

**3rd Biennial Conference on
Asian Current Research
on Fluid Inclusions
ACROFI-III**

and

**14th International Conference
on Thermobarogeochemistry
TBG-XIV**



15-20 September, 2010
V.S. Sobolev Institute of Geology and Mineralogy,
Novosibirsk, RUSSIA

ABSTRACTS

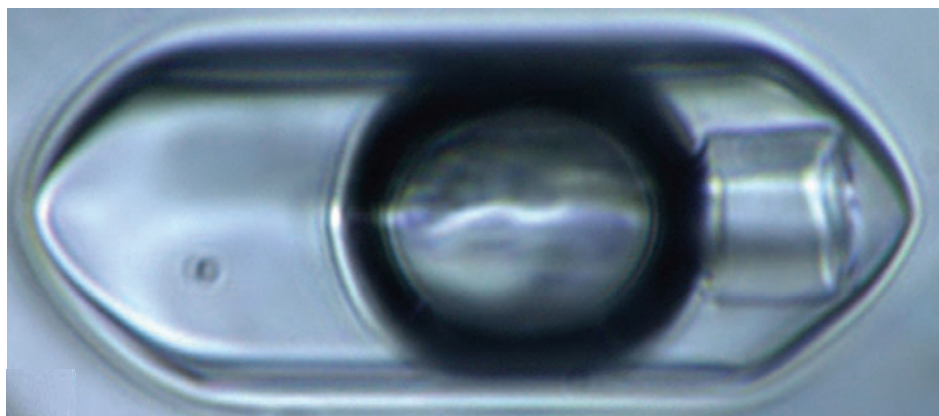
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Compiled and edited by
Victor V. Sharygin



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INTRUSIVES AND ORE FORMATIONS OF GOLD AND RARE METAL DEPOSITS OF UZBEKISTAN

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The territory of Uzbekistan is considered as igneous provinces of the Tien-Shanides – the Urals-Mongolian Fold Belt. There are two regions: the Middle and Southern Tien-Shan. Magmatic processes were acted from rift (O-S), island arc (S-D₁) active continental margin (C₁-P₁) and within plate (P₁-T₁) stages. At this regions are isolated the segments of the earth's crust, where the products of prolonged and diverse magmatism are spatially combined with the polychronic and polygenetic endogenous ore deposits. Areas with the wide and intensive development of magmatic and ore associations are named “ore-magmatic consenters” (Khamrabaev, 2000). Their spatial status is determined by confinement to the bundles of the intersection of the regional faults of sublatitudinal and north-eastern direction. The main characteristic of consenters is the presence in their ranges of polyphase plutons, which have the form of interformational one and multistage laccoliths with the vertical extent of 7-8 kilometers. In the contemporary erosional baring their large protrusions folded are exposed by diorite and by quartz diorite - I phase, by granodiorite - II main phase, by granites - III phase, and by leucocratic granites (alaskite) - IV phase. By them are folded the Kyzylkum-Nurata (Western Uzbekistan), Chatkal-Kurama (Eastern Uzbekistan) and Gissar (Southern Uzbekistan) plutons. According to the geological position, the structural position, the form, the internal structure, the nature of action on the surrounding rocks and other petrological criteria they completely can be defined as batholiths. In the limits of their development the unique and large ore deposits of gold and rare metals are placed. These are supergiant - Muruntau, the deposits of gold and silver of Kokpatas, Kosmanachi, Okzhetspes, Amantaytau in the Kyzylkum desert; Charmitan, Guzhumay, Sarmich, Marzhanbulak, Lyangar, and Koytash in the Nuratau mountains; Kalmakyr, Sary-Checky, Chorukh-Dayron, Kochbulak, Kyzylalma, Chadak in the Chatkal-Kurama mountains. Some ore deposits of tungsten, molybdenum, tin, lithium, niobium, tantalum and other rare metals are connected with skarns, pegmatites and greisens of these batholiths.

The intrusions, compounding the studied batholiths, are formed in the late Paleozoic period (319-274 Ma). Forming homodromic series of

rocks with the calc-alkaline trend of evolution and clearly expressed the increasing trends in quantity of silica and alkalis toward the rocks of final phase. Batholiths have distinguished features in mineral, chemical composition and ore content. Correspondingly, feldspar part is represented in the granitoid rocks of the Kyzylkum-Nurata and Chatkal-Kurama batholiths: 1) high-ferrous by hornblende and by biotite; 2) middle-ferrous by pyroxene, hornblende and biotite. The composition of plagioclase varies: 1) from the andesine (An₄₀) to albite; 2) from labrador (An₆₃) to albite. Potassium-sodium feldspars are: 1) microcline-perthite distinctly latticed; 2) orthoclase – microperthite, microcline-perthite. The accessory minerals for the rocks of the Kyzylkum-Nurata batholith are: ilmenite (I phase); titanite, orthite (allanite), zircon, apatite, ilmenite (II phase); monazite, xenotime, apatite, zircon (III phase); ilmenite, zircon, apatite, gold, tourmaline (IV phase). In the Chatkal-Kurama batholith they are: magnetite (I phase); orthite (allanite), zircon, titanite, apatite, ilmenite (II phase); monazite, orthite (allanite), zircon, magnetite (III phase); apatite, monazite, zircon, topaz, fluorite (IV phase). The differences between rocks of the batholiths are also shown in petrochemical composition, which is expressed by the more silica-acidic, sub-alkaline and peraluminous nature of the rocks of the Kyzylkum-Nurata batholith. The latter is pronounced in the appearance of normative corundum, whose value gradually rises from granodiorites (0,3) to granites (0,7) and leucocratic granites (1,6). In the rocks of the Chatkal-Kurama batholith it is absent, but increase in its quantity is observed with the phenomena of the boundary assimilation of Lower Paleozoic sedimentary-metamorphic rocks in the weakly eroded intrusive bodies. As is known, the values of this coefficient are index of the crustal anatexis nature of magmas for granitoids. Bright confirmation is the high ⁸⁷Sr/⁸⁶Sr values (0,708-0,717) and the identical patterns of distribution rare-earth elements (REE) in the granitoid rocks in the Nuratau and the metamorphic rocks of Precambrian: steep inclination and the deep Eu-minimum. In the Chatkal granodiorite with the predominance of LREE above the heavy Eu-minimum is not expressed distinctly.

The formation of the Late Paleozoic batholiths of Uzbekistan is presented by us: 1) as the result of

the melting of the significant volumes of melts during repeated (from one phase to the next) processing of the rocks of the lower and upper earth's crust by silico-alkaline fluids. This mechanism of formation of magma chambers was predominant in the Kyzylkum-Nurata and Gissar segments and it caused its gold-rare-metal metallogenic specialization; 2) as the result of the mixing of ultrabasic-basic mantle melts with the crustal material. This was reflected in the manifestation of iron-ore-copper-polymetallic, gold-silver and rare-metal mineralization in the Chatkal-Kurama block of lithosphere.

Wide development in their internal, boundary and outlying parts of the small satellite intrusions is the specific feature of the batholiths. They form stocks and dike-shaped bodies and consist of monzogabbro (I phase), syenodiorites (II phase), adamellites (III main phase) and rare-metal leucogranites (IV phase). Regarding the age of batholith rocks (319-293 Ma, C₂-C₃) and small intrusions (293-274 Ma, C₃-P₂) subalkaline associations are formed directly following the apogee of calc-alkaline granite formation. The ⁸⁷Sr/⁸⁶Sr values in late intrusions are low (0,706-0,707). This indicates the possible participation of mantle-derived component in the formation of their melts, which revived the residual chamber of the magmas of batholiths.

Formation of the quartz diorite-granodiorite (adamellite)-granite-leucogranite series of South Tien-Shan is the result of upwards remelting, assimilation, contamination in succession of amphibolites, gneisses and schists of crust section to alkali-silica fluids, alaskite magmas flowing out of ultrametamorphic zones and granite-gneiss cupola (Abdulaev et al., 1953; Letnikov, 2003). Rare-metal (Li, Rb, Cs, W, Mo, Sn, Nb, Ta, Be, TR) granitoids are characterized by high content of boron, fluorite and gold (Akhundjanov et al., 2009).

Diverse mechanisms of the formation and revival of the ore-magmatic systems (palingenic-anatectic, mixing or deep assimilation and meta-magmatism) are the main reasons for metallogenic differences of the Uzbekistan plutonic formations.

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CHAHMESSI EPITHERMAL BASE AND PRECIOUS METAL DEPOSIT, KERMAN COPPER BELT, SOUTH IRAN: INVESTIGATION OF GENETIC RELATION WITH MEIDUK PORPHYRY SYSTEM

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Introduction

Porphyry copper deposits (PCDs) may grade outward/upward into epithermal base and precious metals veins. The porphyry-epithermal transition has been reported from several places (e.g. Brathwaite et al., 2001; Muller et al., 2002). Identification of any genetic relations between epithermal veins and PCDs may serve as a tool in exploration for PCDs.

The Chahmessi Cu-Pb-Zn-Au deposit is located ~1.5 km to the southwest of the Miduk PCD in the Kerman copper belt, south Iran. The country rocks include Eocene andesitic to basaltic volcanic and pyroclastic rocks. An intrusive body of intermediate composition was identified in several boreholes. The deposit consists of a set of four major quartz-sulfide veins and numerous veinlets in dominantly N-NE trending faults and fractures. The veins vary in length and thickness between 100-400 m, and <1m to 10 m, respectively, and display pinch and swell structures. They have been tracked down to a depth of 370 m.

Cross-cutting relations and textures, as evident in the exposures and in the drill cores, suggest that quartz veining and ore formation occurred in at least three stages. The vein materials include quartz, pyrite, chalcopyrite, sphalerite, galena and accessory tetrahedrite. Weathering and supergene processes led to the formation of hematite, goethite, malachite, azurite, cerussite, and smithsonite at the expense of original sulfides above the water table. Minor secondary chalcocite and covellite is developed below water table. On average, the ore minerals constitute 4-5% of the veins. Native gold occurs mostly as inclusions in tetrahedrite and quartz, as well as submicroscopic particles in sulfides. Gold and silver assays vary between 0.1-20, and 20-150 ppm.

The country rocks are weakly to moderately altered to propylitic assemblages, dominated by calcite, and lesser chlorite, sericite and epidote, at the expense of the original plagioclases and mafic silicates. No systematic variations in mineralogy and/or intensity of the alteration can be distinguished with distance from the veins. Whether the alteration is related to the Meiduk porphyry system, or a regional feature unrelated to Meiduk is not known. Propylitic alteration is widespread in

the Cenozoic volcanic rocks in the Kerman copper belt, and elsewhere in Iran.

Alteration associated with vein formation appears to be restricted to thin halos (<1 – 10 m) of silicification, where original silicates are replaced by quartz, as well as scattered zones of argillic/sericitic alteration dominated by illite. The alterations clearly overprint the propylitic assemblage, implying that propylitic alteration predates ore formation at Chahmessi. Argillic alteration is a common feature in epithermal deposits. Absence of argillic alteration at Chahmessi at current exposures might be attributed to the rather deep erosion of the deposit (Modrek, 2009).

The Meiduk PCD (>180 Mt at 0.82% Cu) is associated with an Upper Miocene (12 Ma) composite shallow pluton of granodiorite to quartz-diorite and diorite composition, intruding into Eocene volcanic and pyroclastic rocks of intermediate-mafic composition. The pluton is of high potassium, calc-alkaline affinity and displays features characteristic of continental arc settings (Aliani et al., 2009). Alteration assemblages typical of PCDs are well developed in Meiduk. Fluid inclusions are characterized by high salinities and moderate to high T_H , as in other PCDs. The deposit was emplaced at 3-4 km depth and exhumed to surface around 3-5 million years ago (McInnes et al., 2002).

Fluid Inclusion Studies

Heating and freezing experiments were carried out on fluid inclusions in quartz and sphalerite from the main stage of mineralization at Chahmessi. The inclusions occur in rods and spindles, ellipsoids, circles, irregular elongate and oblate shapes, and negative crystal forms, and vary in size from <5-50 microns. Most measurements were performed on primary fluids inclusions, 5-20 microns in diameter.

Four types of fluid inclusions are distinguished: 1) two-phase, liquid>vapor; 2) two-phase, vapor>liquid; 3) liquid, with a small bubble of vapor; 4) vapor with a small liquid ratio. The liquid-rich inclusions were homogenized by vapor bubble disappearance, and the vapor-rich inclusions homogenized to a vapor phase.

The temperature of homogenization varies

between 175-350 °C (mean= 261 °C) in quartz, and 158-265 °C (mean= 215 °C) in sphalerite. Salinities vary between 0.3-5.5 and 0.1-5 wt% NaCl equivalent in quartz and sphalerite, respectively (Fig. 1). The depth of formation is estimated to be 250-750 m below the paleowater table.

The occurrence of secondary and pseudosecondary inclusions with the same T_H and salinities as the primary inclusions supports the observation that ore fluids were introduced in more than one stage, so that secondary and pseudosecondary inclusions in one quartz and/or sphalerite generation represents primary inclusions in the next generations.

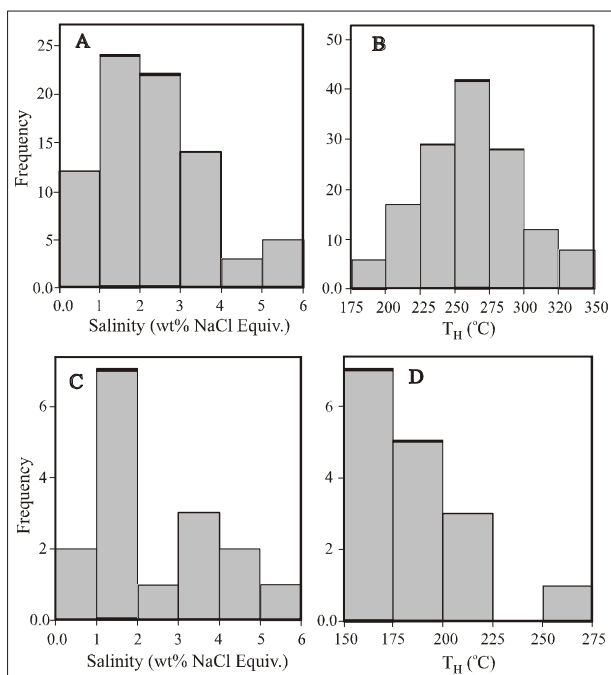


Figure 1. Histograms of salinity and T_H values for fluid inclusions in quartz (A-B) and sphalerite (C-D).

The wide range in T_H and salinity can be explained by boiling and fluid mixing. Boiling is supported by the coexistence of liquid- and vapor-rich inclusions, the occurrence of platy calcite pseudomorphs, and hydrothermal breccias. The stable isotope data suggest the involvement of a magmatic fluid component, and mixing of fluids (Modrek, 2009).

Discussion

With respect to the alteration and ore mineralogy, the relatively high Ag/Au ratios (>3), and the T_H and the salinity data, the Chahmessi deposit can be classified as an intermediate sulfidation epithermal system. Epithermal deposits associated with PCDs are commonly of high sulfidation affinity, deposited from oxidized and acidic fluids, and are characterized by the

occurrence of sulfates and alteration assemblages typical of advanced argillic alteration (e.g. Brathwaite et al., 2001). Our data do not support any genetic links between the Meiduk PCD and Chahmessi. This is also implicated by the depth of formation of the two deposits (3-4 km for Meiduk vs 0.25-0.75 km for Chahmessi). The rather deep erosion at Meiduk would have wiped out any concurrent mineralization at higher levels. The close spatial association appears to be a fortuitous incidence.

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RARE-METAL SILICATE, SILICATE-SALT AND SALT MAGMAS

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Relations between rare-metal ore mineralization and magmatism are one of the pivoting problems in modern petrology and geochemistry. This problem can be solved based on the results of complex studies aimed at the identification of the composition and source of the magmas that produced rare-metal deposits and the role of natural processes able to concentrate ore components. An important role in these investigations is played by the studies of melt inclusions in minerals from ores and rocks sampled at rare-metal deposits. Information provided by such investigations will hopefully shed light onto the complex evolution of natural silicate and salt melts responsible for the origin of rocks at rare-metal deposits, provide insight into relations in the concentrating of trace elements and REE in them, and make it possible to identify processes leading to the generation of ore-bearing magmas.

This paper presents our results obtained by examining silicate, silicate-salt, and salt melt inclusions in minerals from a broad spectrum of rocks and ores from rare-metal deposits in Central Asia related to carbonatite, bimodal, and alkali-granite magmatism. Materials for our studies were collected at rare-metal alkaline carbonatite complexes (Mushugai Khuduk, southern Mongolia, Belaya Zima and Bol'shetagninskii in the Eastern Sayan, Siberia) and at bimodal magmatic associations of elevated alkalinity that include alkali basaltoids, trachytes, pantellerites, comendites, and alkali granites (the Dzarta Khuduk locality, Mongolia, and the Khaldzan-Buregtei massif of alkali rare-metal granites in western Mongolia).

Our important pioneering data on the alkaline carbonatite-bearing Mushugai Khuduk Complex, Mongolia, and related rare-metal deposit include the physicochemical parameters (temperature and pressure) of magma crystallization, the composition of the magmas of the series of volcanic and plutonic rocks and certain ore types related to them. It was established that the rocks composing the complex were produced with the participation of silicate, silicate-salt (silicate-phosphate), and salt melts, with the latter having a highly diverse and unusual composition (predominantly sulfate, phosphate-sulfate, fluorite-sulfate, and chloride-sulfate).

Important results were obtained on the

composition of the magmas responsible for the origin of certain alkali silicate rocks in the Belaya Zima Massif. We discovered Nb-rich melts of composition close to ijolite, with high concentrations of Zr, Th, and LREE. Ore-bearing magmas with elevated Nb concentrations were previously thought to be related only to alkali rare-metal granitoids.

Our detailed data on melt inclusions in fluorite from fluorite carbonatites in the Bol'shetagninskii Massif indicate that these rocks crystallized from a Na-rich carbonatite melt significantly enriched in Mn, Fe, Ba, Sr, Ce, F, and Cl. These data also suggest that these melts had many physicochemical and mineralogical parameters similar to those of lavas of the Oldoinyo Lengai volcano in Tanzania.

Data obtained on inclusions of mineral-forming media in minerals from rare-metal (Nb, Zr, and REE) comendites of the bimodal association of volcanic rocks at Dzarta Khuduk, central Mongolia, testify that the youngest magmatic products of the bimodal series were formed from highly evolved alkaline acid melts with high concentrations of trace elements (Li, Rb, Zr, Nb, and Y), REE (Ce and La), and volatile components (H₂O, F, and Cl). Magmas of this type are rich in fluorides, first of all, in villiaumite and griceite. The identified rare-metal melts were, in fact, ore-bearing magmas, and the alkali-salic rocks of the bimodal association can be regarded as an unusual type of rare-metal ore mineralization related to volcanic rocks.

Studies of melt inclusions in minerals from rare-metal granitoids of the Khaldzan-Buregtei Massif, Mongolia, led us to determine that these rocks crystallized from a magmatic melt with high concentrations of many rare elements (Zr, Nb, Be, Rb, Y, Hf, and Th), REE, F, and volatiles (H₂O, CO₂, and Cl). Our data provide evidence that the elevated rare-metal concentrations in the parental magmas were not caused by any younger overprinted processes.

Analyzing the composition of melt inclusions in minerals from rocks and ores from the deposits, we managed to trace the evolution of silicate, silicate-salt, and salt melts that participated in the origin of the deposits and to identify the role of various magmatic processes that generated ore-bearing magmas. The leading processes were thereby crystallization differentiation and silicate-salt liquid immiscibility. Salt components (P, F, and

S) were determined to have played a determining role in concentrating ore elements in the silicate magmatic melts, up to the origin of ore mineralization.

Our studies of inclusions in minerals from a broad spectrum of rocks and ores from rare-metal ore deposits in Central Asia allowed us to obtain the first data on the rare-metal specifics of the melts that formed these deposits.

BASALT MELTS IN OLIVINE FROM ALKALINE PUMICE OF PRIMORYE

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High concentrations of pyroclastic material (pumice and ash) found in the area of the Tyumen-Ula River in southern Primorye, Russian Far East, were eruption products of the Pektusan volcano at the boundary between China and North Korea. The volcano itself is made up of lava-pyroclastic rocks of trachyte-comendite-rhyolite composition cut by alkali basalt, trachybasalt, and trachyandesite necks and dikes. According to isotopic dates, the volcano was formed over a period of time of >3 Ka. Alkali pumice was brought by the Tyumen-Ula River (whose headwaters originate at the Pektusan volcano) to the Sea of Japan and was then scattered by sea currents along the shore. This material composes a peat-pumice or sand-pumice bed >1 m thick. This bed occurs at a depth of 1-2 m or is exposed at the surface and was traced for more than 50 km north of the mouth of the Tyumen-Ula River. The age of pumice in southern Primorye is 1.5 ± 0.5 Ma, i.e., corresponds to the Early and Middle Pleistocene.

Information on eruption products of the Pektusan volcano is of paramount petrologic importance because it sheds light onto problems related to the genesis of bimodal magmatic series. In this context, it is important to estimate the composition and evolution of the magmas responsible for the origin of compositionally contrasting rocks of the volcano. We are aware of merely very scarce data on the composition of these magmas (Horn, Schmincke, 2000; Guo et al., 2002).

This publication presents our very first data on the composition of melt inclusions in olivine from alkali pumice from Primorye produced by the Pektusan volcano.

The Quaternary pumice whose olivine contains the inclusions examined herein consists of pale gray glass and minor amounts (2-3 vol.%) of sanidine, hedenbergite, magnetite, olivine, apatite, ilmenite, zircon, and chevkinite phenocrysts. The pumice has the following chemical composition (wt.%): SiO₂ – 68.65; TiO₂ – 0.29; Al₂O₃ – 12.42; Fe₂O₃ – 3.62; FeO – 0.89; MnO – 0.09; MgO – 0.10; CaO – 0.22; Na₂O – 5.02; K₂O – 4.43; ZrO₂ – 0.29; Nb₂O₅ – 0.10; $\Sigma \text{TR}_2\text{O}_3 + \text{ThO}_2$ – 0.15; H₂O⁺ – 2.63; H₂O⁻ – 0.48; LOI – 1.06; total – 100.44.

Olivine with coexisting primary melt and crystalline inclusions has the composition For_{74-77} and bears elevated CaO concentrations (up to 0.3

wt.%). The crystalline inclusions are spinel, ilmenite, and titanomagnetite.

Melt inclusions are unevenly distributed in the olivine, are roughly oval in shape, and range from 30 to 70 μm across. These inclusions are usually partly crystallized and contain residual glass, daughter minerals, and gas. The daughter minerals identified in the inclusions are clinopyroxene, ilmenite, titanomagnetite, and apatite. The clinopyroxene is augite with high concentrations of TiO₂ (2.4-3 wt.%) and P₂O₅ (up to 0.8 wt.%) at SiO₂ – 45-46 wt.% and Al₂O₃ – 11-12 wt.%. The ilmenite contains 49 wt.% TiO₂, 44 wt.% FeO, and 6 wt.% MgO. The TiO₂ concentrations in the titanomagnetite reach 14-15 wt.%. The residual glass contains (wt.%): SiO₂ – 60-64; Al₂O₃ – 21; FeO – 4-5.5; MgO – 0.5-1.5; TiO₂ – 0.6-1; CaO – 3.8-5; Na₂O+K₂O – 4-5; P₂O₅ – 1.

According to our thermometric data, the melt inclusions homogenize at 1040-1230°C.

Examination of the glasses under electron microscope allowed us to reveal a significant difference between their composition and that of the pumice. The chemically homogeneous composition of the melt inclusions corresponds to the composition of basalt with elevated concentrations of TiO₂ (2.2 – 3.5 wt.%) and P₂O₅ (up to 0.7 wt.%) at concentrations of SiO₂ from 44 to 52 wt.% and Al₂O₃ – 12-18 wt.%. The contents of alkalis (Na₂O+K₂O) are also relatively high: 4-6.6 wt.%, with an obvious predominance of Na₂O over K₂O. The comparison of the compositions of the melt inclusions and those of the Pektusan volcano alkali basalts show their obvious similarities (Table 1).

Our data provides a good reason to believe that phenocrystal olivine in the alkali pumice was equilibrium mineral and is likely a crystalline fragment of the basalts. The compositional identity of glass in melt inclusions in the olivine and the basalts provides support for this hypothesis.

With regard for K-Ar isotopic dates, which indicate that alkali pumices in Primorye and the basalts correlated with the origin of the shield volcano are roughly coeval (1.5 ± 0.5 Ma and 1.43 ± 0.05 Ma, respectively), it is reasonable to hypothesize that the mixing of compositionally contrasting melts contributed to the genesis of the alkali pumice. Portions of basaltic magma with olivine crystals in it were mingled with mobile acid

melt, and this facilitated degassing and foaming of the liquid. The pressure increase in the magmatic chamber could catalyze an explosive eruption that ejected trachytic pumice with phenocrysts of xenogenic olivine. The pumice in Primorye is thus likely a hybrid rock, which was produced by the mixing of acid and basalt magmas.

Table 1. Chemical composition of glass in olivine-hosted melt inclusions from pumice of Primoye in comparison with basalt of the Pektusan volcano.

Oxide	1	2	3
SiO ₂	43.89	47.32	46.77
TiO ₂	3.55	2.67	3.06
Al ₂ O ₃	12.36	13.85	14.78
FeO	18.92	13.62	12.81
MnO	0.32	0.17	0.21
MgO	6.47	7.79	4.51
CaO	7.7	7.16	6.96
Na ₂ O	3.03	3.07	3.71
K ₂ O	1.41	1.55	2.18
P ₂ O ₅	0.79	0.59	0.64
Cl	0.03	0.03	-
S	0.13	0.08	-
H ₂ O	-	-	0.48
Total	98.6	97.9	99.91*

Note: 1, 2 – glasses in melt inclusions; 3 – basalt (the analytical total is reported with regard for 3.80 wt.% LOI, Sakhno, 2007).

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FORMATION CONDITIONS OF BARITE FROM “BLACK SMOKERS” MOUND AND MINERALIZED VESTIMENTIFERA, TETIS PALEOCEAN: FLUID INCLUSION DATA

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Introduction

Last time the fragments of “black smokers” mounds and mineralized paleovestimentifera were found in massive-sulfide deposit ores of Pontian belt. “Black smokers” mounds are similar in zonality with their modern analogues. Mound coating consists of sphalerite and colloform pyrite. Feeder channels are incrustated with chalcopyrite, sphalerite and barite, sequentially. Similar to modern near-hydrothermal organisms the features of sulfidization for paleovestimentifera at seafloor setting formed pyrite pseudomorphs are observed. Coatings consisting of hydrothermal-sedimentary sulfides (mainly sphalerite) are evidenced about it. But often vestimentifera relics are not served and replaced by barite aggregates filled cavities in vestimentifera bodies. Physico-chemical conditions of barite biomineralization of vestimentifera and “black smokers” mounds of Mesozoic ocean were not studied before. In this abstract we represented first data for these objects. Samples riched of barite from the Killik deposit were used in our study.

Methods

Phase composition of fluid inclusions was studied using Olympus microscope (lens 50^x). Fluid inclusion data were obtained using samples from the Killik deposit: kil-10-1ch – “black smoker” mound fragment, and kil-10-2v, kil-17, kil-10-3v, kil-1 – mineralized vestimentifera shears replaced by barite. Fluid inclusions were studied at Thermobarogeochemistry Laboratory, Geological department, Miass division, South-Urals State University. We used a THMSG-600 heating/freezing stage (LINKAM), allowed to measure temperatures from -196 up to +600°C. Software is a LinkSys32. The sensibility is $\pm 0.1^\circ\text{C}$ within the temperature interval of $-20 - +80^\circ\text{C}$ и $\pm 1^\circ\text{C}$ beyond this range. Salt composition of fluids is estimated using first melting temperatures (Borisenko, 1977). Fluid salinities are calculated using final melting temperatures (Bodnar, Vityk, 1994). Homogenization temperatures are determined at the moment of vapour bubble disappearing during the heating (Roedder, 1987).

Samples

Barite forms tabular semitransparent white crystals and cryptocrystalline masses. Fluid inclusions are 10 μm in size and form groups with

3-5 inclusions. They are not in fractures in barite and can be referred to primary inclusions. Fluid inclusions have crisp boundaries and angular shape. In room conditions (25°C) they are two-phase: light transparent liquid and vapour bubble. Vapour bubbles are crisp, not very big and occupied about 15-20 vol.% of inclusion.

Microthermometric data

According to microthermometric studies fluid inclusions were freezed by temperatures of $-40 - 60^\circ\text{C}$. It was observed due to abrupt mutation of vapour bubble shape in fluid inclusions.

First melting temperatures for inclusions in barite from “black smoker” mound fragment (kil-10-1ch) are $-21 \dots -22^\circ\text{C}$ assuming the prevalence of NaCl in fluid composition. Final melting temperatures are $-1 \dots -3.3^\circ\text{C}$, that testifies about the fluid salinity is from 1.6 to 5.4 wt.% NaCl-equiv. The homogenization temperatures are $125 - 170^\circ\text{C}$. Thus, the fluid salinity formed barite in “black smoker” mound is close to seawater salinity. The homogenization temperatures forms enough restricted interval.

In mineralized vestimentifera replaced by sulfide-barite-quartz aggregate fluid inclusions in barite were studied. The first melting temperatures are $-22.9 \dots -23.9^\circ\text{C}$ (kil-10-2v and kil-17) and show that NaCl+KCl are dominant salts in fluid composition. According to final melting temperatures the salinity is 4–7 wt. % NaCl-equiv. The homogenization of fluid inclusions occurred by $140 - 200^\circ\text{C}$. In kil-10-3v and kil-1 samples rare, but large two-phased fluid inclusions with size of 50 μm were found. They were freezed by temperatures about -40°C . First melting temperatures are $-21 \dots -21.7^\circ\text{C}$, and show that NaCl prevails in fluid composition. Final melting temperatures of fluid inclusions are $-0.4 \dots -3^\circ\text{C}$, and mean the fluid salinity is 0.7–3 wt. % NaCl-equiv., in average (in some measurements is up to 4.5 wt. %). These fluid inclusions were homogenized by $100 - 140^\circ\text{C}$.

Conclusions

Fluid inclusions data of barite from the Killik deposit showed that barite mineralization formed due to water-rich fluids with prevailed NaCl+KCl salts in their composition. Their salinity is in average close to seawater salinity, but has enough broad range of values. For fluid inclusions in barite

replaced vestimentifera bodies, salinity is up to 7 wt.% NaCl-equiv., and more than twice higher than seawater salinity. The presence of KCl was observed during freezing measurements. It testifies that this mineralization was formed due to fluids different in composition from seawater. High salinity in comparison with seawater salinity and KCl presence assume that fluids had probably magmatic origin. Also seawater might be transformed to mineral-forming solution during the interaction with oceanic rocks or evolved during the rising to seafloor (Bortnikov et al, 2004).

Low salinities obtained for fluid inclusions in barite from vestimentifera (kil-10-3v and kil-1 samples) as compared with seawater are determined by the latest their origin and probably diagenetic genesis.

Acknowledgments

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PHLOGOPITE-BEARING PERIDOTITE XENOLITHS IN UDACHNAYA PIPE

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Introduction

The depleted subcratonic mantle lithosphere (SCLM) is not high in the LILE elements which were removed by the high melting degree in the Archean time during the creation of the cratonic lithosphere. Nevertheless, it contains such metasomatic minerals as richterites and phlogopites including highly altered varieties like in MARIDs (Gregoire et al., 2002). In Siberia they are common in the central part of the Siberian craton in the Malo-Botuobinsky region (Sobolev et al., 2010) and abundant in the Sytykanskaya and Komsomolskaya pipes in the Alakit field (Reimers et al., 1998; Ashchepkov et al., 2010) but they are not typical for the Daldyn field with more depleted SCLM. Reported Phl in the contact with huge ilmenite nodules refers to the protokimberlite melts (Pokhilenko et al., 2010). In our study we analysed more 30 new phlogopite-bearing xenoliths from fresh Phl-bearing kimberlite breccia with abundant small peridotite xenoliths.

morphology and assemblages: 1) large phlogopite grains and pockets disseminated in course Sp-depleted harzburgites (SH); 2) veinlets with or without Cpx and Cpx in Sp, and garnet granular peridotites (GGP); 3) symplectites (after garnet) of Sp, Cpx, OPx, Phl in Sp peridotites; 4) intergranular Phl in pyroxenites (Pokhilenko et al., 1999); 5) rims on garnets in porphyroclastic garnet peridotites (PGP); 6) secondary small grains with Al-, Na- low Cpx in all peridotite types, they are frequent in SH and rare in deformed (DP) peridotites.

Major elements of Phl and associated minerals

Phlogopites show enrichment in Ti and Cr. Low-Cr garnets belong to the DP lherzolites, the Cr-rich associations are PGP (Fig. 1) and 4-5 wt.% Cr₂O₃ refers to pyroxene-rich peridotites and pyroxenites. Phlogopite is associated with Cr-spinel (40-57% Cr₂O₃), and secondary phlogopite coexists with low Na-Al Cpx in all peridotites.

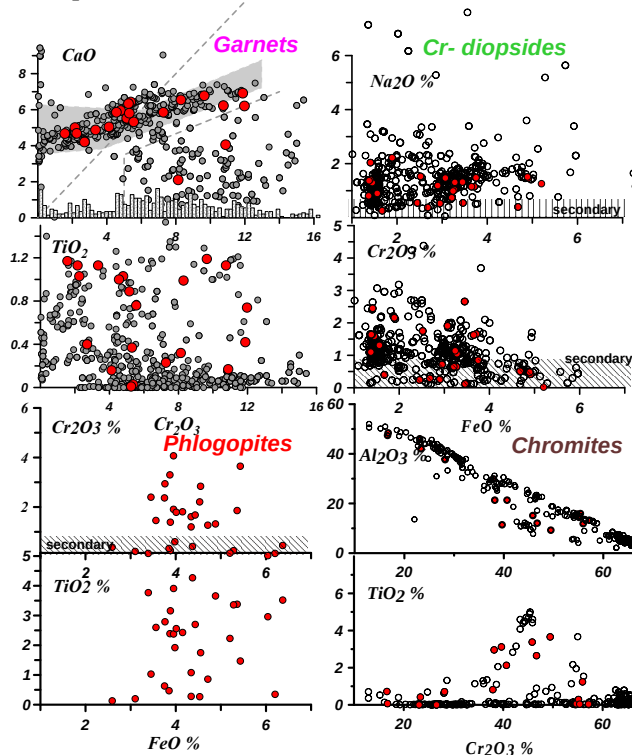


Figure 1. The variations (in wt.%) for minerals in the phlogopite-bearing associations in the Udachnaya pipe (marked by filled circles).

Appearance of phlogopite in xenoliths

The following subdivision were made by

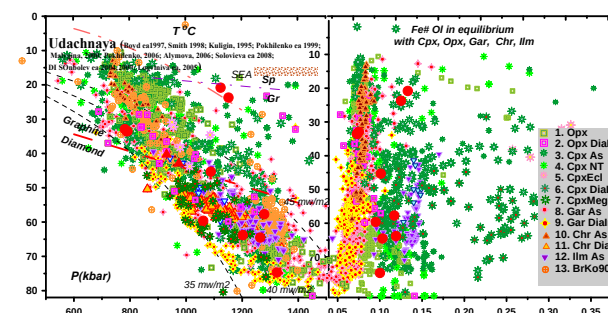


Figure 2. The variations (wt.%) for minerals in the phlogopite bearing associations in the Udachnaya pipe (marked by filled circles).

Calculated pressures and temperatures

The portion of kimberlites indicate Phl-bearing peridotites belonging to three pressure interval 65-50 (DF and PGP), 45-45, 25-15 kbar, (Brey, Kohler, 1990). The monomineral Opx (McGregor, 1974) and Cpx (Ashchepkov et al., 2010) barometers mark adjective branch to 40 kbar close to the protokimberlite PT-path. Phlogopite and Fe-Ti- enriched Cpx are referred to the refertilization path on P-Fe# diagram (Fig. 2). The low-T (and P) associations are less in Fe, Ti and refer to cold geotherm (Boyd et al., 1997). The same set of the PT conditions reveal the large fresh xenoliths found in the lowermost part of the Udachnaya open-pit (Ionov et al., 2011, in press).

Trace elements

Phlogopites show typical sharp difference between high LILE, HFSE and Pb and very low U-Th concentrations (Fig. 3). REE (~0.1 PM) show smooth U-shape pattern. The Cpx associated with Phl in peridotites are also enriched in LILE (Ba) and Ta, Nb and show inclined REE pattern (La/Yb_n ~100) suggesting partial decoupling with phlogopite in trace elements.

Origin of phlogopite-bearing associations

Lowermost horizons of the mantle column beneath the Udachnaya pipe are subjected to the interaction with melts enriched in H₂O and other volatiles, HFSE, and LILE. Direct contacts and inflowing of the dolomite-Phl-rich aggregate including Ilm and Ol without Cpx suggest (Fig. 4) interaction with a carbonatitic H₂O-K-Na-TiO₂-rich melt created newly formed Cpx and associated Phl mostly in deep level. The increase in Fe# in Cpx from the base of the SCLM and decreasing pressure suggest the polybaric differentiation of this melt. The upper most part of the SCLM contains Ti-low association of the early metasomatic stages probably similar to the Alakit field (Ashchepkov et al., 2010b). Secondary phlogopites reflect the fluid interaction in vicinity of kimberlites.

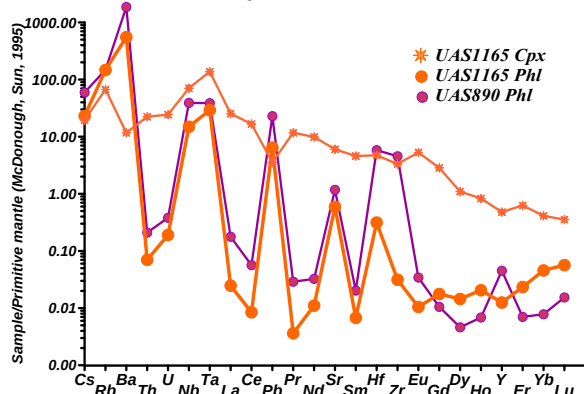


Figure 3. Trace element spiderdiagram for phlogopite associated with Cpx in the Udachnaya pipe.

The sources of fluids and melts

The Ol-Phl-carbonatite aggregates and melt pockets may be derived from the K-rich type-II kimberlites (close to lamproites) (Fig. 4). Such alkali-HFSE-volatile-rich protokimberlite melts which were created megacrystalline associations in the pegmatite-like bodies and the feeder system for kimberlites (Ashchepkov et al., 2010). Many facts show that such melts were from the diamond-generated sources (Logvinova et al., 2008; Wirth et al., 2009). These melts may result from the interaction of Hi-T° kimberlites and carbonated and hydrated due to the subduction lithosphere base. The course Phl melt pockets with low Ti probably reflect the ancient subduction stages close to the time of the Rodinia break up.

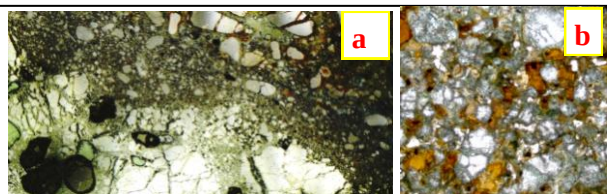


Figure 4. The images of porphyroclastic peridotite with green garnet and Phl rims (a) and Phl-rich magmatic breccia (b).

Conclusions

K-rich phases are common in mantle beneath the Udachnaya pipe and other Daldyn field pipes. They are resulted from the ancient subduction and reflect the interaction of K-rich hybrid protokimberlite melts.

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HYDROUS METASOMATITES IN MANTLE LITHOSPHERE BENEATH THE ALAKIT FIELD

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Introduction

The subcratonic mantle lithosphere (SCLM) beneath Siberia is in general more depleted in bulk rock composition (Ionov et al., 2010) than that reported for South Africa (Gregoire et al., 2002) and other parts of Gondwana which are abundant in metasomatic minerals and show the LILE enrichment as well as the refertilization (Viljoen et al., 2009). Similar processes in large scale are recognized beneath the most of kimberlite pipes from the Alakit region, especially beneath the Sytykansкая, Komsomolskaya and Yubileynaya pipes while the bulk rock compositions here usually is more depleted then in the Malo-Botuobinsky and even Daldyn regions. In the Sytykansкая pipe most of the xenoliths contain mica (Reimers et al., 1998) and amphiboles, which are common also in the Komsomolskaya pipe and mineral concentrates from the Yubileynaya pipe (Ashchepkov et al., 2004). Phlogopite xenocrysts are common in the Krasnopresnenskaya pipe and rare in the Aikhal pipe and nearest kimberlites. Mica occurs in diamonds (Sobolev et al., 2009).

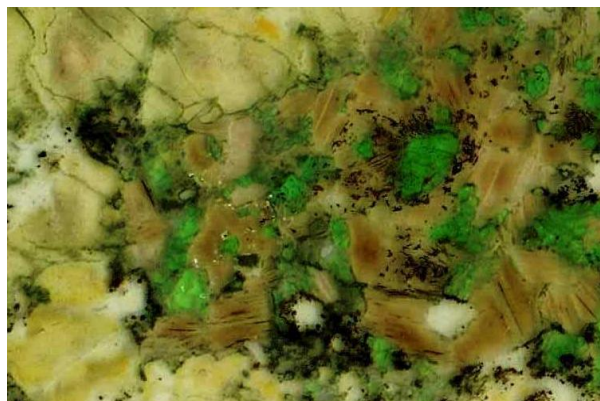


Figure 1. Image of the phlogopite-Na-K-richrichterite-Cr-diopside intergrowth in a xenolith from the Sytykansкая pipe.

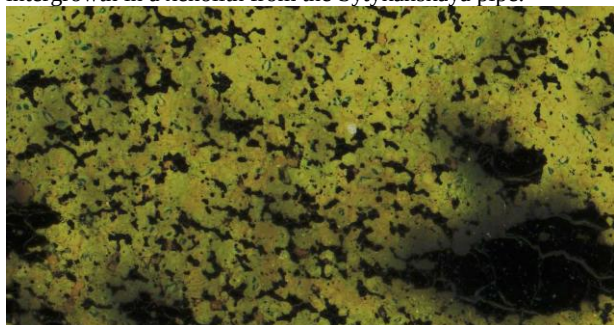


Figure 2. The image of sheared peridotite with Ilm, Cpx and Phl from the Sytykansкая pipe.

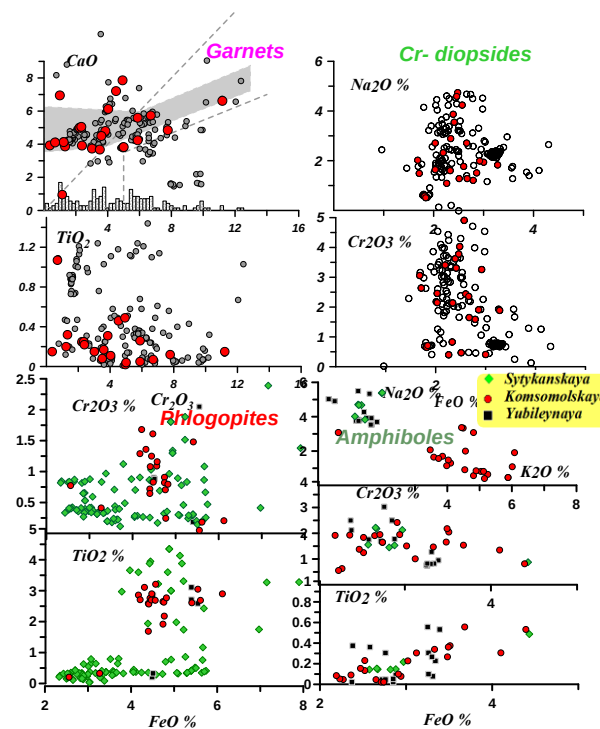


Figure 3. The variations (in wt.%) for minerals in the metasomatic mantle associations beneath the Alakit region.

Metasomatic associations in xenoliths

In the Sytykansкая and Komsomolskaya xenoliths mica is disseminated in most of metasomatic peridotites (MP) or forms the veins and intergranular veinlets (VP) (Fig. 1), sometimes with ulvospinel, ilmenite, rutile and/or Na-K-richrichterite and diopside. Phlogopite is common in green websterites (GW). It associates with ilmenite in deformed peridotites (DP) (Fig. 2). Mica forms xenocrystal intergrowths with rutile.

Major elements of Phl and associated minerals

Phlogopites from the Sytykansкая pipe form two trends on the FeO-Cr₂O₃ and FeO-TiO₂ plots according to the presence of ilmenite. K-richterites are common in the Yubileynaya highly depleted MP xenoliths. They contain up to 3 Cr₂O₃ and up to 0.8 wt.% TiO₂, whereas only K-Na species occur in other pipes. Garnets associated belong to the GW and common lherzolites (Sobolev, 1977) in whole Cr interval (Fig. 3). Pyroxenes associated with metasomatic minerals are enriched in Al and Cr and show large scale variations. Ulvospinel (up to 12 wt.% TiO₂) occurs in veins with ilmenite.

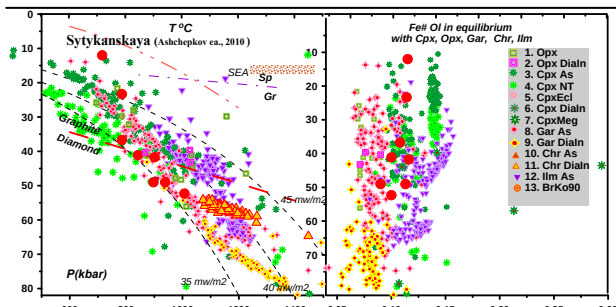


Figure 4. PT-diagram for the Sytykansкая pipe and PT-conditions for the metasomatites according to clinopyroxene (Ashchepkov et al., 2010).

Calculated pressures and temperatures

PT conditions determined according to Cpx thermobarometry (Opx rarely preserved). (Nimis, Taylor, 2000; Ashchepkov et al., 2010) show the general refertilization trend from the base of SCLM to the top of mantle column. Pyroxenites GW are common in 55-40 interval (Fig.2). Ilmenite-bearing associations belong to the lower part of the mantle sequence (Fig. 4). The more Fe-rich refertilization trend is less abundant in hydrous metasomatites.

Trace elements

Phlogopites from kimberlites strongly vary in trace elements. They are enriched in REE and U referring low degree partial melts and fluids. The HFSE-rich associations are less in REE, and La/Yb_n ratios are from the Ti metasomatites from the lower part of SCLM (Fig. 5). The depletion in HFSE is due to association with the rutile and Sr minimum in associations with apatite. The minimum in Pb is due to sulphides which are common in ilmenite-rich associations. Amphibole (K-richterite) shows trace element pattern typical of Cr-diopsides but enriched in Ta-Nb and depleted in U-Th according to partition coefficients (Chazot, 1996).

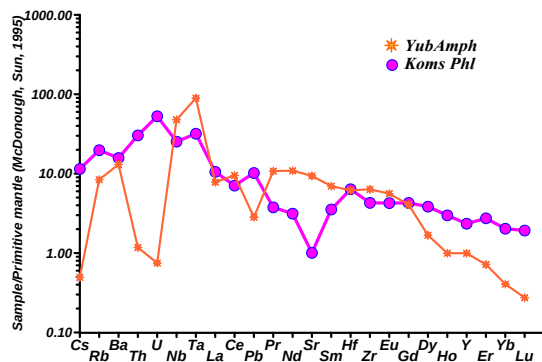


Figure 5. The trace element spiderdiagram for phlogopite and amphibole from the Komsomolskaya and Yubileinaya pipes.

Origin of the phlogopite-bearing associations and sources of the fluids and melts

The discriminated and vein metasomatism without HFSE-(Ti) enrichment according to the ages probably is due percolation of the K-rich fluid in the subduction zones during the rifting processes

of the Rodinia break-up 600-500 Ma ago (Fig. 6).

The refertilization with ilmenite and HFSE enrichment are probably referring to the evolution of the protokimberlite melts in the lower part of SCLM which reveal the carbonatitic features.



Figure 6. Ar-Ar ages of mantle phlogopites from the Alakit field.

Conclusions

The K-Na metasomatism with abundant phlogopites and amphiboles is common of the SCLM in the Alakit region. The most depleted associations were subjected to K-metasomatism. The refertilization by protokimberlites creates the HFSE-enriched metasomatism developed in lower part of the mantle.

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LATE PLEISTOCENE-HOLOCENE MAGMATISM OF SHIVELUCH VOLCANO: THREE TYPES OF PRIMARY MELTS

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Introduction

The products of Holocene eruptions of the Shiveluch Volcano are dominated by compositionally uniform moderately potassic magnesian andesites. Early Holocene rocks are moderately potassic basaltic andesites similar in composition to the rocks of the middle horizons of Old Shiveluch (Pevzner, Babansky, in press). Basic rocks are very rare, and only two Holocene basaltic eruptions have been documented (Volynets et al., 1997).

We attempted to reconstruct the Holocene evolution of the magma chamber of the Shiveluch Volcano by studying melt inclusions in phenocrysts from rocks of different age. Eleven samples of andesite, basaltic andesite pumice and basalt scoria were investigated.

The rocks contain up to 40 vol % of phenocrysts of zoned plagioclase, amphibole, pyroxenes, titanomagnetite and olivine (in basalt scoria). The groundmass of the rock consists of a brownish glass with microlites of plagioclase, pyroxene and magnetite. A characteristic feature of the andesites and basaltic andesites is the presence of relict magnesian olivine rimmed by the Opx–Mt and Cpx–Mt aggregates with peculiar textures. Amphibole develops after pyroxene in such aggregates.

The phenocrysts of the rocks contain crystalline (apatite, titanomagnetite, plagioclase, and amphibole), fluid, and melt inclusions. Fluid inclusions are common of plagioclase.

The melt inclusions show regular outlines and are up to 40 micrometers in size. Most common are two-phase inclusions with glass and about 10 vol % gas. Some inclusions contain larger gas bubble and show variable gas/glass ratios, which probably indicate the entrapment of a heterogeneous gas-melt mixture. The glasses of melt inclusions were analyzed with an electron microprobe (~200 analyses).

Results

Representative analyses of glasses from melt inclusions in rocks of different age are showed in Table 1.

Three types of melts were distinguished: (1) dacitic melt parental for the andesite tephra with ages of 9200 ¹⁴C yr – 1964; (2) basaltic melt

parental for the basalt tephra of the eruption with an age of 3600 ¹⁴C yr, and (3) andesitic melt parental of the Early Holocene basaltic andesite tephra with ages older than 9300 ¹⁴C yr.

The glasses of melt inclusions in plagioclase, pyroxene and amphibole from both andesite and basaltic andesite have similar compositions and differ in composition of the host rocks in higher SiO₂, Na₂O, and K₂O contents. The compositions of rocks and inclusion glasses form separate groups in the SiO₂–K₂O diagram.

No systematic relationships were observed between the compositions of melt inclusion glasses and their host minerals. On the other hand, the petrographic features of the andesites and the chemical similarity of glasses from melt inclusions in plagioclase and amphibole allow us to suppose simultaneous (cotectic?) crystallization of these minerals. The high-Ca composition of plagioclase crystallizing from a silicic melt can be explained by the considerable water content in the melt (Naney, 1983), which is indirectly supported by the low totals of the microprobe analyses of glasses.

The presence of nonequilibrium crystalline phases in the andesite and basaltic andesite tephra (olivine and pyroxene) and peculiar crystal clots may indicate a complex and prolonged fractionation history during the formation of the andesite and basaltic andesite tephra.

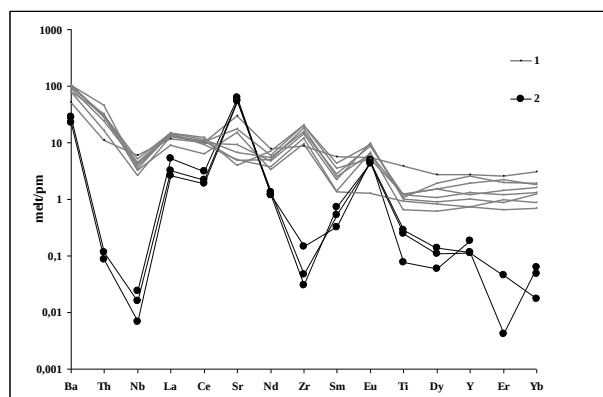


Figure 1. Distribution of the normalized trace elements in the melts of different age. Note. 1 – melts of type (1), 2 – melts of type (3). Normalized after (Sun, McDonough, 1989).

The trace-element characteristics of the Holocene dacite melts (type 1) are significantly different from those of the pre-Holocene andesite melts (type 3) (Figure 1). It can be supposed that

this difference is mainly due to the existence of at least two different magma sources rather than the different degrees of differentiation of a single primary melt. The obtained data support the previous suggestion of Pevzner and Babansky (in press) that the source of melts (or the character of interaction of two coexisting sources) changed dramatically at the Pleistocene–Holocene boundary ca. 9300 ^{14}C yr ago.

We plan to continue thermobarogeochemical studying of the Pleistocene rocks and Holocene basalts. This will clarify the processes of magma evolution of the Shiveluch Volcano as well as to identify the participation of melts of type 2 in the formation of its Holocene rocks.

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Table 1. Representative analyses (wt.%) of glasses from melt inclusions in Young Shiveluch rocks of different age.

Type of melt	(1)			(2)			(3)		
SiO ₂	72,23	74,18	72,89	57,48	57,92	58,44	65,86	63,64	60,68
TiO ₂	0,23	0,26	0,32	0,44	0,51	0,73	0,93	1,15	0,97
Al ₂ O ₃	13,77	13,19	13,86	17,28	19,01	16,55	16,30	16,67	16,4
FeO	1,34	1,36	1,73	7,11	4,38	5,05	4,44	5,40	4,7
MnO	0,07	0,04	0,01	0,15	0,17	0,19	0,17	0,18	0,12
MgO	0,29	0,40	0,55	1,73	1,40	1,85	1,59	2,26	1,76
CaO	1,27	1,31	1,50	6,56	7,11	5,90	3,21	3,96	3,55
Na ₂ O	3,94	2,60	1,01	3,33	4,03	3,59	4,71	5,18	5,27
K ₂ O	2,75	2,33	2,89	2,59	2,99	3,83	2,45	2,34	2,38
P ₂ O ₅	n.a.	n.a.	n.a.	0,86	0,77	0,91	0,52	0,46	0,47
Cl	0,29	0,08	0,14	0,03	0,05	0,04	0,12	0,17	0,12
S	0,07	0,05	n.a.	0,09	0,07	0,06	0,04	0,05	0,02
Total	96,25	95,80	94,90	97,65	98,47	97,14	100,34	101,46	96,44
Age, ^{14}C yr	6900	8000	8100	3600			>Older than 9300		

Note: n.a. – component is not analyzed.

CONTRIBUTION TO UNDERSTANDING THE GENESIS OF ORE-BEARING RARE-METAL GRANITES BASED ON THE MELT AND FLUID INCLUSIONS STUDY

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Introduction

By the example of the Orlovka massif of Li-F granites in Eastern Transbaikalia, the major- and trace-element (Li, Be, B, Ta, Nb, W, REE, Y, Zr, Hf) compositions of the parental melt and the character of its variations during the formation of the differentiated rock series up to forming of lepidolite-amazonite granites with Ta-mineralization, pegmatoids and greisens were quantitatively estimated for the first time on the basis of electron and ion microprobe analyses and Raman spectroscopy of rehomogenized glasses of melt (MI) and fluid (FI) inclusions in quartz and beryl.

Results and discussion

It was shown that the composition of the Orlovka melt corresponded to a strongly evolved alumina-saturated granitoid magma ($A/CNK = 1.12-1.55$) rich in normative albite, poor in normative quartz and similar to ongonite melts. This magma was strongly enriched in water (up to 9.9 ± 1.1 wt.%) and fluorine (up to 2.8 wt.%). Most importantly, this massif provided the first evidence for high B_2O_3 contents in melts (up to 2.1 wt.%). The highest contents of trace elements were observed in the melt from pegmatoid bodies in the amazonite granites of the border zone: up to 5077 ppm Li, 6397 ppm Rb, 313 ppm Cs, 62 ppm Ta, 116 ppm Nb and 62 ppm W. Compared with daughter rock, the Orlovka melt was depleted at all stages of formation in SiO_2 (by up to 60 wt.%), Na_2O (by up to 2.5 wt.%) and, to a smaller extent, in Ti, Fe, Mg, Sr and Ba, but was enriched in Mn, Rb, F, B and H_2O (Badanina et al., 2006).

Two stages were distinguished on the basis of the behaviour of trace elements and fluorine in the melts and rocks. The early stage, from biotite granites of the parental massif to the microcline-albite granites with pea-shaped quartz is characterized by a decrease in Si, Fe, Ca, Mg, Zr and REE and accumulation of Al, Na, Li, Rb, Ta and Nb, which correspond to the ongonite differentiation trend. During the second stage, amazonite-bearing rocks with Li micas and Ta mineralization (columbite-tantalite and microlite) were produced, and the melt was depleted in Al, Na, Li, F, Nb and Ta. A considerable difference appeared between the compositions of rocks and

aluminosilicate melts. There is a paradoxical discrepancy between the high contents of Li, Ta and Nb in the rock (2289, 446 and 263 ppm, respectively) and the low contents of these elements in the melt from the amazonite granites.

The following interpretations can explain the mechanisms of Ta- and Nb-enrichment in rare-metal granites:

1) late-magmatic quartz trapped inclusions of already depleted melt after the fractionation of Li-F micas, albite, topaz, columbite-tantalite and microlite.

2) dramatic depletion of the residual melt in Na, Al, Li, F, Ta and Nb suggests the possible separation of a specific hydrosaline aluminofluoride melt, which accumulated Nb, Ta and REE in some experimental systems. This suggestion was supported by the results of the investigation by MI and FI in beryl from the pegmatoid bodies of Orlovka, which established the coexistence of two types of MI: A-type and B-type (after Thomas et al., 2000) and CO_2 -rich supercritical aqueous fluid (Thomas et al., 2009). The A-type of MI contains mineral phases (>80 vol%) with a small H_2O and CO_2 -rich vapor bubble (<20 vol%). The B-type contains four different phases: a stable aluminosilicate glass, a water-rich solution, liquid CO_2 and a CO_2 bubble. In some MI of the B-type the aluminosilicate glass has crystallized, and the inclusions now contain a H_2O - and CO_3^{2-} -rich solution, liquid CO_2 and CO_2 bubble as well as different mineral phases: polyolithionite, trilitionite, boromuscovite, cristobalite, quartz, beryl, topaz, REE-rich fluorite, albite and pollucite (indicated by Raman spectrometry). Thus, homogeneous aluminosilicate melt split immediately prior to the time of trapping into three different mutually immiscible phases: a relatively volatile-poor slightly peralkaline type-A melt (~12 wt.% H_2O , CO_2 , F, Cl), a volatile- and carbonate-rich strongly peralkaline type-B melt (~30 wt.% H_2O) and a CO_2 - H_2O -rich supercritical fluid containing carbonate ions and sulfur. One of these melts corresponds to a volatile-rich hydrosaline subalkaline melt ($ASI=0.275$), with up to 2.1 % (g/g) Li_2O and up to 3 % (g/g) F. Columbite or tantalite-(Fe) daughter mineral phases in coexisting CO_2 -rich fluid inclusions was identified with Raman spectroscopy. From conservative volume estimation results a

concentration of Ta in this fluid of about 6500 ppm.

3) hydrothermal-metasomatic concept.

To verify the proposed model we did: 1) the assessment of partition coefficients for Ta and Nb in mineral-melt system; 2) the calculation of the saturation's degree of columbite-tantalite in the natural melt; 3) the evolution's study of speciation and impurity composition of columbite-tantalite. The evaluation of $D_{Nb,Ta}^{mineral-melt}$ revealed their dramatic increase in ore-bearing amazonite granites in favor of the melt in comparison with the original granites ($D_{Ta}^{Bt-melt} = 9$, $D_{Ta}^{Lep-melt} = 2.9-7.2$, $D_{Nb}^{Bt-melt} = 8-19$, $D_{Nb}^{Lep-melt} = 4-6.8$; $D_{Ta}^{Mi-melt} = 2.7$, $D_{Ta}^{Amaz-melt} = 0.4-1$, $D_{Nb}^{Mi-melt} = 1.3-3.3$, $D_{Nb}^{Amaz-melt} = 0.03-0.4$), which saturated the melt with Ta and Nb and created conditions for columbite-tantalite crystallization at the magmatic stage.

Morphological features of columbite-tantalite did not show signs of dissolution required in the metasomatic concept. In addition, analysis of the zoned Ta-Nb minerals by the LA-ICP-MS revealed the uniform distribution of REE for columbite-tantalite of all Orlovka massif zones with slope-like form of chondrite-normalized REE distribution spectrum, with a sharp predominance of HREE over LREE, a stable negative Eu-anomaly and the presence of M-shaped tetrad effects T3 and T4 indicating the absence of the abrupt change in the mineral-forming medium typical for silicate melt - aqueous solution transition.

On the other hand, we found that the solubility product (K_{sp}) of mangano-columbite and -tantalite, obtained by analyzing Ta and Nb content in melts of Orlovka's and Etyka's rare-metal granites (after homogenization of crystalline melt inclusions at 2 kbar and 750°C), vary in the range $\log K_{sp}^{Nb}$ from -4,6 to -7,9 mol^2/kg^2 and $\log K_{sp}^{Ta}$ from -5,1 to -8,9 mol^2/kg^2 and have significantly lower rates compared with synthetic haplogranite melts under pressure of 2 kbar and temperature of 800°C $\log K_{sp}^{Nb}$ from -1,6 to -4,1 mol^2/kg^2 and $\log K_{sp}^{Ta}$ from -1,5 to -3,6 mol^2/kg^2 (Linnen, Cuney, 2005). These estimated data impeaches columbite-tantalite crystallization from silicate melt and puts forward the probability of its crystallization from specific hydrosaline aluminofluoride melt, which separation is observed in stable association of Na, Al, Li, F and Ta elements decrease in the residual melt (Badanina et al., 2010).

Acknowledgements

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FORMATION OF SECONDARY FLUID INCLUSIONS IN QUARTZ CRYSTALS AT CONDITIONS OF FAST (CATASTROPHIC) PRESSURE DECREASE

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Introduction

It is known (Ermakov, 1950; Roedder, 1987) that primary, pseudo-secondary and secondary fluid inclusions practically always are simultaneously in the natural minerals. All of them contain thermobarogeochemical information about mineral-forming solutions during certain stages of their activity. Quite often identification of the specified types of inclusions is a difficult and ambiguously solved task. Obviously it is caused by variety of the reasons and mechanisms of their formation.

In the presented work we give results of new experimental data about formation of secondary inclusions in minerals. In particular, possibilities of their formation in synthetic quartz under the influence of slump of pressure and temperature in process of growth of crystals are shown below.

Experiments

We provided two series of experiments for receiving aqueous-hydrocarbon fluid inclusions in synthetic quartz crystals. Crystals were grown on quartz seeds of ZY orientation in mixtures of alkalescent (NaHCO_3) or alkaline solutions (Na_2CO_3 , NaOH) with crude oil and its basic fractions - gasoline, kerosene, diesel fuel and gasoil (27-29 vol. %). As a nutrient, were used the short quartz bars which were placed in the lower hotter zone of autoclaves. Growing of crystals was carried out in autoclaves of 50 ml in volume at temperature 400/450°C (top and bottom of autoclave, accordingly). Autoclave filling was 72 % (with no hydrocarbons). According to PVT-diagram of the solutions, pressure in autoclaves at the specified temperature composed not less than 90 MPa. 10 autoclaves were simultaneously used in experiments of each series. They were placed in a vertical electric furnace. Duration of experiments was 14 days. Stable conditions of the experiments of the both series were changed brutally only after 12 day: one of the autoclaves has unexpectedly exploded. All other autoclaves which were in the furnace have lost tightness under shock wave action, having lost more than 80-90 % of a fluid. Their temperature after explosion has gone down on 70°C, but in 20 minutes was restored completely as well as tightness of autoclaves.

Double-polished plates (2 mm in thickness) were prepared from the grown crystals after experiments. Fluid inclusions in plates were studied

by methods of a gas and liquid chromatography, X-raying, and electron probe microanalysis (Melnikov et al., 2008). Compositions of inclusions were determined using local IR- and Raman spectroscopy, gas chromatography and fluorescent microscopy (Pironon et al., 2000). The phase state and behavior of aqueous-hydrocarbon fluid in inclusions at high temperature and pressure was established in-situ on micro-thermometric stage THMSG-600, Linkam (UK), microscope Amplival (Germany) with a set of long-focal-length lenses, video camera and operating computer. Liquid and gaseous phases in individual fluid inclusions were characterized by IR-spectroscopy (absorption bands in a range of $6000\text{--}2000\text{ cm}^{-1}$, resolution of 4 cm^{-1}), recorded with a help of IR-microscope Continuum and spectrometer Nicolet Nexus (minimal size of the aperture - $5\text{ }\mu\text{m}$).

Results and discussion

Ten wedge-like quartz crystals containing numerous aqueous-hydrocarbon inclusions have been grown in experiments of the first series. The primary tubular and needle-like inclusions were observed in seeds with a relation of phases: $\text{VL1} > \text{G}$, $\text{VL1} > \text{G} > \text{L2}$ and $\text{VL1} > \text{VG} \geq \text{VL2} \gg \text{VSB}$, where V is the volume of phases, and L1 denotes the water phase, L2 denotes the liquid hydrocarbons, G denotes the gaseous phase and SB denotes the semi-liquid and solid bitumen (Fig. 1). Inclusions of cone-shaped, oval, isometric and irregular forms were spontaneously formed in grown layer of quartz (Fig. 2).

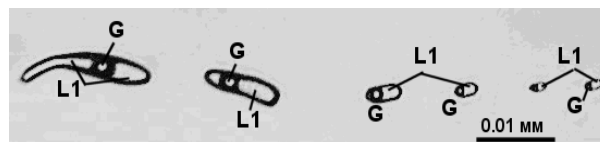


Figure 1. Unlaced primary fluid inclusions in the seed of synthetic quartz from experiments of the first series.

In experiments of the second series the inclusions have kept external morphology of primary inclusions. However, their phase composition and relation of phases have undergone essential changes. The phases of L1 and L2 have disappeared practically; the phase of G has become dominated. Myriads of the smallest secondary gas-dominated inclusions of various forms (with size from shares to the first microns) were formed in healed cracks around all inclusions (Fig. 3, 4).

Formation of secondary inclusions occurred very quickly, at least, within 2 days. A lot of cracks have no exit for limits of seeds and overgrown layer. Such cracks filled with fluid arriving from primary inclusions.

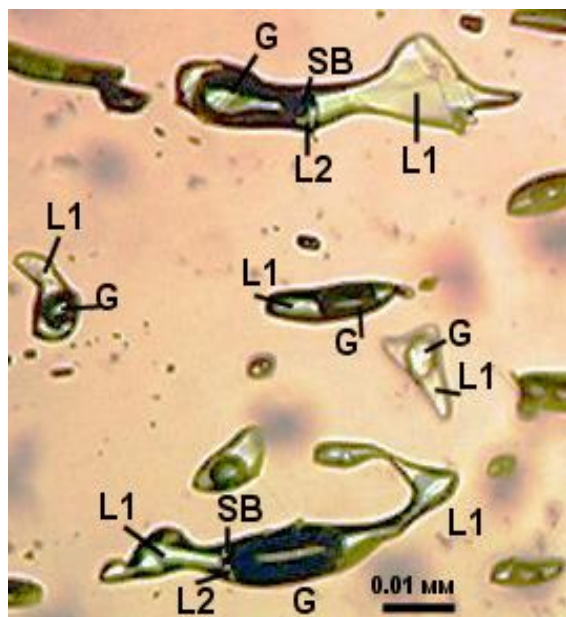


Figure 2. Multiphase primary inclusions in overgrown layer of quartz (growth sector of positive trigonal prism).

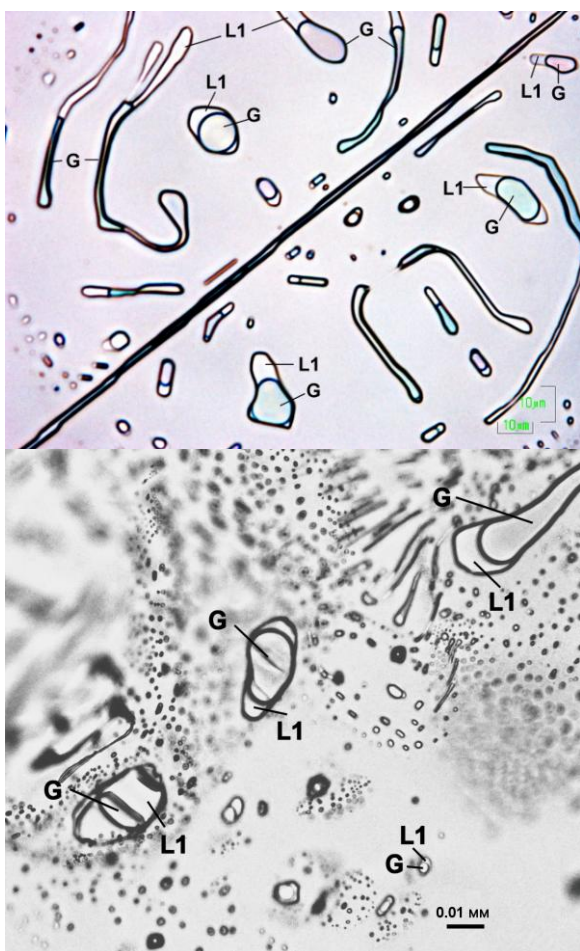


Figure 3. Change of relation of phases in the unlaced inclusions and appearance of numerous secondary inclusions around them.



Figure 4. Change of relation of phases in the large inclusions and appearance of numerous secondary inclusions around them.

Conclusions

Thus, our experiments unambiguously prove that one of the reasons of formation of secondary inclusions in minerals can be a fast (catastrophic) pressure decrease in mineral-forming medium. Simultaneously with this the temperature was decreased for several tens of degrees, but then quickly reached the initial meaning due to constant temperature of environment (furnace). The temperature falls down simultaneously with pressure drop but then very quickly reaches initial meanings due to constant environment temperature. It leads to curing the arisen cracks and to formation in them of secondary inclusions.

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THE PHASE STATE AND BEHAVIOR OF AQUEOUS-HYDROCARBON INCLUSIONS IN SYNTHETIC QUARTZ AT TEMPERATURE 20-400°C AND PRESSURE UP TO 90 MPa

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Introduction

In recent years, artificial inclusions in natural and synthetic minerals are widely used in studies about phase state and behavior of aqueous-hydrocarbon (HC) fluids at wide range of TP-parameters (Sawaki et al., 1997; Dubessy et al., 2000; Teinturier, Pironon, 2003; Teinturier, Pironon, 2004; Balitsky et al., 2005; Balitsky et al., 2007 and many others). These researches are aimed at problems of origin and migration of HC in superficial Earth's crust or at technologies of increasing the reservoir oil recovery and oil refining. Since it is impossible to observe phase state and behavior of hydrocarbons in situ, experimental parameters achieved from fluid inclusions in minerals should provide understanding of HC behavior at wide range of TP-conditions. Minerals trap aqueous-HC inclusions during crystal growth conserving origin states and properties of the aqueous-HC fluid.

Here we report results of our studies of the aqueous-HC inclusions, aiming to determine phase states and behavior of aqueous-HC fluids in wide range of temperature and pressure.

Methods of researches

Crystals of the synthetic quartz containing aqueous-HC inclusions were grown from mixture of alkaline or alkaline water solutions with crude oil (from 0.01 to 50 vol. %) and oil fractions (petroleum, kerosene, diesel oil and gasoil from 12 to 28 vol. %) at temperatures (T) from 260 to 490°C and pressures (P) up to 150 MPa.

The crystals were grown in heat-resisting autoclaves with a volume of 50 and 280 ml under direct temperature gradient (ΔT) conditions. Duration of the growth was varied from 15 to 30 days. The aqueous-HC inclusions were formed in seed (in cavities preliminary prepared by etching) and/or in the overgrown layer spontaneously [8]. Products of experiments were studied by a gas- and liquid chromatography, X-ray diffractometry and electron probe microanalysis (EPMA). Fraction and phase compositions of inclusions were determined using local IR- and Raman spectroscopy, gas chromatography and fluorescent microscopy. The phase state and behavior of the fluid inclusions during heating and cooling were investigated by a micro thermometric method using a comprehensive

device created on the basis of microthermal stage THMSG-600, Linkam (UK), microscope Amplival (Germany) with a set of long-focal-length lenses, video camera and operating computer. Liquid and gaseous phases in individual fluid inclusions were identified by IR spectroscopy (absorption bands in a range of 6000-2000 cm^{-1} (resolution of 4 cm^{-1}) and recorded using IR-microscope Continuum and spectrometer Nicolet Nexus (minimal size of the aperture is 5 μm).

Results and discussion

In total, we grew more than 80 crystals of quartz containing aqueous-hydrocarbon inclusions of the tubular, needle, oval and wrong forms. Size of the majority of the inclusions varied from the tenth of millimeter to 1 millimeter. The inclusions were predominantly three-phase and multiphase. Relations between phase volumes in the inclusions were followings: $VL1 > VG >> VL2$ (Fig. 1a, b), $VL2 \geq VL1 > VG$ (Fig. 1c), $VL1 > VG >> VL2 > VSB$ (Fig. 1d), $VG >> VL1 \geq VL2 > VSB$ (Fig. 1f), $VL2 >> VL1 \approx VG > VL3 > VSB$ (Fig. 1e), $VL1 > VG >> >> VL2 >> VL3 > VSB$ (Fig. 1g), where V is the volume of phases, and L1 denotes the water phase, G denotes gaseous phase (i.e., water pairs, methane and less often propane, ethane and pairs of liquid hydrocarbons), L2 and L3 denotes liquid hydrocarbons, SB denotes semi-liquid and solid bitumen.

Biphasic inclusions in the crystals were found rarely; these inclusions get following relations between phase volumes: $VL1 \geq VG$, $VL2 \geq VG$ and $VL1 \geq VL2$. As usual, their formation is due to the capture of some portions of heterogeneous fluids into inclusions.

The state and behavior of phases in the inclusions at different T and P were recorded in more than 70 videos microfilms.

Our studies showed that oil fractionates with forming the light, middle and heavy fractions after the interaction with hydrothermal solutions at conditions of direct temperature gradient. We observed cracking of the oil fractions at T more than 350-400°C and P more than 70-150 MPa. Cracking results in the increasing of HC gases (methane dominated) and light and middle oil fractions in fluid.

The relationship among water solution, liquid

and gas HC controls heterogeneity or homogeneity of the aqueous-HC fluids. The homogeneous state can be the gas as well as the liquid phase.

In case of $VL1 > VG > VL2$ the fluid forms the biphasic liquid (L1+L2) at $T=300-370^{\circ}\text{C}$ ($P = 30-90$ MPa); the gas phase disappears completely. The analogous biphasic liquid without gas phase were observed in inclusions in the case of $VL2 > VL1 > VG$. In this case, the gas phase disappeared at $227-230^{\circ}\text{C}$. The stable state of such fluids without any gas phase was observed up to $385-405^{\circ}\text{C}$. Further heating resulted in quartz matrix cracking due to explosion of these inclusions. Concentrations of the liquid HC dissolved in the aqueous solution reached 8-10 vol.%. We believe that unlimited solubility can be attained at the higher TP conditions.

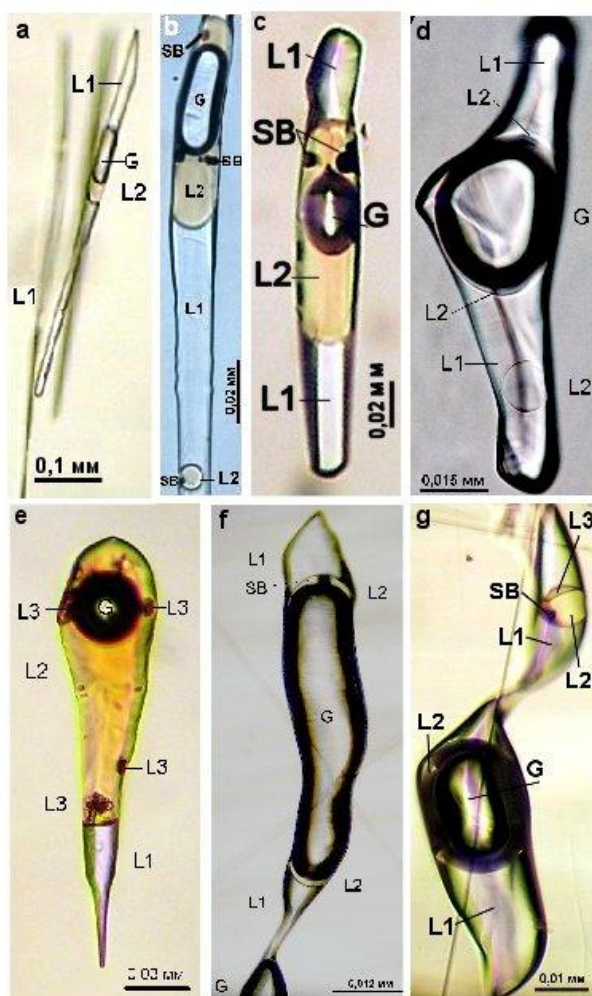


Figure 1. Fluid inclusions with different relations of phases L1, L2, G, SB, L3 (see text).

In the case of $VG >> VL1 > VL2 > VSB$, the phase L2 was dissolved at $T=330^{\circ}\text{C}$ and fluid was converted in biphasic state (G+L1). At $T=350-400^{\circ}\text{C}$, the (G+L1) phase was transformed into homogeneous gas fluid.

In the case of $VL1 > VG >> VL2 > VSB$ liquid HC were dissolved in the water solution completely

at $250-280^{\circ}\text{C}$ with forming the biphasic fluid (L1+G), which at $365-380^{\circ}\text{C}$ was transformed into homogeneous liquid fluid.

At last, in case of $VL2 >> VL1 \approx VG >> VSB$ (such inclusions are formed at interaction of hydrothermal solutions with combustible schist) gas was dissolved in liquid HC at $230-280^{\circ}\text{C}$ with forming the biphasic liquid fluid (L2+L1). Further heating up to $350-360^{\circ}\text{C}$ leads to complete dissolution of the water phase (L1) into the HC phase (L2). Further heating up to $350-360^{\circ}\text{C}$ leads to complete dissolution of the water phase (L1) into the HC phase (L2) with formation of homogeneous fluid.

Conclusions

Thus, the present experimental study evidences that aqueous-HC fluids in Earth's interior exist in various phase states. The relationship between water solution, liquid and gaseous HC and TP parameters controls the phase states and behavior of aqueous-HC fluids.

Our data can be used for determination of the forms of HC migration and conditions of formation of oil-and-gas and gas-condensate deposits.

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EXPERIMENTAL MODELING OF DIAMOND-FORMING PROCESSES IN THE COURSE OF MANTLE METASOMATISM

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Introduction

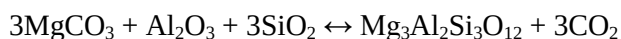
The formation of diamond or graphite in the upper mantle conditions can occur via reduction of oxidized forms of carbon – CO₂ or carbonates (Ryabchikov, 2009). It is experimentally shown, that in the diamond forming processes, concerned with the mantle metasomatism, Fe-sulfides can play a role of reducing agents for CO₂ (Gunn, Luth, 2006; Palyanov et al., 2007). Mantle oxides with variable valence of metals, namely wustite, can potentially act as a reducing agent for CO₂. The present research is directed at the modeling of redox diamond forming reactions in the course of mantle metasomatism and revealing a fluid and melt characteristics.

Experiments

The experimental investigations in the fluid-containing systems MgCO₃-Al₂O₃-SiO₂-FeS and (Ca,Mg)CO₃-Al₂O₃-SiO₂-FeO were carried out at P=6.3 GPa, in the temperature range of 1250-1750°C, with the duration of 20 hours, using a multi-anvil high-pressure apparatus of a “split-sphere” type. The methodical approach was developed to realize in the course of experiments the decarbonation reaction, releasing CO₂, and then (or in parallel) to create conditions for the redox interaction between CO₂ and pyrrhotite/wustite.

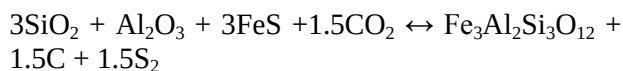
Results

The carbonate-oxide-sulfide interaction, involving pyrrhotite as a reducing agent for CO₂, results in crystallization of pyrope-almandine polycrystalline aggregate and formation of CO₂ fluid, sulfide and carbonate-silicate melts. Diamond growth on the seed crystals was observed in the temperature range of 1250-1750°C, spontaneously nucleated diamond was obtained at 1650-1750°C. The structure of quenched sulfide melt (Fig. 1), containing spheres of carbonate-silicate melt and cavities filled with CO₂, indicates that CO₂ fluid, formed via magnesite decarbonation reaction:



interacts with both carbonate-silicate and sulfide melts. At this interaction CO₂ fluid dissolves oxides, silicates and sulfides and provides the transport of these components. In the course of fluid and sulfide melt interaction the reduction of CO₂ to elemental carbon (diamond or metastable

graphite) occurs:



During this process quantity of FeO in pyrope-almandine increases up to 27 wt.%, sulfide melt enriches in sulfur and at the quench stage crystallizes as pyrite-pyrrhotite aggregate. Diamond and metastable graphite, crystallized via this interaction mainly in the cavities, were formed by excess CO₂ fluid. The occurrence in the cavities of euhedral crystals of garnet, coesite, graphite and diamond, as well as pyrite spheres, are evidence for their crystallization from fluid, and, consequently, for significant solubility of these phases in CO₂-fluid at the experimental conditions.

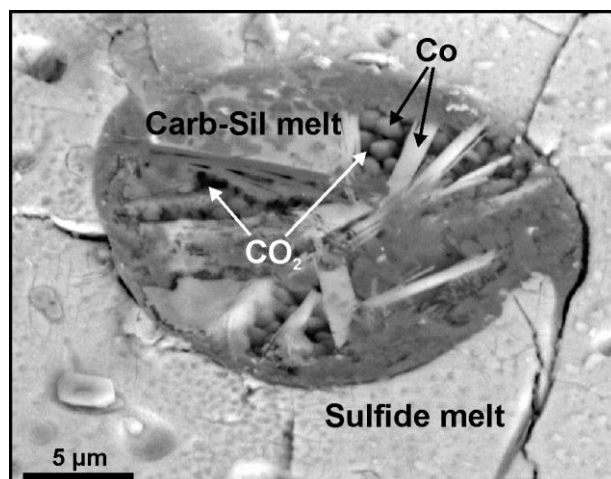
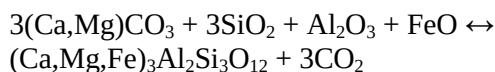


Figure 1. Immiscible sulfide and carbonate-silicate melts, penetrated by CO₂ fluid (shear at the contact with diamond).

Note: Co – coesite; Carb-Sil melt – carbonate-silicate melt.

Diamond seed crystals in the grown layers contain numerous coesite, sulfide and fluid inclusions, in other words, phases crystallized from the components dissolved in the CO₂ fluid.

The carbonate-oxide interaction, using wustite as a reducing agent, results in the crystallization of almandine and CO₂ fluid and carbonate-oxide-silicate melt formation. It was established that CO₂ fluid was generated via reaction:



According to this reaction almandine containing up to 2 wt.% CaO and MgO crystallizes. Interaction of

wustite and carbonate-oxide-silicate melt with CO_2 results in the elemental carbon formation and Fe^{2+} to Fe^{3+} oxidizing (in melt), giving rise to magnetite crystallization during the quenching:

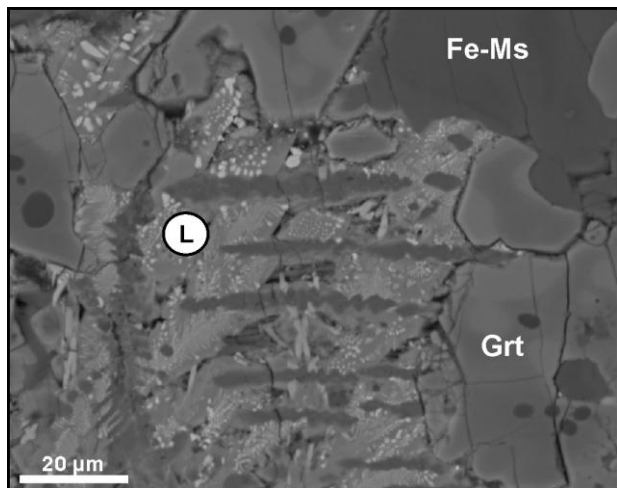
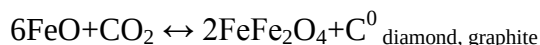


Figure 2. Carbonate-oxide-silicate melt (L) penetrated by CO_2 fluid, at the contact with garnet and Fe-magnesite (1550°C).
Note: Fe-Ms - Fe-magnesite, Grt – garnet.

The processes of partial melting of the carbonate-silicate matrix with subsequent oxidation of a melt by CO_2 fluid resulted in the total wustite-magnetite transformation. Change of $f\text{O}_2$ up to values higher than WM buffer leads to the diamond forming processes taking place only at 1350-1450°C.

Conclusions

Diamond formation processes in the course of carbonate-oxide-sulfide and carbonate-oxide interaction can be described with two principal reactions: decarbonation, accompanied with CO_2 and silicates formation and reduction of CO_2 by sulfide melt or wustite to diamond or metastable graphite. The media for diamond and graphite crystallization is carbon saturated CO_2 fluid and/or carbonate-silicate melt/fluid. It was established, that interaction of CO_2 fluid with carbonate-silicate and sulfide melts results in a saturation of CO_2 with dissolved components – carbonates, silicates, oxides, sulfides and elemental carbon. CO_2 fluid can oxidize carbonate-oxide-sulfide melt, enriching it with Fe^{3+} .

It was experimentally shown, that wustite can partly reduce CO_2 to elemental carbon – diamond or metastable graphite.

Acknowledgements

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MANTLE MINERAL- AND GLASS-HOSTED FLUID INCLUSIONS IN MANTLE XENOLITHS FROM THE CENTRAL PANNONIAN BASIN, HUNGARY: THE SIGNIFICANCE TO DETERMINE THE BULK COMPOSITION IN CO₂-RICH SYSTEM

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Introduction

The main aim of this work is to determine the bulk composition of the studied mantle fluid inclusions to better understand the fluid system that interact with the upper mantle material. Deep-seated fluid inclusions provide useful information and direct evidences on the composition, distribution and role of fluids in the deep lithosphere, which is one of the most active research areas in the earth sciences (e.g., Andersen and Neumann, 2001; Frezzotti, Peccerillo, 2007; Scambelluri et al., 2009; Hidas et al., 2010). Upper mantle xenoliths, containing large amount of fluid inclusions, were selected for this study from localities of Tihany and Szentbékállá (Bakony-Balaton Highland Volcanic Field, Pannonian Basin, Hungary). Besides, synthetic fluid inclusions were also applied to calibrate fluid properties in the mantle xenolith-hosted ones.

Host xenoliths

Both the Tihany and Szentbékállá peridotites are coarse-grained, orthopyroxene-rich spinel peridotites. The Tihany peridotites display poikilitic texture with U-shaped REE characteristic of clinopyroxenes suggesting that a silicic melt reacted with the mantle. The sample from Szentbékállá is a clinopyroxenite-veined peridotite xenolith, referred to also as composite xenolith, representing the crystallization of a mafic melt, which solidified as brownish glass-bearing clinopyroxenite vein in harzburgite wall rock. The peridotite wall rock was affected by modal metasomatism (e.g. clinopyroxene corona around orthopyroxene) by the same mafic melt.

Fluid inclusions at room temperature

Fluid inclusions are, observed dominantly in orthopyroxene subsequently in clinopyroxene and in olivine, occurring in negative crystal shape and in size up to 70 µm. Furthermore, interstitial brownish glass also encloses fluid inclusions. These latter inclusions are characterized by perfectly spherical shape, and sizes up to 65 µm. At room temperature the mantle mineral-hosted fluid inclusions contain mainly one visible phase. By using the definition of Roedder (1984), they can be

classified as either primary (single fluid inclusions or along growth zones) or pseudosecondary fluid inclusions. Rarely solid rhombohedral shaped crystals (up to 15 µm) also occur in the fluid inclusions. The solid-containing fluid inclusions can be characterized as having similar fluid/solid volume ratio (80-85/15-20). During microthermometric studies there was one observable melting event between -56.6 °C to -56.9 °C, typical for pure CO₂ fluid, based on n=98 measurements. Infrared spectroscopy confirmed the dominance of CO₂ in the glass-hosted bubbles. In each case the homogenization occurred into the liquid phase. The homogenization temperature ranged from -55 °C to 28 °C. As a consequence the fluid inclusions show wide range of density between 0.66-1.16 g/cm³ with an average of 1.05 g/cm³. Generally, the smallest inclusions preserved the highest CO₂-density fluid. Room temperature Raman analyses revealed the presence of H₂S as additional volatile and magnesite and quartz as solid phases within the inclusions. In case of the highest density fluid inclusions, peak of dissolved H₂O in CO₂ was also detected even at room temperature. Rarely, focusing at the wall of the fluid inclusions a band of liquid H₂O was also found by Raman spectroscopy.

Fluid inclusions at moderate (≤150°C) temperature

Moderate temperature Raman analysis revealed the presence of H₂O in each fluid inclusion as a characteristic band corresponding to the dissolved H₂O in the CO₂-rich phase (3630-3647 cm⁻¹). Raman spectra have been taken at different temperatures. Comparing the integrated peak area ratio of CO₂ and that of dissolved H₂O at different temperatures, the total homogenization and the relative bulk composition have been determined based on peak ratios (after Dubessy et al., 1989; Fig. 1). The total bulk composition of the fluid inclusions in the Tihany peridotites are as follows: 89-98 mol.% CO₂, 2-11 mol.% H₂O, 0.3-1.0 mol.% H₂S.

Capillary synthetic fluid inclusions

As already pointed out by Chou et al. (2008) the fused silica capsules (capillary fluid inclusions)

can be applied to a wide range of problems of interest in fluid inclusion and hydrothermal research, such as creating standards for the calibration frequency shifts in Raman spectrometers.

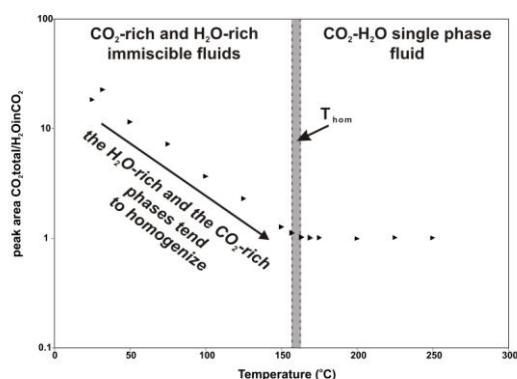


Figure 1. An example for the variation of the CO₂/H₂O peak area as a function of temperature in a fluid inclusion
Note: T_{hom} is the abbreviation of total homogenization temperature.

We applied it to calibrate the molar percentages of the CO₂ and H₂O in natural fluid inclusions calculated by the Raman spectra. The synthetic fluid inclusion set can be characterized by CO₂-H₂O fluid system with high CO₂/H₂O ratios, which is the case in the mantle xenoliths, with a relative amount of H₂O varying between 1 and 6 mol.% (Fig. 2).

25 °C

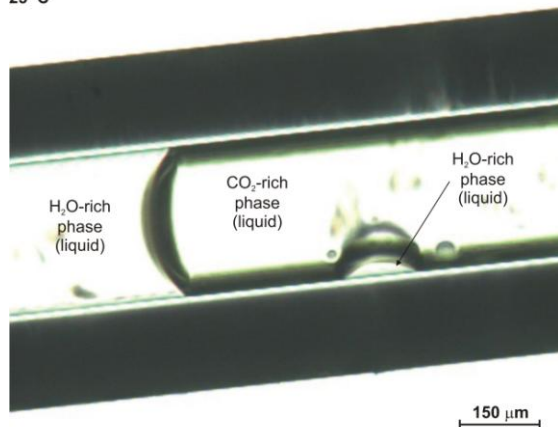


Figure 2. Photomicrograph of CO₂-rich H₂O-bearing synthetic capillary fluid inclusion at room temperature.
Note: the picture was taken after putting the capillary in the centrifuge.

Furthermore, preliminary results of experiments on synthetic capillary fluid inclusions show that the Raman peak position of the dissolved H₂O in the CO₂-rich phase strongly depends on the density of the CO₂-rich phase. Higher the CO₂-density, lower the peak position.

Concluding remarks

1) The fluid inclusions from mantle peridotites represent CO₂-rich, H₂S- and H₂O-bearing fluid

system as proved by Raman microspectroscopy at elevated temperatures. The results suggest that even 11 mol.% H₂O may remain undetected or underestimated if heating experiments compiled with Raman microspectroscopy is not applied.

2) Considering that the magnesite was detected in orthopyroxene- and olivine-hosted fluid inclusions, they are likely a reaction product between the CO₂-rich fluid and the host orthopyroxene and olivine with a co-precipitation of quartz.

3) The use of capillary synthetic fluid inclusions revealed the influence of CO₂ molecules on the perturbation of the energy of the symmetric stretching of the H₂O in CO₂.

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MAGMATIC FLUID EVOLUTION ASSOCIATED WITH EPIZONAL SILICIC PLUTONS

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Introduction

Intermediate composition hydrous silicic magmas emplaced at shallow depths in the Earth's crust show a systematic temporal and spatial fluid evolution history. During and following emplacement, hydrous magmas reach volatile saturation due to pressure decrease ("first-boiling") and crystallization ("second boiling") and exsolve a magmatic aqueous phase. Fluid inclusions that trap the magmatic fluid show room temperature phase relations, compositions, and microthermometric characteristics indicative of their trapping environment. In metal-bearing systems, the magmatic fluids may transport metals from the magma and the distribution of fluid inclusion types can be related to the distribution of metals and provide vectors towards the portion of the system most likely to contain economic mineralization.

Model Description

In this study, aqueous phase stability is modeled as a function of temperature, pressure, and composition of the system. The temperature at any position in the system is based on published numerical models of convective cooling of shallow plutons, and the pressure is based on lithostatic/hydrostatic pressure gradients assuming the boundary between hydrostatic and lithostatic pressure conditions corresponds to the brittle-ductile transition at the 400°C isotherm. The compositions of magmatic aqueous fluid phases are adequately approximated by the system H₂O-NaCl, and thus the PVTX characteristics of the magmatic fluids are easily estimated at any temperature and pressure. The evolution of the room temperature phase relations and homogenization temperatures of fluid inclusions that trap the magmatic fluid at various times and locations in the system are then calculated from the known temperature, pressure, composition and density of the fluid.

The magmatic fluid has been modeled at four different stages during the crystallization of a "Burnham Model" porphyry magma, ranging from immediately following initial volatile saturation to complete crystallization. The distribution of phase fields through a cross-section of the pluton (liquid, vapor, liquid+vapor, vapor+halite) is based on a primary magmatic fluid composition of 10 wt.% NaCl. The fluid inclusion characteristics are then predicted over five depth profiles from the flank to the center of the pluton at each time.

Results

During the earliest stages of crystallization, a halite + vapor field exists in the upper portions of the magmatic system (Fig. 1). Fluid inclusion assemblages (FIAs) trapped in this environment would be characterized by vapor-rich inclusions (without coexisting liquid-rich or halite-bearing inclusions) (Fig. 2). Owing to the low density of the trapped vapor, liquid would not be visible in these inclusions, except in the largest, most irregularly-shaped inclusions. The vapor + halite fields is bounded below by a field in which high salinity liquid and low salinity vapor coexist (Fig. 1), and FIAs trapped in this environment contain coexisting halite-bearing and vapor-rich inclusions (Fig. 2). In the deepest levels of the system, a small vapor field exists along the flanks of the magma body (Fig. 1), and FIAs trapped here will be characterized by vapor-rich inclusions, but with a small amount of aqueous liquid phase visible in most inclusions. Importantly, coexisting halite-bearing and vapor-rich inclusions are restricted to the immediate vicinity of the pluton and do not extend into the surrounding wallrock.

During the intermediate stages of crystallization, the vapor + halite field becomes smaller and moves downward, while the vapor fields along the flanks of the pluton expand and move upwards. The result is that the field in which high salinity liquid and low salinity vapor coexist has become smaller. Fluid inclusions trapped in the upper portions of the system may thus show early coexisting halite-bearing and vapor-rich inclusions followed in time by FIAs composed of only vapor-rich inclusions with no visible liquid. Similarly, in the deep parts of the system along the flanks, early FIAs composed of coexisting halite-bearing and vapor-rich inclusions would be followed in the paragenesis by FIAs composed only of vapor-rich inclusions with recognizable liquid.

With increasing crystallization and downward migration of the melt-rock interface, the vapor + halite field at shallow levels disappears and the high salinity liquid + vapor field also disappears as the liquid field above and the vapor field below expand and merge. As a result, fluids migrating from depth would evolve from "vapor" to "liquid" without crossing a two-phase (liquid + vapor) field. Thus, low density fluids exsolved from the magma at depth could migrate to shallow levels and become liquids, also transporting metals from the

deeper to the more shallow parts of the magmatic system.

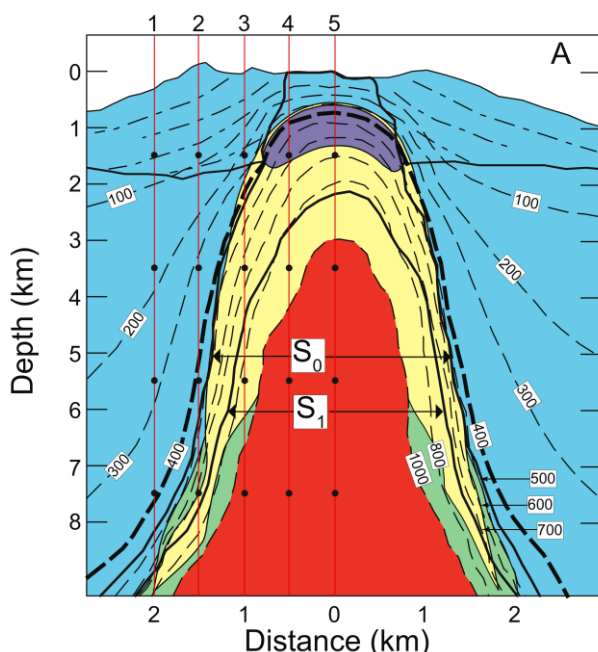


Figure 1. Schematic cross-section of a crystallizing pluton showing fluid stability fields.

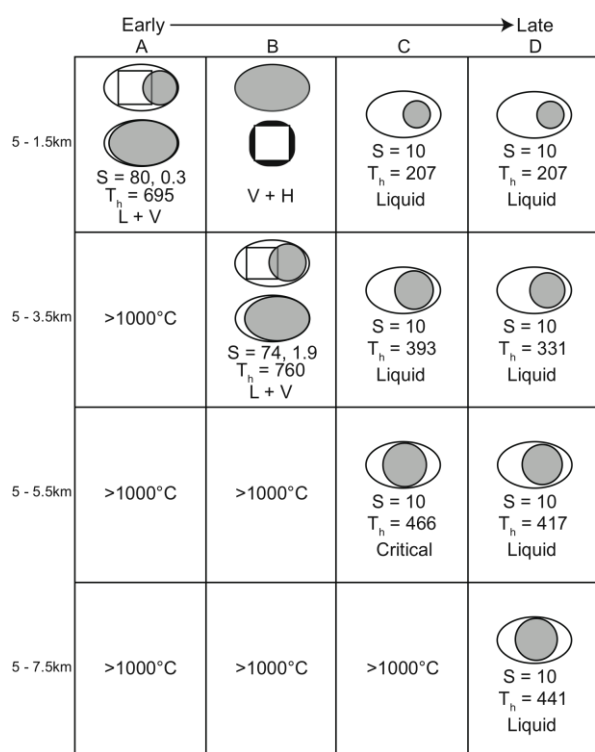


Figure 2. Phase relations of fluid inclusions trapped at different times along depth traverse "5" shown in Figure 1.

The copper ore zone in porphyry copper deposits is centered on the causative intrusive (Sillitoe, 2010). The results of this study are in close agreement with studies that report high-salinity, halite-bearing fluid inclusions coexisting with low-salinity vapor-rich inclusions associated

with veins and alteration in the copper ore zone in the cores of these systems (Nash, 1976; Bodnar, 1995). The model also predicts the existence of inclusions trapped in the one-phase field with near critical density that are characteristic of deeper porphyry systems, as well as a vapor+halite field at shallow levels during the early crystallization history.

The results of this study have implications in exploration for porphyry copper mineralization. Importantly, rocks containing halite-bearing fluid inclusions are predicted to occur only within the pluton and in the immediately adjacent wallrocks, and this also corresponds to the mineralized portion of the system. Fluid inclusions thus provide a tool to direct the explorationist to that part of the magmatic-hydrothermal system that is most likely to host mineralization (Roedder, Bodnar, 1997).

The application of fluid inclusions in exploration for porphyry copper deposits is best applied in regions where little or no outcrop exists, such as in tropical regions. Nash (1976) notes that "Fluid inclusions in quartz survive even severe weathering in the tropics as shown by studies of deposits in Puerto Rico (Cox and others, 1975). Hence, inclusions can be examined in quartz in residual soils or laterite to determine the presence of hydrothermal alteration. By study of the residual quartz grains it is possible to distinguish quartz phenocrysts from hydrothermal and supergene quartz on the basis of fluid inclusion types and abundance. Hydrothermal activity is clearly indicated by appropriate fluid inclusions, even in samples in which weathering destroys all textural and mineralogical evidence of hydrothermal alteration." In this presentation, an example of the application of fluid inclusions in exploration for porphyry copper mineralization in tropical regions will be presented.

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THE ORE AND CARBONACEOUS FORMATIONS OF MARMAROSH MASSIF (UKRAINIAN CARPATHIANS) AS A RESULT OF DEEP-SEATED FLUID INCORPORATION

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Introduction

Connection between regional geological processes and local processes of mineral and ore genesis in the conditions of metamorphism can be established by research of fluid inclusions which represent unique possibility to determine of temperature, pressure and chemical features of these processes. Also fluid inclusions allow defining functioning intervals of mineral-forming solutions, parameters of existence and migration of fluids.

Geological setting of area of investigation

The Marmarosh massif is an important structural element of the Eastern Carpathian Mountains, which differs by the geological features from the other structural-facial zones of the Folded Carpathians. The Marmarosh massif is a result of complicated tectono-magmatic evolution, characterized by formation of multiple multidirectional tectonics. Metamorphic rocks of the massif have been formed under the influence of the processes of medium- and low-temperature metamorphism and metasomatism. Two metamorphic complexes of different ages are distinguished in the geological structure of the Marmarosh massif: the Bilyi Potik complex (amphibolite facies) of Upper-Precambrian age and the Dilove complex (greenschist facies) of Lower-Paleozoic age.

Metamorphic complexes of the Marmarosh massif in Riphean-Early-Paleozoic time have been under the influence of metamorphism and folding, further have been changed overtime by several phases of Alpine tectonogenesis.

Eroded surface of different parts of the metamorphic complex overthrust by slight metamorphized fillite, carbonate and carbonaceous formations of Middle Carboniferous–Permian, terrigenous-carbonate and sedimentary-volcanic sediments of Triassic-Jurassic age and by the thick flysch complex of Cretaceous and Paleogene. The massif is thrust over the Cretaceous black flysch of the Rakhiv nappe.

Foremost Marmarosh massif is known as an ore region. Here are known the stratiform gold ores (polygenic Saulyak deposit), polygenic stratiform ore showings of pyrite-polymetallic ores, showing of iron and manganese ores, closely connected with

carbonaceous rocks. Along with that, here the natural gas shows were fixed. By the mapping drilling within the metamorphic rocks, the powerful enough ejections of natural gas from carbonaceous metamorphic rocks of massif or black flysch of underthrust structures were observed.

Direct relationships between high-grade metamorphized carbonaceous (metaanthracite) formations and ore deposits and hydrocarbon showings to the total genesis of fluids can testify.

Fluid inclusion researches for carbonaceous formations

Fluid inclusions in quartz of uneven-aged metamorphic rocks of massif were investigated. Most inclusions are located along healed fissures, which intersect in various directions. They have small dimensions, preferably less than 0.001 mm, so only in rare cases, made possible the application of thermometric studies (Fig. 1).

Fluid inclusions in quartz from uneven-aged carbonaceous schists of the Marmarosh massif often with sulphide mineralization characterized by predominance of methane (54.7-100 vol.%). Carbon dioxide and nitrogen missing, or their content is limited – 1.2-35.9 and 4.4-19.1 vol.%, respectively (Naumko et al., 2009).

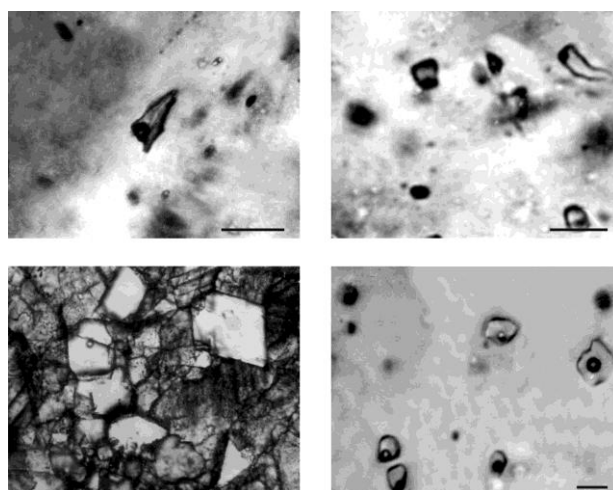


Figure 1. Typical secondary fluid inclusions in quartz from metamorphic rocks of the Marmarosh massif. Scale bar is 20 μm .

Quartz from carbonaceous schists of the Berlebach suite (V- C_{1br}) characterized by methane (59.7-98.6 vol.%). Only in rare cases, the content

decreases to about 7.5-33.1 vol.%. Carbon dioxide (1.9-35.4 vol.%) and nitrogen (0.6-5.4 vol.%) are in subordinate amounts (Fig. 2).

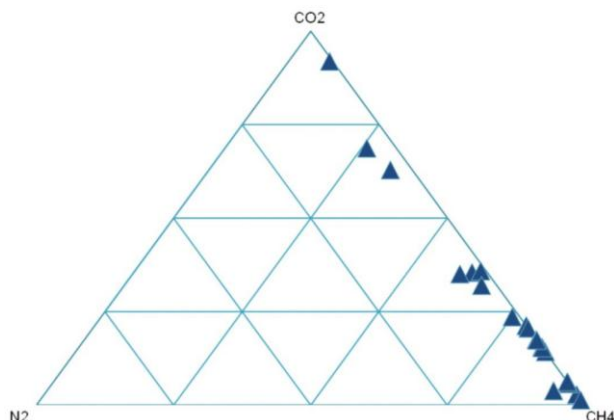


Figure 2. Volatile composition of fluid inclusions in quartz from metamorphic rocks of the Berlebach suite (V-C_{1br}).

In some areas in quartz from the Bilyy Potik and Dilove suites experiencing a sharp predominance of methane (79-94 vol.%) at low content of carbon dioxide and nitrogen. Some samples contain heavy hydrocarbons – C₃H₆ and C₃H₈. Fluid inclusions in quartz of coeval metamorphic rocks of the Chyvchyn Mountains are characterized by total predominance of methane and heavier hydrocarbons in their composition. The homogenization temperature of these inclusions is 250-300 °C.

Fluid inclusion researches for ore formations

Quartz from the Saulyak deposit contains early and late secondary gas-liquid two-phased fluid inclusions with filling 80-90%. Their homogenization temperature was measured by the V.A.Kalyuzhnyi thermometric stage. It was revealed that homogenization temperature of early secondary inclusions in quartz of gold-quartz-mica-carbonate ore type is 260-270°C, whereas that of late-secondary ones – 160-175°C. In quartz of gold-quartz-sulphide ore type fluid inclusions are homogenized at temperatures 150-210°C.

In the volatile phase of fluid inclusions in quartz and carbonates associated with gold within the Saulyak deposit from adit No 2 carbon dioxide and nitrogen dominate (1.56-88.01 and 11.56-88.01 vol.%, respectively). Methane content is 1.38-48.24 vol.%. The same trend is observed in quartz-carbonate rocks from adit No 1 (Fig. 3). Here carbon dioxide (18.05-74.94 vol.%) and methane (12.76-75.28 vol.%) dominate in the gas phase. The nitrogen content is lower (0.28-15.85 vol. %).

Fluid inclusions with remarkable predominance of nitrogen in the gas phase are also known. In particular, inclusions in quartz and barite from the Kamin'-Klyovka sulphide ores show high

nitrogen content (46.45-98.65 vol.%), carbon dioxide and methane are minor (0.81-13.24 and 0.54-46.55 vol.%). In rare cases, the same pattern traced in samples of gold-containing quartz of area within the Bilyy Potik stream, which fluid inclusions contain about 48.0-84.33 vol.% of nitrogen, carbon dioxide and methane are 4.32-28.0 and 11.35-24.0 vol.%, respectively.

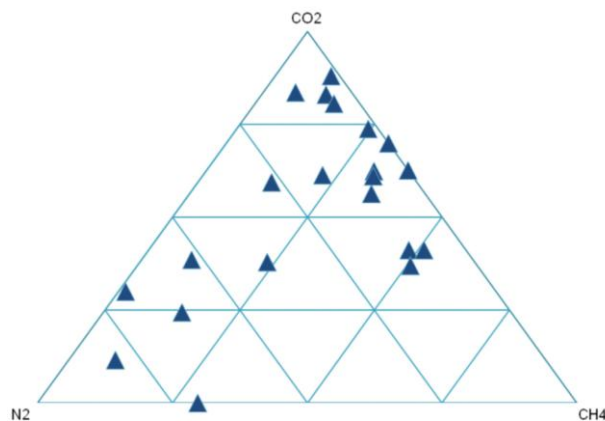


Figure 3. Volatile composition of fluid inclusions in quartz associated with native gold (the Saulyak deposit).

Conclusions

The association of ore showings to tectonic zones, their close relationship with organic matter and carbonaceous horizons indicates that during the geodynamic evolution of the Carpathians there was reusable incorporation of the deep-seated high-temperature fluids, as it was shown by Naumko (2006). Multiple tectonic structure of this region shows that the main channels for the fluids were fault zones of deep origin. By subvertical migration within hydrocarbon-water systems the hydrocarbon and ore components were imposed, which was the reason for the formation of native gold, ores and hydrocarbon deposits within of metamorphic complexes of the Marmarosh massif.

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FLUID REGIME OF LAMPROPHYRE DIKES FORMATION, SE ALTAI AND NW MONGOLIA

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Introduction

Dike complexes of calc-alkaline and alkaline lamprophyres represented by kersantite, minette, camptonite and other rocks, are prominent features for many ore districts with the Sn-sulfide, Sn-Ag, Sb-Hg Ag-Ni-Co, Au-As, Ag-Pb-Zn and other types of mineralization. They are localized independently, and separated in space from the other magmatic rocks, or they can be close in time and in space to the areas of granite and mafic magmatism, that affect the character of associated mineralization. The study of fluid regime of lamprophyre formation is a very important problem in investigation of the mantle-crust ore-magmatic systems and genesis of produced hydrothermal mineralization. A large area of lamprophyre dikes, established by R.V.Obolenskaya (Obolenskaya, 1971) in the composition of the Chuya complex, is located at the SE Altai and NW Mongolia, where it coincides with large ore district with the Ag-Sb, Sb-Hg, Mo-W-greisen, and Ni-Co-As mineralization. The length of the area from North-West to South-East is about 500 km at the width of 200 to 250 km. Two stages of development of the magmatic and ore-forming processes are recognized: 1) dolerite dikes with the age 259.5 Ma and lamprophyre dikes with the age ranging from 250 to 242 Ma; 2) dolerite dikes (242-240 Ma) and later lamprophyre dikes (237-234 Ma). Hydrothermal mineralization associated with these magmatic rocks in space also shows two formation stages: 1) Ni-Co-As and U (258-250 and 240 Ma); 2) Ag-Sb, Cu-Hg-Sb-Ba and Hg (240 and 234-231 Ma). Genetic links of the Ni-Co-As, Ag-Sb and Hg mineralization with mafic and alkaline mafic magmatism are proved not only their close association in space and time, but also by isotope composition of helium extracted from fluid inclusions in the minerals of ores (Pavlova et al., 2008; Pavlova, Borisenko, 2009; Naumov, 2007). Fluid regime of lamprophyre dikes formation was studied on the example of two local areas in the South Chuya and Yustid districts. Host rocks for lamprophyre dikes in the first of them are volcano-sedimentary Cambrian rocks metamorphosed to the different grade, and Devonian black shales in the second one.

Inclusions study

The study is devoted to the primary melt, crystal-fluid, fluid and gaseous inclusions found in

the minerals of lamprophyre dikes (apatite, K-feldspar and pyroxene) and the secondary gas-liquid and gaseous inclusions in xenogenic quartz from lamprophyres (Fig. 1). Melt inclusions from lamprophyre minerals of the South Chuya and Yustid areas are crystallized to a different degree and consist of fine-grained aggregate, gas phase and varying quantity (from 1-5 to 80%) of large solid phases. Orthoclase, phlogopite and albite were found using Raman spectroscopy, and anhydrite, calcite, dolomite, halite, tainialite $\text{KLiMg}_2\text{Si}_4\text{O}_{10}\text{F}_2$, jogannite $\text{Cu}(\text{UO}_2)_2(\text{OH}/\text{SO}_4)_{2.8}\cdot\text{H}_2\text{O}$ and other minerals were observed in completely crystallized inclusions. Heating of these inclusions up to 1100-1200°C resulted in melting of solid phases with formation of immiscible phases of silicate and salt melts. Their volume ratios vary in different inclusions pointing to heterophase state of the melt, which consisted from immiscible silicate, silicate-salt and salt phases. Crystal-fluid inclusions contain varying quantity of solid phases, H_2O solution, and gaseous phase. Moreover, later gas-liquid two- and three-phase inclusions with crystals of NaCl and other salts, and gaseous inclusions were also present. Liquid phase of the inclusions has low eutectic temperature -86°C and salt concentrations ranging from 22 to 35 wt.%, among which Na, K and Fe chlorides predominate. The probability of finding sulfates in solutions of fluid inclusions is consistent with presence of anhydrite and jogannite in the silicate-salt and crystal-fluid inclusions in the minerals of lamprophyres. In the silicate-salt and crystal-fluid inclusions high contents of ore elements are found using LA-ICP-MS: Fe, Mn, Ba, Pb (1 – 0.1%), Zn, Cu, Cs, Sb, Mo, U and Mo (0.001 – 0.1 ppm).

Numerous secondary inclusions of carbonate-sulphate composition and associated high density gaseous inclusions are found in the quartz of granite xenoliths and quartz veins. Composition of gaseous inclusions in the lamprophyres of the South Chuya and Yustid districts is considerably different. Quartz from xenoliths in lamprophyres of the South Chuya district contains abundant secondary gaseous inclusions, which are mainly represented by carbon dioxide (CO_2 100-99.7 mol.%, N_2 0.3-0 mol.%) or nitrogen (N_2 100-0 mol.%, CO_2 18.3-0 mol.%, sometimes H_2S up to 0.04 mol.%) composition. The temperature of CO_2 melting in carbon dioxide containing inclusions ranges from -62.7 to -57°C,

homogenization temperature ranges from -11 up to +18°C, and the density of carbon dioxide from 0.63 to 0.56 g/cm³. Temperature of N₂ homogenization ranges from -164 to -156°C, consistent with its density. No methane was detected in these inclusions.

Quartz from xenoliths contains the secondary carbonate-sulphate inclusions (anhydrite, calcite, velanite $\text{Ca}_5\text{Cu}_2[\text{Si}_6\text{O}_{17}](\text{CO}_3)(\text{OH})_24\text{H}_2\text{O}$, other silicate and gaseous phases) associated with secondary inclusions of high density gases. The secondary gas inclusions in xenogenic quartz from lamprophyres of the Yustid district contain CO₂ from 100 to 92.2 mol.%, N₂ 7.7-0 mol.%, and CH₄ 0.1-0 mol.%. Temperature of carbon dioxide homogenization ranges from +15 to +31°C at the density 0.8-0.51 g/cm³. There are nitrogen-methane inclusions in the interstitial quartz of lamprophyres of the Yustid district, with CH₄ content reaching 3 mol.%, and CO₂ is absent. Gas inclusions discovered in K-feldspar from pegmatite hosted in lamprophyre dikes have N₂-CO₂ composition (CO₂ 78.3 mol.%, N₂ 21.7 mol.%). Considerable difference of methane contents in the gas phase of fluid inclusions in the minerals of lamprophyres from the South Chuya and Yustid districts provide evidence of different redox potentials of magmatic fluids. In our opinion, it can be related to the influence of composition of the host rocks containing lamprophyre dikes: thick (4-6 km) sequence of carbonaceous terrigenous sediments in the Yustid district and metamorphic rocks in the South Chuya district. Methane-nitrogen-carbon dioxide composition of magmatic fluids in lamprophyres found in the black shale sediments is also characteristic of other districts such as northern and southern flanks of the Verkhoysansk fold belt. Nitrogen-carbon dioxide composition is characteristic feature for alkaline mafic rocks hosted by magmatic or metamorphic rocks (Pamir, Aldan shield).

Conclusions

The obtained data indicate that alkaline-mafic magmas which formed lamprophyres of the Chuya complex are highly saturated by fluids. This fact defines the mode of their evolution and formation of immiscible silicate, silicate-salt and salt melts, and magmatogenic fluids. This corresponds to the previously described various schemes of evolution of alkaline-mafic, alkaline-ultramafic, and lamproitic magmas (Panina 1985, 2005; Panina, Usoltseva, 2008; Solovova et al., 1996; Naumov et al., 1988; Andreeva, 2000). An important factor for the endogenic ore formation resulted from these data is the origin of "oxidized" sulphate, sulphate-chloride and sulphate-carbonate fluids at the final

stages of differentiation of such melts. Their high extraction ability is responsible for the extraction from the melt and borrowing from host rocks of the ore elements such as Fe, Co, Ni, U Ag, and Cr, which defines the specific character of metallogeny of alkaline and alkaline-mafic complexes.

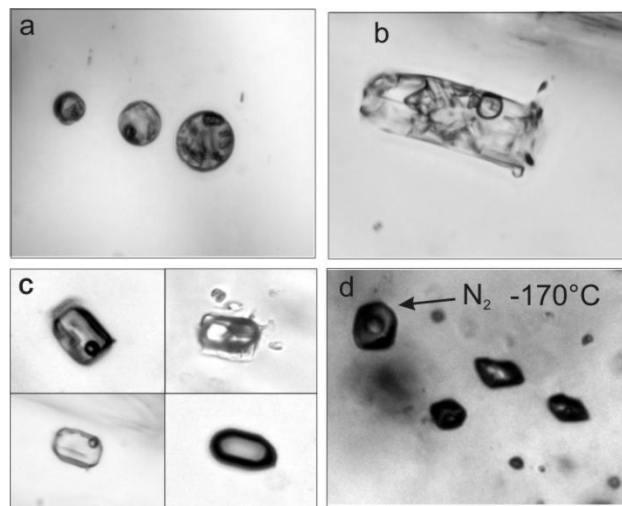


Figure 1. The primary melt (a), crystal-fluid (b), fluid and gaseous (c) inclusions found in the minerals of lamprophyre dikes (apatite, K-feldspar and pyroxene) and the secondary gas-liquid and gaseous inclusions (d) in xenogenic quartz from lamprophyres.

We acknowledge the financial support from RFBR (grants 08-05-00915 and 10-05-00730).

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CONTENT OF AU, SB, TE, AS AND BI IN CHLORIDE-RICH OXIDIZED HETEROPHASE FLUID AT TEMPERATURE 700°C AND PRESSURE 109-124 MPa

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Introduction

Heterophase state of ore-forming fluids has been established for a number of hydrothermal deposits associated with the development of ore-magmatic systems of various geochemical profiles. The process of heterogenization is distinctly manifested at porphyry Cu-Mo-Au, some types of Cu-Ni-Pt (Bushveld), Au-skarn (Au-Cu-Te type), pegmatite (Ermakovskoe Be-deposit) and carbonatite (Mushugai-Khuduk, Krestovskii) deposits which are characterized by oxidized state of ore-forming fluids corresponding to sulphate-sulfide equilibrium (Andreeva, 2000; Borisenko et al., 2006; Naumov et al., 1995; Reif et al., 2004; Zhitova et al., 2004 and many others). The study of ore elements content in syngenetic gas and water-salt inclusions in ore minerals revealed the contrast distribution of metals between the gas and water-salt phases of heterophase ore-forming fluid during formation of these deposits. The study of physico-chemical conditions, responsible for the contrast distribution of ore metals between the phases of heterogenic fluids provide insights into the understanding the reasons of formation of the associated magmatogenic and epithermal mineralization, belonging to one geochemical profile and similar in time of formation.

Inclusions study

To study the regularities of distribution of ore-forming elements (As, Sb, Te, Au, and Bi) between gas and water-salt phases of heterophase hydrothermal oxidized fluid at P-T conditions of its separation from melt we have synthesized fluid and melt inclusions corresponding in composition to supercritical gas and water-salt fluid phases as well as silicate melt phase of hydrothermal-magmatic system (Fig. 1).

In the experiments on synthesis of inclusions in quartz we used autoclave technique with applying golden ampoules (Balitskiy, 2008). Fluid inclusions formed during the quartz growth at 700°C in four autoclaves with various fillings and pressures from 100 to 130 MPa within 5 days in oxidized ($\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$) alkaline environment (with aegirine). The temperature gradient along quartz inoculant was 1.71 °C/cm at temperature 700°C. To provide silica excess necessary for the quartz growth, we loaded Na metasilicate into the ampoule. The aqueous solution contained NaCl 20

wt.%, Rb – 440 ppm, Cs – 430 ppm, Ba – 560 ppm, Te – 150 ppm, As – 100 ppm, Sb – 70 ppm, Bi – 1000 ppm. Rb, Ba and Cs were introduced into the solution as additional inner standards to estimate As, Sb, Bi, and Au concentrations by LA-ICP-MS technique. To prepare a solution containing As, Sb, and Bi we used a chemical extra pure reagents $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Bi}(\text{ClO}_4)_3$, and prefabricated solutions of Sb and As in HCl. Gold was supplied from golden ampoule in which the run was carried out.

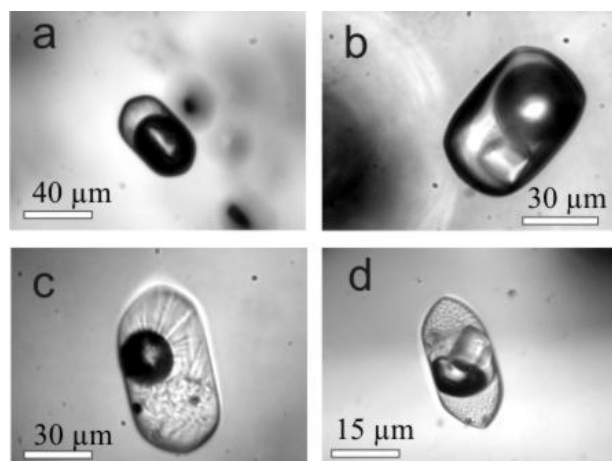


Figure 1. Gas (a), three-phase with halite (b), partly crystallized melt (c) inclusions and combined inclusion (d).

NaCl concentration in synthesized two- and three-phase fluid inclusions was determined by cryometry which allowed us to estimate NaCl concentration in gas and water salt phase present in the autoclave during inclusion trapping. In addition, using Suriray and Kennedy (1962) data for the $\text{H}_2\text{O-NaCl}$ system at high pressures and temperatures we attempted to evaluate the medium pressure during the experiment. The pressure during fluid inclusion trapping was close to 109, 113, 117, 124 MPa while the temperature range of their trapping was 700-690°C (Fig. 2).

Inclusions with no signs of combined trapping were analyzed using LA-ICP-MS techniques to determine As, Sb, Te, Au, and Bi contents. We used glass NIST-614 as an outer standard and Na was used as an inner standard whose concentration was determined by cryometry method. According to microprobe analysis, the resulting experimental silicate melt contained SiO_2 – 73.2-67.6, FeO – 16.2-4.0, Na_2O – 6.1-0.5, Cl 1.1-0.4 wt.%.

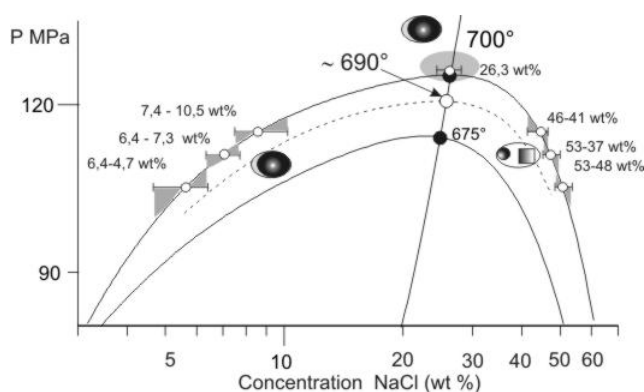


Figure 2. Trapping conditions (T, P) of fluid inclusions and their phase composition and concentration of NaCl. Isotherms 700°C-675°C, showing composition of the coexisting gases and liquids, are according to Sourirajan and Kennedy (1962).

The experimental data indicate that at temperature 700°C the distribution of As, Sb, Te, Au, and Bi in gas and water-salt phases of fluid-magmatic system depend on the pressure. Thus, in supercritical fluid which existed at pressure 124 MPa in equilibrium with silicate melt As concentration reaches (in average) 180 ppm, Sb – 2250 ppm, Au – 66 ppm, Te – 1.4 ppm, Bi – 340 ppm. With pressure dropping below critical point (down to 117 MPa) the gas phase contained in average As – 45 ppm, Sb – 5.5 ppm, Te – 1.9 ppm, Au – 0.2 ppm and Bi – 6 ppm. Water-salt phase at this pressure contained As – 440 ppm, Sb – 690 ppm, Au – 640 ppm, Te – 2.7 ppm, and Bi – 70 ppm. Pressure drop down to 110 MPa results in the enrichment of gas phase in ore elements by more than two orders of magnitude, whereas in the water-salt phase, on the contrary, the concentration is lower at least an order of magnitude As – 90 ppm, Sb – 53 ppm and Au – 22 ppm. A decrease in Te and Bi concentrations in both gas and water-salt phases with pressure increase in our experiments is most likely due to the reaction of these metals with the substance of gold ampoule. No essential changes occur in the concentration of ore elements in silicate melt at pressure increase. Our conclusions are as following:

1) Supercritical oxidized chloride-water fluid coexisting with silicate melt is a powerful extractor of As, Sb, Te, Au, and Bi.

2) Water-salt chloride phase of oxidized heterophase fluid has the highest concentrations of ore-forming elements As, Sb, Te, Au, and Bi at P-T conditions close to subcritical.

3) Pressure decrease results in the formation of ore metal enriched gas fluids due to the strong redistribution of As, Sb, Te, Au, and Bi between water-salt and gas phases.

Conclusion

The experiments confirmed a high metal content in oxidized fluids and an important role of magmatic fluid heterogenization responsible for the geochemical specialization of its individual phases which has been established previously on the examples of numerous natural objects (Borisenko et al., 2006). The separate migration of water-salt and gas phases towards the surface, a change in their aggregate state manifested in permanent heterogenization at the decrease of pressure and temperature, defines subsequent contrast redistribution of ore elements between the newly formed fluid phases. This could explain the spatial and temporal association of mineralization of the same geochemical profiles but different in deep levels in the ore regions with large-scale gold concentration in porphyry, skarn, and epithermal deposits (Kovalenker et al., 2006).

We acknowledge the financial support from RFBR grants 08-05-00915 and 10-05-00730.

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METAL CONTENT IN OXIDIZED SULPHATE FLUIDS OF THE INAGLI ALKALINE MASSIF (CENTRAL ALDAN)

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One of compositionally specific endogenic fluid types is oxidized fluids separating during crystallization of alkaline-mafic, alkaline and ultra alkaline magmatic melts (Andreeva, 2004; Panina, 2000; Naumov et al., 2008; Borisenko et al., 2006). The specific feature of such fluids is the presence of Ca-, Na-, Fe-, K-sulphates along with chlorides of these elements. Gas phase of these fluids is represented by CO₂ and N₂ with no CH₄. The identification of metal content of such fluids is of the utmost interest for interpretation of the genesis of a number of deposits such as carbonatite, TR, U, porphyry Cu-Mo and others. As an example of such oxidized fluids are sulfide-silicate fluids recognized by V.B. Naumov et al. (2008) in the Inagli chrome-diopside inclusions.

The Inagli massif is one of the plutons of K-alkaline rocks confined to the southern framing of the Siberian platform which represent a belt extending from Lake Baikal to Western Aldan and between the northern part of the Aldan shield and Siberian platform in the south as well as in the north of the platform in the eastern Priamur. The specific feature of the Inagli massif of K-alkaline rocks, along with many other massifs from this group (Burpala, Synnyr, Sakun, Murun, Ingili, Bilbinskiy, Konder, and Tomtor), is its differentiation from alkaline-ultramafic rocks to granites (this rock spectrum is fully represented in the Murun and Bilibin massifs) and formation of lamproite rock group as product of intrusive rocks differentiation; many massifs contain carbonatites as the end members of differentiation (Vladykin, Novikova, 2003). In addition to differentiation massifs exhibit features of magmatic segregation. These processes proceed both in silicate magmas and in silicate-carbonate melts-fluids producing ore-bearing hydrothermal solutions (Naumov et al., 2008). Numerous deposits of chromite, apatite, K-Al raw material – synnyrites, ceramic raw materials, (Nb, REE, Ba, Sr)-carbonatites, gems - charoite, Cr-diopside (pegmatites), dianite as well as hydrothermal ore deposits of Pt, Au, Ag, Cu, Mo, Pb, Zn, U, Th, Nb, Ti are associated with these massifs. Therefore, the study of ore content of magmatogenic fluids generated by such massifs in the course of their development is of great theoretic and practical importance.

In addition to melt inclusions described by Naumov et al. (2008) the Inagli chrome-diopside

contains multiphase crystal-rich inclusions ranged from some to 50-80 µm in size (Fig. 1).

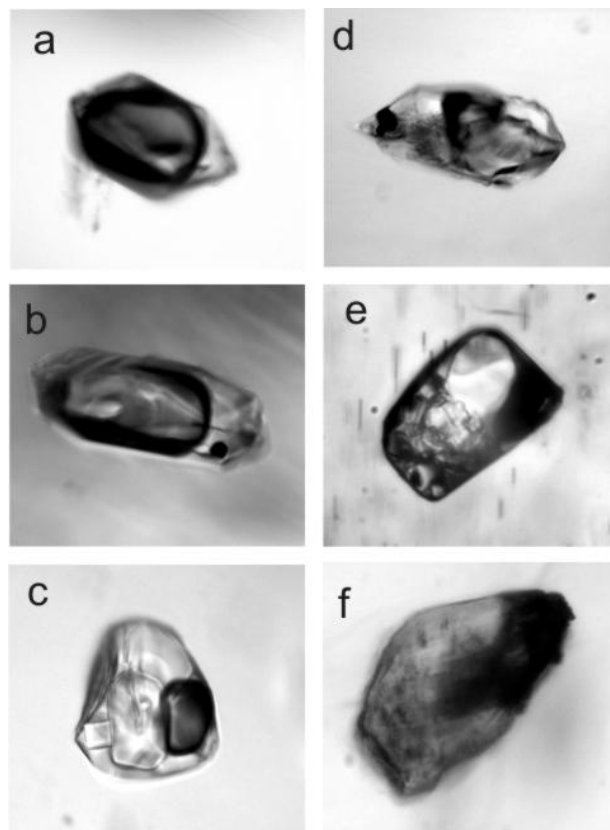


Figure. 1. Gas inclusion (a), gas inclusion with solid phases (b), multiphase crystal-rich inclusions (c, d, e) and melt inclusion (f).

Crystalline phases occupy 70-90 vol. % of inclusion vacuole. Essentially gaseous inclusions in which gas phase drastically prevails over aqueous solution and salt crystals are rarely occurred. The isolated presumably primary inclusions are characterized by stable prevailing of crystalline phases over the gas and aqueous phases. Pseudo-secondary inclusions located in cracks of different orientation are characterized by a greater variation in volume fractions of crystalline phases, aqueous solution and gas. Inclusions contain sulphates of Na, K, Ca, Mg, Ba, and Sr (Naumov et al., 2008). Isolated inclusions referred to as primary ones undergo partial homogenization during heating and decrepitating after gas homogenization though crystalline phases are incompletely dissolved. Occasionally, complete homogenization is observed in small pseudo-secondary inclusions where the aqueous and gas volume fractions are greater as

compared to primary inclusions. The thermometric study of fluid inclusions of sulphate composition has shown that gas homogenization temperature ranges from 595 to 565°C while the last salt phase dissolves completely in the temperature range of 595-519°C.

According to data of LA-ICP-MS analysis of sulphate-rich inclusions and results of microprobe analysis of dry salt residues of inclusion solutions, the average ratio values are as follows: Na/K = 7.7, Na/Ba = 18, Na/Fe = 97, Na/S = 1.2, Na/Cl = 3.5, S/Cl = 3. Ca and Mg determination is difficult due to chrome-diopside mineral matrix.

Nevertheless, the compositional data of silicate-sulphate inclusions in chrome-diopside of the Inagli deposits (Naumov et al., 2008) and, in particular, N₂O content in them permit using Na as an inner standard during estimation of contents of other elements revealed by LA-ICP-MS technique in fluid inclusions. According to LA-ICP-MS data, sulphate inclusions contain S – 2.2 wt.%; Cl – 0.8 wt.%; K – 0.4 wt.%; Mn – 29-14 ppm, Fe – 270 ppm, Zn – 1-0.5 ppm, As – 0.008-0.001 ppm, Mo – 230-70 ppm, Ag – 0.4-0 ppm, Sb – 9-7 ppm, Cs – 280-90 ppm, Ba – 1530 ppm, W – 2 ppm, Pb – 130 ppm, Bi – 0.5 ppm, Th – 0.3 ppm, U – 0.5 ppm (see Fig.). Significant quantities of Co, Ni, Cu, Sn, Au and Hg were not established. Using scanning electron microscopy we identified REE-carbonate, galena, barite, anhydrite in opened vacuoles of multiphase inclusions (Fig. 2).

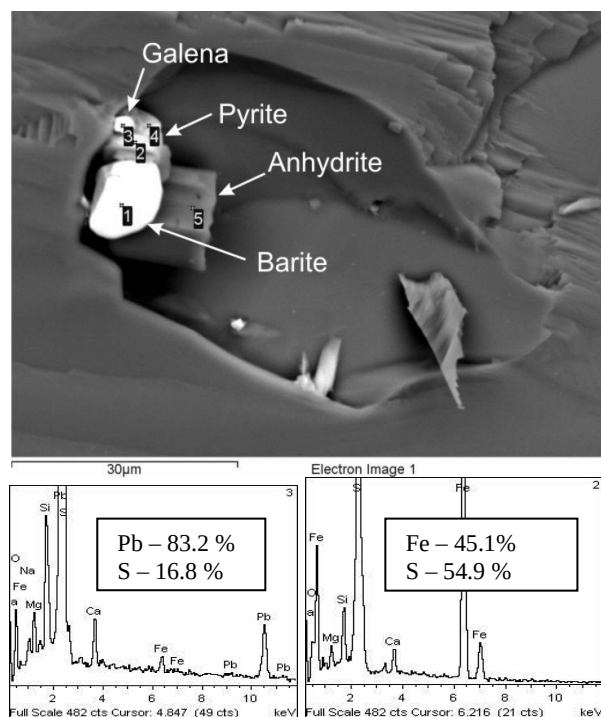


Figure 2. SEM image of an opened crystal-rich inclusion containing daughter phases and ED spectra of galena and barite (LEO 1430VP, OXFORD).

Magmatogenic sulphate fluids of the Inagli massif at the stage of formation of chrome-diopside-bearing pegmatites had a high ore-forming potential and characterized by high S, Mo, Ag, Sb, Cs, Ba, Pb concentrations which exceed clark values of these elements in the Earth's crust. Such high-temperature (519-659°C and higher) and high-concentrated (75-85 wt.% and higher) oxidized magmatogenic ore-bearing fluids might have served as a source of ore-forming components for carbonatite and hydrothermal deposits associated with massifs of K-alkaline rocks.

We acknowledge the financial support from RFBR (grants 08-05-00915 and 10-05-00730).

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INCLUSIONS IN CORUNDUMS AND MARUNDITES OF THE SUTARA DEPOSIT, RUSSIAN FAR EAST

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Introduction

The earliest discovery of corundum in the Sutara golden mine district, which is situated in the Yevreiskaya Autonomous District (Russian Far East, Fig. 1), was actually made as a result of gold mining. In 1943, during site exploration for cassiterite in gold-bearing placers, geologists discovered grey corundum fragments in the alluvium of the Perekhodnaya River. Later, in the vicinity of the mining settlement, large, sometimes well formed blocks of corundum reaching weights of 15-20 kg were discovered. So corundum was worked with the gold. About 2 tons of corundum ore were mined with at 70-80% corundum content.



Figure 1. The Sutara gold mining district.

Geology and materials

At present, there are 4 sources of corundum in the Sutara mining district, two of which (Kurortnoe and Pervomaiskoe) occur in carbonaceous rocks and in the veins of intruding granites. The others (Sutarskoe and Petrovskoe) occur in terrigene-carbonaceous rocks ruptured by granite intrusion. Carbonate rocks on the contact with granites were transformed into marbles. Granite veins are sometimes desilicated and turn into plagioclases. Corundum mineralization is associated with skarns and plagioclases.

In 2009, the authors carried out fieldwork searching for gem quality corundum in the basin of the Sutara River. At the outer limits of the Sutara area, at the Petrovsko-Arkhangelsky site, marundite samples were discovered, and then, in the basin of the streams of the Petrovsky and Mikhaylo-Arkhangelsky, corundum crystals and their fragments.

Corundum rocks – marundites (Fig. 2) – are represented by almost mono-mineral varieties with small amounts of colourless, brittle micas filling the space between corundum crystals. The crystals of corundum are coarse-grained and elongated, reaching up to 5-6 cm in length, and up to 2 cm in thickness. Marundites mainly contain corundum, margarite, and phlogopite.



Figure 2. Corundum-rich rock - marundite.

Accessory minerals are represented by apatite, rutile, tourmaline, ilmenite, biotite, muscovite, garnet, and sillimanite. Diaspore and chlorite are secondary phases. Corundum content reaches 70-90 vol.%, and it is represented by dipyrnidal and rhombohedral crystals typical for marundites and corundum plagioclases.

Corundums from the placers are represented by tabular crystals and their fragments up to 50 mm in size (Fig. 3).



Figure 3. Corundums of the Sutara Deposit.

Most crystals are characterized by polysynthetic twinning observed with a microscope. They are violetish-blue, grayish-blue, blue, and purple in

colour, with the tint varying from very light to dark.

Some samples demonstrate strong pleochroism and vary in clarity from transparent to translucent, and opaque. Painting is often zonal and spotty. Thin sections cut parallel to the pinacoid demonstrate growth zones; alternation of differently coloured bands with sharp borders mirroring crystal facets.

Inclusion study

Mineral inclusions such as zircon, spinel, rutile, monazite, and xenotime have been identified during studies. Spinel and rutile are syngenetic with corundum and located in the growth regions (Fig. 4).

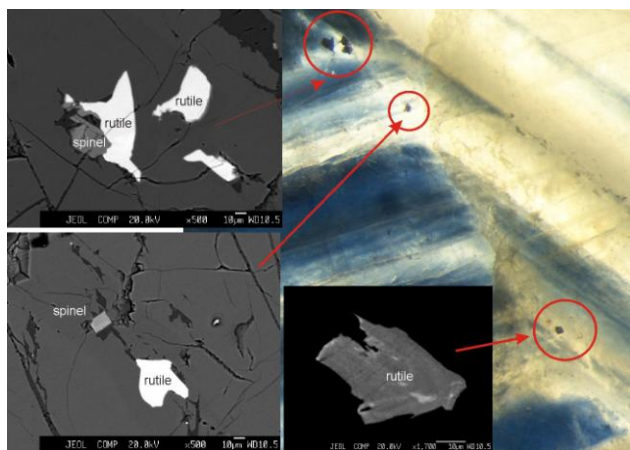


Figure 4. Mineral inclusions in the corundum.

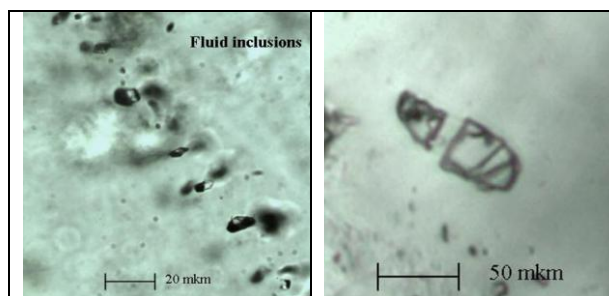


Figure 5. Carbon dioxide inclusions in corundum.

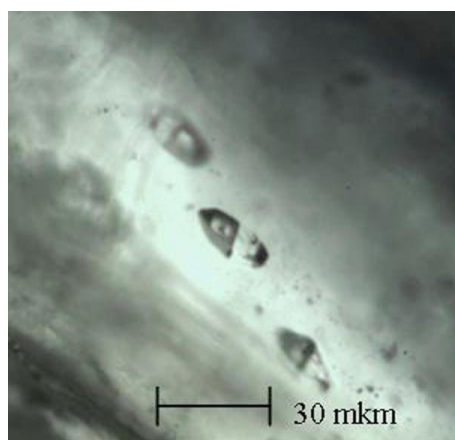


Figure 6. Combined fluid inclusions in corundum.

Corundum contains different fluid inclusions. They are mainly presented by carbon dioxide and combined fluid inclusions (Fig. 5-6). No melt

inclusions are found.

Carbon dioxide inclusions are the indicators of the metasomatic processes occurring at corundum formation.

Results

Corundum mineralization is confined to the carbonaceous rocks and crystalline schists intruded by alaskitic granites. Carbonaceous rocks in the contact with granite are metasomatically altered to opicalcite and serpentine as a result of contact metamorphism. Pegmatite veins, which are developed in the contact zone of granites with carbonaceous rocks, bear corundum mineralization. By their structural peculiarities, rocks covering pegmatite veins are transitional between medium-grained pegmatites and aplites. There is no particular zonality in the vein structure.

We established the presence of outcrops of corundum rocks in pegmatite veins of granite composition cutting opicalcite. This type of corundum mineralization is the result of the desilication of granite pegmatites during intrusion in the metamorphized carbonaceous rocks. Such type has no equivalent in Russia. Common corundum-bearing rocks are the dikes and veins of the corundum syenites and syenite-pegmatites in the alkali syenites or granite gneisses and gneisses contacted with massifs of alkali or nepheline syenites. Such rocks are known in the Il'mensky and Vishnevy Mountains in Russia, the Provinces of Ontario and Quebec in Canada, Madras and Kashmir in India and Sri Lanka. Metamorphic muscovite-sillimanite-corundum and kyanite-corundum rocks in gneisses and crystalline shales are known in Ukraine, Yakutia (the Chaynt deposit), India and other regions.

The fact that corundum mineralization is confined to pegmatite veins of granite composition cutting carbonaceous rocks opens further perspectives of finding analogous corundum occurrences in the Maliy Khingnan Mountains (Xiao Hinggan Ling), where pegmatite veins, carbonaceous rocks and products of their metamorphism are abundant.

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ORE MINERAL ASSEMBLAGES AND FLUID CHARACTERISTICS OF COPPER-GOLD MINERALIZATION IN SAKOLI GROUP OF ROCKS, INDIA - A MAGMATIC LINKAGE

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Introduction

The metapelites and meta-acidic volcanics of the Bhiwapur Formation of Lower Proterozoic Sakoli Supracrustals of Pular, Parsori area, Nagpur District, Maharashtra, India hosts native gold-base metal sulphide-bearing quartz veins $\pm$ carbonate veinlets. The gold-sulphide-quartz $\pm$ carbonate veins are sub-parallel to the transposed schistosity i.e. S_2 planar fabric developed in the area. The metavolcanics are soda-poor, potash-rich, rhyolitic to dacitic and rhyodacitic in composition with normative corundum (varying from 2.9% to 10.1%) and are peraluminous in nature.

The sulphide assemblage comprises chalcopyrite, pyrite, arsenopyrite, sphalerite, pyrrhotite, galena, cobaltite and cubanite. Ore microscopy and mineragraphic studies (by EDX) revealed presence of significant Bi-bearing phases as native bismuth, bismuthinite Bi_2S_3 , tetradyomite Bi_2Te_2S and complex Cu-Bi-Zn-Fe sulphide phases.

Minor wolframite (ferberitic in composition), cassiterite, and secondary scheelite have been identified to occur associated with chalcopyrite and galena. Gold occurs in the native form (1 mm size to 40 to 60 mm) with traces of silver in the following modes:

(A) At chalcopyrite and silicate gangue interface.

(B) As fine to coarse xenomorphic grains included within coarse chalcopyrite and arsenopyrite.

(C) As idiomorphic dispersed grains within microfractures in sulphide and quartz gangue.

(D) As coarse grains in association with chalcopyrite and pyrrhotite forming fracture fillers within arsenopyrite.

(E) As veinlets containing sulphides and tetradyomite pervading the host rocks.

(F) Gold-quartz-carbonate veinlets pervading the major sulphide assemblages.

Fluid inclusion studies

Morphologically, the inclusions assume variable shapes as globular, rectangular, elongated, irregular, spherical, oblate and polyhedral. All the inclusions vary in size from 3

to 30 μ m, with approximate average of 10 μ m in maximum length. Most secondary inclusions having planar disposition along micro fractures have also been recorded. Thermometric studies were undertaken on the morphological types are shown in Table 1.

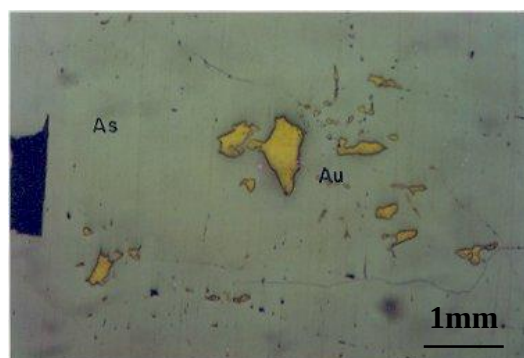


Figure 1. Native gold specks (Au) in arsenopyrite (As).

The T_{fm} data indicated that the ore-forming fluid carried salts of Na, K, Ca, Mg and Fe in varying combinations. The temperature of homogenization, which is also the minimum temperature of entrapment of the fluids are of two ranges: (a) 295°C to 355°C and (b) 195°C to 215°C. These are correlatable with copper-dominated gold-poor and gold-dominated copper-poor mineralization respectively in the area.

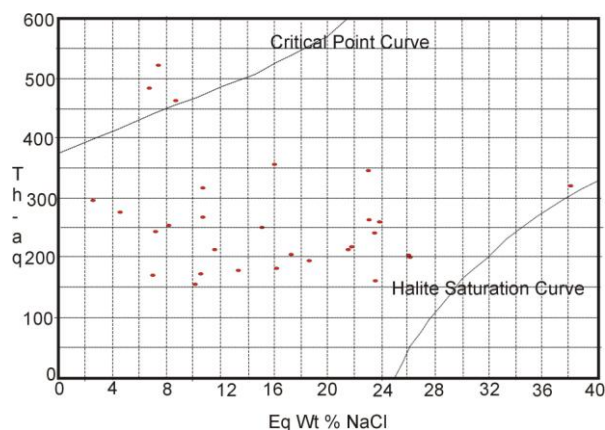


Figure 2. Bivariate plot of Th versus salinity.

Wide variation in salinity of the fluid (I & II) could either be due to mixing of different fluids of contrasting salinity (Fig. 2) (Shepherd et. al., 1985) or entrapment of fluids at different stages

of quartz vein activity hosting mineralization. Mineralizing fluid for gold was of gas-poor, liquid-dominant, moderately high saline nature with poor CO₂ activity unlike Archaean lode gold deposit, where a typically low salinity fluid with major CO₂ ± other gases were present during ore formation (Lindblom et al., 1996).

Moderately hot vapour-rich fluid (400 °C to 530°C: III) are pyrrhotite – pyrite bearing. Such high temperature of homogenization is outside the domain of effective copper and gold precipitation in the area.

The association of native bismuth, bismuth-bearing phases and cubanite marks a temperature constraint of 300°C for the mineralizing fluid. Melting point of native bismuth is known to be between 264°C to 271°C, which in hydrothermal deposits marks the upper temperature limit of their formation (Smirnov et al., 1983). Cubanite lamellae in chalcopyrite suggest that the temperature of formation must have been around 250°C to 300°C (Ramdohr, 1969).

Conclusions

From the interpretative plots of PVTX data

the approximate pressure of the mineralizing copper-gold bearing fluid at the time of entrapment shows a range from 550 bars (0.55 Kb) to 1900 bars (1.9 Kb).

The range of homogenization/entrapment temperature and association of native gold with native bismuth + wolframite + cassiterite + fluorite + tourmaline indicates a pneumatolytic – hydrothermal condition of ore formation (mesothermal). Elemental association in the studied area is more of granitophile character. This may be related to a distant granitic source.

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Table 1. Morphometric and thermometric data for fluid inclusions.

Sl. No.	Types	T _{fm}	T _s NaCl	T _m	T _H
I	L+V	-10.8 °C to -29.4 °C (NaCl +KCl +H ₂ O)		-1.2 to -28.5°C (6.2 to 11.2 wt.% NaCl).	195 °C to 215 °C & 295° C to 355 ° C
II	L +V + S	-11 °C to -51°C (mixed salt + H ₂ O)	273 °C to 344°C (36 to 42 wt.% NaCl equivalent).		167 °C to 300°C
III	V + L	-37.8 °C to -42.2°C (NaCl + FeCl ₂ + H ₂ O).		-21.3 to -24.2°C (23 to 24 wt.% NaCl equivalent)	400 °C to 530°C
IV	L+ V + MS	-37.8 ° C to -50.8°C (mixed salt + H ₂ O).	118 °C to 270°C. (halite). (38.14 to 44.62 wt.% NaCl equivalent)		400 °C to 535°C

CRYOGENIC RAMAN SPECTROSCOPIC CHARACTERISTICS OF NaCl-H₂O, CaCl₂-H₂O AND NaCl-CaCl₂-H₂O: APPLICATION TO ANALYSIS OF FLUID INCLUSIONS

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Introduction

The type and content of salts in aqueous phase are very important for study of fluid inclusions. Since Mernagh et al. (1989), Dubessy et al. (1982, 1992) pointed out Raman spectroscopy can be used to analyze salts in fluid inclusions, many researchers have tried to solve this problem by Raman spectroscopy (Ni et al., 2006). We have analyzed some aqueous samples in NaCl-H₂O, CaCl₂-H₂O and NaCl-CaCl₂-H₂O systems by cryogenic Raman spectroscopy. The experimental results show that some spectroscopic parameters are linear with the contents of salts, and this relation has been used to analyze fluid inclusions.

Experiments and Results

We have confected aqueous liquid with different contents salts (all data are in weight fraction), and got some aqueous liquid in heating-cooling stage and cooled by three times, then, tested by Raman spectroscopy under -180°C. The results were described as follows.

NaCl-H₂O System

The NaCl-H₂O system forms ice and NaCl·2H₂O under -20.8°C. The Raman spectra of NaCl-H₂O system show that NaCl·2H₂O comprise four peaks at -180°C, they are at 3403 cm⁻¹, 3420 cm⁻¹, 3433 cm⁻¹ and 3536 cm⁻¹. The peak at 3420 cm⁻¹ is most strong of NaCl·2H₂O, and its intensity increase with the content of NaCl. The typical peak of ice is at 3091 cm⁻¹. All of that can be seen in Figure 1. The intensity ratios of NaCl·2H₂O to ice also increase with content of NaCl, you can see in Figure 2.

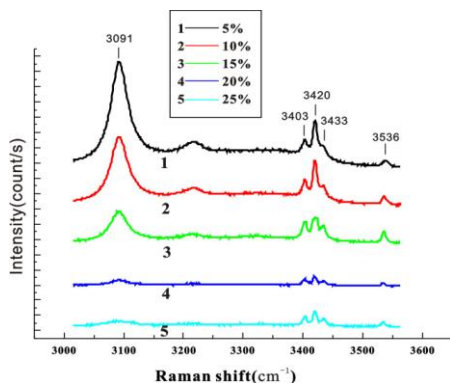


Figure 1. Comparative Raman spectra of NaCl-H₂O system at -180°C after cooled three times.

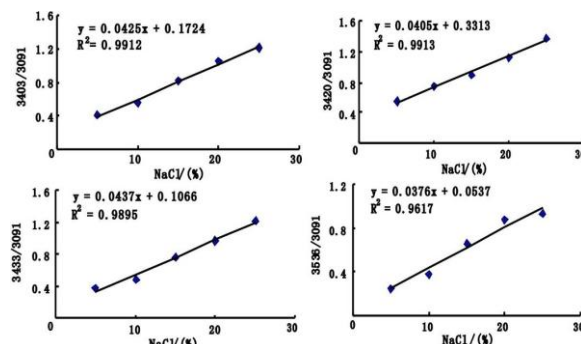


Figure 2. Correlation between Raman spectra intensity ratio of NaCl·2H₂O/ice and content of NaCl.

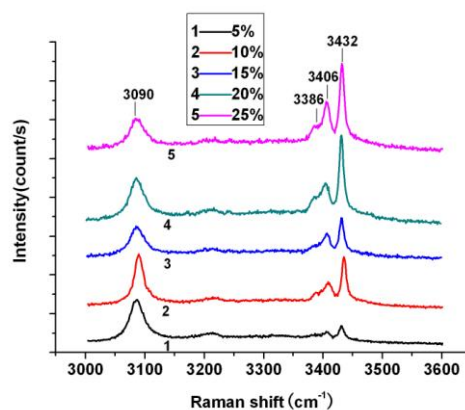


Figure 3 Comparative Raman spectra of CaCl₂-H₂O system at -180°C after cooled three times.

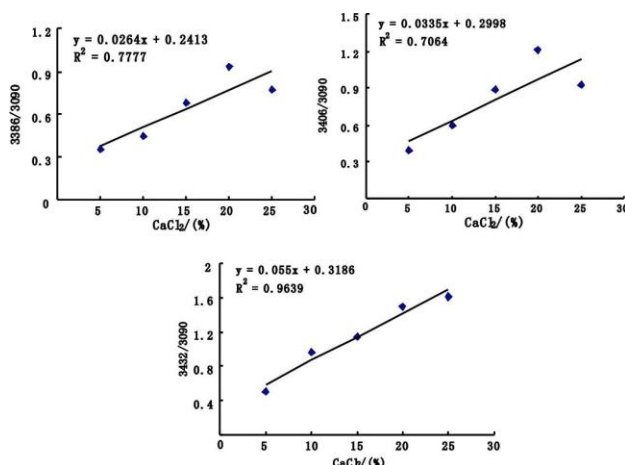


Figure 4 Correlation between Raman spectra intensity ratio of CaCl₂·6H₂O/ice and content of CaCl₂.

CaCl₂-H₂O System

The CaCl₂-H₂O system can form ice and CaCl₂·6H₂O under -49.5°C (Baumgartner, Bakker, 2009). After being cooled three times, the Raman spectra of CaCl₂-H₂O system show four peaks, which are at 3386 cm⁻¹, 3406 cm⁻¹, 3432 cm⁻¹

belong to $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and the peak at 3090 cm^{-1} of ice. The peak at 3432 cm^{-1} is very remarkable, and can be used to identify $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Its intensity increases with content of CaCl_2 , as shown in Figure 3. The intensity ratios of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to ice increase with weight content of CaCl_2 , see as in figure 4. Only ratio of 3432 cm^{-1} to 3090 cm^{-1} gives good linear relationship with content of CaCl_2 .

NaCl- CaCl_2 - H_2O System

The eutectic temperature of NaCl- CaCl_2 - H_2O system is at -52°C . When environmental temperature is under -52°C , the NaCl- CaCl_2 - H_2O system will form ice, NaCl, $\text{NaCl} \cdot 2\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. The weight ratio of NaCl to CaCl_2 is 1:1 for NaCl- CaCl_2 - H_2O system in this study. The Raman spectra of NaCl- CaCl_2 - H_2O system at -180°C indicate that peaks of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ are at 3535 cm^{-1} and in $3380\sim 3450\text{ cm}^{-1}$, see as in Figure 5. The peak of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ at 3403 cm^{-1} is overlapped by the peak of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ at 3406 cm^{-1} , it appears at 3405 cm^{-1} . The peak at 3433 cm^{-1} of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ combined peak at 3432 cm^{-1} of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ into one peak, which appears at 3433 cm^{-1} . The peak at 3420 cm^{-1} is belonging to mixture of NaCl- CaCl_2 - H_2O , its intensity increases with weight content of total salts.

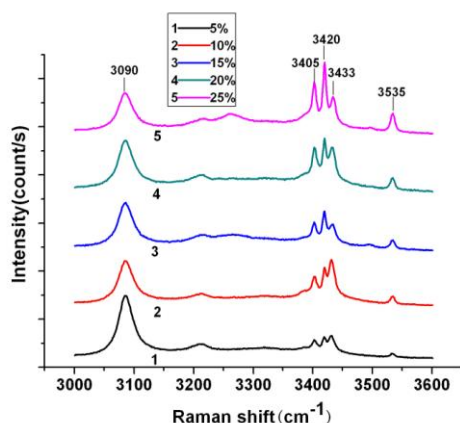


Figure 5 Comparative Raman spectra of NaCl- CaCl_2 - H_2O system at -180°C after cooled three times.

Application of Cryogenic Raman Spectra to Analyze Salts in Fluid Inclusions

We have analyzed some synthetic fluid inclusions and natural fluid inclusions by cryogenic Raman spectroscopy. The synthetic inclusions were synthesized in calcite with 20 wt.% NaCl. The natural inclusions are got from the Dongying sag, China. All these fluid inclusions were analyzed by cooling in heating-cooling stage. The results show that salinity of synthetic inclusion computed by freezing point is below that of cryogenic Raman spectroscopy. The relative error of this study is 1.6%, which is more accurate than results freezing point. So, this work proves that it is credible to get

salinity of fluid inclusions by cryogenic Raman spectroscopy.

Table 1 Results of this study contrast to conventional freezing method.

Samples	Synthetic inclusions	Natural inclusions
Host mineral	calcite	quartz
Freezing point ($^\circ\text{C}$)	16.1	12.8
$I_{3420}/I_{3091}(I_{3092})$	1.1282	1.02
Salinity computed by freezing point (wt.%)	19.53	16.71
Salinity computed by Raman spectra (wt.%)	19.68	17.01
Salinity of synthetic inclusion (wt.%)	20	--
Relatively error of this study (%)	1.6	--

Conclusions

Accurately diagnostic the types of the salt and calculating the salinity quantitatively are the significant for study of fluid inclusions. The traditional method of testing fluid inclusions salinity is cooling. In order to overcome the difficult for observing freezing phase transition, we tested NaCl- H_2O , CaCl_2 - H_2O and NaCl- CaCl_2 - H_2O systems at -180°C by laser Raman spectroscopy after cooling three times. The result demonstrates that the ratio of peak values has linear relationship with salinity. Calibration curves were established by typical ratio of hydro-halite at 3420 cm^{-1} to the ice at 3092 cm^{-1} , and the ratio of antarctite at 3432 cm^{-1} to the ice at 3090 cm^{-1} . The calibration curves have very high correlation coefficient. This method is verified by synthetic aqueous fluid inclusions in calcite and aqueous fluid inclusions in quartz of the well Fengshen 6 from the Dongying sag, China. The work proves that cryogenic Raman spectroscopy can not only identify the types of the salts, but also effectively determine the salinity of fluid inclusions.

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HIGH-PRESSURE MAGMATIC INCLUSIONS IN ZIRCON AND ROCK-FORMING MINERALS OF GRANULITE/ECLOGITE XENOLITHS FROM DIATREMES OF PAMIR

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Introduction

Fluid and melt inclusions in rock-forming minerals and zircon provide essential information on fluid/rock interaction and melting processes at high P and T, notably in domains not accessible to direct observation at the Earth's surface, such as lower continental crust and underlying mantle (Chupin et al., 2001, 2006). Situated on the northern side of the Himalayan collisional orogen, South-Eastern Pamir is in this respect a region of exceptional interest, the continental crust being there extremely thick (70-75 km). Samples of lower crustal (high-pressure granulites) and upper mantle (eclogites, garnet clinopyroxenites and websterites) rocks are brought to the surface as deep-seated xenoliths in Neogene diatremes of alkali basaltoids (Dmitriev, 1976).

Results

At present, primary silicate melt inclusions have been found in garnet and some other minerals from many types of the Pamir deep-seated xenoliths, however in very variable abundance. In bimineraleclogite single primary inclusions occur only in some garnet grains. Similar inclusions are found in garnet, apatite, and quartz from eclogite layers in clinopyroxenite. In sanidine-bearing eclogites melt inclusions are found in many grains of garnet and less often in sanidine, quartz, kyanite, apatite, and zircon. In clinopyroxene from these rocks, only secondary melt inclusions have been found so far. Abundant primary melt inclusions occur in almost all rock-forming minerals of various lower-crustal granulites: garnet, clino- and orthopyroxene, kyanite, scapolite, titanite, quartz, as well as in minerals themselves included in some mineral host: apatite, zircon or monazite in garnet, kyanite or plagioclase.

Almost all inclusions in garnet are decrepitated, much less in other minerals. They contain typically glass, possibly some daughter microcrystallites, and a gas bubble. Freezing and Raman data indicate that this gas is dense CO₂ ($\rho > 0.8 \text{ g/cm}^3$), sometimes mixed with N₂. Cogenetic gaseous and melt inclusions may occur separately in garnet, showing that the early stages of granulite and eclogite crystallization did occur in the presence of both CO₂-saturated melts and a free CO₂-rich fluid phase.

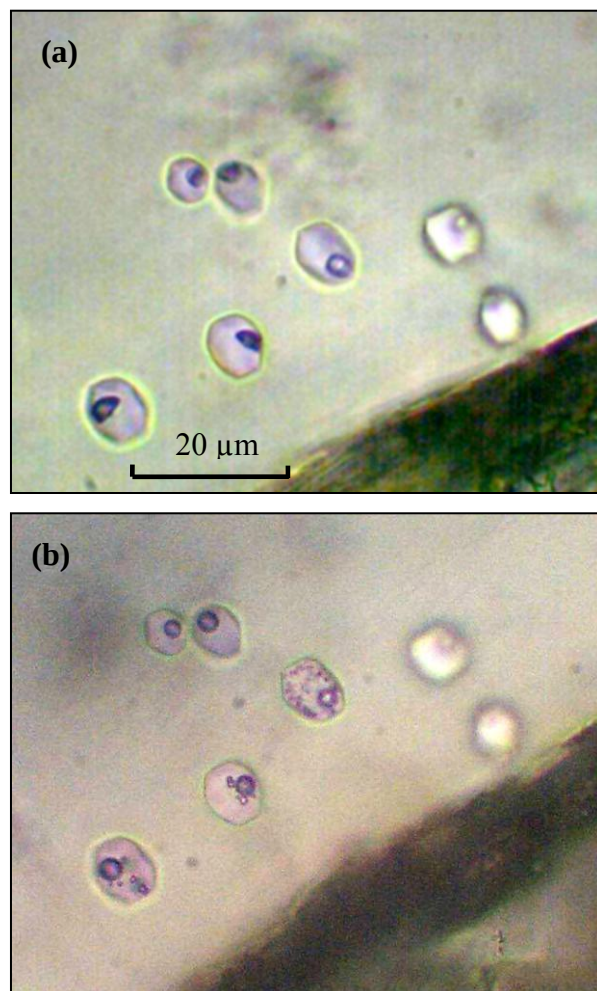


Figure 1. Primary silicate melt inclusions in scapolite from the Grt-Cpx-Pl granulite: a – before heating; b – after heating up to 850°C.

During heating, additional bubbles of dense CO₂ are expelled from the glass of inclusions (Fig. 1), indicating high CO₂ pressure at the time of entrapment (Chupin, Tomilenko, 1995). The determination of homogenization temperatures of melt inclusions in high-pressure minerals is hampered by partial leakage of inclusions (for example, in garnet) or by elastic increase of the vacuole volume (e.g., in quartz) as the external high pressure drops (Chupin, Tomilenko, 1995). With standard heating stages (heating at atmospheric pressure), most inclusions do not homogenize even at 1200°C. In garnet from Cpx-Pl granulite, we could find only one group of visually hermetic melt inclusions which homogenized at 1020°C. Total homogenization of melt inclusions could be

measured under 12 kb external pressure at 1000°C in quartz from massive Grt-Ky granulites. These data are in good agreement with mineral estimates (P above 12 kb and T 940-1000°C). It can thus be assumed that inclusions were formed at peak metamorphic conditions and could survive the transport towards the surface in the basaltic host.

In a more general way, the compositions of melt inclusions in garnet and other minerals of granulites correspond to K-rich acid melts, ranging from dacites to rhyolites. At the early stages all melts are generated in presence of a free CO₂ fluid phase, and their glass shows high-LREE, and low-HREE contents. This pattern could be due to an earlier (deeper) crystallization of garnet, in line with the widespread decrepitation of inclusions in this mineral. The inclusion glass in some Grt-Cpx-Pl (± scapolite) granulites and massive Grt-Ky granulites is enriched in chlorine, suggesting the local influence of salt-bearing aqueous solutions.

By SHRIMP dating of high-pressure zircon crystal (with combined inclusion of melt and kyanite) in kyanite from massive granulite (Fig. 2) two ages were obtained: 14.4±1.6 Ma (possibly the age of host kyanite crystallization) and 64.4±8.7 Ma (possibly the age of protolith or early metamorphism).

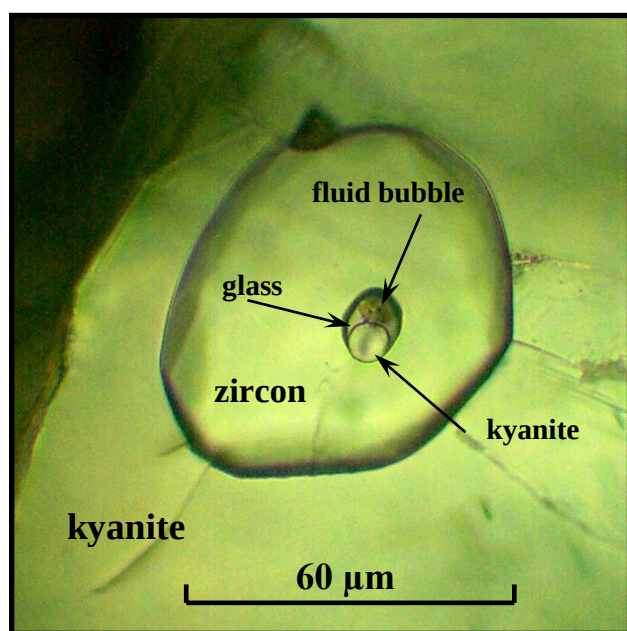


Figure 2. High-pressure combined inclusion (K-rich acid melt + kyanite) in zircon from massive Grt-Ky granulite with 14.4±1.6 Ma age (SHRIMP data).

Conclusions

At > 40 km depth (>12 kb pressure), incongruent melting of K-bearing basic and intermediate high-alumina protoliths may have occurred under South-Eastern Pamir about 15 My ago (preliminary SHRIMP data), producing K-rich

acid magmas. This melting was accompanied by crystallization of Si-poor and Ca-rich minerals (garnet, clino- or orthopyroxene, kyanite, plagioclase and scapolite), which trapped microportions of melts as inclusions.

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3D CONFOCAL RAMAN IMAGING ON FLUID INCLUSIONS IN GARNET AND ON MICRO-DIAMONDS IN QUARTZ

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Introduction

The study of deep fluid or melt inclusions in minerals such as those formed under ultra-high pressure (UHP) conditions, is an ongoing pursuit in the fields of Geology and Mineralogy. In addition, the rare micro-diamond inclusions in Quartz are an area of increased interest for researchers of these fields. Due to these inclusions being rare, a non-destructive technique to study their dimensions and composition would be of immense benefit to the researcher.

Confocal Raman microscopy combines high-resolution microscopy with the chemical sensitivity of Raman spectroscopy, thus allowing non-destructive imaging of chemical properties without specialized sample preparation. Due to the confocal principle, depth information regarding the inclusions can easily be obtained. Not only can thickness and uniformity measurements be performed, but the degree of mixing or segregation of the ingredients within the inclusions can also be determined.

In this paper we present the results of three-dimensional studies of fluid inclusions in garnet and of micro-diamond inclusions in Quartz using confocal Raman microscopy.

Samples and methods

The details of the geological setting that produced the fluid inclusion (the Kokchetav massif, Northern Kazakhstan) have been summarized elsewhere (e.g. Dobretsov et al., 1995; Shatsky et al., 1995) and will not be reiterated here. In this study one exemplary specimen of Grt-Cpx rocks from the Kumdy-Kol deposit and Barchi-Kol area was utilized for detailed fluid-inclusion investigations. The rock composition and the investigation thereof are described in another article presented at this conference (Korsakov et al., 2010).

An octahedral crystal comes from the quartz-tourmaline metasomatic rocks from the Kumdy-Kol deposit. The detail description of these rocks is provided by Korsakov et al. (2009).

The confocal Raman images were collected using a Confocal Raman Microscope *alpha 300R* (WITec). The system was equipped with a frequency doubled Nd:YAG laser emitting at 532 nm which was fiber coupled to the instrument. A 100X NA 0.9 air objective was used for excitation

and detection and the Rayleigh light was rejected using an edge filter. A 50 µm core diameter multimode fiber served as the pinhole for confocality and as the entrance slit to the spectrometer. The spectrometer used was a UHTS300 (see Dieing et al., 2008 for more information) equipped with a back-illuminated CCD camera with peak quantum efficiencies >90% in the detection range. For the measurement on the diamond inclusion an EM-CCD camera was used. The details concerning the functionality and the advantages of these cameras can be found elsewhere (Dieing et al., 2008). A 600 g/mm grating was used to disperse the light. The sample was scanned in X&Y using a highly precise piezoelectric scanner while the movement in the Z-direction was performed by a stepper motor (single step 10 nm). In this way, layer-by-layer, a three-dimensional data set was acquired which consisted of hundreds of thousands of spectra. Further scan details can be found in Table 1. The data sets were evaluated using single variant (e.g. integrated intensity) and multi-variant (e.g. cluster analyses) methods to generate the images displaying the distribution of certain material, their various phases and/or their strain state. The single variant methods were applied to each layer recorded whereas the cluster analysis was applied to the complete data set.

Table 1. Experimental Parameters

	Fluid Inclusions	Micro-Diamonds
Scan Size	60x60x30 µm ³	13x16x15 µm ³
Resolution (pixels)	100x100x20	100x120x12
Integration Time/Pixel	0.132 s	0.020 s
Spectrometer	UHTS300	UHTS300
Grating (grooves/mm)	600 (BLZ 500 nm)	600 (BLZ 500 nm)
Objective	100X air (NA 0.9)	100X air (NA 0.9)
Excitation wavelength	532nm	532nm
CCD Camera	Back-Illuminated CCD (optimized for VIS detection)	Back-Illuminated EM-CCD (optimized for VIS detection)

Fluid inclusions

White light microscopy images of the fluid inclusion samples can be found in another article of this conference (Korsakov et al., 2010).

Following multi-variant data analysis and spectral fitting procedures one image per layer recorded could be generated. These are displayed in Figure 1. The colors correspond to the spectra shown in Figure 2 and the brighter the colors are, the more intense the detected spectra of the component were. It can be seen, that the host garnet (yellow) decreases in intensity from the top layer to the bottom layer due to the attenuation of the signal when passing through more material.

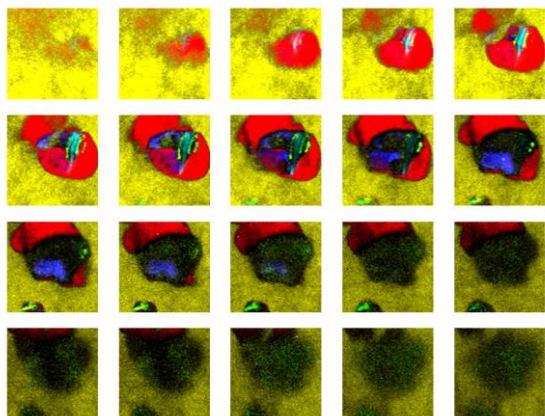


Figure 1. Layer by layer combined color images of fluid inclusion. The top left image is the top layer, whereas the bottom right is the lowest layer (30 μm below the top).

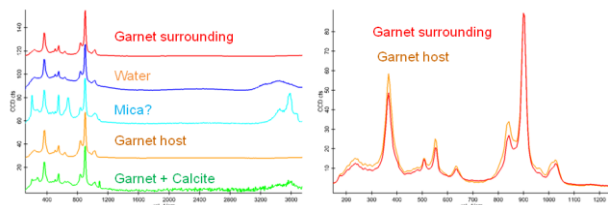


Figure 1. Spectra of the 3D liquid inclusion scan. The colors correspond to the colors in Figure 1. The spectra on the right are normalized to the peak near 900 rel.1/cm to visualize the change in the relative peak intensities of garnet close to the inclusion.

The water phase (blue) is clearly visible and also the phase which might be attributed to Mica (turquoise). The phase containing Calcite (as seen by the peak close to 1086 rel.1/cm) is shown in green. The two garnet phases (yellow/orange and red) are shown as a zoomed view to illustrate the differences in the relative peak intensities. The layer by layer images were exported for each material from the WITec Project Software and imported into ImageJ (public domain software) and here 3D views of the garnet were generated. Since all five phases would have resulted in an overload of information in one 3D image, they were separated into one view for the Garnet phases and one view for the inclusion phases. These can be seen in Figure 3 where the colors again correspond to the spectra presented in Figure 2.

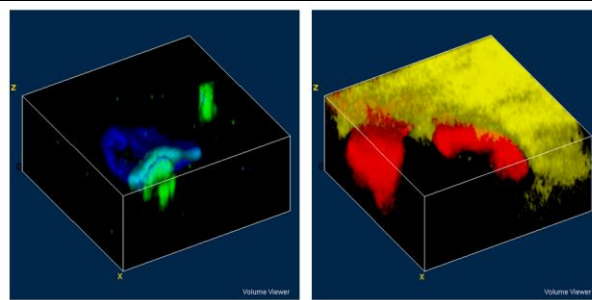


Figure 3. 3D representation of fluid inclusion. The colors correspond to the spectra shown in Figure 2. Left: Water, Mica? and Calcite phase. Right: the two Garnet phases.

Diamond inclusions

The micro-diamond was treated in a similar way as detailed for the fluid inclusions. Figure 4 shows the 3D representation of the diamond and inclusions in the diamond as well as the corresponding spectra. The spectrum of the inclusion is an average spectrum here and more detailed spectra as well as the 3D imaging of the strain within the diamond will be presented during the conference.

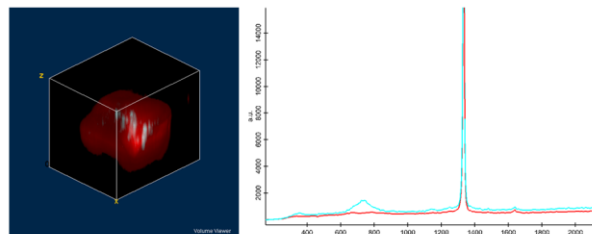


Figure 4. 3D representation of micro-diamond. The colors correspond to the spectra shown on the right.

Conclusions

Confocal Raman imaging allows the non-destructive 3D imaging of various inclusions in a variety of host materials. Its sensitivity to the phases of the minerals and can additionally be used as a tool to identify stresses in the materials.

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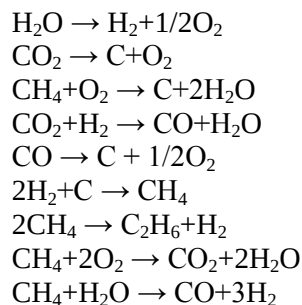
EQUATION OF STATE OF CARBON-BEARING FLUIDS

Duan Z.H.

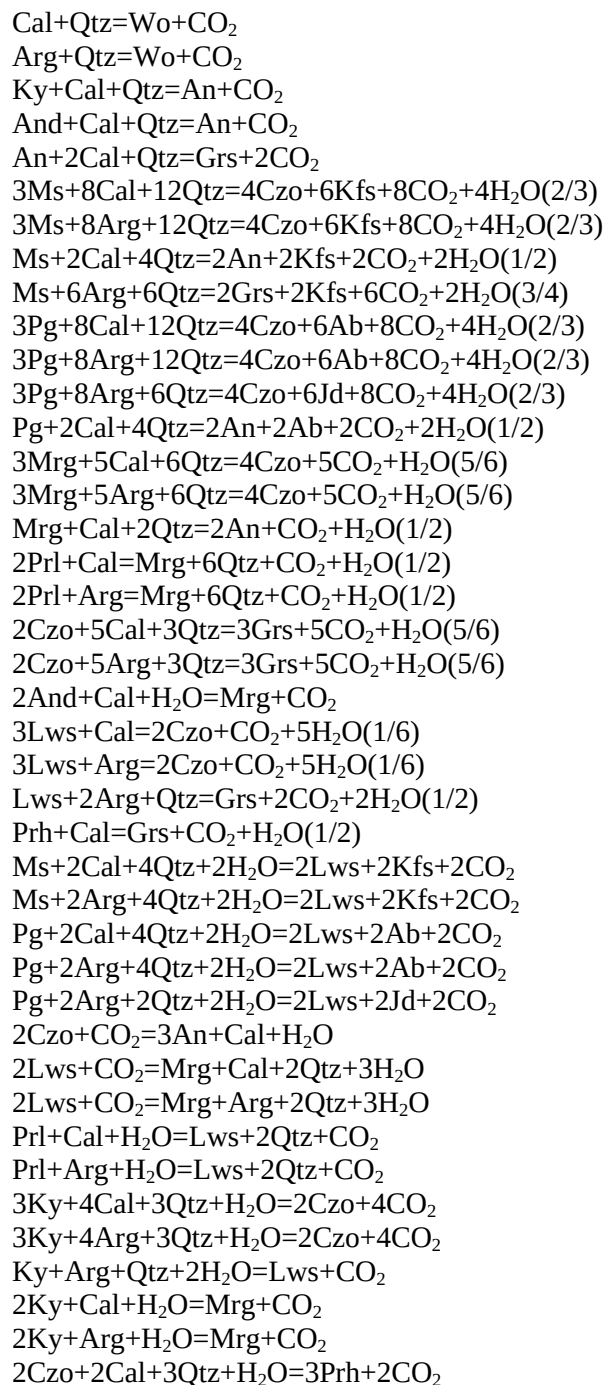
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Carbon plays a pivot role in coupling human and natural systems, bridging energy and environment, connecting time and space, bonding the organic and inorganic world, and exchanging between the Earth's deep interior and the shallow geospheres. Therefore, extensive studies and many ongoing projects have been devoted to the study of carbon budget and global carbon cycling. However, in the past decades, most studies have been focused on the shallow geospheres, little attention has been turned to the Earth's Deep Interior, which accounts for at least 75% of the total carbon budget of the Earth based on different sources of data and rough estimates. Putting in a specific way, in the past even though the carbon budget in the Earth's Deep Interior explains more than 75%, less than 5% of research funding has been allocated to it, far from meeting the needs of the investigation of the global carbon cycle and the development of the Earth System Sciences.

In the Earth's deep interior, carbon can exist in different forms of minerals and fluids (diamond, graphite, carbonates, carbide, discrete carbon in nominally carbon-free minerals, organic and inorganic molecules which compose various C-bearing fluids, carbon in melts, and various mixtures of them). In the study of the deep carbon cycle, we have two basic tasks needing humongous work: (1) identify these different forms of carbon and quantify them; (2) find the various changes between them. These tasks require integrating extensive experimental, computational and observational efforts. For example, even the apparently-looking simple C-H-O fluids; there potentially exists the various speciation reactions under various T-P-fO₂ conditions:



For another example, during slab subduction in the convergent zone, carbonate-bearing pelite may incur various dehydration and decarbonization reactions:



Observational and experimental work is certainly far from sufficient to find out the variety of chemical and phase equilibrium under various T-P conditions, computational methods combined with very limited experimental and observational data seem the only feasible solution to these complicated problems. Equation of state of carbon-bearing fluids is essential in finding the various phase and chemical equilibrium as illustrated above.

Based on thermodynamic approach, *ab initio* molecular potential, and molecular dynamics simulation, we developed equations of state for pure carbon fluids (Duan et al., 1992a), C-bearing fluid mixtures (Duan et al., 1992b), and gas-water-salt mixtures (Duan et al., 1995), general equations of state (Duan et al., 1996; 2000) and molecular dynamics EOS (Duan, Zhang, 2006; Zhang et al., 2007). These EOS not only reproduce hundreds of thousands of laboratory experimental data (sixty thousands of data points) from over one hundred laboratories, but also predict fluid properties exceeding the scope of the experimental data that are tested by the subsequent experiments by a number of international laboratories and have been written into geochemical application codes by many scientists from different countries, and also have been widely applied in various aspects of geochemical researches (such as decarbonization studies, methane hydrate research, study of fluid inclusions, fluids-rock interaction, exploration and development of oil-gas and geothermal energy, study of the origin of the Earth's atmosphere, geological storage of carbon dioxide, and experimental calibration) by more than 1000 researchers from more than 30 countries. In addition, online calculations of these equations are made available: www.geochem-model.org. Recently the EOS has also been used to study the chemical speciation reactions of C-H-O fluids in the mantle (Zhang, Duan, 2009).

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EQUATIONS OF STATE ONLINE CALCULATION FOR THE STUDY OF FLUID INCLUSIONS

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Introduction

Equation of state (EOS) is very important in the interpretation of fluid-inclusion data because it can be used to derive homogenization conditions, isochores, and internal pressures of fluid inclusions. There are many equations or thermodynamic models used in the study of fluids, but most of them lack consistent accuracy over a meaningful temperature-pressure space, yielding unreliable predictions. Therefore, caution must be taken in choosing or developing accurate EOS or models to study fluid inclusions. The objective of this study is to apply the updated EOS or models developed by previous researchers or us to give the most accurate calculation of homogenization pressure and isochores. The online calculation is made available on the website (www.geochem-model.org).

For pure fluids like H₂O, CO₂, CH₄, O₂, N₂, C₂H₆ or H₂S, the best EOS in terms of precision and applicable range is summarized in Table 1.

Table 1. EOS of pure fluids.

Fluid	T(K)	P(bar)	References
H ₂ O	273-1273	0-10000	(Wagner, Pruß, 2002)
	1273-2573	0-100000	(Duan, Zhang, 2006)
CO ₂	216.592-1100	0-8000	(Span, Wagner, 1996)
	1100-2573	0-100000	(Zhang and Duan, 2005)
CH ₄	90.694-625	0-10000	(Setzmann, Wagner, 1991)
	673-2573	0-100000	(Zhang et al., 2007)
C ₂ H ₆	90.352-625	0-700	(Bucker, Wagner, 2006)
O ₂	54.361-1000	0-820	(Schmidt, Wagner, 1985)
N ₂	63.151-1000	0-22000	(Span et al., 2000)
H ₂ S	187.67-760	0-1700	(Sakoda, Uematsu, 2004)

Table 2. EOS or models of binary CO₂-H₂O, CH₄-H₂O and NaCl-H₂O systems

Fluid	T(K)	P(bar)	x _{H2O}	References
CO ₂ -H ₂ O	273-1273	0-10000	0-1	(Duan, Sun, 2003; Mao et al., 2009; Paulus, Penoncello, 2006)
	1273	10000	0-1	
CH ₄ -H ₂ O	273-1273	0-10000	0-1	(Duan, Mao, 2006; Kunz et al., 2007; Mao et al., 2009)
	1273	10000	0-1	
NaCl-H ₂ O	273-1273	P _s -5000	0-1	(Atkinson, 2002; Driesner, 2007)
	1273	5000	0-1	

Note: Ps: vapor pressure of the solutions; x_{H2O}: mole fraction of H₂O

Listed in Table 2 are the temperature-pressure-composition ranges and references for the binary CO₂-H₂O, CH₄-H₂O and NaCl-H₂O systems. Detailed information can be seen from the references. Programs for the CO₂-H₂O-NaCl and

H₂O-NaCl-CH₄ systems can be calculated from the website: <http://geotherm.ucsd.edu/geofluids/run.html>, but a better version is still under development. Once the homogenization temperature and the composition are determined, the internal pressure of the fluid inclusion and the isochores can be calculated. Isochores of the systems listed in Tables 1 and 2 can be drawn online.

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FLUID INCLUSIONS IN HYDROGENIC MINERALS: A TOOL FOR ISOTOPIC PALEOHYDROGEOLOGY

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Introduction

The possibility of analyzing the stable isotope composition of paleowaters trapped in inclusions has long been a tantalizing prospect for paleohydrogeologists and, more recently, researchers studying the paleoclimate using speleothems. Although inclusions could potentially provide direct information about the isotopic composition of paleowaters, paleohydrogeological and paleoclimate applications require reasonably high resolution and analytical precision. The acceptable precision of 1-2 ‰ for δD and ca. 0.5 ‰ for $\delta^{18}O$ has been attained only recently.

Analytical line at Innsbruck University

An analytical line allowing the analysis of stable isotopes of water recovered from fluid inclusions in minerals was built at Innsbruck University. The samples are crushed in a cell with a small internal volume. The working zone of the crusher is kept at 130-150°C to minimize the adsorption of water on freshly crushed calcite and on the internal surface of the cell. The released water is transported by He flow through a heated stainless-steel tube into a computer-controlled cryo-focusing cell (Humble, USA). The temperature and gas-flow parameters are selected so that any CO₂ (and/or other poorly condensable gases) are not trapped, whereas the collection of water is quantitative. Upon completion of cryo-focusing (ca. 5 min) the cell is flash-heated to 280°C at a rate 3600°C/min, which ensures that the released water arrives in the TC/EA conversion unit (Thermo Scientific, Germany) as a discrete pulse. In the TC/EA the water is converted into H₂ and CO through reaction with glassy carbon at 1400°C. The evolved gases are separated in a GC column and admitted, via the ConFlow III interface, into a Delta V Advantage isotopic-ratio mass-spectrometer (Thermo Scientific, Germany). Prior to crushing the line is conditioned by several injections of water with an isotope composition broadly similar (within ± 20 ‰ δD) of the expected composition of the inclusion water. For samples yielding more than ca. 0.2 μl H₂O the precision is better than 1.5 ‰ for δD and ca. 0.5 ‰ for $\delta^{18}O$ (1 σ ; Dublyansky, Spötl, 2009).

Precision

Precision was assessed by repeated crushing of a well characterized natural calcite sample from a deep-seated, low-temperature (ca. 30°C) fossil flow system (Stegbachgraben, Austria). The inner, isotopically homogeneous part ($\delta^{18}O_{\text{calcite}} = -15.12 \pm 0.12$ ‰ V-PDB) of 5-7 cm large, rhombohedral crystals was used. The δD value of fluid-inclusion water measured several times over a one year-period showed variation of 1.1 ‰ (1 σ).

Accuracy

In order to ascertain that the isotopic composition of water trapped in inclusion accurately reflects that of the parent water, multiple analyses were made on calcite collected at the bottom of the two shallow pools in the Obir cave (Carinthia, Austria). The isotope composition of the lake water ($\delta D = -70.1 \pm 0.3$ ‰; $\delta^{18}O = -10.4 \pm 0.06$ ‰ V-SMOW), its temperature (5.2 ± 0.2 °C), as well as the relative humidity ($97-100 \pm 3\%$) at both sampling sites has remained stable over the 2.5 to 5 year-long monitoring periods. The hydrogen isotope compositions measured for fluid-inclusion water in the pool spar matches the lake water ($\delta D_{\text{fi}} = -70.0 \pm 0.3$ ‰) and the oxygen isotope values agree within ca. 0.5 ‰ ($\delta^{18}O_{\text{fi}} = -9.9 \pm 0.4$ ‰). The paired $\delta D_{\text{fi}}-\delta^{18}O_{\text{fi}}$ values plot within 1 ‰ $\delta^{18}O$ of the Local Meteoric Water (MWL) line. We concluded therefore that inclusions in the Obir pool spar preserved the isotope signature of the parent lake water.

Materials for isotopic paleohydrogeology studies

A number of hydrogenic mineral deposits appear to be suitable for fluid inclusion-based isotopic paleohydrogeology studies. Requirements for successful paleohydrogeological application include: (1) the position of the deposits in the hydrogeologic system must be known; (2) deposits must contain sufficient amounts of water in fluid inclusions; (3) inclusions must be primary (or, primary inclusions must dominate volumetrically); and (4) deposits must be datable (U-Th and U-Pb methods are most commonly used).

Cave deposits (speleothems) represent perhaps the most promising paleohydrogeological archive. Calcite of stalagmites and flowstones often exhibits a robust isotopic signal delineating variation in paleoclimate. This allows fluid-inclusion studies to

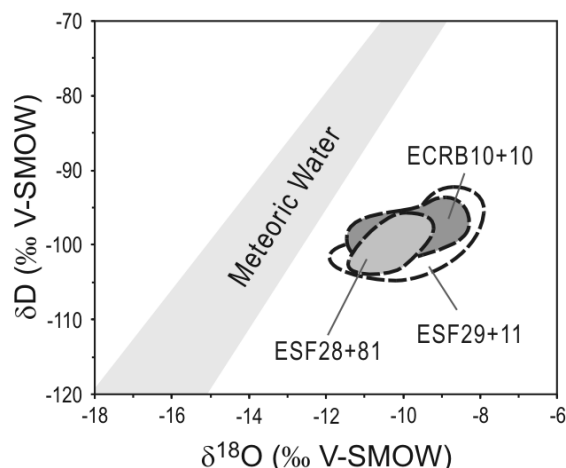


Figure 1. Positive ^{18}O shift in measured δD and calculated $\delta^{18}\text{O}_{\text{fi}}$ values for three samples from Yucca Mountain, Nevada.

target specific climate transitions in the past (see Luetscher et al., 2010; this volume). Subaqueous speleothems, such as mammillary crusts and lake clouds, provide a somewhat attenuated paleohydrogeological record.

Calcite veins representing the discharge sites of a regional aquifer have been successfully used for paleohydrogeological reconstructions (Winograd et al., 1985). Finally, gangue minerals from ore deposits can also be used for broad-scale hydrogeological studies provided the requirements outlined above are met.

Case study: Paleohydrogeology of the prospective nuclear waste disposal site Yucca Mountain, Nevada

Fluid-inclusion isotope data were obtained from low-temperature hydrothermal (40 to 50°C; fluid inclusion data) calcite from Miocene rhyolitic tuffs of Yucca Mountain, Nevada, USA. The paired δD - $\delta^{18}\text{O}$ values ($\delta\text{D}_{\text{fi}} = -105$ to -90 ‰; $\delta^{18}\text{O}_{\text{fi}} = -14$ to -15 ‰) plot close to the Nevada MWL. In contrast, the equilibrium $\delta^{18}\text{O}_{\text{water}}$ values (-10.3 to -7.7 ‰) calculated from $\delta^{18}\text{O}_{\text{calcite}}$ and fluid-inclusion temperatures plot significantly (3.5 to 6.5 ‰) to the right of MWL. The high $\delta^{18}\text{O}$ values suggest that the fluid-inclusion water has re-equilibrated with the surrounding calcite upon cooling from the deposition temperature (40–50°C) to ambient temperature. The strongly positive ^{18}O shift revealed by the equilibrium calculations indicates that mineral-forming water exchanged its O isotopes with rocks at elevated temperatures ($>100^\circ\text{C}$). This implies involvement of the deep-seated hypogene fluids (Dublyansky, Spötl, 2010).

The low absolute $\delta\text{D}_{\text{fi}}$ measured in early, intermediate, and late parts of calcite crusts are consistent with the late Quaternary age of the mineral-forming waters (cf. Winograd et al., 1985;

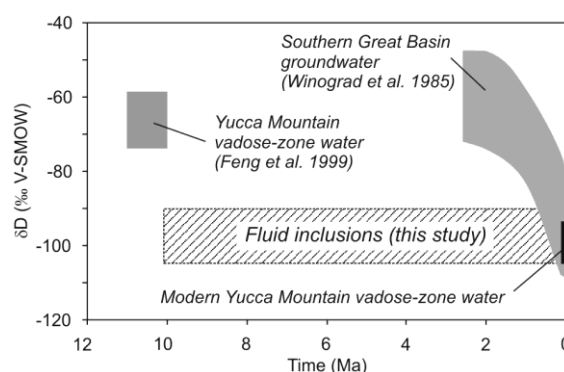


Figure 2. δD values of fluid-inclusion waters in the Yucca Mountain calcite compared with regional paleohydrogeological data.

Feng et al., 1999), but are inconsistent with the continuous, late Miocene to Pleistocene, deposition postulated for the Yucca Mountain calcite (e.g., Whelan et al., 2008).

The fluid-inclusion stable isotope data thus prompted substantial reconsideration of the paleohydrogeologic model for the Yucca Mountain site. The new model includes a stage of circulation of the deep-seated thermal fluids.

Conclusion

Recent improvements in the accuracy and precision of the stable isotope analyses of waters trapped in fluid inclusions in hydrogenic minerals represent a powerful tool for quantitative isotopic paleohydrogeological studies.

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FLUID REGIME OF BARITE ORIGIN IN FLUORITE DEPOSITS OF CENTRAL TAJIKISTAN

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Fluid regime of formation for barite from various mineralogical and genetic types of fluorite deposits in the Central Tajikistan was investigated. This mineral is of the most widely spread in the deposits of quartz-fluorite (Romit) and calcite-barite-fluorite (Krasnaya Kholma) types and in the deposit of optical fluorite (Kuli-Kalon). In addition, its slight amount is noted in other deposits (Bigari Bolo, Ijam). These deposits are located in granites, granodiorites and crystalline schists of Paleozoic age.

Barite formed in the final stages of mineralization in association with quartz, calcite, fluorite, pyrite and galena. It occurs as veins from 10-15 cm up to 1.5-2 meters of thickness, as small grains, nests, phenocrysts and druses are well as formed crystals and thin network of differently oriented veinlets that pervades the country rocks. Aggregates are of granular and plate form with the radiant and sheaf-like arrangement of individuals of unordered orientation. Size of individuals is reaching 5 cm (Faiziev, 1973). There are frequent congestions of "barite rose" type, which are formed with plate crystals. The crystals are tabular and rarely prismatic. The largest individuals were found in the Kuli-Kalon and Krasnaya Kholma deposits, where they reach 20 cm along the axis. Tabular form is a combination of pinacoid and prisms. Color of the mineral is different: white, pinkish-white, reddish-brown, violet. Colorless and transparent difference (optical barite) is widely distributed in the Kuli-Kalon deposit.

Fluid inclusions in barite of investigated deposits were studied by thermobar-geochemistry methods. Studies have shown that samples of barite saturated with single-phase and two-phase inclusions. Size of inclusions is small (0.001 mm), rarely varies from 0.05 to 0.1 mm. Their shape varied: oval, round, elongated, and irregular, sometimes with the elements of crystalline forms. Primary gas-liquid inclusions with the volume of the gas phase from 5-6 to 20-25% predominate (Fig. 1). Secondary inclusions are located in the form of chains, and they are confined to cracks in the mineral. Gas and liquid inclusions are also found.

In barite of the Bigari Bolo deposit (Faiziev, 1975) liquid-gas along inclusions with the gas-liquid ones were found. The content of the gas phase in these inclusions is up to 75-80 vol.% of the vacuoles. Homogenization of gas-liquid inclusions

occurs in the liquid phase, and of liquid-gas ones - to gas, and in the same temperature limit as the gas-liquid does it. This indicates that the boiling of hydrothermal fluids at the time of crystallization of barite in the Bigari Bolo deposit caused, apparently, with sharp decrease in pressure within the system as a result of fracturing.



Figure 1. Primary inclusions in barite.

In the Romit deposit barite crystallized from low salinity (5.5-8.9 wt.% NaCl) Mg-solutions into the temperature range of 235-190°C and a pressure of 380-325 atm. Fluid inclusions in barites (I and II) in the Kuli-Kalon deposit (Faiziev, 1976) with the concentration of 4.7-9 wt.% NaCl are homogenized at temperatures of 240-175 and 170-130°C, respectively, the pressure of the fluid at the same time was 310-190 atm. In the composition of solutions NaCl dominates, KCl is minor component. At the Krasnaya Kholma barite-bearing deposit (Faiziev, 1965) fluid regime gradually reduced during the transition from early to late generations. Here the fluid inclusions have the following parameters: temperature homogenization - 170-155°C (barite I), 115-100°C (barite II), 90-70°C (barite III), and pressure was 225-200 and 170-135 atm, and the concentration of solutions was from 5.5-7 to 1.9-4.3 wt.% NaCl eqv. The aqueous solutions of chlorides of Na and K are presented in the general amount.

The liquid portion of the solution gas-liquid inclusions is sulfate-bicarbonate with low chlorine content. The major cation is Ca, the concentration of which dominates over others.

Thus, these data indicate the similarity of fluid regime during the formation of barite from various mineralogical-genetic types of fluorite deposits of central Tajikistan.

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FORMATION TEMPERATURE OF CALCITE FROM THE KUHILAL NOBLE SPINEL DEPOSIT (TAJIKISTAN)

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The Kuhilal deposit is located in the Ishkashim region of the Gorno-Badakhshan Autonomous Region (South-Western Pamir). It is known from ancient times (VII century) as the source of the famous Badakhshan Lal (noble spinel).

It is localized in the zone of the lower structural-stratigraphic unit of the metamorphic sequence of the Southwestern Pamir – the Goransky series. In this series, the bulk of the sediments are presented with biotite, biotite-hornblende gneisses and migmatites that contain multiple bands, layers and lenses of magnesite marbles.

Since as structure, the deposit is located on the west wing of the Garmchashminsky anticline complicated with folds of the lower orders and with a series of small compressed and often overturned isoclinal folds. The deposit is a unique facility, which combines the original mineralogy, a wide range of minerals and the unique features of the genesis. Various types of non-metallic mineral raw materials of industrial significance are concentrated here.

Transparent jewelry golden-yellow-colored clinohumite occurs along with the noble spinel in the deposit. In addition, an industrial scale developed magnesium silicate (talc, forsterite, enstatite) and Mg-carbonate (magnesite) raw materials are present. Graphite and semi-precious pale green serpentine are also of industrial interest in Kuhilal. All this vast complex of useful components associated with Mg-skarn formations confined to the contact of magnesite marbles and plagiogneiss-migmatite rocks of Archaean age.

Information on physical-chemical conditions of formation of major minerals in Kuhilal deposit (in particular, spinel, forsterite, enstatite, clinohumite, tremolite, and others) can be found in papers of Morozov and Gurevich (1973) and Faiziev et al. (1978). Temperature of the minerals crystallization is in limit of 800-600°C.

Here we present characteristics of calcite, which was crystallized in the regressive stage of skarn formation in close association with clinohumite, anthophyllite (gedrite), tremolite,

quartz, sapphirine, nigrine, talc, phlogopite, etc. All these minerals formed during the replacement over primary skarn minerals, at first over forsterite and enstatite.

Calcite forms nest-shape isolations and small veins composed with transparent and colorless medium- and large-crystal units. Studying of relationship of minerals indicates that the calcite stood before quartz and talc because calcite nodules overgrow with fine-grained chalcedony quartz, and then calcite and quartz clothed around with tiny-flakes talc. Powdery talc is also present in the cavities of leaching in calcite.

Fluid inclusions of 0.01 to 0.05 mm have found in calcite. Their form is oval, isometric, diamond-shaped, elongated. Sometimes the inclusions have shape of negative crystals. In aggregative state they are mostly multiphase crystal-fluid, less single-phase gas.

Aqueous solution in crystal-fluid inclusions is not more than 15-20 vol.%. Content of the gas phase is higher (about 20-25 vol.%). The rest of inclusions' volume belongs to solid phases. There are frequent conservatories with several gas bubbles, or gas is deformed and is located in the interstices of subsidiaries crystals.

Homogenization of crystal-fluid inclusions occurs by stages. Initially, the liquid phase of inclusions disappears, then gradually dissolve solid phase, and then comes the general homogenization of the gas phase (Fig. 1).

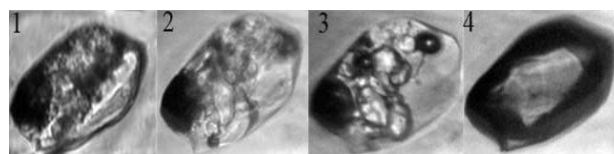


Figure 1. Changes in an inclusion in calcite during heating: 1 - at room temperature, 2 - 515°C, 3 - 590°C, 4 - 690°C.

The temperature of homogenization for inclusions in calcite ranges in the interval 690-670°C. Homogenization takes place exclusively in the gas phase; it indicates a high fluid-content in mineral-bearing medium.

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CHLORINE-RICH MANTLE FLUIDS IN A REGION OF CONTINENTAL FLOOD BASALTS: FLUID INCLUSION STUDIES IN PERIDOTITE XENOLITHS FROM INJIBARA (LAKE TANA REGION, ETHIOPIAN PLATEAU)

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Introduction

Fluid inclusions in mantle rocks provide a unique opportunity to study mantle volatiles, since they can preserve direct evidence of the fluid phases present at depth (cf. Andersen and Neumann, 2001). Since E. Roedder's first studies (1965), it has been evident that CO₂-rich fluid inclusions dominate in the lithospheric mantle. However, overwhelming CO₂ is not the sole component of fluid inclusions. Aqueous fluids of variable salinity have been reported from peridotites in subduction mantle settings (cf., Anderson, Neumann, 2001), and, more recently, intraplate oceanic settings (Frezzotti et al., 2002; Frezzotti, Peccerillo, 2007), pointing to a role of aqueous fluids also in zones of mantle upwelling.

Fluid inclusion study

Petrological and geochemical studies of volatile bearing phases in spinel lherzolite xenoliths (i.e., fluid inclusions, amphibole, and nominally anhydrous minerals – NAM's) from Quaternary lavas at Injibara (Lake Tana region, Ethiopian plateau) show compelling evidence for metasomatism in the lithospheric mantle in a region of upwelling and continental flood basalts. The xenoliths consist of protogranular to porphyroclastic Cl-rich pargasite-bearing spinel lherzolites, metasomatized (LILE and Pb enrichment in clinopyroxene and pargasite) at $T \leq 1000^\circ\text{C}$ (Ferrando et al., 2008).

Lherzolites contain chlorine-rich CO₂ + H₂O fluid inclusions, but no melt inclusions. CO₂ - brines inclusions are preserved only in orthopyroxene, while in olivine and clinopyroxene they underwent extensive interaction with host minerals. In orthopyroxene, liquid H₂O has been observed confined at the cavity borders only in a few large irregularly-shaped inclusions. Water was further identified by Raman analysis (Fig. 1a), and by microthermometric measurements (i.e., clathrates). In olivine, most inclusions are filled by aggregates of talc or clinocllore + magnesite (Raman; Fig. 1b, c, d). In clinopyroxene, rare fluid inclusions contain pure CO₂ and form short alignments along with abundant tiny Cl-rich pargasite inclusions.

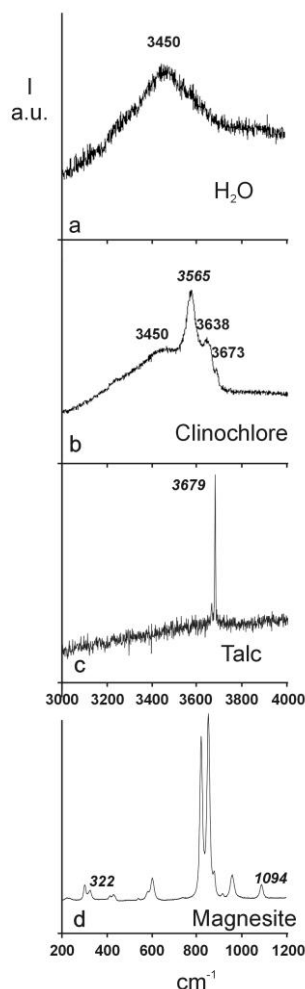


Figure 1. Raman spectra of fluids and minerals contained within fluid inclusions.

From microthermometry and Raman analyses, the metasomatic fluid composition is estimated: $X_{\text{CO}_2} = 0.64$, $X_{\text{H}_2\text{O}} = 0.33$, $X_{\text{Na}} = 0.006$, $X_{\text{Mg}} = 0.006$, $X_{\text{Cl}} = 0.018$, (salinity = 14–10 in NaCl eq. wt.%; $a_{\text{H}_2\text{O}} = 0.2$; Cl = 4–5 mol.%). Fluid isochores correspond to trapping pressures of 1.4–1.5 GPa, or 50–55 km depth ($T = 950^\circ\text{C}$).

In NAM's, synchrotron sourced micro-infrared maps (ELETTRA, Trieste) show gradients for H₂O distribution: olivine incipient hydration is evidenced by local H₂O enrichments up to 200–400 ppm (e.g., inclusions of Mg-phyllsilicates). In clinopyroxene, H₂O contents up to 700–800 ppm

are concentrated in the last 50 μm at grain boundaries, and in intragranular bands at the internal parts.

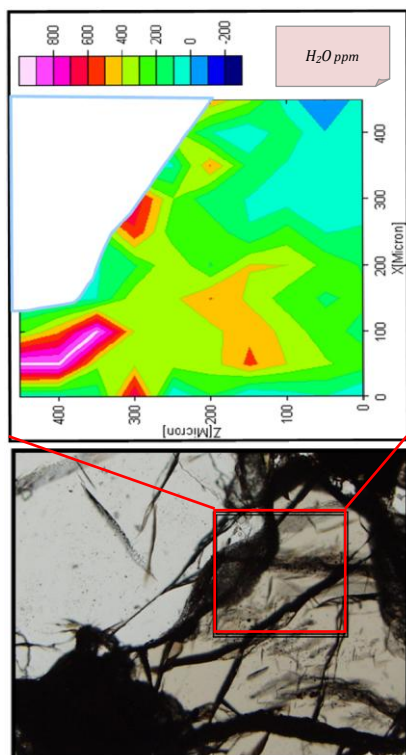


Figure 2. Synchrotron-sourced IR map of H_2O distribution in orthopyroxene containing fluid inclusions.

In orthopyroxene, an increase of OH absorption intensities is systematically observed in fluid-inclusion rich areas. Here, as much as 450 ppm H_2O has been measured, due to additional extrinsic (molecular) H_2O contained in inclusions (Fig. 2). Further, maps revealed positive H_2O gradients moving towards the fluid inclusions: from 80 ppm, at about a 100 μm from the fluid inclusion trail, progressively increasing close to areas containing inclusions up to about 300 ppm (Fig. 2). Similar gradients seem to indicate an effective transition from molecular H_2O into OH-bond, resulting from loss from inclusions through dislocations and other defects.

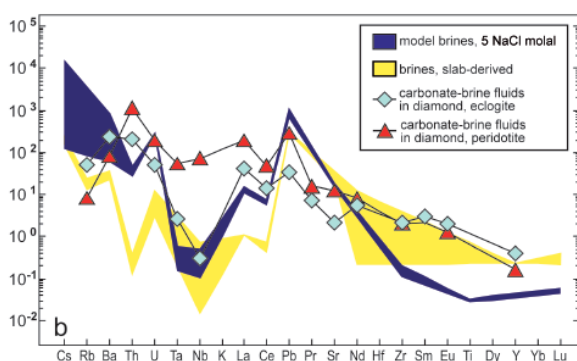


Figure 3. Calculated trace element pattern for brine inclusions (data from Scambelluri et al., 2002; Tomlinson et al., 2009).

Calculated trace-element patterns of metasomatic fluid phases in equilibrium with clinopyroxene and pargasite (5 NaCl molar; Fig. 3; Keppler, 1996), combined with distribution and amount of H_2O in NAM's, delineate metasomatic Cl-, and LILE-rich fluids heterogeneously distributed in the continental lithosphere.

Conclusions

Present data suggest that Cl-rich hydrous fluids were important metasomatic agents in the lithosphere beneath the Ethiopian plateau, locally forming high water content in the peridotite, which may easily melt. High Cl, LILE, and Pb (Fig. 3) suggest the contribution of recycled altered oceanic lithosphere component in metasomatic fluid source. Elemental enrichment by similar fluids may provide an explanation for the geochemical trace-element signature of some LIP magmas (i.e., positive spikes of Ba and Pb). Finally, our findings complement ongoing fluid inclusion research in diamonds and kimberlites (Kamenetsky et al., 2007; Tomlinson et al., 2009), and highlight the important role of chlorine at mantle depth.

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PHYSICO-CHEMICAL CONDITIONS OF ORE DEPOSITION OF GOLD-COPPER AND COPPER MINERALIZATION IN THE BUMBAT ORE CLUSTER, WESTERN MONGOLIA**Gas'kov I.V., Borovikov A.A., Borisenko A.S.***V.S.Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia (gaskov@igm.nsc.ru).*

On the territory of the Ozernaya zone in the Western Mongolia the Bumbat ore cluster is considered as one of the most prospective area for Cu-Au mineralization. It is situated at the south-eastern edge of the Bumbat-Khairkhan Ridge and is composed of island-arc Early Paleozoic volcanogenic and intrusive complexes (Rudnev et al., 2009). Several ore localities with the Cu-Au mineralization are distinguished here, namely Darbi, Three Hills, Altyn Gadas along with a few zones with copper mineralization (Borisenko et al., 2009). They all are spatially confined to plagiogranite intrusion and to small stocks of granodiorites and granite-porphyrries localized at its edges.

Copper mineralization is generally found in a plagiogranite massif and represented by mineralized crush zones with veins and stockworks of quartz-chalcopyrite-bornite composition. Their thickness varies from 0.1-0.5 to 10-15 m and extent – from some meters to 600 m.

Au-Cu mineralization was drilled in the Three Hills and Darbi sites which are located in 20 km from each other. They are represented by sericitized diorites with disseminated pyrite, chalcopyrite, bornite, magnetite and rarely molybdenite. Quartz veins and veined stockworks of quartz-pyrite composition with chalcopyrite, magnetite, hematite, Bi- and Ag-tellurides, galena, molybdenite and native gold with fineness of 850-810‰ are exposed at the Three Hills site. These veins and veined zones contain an elevated Bi, Te, As, Sb, Mo, and Pb concentrations. Gold content in them reaches up to 20 ppm while that of Cu is up to 0.3% and Mo up to 350 ppm. Quartz-pyrite veins and veined stockworks of the same type are wide spread at the Darbi site. They are confined to the exo- and endocontact parts of granodiorite-porphyry stocks or located directly in them. The host rocks are silicified and sericitized to a various degree. Sulfide-quartz veinlets are from some millimeters to 5 cm in thick form linear stockworks. Quartz veins of 0.1-0.2 m thick with sulfide nests and small (up to 0.1 mm) gold nodules are also occurred. The most abundant ore mineral is pyrite which forms crystals up to 1-2 cm in size, the more rarely occurred are chalcopyrite and small segregations (<0.01 mm) of gold and silver tellurides and sulfides as well as of lead telluride (altaite). Gold content in ores vary from tenths to

tens of ppm. Gold fineness is high and varies in the range of 876-1000‰.

U-Pb (SHRIMP) zircon dating for the main types of granitoid intrusions of the Bumbat ore cluster represented by plagiogranite intrusion, granodiorite stock in the Three Hills site, and granodiorite-porphyry stock in the Darbi site, yielded the following age relationships. For this territory the oldest granitoid intrusions are granodiorites hosting Au-Cu mineralization of the Three Hills site (551 ± 13 Ma), a bit younger are plagiogranites of the Bumbat-Khairkhan pluton (534.5 ± 5.7 Ma) hosting copper-quartz veins. The youngest rocks are granodiorite-porphyrries of one of stocks hosting Au-Te mineralization at the Darbi site (524.5 ± 9.8 Ma).

Thus, gold-copper and essentially copper mineralization of the Bumbat region are characterized by various paragenetic mineral associations and are related to different magmatic complexes.

In order to reveal physicochemical conditions of formation for these different manifestations we examined the fluid inclusions in quartz from the samples of quartz-chalcopyrite veins (copper occurrence No.98) and from samples of gold-bearing quartz-sulfide veins (Three Hills and Darbi sites). Fluid inclusions of two generations have been established in quartz of quartz-chalcopyrite veins of the copper occurrence. The first inclusion generation contemporaneous with quartz crystallization is represented by the two-phase inclusions containing the saline aqueous solution, gas bubble and often an opaque ore phase. The homogenization temperatures of first generation fluid inclusions in the explored samples fall into a narrow range of 240-230°C. Overheating of these inclusions up to 350°C causes no inclusion decrepitation indicating the absence of dense gaseous phase in their composition. The solution concentrations do not exceed 5.2 wt.% in NaCl equivalent. Fluid pressure in the inclusions established on the base of homogenization temperature is less than 300-250 bars. Fluid inclusions of the second generation are secondary in nature and are found in the sealed crack plains. These inclusions have a more or less isometric vacuole's shape and contain an aqueous solution and gas bubble. The temperatures of their homogenization are as low as 100-140°C.

Fluid inclusions trapped in quartz of quartz-sulfide veins of the Three Hills Au-Cu occurrence are confined either to crack plains or create isolated groups of the primary inclusions in crystalline quartz. They are represented by essentially gaseous and two-phase water-saline inclusions. The inclusions from quartz groundmass are homogenized at temperatures from 225 to 305°C, 230°C on the average, although the bulk of large inclusions decrepitate prior to complete homogenization at temperature higher than 250°C. The primary inclusions in small drusy quartz crystals have the lowest homogenization temperatures in the range of 160-155°C. Gaseous bubbles in aqueous-saline and in gaseous inclusions contain dense CO₂ observed in a liquid state at 20°C. The relatively wide range of homogenization temperatures (225-305°C) established for inclusions with dense CO₂ indicate a combined entrapment both the liquid aqueous solution and separated gas phase into them. The concentration of water-salt solution in fluid inclusions varies from 12.9 to 9.5 wt.% in NaCl equivalent. CO₂ melting temperature is -57.9°C. This value is somewhat lower than the pure CO₂ melting temperature and may indicate the presence of minor amount of other gases. CO₂ homogenizes into a liquid phase at +10/+20°C that corresponds to a density ranged from 0.86 to 0.79. In the point of homogenization of inclusions containing CO₂ with similar density the values of internal pressure exceed 1700 bar which lead to their decrepitation during heating. The eutectic melting temperature of inclusion solution (-22°C) is close to that of pure water-saline NaCl-H₂O system that suggest that main saline component in an aqueous solution is NaCl. Fluid inclusions in quartz of sulfide veins at the Darbi site have similar parameters. Gas-chromatographic analysis of the samples of gold-bearing sulfide and quartz-chalcopyrite veins has determined the prevailing CO₂ and H₂O in a gaseous phase of fluid inclusions.

Thus, the study of fluid inclusions from quartz-sulfide veins of gold-copper and copper quartz-veined occurrences of the Bumbat region showed considerable differences in the conditions of their formation. It was established that fluid regime of formation of gold-bearing quartz-sulfide veins at the Three Hills and Darbi sites differ substantially from that of veined-type Cu mineralization at the ore occurrence No.98. Gold-bearing quartz-sulfide veins formed with participation of heterophase fluids at temperatures of 155-245°C and pressure of 1700 bar. Average salt concentration in water-saline phase of ore-forming fluid was 12.9-9.5 wt.%, whereas a gaseous phase was represented by a dense (0.86-

0.79) CO₂. The analogous parameters of fluid regime of ore formation are typical for Au-Cu porphyry-type deposits (Ryabinovoe, Endeavour, etc.) and together with geochemical features of these ores (elevated Cu, Mo, Pb, Bi, Te, As, and Sb concentrations) may point to porphyry Cu-Mo type of this mineralization and its large scale. Quartz-chalcopyrite veins of copper occurrences formed from homogenous nearly fresh (< 5.2 wt.% in NaCl equivalent) CO₂-free hydrothermal solutions. Temperatures of mineral formation varied within 230-240°C while the pressure not exceeded 300 bar.

Thus, the presence of fluid inclusions with high water-saline concentrations and gaseous inclusions with dense CO₂ (0.7-0.8) in veined quartz can be considered as the prospecting indicator of gold mineralization of quartz veins in this region.

The work was supported by the grants 09-05-00915, 09-05-00295 from the Russian Foundation for Basic Research.

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THERMOBARGEOCHEMICAL CHARACTERISTICS OF FLUIDS FOR GOLD-QUARTZ VEINS OF THE GERFEDSKOE DEPOSIT (YENISEY RIDGE, RUSSIA)

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Hundreds of quartz veins are known in the metamorphic rocks of the Yenisei Ridge but only few of them are auriferous veins (with commercial gold content) (Seredenko, 1985; Li et al., 1985). The Gerfedskoe deposit, which is located in the South-Yenisei region, is a prominent example of the gold and gold-free quartz veins combination. Ore bodies are located along the large Meister fault which runs in submeridional direction. Structural position of the ore zone as a whole is determined by confinement to anticline limb. The Tatarsky pluton occupies the core of the anticline (Li, 1997). The deposit is represented by sub concordant quartz veins elongated in meridional direction and localized at the contact of Lower Proterozoic Penchenginskaya and Upper Proterozoic Kordinskaya suites. The suites are composed of quartz-chlorite-sericite-carbon schists altered by effusive and carbon phyllite-like schists, respectively.

Intersecting veins are superimposed on the subconcordant meridional quartz veins. Intersecting veins contain similar set of sulfides but they differ in the gold content. The gold content does not exceed 1g/t in some of them and exceeds 10 g/t in the others. The gold content seldom exceeds 1-2g/t in the sub concordant meridional quartz veins (Li et al., 1985).

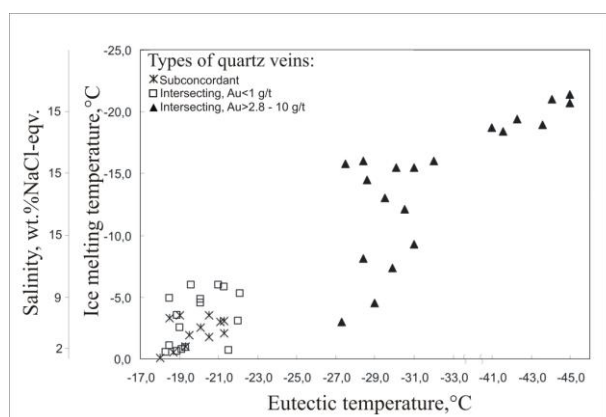


Figure 1. Salinity – composition of fluids from quartz veins of the Gerfedskoe deposit.

Fluid inclusions in quartz of sub concordant and intersecting quartz veins with low and high gold content have been studied by the methods of thermobarometry, cryometry, Raman spectroscopy and gas chromatography. It was found that three types of quartz veins were formed by the fluids

different in composition and thermobaric parameters.

Subconcordant tabular quartz veins were formed by homogenous essentially water-chloride, weakly salt (less than 7.0wt.% NaCl-equiv.) (Fig. 1) fluids in the temperature range of 120 to 230°C (Fig. 2) and pressure of 0.1 to 0.5 kbar.

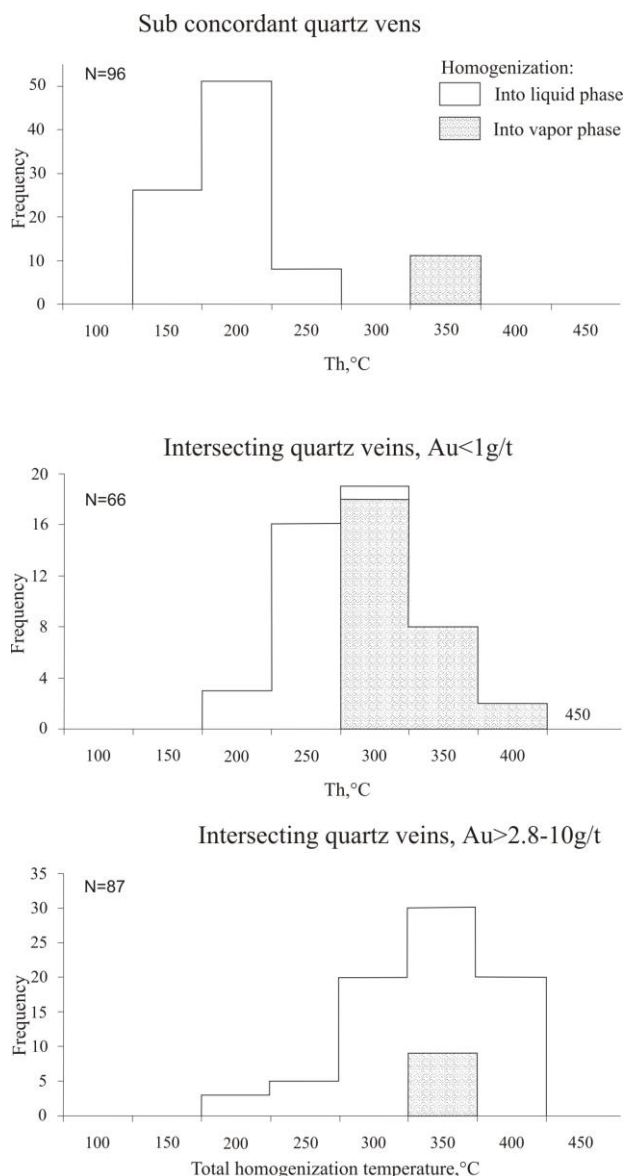


Figure 2. Histograms of homogenization temperatures of fluid inclusions in quartz veins of the Gerfedskoe deposit.

Intersecting quartz veins ($Au \leq 1g/t$) were formed by homogeneous and heterogeneous fluids at the temperatures of 150 to 300°C (Fig. 2) and pressures of 0.1 to 1.7 kbar. Fluids salinity was

growing up to 10 wt.%, NaCl-equiv. Gas component of the fluids is represented by CO₂, N₂, CH₄ and others heavier than CH₄ hydrocarbons (Fig. 3). CO₂/CO₂+H₂O ratio was changing from 0.09 to 0.17.

Intersecting quartz veins with high gold content were crystallized from carbonic acid-water (Fig. 3) heterogeneous fluids with salinity of 6.0 to 23.3 wt.%, NaCl-equiv. (Fig. 1) at temperatures of 150 to 400°C (Fig. 2) and pressures of 1.3 to 2.5 kbar. CO₂/CO₂+H₂O ratio varied within the interval of 0.18 to 0.27.

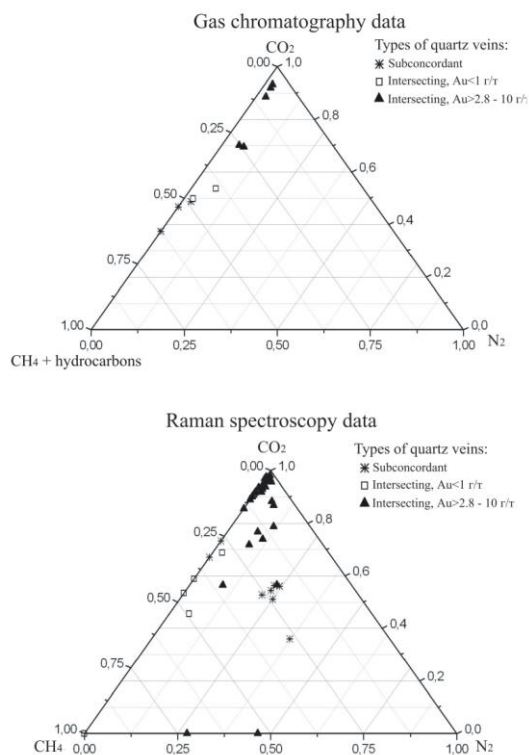


Figure 3. Composition of gas component of the fluids from quartz veins of the Gerfedscoe deposit.

The areas with commercial gold content were formed with the participation of salt, high temperature water-carbon dioxide fluids, which probably extracted gold from weakly auriferous sub concordant and intersecting veins and concentrated gold in the so called “stockwork-like” bodies of the Gerfedscoe deposit.

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COMPOSITION OF MELT INCLUSIONS IN MANTLE XENOLITH MINERALS FROM KIMBERLITES OF THE UDACHNAYA-EAST PIPE (YAKUTIA): RAMAN SPECTROSCOPY DATA

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Introduction

The studies of mantle xenoliths all over the world display the presence of secondary melt inclusions in rock-forming minerals. It mainly focused on study of melt inclusions in minerals from mantle xenoliths from basalts. It was shown that such melt inclusions have predominantly silicate compositions (Schiano, Clocchiatti, 1994; Andersen et. al, 2001). In this paper we present the results of phase analyses of melt inclusions identified in rock-forming minerals from the xenoliths of sheared lherzolites from kimberlites.

Xenoliths of sheared lherzolites are possibly the deepest mantle samples available, and believed to originate from the lithosphere – asthenosphere boundary (Boyd, Gurney, 1986). In general, it is well-known that the nodules have complex history, including partial melting, several stages of metasomatism and deformations. These xenoliths consist of olivine, orthopyroxene, clinopyroxene and garnet. The P-T parameters of last thermal events for 30 samples of sheared lherzolites can be estimated based on the geothermometer of Brey and Kohler (1990) as high as P – 56-75 kbar, T – 1200-1400°C (Agashev et al., 2010).

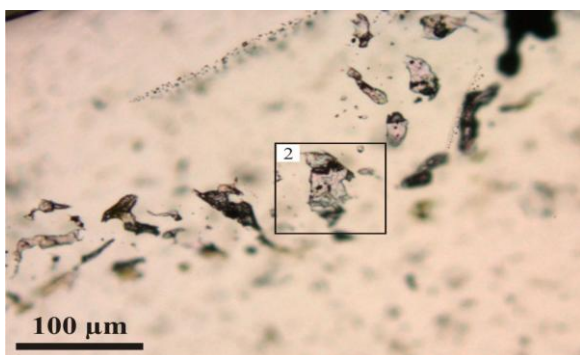


Figure 1. Photomicrograph of secondary melt inclusions in olivine from sheared peridotite xenolith from Udachnaya pipe.

Melt inclusions are present in all primary minerals of lherzolites and are hosted in healed fractures, some of which transect entire grains of host minerals, and therefore are secondary in origin (Fig. 1). They consist of fine-grained aggregate of carbonates, sulphates and chlorides, some translucent crystals, opaque minerals (magnetite, djerfisherite, pentlandite, pyrrhotite) and a vapour bubble (Fig. 2-7). Daughter crystals (up to twenty

in individual inclusions) are represented by silicates (tetraferriphlogopite, olivine), chlorides (halite, sylvite) and various carbonates, sulphates and sulphides (Fig 2-7).

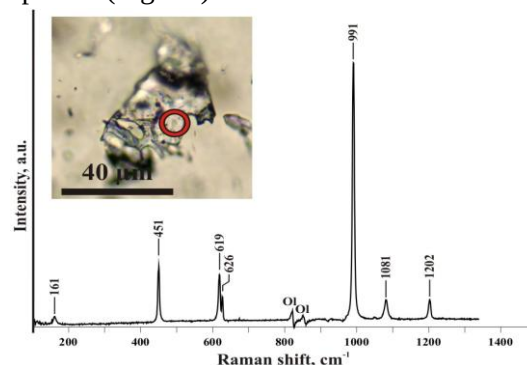


Figure 2. Representative Raman spectra of apthitalite. Note: Ol in all spectra is relict bands of host olivine.

Identification of all daughter minerals, especially those with a submicron size, was not always possible, and this made estimates of the bulk inclusion compositions problematic. In general, main phases are Ca-, Na- and K-bearing carbonates, sulphates, sulfide and chlorides, whereas silicate minerals occupy <15 vol.% of the inclusion volume.

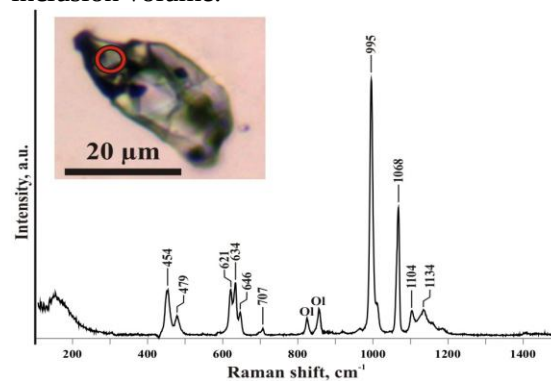


Figure 3. Representative Raman spectra of burkeite.

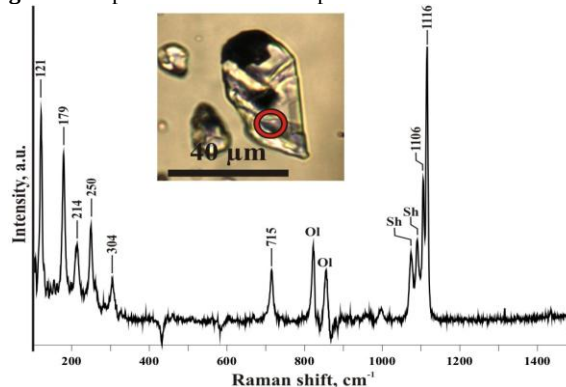


Figure 4. Representative Raman spectra of northupite.

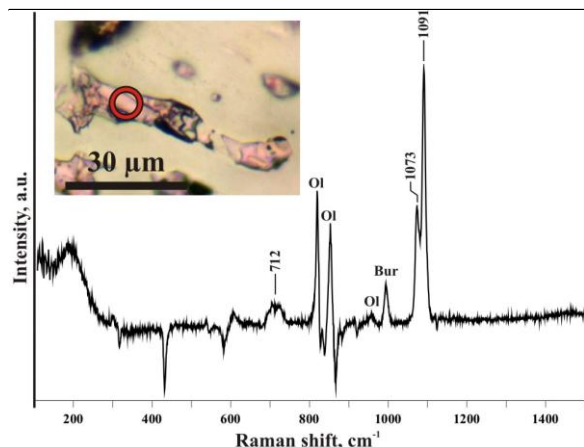


Figure 5. Representative Raman spectra of shortite.
Note: Bur - burkeite peaks.

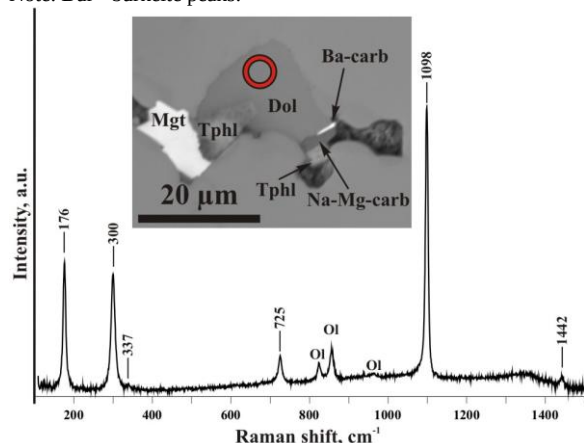


Figure 6. Representative Raman spectra of dolomite.

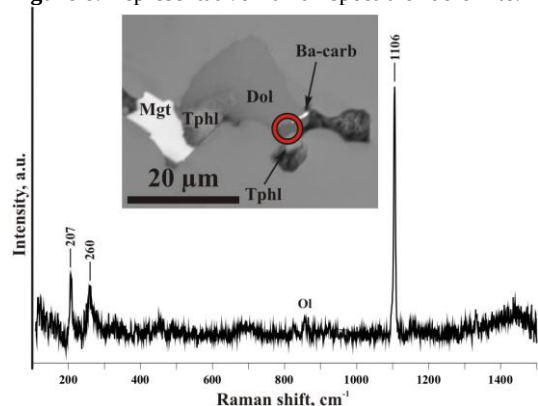


Figure 7. Representative Raman spectra of a Na-Mg-carbonate (eitelite ?, Na, Mg and C were detected by EDS spectra).
Note: Tphl – tetraferriphlogopite, Mgt – magnetite, Dol – dolomite, Na-Mg-carb – Na-Mg-carbonate, Ba-carb – Ba-Na-Mg-carbonate.

Methods

An identification of alkali-carbonates and sulphates in inclusions is problematic due to small size (2-10 μm) and breakdown of these minerals once they are exposed at the surface. The Raman spectroscopy is well known as best non-destructive method of phase identification. Raman spectra were collected at Novosibirsk State University on microspectrometer Horiba Jobin Yvon T64000, with green Ar⁺ 514.5 nm laser (Spectra Physics Stabilite 2017). The identification of minerals was performed by comparison of obtained spectra with spectra from ruff database of Raman spectroscopy,

Results

Unfortunately, the existing database of Raman spectra for rare alkali-bearing carbonates and sulphates is incomplete, nevertheless, the following minerals was found: sulphates - **aphthitalite** $\text{K}_3\text{Na}(\text{SO}_4)_2$ (band at 161, 451, 619, 626, 991, 1081, 1202 cm^{-1} , Fig 2); complex sulphate-carbonate **burkeite** $\text{Na}_4\text{SO}_4\text{CO}_3$ (bands at 454, 479, 621, 634, 646, 707, 995, 1068, 1104, 1134 cm^{-1} , Fig 3); carbonates – **northupite** $\text{Na}_3\text{Mg}(\text{CO}_3)_2\text{Cl}$ (bands at 121, 179, 214, 250, 304, 715, 1106, 1116 cm^{-1} , Fig 4), **shortite** $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ (bands at 712, 1073, 1091 cm^{-1} , Fig 5), **dolomite** $\text{CaMg}(\text{CO}_3)_2$ (bands at 176, 300, 337, 725, 1098, 1442 cm^{-1} , Fig 6). Several additional Raman bands at 207, 260, 1106 cm^{-1} (Fig. 7) were found for **Na-Mg-carbonate**, probably eitelite.

Discussion

Secondary melt inclusions in mineral from the deepest mantle xenoliths from kimberlites have alkali-carbonate compositions. This fact is inconsistent with previous observations, because mainly silicate melt inclusions were identified within the mantle xenoliths. An origin of alkali-carbonate melt inclusions in minerals from the xenoliths is highly disputable. These secondary melt inclusions have similar compositions and ratio of daughter phases as inclusions identified in the olivine from kimberlites (Golovin et al., 2003, 2007; Kamenetsky et al., 2004). Furthermore some kimberlites are characterized by ubnormal high concentration of alkalis and chlorine. Therefore we assume that there is a genetical relationship between origin of secondary melt inclusions in mantle xenoliths and kimberlite magmatism. Inclusions could form prior to entrapment by kimberlite melt. In this case they represent traces of protokimberlite melts and raise an idea about genetic relationship between alkali carbonatites and kimberlites. These inclusions could also form during the transportation of xenoliths by kimberlites at mantle depth or superficially. Thus this model would support the new hypothesis about high concentration of alkali and chlorine in kimberlite melts (Kamenetsky et al., 2007; 2009). In conclusion, whatever the origin (deep mantle or near-surface) and trapping mechanism of the studied melt inclusions, their compositions unambiguously point to high concentrations of alkalis, C, Cl and S in the mantle melts originated at the lithosphere – asthenosphere boundary.

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DISTRIBUTION OF INCLUSIONS IN HALITE FROM CHLORIDE XENOLITH IN UDACHNAYA-EAST KIMBERLITE PIPE

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Introduction

In recent decades many researches have been focused on the role of chlorides in the formation of the mantle rocks. Several recent papers have discussed the possible magmatic origin of alkali chloride and chloride-carbonate xenoliths from kimberlites of the Udachnaya-East pipe, Yakutia. Comagmatic origin of the chlorides from xenoliths to parent kimberlitic magma was concluded on the base of similarity of Sr, Nd and Pb isotopic data in the chloride xenoliths, in the silicate fraction of the groundmass and in the water leachate of the kimberlite groundmass (Kamenetsky et al., 2007). Rare minerals have been described in associations with chlorides (Sharygin et al., 2008). However, they did not remove an ambiguity of the origin of xenoliths.

We have found contrasting inclusion associations at the core and at the rims of chloride xenoliths. Saline melt inclusions have been found exceptionally at the rims (Grishina et al., 2008). These data allowed us to propose the crustal origin of the chloride xenoliths based on partial melting of Cambrian salts leading to heterogeneous trapping of saline melts solely at the rim of xenoliths. The goal of current study is to ascertain the boundary of melting through detailed study of inclusion distribution within the entire xenoliths.

Inclusion types

The most important addition of the current research with respect to previous studies is successive sampling. We have documented the distribution of inclusions within the rounded xenolith #9793, 40 cm in length interlaid with nonsoluble minerals, mainly anhydrite and silicates. Fluid, mineral and combined inclusions have been studied. Chloride-rich waterless inclusions were found to be the most informative ones. They provide essential information on melting processes.

Sylvite in the central part of the xenolith is occurs in halite as abundant tiny (less than 7 µm) idiomorphic inclusions that represent emulsion texture. Under heating more than 500°C sylvite inclusions dissolve in halite with formation of homogeneous solid solution (Na,K)Cl. According to experimental data (Filatov, Vergasova, 2002), the revealed emulsion structure is evidence of disintegration of solid solution KCl-NaCl.

Sylvite in halite of the outer part of the

xenolith form large rounded monomineral inclusions or occur as main phase of crystallized salt melt inclusions. Salt phases in the inclusions occur as monolithic aggregate or some crystals. Polyphase character of sylvite-rich inclusions indicates formation from the melt (Fig. 1).

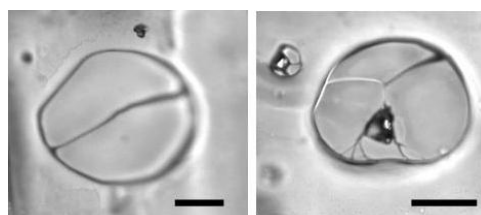


Figure 1. Photomicrographs showing polyphase sylvite inclusions in halite at the rim (scale - 20µm).

Chlorocalcite inclusions are abundant at the centre of the xenolith as euhedral pseudocubic crystals (Fig. 2). Skeletal crystals or twinnings are also common. By contrast, at rims of the xenolith it occurs mostly as tiny rounded solids or dendrites inside salt melt inclusions (Fig. 3, 4b). Embayed crystals of chlorocalcite and sylvite also occur at intermediate zones along with both euhedral and dendritic inclusions. Some chlorocalcite inclusions contain anhydrite (up to 30 vol.%).

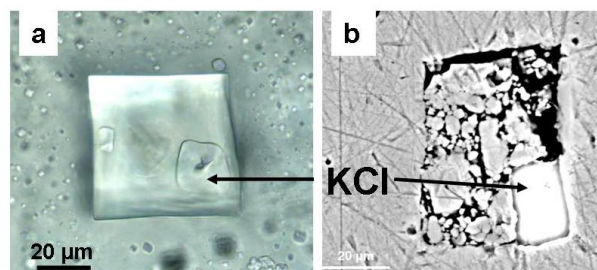


Figure 2. Coeval chlorocalcite and sylvite crystals in inclusions at the core of the xenolith. a – optical (crossed polars), b – an open cavity of chlorocalcite inclusion with KCl crystal (BSE image).

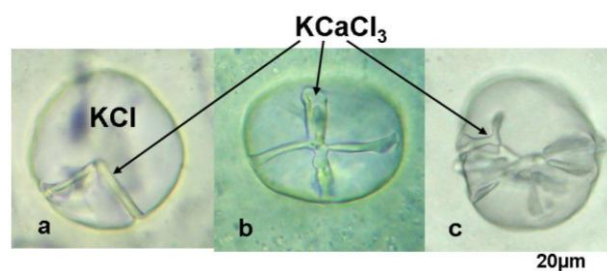


Figure 3. Intergrowths of dendritic chlorocalcite and sylvite at the xenolith rim.

Chlorocalcite sometimes coexist with sylvite in the inclusions (Fig. 2). Their intergrowths display varying volume ratio. However, chlorocalcite is dominating phase in inclusions from the centre of the xenolith, whereas in most cases sylvite prevails in the inclusions from the outer zone.

The CO₂-bearing inclusions occur as combined inclusions with KCl or KCaCl₃ crystals at the centre of the xenolith and CO₂ inside saline melt inclusions are characteristic for xenolith rim (Fig. 4).

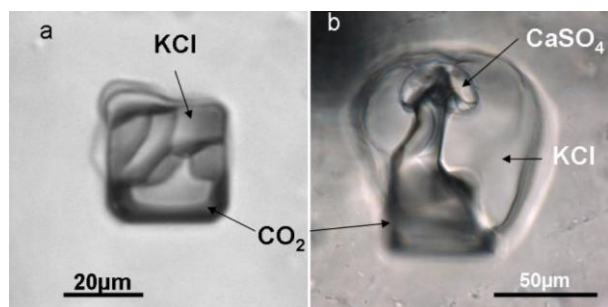


Figure 4. Combined CO₂-bearing inclusions from the central (a) and outer (b) parts of the xenoliths.

Salt melt inclusions have rounded shapes and consist mainly of KCl and CO₂ bubble. Inclusions often contain a round anhydrite and/or chlorocalcite (Fig. 5).

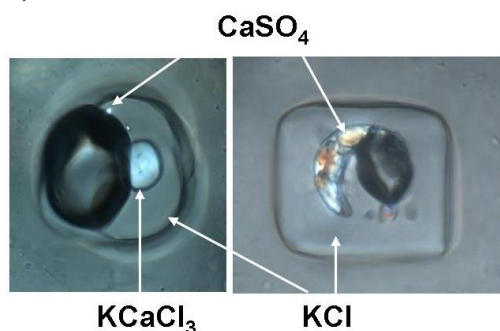


Figure 5. Salt melt inclusions with different phase composition.

Both inclusion associations coexist at the rim of xenoliths, their distribution is heterogeneous but the association II with salt melt inclusions is dominating. By contrast, the association I is concentrated at the centre of the xenolith.

Observed compositional zoning patterns in chloride xenoliths suggest that crystallization took place toward the center and lead to the accumulation of calcium chloride in the residual liquid. Upon reaching the eutectic temperature 495°C in the system KCl-NaCl-CaCl₂ co-crystallization of KCl, 2KCl·3CaCl₂ and the KCl-NaCl solid solution occur (Voskresenskaya, 1961). The composition of the documented inclusions at the center of xenoliths corresponds to that of eutectic phases. The large volume scattering of

crystallized phases suggests crystallization in a heterogeneous environment.

Conclusions

We have observed two contrasting inclusion associations in halite characterized by an inverse ratio of KCl and KCaCl₃. The association I is characterized by Ca-rich inclusions (KCaCl₃ > KCl) and the association II is characterized by K-rich inclusions (KCl > KCaCl₃). These associations have heterogeneous distribution. Both associations is jointly presented throughout the xenolith except for a little domain at the core (nearly 3 cm³), where the association II is absent. At this domain the association I is abundant.

Identifying melted halite matrix at the centre of the xenolith does not contradict the original hypothesis of a crustal origin for halite-rich xenoliths in kimberlite of the Udachnaya-East pipe. Salt rocks belonging to the sediments of the platform cover was captured by kimberlite magma resulting in complete melting of chlorides and partial melting of refractory minerals including anhydrite. Upward transport at extremely high speeds led to rapid crystallization from heterogeneous melt.

Acknowledgements

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TRACE AND MAJOR ELEMENT COMPOSITION OF CARBONATITE MELT INCLUSIONS IN COEXISTING MAGNETITE AND APATITE IN KERIMASI CARBONATITE, TANZANIA: IMPLICATIONS FOR MELT EVOLUTION

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Introduction

Carbonatite melts play an important role in the physical and chemical evolution of the Earth's lithosphere. These melts are effective agents for the transport of transition, rare earth and alkaline earth elements as suggested by numerous studies e.g., Rankin and LeBas (1974), Nielsen et al. (1997), Lee and Wyllie (1998), Sokolov et al. (1999), Panina (2005), Solovova et al. (2006), Guzmics et al. (2008, 2010) and Mitchell (2009).

Results

The Kerimasi calciocarbonatite consists of calcite, apatite, magnetite and monticellite. Apatite and magnetite are abundant in carbonatite melt and fluid inclusions. In addition, silicate melt inclusions occur in magnetite. Calcite contains fluid and S-bearing Na-K-Ca-carbonate inclusions. Our study provides compositional data for quenched S- and P-bearing, Ca-alkali-rich carbonatite melt inclusions in magnetite (Fig. 1) and apatite (Fig. 2). Furthermore, Raman microanalyses on fluid inclusions and bubble phase of melt inclusion have been also carried out. Magnetite-hosted silicate melt inclusions reveal peralkaline composition with normative sodium metasilicate. Magnetite usually hosts perovskite in the melt inclusions. Based on our homogenization experiments, apatite-hosted melt inclusions and forsterite-monticellite phase relationships, temperatures of the early stage of magma evolution are estimated to be in a range of 900-1000°C. At this time three immiscible liquid phases coexisted: (1) a Ca-rich, P-, S- and alkali-bearing carbonatite melt, (2) a Mg- and Fe-rich, peralkaline silicate melt, and (3) a C-O-H-S-alkali fluid. During the evolution of coexisting carbonatite and silicate melts, the Si/Al and Mg/Fe ratio of the silicate melt decreased with contemporaneous increase in alkalis due to olivine fractionation. In contrast, the alkali content of the carbonatite melt increased with concomitant decrease in CaO resulting from calcite fractionation. Overall peralkalinity of the bulk composition in the immiscible melts increased, causing a decrease in the size of the miscibility gap in the pseudoquaternary system studied. The studied melt inclusion data indicate the formation of a carbonatite magma that is extremely enriched in

alkalis showing similar composition to the Oldoinyo Lengai natrocarbonatites.

In case of evolution of trace elements in the studied melts, apatite and perovskite have huge effect on REE fractionation and perovskite also fractionates Nb, U and Th significantly.

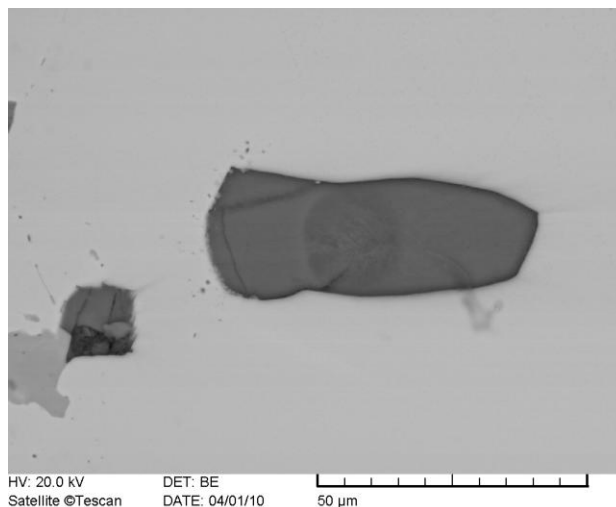


Figure 1. Magnetite-hosted, quenched carbonatite melt inclusion after heating to 880°C (BSE image).



Figure 2. Apatite-hosted, quenched carbonatite melt inclusion after heating to 920°C (photomicrograph, 1N).

Conclusions

Investigating melt inclusions entrapped in co-crystallizing phases is a powerful tool to understand major and trace element evolution of carbonatite melts. The compositions of carbonatite melt inclusions are considered as representatives of parental magma composition contrarily to any

whole rock that contains negligible amount of alkalis. Consequently, implications for magma composition and evolution using bulk rock carbonatite composition should be reconsidered.

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APPLICATION OF FLUID INCLUSION STUDIES ON EXPLORATION OF ORE DEPOSITS IN ARASBARAN METALLOGENIC BELT (NW IRAN)

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Introduction

The Arasbaran Cu-Au Belt, straddling the Iran-Armenia border (NW of Iran) between Latitudes 46° to 47°50' E and 38°-39° N (Iranian part and study area), is one of the worlds premier porphyry-epithermal districts, containing the world class Sungun deposit and some other prospects.

The northern section of the UDMB, also known as Qaradagh Belt (Berberian et al., 1981), or Arasbaran Metallogenic Zone (AMZ), is a major host to porphyry-style Cu-Mo deposits, represented by Sungun, Haftcheshmeh, Kighal and Niaz (Fig. 1), skarn-type base metals, represented by Sungun, Mazraeh, Anjerd (Hassanpour, 2010), and epithermal precious metal deposits, exemplified by Sharafabad, Masjed-Daghi, Sarikhanloo and Safikhanloo (Alirezaei et al., 2008). Compared to the Kerman Belt, however, the evolution of the northern UDMB is poorly known.

The Sungun deposit, with an approved reserve of 500 MT at 0.69% Cu and ~250 ppm Mo, is the largest known porphyry Cu-Mo system in AMZ. Systematic exploration, including 80000 m of diamond drilling, was conducted by NICICO (National Iranian Copper Industries Company) during 1989-2000, and open-pit mining started at 2003. Currently, Sungun is producing 150000 T concentrate per year at 30% Cu.

The geology of the district is dominated by an entirely subaerial upper Eocene to Upper Pliocene calc-alkaline volcanic succession overlying a Cretaceous basement consisting of predominantly limestones and pyroclastic rocks. This transect of the Alpine orogen has been considered to have been a magmatic since the Late Paleocene as a result of a main subduction. The Tertiary succession is herein consists of some volcanic and intrusive units.

Discussion

The studied fluid inclusions from all kinds of mineralizations have been analyzed for temperature and salinity. We have drawn a diagram (Fig. 2) for separating and showing their differentiations for all characteristics. In this research we have obtained a good result for identify kind of mineralization on fluid inclusion patterns.

1. Porphyry type deposits: High salinity and high temperatures.
2. Vein type deposits: Medium to high salinity and high temperatures.

3. Skarn type deposits: Medium to low salinity and high temperatures.
4. Steam heated alterations: Low salinity and medium to high temperatures.

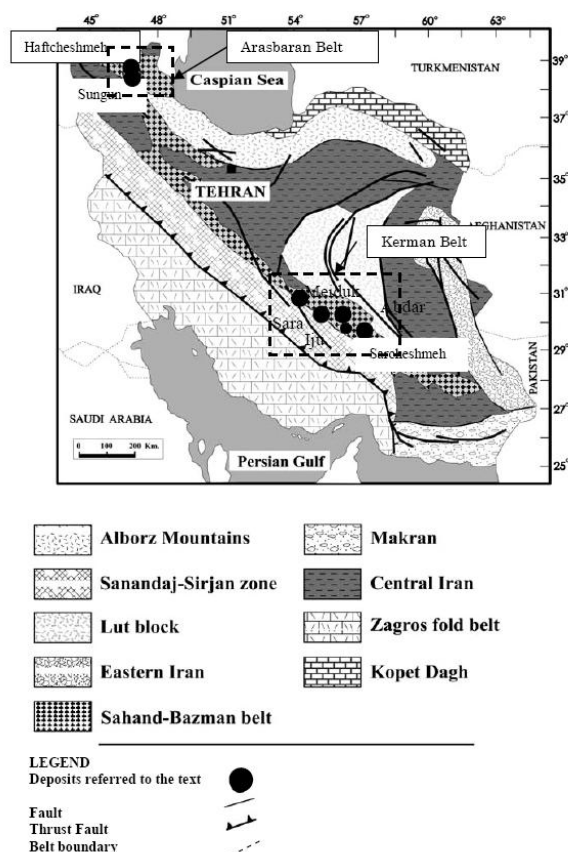


Figure 1. Iran geological zoning map that Arasbaran metallogenic belt and main copper porphyry ore deposits are situated on.

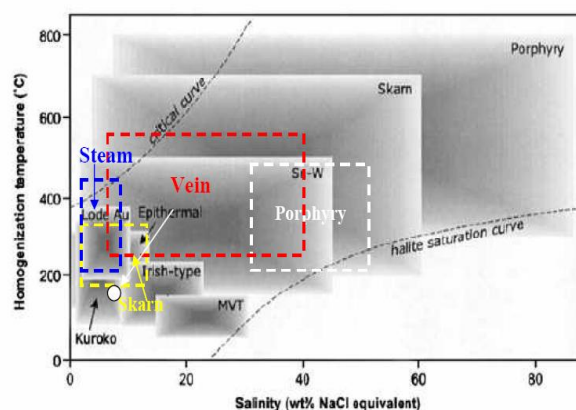


Figure 2. Fluid inclusions for all kinds of mineralization in the Arasbaran metallogenic belt.

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STUDY OF C-O-H BEARING FLUID INCLUSIONS IN PERIDOTITE XENOLITHS FROM JEJU ISLAND (SOUTH KOREA)

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Introduction

One of the most accurate ways to describe the chemical and rheological state of the upper mantle is studying upper mantle peridotites as xenoliths. In this study we give a comprehensive picture of the nature of fluid inclusions in petrologically and geochemically well described spinel lherzolite and harzburgite xenoliths hosted in the Pliocene basalts of the Jeju Island, South Korea. The petrological and geochemical data of the xenoliths combined with the new results obtained from the textural feature and phase chemistry of the fluid inclusions provide better understanding of upper mantle processes and evolution of the mantle beneath the Island.

Fluid inclusions entrapped at mantle conditions are usually CO₂-dominated and additional fluid components, especially H₂O, are rarely recognized (*e.g.* Török, de Vivo, 1995) despite the fact that other evidence suggests that H₂O [the term H₂O, if otherwise not indicated, hereafter refers to molecular water (H₂O) and/or hydroxyl (OH-) regardless of the speciation and hydrogen (H⁺)] is relatively common in the upper mantle. By the reconstruction of post-entrapment evolution of fluid inclusions revealed from metasomatized peridotites this study might contribute to the general knowledge of processes associated with high P-T fluid entrapment.

Geological overview

The Jeju Island is known as an intraplate volcano on the Eurasian Plate showing geochemical signatures of oceanic island basalt (Nakamura et al., 1989). The Island is located close to the eastern margin of the Eurasian plate which is a well-known convergent plate margin; active at least since the pre-Triassic, and now the Pacific Plate is being subducted beneath the Eurasian Plate. Despite the fascinating geodynamic position and evolution of the Island, peridotite studies from South Korea, particularly Jeju Island, are very rare (*e.g.* Choi et al., 2002 and references therein). Hence the general view of the evolution of the sub-continental lithospheric mantle is still enigmatic.

Present day Jeju Island was formed in a ca. 2.5 million years time span by the volcanic activities occurring from the Pliocene to recent on the continental lithosphere showing normal Moho depths. The basal basaltic lavas erupted on Jurassic-

Cretaceous rhyolitic tuff and minor gneiss of unknown age, which are rarely exposed as xenoliths in pyroclasts or recovered in drilling cores (Kim et al., 2003). Four stages of subaerial volcanic activity on the Island have been recognized based on the stratigraphic relationships and radiometric dating (Koh et al., 2004). The mantle xenoliths hosted by alkali basalts outcropped at several localities in the Jeju Island of which Jigriorem, Sangumburi and Sinsanri have been sampled.

Fluid inclusion characteristics

Based on the modal composition, majority of the xenoliths studied here is spinel lherzolite with minor amount of spinel harzburgite, all of them showing coarse grained protogranular-porphroclastic texture. Fluid inclusions in every xenolith are intergranular, crosscutting the rock-forming mantle silicates, and applying the definition of E. Roedder are considered as secondary ones with respect to the formation of the hosts minerals.

The fluid inclusion associations always consist of several hundred negative crystal shaped fluid inclusions ranging in size from 2-3 µm to 50-60 µm. Furthermore, small-sized fluid inclusions (<10 µm), even in olivine, are usually of one-phase at room conditions and show no indication for leakage (*i.e.* no decrepitation halo), whereas the large ones contain two phases (various sized fluid bubble in a liquid phase) or, if single-phase, look empty (Fig 1).

Based on microthermometric experiments, the solid phase melts at -56.6°C (±0.3°C) with no other observable melting events indicating that the trapped fluid is mostly CO₂. In contrast, the homogenization temperatures show a much wider range. The smaller the fluid inclusion, the lower the homogenization temperature, regardless of the host mineral. High density fluid inclusions (1.03-1.10 g/cm³) were found in every xenolith, where sufficient number of freezing-heating experiments could be done. Microthermometric data on the Jeju xenoliths did not succeed to identify volatile components other than CO₂.

Raman analyses were conducted at room and elevated temperatures (+150°C). At room temperatures only the CO₂ was detected, whereas at elevated temperatures, beside the Fermi-diad of CO₂, the peaks of H₂O dissolved in CO₂ were also

observed. Even though the complete homogenization of the fluid inclusion cannot be recognized, at high temperature the distribution of dissolved H₂O in CO₂ is presumably uniform, which allows (semi-)quantification of spectra of the CO₂-rich phase according to the method of Dubessy et al. (1992).

At 150°C, the calculated H₂O content ranges from 3.9 to 9.9 mol% and shows an average value at 5.8 mol%. Recognition of H₂O with routinely used analytical techniques (microthermometry and room temperature Raman spectroscopy) is limited, due to mainly the low concentration of H₂O and its occurrence as a submicroscopic film on the inclusion walls (Berkési et al., 2009).

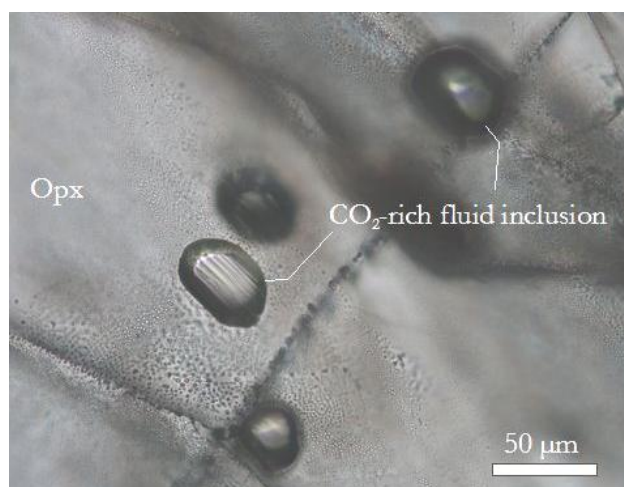


Figure 1 Photomicrograph of fluid inclusions in the Jeju peridotite series. Opx - orthopyroxene.

Conclusion remarks

As summarized, fluid inclusions entrapped at upper mantle conditions in the deep sub-continental lithosphere conditions contain small but significant amount of H₂O that exist as a thin film on the walls of many high-density CO₂-rich fluid inclusions and its detection is prevented by the inadequacy of currently used analytical techniques.

The presence of water in deep-seated fluid inclusions is not the special feature of the upper mantle, but rather reflects the general composition of any fluid inclusion from a sub-continental lithospheric setting.

The widespread occurrence of fluid inclusions in the Jeju peridotite series also indicate that the upper mantle is crosscut by several C-O-H bearing fluid inclusion zones, which could significantly affect the mantle rheology beneath the Island. However, based on the petrographic evidences, the fluid entrapment can be regarded as a late stage event in the evolution of the shallow sub-continental lithospheric mantle.

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DISCOVERY OF TRIPLITE IN THE BAXIANNAO TUNGSTEN DEPOSIT, SOUTHERN JIANGXI, CHINA, AND ITS IMPLICATION TO MAGMA AND FLUID CHARACTERISTICS

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Introduction

Due to the similar ionic radius of Fe^{2+} (0.91 Å) and Mn^{2+} (0.86 Å), two Mn-Fe-bearing phosphate minerals, triplite and zwieselite, usually form a continuous series, with a formula of $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}, \text{Ca})_2(\text{PO}_4)(\text{F}, \text{OH})$ - $(\text{Mn}^{2+}, \text{Fe}^{2+})_2(\text{PO}_4)\text{F}$. They mostly occur in granitic pegmatite and hypothermal rare-metal deposits (Ivanova et al., 1996; Keller et al., 1994; Huang et al., 2002). In recent field investigation of several tungsten deposits in southern Jiangxi, a pink mineral in quartz vein of the Baxiannao wolframite mine was found by the present authors. Laboratory study was then conducted to determine the characteristics of this mineral, which all indicated that it is triplite, the manganese end-member of the triplite-zwieselite series.

The Baxiannao wolframite deposit is located in southern Jiangxi province, the most concentrated tungsten mining district in China as well as in the world. It is a newly discovered tungsten-tin deposit of so-called fracture-alteration type (Zhang, Xie, 1984; Zhu et al., 2006). Two stages of mineralization were recognized: the early-stage quartz-wolframite veins followed by structural fracturing and late-stage hydrothermal superposition of base metal mineralization.

Identification of triplite

The sample was collected in the underground working tunnel of the Baxiannao mine. Pink and transparent triplite clusters occur as paragenetic mineral of quartz and fluorite, forming major gangue mineral assemblage of the ore veins. Based on the observation of hand sample and thin sections, the analyses by using Laser Raman spectrometry, X-ray diffraction, and electron microprobe were conducted in the State Key Laboratory for Mineral Deposit Research, Nanjing University.

Result of Laser Raman spectrometry shows that the determined Raman shift of the sample (425.34, 454.64, 601.12, 981.97, 1040.50, 1073.1 cm^{-1}) is perfectly in accordance with the standard Raman shift of Triplite R050186 in the ruff database (<http://rruff.info/triplite/>), which is 432.08, 453.29, 611.42, 981.69, 1043.40, 1072.33 cm^{-1} , indicating it is triplite.

XRD analysis of the sample shows that the XRD pattern has several groups of strong peaks of d values (2theta/), i.e. 1.639, 1.759, 2.032, 2.110, 2.221, 2.517, 2.602, 2.690, 2.735, 2.864, 3.038, 3.278, 3.442, 3.660, 4.299, and 5.668, respectively. These peak values are also in good accordance with the typical diffraction peaks from the triplite 25-1080 in the PDF Records, which again proves this mineral is the triplite.

Analytic results of the sample on a JEOL JXA-8100 microprobe are shown in Table 1.

Table 1. Electron-microprobe data for triplite from the Baxiannao deposit.

	No.1	No.2	No.3	No.4
K ₂ O	-	0.01	-	-
F	7.21	7.31	7.52	7.94
SnO ₂	-	-	0.04	-
TiO ₂	0.02	-	0.01	-
Na ₂ O	-	-	-	-
WO ₃	0.07	-	-	0.17
CaO	2.12	1.90	1.96	1.75
SiO ₂	0.00	0.02	0.04	0.02
FeO*	7.60	7.78	7.74	7.54
Al ₂ O ₃	0.00	0.01	-	-
MnO	50.59	50.77	50.96	50.19
MgO	2.87	2.88	2.75	2.83
P ₂ O ₅	30.95	30.96	31.51	31.41
2F=O	-3.03	-3.07	-3.16	-3.33
H ₂ O*	1.02	0.93	0.88	0.45
Sum	99.42	99.50	100.25	98.97
Calculated on the basis of P=1				
PO ₄ ³⁻	1.00	1.00	1.00	1.00
SiO ₄ ⁴⁻	0.00	0.00	0.00	0.00
Mn ²⁺	1.66	1.66	1.64	1.62
Fe ²⁺	0.24	0.25	0.24	0.24
Mg ²⁺	0.16	0.16	0.15	0.16
Ca ²⁺	0.09	0.08	0.08	0.07
F ⁻	0.87	0.88	0.89	0.94
OH ⁻ *	0.13	0.12	0.11	0.06

The major components of the sample include manganese (MnO=50.19-50.96 wt.%), iron (total FeO*=7.74-7.78wt%), magnesium (MgO=2.75-2.89 wt.%), calcium (CaO=1.75-2.12wt.%), phosphorus (P₂O₅=30.95-31.51 wt.%), fluorine (F=7.21-7.94 wt.%), and few hydroxyl (H₂O=0.45-

1.02 wt.%). After calculation by taking phosphorus as one standard unit, the simplified chemical formula for the above four samples is $(\text{Mn,Fe,Mg,Ca})_2\text{PO}_4(\text{F,OH})$, almost identical to standard triplite.

Preliminary study of fluid inclusion

Triplite contains fluid inclusions of different sizes, shapes, and gas/liquid ratios. Laser Raman analysis shows that the liquid phase is mainly H_2O , whereas the gaseous phase comprises not only CO_2 , but also CH_4 (Fig. 1).

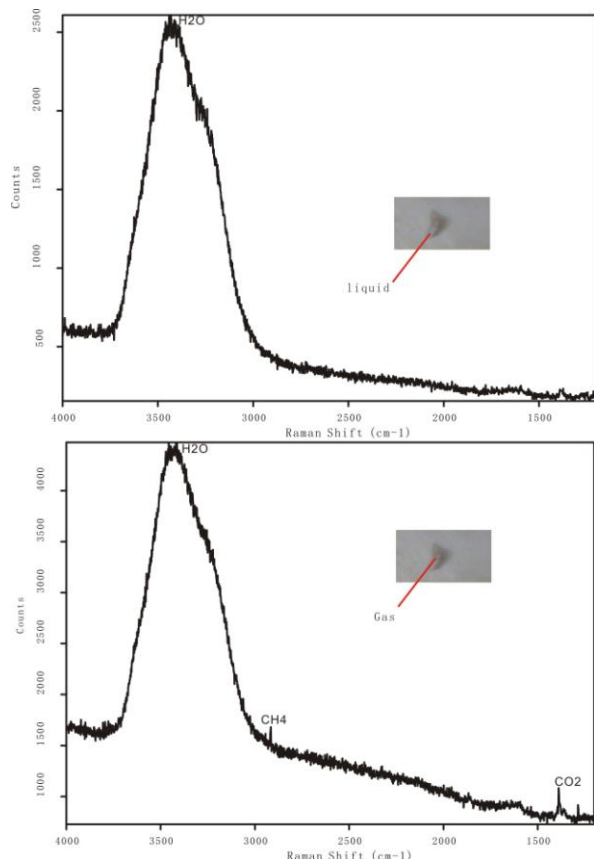


Figure 1. Raman spectra of fluid inclusions in triplites from the Baxiannao deposit.

Conclusion and discussion

A pink mineral was found in the ore vein as a gangue mineral associated with quartz and fluorite in the Baxiannao tungsten deposit of southern Jiangxi. Present study by Laser Raman and XRD identifies that this mineral is triplite. Electron microprobe analysis further proves that it is the Mn-member of the triplite-zwieselite series.

The existence of triplite in the ore vein reveals that the ore-forming fluid was a F- and P-rich solution. It further indicates that the ore-related granite is rich in fluorine and phosphorus. Many studies prove that the rare metal granite is a late-staged, highly-differentiated product of felsic magma, which contains more volatile components such as water, fluorine, phosphorus, boron, and

lithium.

Among all volatile-rich granites, the F-rich one is the most common and important category. Taylor (1992) further divided the F-rich granites into two varieties, i.e. P-rich and P-poor. Although triplite is obviously a P-rich mineral, yet it occurs not only with P-rich granites such as Beauvoir in the French Central Massif and the Yashan granite in Yichun of Jiangxi, China, but also with P-poor granites such as the Shuiximiao granite in Limu of Guangxi, China. The discovery of triplite together with quartz and fluorite in the Baxiannao tungsten deposit suggests that the related granite is most likely attributed to the fluorine-rich category.

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FLUID EVOLUTION IN SIDERITE-POLYMETALLIC VEINS OF WESTERN CARPATHIANS

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Low-grade Variscan basement of the Gemic unit, one of three major tectonic superunits of the Central Western Carpathians, contains more than a thousand of siderite-polymetallic and quartz-stibnite veins distributed parallel to regional metamorphic cleavage. In spite of extensive mining, the origin of the hydrothermal veins remains controversial. The generally accepted metamorphic-hydrothermal model (Grecula, 1982; Žák et al., 1991; Grecula et al., 1995) explained the origin of the hydrothermal veins in terms of mixing of the Variscan metamorphic fluids with meteoric waters leaching and dissolving Permian evaporites. The most recent version (Radvanec et al., 2004; Grecula, Radvanec, 2005a) invoked infiltration of a halite-fractionated seawater into the Gemic basement from periodically flooded Permian rifts/grabens, and the siderite-polymetallic veins were interpreted as conduits of submarine hydrothermal vents (Žák et al., 2005). According to this model, the Gemic veins formed during Middle Permian times, and their evolution, including the final sulphidic stages, was completed before Late Permian (Grecula, Radvanec, 2005b). Such an interpretation explicitly requires very low fluid pressures imposed by a 1-2 km thick autochthonous sedimentary cover overlying tops of some siderite veins, which terminate in lower Permian conglomerates.

The vein infilling formed during successive fuchsite, siderite-barite, quartz-tourmaline, quartz-sulphide, and cinnabar stages named after the dominant mineral. Each stage is typical of unique fluid inclusion composition, which, together with stable isotope, leachate chemistry and geochronological data throws a new light on the origin of the hydrothermal veins.

Siderite stage

Medium salinity (18-26 wt.% total) NaCl-KCl-CaCl₂-H₂O fluid inclusions were trapped in early siderite at temperatures between 140 and 300°C, as indicated by K/Na ratios in leachates. The crystallization temperatures tend to increase from north to southern part of the Gemic unit. Decreasing $\delta^{18}\text{O}$ values reflect increase in temperature during crystallisation of siderite in drusy cavities (Hurai et al., 2002). The $\delta^{18}\text{O}$ values of veiny siderite decrease with depth at the rate of 1.8-2.3 ‰/km in the northern part and 0.9 ‰/km in

the southern part of the Gemic unit. The fluid inclusion isochores and the oxygen isotope gradients converge at temperatures 175-210°C, thermal gradients $38\pm 10^\circ\text{C}/\text{km}$, and a 5.3 ± 1 km depth at the Rudňany deposit. The same parameters inferred for the Rožňava deposit are as follows: temperatures 207-255°C, thermal gradient $19-24^\circ\text{C}/\text{km}$, depth 11.2 ± 0.6 km (Hurai et al., 2008a).

Barite stage

Barite contains primary brine inclusions with widely varying salt concentrations and NaCl/CaCl₂ ratios. The brines are closely associated with high-density ($0.55-0.75\text{ g/cm}^3$) N₂ inclusions in northern part of the Gemic unit, and with high-density (up to 1.02 g/cm^3) CO₂±N₂ mixtures with 0-52 mol.% N₂ in southern part. Metastable high density brines devoid of vapour bubble are diagnostic of a homogeneous fluid trapped at a high pressure. Carbo-aqueous inclusions with variable phase ratios indicate a heterogeneous fluid. Combination of fluid isochores with cation exchange thermometers yielded temperatures 200-300°C and pressures 1.7-4.4 kbar for barite from Rudňany, and 200-240°C, 2-2.4 kbar for that from Krasnohorské Podhradie. Minimum depths and maximum thermal gradients defined by the lithostatic load and average crust density correspond either to 6-14 km and 15-40 °C/km in the north, or 7-12 km and 20-30°C/km, respectively, in the south (Hurai et al., 2008a, b).

Quartz-tourmaline stage

Typical fluid inclusions comprise immiscible carbo-aqueous mixtures with variable phase ratios at room temperature. High salinity brines (23-32 wt.% NaCl eq.) are ubiquitous. Superdense, essentially pure CO₂ inclusions with densities up to 1.197 g/cm^3 were detected in southern part of the Gemic unit. Trapping pressures between 1.6 and 4.5 kbar were attributed to a crack-seal mechanism and changing litho-hydrostatic fluid regimes. Estimated depths of burial and thermal gradients correspond to ~16 km and 12°C/km, respectively (Urban et al., 2006).

Sulphide stage

Sulphide minerals (stibnite, cinnabar) precipitated from moderate to very high salinity brines; locally coexisting with CO₂-rich, low salinity aqueous fluid. Compared to previous stages, the inferred fluid pressures are substantially

lower, except for quartz associated with stibnite in the Čučma deposit, where superdense CO₂ inclusions have been also revealed (Urban et al., 2006). Using a halite liquidus-isochore intersection method, maximal *PT* conditions of the quartz-ankerite-chalcopryrite assemblage at Rudňany was estimated at 180°C and 1-2 kbar. Sphalerite and quartz from the Zlata Idka deposit crystallized at 180-210°C and 0.6-0.75 kbar, as inferred from intersection of halite liquidus (31-34 wt. % NaCl) with isochores of closely spatially associated, essentially pure CO₂ inclusions (Hurái et al., 2008a).

Chemistry of brines

The CaCl₂-rich, high salinity aqueous fluid (18-35 wt. %) found in all mineralization stages corresponds to formation water modified by interaction with crystalline basement rocks at high temperatures. The fluid-rock interaction led to thermogenic sulphate reduction. High brominity (around 1000 ppm in average) is a relic of seawater evaporation and anhydrite precipitation. Additional Br enrichment is attributed to dissolution of organic matter in sediments at diagenetic temperatures.

Radiometric age determinations

U-Pb-Th, ⁴⁰Ar/³⁹Ar and K/Ar geochronology applied to hydrothermal muscovite-phengite and monazite from quartz-tourmaline stage, as well as cleavage phyllosilicates in the adjacent basement rocks and deformed Permian conglomerates corroborated the hydrothermal vein opening during Early Cretaceous and their rejuvenation during Late Cretaceous times. Some Ar/Ar data on hydrothermal muscovite-phengite (Hurái et al., 2008a), as well as unpublished chemical U-Pb-Th data on large (500 µm) hydrothermal monazites with phengite-rich cores indicate the onset of the hydrothermal vein formation in Upper Jurassic times.

Conclusions

The obtained fluid inclusion, stable isotope, leachate chemistry and geochronologic data are inconsistent with the previous models correlating the hydrothermal siderite-polymetallic veins with the Permian rifting. It is proposed, that the early siderite precipitated at increasing temperature in a rock-buffered hydrothermal system during Late Jurassic-Early Cretaceous crustal thickening, as indicated by high fluid pressures and low thermal gradients. Superimposed minerals crystallized in open hydrothermal systems coincident with Late Cretaceous transpressive shearing and extension. The hydrothermal veins can be classified as synorogenic metamorphogenic at the initial stage,

and post-orogenic hydrothermal-metamorphic during the final stages, when input of ore elements from hidden magmatic intrusions cannot be ruled out.

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DEEP FLUIDS AND MELTS IN IGNEOUS XENOLITHS FROM ALKALI BASALTS OF WESTERN CARPATHIANS

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Introduction

Alkali basalt volcanism in the Carpathians is commonly interpreted as a “within-plate” association formed by decompression partial melting of depleted asthenosphere. Isolated volcanic centers originated throughout the whole intra-Carpathian back-arc basin system due to a post-rift thermal subsidence post-dating a Miocene subduction. The alkali basalts frequently contain fragments and nodules of igneous rocks, covering the compositional range from clinopyroxene-dominated gabbroic cumulate, through amphibolite to K-feldspar-dominated syenite (Huraiová et al., 1996; Hurai et al., 1998). Unique in this context is the Pinciná maar, where phreato-magmatic eruptions ejected gabbro, amphibolite, syenite and orthopyroxene granodiorite-tonalite (pincinite) xenoliths, up to 50 cm in diameter. Carbonatized cumulate xenoliths associated with carbonatic micronodules have been also described in lava flow near Mašková (Hurai et al., 2007). Apart from the igneous xenoliths, mantle peridotite nodules are also ubiquitous (Konečný et al., 1995). Zircon (Hurai et al., 2010), plagioclase, K-feldspar, orthopyroxene and olivine mega- and xenocrysts are frequent in effusive and explosive basalts. Some megacrysts contain melt inclusions with unique association of immiscible melt phases.

Isotopic signatures, trace element abundances and fluid inclusions showed that the gabbro-syenite igneous suite is a product of polybaric fractional crystallisation of alkali basalt (Hurai et al., 1998; Huraiová et al., 2005). The pincinite fragments were interpreted as quenched supersolidus anatectic melts formed around the fractionating basaltic magma chambers by dehydration melting of biotite-quartz-feldspar-bearing crust (Huraiová et al., 2005).

Fe- and Ti-oxide melts

The gabbro-syenite suite from the Pinciná maar contains primary CO₂-rich fluid inclusions closely associated with silicate melt inclusions and Fe-oxide globules, which are most abundant in syenite xenoliths. Ti-oxide globules have been described as inclusions in Ti-rich kaersutite from the Hodejov maar (Table 1). Trace element pattern of the Fe-oxide globules indicates a plagioclase-fractionated parental melt. Low totals of electron microprobe analyses together with IR spectra point

to an increased concentration of H₂O, OH and CO₃²⁻ (Hurai et al., 1998). Synchrotron radiation spectroscopy revealed only ferric iron in the Fe-rich globules and dominantly ferrous iron in the associated trachytic glass, thus documenting nearly complete disproportionation of Fe²⁺ and Fe³⁺ during immiscible separation of the coexisting melt phases (Hurai et al., 2008).

Table 1. Representative compositions of Fe- and Ti-oxide globules

Sample Rock	HP-1 gabbro	HO-1 gabbro	PI-12 syenite	HP-3 syenite
SiO ₂	5.94	24.03	13.36	5.03
TiO ₂	0.07	43.49	0.02	0.00
Al ₂ O ₃	0.15	5.16	0.56	0.07
P ₂ O ₅	0.1	1.43		
FeO _{tot}	66.69	10.59		
Fe ₂ O _{3tot}			64.65	71.65
MnO	2.29	0.05	0.09	2.16
MgO	1.03	0.19	0.22	1.10
CaO	0.48	1.79	0.25	0.26
Na ₂ O	0.10	0.01	0.32	0.09
K ₂ O	0.03	0.22	0.03	0.01
Cl	0.04	0.00	0.10	0.07
F			0.07	0.06
Cr			0.03	0.02
Ni			0.56	0.00
Co			0.11	0.08
Cu			0.17	0.00
Zn			0.30	0.00
S			0.02	0.01
Total	76.92	86.86	80.86	80.61

Oxythermobarometry and water content in pincinite xenoliths

Two types of pincinite xenoliths with similar mineral assemblage (plagioclase, quartz, ilmenite, orthopyroxene, intergranular glass) exhibit different redox potential and formation *PT* conditions. Peraluminous pincinite is reduced (6-7 wt.% of total iron as Fe³⁺ in corundum-normative intergranular dacitic glass) and contains high density CO₂ inclusions with minor H₂, CH₄, H₂S, CO and N₂. Equilibrium conditions inferred from Opx-Ilm-Glass assemblage and the fluid isochores corresponded to 1170±50°C and 5.6±0.4 kbar. Metaluminous pincinite is more oxidized (25-27 wt.% of total iron as Fe³⁺) and contains diopside-normative rhyolite-trachyte-dacite glass as well as

carbo-aqueous fluid inclusions with up to 38 mol.% H₂O. Equilibrium *PT* parameters correspond to 740±15°C and 2.8±0.1 kbar (Huraiová et al., 2005).

Despite different formation *PT* conditions and saturation by aqueous phase, the water content in the intergranular glass determined by Raman spectroscopy is rather similar, ranging at 1.9±0.3 wt.% H₂O in the peraluminous pincinite, and 2.1±0.5 wt.% H₂O in the metaluminous pincinite. Silicate melt inclusions in quartz from the peraluminous pincinite contained 0.7 wt.% H₂O. The determined water contents are in conflict with the inferred *PT* conditions, thus indicating water loss and/or changing redox parameters during ascent of the xenoliths to surface.

Multiphase fluid-melt immiscibility in carbonatic clinopyroxenite xenoliths

Two types of carbonatic xenoliths have been identified in a basaltic lava flow near Mašková. One is dominated by Ca-Fe-Mg carbonates with randomly distributed bisulphide globules, Mg-Al spinel, augite, rhönite and Fe-Cu-Ni-Co-sulphides. The second, carbonatic pyroxenite xenolith type, is composed of diopside, fluorapatite, Fe-Mg carbonates, and accessory K-pargasite, ferroan phlogopite, spinel, albite and K-feldspar. All the accessory minerals occur as solid inclusions in diopside or daughter phases in ultrapotassic dacite-trachydacite glass in primary silicate melt inclusions together with calcio-carbonatite and CO₂-CO-N₂ inclusions. Multiphase fluid-melt immiscibility occurs in both xenolith types. The carbonatic pyroxenite is interpreted as cumulate derived from strongly differentiated, volatile-rich, ultrapotassic magma. Formation conditions inferred from Cpx-thermobarometry (~1200°C, 8 kbar) and isochores of CO₂-rich inclusions (6.7-7.5 kbar) points to the parental melt underplating the mantle-crust boundary at the depths of 25-30 km (Hurái et al., 2007).

Carbonate-phosphate-melilitite immiscibility in plagioclase megacrysts

Optically and chemically homogeneous plagioclase megacrystal (An₂₉) from the basaltic diatreme near Hajňačka contains melt inclusions (Fig. 1), up to 2 mm in diameter, with carbonatite (92-98 mol.% CaCO₃, 2-8 mol.% MgCO₃) and phosphate globules embedded in melilitite glass (SiO₂ 45-46, Na₂O 4-5, K₂O 0.8-0.9, CaO 31-32 wt.%). Thin rims around the carbonatite globules have trachyandesite-to-trachyte composition (SiO₂ 60-67, Na₂O 0.3-1.5, K₂O 6.2-8.6, CaO 4-5 wt.%). Despite of unambiguous textural signs for quenched melts, Raman spectra point to well-crystallized Mg-carbonate and apatite. The multi-

phase melts have probably originated due to a low-degree partial melting of the parental plagioclase during ascent in basaltic magma. High content of volatiles in the Ca-phosphate phase (2.3-4.7 wt. % S) is attributed to uptake from the host alkali basalt. Structurally bound phosphorus in the plagioclase may have been the internal source of P for the phosphatic phase exsolved from the carbonatic melt. Owing to a supercooling effect, the associated melts represent most likely non-equilibrium phases.

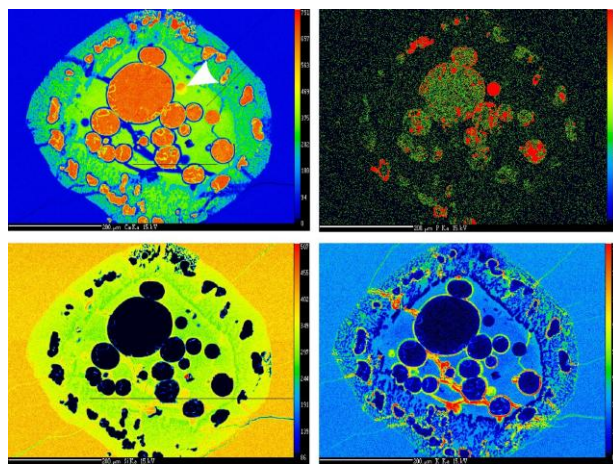


Figure 1. RTG maps (upper row: Ca, P; bottom row: Si, K) of composite melt inclusion in plagioclase megacryst.

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FLUID INCLUSIONS IN CARBONADO DIAMOND AND ITS IMPLICATION TO THE ORIGIN

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Introduction

Carbonado is a natural polycrystalline aggregate of diamond whose origin is still controversial. Carbonado is characterized by a lack of mantle-derived mineral inclusions, a ¹³C-depleted isotopic composition, and radiation effects from radioactive nuclides (Trueb, Buttermann, 1969; Trueb, de Wys, 1969, 1971; Ozima et al., 1991; Kagi et al., 1994; De et al., 1998). Based on these observations, several assumptions on the genesis of carbonado have been proposed: a large impact on the Earth's crust during the Precambrian era (e.g. Smith, Dawson, 1985); transformation of organic sedimentary carbon into diamond in a cold subducted slab (e.g. Robinson, 1978); and radiation-induced diamond formation from organic carbon (Kaminskii, 1987; Ozima et al., 1991; Daulton, Ozima, 1996).

Our recent study on infrared absorption spectra and Raman spectra of Central African carbonado reported the presence of fluid inclusions and high residual pressure in the diamond (Kagi, Fukura 2008). These results suggested that C-O-H mantle fluid was trapped in the carbonado sample and carbonado had grown in the volatile-rich environment in the mantle. However, it was still unclear that the fluid inclusions in carbonado existed inside of diamond grains or in the grain boundaries. In this study, we precisely investigated location of the fluid inclusions from spectroscopic measurements and TEM observations.

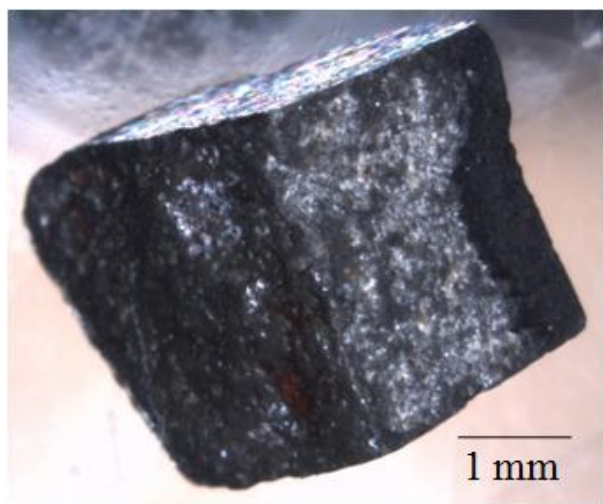


Figure 1. Optical microscope image of carbonado.

Experimental procedures

A carbonado grain with hundreds of micrometer in diameter was heated incrementally at temperatures from 700 to 1100°C under vacuum. After heating at each temperature condition, infrared absorption spectra were measured. Absorption bands assignable to liquid water were observed up to 950°C right before graphitization occurred. This observation strongly suggests that the fluid was trapped inside of diamond grains.

For obtaining direct evidence of fluid inclusion existing inside of a diamond grain, 9 µm × 6 µm and 0.1 µm sized carbonado films were prepared using FIB method. We conducted TEM observations on an FIB-fabricated thin foil of carbonado.

Results and discussion

Figure 2 shows an orientation-contrasted electron microscope image on a polished surface of carbonado sample from the Central Africa. Carbonado consists of diamond grains in diameters ranging from submicron to several micrometers and pores.

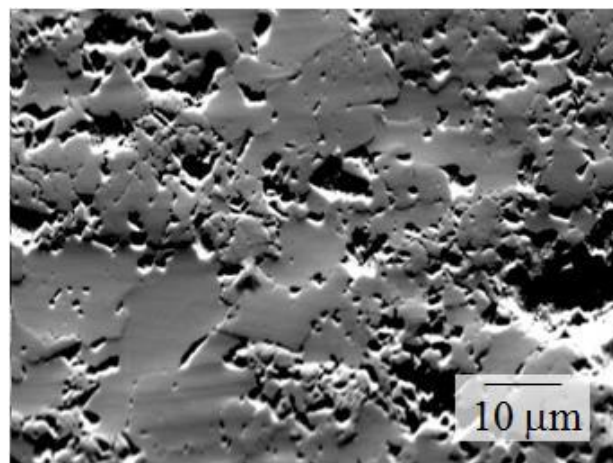


Figure 2. Orientation-contrasted electron microscope image of polished carbonado surface.

The obtained infrared absorption spectra showed that a peak assigned to OH stretching vibration assigned to Si-OH observed at 3625 cm⁻¹ disappeared with increasing heating temperature. In contrast, a peak assignable to molecular water (3401 cm⁻¹) existed until diamond transformed into

graphite after heating at 950°C. These experimental results facts indicate that hydrated minerals existing in the grain boundary of diamond crystals dehydrated by heating and fluid inclusions existing inside of diamond crystals retained until diamond transformed to graphite.

Figure 3 shows a void found in a diamond crystal of carbonado. The void was surrounded by (111) equivalent crystal faces. The octahedral void controlled by crystal habit of host diamond strongly suggests that the void is the negative crystal of diamond. The existence of negative crystal of diamond indicates that the fluid equilibrated with diamond crystals.

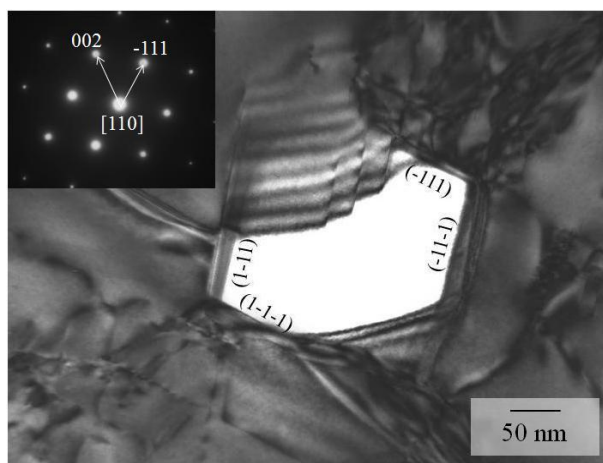


Figure 3. TEM image of a void in FIB film of carbonado obtained using the [110] convergent beam.

Conclusions

We found the fluid inclusions in carbonado diamond. The present study supports that the growth environment of carbonado was in the mantle being rich in C-O-H fluid.

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FLUIDS IN A HISTORICAL SILVER AND COPPER MINING AREA OF VORARLBERG, AUSTRIA

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Introduction

Tyrol and Vorarlberg were once one of the most important Cu and Ag mining areas of Europe. It is well known that fluids are essential for the enrichment of precious metals in the crust. Investigations of fluid inclusions in the minerals of the host rocks of ore deposits allow conclusions of composition, density, pressure and temperature and temporal evolution of the ore-precipitating fluids. This work presents results of a fluid inclusion study of a historical silver and copper mining area in the westernmost part of Austria, which was performed in the framework of an interdisciplinary program called “The **H**istory of **M**ining **A**ctivities in **T**yrol and adjacent areas” (HiMAT).

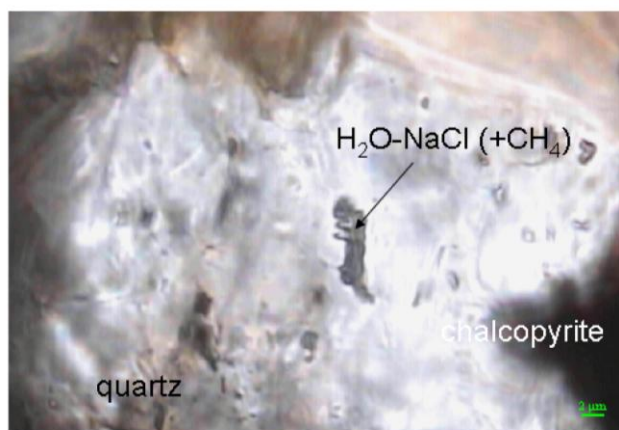


Figure 1. Type 1 inclusions in quartz.

Historical view of the silver-copper mining area

The investigated ore deposit in Vorarlberg is in Bartholomäberg and is part of the Schrunser Becken in the westernmost part of Austria. According to Krause et al. (2004) settlements within the Schrunser Becken go back to Neolithic times. The first evidence of mining activities dates from 842 AD, later they reached a maximum in the Middle Ages with repeated attempts of revitalization in the 18th century. At present, two open pits and several traces of former mining activities such as heaps exist; the investigated samples were taken from the latter.

Petrography

The ores from Bartholomäberg are dominated by chalcopryite and pyrite. Both are altered on the rims and along fractures to covellite and limonite. Fahlore occurs only subordinately. Prevailing

gangue minerals are carbonates, which occur either disseminated throughout the rocks or as veins. Crystals grow frequently into open cavities and are hypidiomorphic to idiomorphic. They host numerous fluid inclusions but they are mostly too small for microthermometric investigations. Quartz is less abundant and occurs sometimes included in the ore minerals and in the central parts of veins and cavities. In veins and fractures it is hypidiomorphic, close to the ore minerals coarse-grained, palisade-like aggregates can be observed. Most of the investigated fluid inclusions are hosted in quartz included in ore minerals or in aggregates.

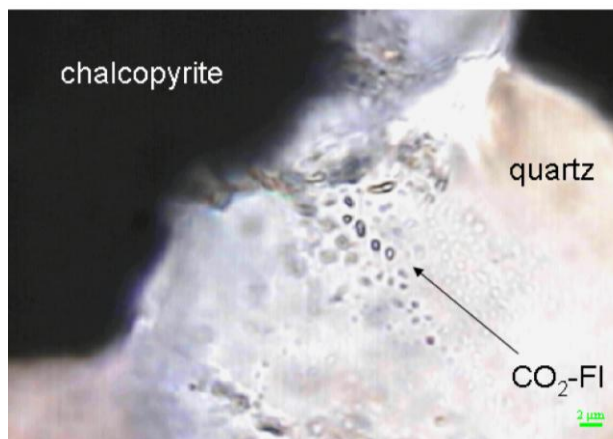


Figure 2. Type 2 inclusions in quartz.

Fluid inclusions

Two types of fluid inclusions could be distinguished (Table 1):

Type 1 inclusions are irregular and elongated and occur mainly close to sulfides in quartz and carbonate (Figure 1). They form single inclusions or clusters and intragranular trails and reach a maximum length of 10 μm in quartz; in the carbonates they are much smaller. They can contain a liquid and a gas bubble, which is not always present. The degree of fill of the two-phase inclusions is high (~0.9) and relatively constant. Sometimes transparent and opaque solids were observed but due to the small size could not be identified. During cooling in the heating-freezing stage freezing was observed around -50°C, melting of a solid T_m occurred between -12 and -1.5°C. During heating the inclusions homogenize into the liquid phase between 99°C and 147°C. These phase transitions are indicative of the H₂O-NaCl system.

In order to check the microthermometric data, Raman spectra of several inclusions were acquired.

The spectra showed three broad bands typical for the vibrational modes of liquid H₂O with dissolved amounts of NaCl. The Raman shift of the lowermost v₁ band was used to calculate salinities which ranged between 4 and 20 wt.% NaCl (Baumgartner, Bakker, 2008). These salinities agree well with the results from microthermometry. Furthermore, a sharp band at 2914 cm⁻¹ in the spectra of some inclusions indicates small amounts of CH₄. Salinities and densities between 0.93 and 1.05 g/cm³ of type 1 inclusions were calculated using the *FLUIDS* package (Bakker, 2003, 2009), and the equations of state by Zhang and Frantz (1987) and Bodnar (1993).

Type 2 inclusions in quartz are similarly to Type 1 inclusions also associated with ore minerals, very small, dark and rounded (Figure 2). Due to their small size and dark appearance they could only be investigated by Raman spectroscopy. They contain CO₂ and sometimes a water-bearing solid phase, probably mica.

Table 1. Properties of the investigated fluid inclusions.

Type	1	2
Host Mineral	Quartz, Carbonate	Quartz
Chemical System	H ₂ O-NaCl± CH ₄	CO ₂
T _m (°C)	-1.5 to -12	
T _h (°C)	99 - 147	
Salinity (wt.% NaCl _{eq})	3 - 20	
D (g/cm ³)	0.93 – 1.06	

Discussion and Conclusions

The chemical composition of the investigated fluid inclusions is dominated by the H₂O-NaCl system. Subordinately additional gas components such as CH₄ and CO₂ could be detected. Opaque phases were also found in the inclusions, suggesting that the ore was transported by aqueous salt solutions. The salinity of the solutions was variable but undersaturated with respect to NaCl, since the homogenization temperatures were low. According to Wilkinson (2001) such inclusions are typical for epithermal ore deposits, which form in low depths in the brittle crust by circulating surface fluids and frequently in zones of increased permeability and heat flow. In this case, the observed homogenization temperatures correspond in a good approximation to the trapping

temperature of the inclusions and thus reveals the formation temperature of the host minerals. On the other hand, parageneses and textures of the main ore minerals chalcopyrite and pyrite suggest high temperatures around 550°C (Bechter, 2009), which agree with the Variscan metamorphic conditions in the investigated area (Maggetti, Flisch, 1993). The Alpine metamorphic overprint in contrast reached only 250-300°C, followed by doming and up-lifting of the Engadin Window at very low temperatures around 100°C. The investigated fluid inclusions therefore most likely represents trapped aqueous, saline, meteoric fluid, which altered the primary pre-Alpine mineralization and caused formation of quartz and carbonate veins.

Acknowledgements

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FLUID INCLUSION STUDY IN OLIVINE PHENOCRYSTS FROM THE GATAIA LAMPROITE

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Introduction

Study of the approximately 1.3 Ma old Gataia lamproite (Banat, Romania) revealed that olivine phenocryst contain large number of silicate melt, fluid and spinel inclusions in different textural positions.

Generally silicate melt and fluid inclusions in igneous rocks provide direct information about the physical and chemical conditions of the magma at the time of entrapment (Frezzotti, 2001). Presence of silicate melt inclusions and fluid inclusions in olivine phenocrysts give a unique opportunity to reconstruct stages in evolution of magma during crystallization.

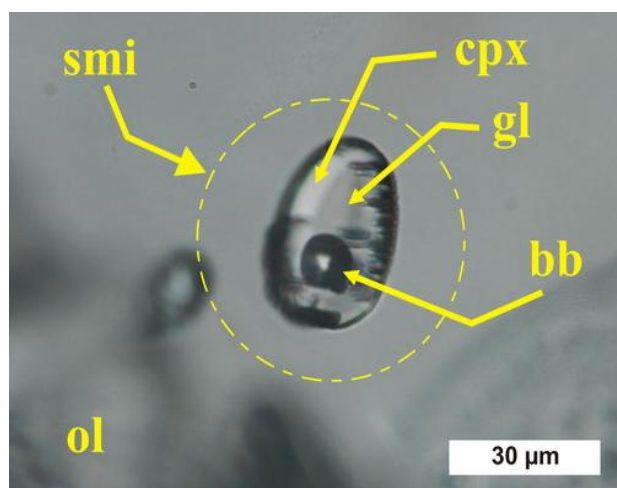


Figure 1. Primary silicate melt inclusion in olivine phenocryst containing clinopyroxene daughter phase, glass and a bubble.

Geological setting

Occurrence of the Gataia Pleistocene lamproite is situated at about 5 km south of Gataia (Banat, Romania) and exposed by exploration drilling. The isolated lamproite volcano, Sumiga hill (198 m above sea level), is located in the southeastern edge of the Pannonian Basin and at the western margin of the South Carpathians along a NE–SW fault system.

The lamproite magma erupted through flat-lying Miocene sedimentary rocks that overlie older crystalline basement that went through an intense lithospheric deformation and orogeny during Cretaceous times. The volcano is built up by sequences of slightly vesicular lava flows intercalated with fallout scoria deposits (Seghedi et al., 2008).

Silicate melt and fluid inclusion study

Based on a detailed optical microscopic study the olivine phenocrysts of the porphyritic lamproite, contain inclusions, apart from the spinel, can be divided into two groups: 1) primary silicate melt inclusions and 2) coeval and coexisted secondary silicate melt and fluid inclusions based on Roedder's classification.

The primary silicate melt inclusions, occurring in the olivine core, are rounded or oval 10 to 25 µm in size (Fig. 1). They consist mostly of alkali-rich glass (gl), clinopyroxene (cpx) daughter mineral and a bubble (bb). The bubble represents 7-12 vol.% of the whole of the melt inclusions. Rarely, accidentally trapped spinel crystals can be recognized in them as well. The secondary silicate melt inclusions occurring along healed fractures running across a part of the host olivine are spherical in shape, 5 to 10 µm in diameter (Fig. 2). These silicate melt inclusions contain only glass (gl) and bubble and show coeval and coexisted occurrence with one - or two-phase fluid inclusions.

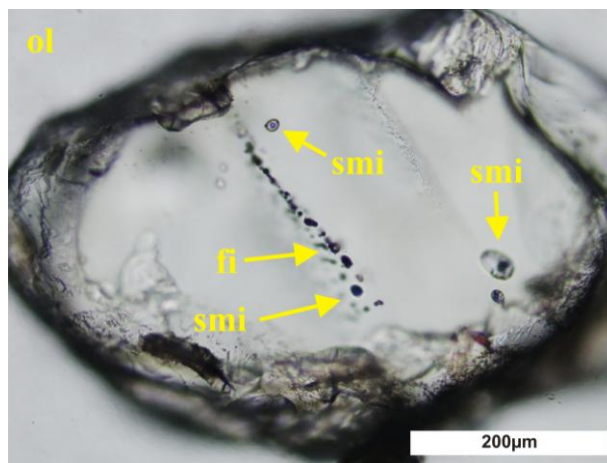


Figure 2. Olivine phenocryst containing primary silicate melt and secondary silicate melt and fluid inclusions.

High-temperature thermometric experiments were performed with the melt inclusions (Danyushevsky et al., 2002). Apart from homogenization of the bubble, we observed the homogenization temperature of the primary silicate melt inclusions between 1140 and 1150°C, which could be a minimum crystallization temperature of olivine phenocryst and spinel inclusions. Low-temperature microthermometric experiments were conducted on the bubbles of the secondary silicate

melt inclusions and the coexisting secondary fluid inclusions. On heating, melting of the solid phase happened at -62 – 61 °C ± 0.5 °C with no other observable melting events indicating that the trapped fluid is CO₂ dominant. The homogenization temperatures of the bubbles of the silicate melt inclusions occurred at 20.8 °C and for the fluid inclusions at 15 °C corresponding to fluid densities of 0.77 g/cm³ and 0.88 g/cm³, respectively (Bakker, 2003).

Raman microspectroscopic analysis was carried out on the bubbles of the secondary silicate melt inclusions and on the secondary fluid inclusions to determine other components next to CO₂. In the bubbles of the secondary silicate melt inclusion presence of CO, CH₄ and N₂ were detected, whereas in the secondary fluid inclusions CO and CH₄ peaks were identified at room temperature.

Conclusion

The homogenization temperatures of the bubbles of the secondary silicate melt inclusions and the secondary fluid inclusions are corresponding to the fluid densities. Applying the determined densities and the widely accepted Duan-equation, a minimum trapping pressure of 5–6 kbar of the coexistence secondary silicate melt inclusions and fluid inclusions can be estimated at the time of entrapment. This pressure value may represent the conditions of a magma chamber (or conduit) in the middle crust. The investigations of the secondary silicate melt inclusions and fluid inclusions in olivine phenocrysts indicate that, besides the crystallized minerals (i.e., olivine and spinel), two different fluid phases were present, a silicate melt and a CO₂ rich volatile that formed by a melt-volatile immiscibility at the time of entrapment of the secondary inclusions in the olivine phenocrysts.

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FORMATION CONDITIONS OF GRANITIC MASSIF IN THE DALNEGORSKY BOROSILICATE DEPOSIT: THERMOBAROGEOCHEMICAL DATA

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Brief geological background

The Dal'negorsky borosilicate Deposit is located in the central part of the Dal'negorsky Ore District in the Primorsky Region (Russian Far East). It is typical calcareous-skarn deposit of boron of industrial value. The deposit is confined to the large block of Upper Triassic reef limestone of the Valanginian olistostromic strata and is a skarn body with boron mineralization. Area of granitoid rocks in the Dal'negorsky District is not large. They occur under skarns at 1100-1400 m depth, there are no outcrops and they are discovered in boreholes only. Their age is 51 Ma according to K-Ar age data. Skarn, boron-silicate, and quartz-carbonatic stages of mineralization were established (Kurshakova, 1976). Most of datolite and some of danburite were deposited during main stage.

Geochemistry of massif

In petrogeochemical features granitoids belong to common and acid intrusive rocks of high-potassium calc-alkaline rock series. By their high contents of alumina and silica they can be attributed in the Tauson's classification to calc-alkaline granites. Granitoids have high K₂O (4.3-4.9 wt.%), Na₂O (3.2-3.6 wt.%) and low Rb (110-140 ppm) that is similar to alkaline granites.

Tectonics of the Dal'negorsk Ore District is represented by combination of basement folded structures and volcanic belt structures that form the Dal'negorsk volcanic-tectonic system of the higher rank. Here, local intrusive-dome structures were revealed (Valuy, 1997), and the Dal'negorsky Massif, which belongs to them, lies inside sedimentary rocks of folded basement that were formed by multiphase diorite-granodiorite-granite intrusives, mainly. Petrogeochemical data on granitoids clarify geodynamic environment of these rocks' formation. In the classification by P. Maniar and F. Piccoli based on step-by-step analysis of petrogenic element composition in granitic system (Sklyarov et al., 2001), most granites fall in the field of post-orogenic granitoids.

For geodynamic classification of granitoids we used the rare earth elements - (Rb, Y, Nb) diagram by J. Piarce et al. The granitoids fall into the area corresponding to granites of volcanic arcs.

Mass-spectrum analysis showed that examined granitoids were characterized by low content of REE and predominance of light REE over heavy

ones. Pronounced Eu anomaly is the evidence of process of fractionation of minerals anomalously rich in Eu.

Granite has common modal composition (in vol.%): quartz - 30, oligoclase - 30, microcline - 30, ferrosalite - 10. Accessory minerals (up to 3-5 vol.%) are represented by actinolite, sphene, apatite, epidote, sphalerite, galena, and covellite. The rock has hypidiomorphic grain structure.

Inclusions study in quartz of granitoids

Quartz phenocrysts of granitoids contain inclusions with different phase composition: melt, gas-liquid, gas-liquid with solid phases, and gas-liquid with essential CO₂. Quartz grains are fissured to different extent due to postmagmatic processes, sometimes so significantly that it is impossible to identify non-modified primary inclusions. Melt inclusions are irregular or isometric in shape (5-30 µm). Most inclusions are characterized by lack of H₂O liquid phase in the fluid part. Its insignificant content was established only by visual and microscopic examination of melt inclusions and control thermometric investigations, which observed no homogenization of fluid part into liquid phase. No coexisted fluid inclusions were revealed. First signs of melting in silicate part are noted in the interval of 500-600°C, and total homogenization was at 800-850°C. Completely homogenized melt inclusions and inclusions containing transparent glass were analyzed using electron probe Jeol microanalyzer JXA-8100. When homogenized, glasses contain 70-79 wt.% SiO₂, alkali content reaches totally up to 9 wt.%, Al₂O₃ - 1.4-4.8 and 15-17 wt.%, FeO - 0.4-0.9 wt.%, CaO - 0.3-1.8 wt.%, Cl - 0.2-0.8 wt.%.

Secondary gas-liquid inclusions of granites are the most prevalent, they are various in shape (10-40 µm in size), and their gas bubble volume is 20-25%. Temperature of homogenization is 250-300°C. In addition, there are gas-liquid inclusions with solid phases of cubic and elongate shape. Apparently, it is halite, judging by its optic and thermometric features. During heating of inclusions with a single solid phase, a gas bubble disappears at 200-220°C, and dissolution of crystalline phase is completed at 230-250°C. During heating of inclusions with two solid phases, a gas bubble disappears at 110-160°C, and dissolution of first crystalline phase occurred at 230-250°C, second

crystalline phase disappeared at 400-430°C. Solution concentration for these inclusions was defined for H₂O-NaCl system depending on temperature of dissolution of solid phases and was equal to 50.8 wt.% of NaCl equivalent.

Cryometric examinations of the gas-liquid inclusions showed that deep freezing (up to -150°C) revealed no signs of “freezing off” of carbon dioxide or other gases that testified to low density of gases or to their presence at insignificant amount. Eutectic temperature of the gas-liquid inclusions is -55°C and -50°C that corresponds to the CaCl₂-NaCl-H₂O and CaCl₂-KCl-H₂O systems, respectively. Eutectic temperature of the gas-liquid inclusions with solid phases is -55°C that corresponds to the CaCl₂-NaCl-H₂O system.

Conclusions

Investigations of Eocenic granitoids of the Dal'negorsk borosilicate deposit give us to make the following conclusions. Petrochemical features of granitoids serve as certain indicators of their formation conditions and indicate their similarity with alkaline granites. By geodynamic environment of forming process and tectonic position they belong to granitoids of continental collision and granites of volcanic arcs.

Based on inclusion study we can conclude that the granite massif was formed from melt of acid composition at 800-850°C and pressure 65-90 MPa. Initial melt that formed the granite massif is characterized by low water content (up to 3.5 wt.%) judging by volume ratio of silicate and fluid phases and lack of coexisted fluid inclusions.

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PHYSICO-CHEMICAL PARAMETERS OF ORE-MAGMATIC SYSTEM AT THE MASSIVE SULPHIDE DEPOSITS OF THE VERKHNEURALSKY ORE DISTRICT, SOUTHERN URALS

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Introduction

The location of the vast majority of the Urals VHMS deposits in central volcanic structures and their paragenetic relation to acidic volcanism are the most reliable attributes. According to the genetic models, the formation of the VHMS systems is related to shallow chambers of acidic magma. The Verkhneursky ore district located in the northern Magnitogorsk trough is attributed to the Uchaly-Alexandrinka structural-formation zone. All economic deposits of the district are hosted in acidic volcanic rocks at the three lithostratigraphic levels corresponding to three rhythms of volcanism. Melt and high density fluid inclusions (FI) of magmatic water in quartz phenocrysts were studied in samples of dacite, rhyodacite and rhyolite. FI studies in minerals from ore bodies and in quartz phenocrysts (secondary FI) from altered country rocks have been carried out also in addition to earlier investigation.

Melt and fluid inclusion study

Two main types of melt inclusions are observed: the devitrified inclusions are the most widespread, whereas vitreous inclusions locally with a gas phase are less frequent. Melt inclusions containing opaque crystals determined as magnetite and sulfide globules (pyrrhotite, pentlandite, chalcopyrite, bornite) are also observed. Glasses were softened at 600-720°C and homogenized at 850-1130°C. Initial melting of devitrified inclusions was at 780-850°C, and total homogenization at 950-1210°C (Karpukhina, 1998). The electron microprobe examination of initially homogeneous or homogenized glasses indicated that the compositions of magmatic melts correspond to rhyolite, occur in the field of tholeiitic series, and are significantly different from the least altered volcanic rocks belonging to calc-alkaline rock series. Three groups of magmatic melt were recognized by the content and variation of alkalis: predominant K-Na and less abundant Na and K. The high content of K₂O in the last group reached 5.0-9.7 wt.%. The recognized groups were observed in acidic volcanics of all three rhythms.

The concentration of volatiles in the

magmatic melts is the following (in wt.%): trace to 6.5 H₂O (by difference between 100% and total components in initially homogeneous or homogenized glasses by an electron microprobe and 4.6-4.7 wt.% in two inclusions analyzed by SIMS), 0.01-0.28 Cl (average 0.13 of 50 inclusions), 0.0-0.42 F (average 0.08 of 37 inclusions). According to examination of 13 melt inclusions, the average content of sulfur is 0.025 wt.% (Naumov, 1999).

Fluid inclusions of magmatic water. Rare FI are observed in quartz phenocrysts in acidic volcanic rocks with the K and Na melt composition of all three rhythms of volcanism (Karpukhina, 2009). FIs homogenize into liquid at 124-245°C. They are frozen in the range of -14 to -37°C with a significantly decreasing gas bubble that is characteristic of aqueous FI. Ice melting temperatures varying from -0.7 to -3.8°C indicate low salinity of the aqueous solution, 1.2-6.2 wt.% NaCl equiv. Calculated the fluid density is 0.80-0.94 g/cm³. Fluid pressure was calculated for 850 and 700°C (minimum homogenization temperature of melt inclusions in quartz and minimum temperature of acidic magma upon eruption). The results obtained show a very high fluid pressure of 7.8-8.7 kbar for 850°C to 5.1-6.8 kbar for 700°C. Similar high-temperature high-pressure aqueous fluids originated in degassing acidic magmatic melts and revealed in many objects around the world. This allows us to indicate the real involvement of these fluids in hydrothermal ore formation of the Ural VHMS deposits.

Fluid inclusion study focused on secondary inclusions in quartz phenocrysts of altered country rocks as well as inclusions in quartz, barite, carbonates and sphalerite from the ore bodies on 5 deposits of the district (Karpukhina, 1995). Palaeotemperature zoning in the deposits has been delimited revealing central linear zones up to 380°C, indicative of ore-transporting channels, as well as zones of lower temperature (to 190-150°C) on flanks. High temperature patterns are also defined for the hanging-wall rocks. The observed temperatures of homogenization (T_{hom}) 375-130°C in minerals from the ore bodies are not connected with the ore composition, but reflect the

diagenetic and epigenetic transformation of ores. T_{hom} of inclusions in fine-grained ores with colloform texture relicts are lower (130-200°C) than in recrystallized aggregates (200-320°C) and vein-form, which have T_{hom} 270-370°C. Salinities of FI in quartz of altered rocks and ores range from 0.8-12.5 wt.% NaCl equiv. Two main types of fluids were distinguished: I - hydrocarbonate-chloride, distributed in ores altered rocks mainly in high-temperature zones and II - chloride with prevalence Na localized on flanking zones of underlying altered rocks. Type I fluid can be interpreted as juvenile based on chemical composition and spatial distribution. Type II fluid seems to attribute to transformed seawater. Evidence for boiling of hydrothermal solutions while approaching the sea-floor was revealed in the altered rocks under the ore bodies on a few deposits. Calculated salinities for CO₂-bearing inclusions are 2-5 wt.% NaCl equiv., CO₂ concentration in fluids reached 40 wt.%, the pressure values for deposits are 0.6-1.6 kbar. Sulphur contents in fluid of vacuoles range from 160 to 250 mg/l and copper – from 0.3 to 1.2 g/kg of solution. Data on isotope composition of hydrogen in sericites from altered underlying rocks in the Uzelguin deposit can be interpreted in favour of sea-water predominance in the fluid composition for deposit, with a certain proportion of juvenile component being more important in the central high-temperature zone of ore-transporting channels and with depth. The sea-water prevalence in the fluid composition agrees with its comparatively low salinity (Baranov, 1988).

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concentration of volatiles and trace elements, crystallization temperatures of quartz in acidic volcanics of the Verkhneursky ore area (Southern Urals). *Geochemistry International* (4), 339-351.

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FLUID REGIME DURING FORMATION OF DEPOSITS OF THE MANGAZEYSKOE ORE FIELD (SAKHA-YAKUTIYA)

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Introduction

Chemistry of mineralizing fluid and PT conditions of ore formation at deposits of the Mangazeykskoe ore field were estimated by individual fluid inclusions study in quartz. In this ore field, gold-rare metal (Trubka), silver-polymetallic (Vasilevskoe, Kuzminskoe, Nizhne-Endybalskoe, Bezmyannoe), and cassiterite-sulphide (Vertikalnoe, Privet) deposits and occurrences are known. They are hosted by a sandstone-slate sequence of the Verchoyansky series (C₂ to J₂) which are intruded by granodiorite-porphyric dykes and by a subvolcanic stock of plagiogranodiorite-porphyrtes. All types of mineralizations are confined to fault zones and spatially separated: gold-rare metal veins (Trubka) occur within the subvolcanic stock in the central part of the ore field, cassiterite-sulphide deposits (Vertikalnoe, Privet) are located in the south-western flank, whereas silver-polymetallic mineralizations (Vasilevsky, Kuzminsky, Nizhne-Endybalskoe, Bezmyannoe) are situated in northern and eastern parts of the Mangazeykskoe ore field. Ores of each type are confined to definite fault systems. The following formation sequence of mineral associations is proposed: early quartz-rare metal – cassiterite-sulphide – late silver-polymetallic.

Research technique

Microthermometric study of fluid inclusions (FI) was performed using a THMSG 600 (Linkam) microscope heating stage mounted on an Amplival microscope. The salt composition of water-salt solutions was defined by eutectic temperatures (T_{eut}). Salt concentration in inclusions was estimated by ice melting temperature (T_m). For inclusions containing aqueous-carbonic fluid it is impossible to estimate concentration of salts by melting temperatures of gas-hydrates, because melting temperatures of gas-hydrates of majority of inclusions exceed +10°C. Therefore, concentration of salts in such inclusions was estimated by T_m and corrected on the basis of measurements of volume parities carbon dioxide and water phases and calculation of concentration of CO₂ in a solution.

Results and discussion

Three types of primary fluid inclusions were

identified in quartz of ore veins. Type I is two or three-phase aqueous-carbonic FI. Type II is two or three-phase vapor-rich FI. Type III is two-phase gas-liquid FI. Vapor-rich FI often coexist with aqueous-carbonic or gas-liquid inclusions, they are confined to the same zones and cracks. This is evidence for phase separation of the fluid to liquid and vapor phases. FI of all types were found in quartz of the Trubka and the Nizhne-Endybalskoe deposits, FI of the type III and II occur in quartz of the Bezmyannoe deposit, and FI of the type III were recorded in quartz of the Kuzminskoe and Vasilevskoe deposits.

The type I aqueous-carbonic inclusions of the Trubka deposit were homogenized (T_{hom}) at 346° to 261°C. Fluid salinity in these FI ranges from 6.6 to 2.0 wt.% NaCl equiv. and concentration of carbon dioxide is 4.4 to 2.5 mol/kg. The T_{eut} range (from -40° to -30°C) indicates that Na and Mg chlorides prevailed in solution (Borisenko, 1977). Dissolution temperature of gas-hydrates ranges from 7.6 to 9.0°C. Carbon dioxide in the type II vapor-rich FI homogenizes into gas at +15.3 to +30.2°C. The T_m values of -58.8 to -58.0°C are lower than melting temperature of pure CO₂ (-56.6°C) and indicate an admixture of volatile gases in vapor phase in these FI. Pressure estimated by an intersection by isochorus and isotherms ranges from 460 to 200 bar.

The type III inclusions homogenize into liquid at from 248 to 186°C. Fluid salinity varies from 9.2 to 5.7 wt % NaCl equiv. Chlorides of Na and Mg are also prevailed among dissolved salts (T_{eut} -40 to -21°C).

In quartz of the Nizhne-Endybalskoe deposit, the type I primary FI homogenizes at 353° to 336°C. Fluid salinity and concentration of carbon dioxide ranges from 14.8 to 3.9 wt.% NaCl equiv and from 3.1 to 1.8 mol/kg, respectively. The T_{eut} range (from -40° to -30°C) indicates that Na and Mg chlorides are also major constituents in the fluid. Dissolution temperature of gas-hydrates ranges from 3.4 to 13.3°C. Carbon dioxide in the type II vapor-rich FI homogenizes into gas at +23.6 to +30.8°C. The T_m values of -58.8 to -57.1°C slightly differ from melting temperature of pure CO₂ (-56.6°C). This indicates the minor admixture of volatile gases in the vapor phase. The estimated

pressures are from 490 to 390 bar.

The type III aqueous gas-liquid inclusions homogenize into liquid at 281 to 162°C. The salinity of trapped solutions varies from 15.0 to 11.6 wt % NaCl equiv. Na and Mg chlorides also prevailed in the fluid (T_{eut} -37 to -21°C).

In quartz of the Bezymyannoe deposit the type III aqueous gas-liquid FI homogenizes into liquid at 249 to 128°C. Fluid salinity varies from 13.3 to 1.4 wt.% NaCl equiv. The T_{eut} range of -37° to -19°C indicates that Na and Mg chlorides are predominated in the solution. Carbon dioxide in the type II inclusions homogenizes into gas at +26.7 to +27.5 and into liquid at +27.2 to +28.5°C. The T_m values vary from -58.3 to -57.3°C and slightly differ from melting temperature of pure CO₂ (-56.6°C). This is evidence for a presence of volatile gases in vapor phase. The pressure is estimated to range from 870 to 230 bars.

In quartz of the Kuzminskoe deposit the type III FI homogenize into liquid at 250 to 220°C. The fluid salinity varies from 10.4 до 9.0 wt.% NaCl equiv. Na and Mg chlorides also prevailed (T_{eut} -37 to -19 °C).

In quartz of the Vasilevskoe deposit homogenization of the type III FI into liquid occurred at 217 to 183°C. The fluid salinity varies from 15.4 to 8.3 wt.% NaCl equiv. Na and Mg chlorides are major salts (T_{eut} -37 to -19°C).

Conclusions

The results obtained evidence that ores in the Mangazeykoe ore field were deposited from fluids contrast in chemical composition and under various physical-chemical conditions.

Gold-rare metal ores of the Trubka deposit and silver-polymetallic ores of the Nizhne-Endybalskoe deposit were formed within hydrothermal systems where all three types of fluids were involved: liquid aqueous-carbonic, gaseous carbon dioxide and aqueous ones. Fluids of the I and II types were formed as a result of phase separation of a mixture of H₂O, CO₂, and Na-Mg chlorides due to pressure or temperature decreasing. Deposition of minerals began at $T \geq 350^\circ\text{C}$ and P from 500 to 200 bars.

Ore formation of the silver-polymetallic Bezymyannoe deposit occurred in hydrothermal system where liquid aqueous and carbon dioxide dominant gaseous fluids were present simultaneously, and they were formed as a result of a phase separation to liquid and gaseous phases at 250°C and 870 bar.

Formation of Ag-polymetallic ores of the Kuzminsky and Vasilevsky deposits took place from aqueous Na and Mg chlorides dominant solutions at T from 250° to 180 °C. It is interesting

to notice that water-salt fluid with moderate salinity formed minerals at 280 to 130°C.

The data obtained allow us to suppose that at least two contrast types of fluid possibly from different sources were involved in ore-forming process in the Mangazeykoe ore field.

Acknowledgements

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FLUID REGIME OF FORMATION FOR GOLD-TELLURIUM-CONTAINING QUARTZ VEINS OF THE BYNGI DEPOSIT (URALS)

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Object of the research

The objects of our fluid inclusion research are beresites and quartz veins within the Byngi gold deposit (Urals). Studied thick quartz vein (called Vostochnaya) contains an impregnated tellurium-sulfide mineralization and is located in an apical part of the blind stock of the plagiogranites which are related to the gabbro-granitic complex. The country volcanogenic rocks were altered into metasomatic rocks - beresites.

Analytical methods

The individual inclusions of the fluid in quartz were studied using a heating and freezing stage Linkam THMSG600. The type of salt system was recognized by temperature of eutectic (T_{eu}), and salinity was calculated by determining the temperature of melting of the CO_2 clathrate hydrate (Diamond, 1992). Density, molar volume and molar portions of components were calculated by the program VX-TERN (Painsi et al., 2008). The pressure and temperature of mineral formation was calculated by using the dolomite-calcite geothermobarometry (Talantsev, 1981).

Results

Fluid inclusions were studied in quartz from samples of brecciated beresite and quartz vein. Results of our research are shown in Table 1 and Figure 1.

Table 1. Salt system and homogenization temperature for quartz-hosted inclusions of studied rocks.

Type of rock (Numbers of incl.)	Type of salt system	Interval T_{eu} , °C	Interval T_h , °C
Brecciated beresite (13)	NaCl-KCl-H ₂ O	22.7-23.1	210-240
Quartz vein (16)	NaCl-KCl-H ₂ O	22.5-23.5	180-220
(29)	NaCl-KCl-H ₂ O	20-23.5	180-220

Primary inclusions in quartz form of negative crystals with short-prismatic or isometric habit and have size up to 15-20 μm in brecciated beresite and up to 25-40 μm in quartz vein. Inclusions are located randomly in host quartz. The volume of gas bubble within inclusions varies from 10 to 40 vol.% (quartz vein) and from 15 to 90 vol.% (brecciated beresite). This indicates that the fluid was heterogeneous as a result of effervescence. The inclusions from the veined and brecciated beresite

quartz are three-phase ($L_{H_2O}+L_{CO_2}+V_{CO_2}$) or two-phase ($L_{H_2O}+L_{CO_2}$) at room temperature. The type of salt system in the quartz vein is NaCl-H₂O and NaCl-KCl-H₂O based on values of the eutectic temperatures (20-23.5°C).

The calculation of other parameters of fluid inclusions in quartz (salinity, density, molar volume and molar portions of components) is shown that there are two groups with different molar portion X_{CO_2} (Table 2). Inclusions with X_{CO_2} less than 0.3 are common of both brecciated beresite and quartz vein. Some inclusions in brecciated beresite have X_{CO_2} more than 0.6.

Table 2. Estimated average characteristics of fluid inclusions in quartz.

Type of rock	Beresite	Quartz veins
V_m (cm ³ /mole)	25.5±2.6	38.1±2.6
ρ (g/cm ³)	0.952±0.043	0.95±0.04
X_{CO_2}	0.64±0.06	0.26±0.05
X_{H_2O}	0.32±0.02	0.71±0.03
X_{NaCl}	0.0083±0.001	0.01±0.05

The fluid salinity is low or elevated (2-8 wt.% NaCl equiv.). There is no any dependence between salinity and homogenization temperature. Inclusions from brecciated beresite and quartz vein are similar in salinity.

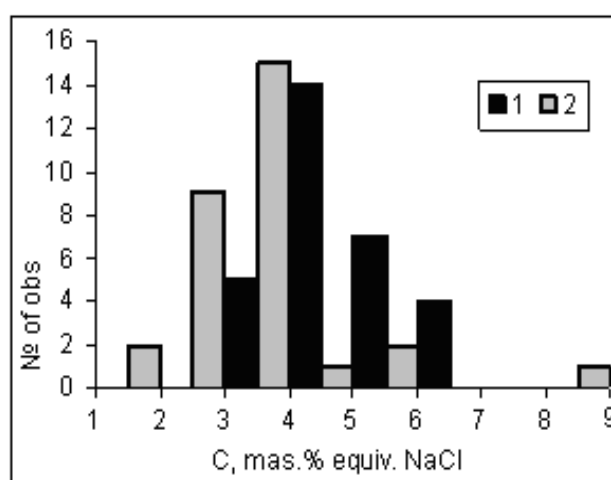


Figure 1. Salinity of quartz-hosted inclusions: 1 – brecciated beresite; 2 – quartz vein.

Calculations of PT-conditions for brecciated beresite and quartz vein based on the dolomite-calcite geothermobarometer are shown on Figure 2. Analysis of this data displays that the process of

metasomatic changes of volcanogenic rocks occurred when PT-parameters changed from $T=465^{\circ}\text{C}$ and $P=1.2$ kbar to $T=170^{\circ}\text{C}$ and $P=0.20-0.34$ kbar. The lowest pressure values assume depth of formation of rocks as 2.5-3.5 km.

The paragenesis of carbonate minerals in the quartz vein suggests $T=360-410^{\circ}\text{C}$, what is higher homogenization temperature of inclusions in quartz in $150-190^{\circ}\text{C}$. Such divergence of pointed temperature amounts could not be explained by the pressure correction value only. It is possible that there is no balance between carbonate minerals and quartz in the vein.

The temperatures of carbonate minerals in brecciated beresite have a wide range that covers whole homogenization temperature interval for inclusions in quartz.

Hereby, the results of the dolomite-calcite geothermobarometry and fluid inclusion study show that quartz vein of the Byngi deposit is formed on the late stages of metasomatic changes inside zone development.

Medium to low salinity of ore-forming carbon dioxide fluid indicates probable link between Au-Te-mineralization and the plagiogranite stock.

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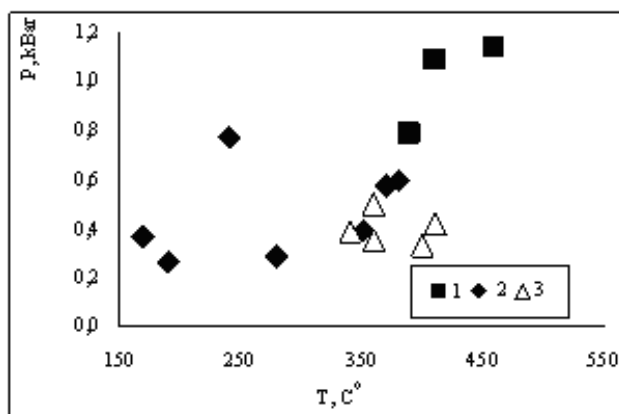


Figure 2. PT-conditions for the carbonate paragenesis: 1 – brecciated beresite, 2 – beresite (Sazonov et al., 1979), 3 – quartz vein.

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MELT INCLUSIONS IN MINERALS OF CA-RICH SI-UNDERSATURATED PARALAVA FROM THE NABI MUSA DOME, DEAD SEA REGION

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Introduction

High-temperature combustion metamorphic (CM) complexes (fossil mud volcanoes, so-called "Mottled Zone" - MZ) are discordantly located within carbonate strata at the western margin of the Arabian petroleum province (Israel, Jordan). Being localized upon the eroded surface of Upper Cretaceous stratum, the MZ complexes are composed mainly of brecciated calcareous sediments of the underlying Cretaceous sequence uplifted from depths of at least 1.5 km.

Petrography of paralavas

Unusual melted rocks were found in the Nabi Musa dome, one of fifteen MZ complexes of the Dead Sea rift valley (Sokol et al., 2010). The foci of the highest-temperature CM rocks and paralavas were found to be localized along conduits and breccia zones. The paralava veins are 0.5-1 m to 4 m long, rootless, and have experienced hydrothermal alteration.

The Nabi Musa paralavas have unusual Si-Ca-rich compositions (71 to 91 wt.% CaO + SiO₂, CaO - 40-51 wt.%) and consequently the other major oxides, except P₂O₅, which are notably lower than other Dead Sea paralavas previously studied. More Si-rich analogous of these paralavas were identified only in the oil fields of Iran and Iraq, where CM events were caused by ignition of gas and oil (McLintock, 1932; Basi, Jassim, 1974).

The freshest coarse-grained paralava (sample 12D) from Nabi Musa was selected for detailed study (in wt.%: CaO - 48.90, SiO₂ - 36.00, Al₂O₃ - 6.00, Fe₂O₃ - 2.80, P₂O₅ - 1.1, MgO - 1.00, TiO₂ - 0.42, Na₂O - 0.40, K₂O - 0.20, SO₃ - 0.2, LOI - 3.00). The paralava contains rankinite (0.02–1.2 mm, 50-70 vol.%), pseudowollastonite (600-900 µm, <10 vol.%), oikilitic melilite (30-40 vol.%). Wollastonite, parawollastonite, Ti-garnet, apatite and cuspidine are minor and commonly occupy interstices between main minerals.

Mineralogy and petrography of melt inclusions

Primary transparent to translucent silicate melt inclusions were found mainly in the cores of melilite, parawollastonite, pseudowollastonite, rankinite and apatite grains (Table 1). The inclusions are from 5 to 150 µm in size and consist of brownish devitrified glass, gas bubble, and

sometimes daughter/trapped crystals (larnite, nagelschmidtite, apatite, opaque minerals). The largest (up to 170 µm) oval inclusions are common of rankinite. They contain fine-grained aggregate of nagelschmidtite and partially devitrified glass (Fig. 1A). Similar inclusions were studied in minerals from the paralavas of the Hatrurim Basin (Sharygin et al., 2006). Secondary melt inclusions are occasionally found in pseudowollastonite. They are small in size and form trails in the host mineral.

Table 1. Representative analyses (wt.%) of minerals from the Nabi Musa paralava (sample 12D).

Phase	PsWo	Ran	Mel	Nag	Lar
	1	1	1	2	2
SiO ₂	51.43	41.16	29.80	29.30	35.27
TiO ₂	0.00	0.00	0.12	0.02	0.04
Cr ₂ O ₃	0.03	0.02	0.02	0.0	0.01
Al ₂ O ₃	0.03	0.00	21.42	0.23	0.88
FeO	0.03	0.13	1.72	0.57	0.44
Fe ₂ O ₃ *	—	—	3.52	—	—
MgO	0.04	0.13	3.25	0.56	0.28
CaO	48.37	58.27	38.30	60.20	62.04
Na ₂ O	0.03	0.09	0.88	1.02	0.17
K ₂ O	0.00	0.00	0.23	0.60	0.00
P ₂ O ₅	0.00	0.00	0.00	6.36	0.00
SO ₃	0.13	0.0	0.0	0.13	0.00
Total	100.10	99.80	98.90	98.98	99.12

Note: * FeO and Fe₂O₃ calculated from mineral stoichiometry; 1 – minerals hosted inclusions; 2 – minerals from heated inclusions.

Thermometry of melt inclusions

Heating experiments were performed for the Nabi Musa coarse-grained paralava (sample 12D). Melt inclusions in melilite (5-30 µm) began to melt between 1100 and 1250°C, but never reached complete homogenization, though several grains were heated even up to 1350°C. Homogenization of melt inclusions in pseudowollastonite (5-25 µm) occurred at 1180°C. Melt inclusions in rankinite (20-170 µm) used for heating experiments are completely crystallized (grayish fine aggregates). The first appearance of melt were observed between 1030 and 1100°C; complete disappearance of gas bubble and in some cases complete melting of crystalline phases occurred at 1280-1300°C. About a half of heating experiments with the melt inclusions in the Nabi Musa minerals were unsuccessful because inclusions were not

homogenized even up to 1320°C (melt + gas bubble) due to possible leakage during heating.

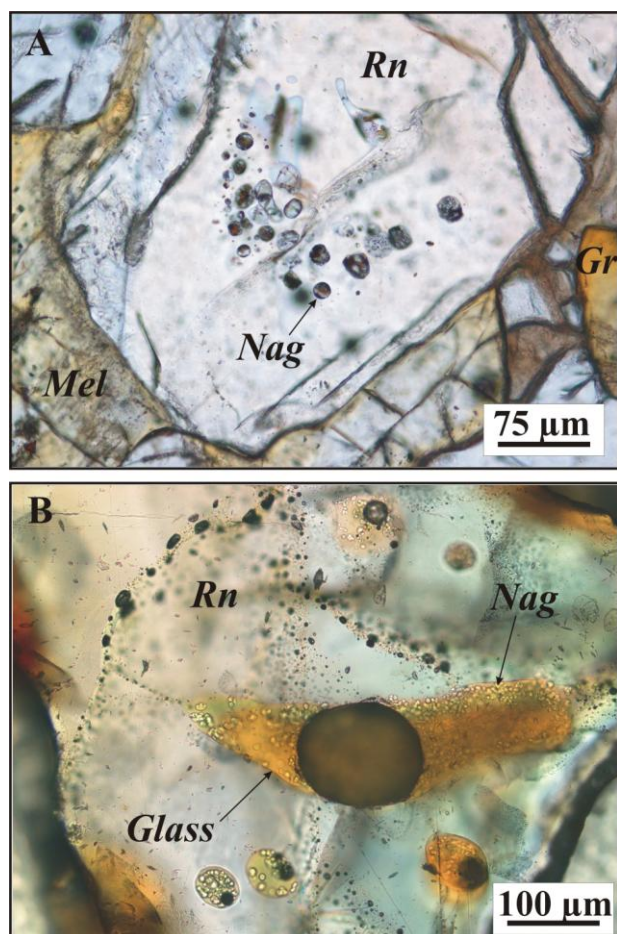


Figure 1. Primary melt inclusions in rankinite.

Note: (a) Unheated inclusions containing brownish glass, larnite, nagelschmidtite, apatite and opaque minerals; (b) heated and then quenched inclusions.

Major element composition of heated silicate melt inclusions

After quenching, the heated inclusions contain brownish to greenish glass, gas bubble and relics of daughter/trapped phases (Fig. 1B). Glasses are low in SiO₂ (36-38.5 wt.%) and high in CaO (42-45 wt.%) and P₂O₅ (0.9-1.9 wt.%). All glasses have notably higher TiO₂ (0.8-2.2), FeO_t (4.3-9.5), alkalis (Na₂O+K₂O – 1.3-3.2), F (1.3-1.9) and slightly higher P₂O₅ than bulk paralava (Table 2). Heated inclusions in rankinite contain relics of nagelschmidtite (up to 6.4 wt.% P₂O₅).

Conclusions

The finding of silicate melt inclusions in minerals of Ca-rich paralavas is quite rare, since the melts of such composition have low viscosity and crystallize very fast. These types of rocks are the non-equilibrium associations and have extremely high temperatures of crystallization, so standard geothermometers are inapplicable to estimate PT-conditions.

In our case the investigations of melt

inclusions along with the other methods provide the opportunity to define precise temperature of rock crystallization.

Due to the bulk composition of the Nabi Musa paralavas (SiO₂+CaO+Al₂O₃ > 90 wt.%) the initial stages of crystallization may be described within the CaO-SiO₂-Al₂O₃ ternary phase diagram. According to the diagram the crystallization had started at T=1600–1400°C.

We failed to melt paralava sample 12D in a furnace even at T = 1500°C, and melt inclusions in rankinite heated to 1320°C were not fully homogenized. Therefore, data on melt inclusions and temperatures from the phase diagram show that the liquidus of melt initial for these rocks lies higher than 1500°C.

Table 2. Representative compositions of glasses of heated melt inclusions in rankinite (paralava 12D).

Glass variety:	Green			Brown		
SiO ₂	38.58	35.74	37.45	36.44	36.59	34.50
TiO ₂	0.62	0.83	0.71	2.21	0.86	1.17
Al ₂ O ₃	5.79	6.19	5.35	4.64	5.30	5.45
FeO	4.26	3.97	3.66	7.76	5.86	9.48
Cr ₂ O ₃	0.05	0.14	0.11	0.02	0.12	0.07
MgO	1.06	1.11	1.10	0.21	0.84	0.65
CaO	43.42	43.22	45.31	42.24	45.03	42.63
BaO	0.10	0.19	–	0.93	0.48	–
Na ₂ O	1.47	1.57	0.95	0.37	0.64	0.48
K ₂ O	1.62	1.62	1.11	1.49	0.72	1.11
P ₂ O ₅	0.86	1.47	1.46	1.59	1.60	1.81
SO ₃	0.66	0.50	0.62	0.01	0.31	0.05
F	1.92	1.29	–	0.12	0.61	–
O=(F,Cl) ₂	0.81	0.54	–	0.05	0.26	–
Total	98.40	97.29	97.82	96.98	98.70	97.41

Acknowledgements

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FLUID INCLUSIONS IN ROCK-FORMING MINERALS OF THE KOKCHETAV GARNET-CLINOPYROXENE DIAMOND-GRADE METAMORPHIC ROCKS

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Introduction

Study deep fluid or melt inclusions in minerals, formed at ultra-high pressure (UHP) conditions, remain one of the most interesting topics. Previous study of fluid inclusions in minerals from UHP metamorphic rocks was mainly focused on inclusions in quartz (Sobolev et al., 1985) and rare in other minerals. Recently sub-micrometric fluid/melt inclusions were identified in diamond from the UHPM metamorphic rocks from the Kokchetav and Erzgebirge (Hwang et al., 2005; Dobrzhinetskaya et al., 2005). But so far the fluid inclusions were not found in rock-forming minerals. In this paper we present the results of fluid inclusion study in garnet and clinopyroxene from diamond-grade, but diamond-free rocks from the Kokchetav massif.

Samples and methods

The geological setting of the Kokchetav massif (Northern Kazakhstan) has been summarized elsewhere (e.g. Dobretsov et al., 1995; Shatsky et al., 1995; Theunissen et al., 2000) and will not reiterated here. In this study, 15 specimens of Grt-Cpx rocks from the Kumdy-Kol deposit and Barchi-Kol area were used for detailed fluid-inclusion investigations.

The Grt-Cpx rock is composed of clinopyroxene (20-60 vol.%), garnet (30-60 vol.%), carbonates (e.g. dolomite or calcite 0-30 vol.%) and minor biotite, K-feldspar and quartz all together less than 15 vol.%. These rocks closely resemble eclogites in hand specimen, but can be distinguished from the later by compositions of garnet (Alm₁₈₋₂₄Sps_{1.5-2.5}Pyr₂₄₋₂₉GrS₄₉₋₅₂) and diopsidic clinopyroxene (sometimes K-bearing).

Mineral compositions were analyzed by a Camebax Micro electron microprobe with a 20-kV accelerating potential and 20 nA specimen current. Microthermometric measurements of fluid inclusions were made on doubly polished, unmounted, 200–400 µm thick sections using a Linkam THM 600 heating / freezing stage coupled to a BH-2 Olympus polarizing microscope, with liquid nitrogen as the cooling medium (minimum temperature of -195°C).

The confocal Raman images were collected using a Confocal Raman Imaging alpha 300R (WiTec). The data set is then evaluated using single variant (e.g. integrated intensity) and multivariant

(e.g. cluster analyses) methods to generate the images displaying the distribution of certain material, their various phases and/or their strain state. Due to the high level of confocality, clear depth scan could also be obtained. Details of the experimental conditions can be found in Table 1.

Table 1. Experimental parameters for confocal Raman images.

	XY Scan	YZ (Depth) Scan
Scan Size	60x50 µm ²	50x20 µm ²
Resolution (pixels)	120x100	100x50
Integration Time/Pixel	0.162 s	0.162 s
Spectrometer	UHTS300	UHTS300
Grating (grooves/mm)	600	600
Objective	100X air (NA 0.9)	100X air (NA 0.9)
Excitation wavelength	532 nm	532 nm
CCD Camera	Back-Illuminated CCD (optimized for VIS detection)	

Fluid inclusions

The fluid inclusions are usually located in the core of the garnet crystals. They may also occur in small domains. The inclusion shape is variable, but predominantly approaching negative crystal (Fig. 1). Almost all inclusions contain different amounts of solid phases (e.g. calcite or mica). Although gas/liquid and solid/(gas+liquid) ratios vary significantly even for adjacent inclusions. Isolated inclusions with negative crystal shape or their clusters are typically primary inclusions. These inclusions are low salinity H₂O inclusions. Ice melting T_m(ice) -3.6 to -0.2°C and homogenization Th=360-380°C were the observable phase transitions. Representative fluid inclusions were analyzed using by Confocal Raman Imaging.

The garnet was polished so that the inclusion remained intact some tens of microns below the surface. As can be seen in Figs. 2c and 3c, the garnet Raman spectra show significant variation in relative peak intensities across the scanned area. The spectra in Fig. 2c and 3c are normalized to the peak near 900 cm⁻¹. Differences are apparent between the red and the magenta spectra (peaks near 850 and 360 cm⁻¹). The orange spectrum represents a calcite in direct proximity to, or as part of the inclusion. This variation is confirmed in the

depth scan (Fig. 3). Here too, spectra are normalized to the peak near 900 cm^{-1} , differences are apparent between the red and the magenta spectra (Fig. 3c). Interestingly, the aqueous phase showed significant variations (Figs. 2f and 3f). Based on the analysis of the Raman spectra and microthermometry, only low salinity H_2O -fluids have been recognized. Changes in garnet peak intensities appear only around the inclusion.

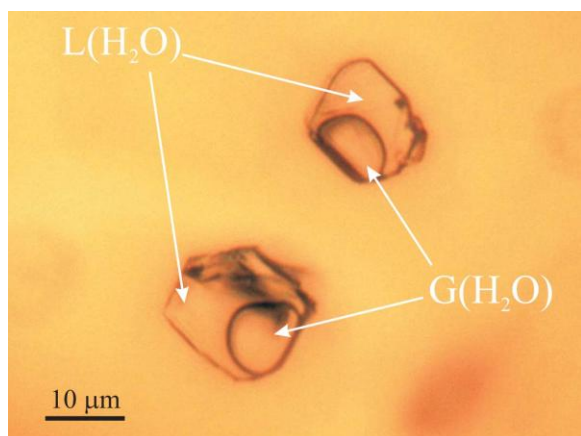


Figure 1. Aqueous fluid inclusions in garnet from calc-silicate rocks (Kokchetav massif, sample GAK101).

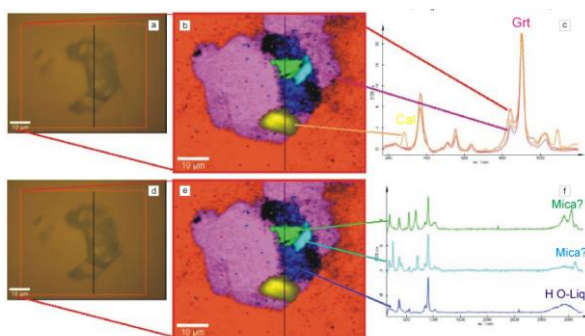


Figure 2. XY Raman Image of the inclusion. The Raman spectra of the garnet (c) and aqueous phase (d) show some significant variations in the relative peak intensities and position. The orange spectrum shows the calcite.

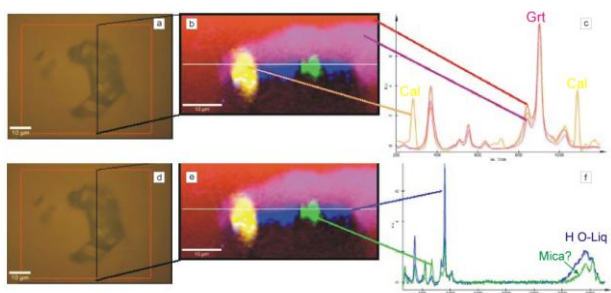


Figure 3. In the YZ (Depth) Scan, the Grt signal again shows some significant variations in the relative peak intensities.

Conclusions

There are several possible mechanisms explaining primary fluid inclusions and small scale heterogeneities in garnet composition associated with such inclusions.

(i) True primary fluid inclusions, which have

formed during growth of garnet cores in the presence of fluid phase. The difference in the garnet compositions then appears due to the reaction between the fluid inclusions and the host-garnet.

(ii) Break-down low temperature and low pressure polyphase inclusions, captured by growing in garnet during prograde stage at peak metamorphic conditions. Recently, these processes were studied experimentally (Perchuk et al., 2008). They found that these processes cause formation of new garnet with a distinctly different composition compared to the initial host-garnet.

(iii) Originally, the inclusions were trapped as melt inclusions. Subsequent crystallization of these melt inclusions liberate some fluid phase, which were dissolved in the melt. Newly formed garnet + solid phases (e.g. calcite, chlorite, mica) occur as daughter or trapped phases in fluid inclusions, would then have crystallized from the melt. Independently from mechanism of origin of these fluid inclusions, newly formed garnet could appear as result of reaction interaction between the inclusions and host garnet.

Acknowledgements

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THE HETEROGENIOUS PHASE EQUILIBRIA IN WATER–SALT (fluoride, carbonate, sulfate)–QUARTZ SYSTEMS

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Introduction

The presence of fluorine, sulfate, and carbonate exerts a significant influence on mass transfer and the entire course of mineral formation. Therefore, experimental investigations of the properties of fluorine-, sulfate-, carbonate-bearing fluids and melts have attracted increasing attention of researchers. Nonetheless, they are still not understood equate.

A distinctive feature of aqueous solutions of such sodium salts, which usually have a negative temperature coefficient of solubility, is the occurrence of critical phenomena in both undersaturated and saturated solutions. In addition, their phase diagrams are complicated by the phenomena of liquid immiscibility. The goal of this study was to experimentally determine the phase state of fluorine-, sulfate-, carbonate-bearing fluids at temperatures of 700–800°C and pressures of 1000–3000 bars.

Experimental results

Fluid inclusions in quartz were synthesized by the method of crack healing at specified pressures and temperatures from solutions containing sodium fluoride, sulfate, and carbonate ($\pm$ chloride). Some experiments have been carried out in the presence of albite gel. The experimental sample contained two types of inclusions, two phase (gas + liquid) and three phase (gas + liquid + crystal), which indicated the coexistence of two immiscible fluids, with low and high concentrations, under the experimental conditions. The four-phase inclusions (gas + crystal + liquid1 + liquid2) are found in some samples and contain the second liquid, which is more viscous than the water phase. It resembles glass from natural melt inclusions, and it will be hereafter referred to as glass.

NaF-bearing fluid

A comparison of the results of 700°C, 2 kbar experiments with NaF or NaF+NaCl solutions showed, despite the difference in the composition of initial fluid mixtures, the two-phase inclusions are similar to each other and have similar ice melting temperatures. However, the range of homogenization temperatures of the inclusions formed in chloride–fluorite solutions is much narrower compared with the inclusions synthesized in a pure fluoride solution. This probably indicates

that the phase boundary for the pure fluoride system passes immediately near the point of experimental conditions.

In the 800°C - 2 kbar inclusions a crystal sometimes appeared in the two-phase inclusions during heating and did not disappear up to the temperature of vapor dissolution (377–397°C). When temperature increased up to 465°C, no changes were observed in the inclusions containing glass and vapor. During the heating of the three-phase inclusions with glass and liquid, the glass crystallized, and the newly formed solid phases dissolved in the range 150–400°C without homogenization. If a solid phase was present instead of liquid in an inclusion, liquid appeared in the vapor bubble, and partial homogenization to this liquid was observed at 397–398°C. Complete homogenization was never observed, because the inclusions began to decrepitate at 380–400°C, and heating was stopped.

Of special interest is the composition of the glass phase. In some experiments, the surface of quartz appeared glazed after quenching. The surface glass layer was analyzed with an electron microprobe, although its composition could be somewhat modified by the loss of water and probably other components. In addition to SiO₂ (75–79 wt.% in various experiments), the glass contained 1.6–4.8 Al₂O₃, 0 – 5.9 Na₂O, and 0.5–1.0 wt.% F. At 800°C and 2 kbar, the equilibrium of a substantially aqueous fluid + silicate-salt-aqueous liquid (so-called heavy fluid) $\pm$ solid phase is possible in the ternary system. A heavy fluid is most likely an intermediate compound of SiO₂, H₂O, and NaF, that is, sodium hydrosilicates or malladrite. The composition of the pseudohexagonal crystalline phase in opened inclusion by microprobe data is close to malladrite, despite a significant deviation in F content: 16.8–34.1 SiO₂, 24.8–31.0 Na₂O, 35.9–40.0 wt.% F.

Na₂SO₄-bearing fluid

Two-phase inclusions synthesized at 700°C and 1 kbar homogenized to both liquid and gas phases, sometimes with critical phenomena. So fluid of the inclusions has a near critical density. The three-phase inclusions were heated up to 600°C; at temperatures above 450°C, rather intense dissolution of salt crystals began, but almost all inclusions decrepitated at 530–582°C.

Two- and three-phase inclusions with Na_2SO_4 contents of 6.7–12.7 and 60–70 wt.% (roughly) were synthesized at 700°C and 2 kbar.

The cryometric investigation of the two-phase inclusions, synthesized at 800°C and 3 kbar, showed that they can be divided into two groups on the basis of salt content: 4.0–0.6 and 10.3–23.2 wt.% Na_2SO_4 .

The salt phase in three- and four-phase inclusions was not completely dissolved, because extensive leakage of inclusions began at 400–410°C.

Na_2CO_3 -bearing fluid

Two-phase inclusions, synthesized at 700°C and 1 kbar filled to various degrees were observed in the samples. The vapor phase occupies ~70% of inclusion volume in some varieties and less than 25 vol.%, in the other varieties. In addition, inclusions with an intermediate filling coefficient were observed. Homogenization to gas occurred at 382–383°C, sometimes during boiling. Essentially liquid inclusions were not homogenized during heating up to 550°C.

Complex unmixing processes took place in the inclusions synthesized under the conditions of the upper heterogeneous region. All our observations suggest that coarse dispersed emulsions of two liquids exist in the upper heterogeneous region: an essentially aqueous phase and a water-rich silicate-dominated phase.

The thermometric investigation of inclusions that trapped fluid phases immiscible under experimental conditions showed that they can, in turn, become heterogeneous at temperatures of approximately 200–400°C. Under such conditions, three or four noncrystalline phases can be in equilibrium (Fig. 1).

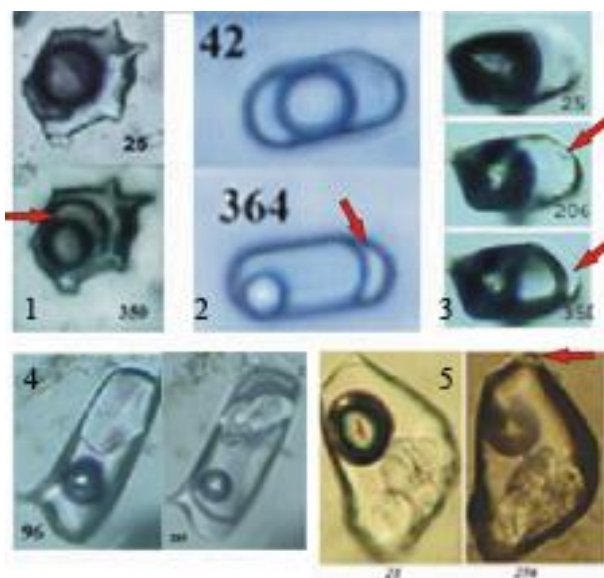


Figure 1. Liquids separation at unsaturated (1, 2) and saturated (4) solution and glasses (3, 5) under heating..

During the thermometric measurements, another liquid phase appeared in the inclusions at approximately 200°C; i.e., the liquid separated into two phases (indicated by arrows in Fig. 1). The newly formed liquid may have both smaller (Photo 1 in Fig. 1) and greater (2, 4 in Fig. 1) density than residual liquid phase. Phenomena of liquid separation occurred in any studied solutions: NaF-bearing inclusions (3 in Fig. 1), Na_2SO_4 -bearing inclusions (2, 4, 5 in Fig. 1) and Na_2CO_3 -bearing inclusions (1 in Fig. 1).

Conclusions

1. The experiments supported the possibility of equilibria between three and four noncrystalline phases in the ternary H_2O – SiO_2 –salt (II) system. The field of inhomogeneous fluid is very wide and its lower boundary extends to temperatures of approximately 200°C at corresponding pressures (approximately 400 bar).

2. The possibility of the formation of heterogeneous fluids increases considerably in multicomponent fluid–silicate systems. Heterogeneous equilibria are probably an essential stage in the evolution of natural fluids. They are accompanied by the redistribution of components between the immiscible phases. Heterogenization of fluids is the most important mechanism of matter redistribution in the establishment of heterogeneous equilibria. Separation of the heavy fluid phase enriched in silicates, salts, and ore components can lead to the development of various superimposed processes with changeable external conditions.

3. The fluid phases separated during the magmatic stage undergo, in turn, unmixing in response to further cooling and decompression. This process may happen to temperatures as low as 180–200°C. Thus, fluid immiscibility phenomena can occur in several stages.

4. When a portion of the heavy fluid is entrapped in inclusions, the latter can be identified as melt inclusions.

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COMPARATIVE SILICATE MELT INCLUSION STUDY OF TWO VOLCANOES (HEGYESTŰ AND HALÁP) IN THE BAKONY-BALATON HIGHLAND VOLCANIC FIELD, HUNGARY

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Introduction

Primary silicate melt inclusions in early phenocrysts of mafic volcanic rocks are the best opportunities to obtain direct information on physical conditions and chemical processes of the upper mantle (Roedder, 1984). In this study, two OIB type post-extensional alkali basalt volcanoes (Hegyesztű and Haláp) were selected in the Bakony-Balaton Highland Volcanic Field (Western Hungary) with different ages (7.9 Ma and 3.0 Ma, respectively) and slightly different modal and major and trace element compositions (Embey-Isztin et al., 1993). We used primary silicate melt inclusions (SMI) hosted in olivine phenocrysts of the two volcanoes to compare their original chemical features.

Methods

The bulk modal and chemical compositions of the primary multiphase silicate melt inclusions and crystallization sequences of the melt within the SMIs determined by homogenization experiments using high temperature Linkam and Vernadsky stages, and a furnace technique. Fluid phases occurring in the SMIs and coexisting and coeval fluid inclusions were studied by microthermometry and Raman microspectroscopy. To determine the chemical compositions of solid phases of the unheated SMIs and homogenized glassy SMIs, we applied EMPA for major elements and SIMS for trace elements.

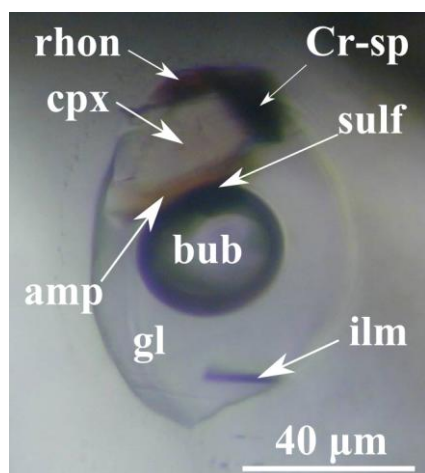


Figure 1. Photomicrograph of olivine-hosted partially crystallized silicate melt inclusion with large CO₂ bubble, Haláp volcano.

Note: cpx - clinopyroxene, rhon - rhönite, amp - amphibole, sulf - sulfide, gl - glass, bub - CO₂ bubble, sp - spinel, ilm - ilmenite.

Bulk compositions of the SMIs

The modal compositions of the studied olivine-hosted SMIs (Fig. 1-2) are similar in both localities, but characteristic differences were also recognized. One of the major daughter minerals is clinopyroxene which is common and similar in chemistry both in Hegyesztű and Haláp. Other principal crystalline phase is rhönite found in Hegyesztű (Fig. 2), and coexisted amphibole and rhönite can be observed in Haláp (Fig. 1) (Sharygin et al., 2007). The highly silicic residual glass with high alkali content and CO₂-rich gas bubbles occur among the daughter minerals in both SMIs.

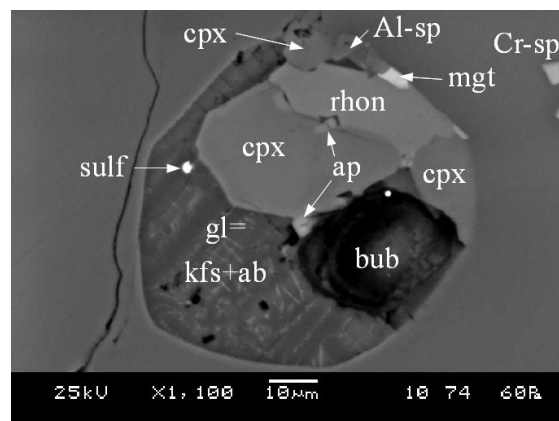


Figure 2. BSE image of olivine-hosted partially crystallized silicate melt inclusion, Hegyesztű volcano. Note: cpx - clinopyroxene, sp - spinel, rhon - rhönite, mgt - magnetite, ap - apatite, sulf - sulfide, gl - glass, bub - bubble, kfs - K-feldspar, ab - albite.

Both bulk compositions of SMIs are alkali mafic melts. However, Hegyesztű shows higher alkalis, TiO₂, Al₂O₃, CaO and lower silica, MgO, FeO compared to that of Haláp (Fig. 3).

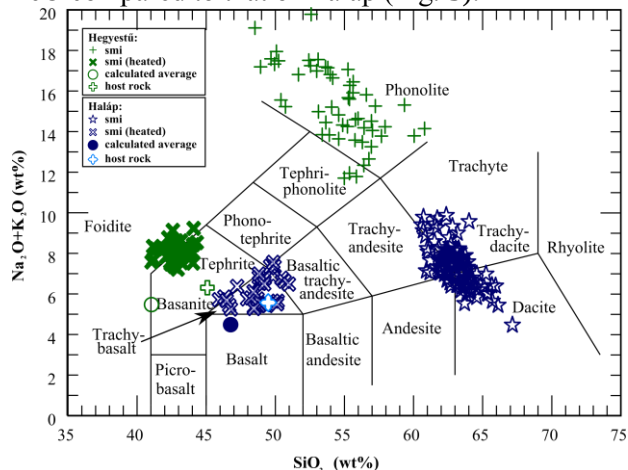


Figure 3. TAS diagram for the calculated and measured bulk chemical compositions of SMIs and their residual glasses. Compositions of the host basalts are also shown for comparison.

Both melts are relatively volatile-rich, the CO₂ content of the Hegyestű melt is 2 wt.% and that of Haláp is ~1.5 wt.%. A small amount of CO (max. 9 mol.%) at both localities and CH₄ (max. 2 mol.%) in the Haláp samples were detected in the CO₂-rich fluids inclusions.

Trace element distributions of the SMIs from both localities are similar to the host rock, although some slight differences can be observed (Fig. 4-5). The SMIs hosted in olivine phenocrysts from Hegyestű are richer in trace elements compared to the host rock (Fig. 4). Furthermore, SMIs from Haláp show lower Sr and heavy rare earth element contents than host alkali basalts indicating different melt source and/or partial melting process (Fig. 5).

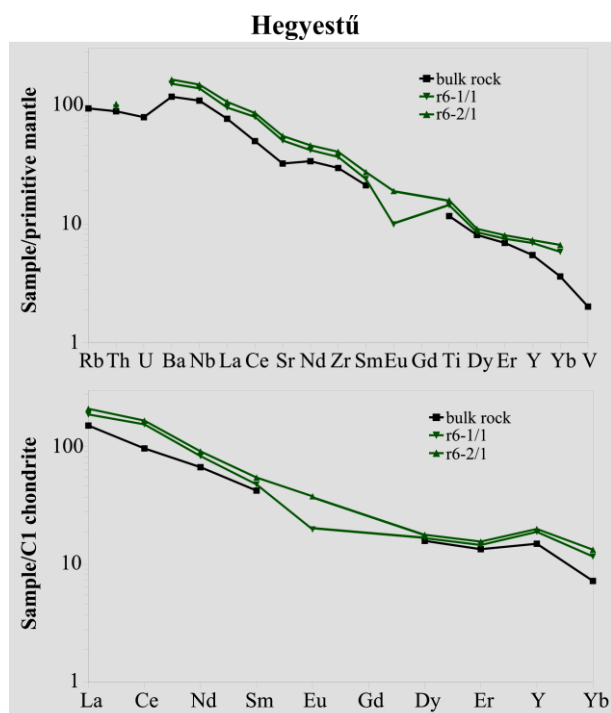


Figure 4. Trace element composition of SMIs in the Hegyestű olivine phenocrysts compared with the host rocks. Note: compositions are normalized for primitive mantle (McDonough and Sun, 1995) and C1 chondrite (Nakamura, 1974).

Discussion and conclusions

The evolution of the magma droplets entrapped in olivine phenocrysts at both localities can be characterized by an early sulfide-silicate immiscibility, as well as crystallization of daughter minerals at magma chamber level.

The solidification continued and CO₂ separation from the silicate melt happened particularly at conduit level. This process in the Hegyestű SMIs follows a definite trend: sulfide bleb → Al-spinel → rhönite → Ti-augite → apatite ± rutile ± ilmenite → CO₂ + glass (Kóthay et al., 2005).

The Haláp SMIs show a slightly different and more variable crystallization sequence: Al-rich spinel + sulfide bleb → rhönite + amphibole +

clinopyroxene → apatite + ilmenite → CO₂ + glass. This indicates more variable chemical composition of the mafic melt compared to the homogenous Hegyestű melt.

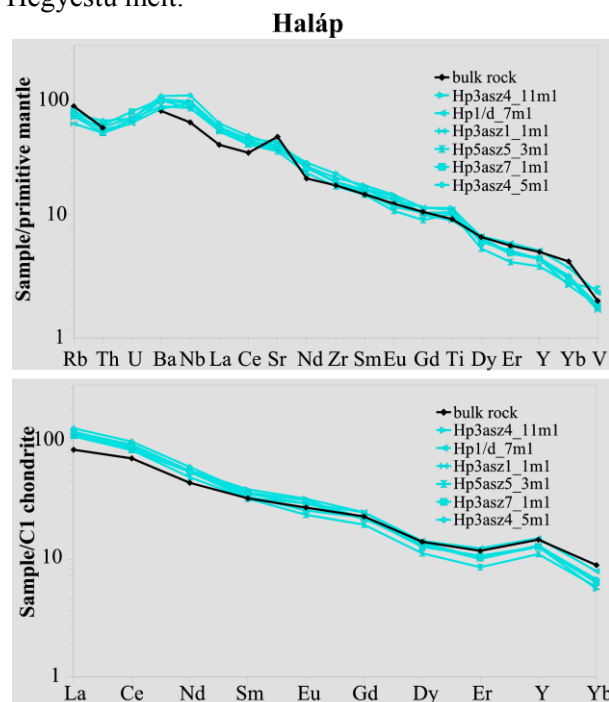


Figure 5. Trace element composition of SMIs in the Haláp olivine phenocrysts compared with the host rocks. Note: compositions are normalized for primitive mantle (McDonough and Sun, 1995) and C1 chondrite (Nakamura, 1974).

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MELT INCLUSIONS IN MINERALS FROM HOLOCENE TEPHRAS OF AVACHINSKIY VOLCANO, KAMCHATKA

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Introduction

Melt inclusions presents melts trapped by minerals during their growth in magma chambers and at ascending to the surface. Several recent studies of melt inclusions in island-arc rocks revealed a strong bimodality of the compositions and scarcity of intermediate melts with $\text{SiO}_2=59\text{--}66$ wt.% (e.g. Naumov et al., 1997; Reubi, Blundy, 2009). These observations were used to interpret the origin of island-arc andesites by magma mingling and crystal accumulation rather than by fractional crystallization of basaltic magmas. Whether or not all island-arc volcanoes are equal with this respect remains not clear. On the other hand, most investigations of melt inclusions in island-arc rocks were focused on inclusions from one or two minerals (e.g., Naumov et al., 1997; Tolstykh, 2002). It cannot be excluded that such data sets are biased and not representative for large volume and heterogeneous magma systems.

In this work we report results of a systematic study of melt inclusions in 6 minerals from 61 tephra samples from the Avachinskiy volcano in Kamchatka. These samples represent 40 Holocene eruptions of this volcano including: 1) early phase of rare and voluminous andesitic eruptions (7.25–3.5 ky BP) and 2) later phase of frequent eruptions of basaltic andesites associated with the construction of the Young Cone (3.5 ky BP to present) (Braitseva, 1998). We use the data to reconstruct the evolutionary path of the Avachinskiy melts prior eruptions and the changes in the magma feeding system beneath this volcano which occurred during the last ~7,000 years.

Results

In the course of this study we have analyzed ~500 melt inclusions in *Ol* (60 an.), *Cpx* and *Opx* (300 an.), *Amph* (60 an.), *Pl* (30 an.) and *Mt* (40 an.). All analyses were performed with the help of JEOL JXA 8200 wave-length dispersive electron microprobe at the IFM-GEOMAR (Kiel, Germany). The results are shown in Figure 1.

The melt inclusions span a large range of compositions from basalts to rhyolites. Both melt inclusion and host rock compositions plot predominantly along the line dividing low- and middle-K island-arc series (Fig. 1).

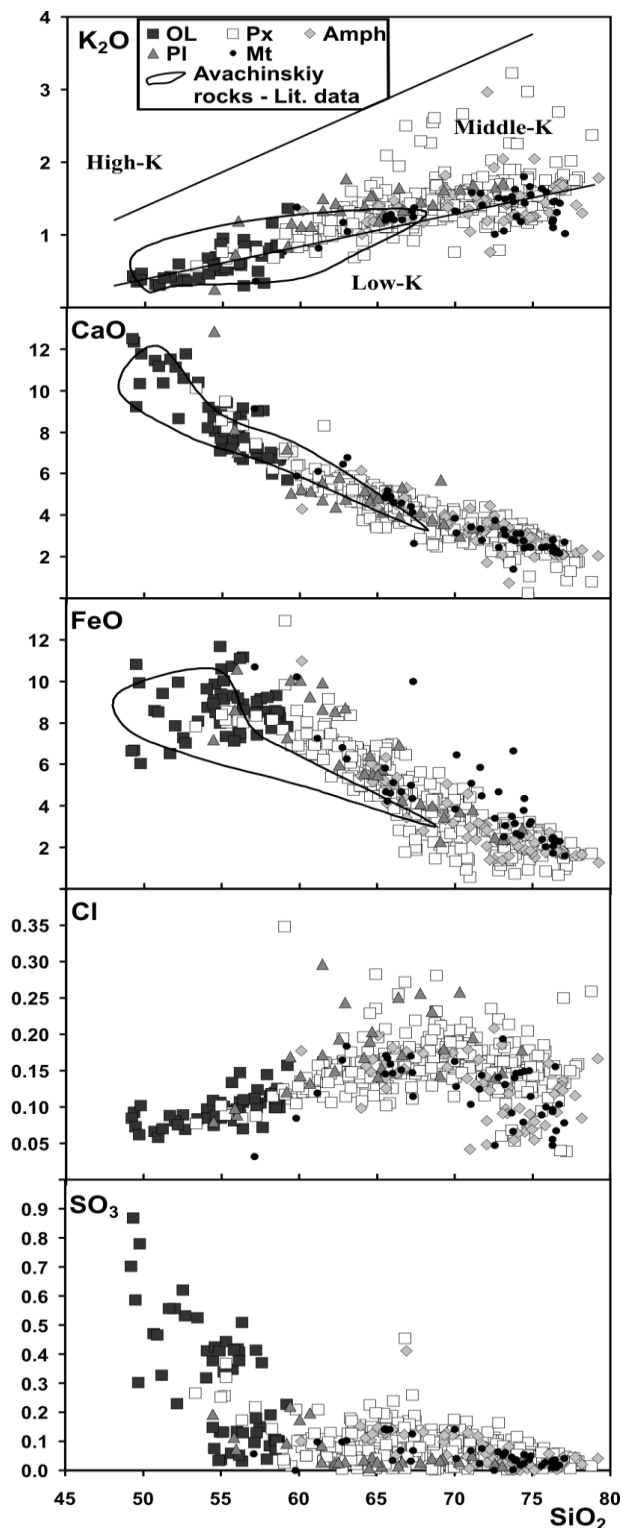


Figure 1. Composition of melt inclusions in different minerals from tephra samples of the Avachinskiy volcano. Field of whole rock compositions is shown after (Bindeman et al., 2004; Castellana, 1998). All concentrations are in wt.%.

The trends of major elements are continuous, and no apparent bimodality is observed in the data set. Most of the major element variability can be explained by fractional crystallization from parental basaltic melts. The most primitive crystallizing assemblage is represented by *Ol* and *Cr-Sp*. Judging from decreasing CaO content in primitive melts, *Cpx* also jointed *Ol* at very early stages of crystallization. *Plag* appears on liquidus at ~52-53 wt.% SiO₂. *Mt* and *Ilm* started to crystallize at ~57 wt.%. Significant change of crystallizing assemblage occurred at ~60-62 wt.% of SiO₂, when *Opx* replaced *Ol* and *Amph* and *Ap* become stable. Paragenesis of *OPx*, *CPx*, *Amph*, *Pl*, *Mt*, *Ilm* and *Ap* dominated the following evolution of melts toward strongly acid compositions with 78-80 wt.% SiO₂.

Studied melt inclusions are rich in volatile components. Judging from low totals of microprobe analyses the amount of H₂O in parental basaltic melts was at least 2-3 wt.% and increased up to 5-6 wt.% in more silicic melts. SO₃ content was as high as 0.9 wt% in basaltic melts and decreased rapidly with increasing SiO₂. Cl concentrations in mafic melts were ~0.07 wt.% and increased to ~0.20-0.25 wt% at SiO₂~70 wt.% and then decreased in more evolved melts, probably, due to separation of Cl-rich hydrous fluid from evolved magmas.

In comparison with host rocks, melt inclusions have in general more silicic compositions, and this difference increases with increasing SiO₂ content in the host rocks. For example, melt inclusions from rare basalts of the Avachinskiy volcano have SiO₂ similar or slightly higher than host rocks. Melt inclusions in basaltic andesites (SiO₂=53-57 wt.%) of the later stage of volcano formation (<3500 ky BP) have SiO₂ which is typically ~6-8 wt.% higher than their host rocks. Melt inclusions in andesites (SiO₂=57-63 wt.%) of the earlier stage (3500-7250 ky BP) are mostly rhyolitic (SiO₂>70 wt.%). Because the composition of erupted magmas is shifted to more mafic compared to melt inclusions, accumulation of minerals was likely very important process at the origin of all Avachinskiy rocks.

Magma mixing also played an important role in the origin of Avachinskiy rocks as evident from occurrence of contrasting matrix glasses in single tephra samples and from inverse and rhythmic zoning of minerals. In most cases, the contrasting compositions can be related to each other by fractional crystallization process. Thus, mixing of less and more evolved magmas could plausibly occur during periodic replenishment of magma chamber with more primitive melts.

Some studied silicic melt inclusions in *CPx* and *Amph* have relatively K-rich compositions and cannot be related to parental basaltic melts by simple crystallization process. These melts are

considered to be exotic and can be formed by localized melting of hydrothermally altered wall rocks beneath volcano. The proportion of the exotic melts is however relatively minor compared to the predominant less K melts, and thus crustal melting was likely not a major process to generate acid melts of the Avachinskiy volcano.

Conclusions

New data on composition of melt inclusions from the Avachinskiy volcano allowed us to reconstruct the entire evolutionary path of its parental melts evolved from basalts to rhyolites. Melt inclusions in different minerals form coherent trends of major elements, which can be well explained by fractional crystallization. Unlike other island-arc volcanoes, the Avachinskiy melts do not display bimodality of SiO₂ content. Melts of intermediate compositions are relatively abundant but they were found in less evolved rocks than andesites. In general, our data demonstrate that melt inclusions in typical arc rocks have systematically more Si-rich compositions compared to their host rocks, and this difference increases with increasing SiO₂ in rocks. This observation implies that evolved rocks of island-arc volcanoes are indeed products of magma mixing and accumulation of minerals, which crystallized from more evolved melts. While the majority of island-arc rocks are andesites, it is therefore not surprising that large number of highly evolved rhyolitic melt inclusions were analyzed by researchers in these rocks.

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ON THE PRESSURE ESTIMATE METHODOLOGY USING CO₂-BEARING FLUID INCLUSIONS

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Introduction

Like in any other science, repeatability is a crucial requirement to analytical data obtained from fluid inclusion studies. Notably, in this regard, that among the three important characteristics of natural fluid systems (i.e., pressure-temperature-salinity), temperatures and salinities are determined quite precisely by phase transitions, i.e., more or less directly, whereas pressure is estimated with much less accuracy. Such pressure estimates made by calculation often show significant discrepancy and lack of compatibility while using various methods of the pressure estimates (Kryazhev, 2010). It can be demonstrated that this discrepancy is caused by generally limited applicability of some of these methods.

Pressure estimate methods for CO₂-bearing fluid inclusions

The pressure estimate methods employing data on the CO₂-bearing fluid inclusions are very often used in fluid inclusion studies. This is due to broad occurrence of such fluid inclusions in hydrothermal minerals and generally advanced knowledge of the CO₂-H₂O and CO₂-H₂O-NaCl fluid systems.

There are two major methods usually applied the pressure estimates using CO₂-bearing fluid inclusions, namely:

(1) the method based on the experimental data of CO₂ properties and its solubility in water (Fig. 1) and saline solutions under elevated temperatures and pressures (e.g., Kalyuzhnyi, 1982; Roedder, 1984); the major source of errors while using this method is un-accountability of various admixtures found in natural fluids (mainly CH₄+N₂) and their influence on the CO₂ homogenization temperature, as well as inaccuracy of CO₂-H₂O volume fractions measurement in the inclusions (Kryazhev, 2010);

(2) the method based on the equation of state (EOS) determined for the CO₂+H₂O±NaCl system; on this basis, in particular, Brown and Lamb (1989) suggested a diagram package intended for more precise determination of fluid inclusion entrapment pressures and temperatures (Fig. 2). Also, various computer programs for calculating pressures using fluid inclusion data were established (e.g., FLINCOR, Brown, 1989; FLUIDS, Bakker, 2003).

A comparison of pressure estimates obtained by the two methods mentioned is given in Table 1.

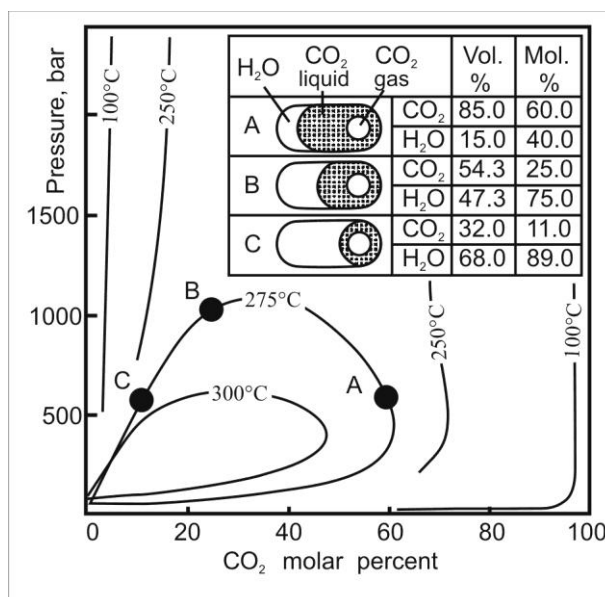


Figure 1. PTX-diagram for the CO₂-H₂O system (Roedder, 1984).

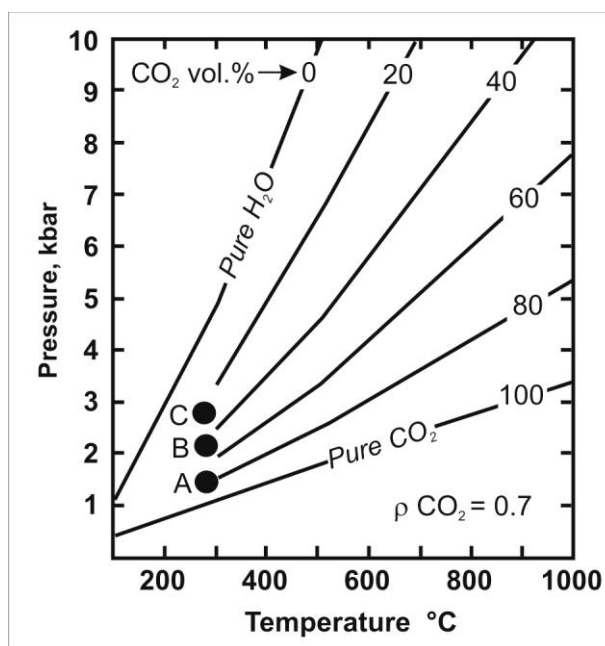


Figure 2. PTX-diagram for the CO₂-H₂O system (Brown and Lamb, 1989).

Fluid compositions corresponding to the fluid inclusions shown on Fig.1 are plotted on condition that the T=275°C.

Table 1. Comparison of the pressure estimates (bars) obtained by various methods.

Method	Fluid inclusions (Fig.1, Fig. 2)		
	A	B	C
Experiment (Fig 1)	575	1000	575
Diagram (Fig 2)	1300	2000	2500
All EOS in packages FLINCOR, FLUIDS	1080–1160	1220–1530	1655–2245

It shows that the model data have significant discrepancy with the experimental results. This may be in part explained by a non-linear character of isochors in the CO₂-H₂O system (cf. Roedder, 1984). It should be noted as well that the diagram (Fig. 2) gives no way of plotting the fluid compositions corresponding to the fluid inclusions A and C (Fig. 1) that are illustrative of possible presence of coexisting two distinct fluids with different composition and density in equal *PT* conditions.

It is worth to consider in more detail main reason for this discrepancy.

Weakness of the EOS method

While using the EOS method, it is often assumed that the “isochors” for mixed H₂O-CO₂ fluid systems can be calibrated in the *PT* field between the isochors of pure water and pure carbon dioxide of various densities; thus, the most precise interpolation of these “intermediate isochors” in the corresponding *PT* field is considered to be the fundamental approach in obtaining the respective pressure estimates (Fig. 2).

However, using this approach, no attention is paid on the fact that various phases found inside fluid inclusions can not be regarded as isochoric systems. The conclusion that the isochors for the H₂O-CO₂ fluid inclusions can be found in the *PT* field between the isochors of the pure components is based just on general assumption that appears to be fundamentally wrong. Such approach can be expressed like calculation of some intermediate pressure between those found for autoclaves filled in by pure water and dense carbon dioxide. In our opinion, this approach is not applicable to fluid inclusion systems.

Under rising temperature, compositions and volumes of the CO₂ and H₂O phases found inside fluid inclusions are constantly changing, and the corresponding isochors change their positions respectively. In the homogenization point, the both components are evenly distributed within the entire fluid inclusion volume. In accordance with the fundamental Dalton Law, total pressure of the mixed H₂O-CO₂ fluid is equal to a sum of partial (H₂O and CO₂) fluid pressures calculated under assumption if each component occupied the entire inclusion volume under the same temperature.

For example, the maximal internal pressure calculated for homogenization of H₂O-CO₂ fluid inclusion containing (at room temperature) 50 vol.% CO₂ with the density of 0.7 g/cc should be considered as a sum of internal pressures of two fluid inclusions of the same volume, one containing vapour with the density of 0.5 g/cc, and another one containing CO₂ with the density 0.35 g/cc. At

400°C, this sum would not exceed 400 bars ($P_{\text{H}_2\text{O}}$) plus 470 bars (P_{CO_2}), i.e., 870 bars. It can be seen that this value is significantly less than the value of 2500 bars obtained from Fig. 2 and the FLINCOR/FLUIDS-programmed calculations.

The above estimate is valid for ideal gases (note, that the corresponding equations of state are based of the respective ideal gas properties). However, while studying fluid inclusions, one should consider quite dense gases and liquids, and the combined fluid pressure will be always much lower than the sum of the component partial pressures. That is the reason why determining physical-chemical conditions of hydrothermal mineralization using CO₂+H₂O±NaCl fluid inclusions should include “solubility” and “miscibility” as the basic terms, and experimental data on the respective mixed fluid systems should be considered as the only reliable source of information.

Conclusions

The CO₂-bearing aqueous fluids are among the most common fluid systems found in fluid inclusions and they are often used for pressure estimates. However, broad pressure variations of mineralizing fluids reported in some publications reflect the low accuracy of pressure estimate methods used rather than actual conditions of mineralizing processes occurred in natural systems.

To obtain the most reliable estimate of the pressure from CO₂+H₂O±NaCl fluid inclusion properties (phase volume fractions and phase transition temperatures), it is necessary to take into account the solubility of carbon dioxide in NaCl-H₂O solutions at high temperatures and pressures.

The thermodynamic (based on equations of state) modeling method (e.g. Brown and Lamb, 1989; Brown, 1989; Bakker, 2003) is totally not applicable for the purpose of pressure estimating.

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PHYSICO-CHEMICAL PROPERTIES OF THE ORE-FORMING FLUIDS ON THE BAKYRCHIK GOLD DEPOSIT (EASTERN KAZAKHSTAN)

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Introduction

Bakyrchik (Eastern Kazakhstan) is typical gold-sulfide deposit in "black shale" (Novozhilov, Gavrilov, 1999). The ore bodies at Bakyrchik are localized in a regional zone of strong cataclasis and shearing occurred within carbonaceous-terrigenous C₁₋₂ sequence. Disseminated Au-bearing pyrite and arsenopyrite occur along quartz veins in cataclased host rocks and in clasts of these rocks found in quartz and adjacent cataclasites.

Although the deposit has been long studied, virtually no information has been reported regarding the fluid inclusion characteristics.

Material and methods

The fluid inclusion data were obtained from studying of four samples stored in TsNIGRI museum (collected in 1978-1982):

BK-1 – brecciated quartz vein mineralized with abundant Au-bearing fine-grained needle-like arsenopyrite (from open pit);

BC-2 – massive quartz vein with rare microcrystals of arsenopyrite (drill hole, from a depth of 250 m);

BC-3 – similar vein (from a depth of 500 m);

BL-4 – quartz vein with native gold from a granitoid stock (C₃-P₁) located 5 km from the Bakyrchik deposit. This sample may be considered as representative of intrusive-related Au mineralization occurred in the Bakyrchik district.

The fluid inclusions were studied in order to estimate temperature, pressure, salinity and composition of the ore-forming fluids produced the Au mineralization. The microthermometric measurements were carried out on doubly-polished wafers using heating-cooling stage.

The bulk fluid composition analyses were conducted for 1 gram of monomineralic quartz samples crushed to 0.25-0.5 mm; this was followed by sample cleaning in HNO₃ aqueous (1:1) solution and then by water-flow electrolytic cleaning in ultrasound bath for 3 hours. Following this procedure, the samples were dried and put into a glass reactor vacuumed at 110°C and filled in by helium.

The opening of fluid inclusions was conducted by heating to 400°C or by crushing with the use of vibration and corundum balls. The gases extracted were introduced into a gas chromatograph equipped

by gas flow divider to allow simultaneous determination of H₂O, CO₂, CH₄. Then, the crushed or heated sample was leached with deionized water in ultrasound bath. The aqueous extract was separated by centrifuging and then analyzed by ion chromatography for Cl, F, SO₄, NO₃ and by ICP-MS for other elements. The second (blank) extract analysis data was subtracted from the results.

Results and discussion

Two fluid inclusion types were identified, namely: (1) primary inclusions occurred in isolated clusters in some quartz crystals, and (2) secondary inclusions occurred in trails along healed fractures.

The inclusions of the both types contain CO₂ and H₂O in variable proportions (Table 1). Also, the inclusions of pure CO₂ occur in association with H₂O-CO₂ secondary inclusions. CO₂ triple point of all inclusions ranges from –57.0°C to –56.6°C. Gas chromatography analysis indicate a presence of CH₄ (1–5 mol.%).

Table 1. Fluid inclusion PTX-properties (results of microthermometric measurements).

Sample	Type	NaCl wt.% equiv.	CO ₂ mol. %	T _i , °C	P kbar
BK-1	P	5.0–6.5	10	280–300	1.0
BC-2	S	4.5–5.5	5	230–250	1.1
	P	3.5–4.5	12	300–315	1.2
BL-4	S	8.0–8.3	6	225–235	1.3
	P	7.0–7.5	15	315–350	1.4

Types of fluid inclusions: P – primary, S – secondary. More than 20 individual fluid inclusions were analyzed in each group.

The salinity of the ore-forming fluids estimated from clathrate melting temperatures (Darling, 1991) ranges from 3.5 to 8.3 wt.% NaCl equiv. As follows from the bulk analysis, the total mineralization of the solutions found in the inclusions is not exceeding 20 gram/litre.

The maximum entrapment pressure for the primary inclusions was estimated based on the data for carbon dioxide solubility in 6 wt.% NaCl solution (Takenouchi, Kennedy, 1965).

The minimum entrapment pressure for the secondary inclusions was estimated using the density of the CO₂ inclusions and homogenization temperature of coexisting CO₂-H₂O inclusions (Kalyuzhnyi, 1982). The results obtained by two methods are in close agreement (Table 1).

Table 2. Fluid inclusions composition (results of bulk analysis).

Sample	BL-4	BC-3	BC-2	BK-1	
Opening method	Heating (to 400°C)				Crushing
H ₂ O ppm	1704	1248	1562	3347	2560
Contents of major components, g / kg H ₂ O					
Na	0.85	1.75	1.51	0.69	3.48
K	0.08	0.13	0.16	0.44	1.02
Ca	<0.01	<0.01	<0.01	1.10	0.05
Mg	<0.01	<0.01	<0.01	0.11	0.02
HCO ₃	2.4	4.7	3.5	6.0	10.4
Cl	<0.05	<0.05	0.32	0.24	0.37
SO ₄	<0.3	<0.3	<0.3	13.98	<0.3
F	<0.05	<0.05	<0.05	<0.05	<0.05
Total	2.4	4.7	3.8	20.2	15.3
CO ₂	99	101	73	114	145
CH ₄	1.1	0.6	0.7	0.4	2.5
Contents of trace elements, mg / kg H ₂ O					
B	128	194	185	123	144
Li	4	17	37	0.2	0.3
Rb	0.1	0.1	0.2	0.7	0.7
Sr	1.3	0.0	0.0	13.4	0.0
Ba	0	0	0	12.4	0.2
As	140	46	44	47	48
Sb	105	128	80	27	2
Ge	1.1	1.5	1.5	0.5	0.7
Fe	55	0	0	77	1
Cu	0	0	0	31	11
Zn	0	0	3	447	6
Pb	0	0	0	0.6	0.4
Bi	0.25	0	0	0	0
Mo	0.03	0.00	0.02	0.07	0.00
Sn	0.06	0.05	0.06	0.46	0.0
Hg	0.00	0.00	0.15	0.17	0.14
Ag	0.00	0.00	0.00	0.18	0.01
Au	0.00	0.04	0.07	0.00	0.21
Component mole ratios					
CO ₂ /CH ₄	32	60	40	99	21
CO ₂ /H ₂ O	0.04	0.04	0.03	0.05	0.06
Na/K	17	23	16	3	6
K/Rb (10 ³)	1.7	2.1	2.1	1.3	3.2
As/Ge	125	31	29	96	71
As/Sb	2.2	0.6	0.9	2.8	41

All fluid inclusion types are similar in composition and entrapment pressure. It can be assumed that primary and secondary fluid inclusions in all samples represent the different parts of a single ore-forming hydrothermal fluid system. The fluid inclusion properties suggest an isobaric regime of fluid cooling at each level of the system at a thermal gradient of around 50°C/km.

The phase (Na, K)HCO₃ is the most abundant component in the solutions entrapped in the fluid

inclusions (Table 2). B, Li, Rb, As and Ge are also present in the solutions.

The fluid inclusions in quartz with abundant Au-bearing arsenopyrite (sample BK-1) contain elevated amounts of S, Ca, Mg, Sr, Ba, Sb, Cu, Zn, Pb, Mo, Sn, Ag. The significant disparity between the results of bulk analysis obtained by different fluid inclusion opening methods suggests that the elements specified above are in a form of daughter solid phases and/or microprecipitates (sulfates and sulfides) deposited on the inclusion walls (Kryazhev et al., 2008).

As sulfur had a dominant role in the ore-forming fluid system, revealing the sulfur source is of the most interest. The sulfur isotope composition in Au-bearing arsenopyrite and pyrite falls within a narrow range ($\delta^{34}\text{S} = -1.5 \pm 2\%$, 200 analyses, TsNIGRI, 1978-1982). The sulfur in diagenetic pyrite from the hosting sedimentary rocks has a different isotope composition ($\delta^{34}\text{S}$ ranges from -5 to -21 ‰). These data allow us to draw a conclusion on a deep source of sulfur in the ore-forming hydrothermal system.

Conclusions

The main properties of the ore-forming fluids on the Bakyrchik gold deposit are as follows:

- relatively low salinity (< 5 wt.% NaCl equiv);
- (Na, K)HCO₃ is the most abundant salt;
- relatively low CH₄ content (CO₂/CH₄ > 20);
- temperature ranges from 315 to 230°C;
- isobaric regime of fluid cooling at a depth of 4–5 km (at a pressure of 1–1.2 kbar) result in CO₂ content decrease from 12 to 5 mol.%;
- constant level of As content in the solution (45–50 mg/kg H₂O);
- deep source of sulfur ($\delta^{34}\text{S} = -1.5 \pm 2\%$).

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FORMATION CONDITIONS OF W- AND SN-W-ORES ASSOCIATED WITH LI-F-GRANITES (DEGANA DEPOSIT, RAJASTAN, INDIA AND TIGRINOE DEPOSIT, FAR EAST, RUSSIA)

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Introduction

A major subject of our investigation is the examination of the formation conditions of W- and Sn-W deposits associated with Li-F granites of different age from various regions. To solve this problem a study of the tungsten deposit Degana (Rajasthan, India) and the Sn-W deposit Tigrinoe (Far East, Russia) has been performed. A preliminary part of our work is an estimation of formation conditions of the ore mineralization.

Methods

The parameters of ore-forming fluids were estimated by a study of fluid inclusions (FI). A microthermometric study of individual FI was performed on a Linkam THMSG 600 thermostage with a microscope that was equipped with a 50x Olympus long-focus objective and a video camera. The composition and salinity of fluids were determined by standard methods (Roedder, 1984), the pressure and density of fluids were calculated with the FLINCOR program.

The petrographic study of FI was carried out before their heating and freezing measurements. The understanding of results obtained was making on a basis of an exacting analysis of the ore mineralogical composition with account of a structural tectonic situation during an ore deposition.

Degana Tungsten Deposit

In the Degana area a suite of mineralized granitic rocks are emplaced within phillites of the Delhi Supergroup. Greisen-bordered quartz veins in two-mica granite and phillite, and stockwork veinlets within intrusion breccia carry wolframite mineralization. The presence of zinnwaldite, topaz and fluorite in all the members of the granite suite, ore bodies and altered wall rocks is a unique feature of this deposit. The granitic rocks of Degana are peraluminous, enriched in Rb (650-1070 ppm) and depleted in Sr (8-22 ppm), as a result of which Rb/Sr ratio is abnormally high. Abnormally high concentration of Li and F (510 and 9500 ppm, IGEM, 1972) in the granites, greisen and tungsten ore bodies is indicated by the presence of Li-mica, topaz and fluorite. K-Ar radiometric dating of zinnwaldite and muscovite from wolframite lodes (IGEM, 1972) has indicated ages of 860-870±25

Ma. Wolframite lodes commonly show crustification with zinnwaldite/muscovite lining the vein walls and quartz occupying bulk of the veins along with disseminated topaz, fluorite and wolframite of ferberitic composition.

Samples from granite-hosted quartz-wolframite veins and breccia-hosted ones were studied. Quartz is cut by fractures, recrystallized and contains a lot of FI of various generations. We examined primary FI in unbroken quartz crystals in close contact with wolframite.

Two types of primary FI are found in quartz crystals of this type from both ore bodies: 1 - two-phase (V+L) FI and 2 - vapor-rich ones somewhere covered by liquid along vacuole sides. These FI are located into the same growth zones and were trapped synchronously. This is evidence for fluid phase separation during a mineral deposition.

Two-phase (V+L) FI in quartz from breccias have $T_h=454-310^\circ\text{C}$ (Table 1). They contain Na-Cl solutions with a salinity from 9.6 up to 26 wt.% NaCl equiv. ($T_{\text{ice melting}} = -6.3 - 18.8^\circ\text{C}$, in some FI the salt-hydrate is the last melting crystal). Phase changes in many vapor-rich FI were not observed during the heating and freezing measurements. In some FI we observed only freezing and melting of CO_2 ($T_{\text{melting}} = -59.5 \dots -57.8^\circ\text{C}$). All vapor-rich FI are filled with low density $\text{CO}_2\text{-H}_2\text{O}$ fluids. The pressure is likely to be similar to the pressure of a saturated vapor of the system NaCl- H_2O and calculated for the temperature of 450-300°C is equal to 468-94 bars.

Two-phase FI in quartz from granites (Table 1) homogenized at $T=420-260^\circ\text{C}$. The solutions in these FI also have Na-Cl composition and salinity of 23 to 9 wt.%. The main component in single-phase vapor-rich FI is liquid CO_2 with a small admixture of another gases, probably CH_4 ($T_m \text{ CO}_2 = -60 \dots -58^\circ\text{C}$). The CO_2 homogenization occurs into a liquid at 5 to 19°C. The pressure calculated temperature of 250-400°C is equal to 1400-800 bars. It should be note that we could determine T_h only for the smallest FI at the heating velocity of 1-3°/min because two-phase FI are often decrepitated under the heating. It is also evidence for high pressure during the mineral formation.

The wolframite deposition temperature at the Degana deposit adjusted for pressure correction reaches up to 500°C.

Table 1. Physicochemical parameters for quartz-hosted inclusions at the Tigrinoe and Degana deposits (microthermometric and calculated data).

Parameters	Degana		Tigrinoe
	granites	breccias	breccias
Th, °C	420-260	454-310	416-318
Teut, °C	-32...-24	-33...-25	-30...-23
C, wt. %	23-9	26-10	5.8-0.8
D, g/cm ³	0.93-0.77	0.96-0.80	0.74-0.50
P, bar	1400-800	468-94	299-92

Note: D – density of water-salt fluids.

Tigrinoe Tin-Tungsten deposit

Sn-W mineralization of the Tigrinoe deposit is associated with the granite stock that is a final phase of the Tigrinyi intrusive buried at the depth. The granitoids belong to the family of alkaline high-aluminous Li-F leucogranites and can be considered as a young analogue (85-90 Ma) of the Degana granites. The main-ore-bearing zone of the deposit corresponds to a linear stockwork formed by a thick net of veinlets in greisenized sedimentary and intrusive rocks. Greisens consist of quartz-topaz-micaceous aggregates. At the deep horizons, zinnwaldite and fluorite are observed. Within the stock, a pipe-like body of a hydrothermal explosive breccia is found. It is considered as a channel for an ascending of ore-forming fluids from the depth (Gonevchuk et al., 2005). Earlier aggregates are composed of greisens with cassiterite, wolframite, stannite, and arsenopyrite. Lately, quartz-feldspar veins with wolframite, cassiterite and zinnwaldite as rims along a selvage were formed. These veins concentrate the major ore mineralization.

Fluid inclusions are examined in coarse-crystalline quartz from wolframite-cassiterite veins. At a room temperature FI in quartz are similar to FI from veins of the Degana deposit. Two-phase and monophasic FI in quartz were trapped synchronously indicating the existence immiscible liquid aqueous and vapor-rich fluids. Two-phase FI in quartz homogenized at 410 to 318°C contain identical Na-Cl solutions but with lower salinity 5.8-8.0 wt% (Table 1). The some vacuoles of single-phase FI contain isotropic salt crystals. The phase changes in single-phase FI are not observed at a microthermic study, FI are trapped a low density fluid. The pressure calculated as the pressure of a saturated vapor of the system NaCl-H₂O for a range of 410-300°C and corresponding fluid concentrations is lower than 300 bars.

The pressure correction in this case does not exceed 30°. Wolframite and cassiterite deposition occurred at the temperature up to 450°C.

Conclusions

1. Temperatures of ore forming fluids at the Degana deposit reached 500°C, whereas at the Tigrinoe deposit did not exceed 450°C.
2. The ore formation at the Degana and Tigrinoe deposits occurred due to fluid phase separation into liquid aqueous fluid with moderate and high salinity and vapor-rich fluid.
3. The aqueous fluids display similar Na-Cl composition at both deposits. Their salinity deposit corresponds to dilute brines at the Degana deposit whereas at the Tigrinoe deposit it was rather low saline.
4. The vapor-rich fluid at the Degana deposit had H₂O-CO₂ composition with a little admixture, probably, CH₄. The gas composition at the Tigrinoe deposit did not analyze.
5. The pressure in ore forming systems at the Degana deposit was higher. The pressure in breccias zones was significant lower than in granites.

The data obtained allow assuming that a chemical composition of ore-forming fluids at the deposits associated with Li-F-granites of different age was similar. The difference between temperatures, salinity and pressure in fluid systems at the Degana and Tigrinoe deposits can depend on geological and structural environment of the ore body formation.

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EXSOLUTION FLUID INCLUSIONS IN MINERALS AND THEIR TRAPPING

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Introduction

Exsolution solid inclusions are common inclusions in magmatic minerals. They are formed during diagenetic transformation of minerals as a result of disintegration of solid solution. The last one is often identified as a synonym to mixed crystal (Cary et al., 1972). The homogeneous crystal, formed in high temperature conditions, traps large quantity of isomorphous admixtures which segregate and isolate in a separate crystalline phase with no change of total composition of the system and primary crystal integrity when the temperature is decreasing. The isolated phase exists in a crystal-host as the inclusion of mineral with three-dimensional similarity of structure. Mixed crystals are characterized by comparatively equal and visually regular distribution of isostructural mineral inclusions.

Solid solutions of non-isomorphous matters

At the time G.G. Lemmlein (1948) noticed the existence of two types of solid solutions and accordingly two types of mixed crystals: normal (mixture of two matters with three-dimensional similarity of structure) and anomalous (with two-dimensional similarity of structure). The possibility of formation of solid solutions with non-isomorphous matters is confirmed by the theory of structure of crystals (Vainshtein, 1979) and by the example of their synthesis (Chernov, 1980). Mineral particles and cavities may appear in crystal's body after its formation as a result of disintegration of oversaturated solid solution of admixture atoms, own internode's atoms or vacancies, trapped by a growing crystal. Non-equilibrium concentration of admixtures, oversaturation of solid solution with admixtures, increasing while the temperature is decreasing, and aspiration of crystal to the minimum of internal energy are the motive force.

The findings of unusual inclusions in magmatic minerals (Fig. 1) verify disintegration of non-isomorphous solid solutions. Location of inclusions in fayalite is typical of solid solution disintegration structures, however neither magnetite nor mica are isostructural with a mineral-host. Mica always margins the magnetite crystals. Constant correlation of these minerals in almost all inclusions is more typical of high-ferrous melt crystallization products.

It is segregation of non-isomorphous

admixtures that explains formation of refractory mineral inclusions, taking not their own, but the shape of comparatively low temperature mineral-host. Fluorite from the Azov and Yastrubetsky syenite stocks of the Ukrainian Shield abounds with such exsolution inclusions. Isometric cubes of zircon and apatite, flattened cubes of amphibole and mica, flattened octahedrons of mica and albite together with the larger inclusions of these minerals are typical of the particular zones in the fluorite crystal (Kulchytska, 2007). While the temperature is decreasing new admixtures are involved in the process of disintegration, and composition of the new formed inclusions changes naturally.

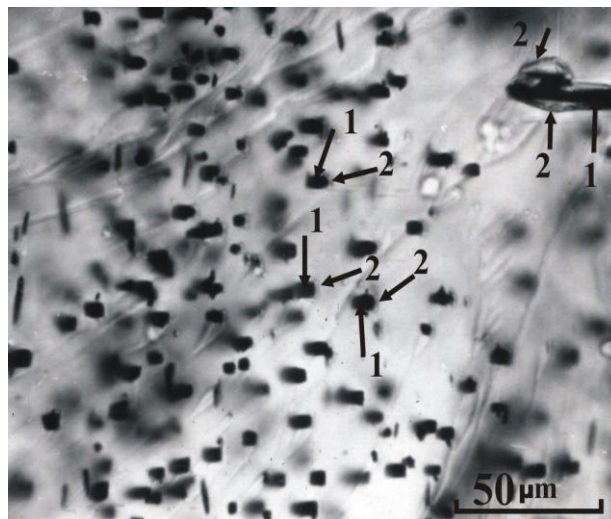


Figure 1. Exsolution of magnetite + annite inclusions in fayalite. Azov stock, Ukraine. Note: 1 – magnetite; 2 – annite.

Solid solutions with volatile components

If non-isomorphous admixtures in a crystal are volatile components, then disintegration of such solid solution will be accompanied by separation of fluid phase, forming liquid exsolution inclusions in favorable conditions. Admixtures on the surface of internal pores and other defects of crystal should be added to the volatile admixtures in the crystal lattice. As G.G. Lemmlein (1948) considered, phenomena of "internal adsorption" and interstices in the defect places of crystal should be compared with phenomena of formation of liquid inclusions in it.

Exsolution of volatile admixtures is more sensitive to internal pressure change in a crystal, therefore the liquid exsolution inclusions are more typical of vein minerals, appearing in the conditions of pressure gradient. Exsolution inclusions with

volatile components may be also solid (for example, carbonates) or gaseous.

E. Roedder (1984) used classification scheme for inclusions, based on their origin: primary, secondary and pseudosecondary inclusions. He defined liquid inclusions in metamorphic quartz, appearing as a result of internal isochemical processes, as a separate type of *exsolution inclusions*. Absence of components exchange with an intergranular fluid phase was considered by E. Roedder as the main peculiarity of such inclusions' formation.

Exsolution or diagenetic inclusions

The term "*exsolution inclusions*" is firmly attached to the products of disintegration of isomorphous solid solutions in the Russian-language scientific literature. As disintegration of isomorphous and non-isomorphous solid solutions, compression of mineral, removal of defects and healing of internal cracks, take place during the diagenetic stage, we propose to classify inclusions formed in this stage as *diagenetic*, as well as proto-, syn- and epigenetic. Therefore, classification of inclusions in minerals will be the following (Fig. 2).

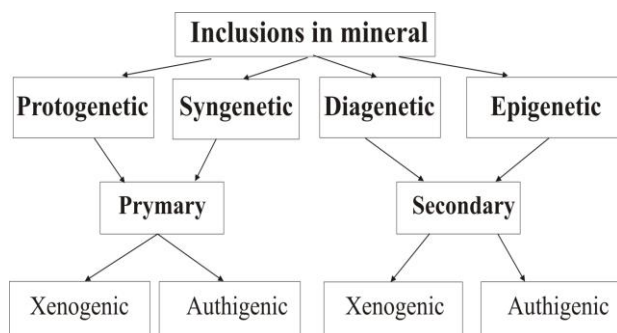


Figure 2. Genetic classification scheme for inclusions in minerals.

In relation to a crystal-host the diagenetic inclusions will be secondary because they are formed in the crystal body after its crystallization. At the same time they should not be considered as epigenetic, because formation of inclusions is related not to destruction, but the crystal improvement. The diagenetic inclusions may be localized in particular crystal zones as primary or in the healed internal cracks as secondary inclusions. Inclusions in particular zones are usually fine; there are a lot of them and they often form (underline) the zonality of crystal. Cracks, healed with the diagenetic inclusions, usually do not have clear borders. The rectilinear stripe with inclusions, crossing several crystals simultaneously, underlines secondary nature of inclusions. Such inclusions are especially typical of veined quartz.

The diagenetic inclusions are comparable by

comprehension with primary-secondary inclusions in the N.P. Ermakov (1950) classification scheme for inclusions, secondary inclusions of syngenetic cracks in the G.G. Lemmlein (1959) scheme, secondary early inclusions in the V.A. Kalyuzhnyi (1982) classification scheme.

Conclusions

Exsolution inclusions are formed in crystals not only as the result of disintegration of isomorphous solid solutions. Segregation (exsolution) of structural and non-structural admixtures with formation of secondary diagenetic inclusions – solid, liquid and gaseous, takes place in the diagenetic stage of compression of mineral. The diagenetic inclusions are not less informative than primary syngenetic inclusions. It is important to define correctly what stage of crystal transformation they characterize.

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PRIMITIVE MELT OF ICELAND MANTLE PLUME: MELT INCLUSIONS DATA FOR THE KISTUFELL VOLCANO

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Introduction

Kistufell (64°48'N, 17°13'W) is a table mountain located in the neovolcanic northern rift zone (NRZ) at the NW margin of the Vatnajökull ice cap (Fig. 1). The central axis of the Icelandic plume is thought to be located below this region (Breddam, 2002). The precise age of Kistufell is not known. However, the high eruptions frequency of picrites and olivine tholeiites was in early postglacial times (Jakobsson et al., 1978).

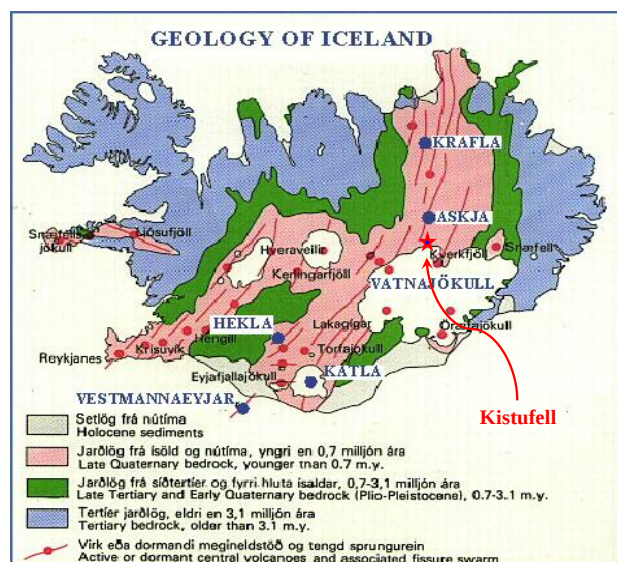


Figure 1. Kistufell volcano on the geological map of Iceland.

In this paper we report new data on the composition of parental melts for the Kistufell volcano based on the detail study of naturally quenched glass inclusions in olivine phenocrysts and matrix glasses.

Methods

Major and trace elements were determined by EPMA on a Jeol JXA 8200 SuperProbe Electron Probe Microanalyzer and with Laser-Ablation mass spectrometry with Inductively Coupled Plasma (LA-ICP-MS) at the Max Planck Institute for Chemistry (Mainz, Germany). Fractional crystallization of melts was simulated using the olivine-liquid equilibrium models of Ford et al. (1983) and Herzberg and O'Hara (2002) by the PETROLOG software (Danyushevsky, 2001). Correction for Fe-Mg exchange between melt

inclusions and the host olivine was applied using the same models for olivine-melt partition and software of Danyushevsky et al. (2000).

To estimate the initial FeO content in melt inclusions we used strong linear correlation between the contents of FeO and $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratios in the pillow lavas and gyaloclastites of Kistufell obtained in this study (Fig. 2).

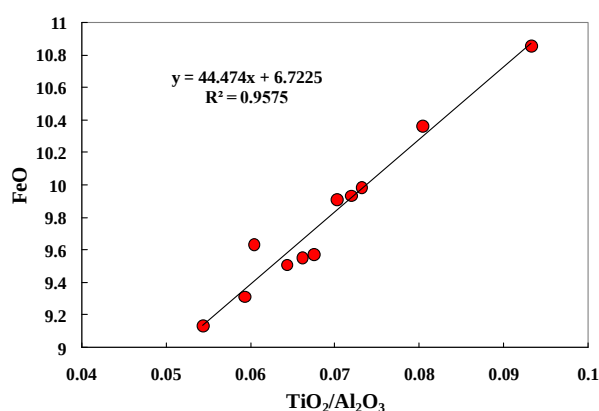


Figure 2. FeO vs $\text{TiO}_2/\text{Al}_2\text{O}_3$ in lavas and gyaloclastites of Kistufell.

The $\text{Fe}^{2+}/\text{Fe}^{+3}$ ratio of melt was determined from the composition of chrome spinel and the model of the spinel-melt $\text{Fe}^{2+}/\text{Fe}^{+3}$ partitioning (Maurel, Maurel, 1982). It corresponds to oxygen fugacity ($f\text{O}_2$) near the NNO buffer and slightly differs between samples (Fig.3).

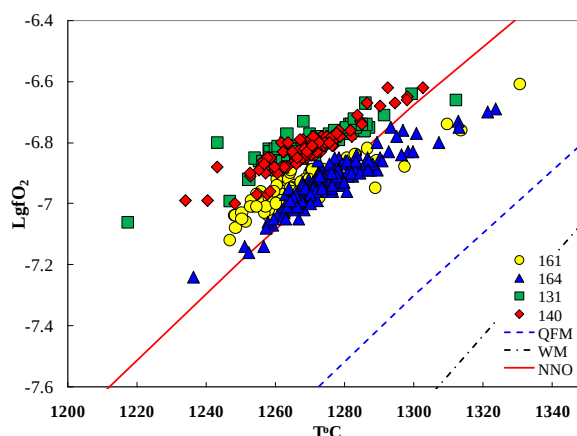


Figure 3. Oxygen fugacity during crystallization of the Kistufell melts. Different symbols indicate different samples.

Composition of trapped melt

The studied melt inclusions were trapped by

olivine phenocrysts ($Fo=88-89.6$) in the temperature range of 1240-1330°C (Fig. 4). These temperatures were calculated for 1 bar pressure and thus should be considered as minimum estimate.

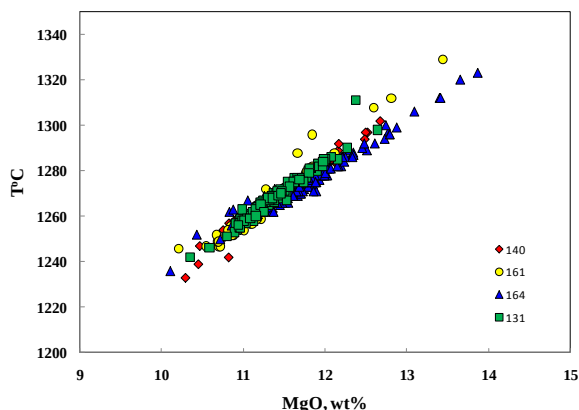


Figure 4. Calculated temperature of trapped melts.

Melt composition corresponds to depleted olivine tholeiite or picrite with very low contents of K and Cl. Most inclusions are sulphur-undersaturated (Fig.5).

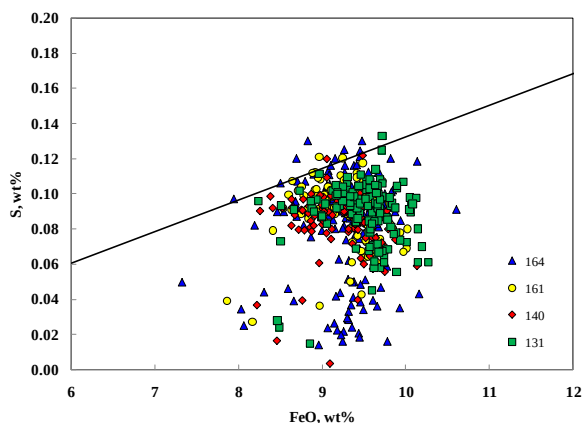


Figure 5. S vs. FeO in melt inclusions. Line shows saturation of basaltic melt with sulfide melt (Mathez, 1976).

Trace element compositions of trapped melts are similar to matrix glass (Fig. 6) and to central Iceland in general (Breddam, 2002). Typical are strong depletion in Th, U, Pb and relative enrichment in Sr. Positive Sr anomalies could result from interaction of the ascending magmas with gabbroic cumulates at the crustal depths (Gurenko, Sobolev, 2006).

The Fe/Mn and Ni/Mg ratios of olivine phenocrysts suggest mostly peridotitic source of the Kistufell parental melt, however, with distinct admixture (around 30%) of pyroxenite derived melt (Sobolev et al., 2007, 2008).

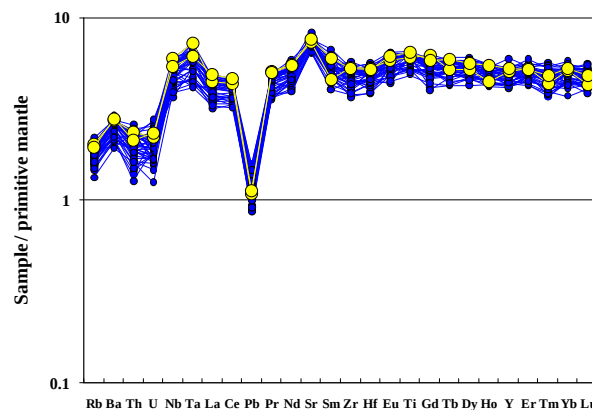


Figure 6. Concentrations of incompatible elements. Blue - melt inclusions, yellow - pillow glasses.

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METAMORPHIC AND FLUID EVOLUTION IN CENTRAL CRYSTALLINES OF KUMAUN HIMALAYA, INDIA

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Introduction

The Himalayan orogen is a product of the Cenozoic collision between the Indian and Eurasian plates. P-T-X characterization of crystalline rocks throws light on petrotectonic evolution and exhumation history of these rocks. The studied transect around Dhakuri (longitude 79°51' to 79°58' E and latitude 30° 4' to 30° 8' N) is a part of the Munsiri formation, Main Central Thrust Zone, Central Crystallines, Kumaun Himalaya, India. The Munsiri Formation is bounded by the Munsiri Thrust at the base and the Vaikrita Thrust at the top (Valdia et al., 1999).

Metamorphic rocks

The rocks of the area have been subjected to at least three phases of deformation and metamorphism. The studied transect documents the Barrovian sequence of metamorphism which has been inverted. The metamorphic zones include chlorite-biotite zone, garnet zone and staurolite zone. At places mylonitic effect has been noticed. The metamorphites of the area include chlorite-mica schists, garnet-mica schists, staurolite-garnet-mica schists of different metamorphic zones, amphibolites which are both garnet-bearing and garnet-free, augen gneisses and gneisses. The pelitic schists occur interbedded with the quartzites. In the present study we present data on petrography, geothermobarometry, fluid inclusion petrography and microthermometry. Textural features in different rocks are suggestive of the following reactions:

Fe-rich Al-poorer Chlorite + Muscovite => Biotite + Fe-poor Al-richer Chlorite + Quartz + V;
 Fe (rich) Chlorite + Quartz => Fe-Garnet + V;
 Garnet + Biotite + H₂O => Chlorite + Muscovite + Quartz;
 Garnet + Chlorite + Muscovite => Biotite + Staurolite + Quartz + V;
 Chlorite + Muscovite => Staurolite + Biotite + Quartz + V.

Fluid inclusions in garnet-hosted quartz

Fluid inclusions of various types are observed in quartz grains hosted by garnet.

Type (1): Monophase liquid inclusions

They contain mainly carbonic liquid and are <10 μm in size and rounded or elliptical in the shape. These inclusions are usually isolated; some

of them occur in trails (Fig. 1). In one trail, containing monophase liquid inclusions, a C-shaped inclusion is observed. Such unusual shape could be an example of exhumation of the host mineral. Two inclusions with heart shape are also found. Such typical shapes may form due to the pressure from the surrounding environment.

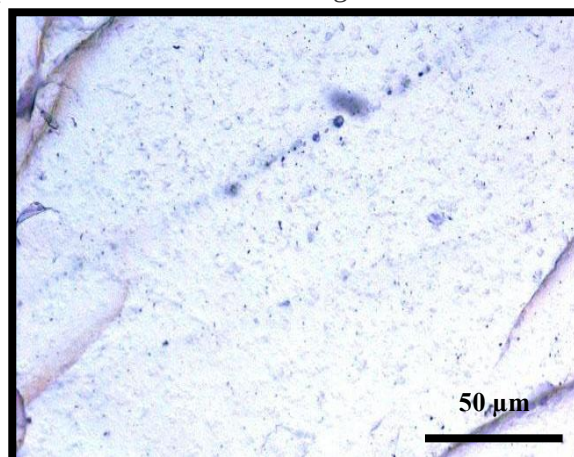


Figure 1. Trails of biphase and monophase inclusions in quartz.



Figure 2. Biphase inclusions in quartz.

Type (2): Monophase vapour inclusions

Such inclusions contain low density CO₂ vapour and could be primary in nature. Their size is <5-10 μm.

Type (3): Liquid-rich biphase inclusions

These are of various shapes: rounded, elliptical, cubic or irregular (Fig. 2). Some stretched inclusions (Fig. 3) also observed which is due to the surrounding pressure. Moving bubble is identified in some inclusions. It occupies 30- 40 vol.% of inclusion.

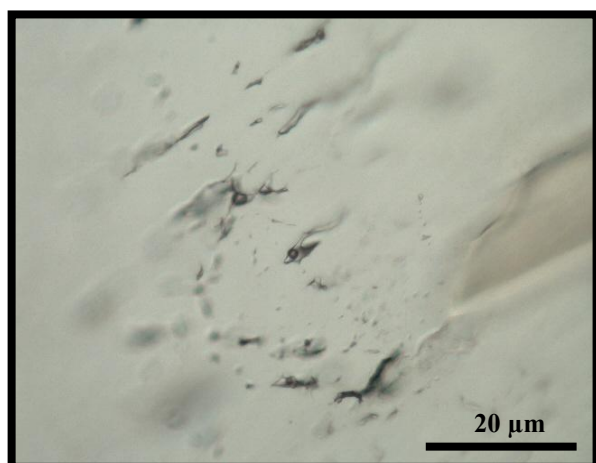


Figure 3. Stretched inclusions in quartz.

Type (4): Vapour-rich biphase inclusions

They are very scarce. Vapour content is up to 80 vol.% in such inclusions.

Type (5): Biphase immiscible inclusions

The inclusions contain both liquid and vapour phase. Immiscible inclusions with heterogeneous bubble ($\text{LCO}_2 + \text{VCO}_2$) are most abundant. The bubble may occupies 70-80 vol.% of inclusion.

Type (6): Inclusions with solid phases

These inclusions consist of liquid, vapour phase ($\text{CO}_2?$), and crystal phase of NaCl (halite) (Fig. 4).

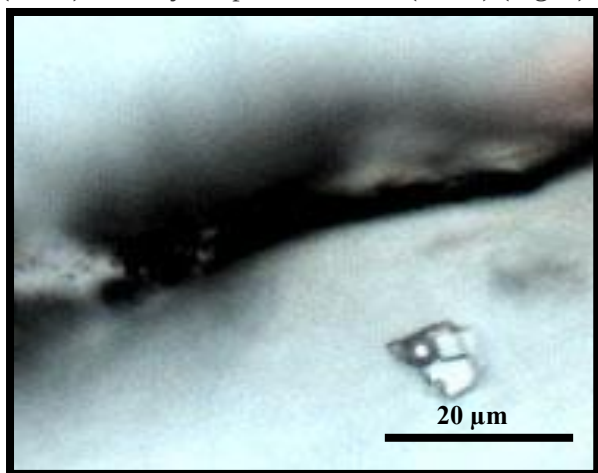


Figure 4. Multiphase inclusion in quartz.

Fluid inclusions in rock-forming quartz

The inclusions are mainly isolated, rarely clustered in group (4-5 inclusions); some trail sequence is also observed. Some inclusions are very minute in size to be identified properly phase composition. They are of various size, mostly <5-10 μm . They are rounded, semi-rounded and tabular in shape. Some inclusions are stretched, showing pressure direction. Mostly biphase inclusions are observed. Carbonic and immiscible carbonic inclusions are also identified. Moving bubble is visible in most inclusions. Some inclusions show partial leakage, it may be due to the environmental pressure. Halite and other solid phases are observed in some inclusions.

Inclusions in rock-forming garnet

The primary inclusions in garnet are biphase and monophase in composition. Biphase inclusions are aqueous-carbonic, <5-15 μm in size and occur as isolated inclusions or in trails. Monophase inclusions contain carbonic fluid; they are also isolated and small in size (<10 μm). Secondary inclusions form small trails which cuts the host garnet. They are irregular in shape.

Discussion

Fluid inclusions trapped by early quartz represent the earlier fluid ($\rho\text{CO}_2 = 0.98 \text{ g/cm}^3$) preserved in the metapelites; pressures obtained from isochors are 3.8 kbar at 500°C and 3.2 kbar at 400°C. Primary fluid inclusions in garnet are monophase carbonic and biphase aqueous-carbonic. They indicate growth of garnet during metamorphism. Their CO_2 density is slightly lower (0.95 g/cm^3) and calculated pressures are 3.6 kbar at 500°C and 2.9 kbar at 400°C. Fluid in early quartz may represent pre-garnet prograde formation. The P-T conditions of metamorphism for pelitic rocks of the area may have been estimated according to the pertinent models of geothermobarometry such as garnet-biotite thermometer, titanium content in biotite, Al^{IV} content in chlorite, garnet-muscovite-biotite-plagioclase barometer, THERMOCALC (Holland, Powell, 1998) using electron microprobe data of coexisting mineral phases in different metamorphic zones. A drop in pressure from 7.8 to 5.0 kbar has been noticed suggesting decompression.

The isochor for the dense CO_2 in garnet when compared to mineral phase P-T conditions (cf. $480 \pm 25^\circ\text{C}/5.6 \text{ kbar}$) imply a post-peak re-equilibration of the fluid, consequently the retrogression of these pelites. Fluid-rich inclusions population is found in the late quartz grains. Carbonic inclusions, monophase at room temperature, biphase carbonic, biphase aqueous-carbonic and triphase aqueous inclusions are observed. Biphase aqueous-carbonic inclusions show total homogenization at 219-270°C and triphase inclusions - at 335-385°C. The carbonic inclusions present in the garnet-mica schists of the investigated area suggest that the fluid infiltration through deep-seated fractures occurred during metamorphism related to thrusting and uplift.

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FLUID MIXING AND BOILING DURING LATEST STAGE OROGENIC GOLD MINERALIZATION AT BRUSSON, NW ITALIAN ALPS

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Introduction

A current problem in the genesis of orogenic gold deposits is the influence on gold solubility of reactions between the ore-bearing fluid and the wall rocks of the deposits. In this context, we are investigating fluid inclusions in hydrothermal quartz-carbonate-sulphide veins from the abandoned Fenilia Mine at Brusson, northwestern Italian Alps.

Results

Studied quartz samples contain early primary and pseudosecondary inclusions that can be approximated by the $\text{CO}_2\text{--H}_2\text{O--NaCl}$ system. Two types are observed (Fig. 1): first, abundant low- XCO_2 $\text{L}_{\text{aq}}\text{L}_{\text{car}}\text{V}$ inclusions that homogenize to liquid at $\sim 230^\circ\text{C}$ and have an aqueous salinity of 3.7 mass% $\text{NaCl}_{\text{equiv.}}$; second, high- XCO_2 $\text{L}_{\text{aq}}\text{L}_{\text{car}}$ inclusions with similar homogenization behaviour and an aqueous salinity of 2.2 mass% $\text{NaCl}_{\text{equiv.}}$. These inclusions are present only in late pseudosecondary assemblages. The two contrasting inclusion types were described by Diamond (1990) and interpreted to have formed during boiling (phase separation into “vapour” and “liquid”) of the low- XCO_2 -type ore-bearing solution.

New charge-contrast imaging has revealed fine overgrowths of quartz on the main-stage crystals (quartz zone 3 in Fig. 2c). These host late-primary inclusion assemblages, which consist of rare low- XCO_2 $\text{L}_{\text{aq}}\text{L}_{\text{car}}\text{V}$ inclusions (identical to those described above) coexisting with abundant $\text{L}_{\text{aq}}\text{V}$ inclusions. The latter were previously unknown at this deposit. Their carbonic phases have variable volume fractions [$\varphi_{(\text{car})}$] ranging from 0.075 to 0.47 ($\pm 4\%$) (Fig. 1a). These inclusions homogenize at $\geq 180^\circ\text{C}$ via the transition $\text{L}_{\text{aq}}\text{V} \rightarrow \text{L}_{\text{aq}}$.

Raman analysis revealed CO_2 , CH_4 and N_2 within the carbonic phases of all $\text{L}_{\text{aq}}\text{V}$ inclusions, but the molar ratios of the gases vary systematically. In Fig. 1b these analyses reveal a linear array stretching from compositions close to those of low- XCO_2 $\text{L}_{\text{aq}}\text{L}_{\text{car}}\text{V}$ and high- XCO_2 $\text{L}_{\text{aq}}\text{L}_{\text{car}}$ inclusions (end-member no. 1 in Fig. 1) to compositions of about 4.4 mol.% CO_2 , 91.4 mol.% N_2 and 4.2 mol.% CH_4 (end-member no. 2 in Fig. 1). Quartz-vein samples hosted by calcite marbles contain $\text{L}_{\text{aq}}\text{V}$ inclusions with relatively more methane in their carbonic phases (end-member no. 2b in Fig. 1b).

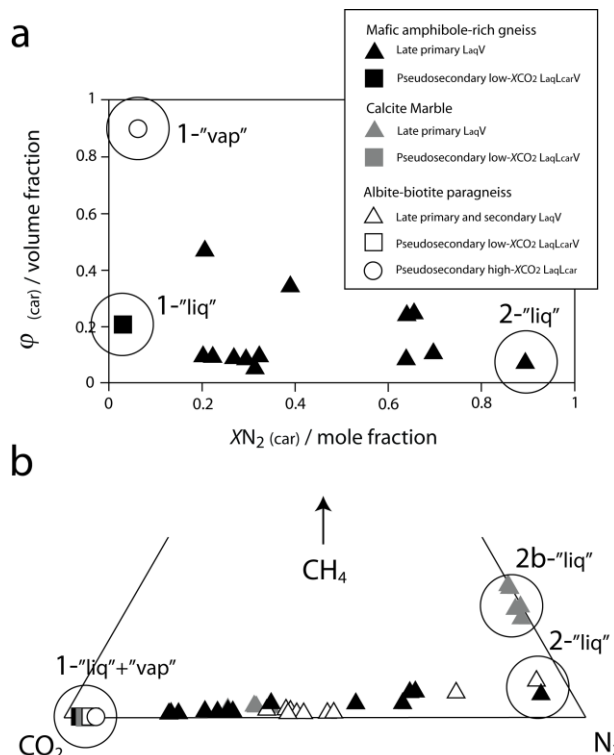


Figure 1. (a) Relationship between $\varphi_{(\text{car})}$ and $\text{XN}_2(\text{car})$ (b) molar composition of carbonic phase in sampled inclusions.

Quantitative LA-ICP-MS analyses show that inclusions at and near the end-member no. 1 in Fig. 1 have higher As and lower Sr contents than those nearer end-member 2. The Sr content in $\text{L}_{\text{aq}}\text{V}$ inclusions is higher where the vein is hosted by calcite marble rather than other wall rocks.

Discussion

The carbonic phases of the late primary $\text{L}_{\text{aq}}\text{V}$ inclusions have variable volume fractions [$\varphi_{(\text{car})}$] (Fig. 1a), which, along with element partitioning data, is diagnostic of boiling. The liquid end-members 1, 2 and 2b are mutually miscible at the entrapment temperature of the low- XCO_2 liquid, 230°C . Therefore, the linear compositional trend of the late primary $\text{L}_{\text{aq}}\text{V}$ inclusions in Fig. 1b can be interpreted as a mixing line. Combining both interpretations, it appears that boiling and mixing occurred simultaneously in the vein system during precipitation of quartz zone 3 (Fig. 2c).

End-member 2b (Fig. 1b), hosted by calcite marble wall rocks, has relatively more methane than end-member 2, hosted by gneisses. This suggests that the composition of $\text{L}_{\text{aq}}\text{V}$ inclusions

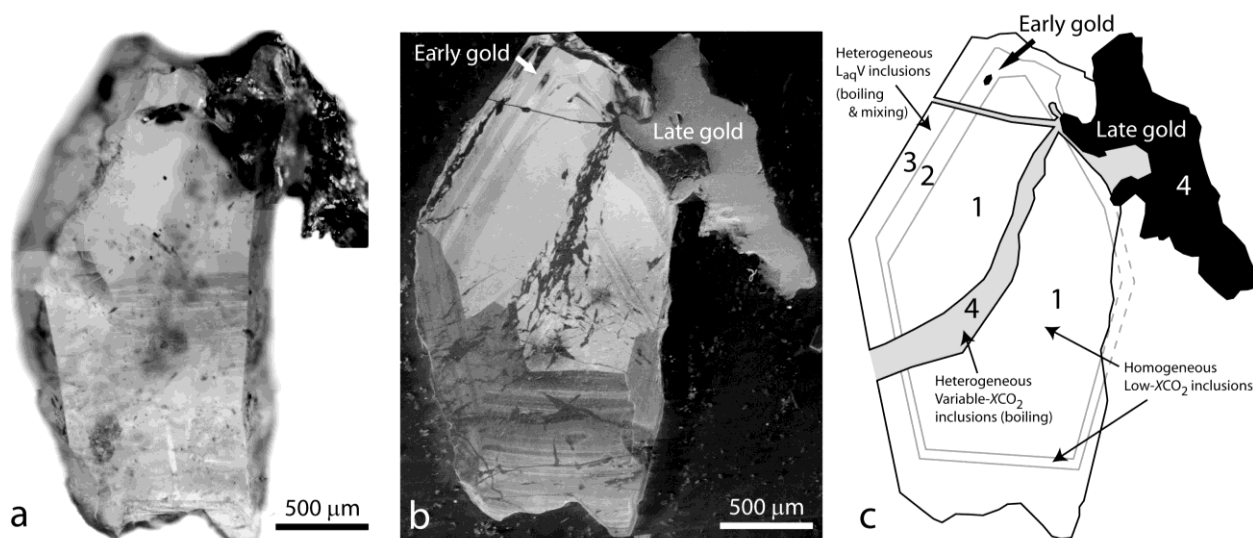


Figure 2. (a) Photograph of quartz crystal with free gold deposited on the surface. (b) SEM charge-contrast image of a polished section through this crystal. (c) Schematic interpretation of the charge-contrast image in b. See text for further details.

represents pore fluid from within the wall rocks around the vein. This hypothesis is further supported by our LA-ICP-MS data.

The quartz sample in Fig. 2 exhibits two generations of gold: small inclusions within a late growth zone (Early gold in zone 2, Fig. 2c); and free gold mostly overlying the outer crystal surface (Late gold, Fig. 2c). Charge-contrast imaging reveals that this late gold is younger than the fine crystal growth zone 3 (Fig. 2c) that hosts the late primary $L_{aq}V$ inclusion assemblages. The late gold is also in direct contact, and therefore coeval, with healed fractures (zone no. 4 in Fig. 2c) that host a secondary assemblage of variable- XCO_2 inclusions (including both low- XCO_2 $L_{aq}L_{car}V$ and high- XCO_2 $L_{aq}L_{car}$ types). No $L_{aq}V$ inclusions are present in zone 4.

These new temporal and compositional deductions are used to reconstruct the history of quartz growth in the Fenilia vein (Fig. 3). First, a low- XCO_2 -type carbonic liquid forms main-stage quartz (zone 1 in Fig. 2c) and alters the adjacent wall rock (Fig. 3-1). Subsequent simultaneous precipitation of gold and quartz (Fig. 3-2) is presumably triggered by cooling or by wall-rock reactions. Progressive cooling and reduction in fluid pressure owing to on-going uplift of the Western Alps induces boiling of the main-stage fluid (Diamond, 1990; Fig. 3-3). Pore fluid from the wall rocks simultaneously seeps into the open vein, where it mixes with boiling carbonic fluid. At this moment the late primary $L_{aq}V$ inclusions are trapped (zone 3 in Fig. 2c). Finally (Fig. 3-4), a new pulse of boiling, ore-bearing carbonic fluid enters the mine level, fracturing the existing quartz crystals and depositing the late gold on top of them

(zone 4 in Fig. 2c). Without any evidence for wall-rock pore waters at this stage, it seems most likely that partitioning of gold-complexing ligands (aqueous HS^- and H_2S) from the liquid into the carbonic vapour triggered deposition of the late gold.

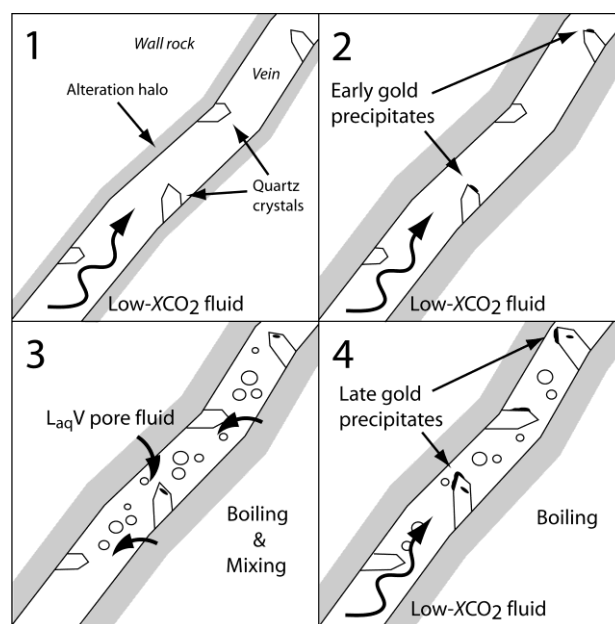


Figure 3. History of quartz veins at Fenilia. See text for further details.

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FLUID INCLUSIONS AND H-O ISOTOPE COMPOSITIONS OF QUARTZ VEINS IN HP-UHP METAMORPHIC ROCKS FROM CHINESE CONTINENTAL SCIENTIFIC DRILLING PROJECT (CCSD)

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Introduction

The Chinese Continental Scientific Drilling (CCSD) project is located in the Donghai County, Jiangsu Province. It is drilled to a depth of 5158 m through the southern limb of the eastern part of the well-known Dabie-Sulu ultrahigh-pressure (UHP) metamorphic belt (Xu et al., 2004). The drill cores obtained from the main hole of CCSD consist chiefly of eclogites, gneisses, ultramafic rocks, schists and quartzites (Zhang et al., 2005). Ubiquitous quartz veins have been recognized in the eclogites and gneisses.

Fluid inclusions in quartz

By microthermometric measurement and Raman analysis, four types of fluid inclusions are found in these quartz veins (Fig. 1-2). They are: (1) brine (NaCl-H₂O) inclusions (type I), which can be subdivided into high salinity (type Ia), medium-high salinity (type Ib), medium salinity (type Ic) and low salinity (type Id) brine inclusions, (2) N₂-CH₄ pure gaseous inclusions (type II), (3) Calcite daughter mineral-bearing inclusions (type III), (4) CO₂-NaCl-H₂O and pure CO₂ inclusions (type IV). The type III and IV ones are first discovered in the CCSD quartz veins (Xu et al., 2006a). Type Ia, Ib, II, III and IV inclusions mainly occur as primary ones in quartz veins in eclogites and gneisses, indicating that they were probably captured in decompression-recrystallization stage of the HP-UHP metamorphic rocks. Type Ic and Id inclusions occur mostly as secondary ones in matrix quartz in eclogites and gneisses, implying that they were captured in the later retrograde stage. The H₂O-carbonate inclusions and CO₂ inclusions occurring as primary ones, suggest that a part of the quartz veins and their host rocks might have undergone UHP metamorphism.

Isotopic analyses show that that D_{H₂O} and ¹⁸O_{H₂O} values of the fluid inclusions in quartz veins are -97 ~ -69 ‰ and -11.66 ~ 0.93 ‰, respectively, indicating that the protoliths of some CCSD HP-UHP metamorphic rocks reacted with meteoric water at high latitude near the surface before being subducted to great depths (Xu et al., 2006b, 2007). In addition, the $\delta^{18}\text{O}$ of the quartz veins and fluid inclusions vary greatly with depths along the drill

hole (Fig. 3). In the CCSD main drillhole profile lower $\delta^{18}\text{O}$ values occur at depths of ~900 m to 1000 m and ~2700 m, and higher values at depths of about 1770 m and 4000 m correlating roughly with those of wall rock minerals. Given that the peak metamorphic temperature of the Dabie-Sulu ultrahigh pressure metamorphic rocks is about 800°C or higher, much higher than the closure temperature of oxygen isotope in quartz under wet conditions, such synchronous variations can be explained by re-equilibration. By contrast, δD values of fluid inclusions show a different relationship with depth (Fig. 3). This is likely because oxygen is a major element of both fluids and silicates, and is much more abundant in the quartz veins and silicate minerals than is hydrogen. The oxygen isotope composition of fluid inclusions is thus more susceptible to late-stage re-equilibration with silicate minerals than the hydrogen isotope composition. Therefore, the different δD and $\delta^{18}\text{O}$ patterns imply that there was dramatic fluid migration, whereas the covariation of oxygen isotopes in fluid inclusions, quartz veins, and wall rock minerals can be better interpreted by re-equilibration, likely during exhumation.

Quartz veins in the Dabie-Sulu UHP metamorphic terrane are the product of channelized high-Si fluids (Sun et al., 2007, 2010). Given that channelized fluid migration is much faster than pervasive flow, and that quartz veins formed through precipitation of quartz from high-Si fluids, the abundant quartz veins indicate significant fluid mobilization and migration within this subducted continental slab. Many mineral reactions can produce high-Si fluids during subduction and exhumation. For UHP metamorphic rocks, major dehydration during subduction occurred when pressure-temperature conditions exceeded the stability of lawsonite. In contrast, for low temperature eclogites and other high pressure metamorphic rocks with peak metamorphic P-T conditions within the stability field of lawsonite, dehydration and associated high-Si fluid release may have occurred as hydrous minerals were destabilized at lower pressure during exhumation. Because subduction is a continuous process whereas only minor fraction of subducted slabs are

exhumated back to the surface, dehydration during subduction is more prevalent than exhumation even in subducted continental crust, which is considerably drier than oceanic crusts (Sun et al., 2010).

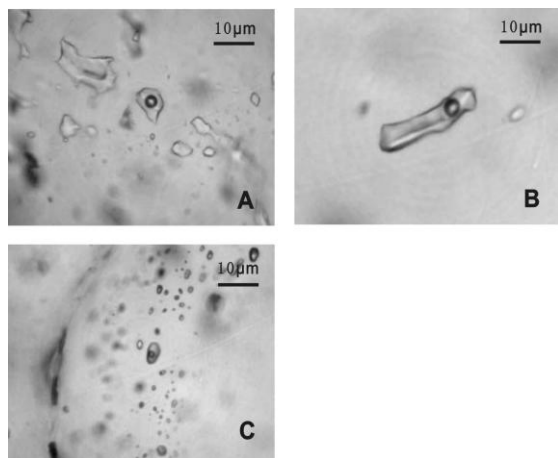


Figure 1. Microphotographs of fluid inclusions in quartz veins from HP-UHP metamorphic rocks from CCSD.

A. High salinity brine inclusions (1a), sample 05044, B. Medium-high salinity brine inclusions (1b), sample 05062, C. Medium and low salinity brine inclusions (1c and 1d), sample 05017.

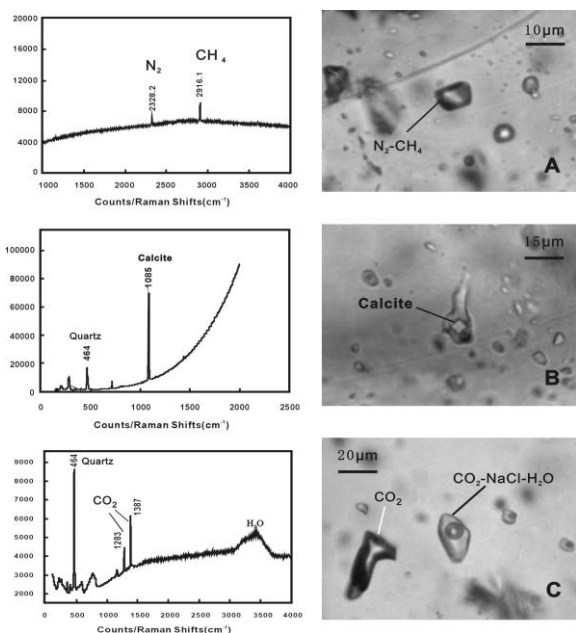


Figure 2. Laser Raman spectrum and microphotographs of fluid inclusions in quartz veins from HP-UHP metamorphic rocks from CCSD.

A. N_2 - CH_4 inclusions (type II), sample 03558. B. Calcite daughter mineral-bearing inclusions (type III), sample 06031. C. CO_2 - $NaCl$ - H_2O inclusions (type IV), sample 05066.

Acknowledgements

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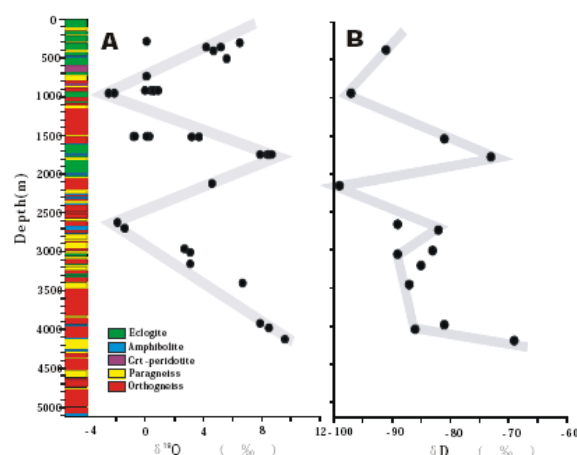


Figure 3. CCSD profile of $\delta^{18}O$ isotopic composition of quartz veins (A) and δD of fluid inclusions in quartz veins (B).

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GENESIS AND MINERALIZATION OF GOLD-BEARING QUARTZ VEINS IN XIAO QINLING GOLDFIELD, CENTRAL CHINA

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Introduction

The Xiao Qinling area is located within the Qinling orogenic belt, a major structural zone situated between North and South China Blocks. The Xiao Qinling goldfield, one of the three biggest gold production areas of China, is situated in border region of the Henan and Shannxi Provinces. Gold deposit in the Xiao Qinling area is one of the most important gold metallogenic types in China. The principle type of gold mineralization in the area is gold-bearing quartz veins structurally controlled by orogenic faults and shear belts. Gold-bearing quartz veins are hosted in the Taihua Group, set of Late Archean amphibolite-granulite facies metamorphic rocks with many Mesozoic giant granite intrusions. Chronology studies show that metallogenic epoch of gold deposits is Mesozoic (Wang Yitian et al., 2002). Genesis and origin of gold-bearing quartz veins remain controversial after more than 50 years studies including field mapping and exploration, ore mineralogy, fluid inclusion and geochemistry. Many hypotheses for genesis of gold-bearing quartz veins have been proposed such as generated by metamorphism, granitic magmatism or even devolatilization of mantle-derived fluids through fault system (Jingwen et al., 2003; Jiang et al., 1999; Shaoru et al., 1998). This work presents the basic geologic background and mineralization of gold-bearing quartz veins by means of records of fluid inclusions in the Xiao Qinling area.

Regional geology

The Xiao Qinling goldfield is located on the Qinling orogenic belt which represents an easterly trending structural boundary lies between the North China Block (NCB) and the South China Block (SCB). The Qinling orogenic belt originated from a shallow elongated basin separating the stable regimes to the north and south of China. Indosinian (Triassic) tectonic made final closure of the Qinling basin. Gold-bearing quartz veins are solely hosted in the basement assemblage of the Taihua Group, which is generally tilted or complexly folded, fault-bounded. Litho of the Taihua Group is Archean metavolcanic rock of intermediate to basic composition and quartzite. Details about tectonic evolution and structural context are described by Shao (2000).

Regional magmatism in the Xiao Qinling area

has occurred frequently and with strong intensity. Period of magmatic peak activity was late Mesozoic. Mesozoic biotite granite, whose isotopic age of 108-130 Ma, is the largest occurrences of granite in the area. Much of magma generated was anatectic melts of granitic composition and metallogenic processes associated with this activity produced gold deposits. It correlates with the formation time of the gold-bearing quartz veins in the Xiao Qinling area (Wang Yitian et al., 2002).

Alteration, mineralization and deposit type

The microscopic study of thin and polished sections shows that the quartz veins experienced strong alteration characterized by altered mineral assemblage, such as sericite, carbonate, chlorite and silicification. An alteration envelope is typical for the mineralized veins. Potassic and silicic alteration sequences are found closest to the vein system, followed by carbonate + potassic alteration. Sericite, kaolinite and chlorite assemblages complete the outer envelope alteration sequence. Boundaries between these sequences are not distinct and appear to be very gradual over distances of centimeters to more than one meter. The style of alteration is typical of most mesothermal hydrothermal systems in that it is zoned from an outer propylitic assemblage (chlorite-carbonate) to an innermost silica-sulphide zone. The centre of the system is occupied by massive quartz in a single or multiple parallel veins. Veins were forcibly injected, or injected syntectonically, as evidenced by large blocks of host rock that are locally assimilated by the vein.

Typical minerals found in the sulfide zones are native gold and silver, pyrite, chalcopyrite, siderite, galena and sphalerite. It seems that the grade of gold increase with the higher content of sulphide, which is principally in the form of galena with lesser pyrite and chalcopyrite.

Two types of gold-bearing quartz veins are found in the district. The first is a quartz-pyrite system and the second is a quartz-polymetallic sulfide stage type. Abundant fluid inclusions were found contained in gold-bearing quartz veins.

Fluid inclusion and genesis of gold-bearing quartz vein

Double polished thin sections of the gold-

bearing quartz veins and 101 inclusions trapped in quartz were studied. Melting and homogenization temperatures were measured on a heating/cooling microscope stage of Linkam THM 600 and a Leitz DMRX 45× long distance objective at the Geology Department of Chang'an University. Fluid inclusions are more abundant in the quartz crystals than in the other minerals of the veins. Most fluid inclusions, occurred in clusters, are in the range of 2-15µm in size. Three types of fluid inclusions in the gold-bearing quartz veins at the area are identified: 1) gas-rich inclusions; 2) liquid-rich inclusions; 3) multiphase inclusions. Multiphase inclusions, mixed with aqueous and CO₂, have been observed in gold-bearing quartz veins. H₂O inclusions, including two phases, are the most abundant. Homogenization temperatures of aqueous fluid inclusions range from 110 to 670°C which exhibit low and high peaks ranged in 120-160°C and 270-350°C, respectively. The salinity of aqueous inclusions, based on ice melting, varies between 2.8 and 12.8 wt.% NaCl. CO₂ fluid inclusions include three phases, an outer aqueous liquid, and inward by a carbonic liquid and centered with carbonic vapor bubble. CO₂ fluid inclusions homogenize to a liquid phase at temperatures of range from 23 to 30°C and exhibit a relatively low density range from 0.68 to 0.71 g/cm³.

Fluid inclusions of three phases of H₂O-CO₂ as well as two-phase aqueous inclusions are the main fluid inclusion types in the gold-bearing quartz veins of the Xiao Qinling goldfield. Geology and microthermometry of fluid inclusions indicate that the gold-bearing fluids sourced from two mixed fluids of granitic intrusions with meteoric origin. Mesozoic magma activities related with granitic intrusions are the main source of CO₂ fluid with higher temperature and salinity.

The gold-forming fluid was originated from the mixing of magmatic solution with meteoric water and modified by reaction with Archean wall rock during mineralization. Au was liberated from the Archean metavolcanic rock of the Taihua Group. Both of CO₂-rich fluid and meteoric fluid are of great importance in the transport and deposition of gold in quartz veins.

Conclusions

Gold-bearing quartz vein deposit in the Xiao Qinling area, central China, is one of the most important gold metallogenic types in China. Networks of shear, fault and fracture systems in the Da Yueping anticline structurally control gold-bearing quartz veins. The style of alteration is typical of most mesothermal hydrothermal systems. Gold-bearing quartz veins are associated with Mesozoic granitic intrusions in that magma was an

important part of mineralizing process. Mineralization related with meteoric fluid as well as tectonic activities.

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OIL INCLUSIONS IN MINERAL VEINS FILLED IN FRACTURES: INDICATION OIL MIGRATION INTO COMPACTED SANDSTONE IN ORDOS BASIN, NORTH CHINA

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Introduction

Fluid inclusions together with host vein minerals filled in fractures recorded fluid flux along fractures occurred during various phases of basin evolution. Oil inclusions hosted by vein-filling minerals have been considered as evidence for oil migration through fractures (Barker et al., 2006).

Fractures have been thought vital important for oil migration into compacted sandstone reservoir with very low permeability in the Ordos basin where Upper Triassic fluvio-lacustrine delta sediments in the Yanchang Formation is an important commercial oil beds (Liu et al., 2000). The aim of this study is to employ oil inclusions of vein minerals filled in fractures cutting compacted sandstone reservoir of the Yanchang Formation. The Ordos basin in order to unravel origin and geologic conditions of oil fluid encountered during fracture mineral precipitation.

Geology setting

The Ordos basin, the second largest oil/gas production basin in China, is a depression basin developed on the base of the North China Craton. The Paleo-Tethys floor collided with the Asian-European plate caused subsidence of the area of the Ordos basin during Early Triassic (Liu, 1998; Li et al., 2008). Upper Triassic fluvio-lacustrine sediments, the Yanchang Formation consisted of deltaic fluvial system, is one of the most important commercial oil bed in China. Traditionally the Yanchang Formation was divided into 10 oil beds, named Chang 10 to Chang 1 from the bottom to the top. Sedimentary sequence of the Yanchang Formation represents a whole terrestrial basin evolution from subsidence (Chang 9) to most lake expansion (Chang 7), then to fade (Chang 6) and to extinction (Chang 1). Oil shale and black mudstone of Chang 7, deposited at the most Ordos lake expansive stage of Later Triassic, have been proved the high quality source rock of the Yanchang oil beds. Oil beds for commercial production are mainly delta channel sand bodies of Chang 2, Chang 3 and Chang 6. However, many exploration results had shown that sand bodies of Chang 8 and Chang 9 underlying Chang 7 source rocks are big potential for exploration.

Fractures and its fillings in oil beds

Samples of compacted fine grain sandstone

with veins filled fractures of Chang 8 oil bed of the Yanchang Formation were taken from drill cores of three exploration wells in the Yingwang oilfield located at east center of the Ordos basin. Almost all fractures, filled with mineral veins or mineral crystals, are vertical to the bedding stratification (Fig. 1-1) which is almost horizontal in most area of the basin. Some drill cores with fracture filled by mineral crystals are brooked to two parts naturally when they got out of the drilling hole. The surface of fractures is flat and smooth which looks as cut by knife. There are numerous calcite and quartz crystals with nearly one cm in length developed on surface of naturally brooked fracture (Fig. 1-2).

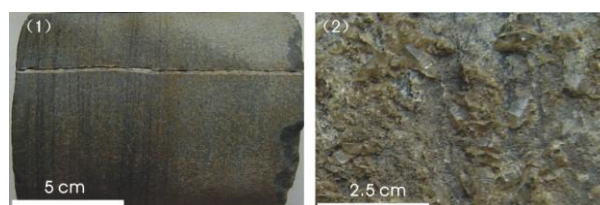


Figure 1. Vertical fracture to bedding stratification.

(1) fracture filled by mineral veins; (2) calcite and quartz crystals developed on the surface of natural opened fracture.

Oil inclusions

Calcite veins filled in fractures or crystals developed on fracture surface together with sandstone were doubly polished to be thin-section (about 0.3 mm) for observation under both white transmitted light and incident UV light. Plenty and large fluid inclusions were found in calcite veins filled in fractures or well-crystallized calcite and quartz developed on fracture surface cutting sandstone. The vapour bubble of inclusions shows Brownian movement at room temperature. The majority of the fluid inclusions occurred in distinct planes as they occurred along growth zones or as clusters in the host crystals (Fig. 2), which indicate that they are likely to be of primary origin.

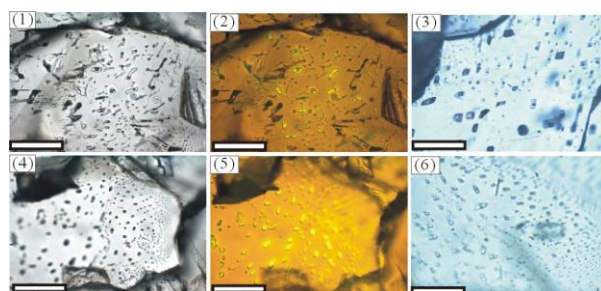


Figure 2. Oil inclusions in calcite of veins under microscope (details see text). Length of bar is 100 μ m.

Two types of fluid inclusions are distinguished by means of microscopic observations at room temperature. The type 1 inclusions, the most abundant inclusions with shape of elongate, tubular or irregular, consist of three phases: two liquids and a small vapour bubble (Fig. 2-1 to 2-3). Two liquid phases of inclusions can be easily distinguished under incident UV light which oil liquid fluoresces is bright yellow but aqueous colorless. The shape of the fluorescing oil in the center of inclusions under both normal illumination and incident UV light (Fig. 2-2) does not exactly match the shape of the liquid portion under white light (Fig. 2-1) because of a small rim of water. Freezing studies (see below) also indicate that these two liquid phases of inclusions are made up oil with aqueous.

The second type inclusions (Fig. 2-4 to 2-6), with shape of oval and elongate, consists of either monophasic oil liquid, or liquid with a small vapour bubble. Figure 2-5 is the same inclusions as in Figure 2-4 under white light but under both normal illumination and incident UV light. Note the whole liquid phase of the type 2 inclusions is fluorescent with bright yellow (Figure 2-5) indicated capture of matured oil. Both type 1 (Figure 2-3) and type 2 (Figure 2-6) inclusions occurred with the direction along crystal growth zone indicate their primary nature. Necking is found but not common in both two types of inclusions.

Chemistry of oil inclusions

Chemistry of oil inclusions was detected in-situ with microanalysis techniques of fluorescence microscopy and Micro-Fourier transform infrared (Micro-FTIR) spectroscopy. Laser Raman study was hindered because of fluorescence of inclusions. Fluorescence of oil inclusions is of bright yellow colour with a major peak at 500-530 nm which correlates with matured oil. Micro-FTIR spectra of oil inclusions exhibit distinct strong absorption of aliphatic bands with four peaks in the range of 2800-3000 cm^{-1} . It is possibly relating to the stretching bonds CH_2 and CH_3 and thus pointing to the presence of alkanes. Micro-FTIR spectra of oil inclusions with aqueous show weak absorption band of water at 3400 cm^{-1} , but the band of 1600-1700 cm^{-1} region is complex which formed by absorptions of aromatic $\text{C}=\text{C}$ and ketonic $\text{C}=\text{O}$. Micro-FTIR spectra reflect that compound of oil inclusions is dominated by aliphatic and aromatic organic matter. Organic chemical characteristics derived by GC-MS of the extracts from inclusion oil captured by vein minerals suggest that oil charged was generated from matured source rocks which deposited in an anoxic environment, and dominated by terrestrial mixed type I and type II kerogen. The overall organic geochemistry of

inclusion oil is comparable to that of Chang 7 source rock overlying Chang 8 oil beds.

Microthermometric study of oil inclusions

Homogenization temperature (T_h) of inclusions was measured using a Linkam THMSG 600 heating-freezing stage. No discernible ice was seen during freezing until temperature of -80°C to the type 2 inclusions contained pure oil without aqueous and thus no melting temperatures of pure oil inclusions were measured. However, in most cases, small ice was seen when freezing to type 1 inclusions with aqueous. The ice melting temperatures of the type 1 inclusions with aqueous range between -1.8 to -2.5°C . This indicates that the entrapped fluid of the type 1 inclusions has a salinity range of 3.06 to 4.18 wt.% NaCl equivalent. On heating the vapour bubble of all inclusions moves more quickly and the whole inclusion homogenized to liquid phase by final disappearance of vapour bubble at temperature of 62 to 123°C (with peak value of 107°C for 46 inclusions). This indicates that T_h of vapour phase to liquid phase of oil inclusions occurred over the temperature range of 62 - 123°C . This temperature condition for oil migration along fracture is coincided with that of oil generated from Chang 7 source rock overlying Chang 8 oil bed.

Conclusions

Abundant primary oil inclusions contained within vein quartz and calcite filled in fractures cutting compacted fine grain sandstone of Upper Triassic Chang 8 oil bed in the Ordos basin show fluoresces with bright yellow color and a range of T_h from 62 to 123°C . Organic geochemistry and temperature condition for inclusion oil migration along fractures are coincided with that of oil generated from Chang 7 source rocks overlying Chang 8 oil bed. Oil within fluid inclusions trapped in veined quartz and calcite represents episode of secondary oil migration from Chang 7 source rocks through fractures downwards to Chang 8 oil bed which consisted of compacted fine-grained sandstone with very low permeability.

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STUDY ON MELT INCLUSIONS IN ZIRCON IN IGNEOUS ROCKS FROM VARIOUS REGIONS IN CHINA

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Introduction

Melt inclusions in accessory mineral zircon in igneous rocks preserved the early crystallization temperature, components, and phase changing features of magma during petrogenetic processes. During this study, melt inclusions in zircon from over 20 igneous rocks from different regions in the northwest, southwest, east, and south of China were studied. Types of igneous rocks included granites, alkaline rocks and basalts. Some interesting data was collected. Different types of melt inclusions are widespread in zircons from these 20 rock samples.

Types of inclusions in zircon

Based on phase features and ratios, they were classified into single phase solid inclusions (Agl, CSi, CFe, CP₂O₅), two-phase melt inclusions with amorphous and crystalloid, multi-phase melt inclusions (Csi + Agl + V) and immiscible melt inclusions (Agl + nCsi + nCFe + V). Different types of inclusions were found co-existing in a same zircon, which indicates the heterogeneity and immiscibility of magma.

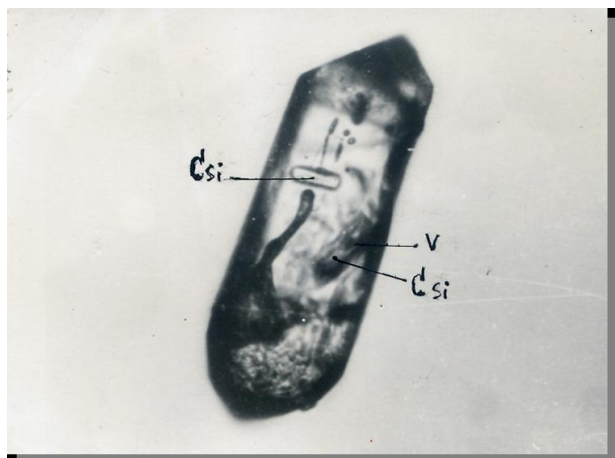


Figure 1. Solid inclusions and two-phase inclusions in zircon.

Shapes of melt inclusions

Most inclusions in zircon are in shapes of ellipses, strips, or irregular. Their long axis is often parallel to the C axis of the host crystal and sizes vary from 3x6 μm to 20x60 μm; a few up to 6x142 μm. Gaseous phase is 1-25 vol.%.

Homogenization temperature of melt inclusions in zircon

Methods used to measure the homogenization temperatures of melt inclusions in zircon include

homogenization method, oil immersion and quenching method.

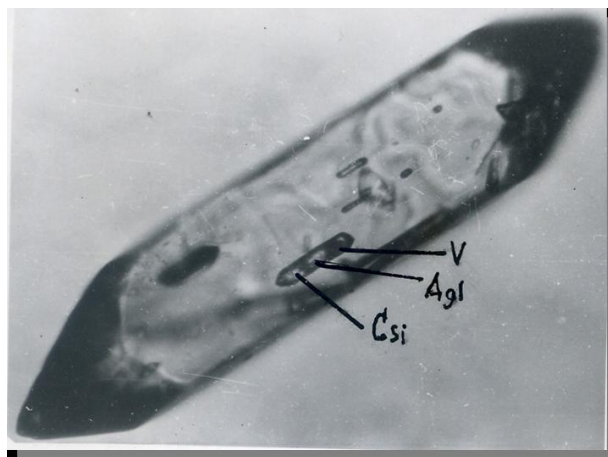


Figure 2. Three-phase melt inclusions in zircon.

Granite: Among granites in different regions related to REE-, W-, Sn-, Au-bearing deposits the temperature of first melting in melt inclusions in zircon from quartz porphyries is fixed at 700-900°C. Their homogenization temperature (T_{hom}) is 789-1200°C. REE-bearing granite in Raoping, Guangdong shows T_{hom} at 1020-1180°C; Sn-bearing granite in Gejiu, Yunnan - at 800-1200°C; W-bearing granite in Lianhuashang, Guangdong - at 950-1000°C; Au-bearing granite in Taishang, Shandong - at 780-980°C, and in Hetai, Guangdong - at 900-950°C. It appears that REE-, W- or Sn-bearing granites have higher homogenization temperature than the one of Au-bearing granite.

In the same region, melt inclusions formed in earlier stages have higher homogenization temperature than the ones formed later. For instance, in Gejiu Yunnan, earlier stage of the Louchahe and Masong porphyritic biotite granite is 900-1200°C, second stage of the Shenxianshui medium granular biotite granite is 800-1200°C, and later stage of the Laoka fine to medium granular biotite granite is 800-1000°C.

Homogenization temperatures of melt inclusions of different ages are also different. The ones in the Shanxi granite is 950-1100°C. In the same region, elder Proterozoic granite (Erxianzi Massif) is 950-1000°C, upper proterozoic Hannan Massif and Yanshan Dongjiangkou Massif is 950-1100 °C, some higher than 1100°C. Therefore, the crystallization temperature of newer granite is higher than the older ones.

Intermediate to Acidic Rocks: In the middle and lower reaches of the Yangtze River in eastern China, iron and copper associated intermediate to acidic intrusive rocks, granodiorites, are widely spread. Homogenization temperature of melt inclusions in zircon from these rocks is 740-1080°C. In same massifs, homogenization temperatures are various from different lithofacies. For example, in the Xiashu Massif in Gaozi, Jiangsu, the edge phase is 900-1080°C, the transition phase is 880-900°C, and the core phase 740-840°C. That is it gradually reduced from the edge to the center. In addition, the later time quartz diorite in the region is 720°C, which is lower than the early intrusive rock.

Alkaline rocks: Abundant two-phase and three-phase melt inclusions were found in zircons from alkali syenites in Saima, Liaoning. Inclusions are composed of amorphous and crystalloid silicate and 20-40 vol.% of gas. They are in shapes of square or ellipse and in sizes of 20x20 µm to 20x40 µm. The initial melting temperature of inclusion is 740-840°C and homogenization temperature is 950-1000°C. These rocks are magmatic in origin.

Mafic rocks: Two-phase and three-phase melt inclusions were mainly found in zircons from basalts in Penglai, in Hainan and Leizhou Peninsula, Guangdong. Inclusions are composed of amorphous and crystalloid silicate and 25-30 vol.% of gas. They are in sizes of 17x30 µm to 50x40µm. The initial melting temperature of melt inclusions in zircon from the Penglai basalt is 740-810°C, and the homogenization temperature is 1040-1120°C. Melt inclusions in zircon from basalt in the Leizhou Peninsula show 740-820°C for initial melt temperature and 1050-1080°C for homogenization.

Composition of melt inclusions in zircon

Melt inclusions in zircons from the Gejiu and Hetai granite and in zircons from the Hetai mylonite were selected for SEM/EDS analyses.

Ten points at the edge and center of melt inclusions in zircon and 3 points in the host zircon from Gejiu were analyzed (Ref. to Table 1 for part of the results, in wt.%): SiO₂ - 52.9-75.1, Al₂O₃ - 3.3-35.9, ZrO₂ - 0.8-17.9 (average 6.8), Cr₂O₃ - 0.2-5.7, FeO - 0.3-4.6, other components are minor. Their component is classified as zirconium bearing silica-aluminate and glass. Compared with the host zircon, melt inclusions are higher in Si, Al, Ca, Na, K, Ti, Cr, and Fe and lower in Mg, Zr, and P. Melt inclusions are also higher in P, Zr, Ti, Cr and lower on Na, K, Ca, Fe and Si than their protolith. This suggests the nature of early zirconium-bearing silica-aluminate magma.

Sixteen points were analyzed for melt inclusions in zircons from the Hetai granite and

mylonite. Zirconium-bearing silicate glass, zirconium- and sulphur-bearing silicate glass, iron-bearing zircon, calcium-bearing silicate glass, and daughter minerals were detected in zircon-hosted melt inclusions from granite. Zirconium-bearing silicate glass and aluminum-bearing daughter zircon were found in melt inclusions from mylonite. Melt inclusions have high Zr, P and Fe, which implies the early magma nature.

Table 1. SEM/EDS analysis of melt inclusions in zircons from the Gejiu Granites.

No. of sample		1	2	7	ACMI	ACZc	ACGZc
Position		M	E	Zc			
Composition, wt. %	SiO ₂	52.89	65.66	34.55	66.83	33.97	67.32
	Al ₂ O ₃	35.9	18.85	2.02	15.93	1.42	15.31
	MgO	0.68	0.31	0.80	0.53	0.72	0.62
	CaO	1.44	1.16	0.15	1.13	0.05	1.96
	Na ₂ O	0.76	1.18	0.86	1.48	0.79	3.05
	K ₂ O	3.03	3.63	0.22	2.83	0.07	5.57
	TiO ₂	1.25	0.58	0.22	0.55	0.08	0.46
	Cr ₂ O ₃	0.45	0.21	0.29	0.45	0.097	0.00
	ZrO ₂	1.27	5.89	43.96	6.79	46.40	0.00
	P ₂ O ₃	0.36	1.78	16.6	2.43	16.29	0.20
	FeO	1.93	0.74	0.30	0.97	0.01	3.68

Note: M - middle part of melt inclusion, E - edge part of melt inclusion, Zc - host zircon, ACMI - average composition of melt inclusions, ACZc - average composition of host zircon, ACGZc - average composition of Granite.

Conclusions

The findings of this research indicates that studies on melt inclusions in zircon in different types of igneous rocks would help to understand the temperature and compositions of magma at their early crystallization stage and the phase equilibrium evolution features of magma at heat condition. This is very important to resolving the physicochemical conditions of magma evolution and petrogenesis theory research.

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CALCULATION OF MELT-VOLATILE FLUID INCLUSIONS IN MANTLE ROCKS: APPLICATION OF THE MELT ACTIVITY EQUATION

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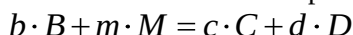
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Introduction

The melt -volatile fluid inclusions bearing two different components, which include two kinds of immiscible melt and volatile phase fluid inclusions trapped under high temperature and high pressure. Because of the volume ratio of melt and volatile phase is different, and their total homogenization temperature is far different, the most total homogenization temperature is higher to trapping temperature. Because of those inclusions will be cracked and leaked out the components before far from total homogenization temperature under heating-freezing stage, it is difficult for us to obtain the formation temperature and formation pressures.

Commonly appear the mineral, melt and volatile at crystallization time in mantle rock. The solubility of volatility is less in mineral and melt, like B.W.Murck index that rich CO₂ volatility phase coexist with melt phase in the deep (lower crust and upper mantle). So may consider the melt-volatile fluid inclusions have two independence phases: melt phase and volatile phase, can calculate formation temperature and pressure by calculating method for immiscible fluid inclusions.

(1) **Melt phase** may be listed an equilibrium reaction of paragenetic host mineral (B, C, D) with melt (M). The formula of reaction express as:



When reaction arrives at equilibrium state, under any temperature and pressure the change of Gibbs Free Energy ΔG is 0.

By formula, can obtain the activity equation:

$$m \cdot \ln a_M = \Delta G^0 / RT + \ln \frac{a_C^c \cdot a_D^d}{a_B^b}$$

Nicholls et al. (1971, 1972) calculated to the melt activity equation of common reaction:

$$\lg a_M = \frac{\Delta G^0}{2.303RT} = A/T + B + C(p - p^0)/T$$

($p^0=10^5$ Pa).

In the formula, A, B and C are the calculating constant, which can look up by many of the literatures, books about thermodynamics and physical chemistry of rocks.

To require higher precision, the change of Gibbs Free Energy ΔG is:

$$m \cdot \ln a_M = \Delta G^0 / RT$$

$$= A \cdot (\ln T - 1) + B \cdot T + C \cdot T^{-1} + D \cdot T^{-2} + E$$

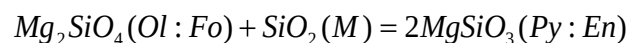
In the formula, A, B and C are also the calculating constant, which can look up by same literatures, and books.

(2) **Volatile phase** may be listed an isochore with univariant function bearing temperature and pressure, which isochore generally make use of equations of state (EOS). Shall choice the appropriate EOS such as the cubic type(R-K, S-R-K, P-R), corresponding states type, Virial equations, multi-parameter equations (B-W-R and L-K type), perturbed hard-sphere equations.

United the melt activity equation to EOS of volatile phase, and solved the simultaneous equation, can obtain formation temperature and pressure at the same time due to uniting equation is the concealed function with two variable of temperature and pressure.

Example 1: the melt-volatile fluid inclusions in mantle xenoliths in Cenozoic basalt, Liuhe in the Jiangsu province.

According as the paragenetic association of minerals can be listed the reaction of minerals to melts:



Using SiO₂ melt activity equation, namely formula 8 in Nicholls et al. (1971), thereby have:

$$\ln a(SiO_2)$$

$$= 0.045(\ln T - 1) + 0.186 \times 10^{-3} \cdot T - 2198.2/T$$

$$+ 0.148 \times 10^5 / T^2 + 0.6433 + 2 \ln a_{En} - \ln a_{Fo}$$

Under heating-freezing stage have measured the freezing point of gas-liquid CO₂, and have calculated the fluid density (g/cm³), afterward have incoming modified Redlich-Kwong EOS:

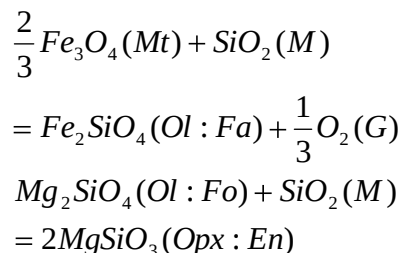
$$p = \frac{R \cdot T}{V - b} - \frac{a(T)}{\sqrt{T} \cdot V \cdot (V + b)}$$

So the formation temperature ($T \approx 1250$ - 1350°C) and pressure ($P \approx 1076.5$ - 1357.2 MPa) can be obtained. Calculating result is completely accord with Xia (1984) to determine the pure CO₂ inclusions in same area and rocks.

Example 2: the melt-volatile fluid inclusions in Cenozoic basalts and mantle xenoliths, Datong in the Shanxi province.

According to the paragenetic mineral characterization in the rocks of this region and

using the minerals-melt activity equation in equilibrium, establishing the relation of temperature to pressure, therefore two activity reactions can be listed.



Based two activity reactions can obtained two correspond melt activity equations. Measured the mineral's composition, gained the each activity, $a_{Fa}=(x_{Fa})^2$; $a_{Fo}=(x_{Fo})^2$; $a_{En}=x_{En}$; $a_{Mt}=x_{Mt}$, substituted into the melt activity formula:

$$\begin{aligned} & 9304/T - 3.407 + 0.3689(p-1)/T \\ & + \log a_{Fa} + \log a_{Fo} - 2 \log a_{En} - \frac{2}{3} \log a_{Mt} \\ & + \frac{1}{3} \log f_{O_2} = 0 \end{aligned}$$

Under heating-freezing stage have determined the freezing point of gas-liquid CO₂ in inclusions are from -6.0 to ~-11.5°C, and have calculated the fluid density ~0.9571-0.9910 g/cm³ using CO₂ density formula, afterward have substituted into Redlich-Kwong EOS to modified by Holloway (1981).

Uniting the melt activity equation and gas-liquid fluid Redlich-Kwong EOS, the formation temperature (T≈1250-1710°C and pressure (P≈841.7-1152.1 MPa) so can be calculated.

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COMPOSITIONAL VARIABILITY OF HIGH-DENSITY FLUID NANOINCLUSIONS IN ALLUVIAL NORTHEAST SIBERIAN DIAMONDS

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Introduction

The problem of the origin of alluvial Northeast Siberian diamonds is still a subject of controversy. These placer deposits (in particular, in the Ebelaykh area) are highly productive. The source rocks for these diamonds remain unidentified. Their ones of the typical characteristics of these alluvial diamonds differ from those of diamonds from kimberlite bodies, which are located in above mentioned region.

The most important information about diamond-forming media can be obtained by studying of submicron inclusions, located in the central zone of diamonds because they were trapped at the earliest stage of diamond nucleation and are the deepest available samples of mantle fluids. Navon (1999) has concluded that inclusions similar to these ones carry high-density fluids (HDFs) with compositions varying between hydrous-silicic, carbonatitic and saline end-members. Klein-BenDavid et al. (2009) defined high-Mg and low-Mg carbonatitic end-members in kimberlitic diamonds. Earlier, we have revealed, that HDF nanoinclusions in kimberlitic diamonds represent the multiphase assemblages, consisting of minerals and fluids (Logvinova et al., 2008). The bulk composition of fluid inclusions in the Ebelaykh diamonds has been studied by Tomilenko et al. (2001). It was shown that these fluids consist of CO₂, H₂O and hydrocarbons heavier than CH₄. Here we show for the first time the data on the internal morphology, mineralogy, chemical composition and crystallography of the phases composed HDF nanoinclusions in alluvial diamonds.

Samples

Two populations of diamonds from Northeast Siberian Platform placers (Ebelyakh area) have been studied. The Population I includes rounded single-crystals (dodecahedrons, octahedrons and irregular stones) with laminar structure and a black central zone rich in microinclusions. Some of them frequently exhibit growth twinning. They are strongly deformed during nucleation stage, are characterized by varying carbon isotopic composition from $\delta^{13}\text{C}$ -2,2 -9,8‰ in peridotitic diamonds to $\delta^{13}\text{C}$ -16,5-24,5‰ in eclogitic ones (Koptil, 1994), varying nitrogen content from 50 to

1400 ppm (mainly uniform distribution over the crystal). Mineral inclusions in them (58%) are predominantly related to the eclogitic suite (Sobolev et al., 1999).

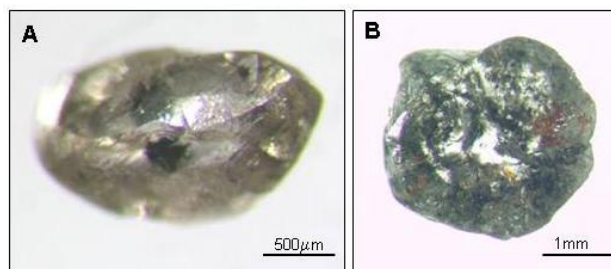


Figure 1. Photomicrographs of the Ebelaykh diamonds of the Population I (A) and Population II (B).

Population II diamonds are represented by rounded dark crystals related to variety V according to the classification by Orlov (1977). They have their own typical features: dark color due to abundant black microinclusions and high dislocation density; mosaic-block internal structure (Ragozin et al., 2002); very light carbon isotopic composition ($\delta^{13}\text{C}$ 19-23 ‰) (Koptil, 1994); varying nitrogen content from 1100 to 2700 ppm, aggregation states – 30-42% homogeneous (IaB) and nearly total absence of mineral inclusions.

Methods

The CL characteristics were studied using scanning electron microscopy (LEO-1430 VP). Nitrogen contents have been measured by Fourier transform Infrared (FTIR) Bruker Vertex 70 spectrometer using of HYPERION 2000 microscope. Phase composition of nanometer-sized inclusions in diamonds was studied by Transmission Electron Microscope (TEM) techniques such as electron diffraction; analytical electron microscopy including line scanned elemental mapping electron energy-loss spectroscopy, high-resolution electron microscopy.

In total, 63 nanoinclusions in 20 Ebelyakh diamonds have been studied conducted a FIB/TEM method.

Results and discussion

Nanoinclusions in diamonds of both populations carry HDFs. Diamonds of Population I are characterized by two types of HDF nanoinclusions: 1) multiphase high-Mg

assemblages, which include solid phases (magnesite, dolomite, clinohumite, Fe-spinel, graphite) and fluid bubbles; 2) sulfide melt nanoinclusions in association with halides (KCl, NaCl), high-Si mica and fluid bubbles. All of them ranging from 5 to 200 nm in diameter are reflecting the diamond habit. Sulfides, as well as the other inclusions in diamonds, are derived from the two principal rock types occurring in the deep lithosphere, peridotite and eclogite. Amount of Ni in the monosulfide solid solution has been used as indicator. Among Population I diamonds high-Ni sulfide nanoinclusions are predominate. Sulfides are homogeneous in composition within one sample. The Ni/(Ni+Fe) ratio of these inclusions varied from 0.038 ± 0.04 to 0.075 ± 0.02 . Still closed fluid bubbles were identified as moving absorption contrast due to density fluctuations caused by the electron beam. Bubbles contain high content of K, Cl, O. EDX spectra before and after opening one of the fluid bubbles show that only Cl-content is decreased. Therefore it was assumed that these fluid bubbles contain gas phase. All of these diamonds are strongly deformed. A lot of dislocations are found around nanoinclusions. All of the observed phases have been identified by diffraction patterns and chemical composition. To determine the carbonate phases we additionally used the electron energy-loss spectra.

The constant Ni/Ni+Fe in sulfide inclusions, the presence of varying amounts of alkalis, gaseous fluids and water-bearing silicic phases, and association with carbonatitic melts suggest the presence of sulfide melts in these diamonds and can be an evidence of immiscibility between the melts. Sulfide melt dissolves carbon well. The continual presence of sulfide with graphite and fluid confirms the assumption of diamond nucleation from sulfide-silicate melt. Sulfide melt is a less efficient diamond-forming medium as compared to carbonate, carbonate-silicate-fluid systems. However, the role of sulfides in the diamond genesis may appear in the reactions with fluid.

Population II diamonds are richer in nitrogen and carry low-Mg carbonatitic HDFs, rich in Ba, Sr, P and K. HDF nanoinclusions consist of several phases: Ca-Ba-Sr-carbonates, Ca-Fe-carbonates, K-Ba-phosphates and Ba-sulphates, graphite, fluid bubbles and less Ti-silicate or Ti-oxide (not exactly identified). Sulfur observed in EDX-spectra is closely related to Ba-sulphates. Separately NaCl, KCl nanoinclusions have been identified. Fluid bubbles evidently contain H₂O, CO₂ and heavier hydrocarbons.

Conclusions

- 1) Preliminary results prove that diamonds

from Northeast Siberian Platform placers are characterized by compositional variability of the parental medium (high-Mg carbonatitic, Ba,Sr-rich carbonatitic and sulfide-silicate-brine HDFs) and suggest at least three different sources.

- 2) The sulfide melts can coexist with hydrous-silicic melts and brine as well and add another branch to the diamond forming fluid system, thus enlarging the range of trace elements that may be transported by such fluids.

- 3) The composition of high-Mg HDFs is closer to that of near-solidus melts of saturated carbonate peridotites. Thus, it should be possible to produce the Mg-rich HDF either by incipient melting or by cooling and crystallization of a proto-kimberlitic melt at depth.

- 4) The source rock for the low-Mg carbonatitic HDFs detected in diamonds, in the view of the first reported data and previous ones as well, can be subducted rocks of the oceanic crust. The extreme enrichment of these HDFs in incompatible elements can be attributable to the interaction of saline fluids, which bring Ba, Sr, K, Cl, with carbonate-bearing eclogite rock.

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STABLE ISOTOPE COMPOSITIONS OF FLUID-INCLUSION WATER FROM AN ALPINE SPELEOTHEM: IMPLICATIONS FOR PALEOCLIMATE AT THE PLEISTOCENE-HOLOCENE TRANSITION

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Introduction

An analytical line allowing the analysis of stable isotopes of water recovered from fluid inclusions in minerals was built at Innsbruck University. Water is released from samples by heated crushing in a He flow and, after cryo-focusing, is decomposed by reaction with carbon at 1400°C. The evolved H₂ and CO are separated in a GC column and delivered, sequentially, into an isotope ratio mass spectrometer (DELTA V Advantage; Thermo Fisher Scientific). A minimum of 0.1 µL of water is needed to achieve a precision sufficient for paleoclimatic applications (1.5 ‰ for δD; 0.5 ‰ for δ¹⁸O; 1σ; Dublyansky, Spötl, 2009).

Speleothems, secondary calcite deposits formed in caves, offer unique insights into past continental climate and environments. Stable isotope analyses at sub-annual resolution offer valuable records of past changes in the isotopic composition of precipitation. Paleoclimatic interpretations of isotopic patterns in speleothems, however, are hindered by the fact that the δ¹⁸O_{calcite} reflects both, the δ¹⁸O_{precipitation} and the cave temperature. Measurements of δ¹⁸O and δD of water trapped in fluid inclusions have the potential of providing direct information of δ¹⁸O_{precipitation}, allowing separating the two controlling factors.

Stalagmite from Bärenhöhle

Bärenhöhle, a nearly 1 km-long cave system located on the northern ridge of the Alps, hosts a significant number of Holocene speleothems. A 140 cm-long, naturally broken stalagmite BH-1 was sampled for paleoclimate investigations.

28 U-Th MC-ICP-MS analyses revealed that the stalagmite was deposited between 13.8 and 7.8 ka (= thousand years before the year 2000). Age modeling suggests a rather constant growth rate of ca. 100 µm·a⁻¹ until ca. 11.5 ka, followed by a 3-fold increase.

The calcite fabric shows a laminated pattern with porous laminae formed at high growth rate during the summer season and slower-growing compact winter laminae. The oxygen isotope composition of calcite, measured at 200 µm-increments along the stalagmite growth axis, shows an abrupt decrease of nearly 2 ‰ between 12.9±0.1 and 11.6±0.1 ka, in good agreement with stable

isotope records from Greenland ice cores (Rasmussen et al., 2006). This isotopic excursion, known as the Younger Dryas stadial, reflects a cold spell which occurred during Termination I, and gave rise to a well-documented glacier advance in the Alps. Estimates of the amount of cooling derived from various environmental archives range between 1.5 and 7.6°C.

This study attempts an independent quantification of the Younger Dryas cooling employing the isotopic composition of aqueous fluid inclusions trapped in speleothem calcite.

Fluid-inclusion study

Fluid inclusions were analyzed along a 400 mm-long section of stalagmite BH-1 deposited between 13.5 and 11.1 ka. 14 individual growth zones, each averaging 50 years, were analyzed in duplicate or triplicate. Overall, 30 sub-samples, 300 to 1200 mg each, were crushed for fluid-inclusion analyses.

Results

The average water content in stalagmite BH-1 is 0.54±0.35 µL/g CaCO₃. Five sub-samples yielded too small amounts of water, and five others were discarded because of secondary isotopic fractionation effects.

The validated data plot within analytical errors along the Global Meteoric Water Line (Fig. 1), suggesting that site-specific fractionation was negligible. The data show a statistically significant correlation between the stable isotope values of the fluid-inclusion water (δD and δ¹⁸O) and the δ¹⁸O values of the host calcite (R²= 0.54). Similarly to the δ¹⁸O_{calcite}, the fluid inclusions' isotope values exhibit a strong depletion centered at 12.4 ka (Figure 2). The amplitude of the change is 8.5‰ for δD and ca. 1‰ for δ¹⁸O.

Discussion

Monitoring of the Bärenhöhle drip sites suggests that hydrological transport is rapid with only limited mixing occurring in the soil and epikarst. Therefore, water trapped in fluid inclusions in the speleothem calcite is assumed to be representative of local karst recharge.

Taking into account that (a) in the BH-1

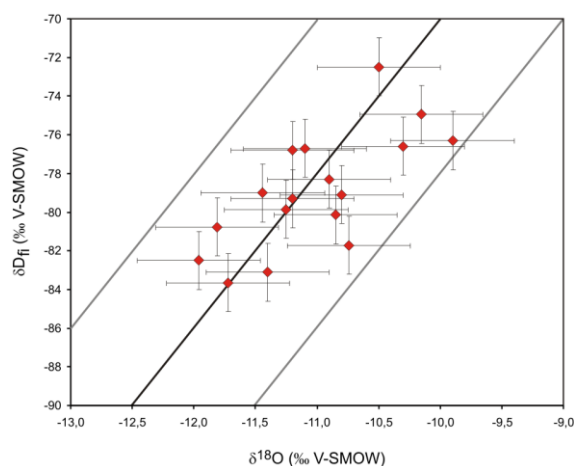


Figure 1. $\delta^{18}\text{O}$ and δD values measured in fluid-inclusion water plotted relative to the Global Meteoric Water Line. Gray lines show a ± 1 ‰ envelope on both sides of the GMWL.

stalagmite laminae representing summer growth are volumetrically dominant (ca. 3 times thicker than winter laminae), and that (b) fluid inclusions mostly occur in the summer laminae, both the calcite growth and the fluid-inclusion record are clearly biased towards the summer season.

The fluid-inclusion results suggest that $\delta^{18}\text{O}$ of the summer precipitation decreased by 0.8 ± 0.5 ‰ during the Younger Dryas. Considering a temperature sensitivity of 0.5 ‰/°C of $\delta^{18}\text{O}$ of summer precipitation in Europe (GNIP database) we infer a decrease in the summer air temperature between 0.6 and 2.5 °C. These values are near the lower end of the summer temperature estimates based on the depression of the tree line (Kerschner, 2009) and based on chironomids and other bio-indicators from alpine lake sediments (Heiri, Lotter, 2005; Ilyashuk et al., 2009).

The observed negative $\delta^{18}\text{O}$ anomaly recorded in the speleothem calcite, however, is larger than the combined effect of summer precipitation $\delta^{18}\text{O}$ decrease and equilibrium fractionation due to lower cave air temperatures. Kinetic effects during calcite precipitation can be safely ruled out (they would cause the opposite effect, i.e. an increase in $\delta^{18}\text{O}_{\text{calcite}}$). In order to reconcile the calcite and the fluid-inclusion stable isotope compositions a dramatic cooling during Younger Dryas winters has to be invoked, which manifests itself in the low winter laminae-calcite isotope values via the temperature-dependent fractionation.

Conclusions

In this study we obtained a preliminary estimate of the summer temperature change during the Younger Dryas in the Alps using the fluid-inclusion signature from speleothem calcite. This new approach also opens the door to extract winter

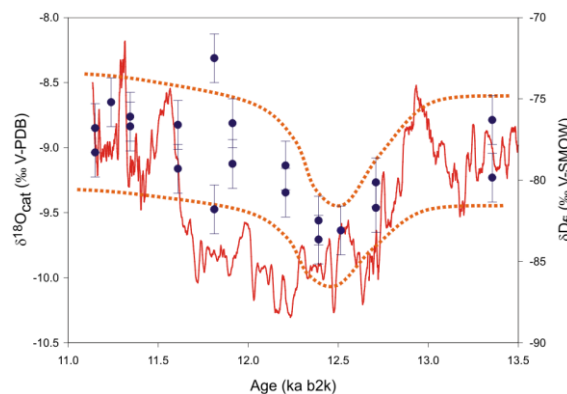


Figure 2. Evolution of $\delta^{18}\text{O}_{\text{calcite}}$ and δD of fluid-inclusion water in time. The combination of the two isotope systems provides a basis for paleotemperature reconstructions.

temperature estimates, because the cave interior air temperature closely approximates the mean annual air temperature of the atmosphere outside the cave. Winter temperature proxies are rare and our preliminary data suggesting very cold winter temperatures are consistent with inferred paleoceanographic changes in the North Atlantic (e.g., Denton et al., 2005). When combined with independent oxygen isotope data from benthic ostracods (e.g., von Grafenstein et al., 1999) our approach has a high potential for yielding validated isotope-inferred paleo-seasonality data.

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LOWER CRUSTAL SCAPOLITE CRYSTALLIZATION FEATURES (GRANULITE XENOLITHS FROM DIATREMES OF THE PAMIR): RESULTS OF MAGMATIC INCLUSION STUDY

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Introduction

Scapolite is a framework silicate comprising an isomorphic series marialite $3\text{Na}[\text{AlSi}_3\text{O}_8]\cdot\text{NaCl}$ – meionite $3\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]\cdot\text{Ca}[\text{CO}_3, \text{SO}_4]$. Stability of this mineral in a wide range of PT parameters makes it a widespread mineral of metamorphic and metasomatic rocks. Primary magmatic scapolite is relatively rare (for example, Goff et al., 1982). High-Ca scapolite according to experimental data (Goldsmith, Newton, 1977) is crystallized preferably at elevated PT parameters. High partial pressure of CO_2 typical for granulite facies metamorphic rocks seemingly should provide favorable conditions for crystallization of high-Ca scapolite in the lower crustal settings. Such scapolite is found in eclogite-like rocks and granulites (Sobolev, 1960; Knorring, Kennedy, 1958). Scapolite-bearing granulites are distinguished among compositionally unique abyssal derived xenoliths from Neogene fergusonite diatremes in the South-Eastern Pamirs as well (Dmitriev, 1976). The study of melt inclusions in minerals of scapolite-bearing granulites from the Pamirs allowed us to obtain the first data on crystallization of scapolite at lower crustal conditions with participation of CO_2 -saturated melts (Chupin et al., 2006).

Results

The studied xenolith of scapolite-bearing granulite (Sample 1324 from the collection of E.A. Dmitriev) is fine- to medium-grained patchy rock. The distribution of leucocratic minerals varies from 20 to 70% in different parts of the xenolith. The rock consists of garnet (Mg#-40–46; composition: almandine_{41–44}, pyrope_{25–36}, grossular_{17–29}), clinopyroxene (salite with jadeite content 6–8 mole %), K-plagioclase ($\text{Ab}_{38–49}\text{An}_{41–52}\text{Or}_{6–9}$), titanite, scapolite, quartz, insignificant amount of K-feldspar, graphite, biotite, accessory apatite, ore phases, rutile, zircon, and carbonate. The primary high-Ca scapolite ($\text{Me}_{67–69}$ with Cl up to 0.9 wt.%) is present as major component (approximately 15 vol.%). Garnet encloses primary small quartz grains, carbonate (dolomite with FeO up to 7.0 wt %), rutile, zircon, apatite, and ore mineral. Small grains of quartz and carbonate (calcite with FeO up to 10.5 wt.%) are fixed in clinopyroxene as well. Mafic minerals are intensely altered along edges of grains. The central parts of garnet grains are

characterized by similar compositions, whereas the composition of their rims is variable. Some garnet and clinopyroxene grains have a weak progressive metamorphic zoning.

Primary melt inclusions occur in all the major and accessory minerals from Sample 1324 (Fig. 1). Such inclusions were firstly discovered in scapolite from the Pamir xenoliths. The inclusions are usually 5–15 μm across. They can be as large as 40–60 μm in quartz and titanite grains. Their phase composition at 20°C is glass + heterogeneous fluid bubble (gas and liquid) + one or two daughter microcrystals. Practically all the inclusions in garnet are partly decrepitated (Fig. 1a), while inclusions in quartz and scapolite are usually hermetic. Inclusions in quartz have the negative form of its high-temperature modification (Fig. 1c), which allows the minimal temperature of quartz crystallization to be estimated. At a pressure of 15 kbar, the high-temperature quartz modification is stable at temperatures above 940°C (Cohen, Klement, 1967).

Garnet and scapolite host primary fluid inclusions that are syngenetic with melt ones (Fig. 1b). The fluid inclusions reach 10–15 μm across. Most of these inclusions are partly decrepitated. The joint trapping of fluid and melt inclusions results in formation of combined inclusions with anomalously large fluid vacuoles (Fig. 1b). The cryometric study reveals that primary fluid inclusions and fluid phase of melt inclusions are mainly represented by CO_2 with a density of $\sim 0.75 \text{ g/cm}^3$. Taking into account partial leakage of inclusions, the real density of CO_2 in inclusions was substantially higher.

The melting temperatures of daughter liquidus crystalline phases (1000–1020°C) were taken for the trapping temperatures of examined melt inclusions (Schiano, Clocchiatti, 1994; Szabo et al., 1996). This is consistent with the average temperature ($\sim 1020^\circ\text{C}$) based on a garnet-clinopyroxene thermometer (Powell, 1985).

Occurrence of syngenetic melt and fluid inclusions suggests that early garnet and scapolite were crystallized in presence of the CO_2 -saturated melt and free CO_2 -rich fluid. At temperatures of 1000–1020°C (probable temperatures of inclusion trapping), the fluid pressure for CO_2 inclusions with a density of approximately 0.75 g/cm^3 was ~ 4 kbar. This is the minimal value of the pressure because of

partial decrepitation of fluid inclusions in garnet or elastic expansion of inclusions in scapolite under the pressure release. The pressure estimated for the examined granulite using a garnet–clinopyroxene–plagioclase–quartz geobarometer (Perkins, Newton, 1981) is 13–15 kbar.

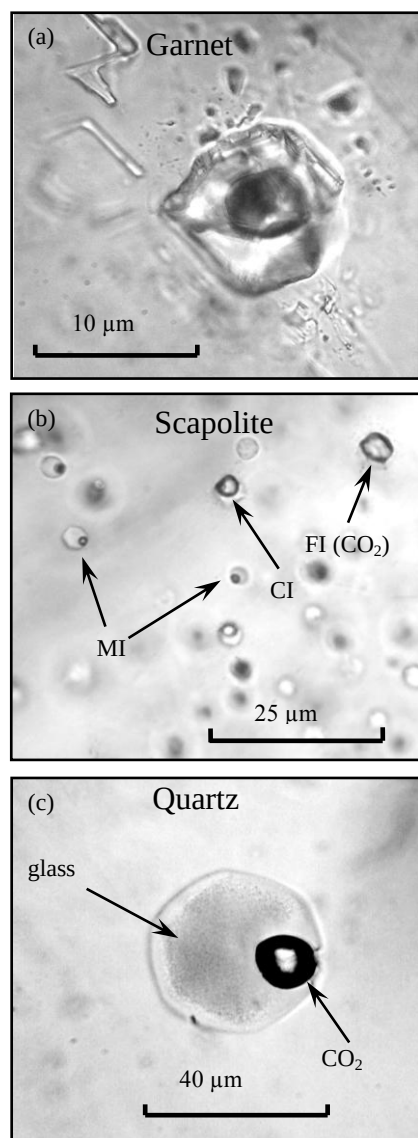


Figure. 1. Primary melt and fluid inclusions in minerals of scapolite-bearing granulite: (a) garnet, (b) scapolite, (c) quartz. Inclusions: (MI) melt, (FI) fluid, (CI) combined.

According to microprobe data, compositions of glasses in primary melt inclusions from all minerals of Sample 1324 correspond to high-K acid (from rhyodacites to rhyolites) melts of normal to elevated alkalinity. Melt inclusions in all minerals (with the exception of scapolite) have elevated Cl contents (up to 0.8 wt %). The calculated CO₂ content in quartz-hosted melt inclusions amounts to 1.0 wt.%. According to ion microprobe data, the water content in melt inclusions varies from 1.6 to 0.8 wt % in quartz (four analyses) and from 4.1 to 1.7 wt % in titanite (two analyses). Melt inclusions in quartz and scapolite are characterized by high contents of LREE, low contents of HREE, and high

contents of Th and Nb (up to 72 and 18 ppm, respectively).

Conclusions

The formation of acid high-K melts with high CO₂ and Cl contents can be explained by incongruent melting of high-Ca substrate in the lower crustal settings (pressure >13 kbar, temperature ~1000°C). The incongruent melting was accompanied by crystallization under peritectic conditions of Si-poor and Ca-rich minerals (garnet, clinopyroxene, titanite, plagioclase, and scapolite), which trapped microportions of melts as inclusions. Probably scapolite crystallized instead of plagioclase when high CO₂ (~1 wt.%) and Cl (up to 0.8 wt.%) concentrations were reached in melts and in presence of CO₂-rich fluid.

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INTRA-PLATE ORE-GENERATING FLUID-MAGMATIC SYSTEMS OF THE CHATKAL-KURAMA REGION, UZBEKISTAN

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Study of intra-plate acid magmatism in folded regions is one of the pressing problems in petrology and metallogeny. Currently, rare metal ongonite-leucogranite associations, which are formed by large granitoid batholiths, are indicators of continental intra-plate geodynamic situation. Within western Tien Shan similar rocks are found in the Sarydjaz tin ore district of the Inilchek ore area, in the Sargardon tungsten deposit and in the Shavazsay lithium deposit.

In recent years (2005-2009) ongonites and ongorhyolites, rare metal leucogranites were examined us within the Karakushhana-Bashkizylsey, Kelenchek-Tashsey, Yertashsey and Chetsu-Shavkatli areas. Exotic varieties of these rocks are first identified: aegirine ongorhyolites (Yertashsay neck) and fayalite ongonites (Angren dike). These rocks are related to areas of deep faults with manifestations of lithium, beryllium, tantalum, niobium and rare-earth metals. Studies have shown that rare-metal magmatism in western Tien Shan is also characterized by traditional mineralization (W, Mo, Sn, U, Th, fluorite) and occurrences of niobium, tantalum, rare and other metals. Association of rare-metal acid rocks form stocks and necks of ongonites, ongorhyolites and the small intrusives of leucogranites. As a result of complex geological, petrographic, mineralogical and geochemical studies petrologic models of formation for deposits closely associating with ongonite-leucogranite magmatism were made and deposit types were divided.

The first type is the explosive-intrusive fluidized Shavazsey lithium deposit which related to the Takeli-Karakushhana paleovolcano. Since Lower Permian ore formation connected with granite-rhyolite magmatism was in the following sequence: 1) appearance of tuffs of basic composition and accumulation of them together with peraluminous rocks in lava lake conditions; 2) formation of dikes and sills of trachydolerites, syenite-porphyrtes and trachytes; 3) injection of fine clastic-agglomeratic tuffs of ongonitic composition; 4) formation of multi-stage sills, dikes and necks of ongorhyolites. The mineralization in these ore deposits is a product of fluid-saturated melts from the lower mantle.

The second type is an extrusive-intrusive mineralization in the Yertashsey area. Its formation is related to neck-like bodies of alkaline

ongorhyolites and, possibly, with depth to rare-metal alkaline leucogranites. The peculiar features of these rocks are: mineral isolations, consisting of aegirine, quartz and fluorite, the presence of rare earth minerals, rutile, sphene and Cr-spinels. Ores are enriched in W, Mo, Sn, Nb, Zr, HF, U, Th, and REE. The data reveal a significant role of the melt mantle fluids for the association alkaline ongorhyolite-leucogranite.

The third type is apogranite-intrusive-deposits with tantalum-niobium and rare-earth metals in the Kelenchek-Tashsay area. Here mineralization is localized in albities (apogranites) within granites of the Arashan intrusive. Rare-metal leucogranites occur as dikes among these rocks. Dike swarms are expected to move with the depth of the stock. Leucogranites are characterized by an abundance of volatiles and fluorite, associating with minerals of Ti, Nb, REE, U and Th. Ores are enriched in Rb, Cs, Hf, Nb, Ta, W, Au, As, Sn, U, Th, and REE. Content of REE in albities is 0.1-0.2 wt.%. The third type of apogranite-intrusive mineralization also includes rare-metal ore deposits of tin, molybdenum and tungsten in the Chetsu-Shavkatli area. Within this area, the authors identified dikes of fayalite ongonites and their intrusive analogues - stocks of fayalite rare-metal leucogranites with traditional rare-metal and rare-earth mineralization. Their complex study was based on petrography, mineralogy, geochemistry and fluid inclusions. High clarks of Sn, Nb, W, Mo, Cs, U, Th, Hf, REE, Sb, As, Au, etc., point out melt geochemical specialization of these elements; the abundance of volatiles and fluorite, fluorapatite and primary fluorcarbonates associating with minerals of Ti, Nb, Sn, Mo, W and REE (Ti-magnetite, ilmenite, ilmenorutile, Nb-rich rutile, fergusonite, rizerite, yttrapatite, rabdophanite, yttrorhite, baestnasite, synchysite, lanthanite, allanite, chevkinite, cassiterite, molybdenite, scheelite, etc.). Among accessories in fayalite ongonites and leucogranites minerals with the yttrium subgroup REE essentially prevail over those with the cerium subgroup. According to apogranite-intrusive model for rare-metal deposits, formation granosyenite-porphyry bodies of ongonites and leucogranites seems to be the result of contact metasomatism and pyrometamorphism that took place under the influence of fluids from ongonitic melt. Non-traditional localization of rare-metal mineralization

in granosyenite-porphyries is possibly due to concentration of ore-generated heterogeneous fluids separated from ongonitic melt. This scientific prediction was probated during study of hybrid granosyenite-porphyries and metasomatic rare-metal leucogranites of intrusive zone at Shavkatli and fayalite ongonites from the exocontact zone the Angren dikes.

The fourth type is exogreisen fluorite and tungsten mineralization in the Sargardon-Shabrez area. Here at depths of 800-1000 m rare-metal leucogranites are embedded in large intrusive body (intrusive in intrusive granites). Dikes of ongonite are placed into more ancient granite intrusive naked on the surface. They associate with others rocks represented by quartz diorites and granosyenite-porphyries. Formation of ore field is related with fluids derived from leucogranite melt.

The formation of above ranked rare-metal deposits in the Chatkal-Kurama region (western Tien Shan) is seems to be product of fluid-saturated high fluorine rare-metal acid magmatism, manifested in the intra-plate stage of development of the region. Invasion and crystallization of these ore-containing melts from different levels of the Earth's crust have led to formation of: rare-metal leucogranite intrusives with W, Sn, Mo, Nb, Ta, Be, Li and fluorite in hypabyssal facies (the Sargardon greisen deposit); albitites with Ti-Nb-Ta-REE (+ Zr, Hf, Au, U, Th, etc., the Kelenchek-Tashsay area) and non-traditional ore deposits and mineralization zones with tin, niobium and REE (the Chetsu-Shavkatly area); fluidized explosive-intrusive type of rare-metal rocks of subvolcanic facies with Nb, Ta, Zr, Hf, W, Mo, Au, U, Th, REE and fluorite (the Shavazsey area) and mineralization in the Yertashsey area. The origin of melts is represented as a result of interaction of residual granitic and alyaskitic magmas with ore-generating intratelluric fluids.

FLUID INCLUSIONS STUDIES OF Pb-Zn-(Ag) DEPOSITS FROM NE PORTUGAL

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Fluid inclusion (FI) studies of Pb-Zn-(Ag) deposits are being carried out in NE and W Portugal. We present the results for three of the deposits in the Bragança district NE Portugal: Ferronho, Vale da Madre and Olgas. The study of these deposits encompasses mineralogical, geochemical and petrographical studies together with fluid inclusions. In this work we present the results of petrographic and microthermometric study of FI for the three deposits mentioned above. These deposits of the Bragança district were explored during few years in the XXth century. They are Pb-Zn vein deposits some richer in Cu as Olgas, others in Ag as Ferronho, with occasional occurrence of Bi and Sb in minor quantities.

Geology and mineralogy

The studied deposits are situated in the southern part of the Bragança district in NE Portugal. These are vein type deposits with main quartz gangue which formed in fractures related to the later stages of the Variscan orogeny. The veins cross lithologies of Ordovician age that consist of phyllites and quartzites of the Autochthonous Transmontano Formation. The three deposits form a larger lineament together with other deposits which runs parallel to a main NNE-SSW regional fault known as the “Vilariça fault”. These deposits, as well as other Pb-Zn and Sb mineralizations from NE Portugal, are not spatially related with the two micas syntectonic granites as they occur installed in later fault structures (Noronha et al., 1998, 2006).

The main veins are mostly subvertical with directions ranging from N25°E (Olgas) to N40°E (Ferronho) with thicknesses ranging from 0.10 to 2.5 m. They are composed of brecciated (Ferronho, Vale da Madre) to coarse quartz (Olgas). Brecciated quartz exhibits cockade textures in which quartz envelopes fragments of the wall-rock. There exists several generations of quartz. We have identified mainly three generations: quartz I, which is earlier massive milky quartz, quartz II which is translucent euhedral mosaic sometimes zonal and quartz III which is clear euhedral crystals in comb texture. The first sulfides to occur are arsenopyrite and pyrite which are contemporary with quartz I and then sphalerite and chalcopyrite which are contemporary with quartz II. Galena occurs after quartz II in fractures that cross-cut the milky quartz I and the euhedral translucent quartz II. Later in the

paragenesis covellite, acanthite, anglesite, cerussite, pyromorphite and oxides of Pb, Fe, Cu and Mn appear.

Fluid inclusion petrography

All of the studied FI are hosted by quartz. Petrographical studies allowed us to identify different assemblages of FI: 1 – isolated; 2 – defining crystal growth zones; 3 – in intragranular planes; 4 – in transgranular fluid inclusion planes (FIP), or transgranular trails or swarms; 5 – in intergranular planes (Van den Kerkhof, 2001). The studied FI can be classified according to Roedder's criteria (1984) as primary (cases 1, 2 and 3), pseudosecondary (3) and secondary (4 and 5). Sometimes it is difficult to distinguish between intragranular and transgranular planes and trails because of the limitation in the third dimension – thickness of the plate (~100µm). It is usual to find FIP crossing through quartz I or II composed by the same type of FI that are primary in quartz III. Most of the studied FI from these deposits are secondary and pseudosecondary in quartz I and II, which are the most common FI and the ones that are related to the main ore (Pb) stage (Fig. 1). Some primary and pseudosecondary FI related to earlier events (As, Fe, Zn, Cu) were also studied as well as some secondary related to later stages of fluid circulation present in quartz III. The studied FI present frequently an oval, rectangular or negative crystal form, they are two-phase aqueous FI, with sizes ranging from 5 to 60 µm and constant Flw inside the same family of FI (most common 0.80).

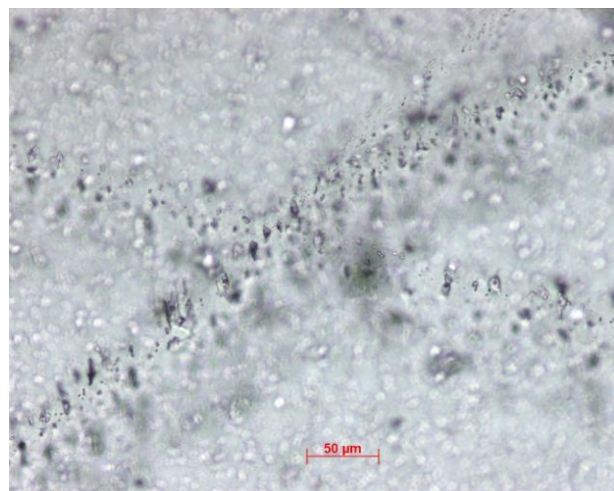


Figure 1. Crossing trails of secondary FI in sample F3-7 from the Ferronho deposit.

Microthermometry results

The microthermometric analyses were carried out mainly in pseudosecondary and secondary inclusions. In total 251 FI from the three deposits were so far analyzed, although in some cases results for the pair ice melting temperature (T_{mi}) and homogenization temperature (T_h) were not obtained. Salinities were calculated for wt.% of NaCl, although presence of Ca^{2+} is probable as indicated by T_e temperatures. Microthermometric results were summarized through the use of basic statistics in the data presented in Table 1.

Table 1. Microthermometric data.

Deposit (n)	T_e	T_{mi}	T_h	Salinity
Ferronho (100)				
F1 (3)	-52.3 (± 2.7)	-6.3 (± 2.7)	343 (± 30.4)	9.59
F2 (55)	-53.9 (± 0.65)	-1.1 (± 0.07)	212 (± 4.65)	1.90
F3 (14)	-54.3 (± 0.73)	-3.6 (± 0.12)	161 (± 2.55)	5.86
F4 (13)	-53.3 (± 1.17)	-8.75 (± 0.3)	149 (± 2.3)	12.56
F5 (12)	-57.6 (± 1.52)	-16.2 (± 0.66)	107 (± 0.76)	19.60
Vale da Madre (75)				
F1 (41)	-55.7 (± 1.26)	-3.8 (± 0.27)	255 (± 5.9)	6.15
F2 (28)	-52.5 (± 1.1)	-1.17 (± 0.08)	203 (± 7.2)	2.02
F3 (2)	-61.9 (± 4.1)	-2.3 (± 1.1)	133.5 (± 8.5)	3.87
Olgas (58)				
F1 (48)	-49 (± 1.4)	-0.37 (± 0.04)	171 (± 5.15)	0.65
F2 (8)	-47 (± 4.65)	-5.4 (± 0.02)	192 (± 7.02)	8.41

Note: All values for temperatures are in °C and are means with standard error. Salinity is in wt.% NaCl.

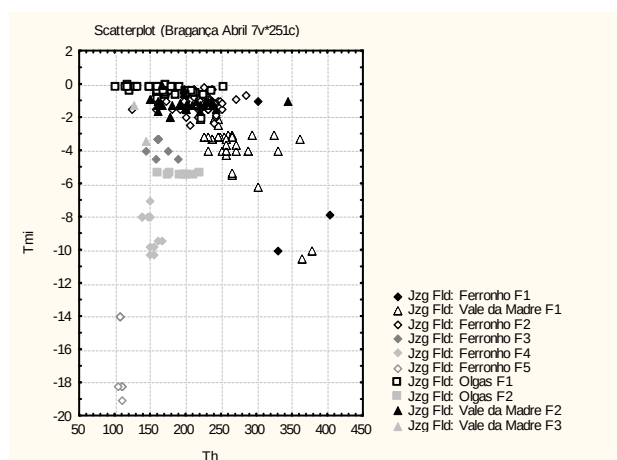


Figure 2. T_{mi} versus T_h diagram discriminating different “fluids” for the three studied deposits.

Plotting a diagram (Fig. 2) of T_{mi} versus T_h together with the petrographical characteristics of

the inclusions allowed us to define different subsets of “fluids” which we named F1, F2 ... These are subsets of FI with similar characteristics that represent stages of the mineralizing fluid during these ore deposits formation. These “fluids” correspond to three main events: early (As-Fe-Zn-Cu) mineralizing stage – Ferronho F1 and Vale da Madre F1; main stage of Pb ore deposition – Ferronho F2, F3, Vale da Madre F2, F3 and Olgas F1 and F2; late fluids - Ferronho F4 and F5.

Conclusions

We conclude that in these deposits it is possible to distinguish several types of fluids that correspond to different stages of evolution: F1 (Ferronho and Vale da Madre) - earlier fluids, responsible for a stage of the hydrothermal system richer in Fe-As-Zn-Cu; F1 (Olgas), F2 and F3 with a wide range of homogenization temperatures, (300°C to 100°C) and salinity that varies from 8.41 to 0.65 wt.% NaCl; F4 and F5 are later fluids.

Lowering of temperature and entrance of a more saline fluid in the system is the mechanism we believe responsible for the ore deposition (Marques de Sá, Noronha, 2010). This fluid evolution is similar to the one registered on later stages of W-Sn vein deposits in North Portugal (Noronha, 1990). The results suggest that in these deposits the catalyser of the mineralization process was a mixture of fluids with different characteristics and possibly some boiling off as evidenced by the dispersion of the values of T_h (Roedder, 1984; Loucks, 2000).

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EDIACARAN SEAWATER TEMPERATURE: EVIDENCE FROM INCLUSIONS OF SINIAN HALITE

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Introduction

Seawater temperatures throughout Earth's history illustrate a long-term cooling trend from nearly 70°C at ~3500 Ma to around 20°C at ~800 Ma. The terminal Neoproterozoic prior to the "Cambrian Explosion" is a key interval in evolutionary history, as complex multicellularity appeared with the advent of the Ediacaran fauna. These organisms were likely the first that required higher levels of atmospheric and dissolved marine oxygen for their sustainability. It is known that most modern macroinvertebrates are intolerant of temperatures in excess of 45°C. Perhaps more importantly, these high seawater temperatures limit the potential of dissolved oxygen, and therefore become an integral part of this evolutionary story. Previously, our understanding of seawater temperature during the terminal Neoproterozoic comes only from ¹⁸O/¹⁶O and ³⁰Si/²⁸Si ratios ascertained from a limited number of cherts. Isotopic ratio methods for assessing seawater temperatures are inherently indirect and have a wide range of oscillation.

Methods and results

However, maximum homogenization temperatures ($T_{h,max}$) of primary fluid inclusions in halite provide a direct means of assessing brine temperature, and have been shown to correlate well with average maximum air temperatures.

The oldest halites date to the Neoproterozoic–Lower Paleozoic (~700–500 Ma), and Ediacaran representatives can be found in Sichuan Province, China, which do preserve primary fluid inclusions for analysis via cooling nucleation methods. We utilized halite samples from the Changning-2 well, correlative to the Denying Formation (551–542 Ma), to provide a direct assessment of terminal Neoproterozoic seawater temperature. Our measurements indicate that seawater temperatures where these halites formed are highly similar to tropical Phanerozoic seawater temperature estimates.

Conclusion

From compiled paleotemperature data, the decline in seawater temperatures over the course of the Proterozoic, accompanied by the reduction of

seawater salinity with the sequestration of salt in massive halite deposits in the Neoproterozoic, allowed the ocean system to accumulate more dissolved oxygen, and potentially paved the way for the evolutionary innovation of complex multicellularity.

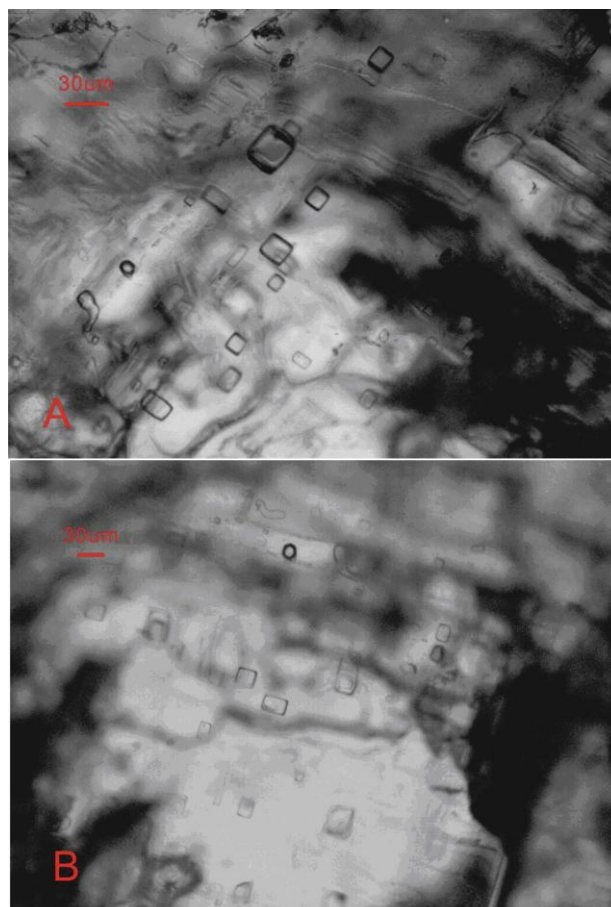


Figure 1. Primary fluid inclusion textures in the Ediacaran halite.

Acknowledgments

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URANIUM-COPPER SYSTEMS IN WESTMORELAND REGION, NORTHERN AUSTRALIA: FLUID INCLUSION STUDIES AND GEOCHEMICAL MODELLING OF BASINAL FLUIDS

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Introduction

The Westmoreland region is located 1250 km southeast of Darwin. Over 104 mineral occurrences are recorded in the Westmoreland region, including 38 uranium occurrences (some with gold) and 52 copper occurrences (Fig. 1). The three largest uranium deposits are Redtree, Huarabagoo and Junnagunna. These three deposits have a collective inferred and indicated resource of 23.6 kt U_3O_8 at 0.07 to 0.09 wt.% U_3O_8 (Mernagh, 2010).

The Westmoreland region is flanked on the southeast by the Paleoproterozoic Mt Isa Inlier and the Neoproterozoic South Nicholson Basin and in the northwest it is overlapped by Mesoproterozoic sediments of the McArthur Basin (Ahmad, Wygralak, 1990). The northern McArthur Basin is well known for its association with unconformity-related uranium mineralization but the potential for unconformity-related uranium deposits in the southern McArthur Basin and adjacent Westmoreland region has not been fully recognized. The oldest rocks in the Westmoreland region are quartzites and carbonaceous sediments

of the Murphy Metamorphics which are unconformably overlain by the felsic Cliffdale Volcanics and intruded by the comagmatic Nicholson Granite. The McArthur Basin sequence unconformably overlies these units with the oldest formation being the relatively oxidised Westmoreland Conglomerate which is conformably overlain by the mafic Seigal Volcanics. Uranium-copper mineralization occurs close to the upper contact of the Westmoreland Conglomerate with the Seigal Volcanics, as well as within the overlying volcanic rocks, and in dyke-filled fault zones.

Fluid inclusion studies

Fluid inclusion studies have been carried out on quartz veining from Jackson's Pit and Eva uranium mines and the Dianne and St Barb copper prospects in the Westmoreland region. Primary fluid inclusions occur in growth zones in quartz veins with minor chlorite, hematite and secondary copper or uranium minerals. Many low temperature inclusions show signs of necking down and these

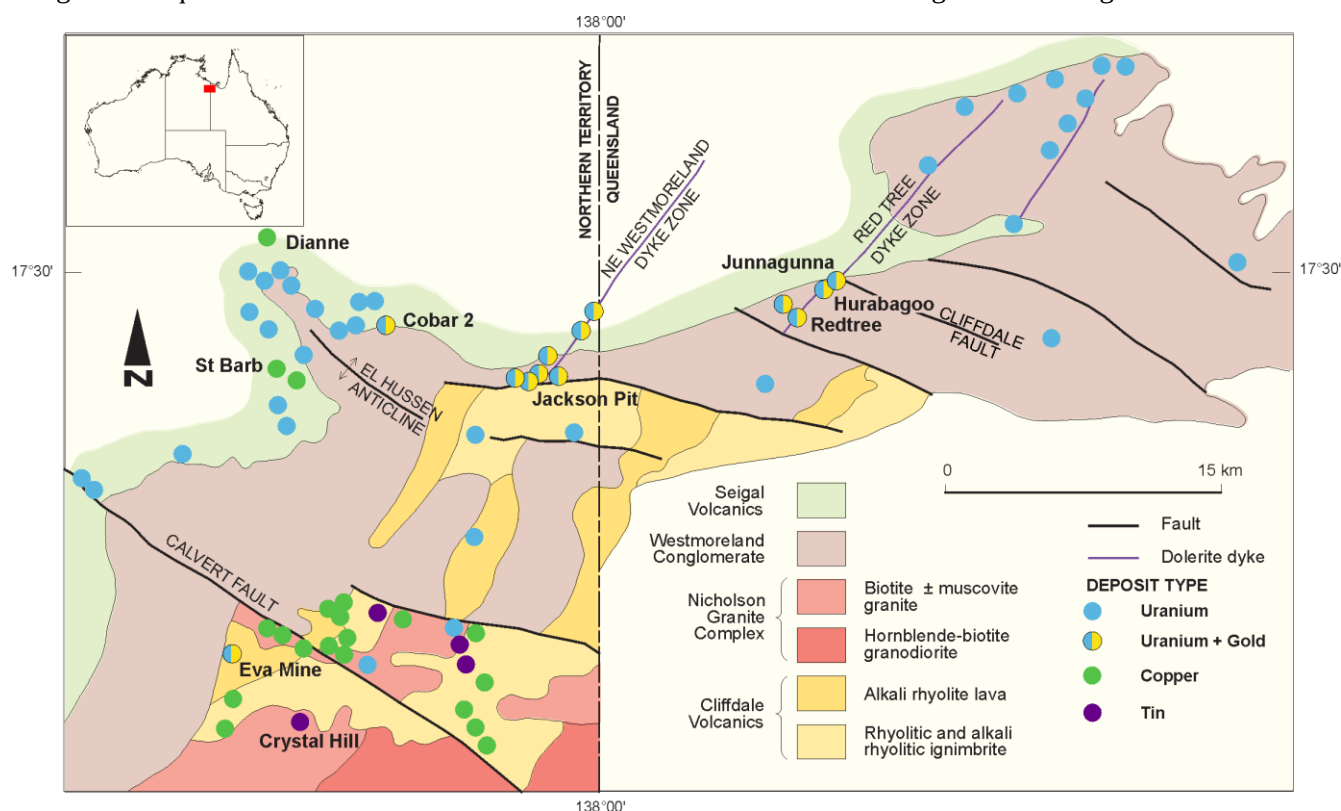


Figure 1. Geological setting of mineral deposits and mineral occurrences in the Westmoreland uranium field (modified from Lally, Bajwah, 2006).

were avoided where possible.

Four types of inclusions have been observed in mineralized quartz veins. Type A, vapour-rich inclusions, contain 30-100 vol.% vapour with varying amounts of $\text{CO}_2 \pm \text{N}_2 \pm \text{CH}_4$. Type B, liquid-rich inclusions, contain up to 30 vol.% vapour. Type C inclusions are liquid-only. Type D, three-phase (vapour + liquid + solid) liquid-rich inclusions, contain a small daughter crystal.

Type A, vapour-rich inclusions and some Type B, liquid-rich inclusions homogenized over the range 171 to 385°C. Other Type B and Type D inclusions typically homogenized between 100 and 240°C with a mode around 120°C, while the presence of liquid-only inclusions suggests trapping at temperatures below 50°C. This may indicate three phases of fluid flow in the region with progressively cooling fluids.

Eutectic melting temperatures as low as -79.8°C in Type B and C inclusions suggest the presence of CaCl_2 and other salts in the fluids. Final ice melting temperatures for Type B and C inclusions fall into two groups. The first group has final melting temperatures below -10°C while the second group shows final melting above -10°C and more typically close to 0°C indicating the presence of low salinity fluids. This suggests mixing between saline basinal fluids and low salinity meteoric fluids that continued down to temperatures below 50°C.

Geochemical modelling

We have applied chemical modelling to the Westmoreland region, using the fluid inclusion data and the geology to constrain the composition of the rocks and fluids in the models. The initial fluids were also assumed to be in equilibrium with the atmosphere. The results show that these fluids are capable of transporting significant quantities of both uranium and copper species. Both these metals will precipitate by interaction of the fluid with the originally Fe^{2+} -rich matrix of the Westmoreland Conglomerate. The interaction of the Westmoreland Conglomerate with the oxidized fluids has resulted in the more oxidized assemblage that currently exists. The modelling also indicates that subsequent fluid flow after uranium and copper precipitation would remobilize the minerals once again. Therefore, preservation of uranium mineralization in the Westmoreland Conglomerate will only occur if there is a cessation of fluid flow after mineralization.

Furthermore, fluids that penetrated deeper into the basin and also interacted with the Nicholson Granite were more likely to form copper-rich deposits when they initially interact with the overlying Seigal Volcanics but uranium-rich

deposits could form at temperatures above 150°C, if fluid flow continued, causing re-dissolution of the copper that precipitated earlier. Therefore, this modelling has demonstrated that higher temperature basinal fluids (up to 200°C), such as those associated with unconformity-related systems, may form high-grade uranium mineralization near the contact with or within mafic volcanics.

The modelling has demonstrated that both uranium and copper mineralization may be associated with unconformity-related systems. It has also demonstrated that fluids in the Westmoreland region were capable of simultaneously transporting uranium and copper and that mineralization was most likely to occur at or above one of the unconformities in this region or when oxidized basinal fluids interacted with reduced mafic dykes or mafic volcanics. In these models, the formation of uranium-rich or copper-rich deposits depends on the degree of fluid-rock interaction which, in turn, controls the oxidation state of the fluid.

The modelling also shows that these deposits are readily remobilized by later interaction with oxidized fluids. Therefore, this suggests there is potential for similar styles of mineralization in the vicinity of carbonaceous sediments and mafic volcanic units of the overlying McArthur Basin. However, one of the most important constraints is the presence of a suitable source rock for both uranium and copper. Rarely are both present. They are in the Westmoreland region (Cliffdale Volcanics for uranium and mafic volcanics or Nicholson Granite for copper).

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FLUID INCLUSIONS OF VEINLETS AND IMPREGNATES IN SEDIMENTARY STRATA OF THE LOPUSHNA OIL FIELD (UKRAINIAN CARPATHIANS)

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Introduction

The Lopushna oil field is located in the thrust structures in the south-eastern part of the Outer zone of the Carpathians Foredeep – a constituent of the Carpathian oil and gas province. Oil deposits are confined to Jurassic, Cretaceous and Paleogene rocks of the platform overlapped by the Folded Carpathians. The reproduction data of thermobaric and geochemical parameters of migration and geochemical specialization of fluid inclusions in minerals of the post-sedimentogenous veins in sedimentary strata of oil and gas fields show promising value of such studies for prediction of new pools of hydrocarbons (Naumko, 2006).

Object of research

We studied fluid inclusions of vein minerals and impregnations in uneven sedimentary layers of the Lopushna oil field. The veins are filled mainly with calcite, sometimes with admixtures of quartz and anhydrite. Fluid inclusions are very small (0.01-0.001 mm and less), often of irregular shape, unevenly mineral saturate grains (Fig. 1). By phase composition gas-liquid inclusions with filling from 70 to 95 % predominate. Sometimes fluid inclusion with hydrocarbons are available in calcite. Homogenization of gas-liquid fluid inclusions in calcite within the limits of various fields of this region ranges from 110 to 218°C (in liquid phase).

The sustained homogenization temperatures of fluid inclusions in the gypsum-anhydrite segregations in adjoining rocks of the Lopushna field average out from 195 to 215 °C (in liquid phase) (Naumko et al., 1999).

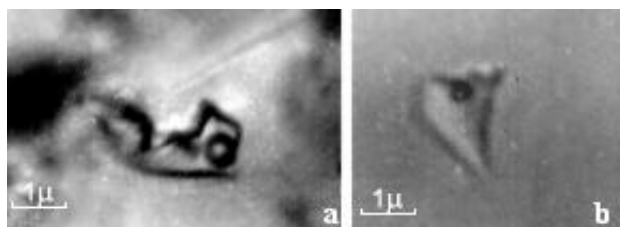


Figure 1. Fluid inclusions in calcite (a) and quartz (b) from veins of the Lopushna oil field.

Volatiles of fluid inclusions

Composition of volatiles of fluid inclusions and closed pores in minerals of veins (mainly calcite, sometimes – quartz and anhydrite) and of adjoining rocks (limestones, argillites, sandstones)

was established by mass spectrometric analysis (mass spectrometer MSH-3A). Volatile components from the same sample batches (200 mg and +1-2 mm fraction) are disengaging oneself as a result of their mechanical milling in a high vacuum.

The relative gas saturation (ΔP) – as an increase of pressure in the affected system of mass spectrometer with respect to its initial value of about $1 \cdot 10^{-3}$ Pa and the water saturation (C_{H_2O}) – as the relative content of steam water (absorber - P_2O_5) in total volume of volatiles were determining. It is established that in all samples of calcite from the veins, consisting of gas after absorbing water vapour predominates methane (86.0–94.6 vol.%) with admixtures of N_2 and CO_2 (Fig. 2). A vapour of water in most investigated samples was determined in significant quantities (69.7–96.1 vol.%).

Especially high concentrations of methane have samples from wells that have a flow of oil. It is typical that within the Lopushna field methane content is higher in veins than in adjoining rocks (see Fig. 2). It should be noted that in samples of the quartz-calcite and calcite- anhydrite veins methane is absent.

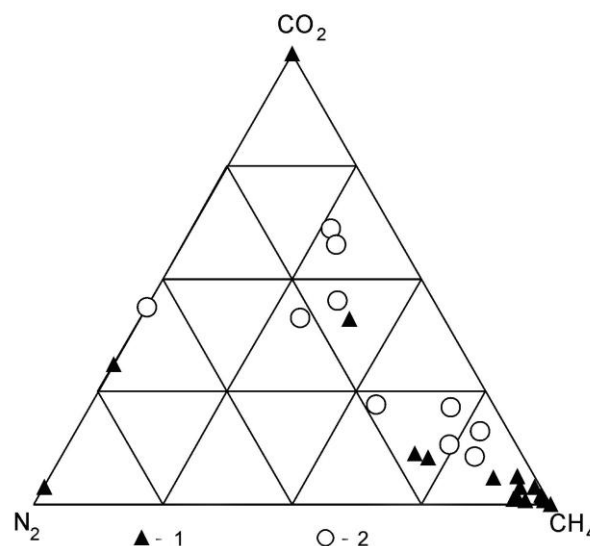


Figure 2 Composition of volatiles of fluid inclusions in minerals of veins (1) and adjoining rocks (2).

Other hydrocarbon compounds are also found in small amounts: ethane (up to 3.5 vol.%) and propane (up to 11.0 vol.%).

The second is the contents of carbon dioxide, occurred in samples from most wells. Overall, for

many different intervals of wells is characteristic sharp prevalence of CO₂ in gases from adjoining rocks (limestone, sandstone, siltstone) compared with gas containing of vein minerals. Nitrogen predominates in the anhydrite-calcite veins of the Stebnyk suite (96.1 vol.%), and its high content for sediments of the Santonian stage (K₂) (69 vol.% in quartz-calcite veins, 56.3 vol.% – in limestones) is typical. Significant is value of ΔP , which gives an idea of the relative gas saturation of the mineral forming fluid. For the investigated samples it varies to a considerable extent mainly within the limit of 1.0 Pa, in some wells reaching 6.93 Pa (Naumko et al., 2007).

It should be noted the high relative water saturation of fluids that determined by indicator C_{H2O}, which shows percentage composition of water in relation to the amount of remaining volatile components of fluid inclusions and closed pores, which was revealed during milling of samples. This value is large enough for vein calcite (96.1-69.7 vol.%) and also for adjoining rocks (86.7-77.8 vol.%).

So, the main component in the gas of fluid inclusions in mineral from veins is methane, and for adjoining rocks – carbon dioxide and nitrogen. It testifies, to that for the fluids at the time of the fissures healing and together with forming of veinlet-impregnated mineralization within oil field, among volatiles, the presence of the major content of saturated hydrocarbons, mainly methane, is inherent.

Conclusions

Within the Lopushna oil field the post-sedimentogenous transformations of sedimentary strata occurred at temperatures up to 200°C, which contributed to preservation of hydrocarbons in the whole stratigraphic range of productive thicknesses. The main volume of gas of inclusions in vein minerals presented by methane is characterized especially by high concentrations from productive zones and by their generally much higher content in comparison with the veins in the adjoining rocks. It testifies to its gas underlay from deep-seated site, once again confirming the notion about the deep-seated specialization of mineral forming fluids of the Folded Carpathians.

At the same time, in the adjoining rocks the carbon dioxide and nitrogen generally dominated as a result of catagenetic transformations of dispersed organic matter in them. Almost all samples are characterized by high relative gas and water saturation. All these facts indicate the transfer of hydrocarbons composed of heterogeneous carbohydrate-water system.

Migration processes stand out here by the

presence of at least two stages of influxes of hydrocarbons containing fluids divided by temperature-time stretch (Naumko, 2006), one of which appeared between Middle and Upper Pliocene. Migration proceeded first by vertical longitudinal and transverse deep faults that divide some blocks of field, and after laterally within concrete structures through the collectors that from the top and bottom by impermeable strata are limited (fluid-confining strata).

Comparison of volatiles of fluid inclusions, in water soluble and free gases and salt composition of solutions of the inclusions and formation water testifies to their inflow as a part of deep-seated high-temperature deep fluid (Naumko, Svoren', 2003) from a single homogeneous source. The data of isotopic analysis of carbon and oxygen in calcite from veins and adjoining rocks testify to that (Naumko et al., 2006).

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PHYSICO-CHEMICAL PARAMETERS OF TIN AND TUNGSTEN ORE DEPOSIT FORMATION

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Based on our database including above 18500 references on the fluid and melt inclusions in minerals we present the generalization on physico-chemical parameters of the tin and tungsten ore deposits and non-economic localities. The database compiles 320 worldwide Sn and Sn-W objects and 253 W and W-Sn objects. For most typical minerals (quartz, cassiterite, wolframite, scheelite, topaz, beryl, tourmaline, fluorite and calcite) the histograms of homogenization temperature of fluid inclusions are presented.

Results

The majority of 463 cassiterite determinations correspond to 300-500°C interval with the maximum at 300-400°C, whereas similar data for 453 wolframite and scheelite are in the range 200-400°C with the maximum at 200-300°C. The representative data on pressure estimates of hydrothermal fluids for the Sn (330 determinations) and W (430 determinations) objects is discussed. The total pressure data range on preceding, ore and post-ore stages is rather broad: from 70-110 bar up to 6000-6400 bar. High pressures of ore preceding stages could be interpreted in terms of the genetical link with acid magmatism. About 50% of pressure data correspond to 500-1500 bar interval. The total salinity and temperature range of mineral-forming fluids of Sn (1800 determinations) and W (2070 determinations) is very broad: 0.1-80 wt.% eq. NaCl and 20-800°C. The predominant part of the data correspond to salinity of <10 wt.% eq. NaCl (~60%) and 200-400°C (~70%).

The average volatile composition of fluids was calculated using different methods. It was found that H₂O, CO₂, CH₄ and N₂ are main components.

The W-ore deposits are characterized by higher CO₂ content than the Sn-ore deposits. Raman-spectroscopic data on fluid gas composition are presented in Table 1 and Figure 1. The W-ore deposits are characterized by predominantly CO₂-fluids with lower (but sufficiently high) CH₄ and N₂ content. The fluid inclusions in ore minerals showed that fluids in cassiterite are significantly enriched in CO₂ (63.8 mol.%) in relation to average CO₂ content of the Sn-ore deposits. The CO₂ data for wolframite are substantially lower (43.3 mol.%).

Tin and W concentration in magmatic melts and mineral-forming fluids were evaluated by use of individual inclusion analyses. The mean geometrical value of the Sn content in melts was found as 77 ppm (confidence interval +520/-67) of 605 determinations. Mean Sn-content in fluids (253 determinations) is 132 ppm (+630/-109). For tungsten the following parameters were found: mean value for the magmatic melts (489 determinations) is 5.5 ppm (+60/-5.0) and in mineral-forming fluids those are 30 ppm (+144/-25) for 391 determinations.

Acknowledgements

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Table 1. The average composition (mol.%) of gaseous phase in natural fluids from worldwide objects (Naumov et al., 2009; Mironova, 2010) in comparison with fluid inclusion composition of the Sn-ore and W-ore deposits.

	CO ₂	CH ₄	N ₂	H ₂ S
Natural fluids* (Naumov et al., 2009; Mironova, 2010)	65.9	20.1	13.4	0.57
Tin ore-deposits (181)	43.2	41.5	20.1	0.16 (73)
Tungsten ore-deposits (188)	56.1	30.7	13.2	0.01 (69)

* - additionally contain 0.03 mol.% of H₂ and CO. The number of determinations is shown in parentheses.

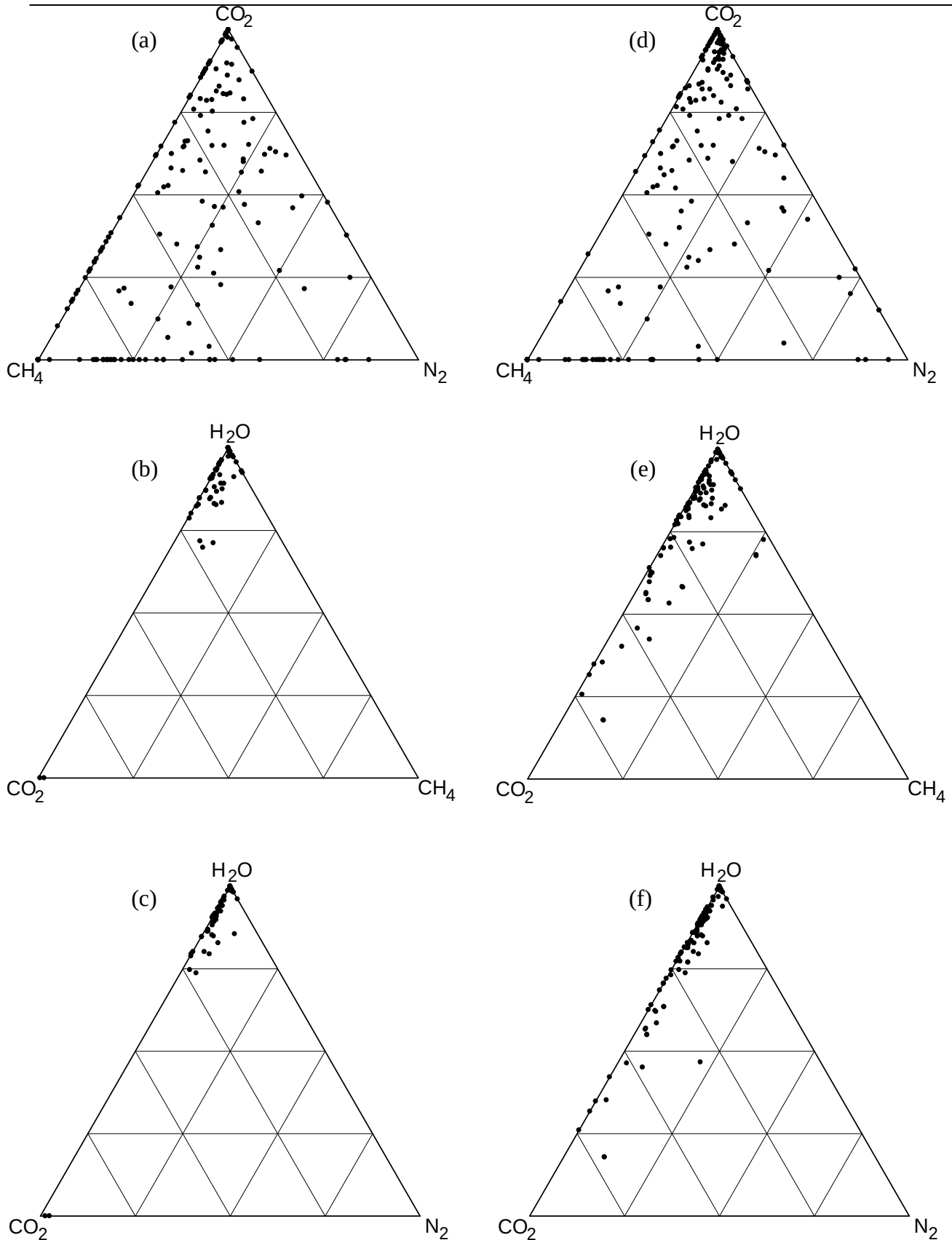


Figure 1. Diagrams showing proportions of gas components in natural mineral-forming fluids from the Sn-ore (a-c) and W-ore deposits (d-f). Number of determinations: (a) 180, (b) 61, (c) 61, (d) 188, (e) 112, (f) 112.

PECULIAR MELT INCLUSIONS IN QUARTZ PHENOCRYSTS OF ROȘIA MONTANĂ DACITE BRECCIA HOSTED EPITHERMAL AU-AG DEPOSIT (ROMANIA)

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Introduction

The epithermal Au-Ag deposit Roșia Montană is located within the gold-mineralized province of the Apuseni Mountains. The deposit is related to Neogene volcanism and composed by pipes of mineralized explosion breccias formed inside of dacitic diatremes that have been intruded through volcanogenic-sedimentary and sedimentary rocks of Cretaceous age. The isotopic age of dacites is 13.61 ± 0.07 Ma (Kouzmanov et al., 2005). Fragments of breccias are strongly altered hydrothermally and cemented by quartz gangue material comprising also rhodochrosite, pyrite, arsenopyrite, chalcopyrite, sphalerite, galena, fahlore, silver sulfosalts and gold. Breccia pipes are surrounded by zones of anastomosing veins and disseminated mineralization. The processes of hydrothermal alteration are best manifested in dacites as advanced argillization, adularization, sericitization and silicification.

Melt inclusion study

Crystalline and melt inclusions were studied in large (up to 2 cm) bipyramidal quartz crystals from the dacitic and rhyolitic Cetate and Cărnăk subvolcanic bodies. The fluid inclusions in similar quartz phenocrysts have been earlier considered in Wallier et al. (2006). The melt inclusions were analyzed with an electronic microprobe Cameca SX-100 (in Moscow, Russia) and with an ion microprobe IMS-4f (in Yaroslavl, Russia). The following minerals were identified among the crystalline inclusions: plagioclase (An_{51-62}), orthoclase, amphibole (F - 0.19 wt.%, Cl - 0.04 wt.%), zircon, magnetite (TiO_2 - 2.8 wt.%) and an iron sulfide. The size of the majority of melt inclusions did not exceed 10-15 μm , only sometimes they reached 25-30 μm . The analysis of glasses of these inclusions has allowed identifying various melt types (Fig. 1).

The first type of melt according to analyses of 7 inclusions is very unusual, not described yet in the literature (in wt.%: 75.7 SiO_2 , 0.21 TiO_2 , 5.5 Al_2O_3 , 6.1 FeO, 0.13 MnO, 1.9 MgO, 3.1 CaO, 3.0 Na_2O , 2.9 K_2O , 0.07 P_2O_5 , 0.04 Cl). A ferroan phlogopite could be a source of such high contents of Fe, Mg and K.

The second melt type, also from analysed 7

inclusions, on the contrary, is typical of felsic magmas (in wt.%: 76.4 SiO_2 , 0.08 TiO_2 , 13.3 Al_2O_3 , 0.6 FeO, 0.09 MnO, 0.2 MgO, 3.2 CaO, 4.0 Na_2O , 1.8 K_2O , 0.06 P_2O_5 , 0.06 Cl). Comparison of these melt compositions reveals essential difference in Ti, Al, Fe, Mg, Na and K.

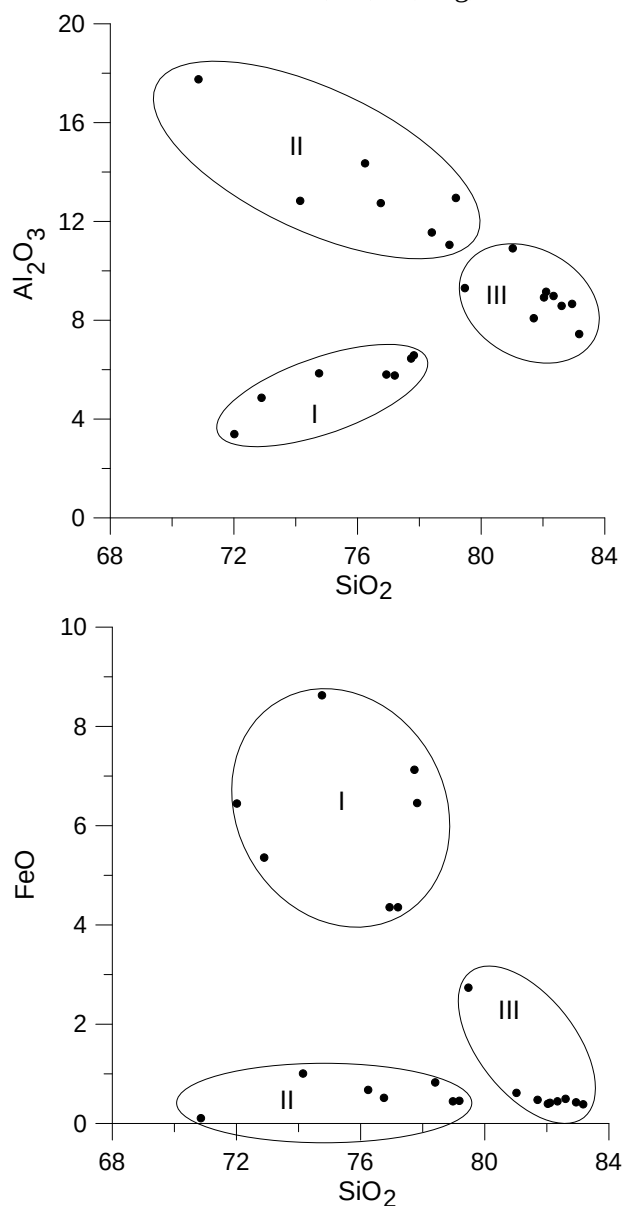


Figure 1. Variation diagrams $SiO_2 - Al_2O_3$ and $SiO_2 - FeO$ for compositions of melt inclusions in quartz phenocrysts from Roșia Montană.

For the third melt type, from the data for 9 inclusions, it is seen much higher silica content

and rather ordinary concentration of alumina (in wt.%: 82.0 SiO₂, 0.12 TiO₂, 8.9 Al₂O₃, 0.7 FeO, 0.07 MnO, 0.3 MgO, 1.4 CaO, 3.6 Na₂O, 1.7 K₂O, 0.05 P₂O₅, 0.03 Cl). The high total content of components in analyses of melt inclusions (98.5-99.7 wt. %) attest a low water content of these melts. Due to small sizes of studied inclusions, only one of them, belonging to the second melt type, we succeeded to analyze with the ion microprobe. Data obtained for 28 elements (in ppm) are as follow: 1700 H₂O, 3.8 F, 10.3 Li, 0.69 Be, 5.7 B, 12.1 Y, 7.1 La, 15.0 Ce, 1.3 Sm, 6.4 Nd, 0.25 Eu, 1.5 Gd, 1.6 Dy, 1.4 Er, 1.6 Yb, 1.2 Cr, 6.7 V, 25.5 Rb, 20.0 Zr, 6.2 Nb, 111 Sr, 191 Ba, 0.68 Hf, 0.66 Ta, 1.94 Pb, 2.73 Th, 1.37 U, 21.6 Cu.

Acknowledgements

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HYDROTHERMAL FLUIDS AND VEIN-TYPES IN THE OROGENIC GOLD-BEARING HUTTI MASKI GREENSTONE BELT, KARNATAKA, INDIA

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Introduction

Evolution of hydrothermal fluids and emplacement of veins of various generations is an important problem that needs to be addressed in understanding gold mineralization in greenstone belts. The present study attempts to document the nature of different fluids that have been observed in hydrothermal veins of various generations in the Hutti-Maski schist belt, the major gold-producing greenstone belt of India.

In the Hutti-Maski schist belt gold mineralization is associated with discrete shear zones that localize fluid flow. The major zone of gold mineralization is located in the north-western part of the belt ($\sim 76^{\circ}38' - 76^{\circ}50'N$ and $16^{\circ}14' - 15^{\circ}50'E$) and is the site of the Hutti gold mine. The schist belt comprises metavolcanics and subordinate metasedimentary rocks and is surrounded by gneisses, granites and granitoids. The metavolcanics include abundant pillowed basalt and thin units of felsic volcanics of dacitic composition. Metasediments include banded hematite quartz, chlorite schists and rare carbonate rocks. In the Hutti deposit, gold occurs in nine sub-parallel quartz reefs that trend NNW (dip $\sim 70^{\circ}$ westward) and in altered wall-rocks that occur beside it. The structural setting of the Hutti schist belt indicates that the terrain experienced four phases of deformation of which the first two deformations (D1 and D2) have pronounced effects (Roy, 1979; 1991). Veins of quartz, scheelite, calcite and rare barite are associated with different episodes of deformation in the schist belt.

Vein-types studied

In the Hutti schist belt, quartz veins are basically of two types. These can be classified as quartz veins related to the D1 deformation (D1 quartz) and quartz veins associated with shear zones (Sm quartz). Chronologically the Sm quartz veins may post-date the D1 quartz veins although on the basis of field data both are inferred (Roy, 1991; Nevin et al., 2010) to result from the first phase of deformation. The other veins studied include scheelite veins related to the Sm quartz and post-ore barite and calcite veins.

Fluid inclusion petrography of vein-types

The D1 quartz veins were collected from the surface exposures. These represent quartz veins that

are tightly folded into isoclinal folds and those that occur on the limbs of such folds. Fluid petrography on D1 quartz shows that there are two types of primary fluid inclusions i.e. monophasic (Type I) fluid inclusions and biphasic (Type II) fluid inclusions. The Type I inclusions mainly appear as three dimensional arrays of small ($<20 \mu m$) irregular inclusions. The Type II fluid inclusions are small ($5-20 \mu m$), sub-rounded to irregular in shape and possess variable degree of fill (L:V = 90:10 to 10:90). In some carbonic fluid inclusions the vapour bubble adheres to a small solid graphite grain. Such fluid inclusions are classified here as biphasic fluid inclusions.

The D1 quartz samples also contain secondary monophasic, biphasic and polyphasic aqueous fluid inclusions. Polyphasic fluid inclusions are elongated and irregular and may contain one or more daughter crystals with or without a vapor phase.

Sm quartz veins occur parallel to mylonitic foliation of shear zones and are sheared and recrystallized to variable degrees. Porphyroclasts of quartz embedded in recrystallized matrix in these quartz veins contain fluid inclusions. Despite the high degree of deformation undergone by the porphyroclasts, they are seen to contain the Type I fluid inclusions $5 \mu m$ to $20 \mu m$ in size in clusters and as isolated fluid inclusions and within the body of the porphyroclasts. The Type II fluid inclusions that occur as isolated fluid inclusions in the body of porphyroclasts are very few and these vary in size from $7 \mu m$ to $15 \mu m$ and have variable degree of fill (L:V = 90:10 to 20:80). Other monophasic, biphasic and polyphasic fluid inclusions occur in fracture trails that cut across porphyroclasts of the sheared quartz. More detailed work on quartz veins related to Hutti shear zone can be found in Pandalai et al. (2003).

Fluid inclusion petrography reveals that scheelite has the Type I and Type II primary fluid inclusions (Nevin, Pandalai 2008). The Type I inclusions are mostly irregularly shaped inclusions of $5 \mu m$ to $20 \mu m$ size. The Type IIa are carbonic fluid inclusions ($5-25 \mu m$ in size) of slightly dark hue and of rectangular, oval or irregular shape. The Type IIb are aqueous inclusions of $\sim 10-12 \mu m$ size that are common in scheelite. The fluid inclusions are slightly pinkish in appearance with a liquid to vapor ratio of 90:10 to 80:20. The polyphasic fluid inclusions reported in quartz veins of Hutti

(Pandalai et al., 2003) are not observed in scheelite.

Calcite and barite veins studied are post-ore veins and the fluid inclusions in them belong to the Type I and Type II categories. While in barite, the fluid inclusions are either primary or pseudo-secondary in nature (Nevin, Pandalai, 2010), calcite shows primary, pseudo-secondary and secondary fluid inclusions.

Laser-Raman and microthermometric studies

The Laser-Raman and microthermometric studies were carried out on fluid inclusions of the above-mentioned vein samples. D1 and Sm quartz and scheelite show presence of CO₂, CH₄ and H₂O with or without graphite. Similar studies on the primary fluid inclusions on the post-ore barite and calcite veins reveal that they are aqueous in nature.

The summary of microthermometric studies on primary fluid inclusions discussed above is given in Table 1. Microthermometric studies indicate that the D1 quartz, Sm quartz and scheelite contain carbonic and aqueous primary fluid inclusions whereas post-ore barite and calcite primarily contain only aqueous fluid inclusions.

Conclusions

The fluid inclusion studies of the D1 quartz, Sm quartz and scheelite indicate that while during the first phase of deformation fluids have evolved

from a fluid of CO₂-CH₄-H₂O-NaCl composition, fluids of the post-ore hydrothermal episodes are purely aqueous in nature. While early gold-bearing fluids were reduced, post-ore hydrothermal fluids record a relatively more oxidized condition.

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Table 1. Microthermometric data of primary inclusions in different types of vein samples (a: CO₂-CH₄-H₂O-NaCl; b-i: low-salinity H₂O-NaCl; b-ii: high-salinity H₂O-NaCl; c: low X_{CO₂}, H₂O-CO₂-CH₄-NaCl).

Sample			Tf	Tm CO ₂	Te	Tm ice	Tm CLA	Th CO ₂	Th total
D1 Quartz	Monphase		-124 to -96	-72 to -62				-25.4 to 7 (L)	
	Biphase	a	-116 to -90	-72 to -66			9 to 14	-12 to 9 (L)	291 to 324 (L)
		b-i	-40 to -35			-2 to -1			
		c	-56 to -43			-5 to -2	7.2 to 16		280 to 283 (L)
Sm Quartz	Monphase		-100 to -80	-62 to -56.6				-10 to 16 (L)	
	Biphase	a	-96 to -82	-57 to -56.6			6 to 9.8	-6.1 to 29 (L)	236 to 316 (V)
		b-i	-51 to -33		-32 to -23	-2 to -0.9			
Scheelite	Monophase		Changes not observed may contain CH ₄ (?)						
	Biphase	a	-96 to -80	-80 to -57.1		-24 to -1.4	6.3 to 18		225 to 406 (L)
		b-i	-56 to -35		-40 to -24	-8 to -1			130 to 196 (L)
		b-ii	-84 to -60		-54 to -38	-25 to -11.6			133 to 163 (L)
Barite	Monophase		-80 to -45		-45 to -30	-14 to -10			
	Biphase		-65 to -43		-45 to -30	-14 to -6			150 to 125 (L)
Calcite	Monophase		-55 to -42		-37 to -24	-2 to -0.7			
	Biphase		-50 to -42		-37 to -24	-6 to -0.7			80 to 130 (L)

PHYSICO-CHEMICAL CRYSTALLIZATION CONDITIONS OF LEUCITE-WOLLASTONITE MELILITOLITES AND CONTACT WOLLASTONITE-ANORTITE-PYROXENE ROCKS OF COLLE FABBRI (CENTRAL ITALY)

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Introduction

Leucite-wollastonite melilitolites make up the central part of the subvolcanic body at Colle Fabbri. Wollastonite-anortite-pyroxene rocks occur at the contact with host pelites on the periphery of the body (Stoppa, Sharygin, 2009). Melilitolites of Colle Fabbri, the same as other high-potassium Ca-rich rocks from the ULUD province, are referred to kamafugite series (Stoppa et al., 2002). However, the subvolcanic body at Colle Fabbri differs from volcanic structures of the ULUD in phreatic explosion with extrusive breccias and underground explosions (Stoppa, Rosatelli, 2009). The distinctive feature of Colle Fabbri is the presence of wollastonite in rocks. Wollastonite is absent in all other rocks of the ULUD and is not common of typical kamafugites.

Petrography of rocks

Leucite-wollastonite melilitolite consists of nearly equal amounts (35-40 vol.%) melilite and wollastonite and a minor amount of leucite, plagioclase, Ti-garnet, apatite, magnetite, and Fe-Ni-sulfides. The *contact wollastonite-anortite-pyroxene rock* consists of phenocrysts of clinopyroxene and wollastonite (25-28 vol.%) and plagioclase microphenocrysts. Fine-grained groundmass is represented by plagioclase, clinopyroxene, ore phases and glass.

The chemical composition of Lc-Wo melilitolites is drastically undersaturated in SiO₂ (about 42 wt.%) with a low content of Al₂O₃ (10.7 – 11.2 wt.%) and extremely high CaO (37.3 – 38.5 wt.%). Despite the presence of leucite in the rocks, the total amount of Na₂O+K₂O is low (1.4-1.9 wt.%). The contents of MgO (1.6-2.4 wt. %) and FeO (3.3-3.7 wt.%) are low. The contact Wo-An-Px rock compared to Lc-Wo melilitolite has higher concentrations of SiO₂ (up to 53.1 wt.%), Al₂O₃ (up to 13.8 wt.%) and lower contents of CaO (18.2 – 22.9 wt.%).

Melt inclusions in minerals

Melilite grains (Table 1, an. 1) from Lc-Wo melilitolite contains single partly crystallized melt inclusions (up to 50 µm). Their phase composition is glass, garnet (Table 1, an. 4), ore phases and gas bubble (Fig. 1). Inclusions homogenize at 1320 ± 15°C.

Glasses from unheated inclusions are nonuniform (Table 1, ans. 2 and 3): compared to rims, the core of inclusions contains more Si, Al и K. They also contain Ti and P, but considerably lesser Ca and lack Fe and Mg. The rims of inclusions are characterized by the total absence of Ti and P. This nonuniformity suggests that the melt conserved in the inclusions is heterogeneous.

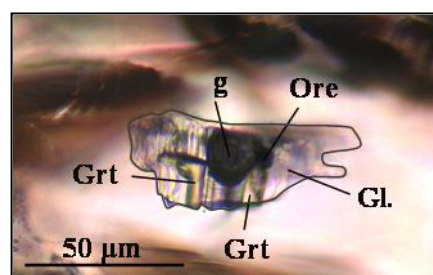


Figure 1. Melt inclusion in melilite from Lc-Wo melilitolite (transmitted light).

Table 1. Chemical composition (wt.%) of phases from inclusions (2-4) in melilite (1), Lc-Wo-melilitolite.

Oxide	melilite	glass	glass	garnet
	1	2	3	4
SiO ₂	35.76	50.45	46.81	29.62
TiO ₂	0.00	1.27	0.00	21.28
Al ₂ O ₃	17.36	22.06	20.74	18.21
FeO	2.47	0.00	1.57	1.36
MgO	6.10	0.00	1.32	0.00
CaO	38.30	6.49	16.67	28.70
K ₂ O	0.00	17.23	12.90	0.83
P ₂ O ₅	0.00	2.50	0.00	0.00
Total	99.99	100.00	100.00	99.99

In the phenocrysts of *wollastonite* (Table 2, an. 1) from contact Wo-An-Px rocks we also found colorless and brownish, partly crystallized inclusions (<20 µm). Their phase composition is glass, Ca-silicate (Table 2, an. 6), and a gas bubble (Fig. 2). The homogenization temperature of inclusions is slightly higher than 1210°C.

The chemical composition of unheated glasses varies considerably in the contents of Si, Al, Ti, Fe, Mg, Ca Na and K (Table 2, ans. 2 and 3). The composition of heated glasses varies as well (Table 2, ans. 4 and 5). Heated inclusions compared to unheated ones contain more Fe, Mg, and Ca, but are less enriched in Si, Al, Ti and alkalis. The evolution of chemical composition from heated to unheated inclusions is not pronounced with

deviations for nearly all components. This is most probably related to the contamination of initial magma by host pelites and addition of major components as SiO_2 , Al_2O_3 and alkalis into the melt.

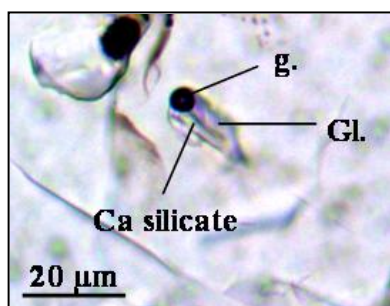


Figure 2. Melt inclusions in wollastonite from contact Wo-An-Px rock (transmitted light).

Table 2. Chemical composition (wt.%) of phases from inclusions (2-6) in wollastonite (1) from contact Wo-An-Px rock.

Oxide	Wo	Glass of unheated inclusions		Glass of heated inclusions		Ca silicate
	1	2	3	4	5	6
SiO_2	53.81	57.86	72.80	57.11	71.82	57.73
TiO_2	0.00	0.30	1.17	0.00	0.72	0.00
Al_2O_3	0.00	20.61	12.03	13.51	10.71	2.40
FeO	0.00	2.29	0.91	3.52	1.00	3.94
MgO	0.96	0.48	0.04	1.71	0.00	1.86
CaO	45.22	12.80	2.34	21.97	6.81	32.46
Na_2O	0.00	1.52	0.66	0.00	0.00	0.00
K_2O	0.00	4.35	6.70	2.16	8.91	1.60
ZrO_2	0.00	0.07	0.21	0.00	0.00	0.00
P_2O_5	0.00	0.29	0.07	0.00	0.00	0.00
Total	99.99	100.50	96.92	100.00	100.00	99.99

Glassy inclusions were also found in *anorthite* (Table 3, an. 1) of contact rock (Fig. 3). Their size reaches 20-30 μm . The brownish glass of inclusions contains colorless Si-rich glassy globules with a gas bubble of about 1.5 μm in size.

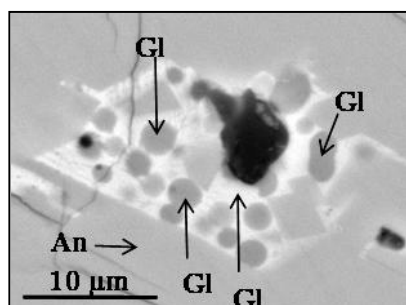


Figure 3. Melt inclusion in anorthite from contact Wo-An-Px rock (reflected light).

The chemical composition of brownish glass (Table 3, an. 2) of unheated inclusions in anorthite, compared to colorless globules (Table 3, ans. 3-5) contains more Fe, Ti and less Si. This also

evidences that the melts trapped in inclusions are heterogeneous and supports the assumption that the host pelites, which were not completely dissolved in the initial magma melt, were contaminated by magma.

Table 3. Chemical composition (wt.%) of inclusion glasses (2-5) in anorthite (1) from contact Wo-An-Px rock.

Oxide	An	Glass	Glass	Glass	Glass
	1	2	3	4	5
SiO_2	47.12	57.36	66.15	68.33	74.07
TiO_2	0.00	1.13	0.00	0.00	0.00
Al_2O_3	32.55	6.37	10.65	10.62	10.09
FeO	0.75	7.99	4.03	3.22	1.58
MgO	0.00	3.60	1.34	0.78	0.85
CaO	18.65	21.66	13.88	13.00	6.95
Na_2O	0.90	0.00	0.00	0.00	0.63
K_2O	0.00	1.88	3.94	4.04	5.81
Total	99.97	99.99	99.99	99.99	99.98

Conclusions

Therefore, thermometric data suggest that the crystallization of leucite-wollastonite melilitolites started at $1320 \pm 15^\circ\text{C}$. The contact wollastonite-anorthite-pyroxene rocks formed at temperatures much lower than 1210°C .

The inhomogeneity in the composition of inclusions in melilite of Lc-Wo melilitolite and in the composition of inclusions in wollastonite of contact Wo-An-Px rocks and the presence of immiscible glasses in anorthite inclusions of the contact Wo-An-Px rocks suggests heterogeneity of melts conserved in the inclusions. This can be, to some extent, related to the assimilation of host pelites.

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TITANIUM ORE FORMATION AND RELATION TO UHP ECLOGITES, DONGHAI, CHINA: AN INFRARED MICROTHERMOMETRIC STUDY OF FLUID INCLUSIONS IN RUTILE

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Introduction

The Dabie-Sulu belt between the North China plate and the Yangtze plate is one of the largest ultrahigh-pressure (UHP) metamorphic belts in the world and is the product of plate subduction and continental collision (Xu et al., 2003). The Sulu UHP metamorphic belt near the Maobei village of the Donghai county, Jiangsu Province was sampled by a 5000 m-deep drill hole of Chinese continental scientific drilling project (CCSD) (Xu et al., 2005).

In the Donghai area titanium-rich rutile eclogites are not only the host but also the parent rocks of the rutile deposit. The eclogites in gneiss are most rich in rutile and most economic. The proved rutile reserves in the Donghai area amount to 300×10^4 t. In particular, the Maobei rutile deposit is hosted in rutile-rich eclogites with a reserve of over 100×10^4 t; and the largest stratiform ore body lies on the east flank of the Niushan-Ahu overturned anticline, extending 2820 m in near north-south direction and ranging from 4 to 210 m with an average of 130 m in width (Fan, 1997).

A systematic infrared thermometric study on fluid inclusions was carried out in rutile from the CCSD eclogites in the Donghai area, eastern China. This work aims to directly obtain the information of the composition and property of mineralizing fluids of rutile deposits, and further to gain insight into the process and evolution of fluids during subduction and exhumation of the Sulu UHP metamorphic belt.

Analytical methods

Doubly-polished thin sections were prepared from samples of rutile-bearing eclogites. By using BX51 infrared microscope, the images of fluid inclusions in the thin sections were transformed to the monitor through a high-resolution camera for observation. The fluid inclusions in rutile were selected for microthermometric measurements, which were carried out on the Linkam-THMS600 heating-freezing stage made in UK (temperature range: -195°C – $+600^\circ\text{C}$). The stage was calibrated by measuring the melting points of pure water inclusion (0°C), pure CO_2 inclusion (-56.6°C) and potassium bichromate (398°C). The accuracy of measured temperatures is about $\pm 0.2^\circ\text{C}$ during cooling and about $\pm 2^\circ\text{C}$ between 100 – 600°C . The

compositions of individual (single) inclusions in some translucent rutile were also analysed on a Renishaw RM2000 Raman microprobe using an Ar ion laser with a surface power of 5 mW for exciting the radiation (514.5 nm); the detector CCD area is 20 and the scanning range of spectra was set between 200 – 3800 cm^{-1} with an accumulation time of 60s for each scan. All the fluid inclusion studies were carried out in the State Key Laboratory for Mineral Deposit Research, Nanjing University.

Type and occurrence of fluid inclusions in rutile

Petrographic observations show that rutile in eclogites has three occurrences, that is occurs as: (1) fine-grained euhedral crystals included mainly in (the cores of) garnet, omphacite, phengite, and subordinately in zoisite and quartz; (2) euhedral to subhedral grains with smooth boundary in equilibrium with garnet, omphacite, phengite and kyanite; (3) discrete and bead-like veinlets, aggregates and megacrysts filling in cleavage, cracks and grain boundaries of garnet, omphacite and phengite.

Rutile occurred as veinlets, aggregates and megacrysts was formed after the peak UHP metamorphism, probably during retrograde metamorphic stage. Fluid inclusions with relatively large size are widespread in it and are used for this study.

Three types of fluid inclusions in rutile were recognised: aqueous (H_2O) (Type I), CO_2 - H_2O (Type II) and CH_4 -bearing (Type III) inclusions.

Conclusions

(1) Three types of fluid inclusions, aqueous (Type I), CO_2 - H_2O (Type II) and CH_4 (Type III) inclusions, are present in the rutile formed in the retrograde metamorphic stage of eclogites in the Donghai area of Jiangsu province, China. The Type I and II inclusions were trapped during the eclogite-facies recrystallization and early amphibolite-facies retrogression stages, whereas the secondary H_2O inclusions were trapped in the amphibolite-facies retrogression or even later during the exhumation history of the UHP rocks. The Type III inclusions were probably trapped in the late exhumation stage.

(2) Concentration and mineralization of rutile took place mainly during the exhumation of the

UHP metamorphic rocks: in the recrystallization of eclogites and/or the early amphibolite-facies retrograde metamorphism, with the decrease in pressure and fluid salinity the solubility of rutile in fluids decreased, and rutile was deposited when the fluids flew along joints and fissures in the eclogites.

(3) Infrared microscopy is a new approach to study fluid inclusions in translucent and opaque minerals and fluid inclusions in rutile provide the constraints on the composition and properties of the fluids present during the exhumation of UHP metamorphic rocks and on the uplift history of the metamorphic terrain, as well.

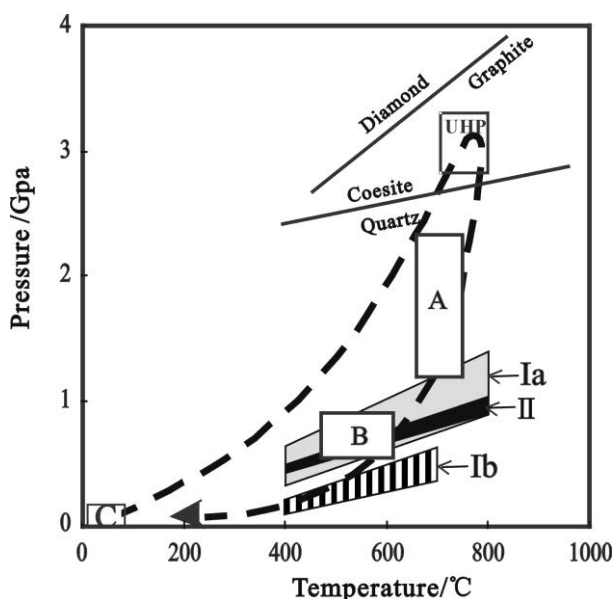


Figure 1. P-T path of eclogites from the Sulu ultrahigh-pressure metamorphic belt and fluid inclusions isochors in rutile (modified after Zheng, 2004; Shen et al., 2005).

UHP - ultrahigh-pressure eclogite-facies metamorphic stage; A: eclogite-facies recrystallization stage; B: amphibolite-facies retrogression stage; C: near surface conditions before subduction; Ia: range of isochors for primary and pseudosecondary H₂O inclusions; Ib: range of isochors for secondary H₂O inclusions; II: range of isochors for CO₂-H₂O inclusions.

Acknowledgments

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THE KEY CHARACTERISTICS OF THE FLUID INCLUSIONS IN THE GOLD DEPOSITS IN THE SANANDAJ-SIRJAN ZONE (SSZ), IRAN

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Introduction

The Sanandaj-Sirjan Zone (SSZ) in the Arabia-Eurasia collision zone, trends NW-SE, has been evolved during a complex geological history that lengthened Late Precambrian to Tertiary, accompanied by multiple deformation events and local green schist to amphibolite facies metamorphism (Mohajjel et al., 2003; Moritz et al., 2006). It is located between two main tectono-sedimentary units of central Iran (CI) and the Zagros Fold-Thrust Belt (ZFTB) (Fig. 1). Subduction of the Neo-Tethyan sea floor under CI along the SSZ has occurred prior to the Middle Triassic (Berberian, King, 1981). The SSZ represents a polyphase deformation, in which the youngest has been identified as a consequence of the collision between Arabia and Eurasia which resulted in southward propagation of the fold-thrust belt (Alavi, 1994). Extension-related successions in the SSZ are mainly occurred in Late Triassic (Mohajjel et al., 2003). An exhumed metamorphic ductile-brittle sheared belt, the SSZ appears to be a promising area for further studies on the syn-orogenic gold deposits (e.g. Heidari et al., 2006; Moritz et al., 2006; Padyar et al., 2009). In this study, we report the fluid inclusion characteristics of the gold mineralization in the shear zones in the SSZ (Fig. 1). They are resulted from post dated metamorphism shearing zone crosscutting the host rocks and located in the Muteh and Saghez (including three deposits: Qolqoleh, Kervian, Ghabaghlogh).

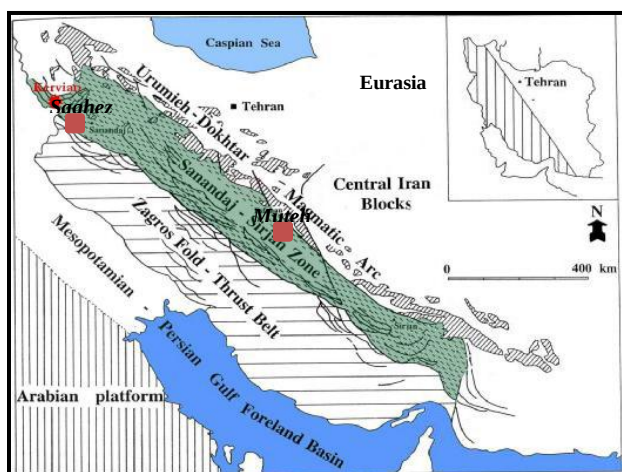


Figure 1. Location of the Muteh and Saghez gold deposits displayed in red square are situated in the SSZ. SSZ is highlighted in a green belt.

Table 1. Summarized results for four types of the fluid inclusions in the Saghez complex.

type	Tm CO ₂ (°C) Mean	Tm H ₂ O (°C) Mean	Tm clath (°C) Mean	Th CO ₂ (°C) Mean	Th(°C) Mean
Ia		-0.7 - -12.5			180-360
Ib			2-12.6		
IIa	-57.8 - -59.1	-5.4 - -10.9		18-30	250-400
IIb					(Td)
III	-58 - -58.8	-7 - -11.5	2.6-13.1	23-24	370-420
IV	-58 - -60.9			20-26	

Continuation of Table 1.

Category	type	Phases	Tm CO ₂ (°C) Mean
Aqueous	Ia	L+V (a - clathrate detected)	
	Ib	(b - clathrate not detected)	
Bicarbonate	IIa	Triphase, aqueous bicarbonate	-57.8 - -59.1
aqueous	IIb	a=homogenized to liquid b=homogenized to vapor	
aqueous ± bicarbonate and solid	III	aqueous ± carbonic + solid (homogenized to liquid; solid does not melt).	-58 - -58.8
Bicarbonate	IV	Mono-, bicarbonate	-58 - -60.9

Gold deposits in the Saghez complex

This complex is located in the NW end of the SSZ and includes three deposits: Qolqoleh, Kervian and Ghabaghlogh. Gold mineralization is mainly concentrated along the ductile shear zones. The host rocks of the gold deposits are predominantly acidic to basic, highly deformed metavolcanics with mylonitic foliation; the deposit consists of pyrite, chalcopyrite, arsenopyrite and pure gold. Hydrothermal alteration associated with ore formation consists of quartz, mica, carbonate and feldspars. The results of the petrographic and fluid inclusion microthermometry carried out on the sulfide-bearing siliceous lenses are presented in Table 1.

According to Table 1, the melting temperature within a range for CO₂ (-60.9 to -57.8°C) indicates some other dissolved gas such as N₂ and CH₄. Total homogenization temperature 180-390°C, Maximal Td (350-400°C) and salinity (2-14 wt.% NaCl) are estimated in this study. Two main sources for the fluid inclusions are implied because of the range of density and salinity those alter. The fluids with metamorphic origin are shown by high salinity-high temperature conversely, the fluids originated from the meteoric water are indicated by the low salinity-low temperature. We consider fluids arise from intrusive bodies or evaporate layers in charge of high salinity too. The thermobarometric study estimates a depth of mineralization around 10-16 km.

Gold deposits in the Muteh complex

The Muteh complex hosted by metamorphic rocks of the SSZ is located about 240 km southwest of Tehran (Fig. 1). The gold mineralization occurs within the Early Carboniferous - Devonian metamorphic complex and the metamorphic rocks consisting of gneiss, marble, amphibolite, schist, phyllite, and quartzite. The extensional zones host the gold deposits and an intensive alteration is a dominated feature along normal faults which causes alteration mineralogy, including quartz, sericite, kaolinite, epidote, and tourmaline.

Moritz et al. (2006) have identified four fluid inclusion types on the basis of the number of phases at room temperature and their microthermometric behavior. These results are in harmony with the isotopic studies (Moritz, Ghazban, 1996) where $\delta^{18}\text{O} = 2.12\text{‰}$; this value implies interaction between metamorphic-magmatic fluids and the meteoric water during gold mineralization.

Conclusions

Comparing the two case studies in this paper, we conclude that metamorphism processes facilitate the hydrothermal fluid circulation and gold deposition as a reduced sulphide mixed with meteoric water that deposited in the form of infilling siliceous veins. The fluid inclusions seem to be characteristics of the orogenic gold deposited in the green schist-amphibolite facies.

Exhumation of metamorphic host rock complex perhaps coincides with magmatic activity in the SSZ caused the type I fluid inclusions; and during the later extensional phases it underwent mixing with the meteoric water which causes the gold deposition in the studied areas.

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INTERPRETATION OF THE EVOLUTION OF HIGH- AND LOW-SALINITY AQUEOUS FLUID INCLUSIONS IN SHEAR ZONE HOSTED OROGENIC GOLD DEPOSITS: A CASE STUDY OF THE HUTTI GOLD DEPOSIT, KARNATAKA, INDIA

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Introduction

Physico-chemical changes in a predominantly $\text{CO}_2\text{-CH}_4\text{-H}_2\text{O-NaCl}$ fluid system are recognized to be causative factors in deposition of gold in shear-zone related orogenic gold deposits. The physical processes that cause progressive deformation in the shear zone often result in phase separation in low-salinity $\text{CO}_2\text{-CH}_4\text{-H}_2\text{O-NaCl}$ fluids. It is well known that changes in fluid chemistry as a result of such phenomena are important factors in destabilization of gold bisulfide complexes that leads to precipitation of gold (Groves et al., 2003). Previous studies have shown that most greenstone-hosted orogenic gold deposits have resulted from fluids of relatively low salinity (< 12 wt.% NaCl equiv.). Aqueous fluid inclusions of high salinity have been reported from auriferous quartz veins of such deposits (Robert, Kelly, 1987; Boullier et al., 1998; Pandalai et al., 2003).

The Hutti gold deposit is located in the Hutti-Maski schist belt ($\sim 76^\circ 38' \text{N}$ and $16^\circ 14' \text{E}$) of the Karnataka State of India. Here gold is associated with nine sub-parallel and sub-vertical quartz reefs which contain a diverse variety of fluid inclusion types that includes aqueous inclusions of high and low salinity and carbonic ($\text{CO}_2\text{-CH}_4$ -containing) fluid inclusions. Surface samples of quartz of the first phase of deformation (D1-quartz), auriferous quartz vein samples from the Hira Buddini deposit located in the Hutti-Maski schist belt and scheelite samples from the Hutti deposit also contain a similar array of fluid inclusions (Nevin et al., 2010). The purpose of this work is to discuss the evolution of fluids of varying salinity and to identify a mechanism that may lead to generation of such fluids in a shear zone undergoing progressive deformation.

Hutti-Maski Schist Belt

The Hutti-Maski schist belt comprises metavolcanics and subordinate metasedimentary rocks and is surrounded by gneisses, granites and granitoids. The structural setting of the Hutti schist belt indicates that the schist belt experienced four phases of deformation of which the first two (D1 and D2) are more pronounced (Roy, 1973; 1991). Details of mineralization can be seen in Nevin et al. (2010), Mishra and Pal (2008) and Pandalai et al. (2003) among others.

Fluid inclusions

Fluid inclusions were studied in quartz and scheelite samples. Quartz samples from the auriferous laminated veins of the Hutti deposit show a high degree of shearing and recrystallization. The D1-quartz samples from veins exposed at the surface and extension veins of the Hira Buddini deposit are less sheared. In sheared and recrystallized quartz samples, fluid inclusions are present only in porphyroclasts embedded in a matrix of smaller recrystallized grains. The less sheared D1-quartz samples show large grains of quartz with boundaries marked by decrepitated fluid inclusions. Five types of fluid inclusions have been identified in laminated quartz veins related to the Hutti shear zone (Pandalai et al., 2003). They are also observed in the D1-quartz and the quartz veins of the Hira Buddini deposit. The fluid inclusions are re-classified here as follows: (i) monophasic carbonic fluid inclusions – Type I; (ii) low-salinity (0-14 wt.% NaCl equiv.) biphasic aqueous fluid inclusions – Type IIa; (iii) high-salinity (16-23 wt.% NaCl equiv.) biphasic aqueous fluid inclusions – Type IIb; (iv) low-salinity (0-8 wt.% NaCl equiv.) biphasic $\text{CO}_2\text{-CH}_4\text{-H}_2\text{O-NaCl}$ fluid inclusions – Type IIc; (v) high-salinity (28-40 wt.% NaCl equiv.) polyphasic aqueous fluid inclusions – Type III; (vi) rare carbonic inclusions with halite $\pm$ nahcolite – Type IV. The petrographic relationships among these fluid inclusions as seen in samples of the D1-quartz are shown in Fig. 1.

Aqueous biphasic fluid inclusions of high and low salinity (Types IIa and IIb) occur in clusters within porphyroclasts of sheared laminated quartz veins and within the grains of D1-quartz. Typically Type IIa and IIb fluid inclusions are 5 to 15 μm in size and of subhedral form. Type IIa fluid inclusions are also seen along thick healed fractures that traverse the porphyroclasts and quartz grains. (Small, <5 μm , late-stage Type IIa fluid inclusions in thin fracture trails corresponding to a late-stage of brittle deformation, that cut across porphyroclasts and the recrystallized matrix are also observed but are not considered further here).

The Type IIc fluid inclusions are irregular in shape, of 2 to 25 μm in size and occur both along fractures and within porphyroclasts and grains. The Type III fluid inclusions usually contain one (halite) daughter crystal, and less commonly up to

three daughter crystals.

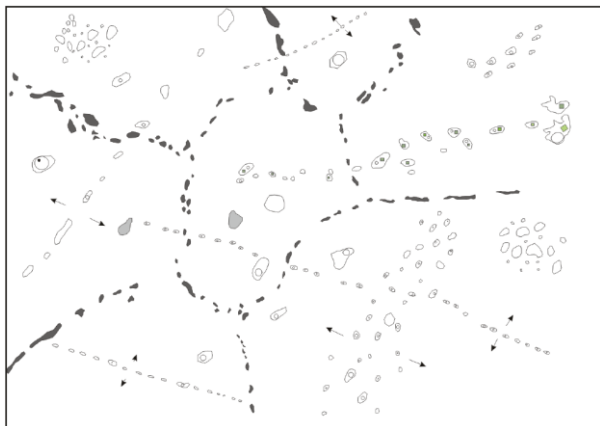


Figure 1. Schematic diagram of petrographic relationships among fluid inclusion types in the D1-quartz as described in the text.

The Type III fluid inclusions often do not have a vapour bubble initially, but on cooling a vapour bubble develops that persists at room temperature. On heating, the Type III fluid inclusions final homogenization (~ 150 - 290°C) takes place into the liquid phase by disappearance of the solid with vapour phase disappearance between ~ 100 to 140°C . The Type III fluid inclusions have a flat subhedral to oval appearance and occur on trails that cut across porphyroclasts and grains. The subhedral Type III fluid inclusions are larger than the oval fluid inclusions and have deformed morphologies. In sheared quartz, the trails of these fluid inclusions can be traced from one porphyroclast to another across recrystallized quartz. In the recrystallized matrix their trace is seen in the form of sparsely distributed decrepitated fluid inclusions along trails. Laser-Raman studies on these fluid inclusions have shown them to be purely aqueous in nature. The petrography of the Type III fluid inclusions establishes that they are formed before the recrystallization of sheared quartz is completed.

Fluid evolution model

The Type-I, Type IIa, IIb IIc and Type III fluid inclusions are interpreted as evolving from a single source of CO_2 - CH_4 - H_2O - NaCl fluid in a system undergoing cyclic episodes of shear failure. Initially, as stress builds up in a shear zone, grain-scale fracturing and creep-induced rotational dilatancy in rock rocks around the shear zone cause fluids to move out into country rocks. Decrease in fluid pressure causes unmixing into H_2O -rich and H_2O -poor low-salinity phases and sometimes into two H_2O -rich phases, one more saline than the other. Although these fluids may accumulate initially in interconnected chambers, increase in stress may cause necking and isolation of these unmixed fluids into sequestered unconnected fluid

chambers. Collapse of such chambers with further increasing stress causes their re-injection into the central part of the shear system where they are entrapped in various secondary modes in quartz of previous cycles of shear failure and as primary fluid inclusions in quartz that precipitates in the inter-seismic period.

Conclusions

Isolation of unmixed fluids of varying composition in unconnected chambers of an evolving shear system is inferred to be a principal cause for generating primary and secondary fluids inclusions of high and low salinity in quartz undergoing cyclic shear deformation. The similarity of inclusion types of the D1-quartz and quartz in shear zones that host gold shows that the phenomena of fluid evolution took place at larger and smaller spatial scales over a large temporal part of the first cycle of deformation of the Hutti orogen.

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A MICROSOFT EXCEL 2007 AND MS VISUAL BASIC MACRO BASED SOFTWARE PACKAGE FOR COMPUTATION OF DENSITY AND ISOCHORE OF FLUID INCLUSIONS

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Introduction

Computation of density of inclusion fluid and the corresponding isochore on P-T space is an exercise that every fluid inclusionist has to carry out. The calculation procedures are based on P-V-T-X relationship in relevant fluid systems. Irrespective of the complexity of phase relationship (topology of stability fields of vapor, solid, liquid and their coexistence and mutual solubility) equations of state need to be formulated for computation of density and isochore. These equations of states result from rigorous thermodynamic treatment or empirical fit to volumetric measurements or molecular dynamic simulations. An end user has to implement the best available equation of state to compute the parameters from raw inputs of microthermometric data. Many workers have written computer codes in many high level languages for computation of density and isochores. FLINCOR (Brown, 1989) was the first to implement a Graphical User Interface (on Windows environment) based package for construction of isochores in a multitude of fluid systems. Extensive computer modeling of fluid system and generation of computer codes has been done by Bakker (2003) which can be used by fluid inclusionists. However, the programs and packages developed by Bakker (op. cit.) are sometimes a bit complicated to be used by one and all. The present work is an attempt to design a simple and user friendly software package to analyze fluid inclusion microthermometric inputs and present the output graphically. All users of the Microsoft Windows operating system are familiar with the Excel spreadsheet where much computational and graphic functionality are implemented. MS Excel can be suitably linked to any code written in MS Visual Basic through a Macro and the user can carry out any computational task by implementing the Macro. Visual Basic Macros have almost become common programming practice.

Program logic and design

Microthermometric parameters on natural fluid inclusions are finite in number. Again, the different compositional varieties of fluid inclusions have fixed number of such parameters. For example, an aqueous-carbonic inclusion (considering pure CO₂) can have only four parameters – temperature of

melting of CO₂ (T_{m,CO_2}), temperature of melting of clathrate ($T_{m,clath}$), temperature of homogenization of carbonic phase (T_{h,CO_2}) and temperature of total homogenization (T_t). Entry of these four parameters automatically identifies the system as H₂O-NaCl-CO₂. Calculation of density and pressure-temperature values corresponding to isochore in the one-phase field then can be computed by using the best available equation of state applicable in a wide range of temperature, pressure and compositions. The user is not prompted for any further input on the choice of system or the equation of state to be used. The present design has followed this strategy. There are a number of fields in the Excel worksheet designated as input parameters such as temperature of last ice melting (T_m), temperature of liquid-vapor homogenization (T_h), mode (L/V), temperature of dissolution of halite (T_s) and parameters in H₂O-NaCl-CO₂ system as stated already. Parameters such as 'System', 'Salinity' and 'Density' are appended as output parameters after computation. Enabled Macros are displayed as buttons which are activated on clicking to execute the calculation of densities and plotting of data. Three types of graphical presentation required by fluid inclusionists have been implemented – histograms, scatter plots and isochores. The first two types of plots are generated by selecting data (or pairs) from designated fields in the worksheet such as ' T_h ', 'Salinity', etc. Pressure-temperature values corresponding to isochore of any particular inclusion is done by selecting data from a record and plotting on P-T space with user defined range in the parameters. Provisions for plotting of more than one isochore on a single plot have been implemented for P-T estimation from intersecting isochores.

Present status of implementation

At present, four systems have been implemented: (1) NaCl-H₂O, (2) pure CO₂, (3) CO₂-CH₄ and (4) H₂O-NaCl-CO₂. In (1) the regression equation of Bodnar (1983) is used for density calculation and the equation of Bodnar and Vityk (1994) is used for isochore construction. MRK equation of state (Holloway, 1977; Bowers, Helgeson, 1983; Parry, 1986) is used for isochore construction in pure CO₂, and H₂O-NaCl-CO₂ systems. Calculations of density and X_{CO_2} at minimum pressure of entrapment are done adopting

a modified procedure outlined in Panigrahi and Mookherjee (1997). For calculation of density in CO₂-CH₄ system, a slightly different procedure has been adopted. The equation provided in Parry (1986) for density calculation in pure CO₂ has been used where the critical temperature (T_c) and critical density (d_c) of pure CO₂ is replaced by the same parameters in CO₂-CH₄ mixture at specified value of X_{CH₄}. This is accomplished by fitting the experimental data of Kreglewski and Hall (1983) on critical temperature and density in CO₂-CH₄ mixtures. The data is accurately fit by a third degree polynomial in X_{CH₄}. Pressure-temperature calculation corresponding to isochore in this system is done again by using the MRK equation with the non-ideal parameters for CH₄ and interaction parameters for CO₂-CH₄ taken from Bakker (1999). A user only has to provide X_{CH₄} determined either from Raman spectroscopy or graphical method, as input in an appropriate field in the Excel worksheet. The values of density obtained for CO₂-CH₄ mixtures in this method match well with values obtained by using FLUIDS package of Bakker (2003). The program is also provided with a HELP file explaining the terms and various functionalities.

Conclusion and future developments

The program is expected to cater to the need of fluid inclusionists at large because of its user friendliness. The program is under revision for incorporating other important electrolyte and gas mixtures. Revision of the program is also underway for incorporation of EOS developed through molecular dynamic simulations in different systems.

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HETEROGENEITY IN FLUID CHARACTERISTICS IN THE GRANITE-GREENSTONE ENSEMBLE OF THE EASTERN DHARWAR CRATON: A SYNOPSIS OVERVIEW

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Introduction

The granite-greenstone ensemble of the Eastern Dharwar craton has been the focus of attention by virtue of its auriferous schist belts. Considerable efforts have been put to understand the metallogeny of gold in relation to evolution of these schist belts. Fluid inclusion studies have been carried out by many workers on the auriferous Kolar, Hutt-Maski, and Jaonnagiri schist belts in order to identify the phase(s) of fluid as possible carrier of the noble metal (Mishra, Panigrahi, 1999; Pal, Mishra, 2002; Mishra et al., 2005; Panigrahi, Gupta, 2007; Saravanan et al., 2009). A metamorphogenic CO₂-bearing fluid has been identified as the carrier of gold and immiscibility of the homogeneous aqueous-carbonic fluid has been ascribed as the mechanism of deposition in most of these occurrences with a few exceptions. The present study is an attempt to work out the spectrum of fluid activities in the Eastern Dharwar craton focusing on the Ramagiri-Penakacherla schist belts where there is a dearth of information on fluid characteristics. The work is primarily aimed at understanding the role of the younger granitoids in mineralization/enrichment of gold in these schist belts.

Background Information

Figure 1 is the geological map of a part of the Eastern Dharwar Craton showing the Ramagiri-Penakacherla schist belts within the Peninsular Gneissic (PG) (TTG gneiss) along with younger granitoids (Closepet being the most prominent one) and the shear zones. A nearly NE-SW transect from Hiriya to Anantapur was chosen for study. Samples of quartz veins in PG and schistose rocks from the two schist belts were collected; the present status is based on four samples studied from the PG and Ramagiri schist belt as shown in Fig1.

Fluid inclusion studies

Fluid inclusion assemblages in the quartz veins in the PG include: (1) Aqueous-carbonic inclusions ($L_{aq} + L_{carb} + V_{carb}$) occurring as non trail-bound in random three dimensional network and also on intersecting healed fractures in the host quartz. There is appreciable variation in their aqueous to carbonic phase proportions. (2) Aqueous biphasic ($L + V$) inclusions also occur as primary non trail-bound inclusions on the same plane. Samples studied from the auriferous Ramagiri schist belt

have (1) aqueous-carbonic inclusions with variable ratio of the aqueous and carbonic component, occurring both as non trail-bound as well as trail-bound; (2) pure-carbonic inclusions also exhibiting similar mode of occurrence, (iii) aqueous-biphasic ($L+V$) inclusions mostly as part of three dimensional network and rarely as trail-bound, and (iv) polyphasic inclusions ($L+V+S$) with halite as the solid phase occurring mostly as trail-bound inclusions. Thus, there seem to be a difference in fluid characteristics in the two domains. In the PG domain, the carbonic component of the aqueous-carbonic inclusions is pure CO₂, whereas the same in the auriferous Ramagiri schist belt contains variable proportions of methane as confirmed from Laser Raman microspectrometry. Absence of pure carbonic inclusions in the PG domain indicates that the fluid evolved mostly in the one-phase miscible region. Raman spectroscopy has also revealed suspected presence of N₂ in the carbonic inclusions.

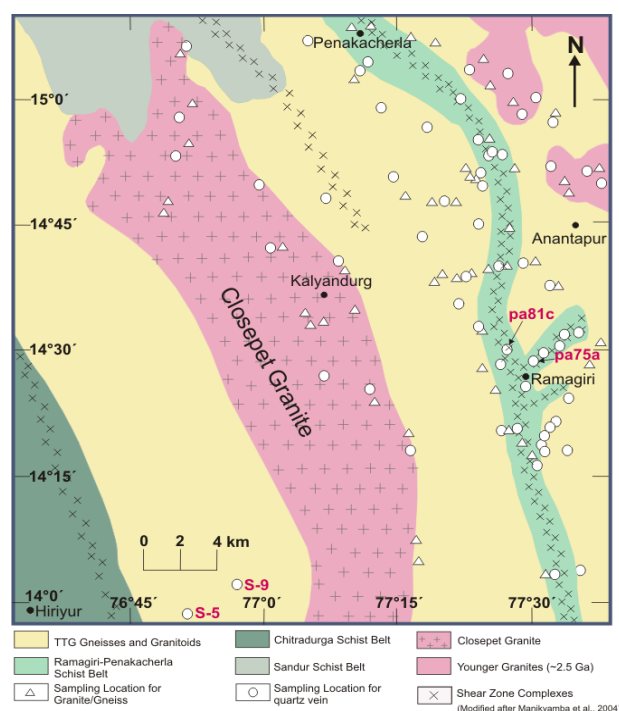


Figure1. Geological map of a part of the Eastern Dharwar craton showing the oldest Peninsular Gneiss, the schist belts and younger granitoids. Simple points are marked as white circles and those examined for fluid inclusions are marked red.

Microthermometry of the aqueous-carbonic inclusions has been the most difficult exercise in samples from both domains with most inclusions leaking without total homogenization at

temperatures beyond 200°C. So far, only five aqueous-carbonic inclusions (regular shaped, small and non trail-bound mode of occurrence) from the Ramagiri domain furnished total homogenization temperature in the range of 269 to 339°C. These temperatures of total homogenization, with the salinity of the aqueous phase determined from clathrate melting temperatures, yielded minimum pressure of entrapment from 1500 to 3400 bars with mole fractions of the carbonic phase between 0.014 and 0.32. Computations of these parameters are on the basis of PVTX relationship in H₂O-CO₂-NaCl system following the procedure outlined by Panigrahi and Mookherjee (1997). Pure carbonic inclusions in the same domain furnish temperature of homogenization in the range of 11.8 to 15.3°C, furnishing moderate densities. Only one set of coexisting pure-carbonic and aqueous biphasic inclusions yielded pressure and temperature conditions of entrapment as 1380 bars and 240°C respectively. This temperature and pressure corresponds to the immiscible regime in the fluid in the Ramagiri domain. Aqueous inclusions in the PG domain are restricted in their salinity and homogenization temperature to 15-18 NaCl wt.% equivalent and 150-170°C. The same type of inclusions in the Ramagiri domain exhibit a greater spread in salinity and homogenization temperature (1.4-16.9 NaCl wt.% equivalent and 160-275°C respectively). Halite-bearing polyphase inclusions in the Ramagiri domain furnish temperature of dissolution of halite in a restricted range of 214 to 259°C corresponding to salinity range of 32.6 to 35.4 wt.% NaCl equivalent.

Discussion and conclusion

Data presented here are too sparse to lead to any firm conclusion on origin and evolution of fluids in relation to gold mineralization. However, a few points seem significant and need further attention.

(1) Fluid in the PG domain is devoid of CH₄ as against its CH₄-bearing nature in the Ramagiri domain. Previous work on the auriferous Hutti and Jonnagiri schist belts (Pal, Mishra, 2002; Panigrahi, Gupta, 2007; Saravanan et al., 2009) generally agree on a CH₄-rich nature of the fluid although the significance of the same in gold mineralization has not been discussed.

(2) Halite-bearing polyphase inclusions were reported from the Hutti-Maski schist belt (Mishra et al., 2005; Panigrahi, Gupta, 2007). Presence of these inclusions in a sizable population does indicate that a high saline and moderate to high temperature fluid of possible magmatic parentage was active whose potential as a either a carrier or mobilizing agent of gold has not been evaluated.

(3) The Ramagiri domain does conform to the pressure-temperature regime of the CO₂-bearing fluid and its subsequent splitting as observed in other gold producing zones and prospects in addition to its methane-bearing nature. Although the former has often being discussed as the mechanism of gold deposition in hydrothermal fluids, the latter has not been examined in the context of gold transport.

Further fluid inclusion data are being generated to address the issue of the possible role of younger granitoids in metallogeny of gold in the Eastern Dharwar craton.

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PHYSICO-CHEMICAL CRYSTALLIZATION CONDITIONS OF PICRITE PORPHYRITES AND OLIVINE MELANEPHELINITES FROM THE GULI MASSIF (POLAR SIBERIA)

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Introduction

One of the most important tasks of modern petrology is to establish the composition of primordial magma/magmas, from which complex alkaline-ultrabasic carbonatite intrusions formed. Some researchers believe that all rock varieties of intrusions were formed from one alkaline-picrite (Yegorov, 1991) or meimechite (Sobolev et al., 1991; Ryabchikov et al., 2009) magma during its evolution. Others (Rass, 2000) think that the formation of massifs was contributed by several primary magmas. The composition and crystallization temperature of meimechite melts has been characterized most completely. We used the methods of thermobarogeochemistry for studying picrite porphyrites and olivine melanephelinites of the Guli massif, whose composition is ultrabasic and enriched in Ca and alkalies (Table 1, ans. 1 and 2).

Table 1. Average composition of rocks and heated inclusions in minerals, wt. %

	Rocks		Inclusions			
	1	2	3	4	5	6
SiO ₂	40.38	42.04	43.07	45.00	43.00	53.53
TiO ₂	3.63	2.77	5.51	3.28	3.68	0.26
Al ₂ O ₃	2.56	10.48	7.35	15.74	12.47	21.35
FeO	12.82	11.47	13.93	7.50	9.13	2.88
MnO	0.17	0.17	0.17	0.13	0.19	0.06
MgO	20.90	13.66	7.31	4.46	5.84	3.66
CaO	8.08	10.38	13.60	8.57	12.30	7.03
Na ₂ O	0.28	3.38	2.52	5.67	4.82	6.51
K ₂ O	1.71	0.72	2.98	3.72	3.07	1.70
BaO			0.05	0.20	0.14	0.00
SrO			0.05	-	0.06	0.00
P ₂ O ₅	0.65	0.37	0.11	0.94	0.82	0.03
Cl			-	0.09	0.07	0.00
SO ₃			-	0.48	0.26	0.03
Total	91.18	95.44	96.65	95.78	95.85	97.04

Note. Rocks: 1,3 - picrites, 2,4-6 - Ol melanephelinites. Host mineral: 3, 4 - Ol, 5,6 - Cpx.

Melt inclusions in minerals

In *olivine* of *picrite porphyrites* melt inclusions are distributed no uniformly, are of rounded and prismatic-rounded shape with dark-brownish color. In picrite porphyrite with glassy groundmass inclusions are vitrified and those with fine-crystallized basis are partly or completely crystallized. Glass in glassy inclusions softens at about 1070°C. At 1150°C one can observe very

small light and dark phases. At about 1280°C, the content of vacuole is melt with a gas bubble. At 1340°C, the gas bubble became smaller. Further heating was stopped for technical reason. Partly and completely crystallized inclusions contained clinopyroxene, nepheline, perovskite, magnetite and Mg-Fe-carbonate. On heating, the content of inclusions becomes lighter, some daughter phases melt and at 1125°C a few gas bubbles are observed. Homogenization temperature of inclusions exceeds 1300°C.

In *olivine melanephelinites* melt inclusions were found in olivine and clinopyroxene phenocrysts. *Clinopyroxene* contains abundant melt inclusions, occasionally to two or three tens in the field of microscope. The size of inclusions ranges from few to 30-50 µm. Primary inclusions are arranged randomly and occur near the growth zones of host mineral. The inclusions are fine- or coarse-crystallized and are of irregular and rounded-prismatic shape. Among daughter phases we observed clinopyroxene, apatite, phlogopite, magnetite (spinel), nepheline, and amphibole. Melting of daughter phases begins at about 870-970°C. At 1030-1050°C, a gas bubble appears, which moves along the vacuole at 1080°C. At 1140-1180°C all daughter phases, except ore phases, melt and the gas bubble reduces in size. The ore phase melts completely for 20-30°C before homogenization of inclusion content at 1200-1230°C.

Olivine also contains abundant inclusions. They are mainly coarse-crystallized and vary in sizes. Among daughter phases we observed nepheline, clinopyroxene, apatite, phlogopite, and magnetite. Melting of crystal phases starts at about 870°C. At 1200-1270°C, the crystal phases did not melt completely but the gas bubble appreciably decreased in size. We stopped heating the inclusions because of the intense darkening of host olivine.

In *picrite porphyrite* the glasses of heated inclusions from olivine (Table 1, an.3) have ultrabasic alkaline-rich composition. Compared to the rock (Table 1, an. 1), they are more enriched in Si, Al, Ca, and alkalies (with minor predominance of K over Na) and are depleted in MgO (to 6-7 wt.%). Their composition is similar to that of melanephelinites from the Krestovsky massif.

In *olivine melanephelinites* the glasses of

homogenized inclusions in *clinopyroxenes* (Table 1, an.5) compared to inclusions in olivine of picrite porphyrites (Table 1, an 3) are more enriched in Si, Al, alkalis (at Na-type alkalinity), Ba, Cl, and S, but contain less Ca and Ti. Their composition corresponds to that of nephelinites. In most differentiated melts conserved in inclusions (Table 1, an.6) the concentration of Si, Al, and Na increases and that of Mg, Ca, and K, on the contrary, decreases. They are free in Ba, Cl, S and P. Their composition is similar to that of trachydolerites.

In *olivine* of melanephelinites we analyzed the composition of residual glasses heated to 1180-1270°C. After heating, the inclusions in addition to glass contained ore minerals and clinopyroxene. Compared to the composition of homogenized inclusions in clinopyroxenes (Table 1, an. 5), residual glasses from inclusions in olivine (Table 1, an. 4) are more differentiated, contain still more Si, Al, alkalis, Ba, P and much less Mg and Ca.

Geochemistry

Vitrified melts in clinopyroxenes of *melanephelinites* are considerably enriched in incompatible elements: LILE, LREE and MREE (two orders of magnitude) and HREE (one order of magnitude) higher than the mantle level. The patterns of trace elements normalized to primitive mantle (Taylor, McLennan, 1985) have a negative slope and many large anomalies: negative Hf and positive Gd and Er, Yb (Fig. 1). The melts conserved in olivine of *picrite porphyrites* in the enrichment with incompatible elements are similar to the melts from which olivine melanephelinites crystallized. In contrast to the latter, melts from picrites contained less Ba, Th, U, La, and Ce and more HREE. The normalized pattern of trace elements in the melts from picrite porphyrites is in general similar to the pattern of inclusions in olivine melanephelinites. They also have marked negative Hf and positive Gd and Er, Yb anomalies.

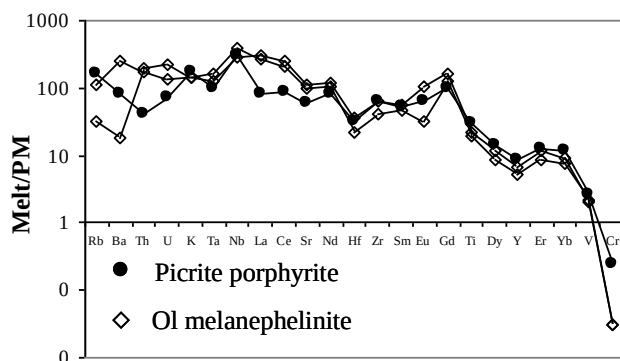


Figure 1. The pattern of trace elements in melt inclusions from clinopyroxenes of picrite and olivine melanephelinite.

Conclusions

The data obtained suggest that picrite porphyrites and olivine melanephelinites are a single genetic series of differentiates of one and the same magma. Conservation of melts of nephelinite and trachydolerite compositions in clinopyroxenes of melanephelinites evidences that this magma during its further evolution could be the source for the formation of alkaline rocks typical of alkaline-ultrabasic carbonatite intrusions.

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FEATURES OF CRYSTALLIZATION OF THE ONGONITIC MAGMA FROM MELT AND FLUID INCLUSIONS STUDIES IN ROCKS OF THE ARY-BULAK MASSIF

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Introduction

The Ary-Bulak massif (East Transbaikalia) has a mushroom-like shape with a maximum horizontal section under the Quaternary sediments as ~700x1500 m and flat inclination angles relative to host sedimentary-volcanogenic rocks (schist and effusives). The porphyric ongonites, composing the major part of the massif, gradually transit into the aphyric rocks on the south-west endocontact zone of wide up to 100 m (Peretyazhko, Savina, 2010b).

Results of melt and fluid inclusion studies

The data on melt inclusions indicate the immiscibility of fluoride and silicate melts during the crystallization of the ongonitic magma. Melt inclusions with fluoride glasses of different composition are found in quartz phenocrysts in each studied rock sample (Peretyazhko et al., 2007a, 2007b; Peretyazhko, Savina, 2010b). The ongonitic melt at different stages of its evolution demonstrated significant concentrations of trace elements (Cs, B, Be, Li, Rb, Nb, Ta) and also had rare isolations of silicate melts with very high cesium content (Peretyazhko et al., 2007a). Each studied rock sample includes scarce melt inclusions in quartz phenocrysts with glasses show cesium concentrations up to 17 wt%. Silicate glasses rich in Cs in melt inclusions also contain a permanent As impurity (up to 2-4 wt.% As₂O₃).

Low-density magmatic fluids of P-Q type – vapor solutions presumably NaF-containing with an insignificant impurity of chlorides participated in the crystallization of porphyric rocks of the massif (Peretyazhko, 2009). Penetrating into the aphyric zone, the magmatic fluid of P-Q type, coexisting with the melts in the residual magmatic chamber, cooled down, changed the composition and its features began to correspond to the water-salt system of the first type. As a result the magmatic fluid boiled and separated into immiscible phases – salt brine with very high Cl, F, K, Cs, Mn, Fe, Al concentrations, impurities of S, As and a low-density vapor solution. Quartz phenocrysts in the aphyric rocks occurring on south-west endocontact zone of the massif contain rare melt and syngenetic fluid inclusions – vapor solutions and brines in healed cracks. The inclusions of brines (crystalline phases occupy up to 70-80 vol.%) were homogenized into the liquid after solid phases dissolution (150-650°C) at high temperatures (450-

700°C). The features of dissolution-crystallization of phases in brine inclusions as well as the data of microprobe analysis of inclusions indicate that the crystalline phases are chlorides, fluorides (NaCl, KCl, (K,Cs)Cl, KF, NaF), as well as most likely crystalline hydrates of MnCl₂·nH₂O, FeCl₃·nH₂O, KF·nH₂O, AlF₃·nH₂O type (Peretyazhko, Savina, 2010b).

Discussion

The crystallization of the ongonitic magma in the chamber with the size and shape like the Ary-Burak massif has could last not more than 1500-2500 years (Peretyazhko, Savina, 2010b). The calculations of density, viscosity and Reley criterion for the ongonitic melts done using the composition of silicate glasses of melt inclusions suggest intensive convection melts flows in the residual magmatic chamber. The porphyric and aphyric rocks rich in Ca and F generated from immiscible silicate and calcium-fluoride melts rich in oxygen and F-Cl-containing water magmatic fluids of different types (Peretyazhko et al., 2007b; Peretyazhko, 2009).

Isolations of calcium-fluoride glasses, being crystallized to a different degree, are found in each sample of porphyric ongonite even if it contains <0.1 wt.% Ca (Peretyazhko, Savina, 2010b). Calcium-fluoride glasses available in fluidal aphyric rocks from the endocontact zone and its trace contents in porphyric ongonites all over the massif suggest that the ongonitic melt prior to its intrusion into the magmatic chamber already had of calcium-fluoride melt isolations. We suppose that oxygen (10-16 wt.%) contained in calcium-fluoride melts prevented fluorite crystallization to a relatively low (500-600°C) temperature (Peretyazhko et al., 2007b). The increase of fluid pressure up to 200-400 bars during the magma degassing led to pressing of immiscible melts of low viscosity (calcium-fluoride and residual silicate rich in fluorine and water) in the interstitial space between minerals of the magmatic “porridge” on the crystallization front (Peretyazhko, Savina, 2010b).

Studies of melt and fluid inclusions indicated that the ongonitic magma contained crystalline phases and silicate melts with water-salt fluids of different types, fluoride melts which in terms of component ratio are similar to fluorite, sellaite, cryolite, chiolite and more complicated

alumofluoride composition as well as silicate melts with anomalous Cs and As contents (Peretyazhko et al., 2007a, 2007b; Peretyazhko, Savina, 2010b). The data on melt inclusions thermometry in quartz phenocrysts from one of porphyric ongonite sample show that the cryolite-like melt can be completely dissolved in silicate melt rich in fluorine (7-9 wt.%) at temperatures higher than 700-720°C. Taking into account the cryolite-like phase such a silicate melt in the homogenous state is alkaline ($A/CNK < 1$). When alkaline silicate melts cooled down to a temperature lower than 700°C they most likely liquated and immiscible silicate ($A/CNK = 1$) and cryolite-like melts. Isolations of other fluoride melts (calcium-fluoride, sellaite, alumofluoride with different ratio of Al, F, Na, Ca, Mg) were immiscible between each other and silicate melts in the ongonitic magma at temperatures over 500-600°C.

Fluoride melts started to be liquated in the ongonitic magma as a result of local increase of the alkalinity in the original silicate melt and significant increase of fluorine content. The main components of the fluoride melts (F, Ca, Al, Na, Mg) were extracted from the ongonitic magma. Moreover, almost all Ca was accumulated in isolations of calcium-fluoride melts.

Fluoride-silicate liquid immiscibility in the ongonitic magma gave rise to tetrad effects of M-type in chondrite-normalized REE patterns as well as low (9-17) non-chondrite Y/Ho ratio in rocks from the massif (Savina, Peretyazhko, 2009; Peretyazhko, Savina, 2010a). The redistribution of lanthanoids between immiscible liquid fluoride and silicate melts in the ongonitic magma led to tetrad effects of M-type in REE patterns of silicate melts, while from experimental data REE distribution of fluoride melts demonstrate significant tetrad effects of W-type.

The lack of cryolite and chiolite among minerals, composing the porphyric ongonites point out the disappearance of alumofluoride melts at a magmatic stage. Such melts most likely actively react with products of the ongonitic magma crystallization and their major components (Na, Al, F) participated in formation needle-shaped topaz of the late generation, Na-sanidine from the rock matrix and were included into magmatic fluids. The crystalline phase $(K,Cs)Cl$ and As impurity in inclusions of brines from quartz phenocrysts of aphyric rocks showed that Cs and As were partially transported by magmatic fluids (Peretyazhko, Savina, 2010b).

The marginal zone (50-100 m thick) of aphyric and porphyric rocks rich in Ca and F on the south-west endocontact of the massif most likely generated as a result of the local decompression of

the magmatic chamber in near-surface conditions that resulted in quenching of the calcium-fluoride melts accumulated at the crystallization front. The degassing of magmatic fluids enriched in fluorine through the marginal zone of the massif gave rise to crystallization of prosopite $CaAl_2F_4(OH)_4$ and water-calcium alumofluorides (Peretyazhko et al., 2007b), submicron fluorite crystals in calcium-fluoride glasses, and was associated with increase in concentration of water (up to 2-4 wt.%) and impurity elements (Sn, W, Cs, Rb, Ta, Be, Zr, Hf, Sb, As, Sc), decrease in concentrations of all lanthanoids in particular heavy (Savina, Peretyazhko, 2009; Peretyazhko, Savina, 2010b). The calcium-fluoride glasses were partially replaced by dickite or kaolinite, that was stimulated by permanent Al and Si impurities (Peretyazhko et al., 2007b).

Conclusions

The fluoride-silicate liquid immiscibility, silicate melts with anomalous Cs and As contents, changes in the composition and features of magmatic fluids leading to boiling and separation of brines or salt melts indicate complicated fluid-magmatic interaction and heterogeneous state of the ongonitic magma during the crystallization of rocks of the Ary-Burak massif. Low viscosity and high mobility of silicate melts rich in fluorine and water, intensive convection flows of melts in the residual magmatic chamber and the increase of fluid pressure during degassing contributed to these processes.

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THE ENTRAPMENT OF MELT INCLUSIONS DURING THE GROWTH OF LEUCITE CRYSTALS: MELTING EXPERIMENTS

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Introduction

The study of silicate melt and fluid inclusions in minerals of volcanic rocks allows for obtaining the important information on P-T conditions of their generation, chemical composition and evolution. The leucite crystals often contain a lot of inclusions. There are some methodic problems to obtain true temperatures for leucite crystallization in different rocks (Bazarova, Krasnov, 1975) due to the initial leakage of inclusions or leakage during heating. Possibly, it occurs owing to the transition of cubic leucite into tetragonal leucite at temperatures of 625-650°C and further twinning (Bragg, Claringbull, 1965).

The purpose of this paper is obtaining new data on initial crystallization stages of natural alkaline melt. The experimental simulation of leucite crystallization in natural melts allows studying the peculiarities of inclusion trapping during the crystal growth. This investigation was performed on a heating stage designed by the authors (Petrushin et al. 2003).

Investigated rocks

Orendite (sanidine-phlogopite-leucite lamproite) from the Zirkel Mesa outcrop, Leucite Hills (Wyoming, USA) was chosen as a starting material for experiments on melting and crystallization (Günter et al., 1990). Depending on the regime of cooling of primary magmas, lamproites greatly vary in crystallinity, forming varieties from glassy (up to 85 vol.% of glass) up to holocrystalline with similar chemical compositions.

The orendite is SiO₂-rich (up to 57 wt.%), has a high content of K₂O (up to 11 wt.%), and high peralkaline index (K₂O+Na₂O)/Al₂O₃ (up to 3) (Table 1). These rocks form volcanic cones and lava flows. Holocrystalline specimens of orendites without secondary alteration were selected for the experiments. The rocks contain phlogopite phenocrysts (10-15 vol.%) in the groundmass consisting of leucite (30-35), sanidine (20-30), diopside (10-15), K-richichterite (up to 5), apatite (up to 1.5), priderite (< 1) and interstitial glass (up to 5 vol. %). Xenogenic olivine and Ca-Ba-Sr-carbonates and barite sometimes occur in the rocks. Phlogopite phenocrysts (1.5-2 mm) are likely to crystallize at a depth on the early stage of primary magma evolution, whereas the groundmass has been formed on the surface.

Table 1. Chemical composition of investigated rock (XRF, SIMS data).

Components.	wt.%	Trace elements (ppm)	
SiO ₂	56.62	Cr	384
TiO ₂	2.68	Ni	253
Al ₂ O ₃	10.86	Co	1838
FeO	3.94	Ba	2433
MnO	0.13	Rb	284
MgO	6.83	Zn	104
CaO	4.11	Cs	2
Na ₂ O	0.58	Li	10
K ₂ O	11.5	Pb	10
P ₂ O ₅	1.37	Cu	892
LOI	1.5	Sr	2092
Total	100.12		

Magmatic inclusions in natural leucites from orendites

Leucite in the orendites as well as in the cognate wyomingites occurs as euhedral grains without twinning. It contains the coexisting primary silicate melt and fluid inclusions, which predominantly decorate the growth zones in the host crystals. The sizes of inclusions are usually 2-5 µm, sometimes up to 10-20 µm. They are oval, rounded, and occasionally dumbbell-like in shape. The quenched melt inclusions containing fresh greenish silicate glass are most common (Fig. 1a). The phase composition of large melt inclusions varies from glass to glass + gas ± daughter/trapped crystals (Sharygin, Bazarova 1991). In some melt inclusions a gas bubble is partially or completely filled by carbonate or barite (Sharygin, 2001). Chalcopyrite and barite have been observed as daughter phases of leucite-hosted melt inclusions in the Zirkel Mesa rocks (Mitchell, 1991).

Run procedure

The liquidus temperature of the samples is determined according to the standard procedure to obtain the equilibrium between crystal-melt that is termed as the approach in two ways. In our case it is made by the commencement of crystallization or leucite melting – first crystallizing phase (Petrushin et al., 2003).

Results

The dynamics of homogenous generation of crystallization centers, formation and entrapment of

primary inclusions of the melt glass with their conservation were traced in the experimental products (Fig. 2). The glassy melt inclusions in leucite are predominantly monophasic, but there are separate inclusions with the gas bubble, that is specified by dry experimental conditions.

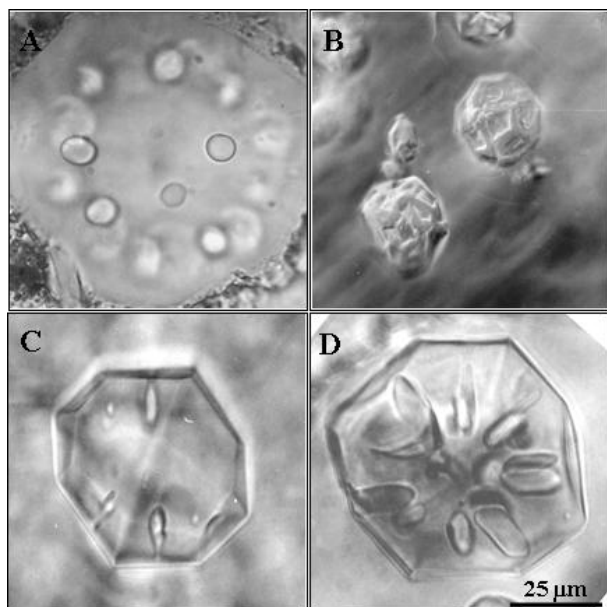


Figure 1. Silicate melt inclusions in natural and synthetic leucites: A – silicate melt inclusions in natural leucite. B – the pits on the faces of synthetic leucites. C-D – silicate melt inclusions in the synthetic leucites.

The experimental products show different stages of growth of leucite crystals, which allow judging of mechanism of melt inclusions trapping. On moderate supercooling of 20–40°C, the morphological evolution of leucite crystals in the process of growth at stable temperature is observed. After generation, pure small (up to 1–3 µm) idiomorphic crystals are originally formed. Thereupon, pits appear on their faces (Fig. 1, B). At the stage of skeletal growth with the predominant development of apical and ridge forms these pits become deeper (Fig. 1, C). During the final stage, the edges grow over with the formation of flat-faced «box-like» tetragonal-trioctahedral crystals with skeletal interior structure and inclusions of melt glass along the growth sectors (Fig. 1, D).

Conclusions

The obtained data allow comparing morphology of synthetic and natural inclusions in leucites. The shape of the melt inclusions in the experimental leucite (negative crystals) (Fig. 1, D) is more elongated than the shape of the inclusions in leucite from the natural rocks (Fig. 1, A). It may be explained by a higher rate of crystal growth in the experiments.

In both natural and synthetic crystals the central and outermost zones are free in inclusions,

but the middle part contains a great deal of inclusions. Similar distribution suggests that the capture of inclusions occurred on the skeletal stage of crystal growth. The smooth difference in inclusion shape in natural and synthetic leucites is likely to explain by cooling kinetics. The cooling in lava flows was slower than in the run products and it may explain the more rounded shape of inclusions in natural leucites. The absence of skeletal leucite crystals in the Zirkel Mesa natural rocks may indicate that the supercooling of lamproitic melt was less than 50°C.

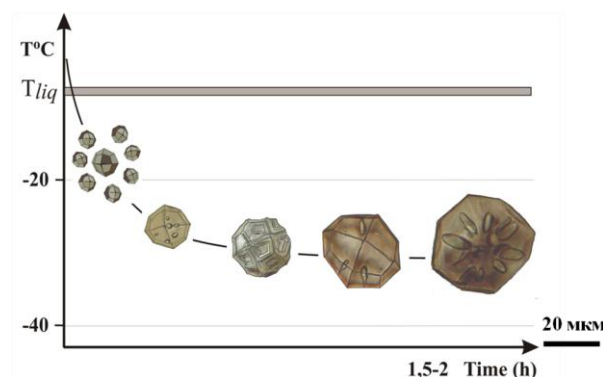


Figure 2. The dynamics of melt inclusions entrapment in thermal experiments.

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CO₂-RICH FLUID INCLUSIONS IN UPPER MANTLE XENOLITHS FROM THE CAMEROON VOLCANIC LINE

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Introduction

We have studied upper mantle xenoliths from alkali basalts outcropped at Nyos and Barombi Lakes, which are situated along the Cameroon Volcanic Line (CVL). Based on the results of previous study (Tanyileke et al., 1996), the outgassing CO₂ in waters of the crater lakes along the CVL can be derived from a degassing mantle, also Touret et al. (2010) concluded that the CO₂ could have been originated from the basalt magma chamber. This is the first fluid inclusion study from mantle of the CVL continental sector, dealing with fluid inclusion-rich upper mantle xenoliths, which might be regarded indeed as a source of the CO₂ that erupted from the Nyos Lake and killed about 2000 people and animals in 1986.

Geological overview

The western part of Cameroon displays an alignment of Tertiary to recent alkaline volcanoes, plutons and grabens extending over more than 1600 km which is called as Cameroon Volcanic Line (CVL). The CVL stretches from the Atlantic oceanic island of Palagu through the Gulf of Guinea and within the African continent to the Lake Chad. Recently, the CVL has been considered as being a huge lithospheric crack tapping a hot deep asthenospheric sector. The Nyos and Barombi host alkaline basalts are 1.5 to 0.2 Ma old (Déruelle et al., 2007), their pyroclastic deposits contain large number of ultramafic xenoliths (Temdjim et al., 2004; Teichou et al., 2007), and eight selected peridotites are presented here.

Ultramafic xenoliths

The studied peridotite xenoliths are spinel lherzolites with protogranular and porphyroclastic texture showing lithology and mineral chemistry similar to the other xenoliths from the continental sector (Lee et al., 1996; Dautria, Girod, 1986) along the CVL, and also to the average sub-continental lithospheric mantle (Downes, 2001).

Fluid inclusions

Based on fluid inclusion petrography, two generations of fluid inclusions can be distinguished in the xenoliths (Fig. 1). The Generation 1 fluid inclusions can be seen randomly in olivine and orthopyroxene in the Nyos peridotites. These fluid inclusions have negative crystal shape with 50 µm

average size, and they are partly or completely decrepitated. This population of fluid inclusions is considered as older generation of fluid inclusions.

The Generation 2 fluid inclusions occur in all the mantle silicates, including clinopyroxene, orthopyroxene and olivine, in both Barombi and Nyos xenoliths. These inclusions are trapped along healed fractures; however, they can also be found in the neighborhood of the older decrepitated inclusions, in case of the Nyos peridotites, with size of generally 8-30 µm. This population of fluid inclusions is considered as younger generation fluid inclusions. They can be divided into two subgroups: the generation 2A fluid inclusions show negative crystal or spherical shapes, whereas the generation 2B fluid inclusions show irregular, oval or vermicular shape.

Solid phases, namely carbonates, in the younger generation (2A and 2B) fluid inclusions (10-20%) were identified under polarized microscope.

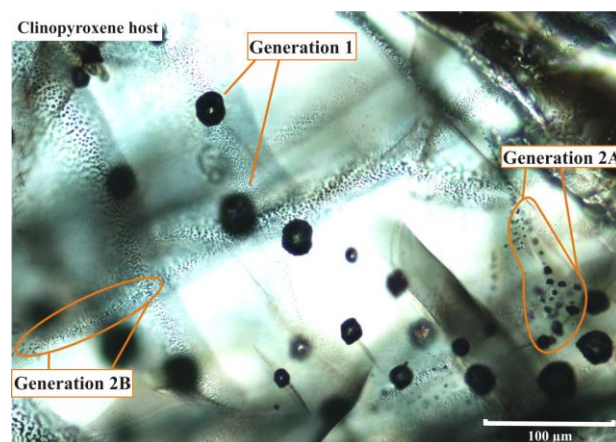


Figure 1. Photomicrograph of clinopyroxene hosted two generations (generation 1, 2A and 2B) CO₂-rich fluid inclusions in the Nyos peridotites.

Microthermometric measurements were carried out on the generation 2A fluid inclusions because they show textural equilibrium with the host silicates in mantle xenoliths. Neither generation 1 nor generation 2B fluid inclusions are considered in this study.

In the studied generation 2A fluid inclusions for both Barombi and Nyos peridotites similar last melting temperatures were observed. In the Barombi xenoliths melting temperature yields in very narrow range between -57.9 and -56.6°C, and in the Nyos samples it shows a range between -58.1

and -56.6°C . The decreasing of the melting temperatures of CO_2 suggests presence of minor amount of other component(s), for instance CH_4 and N_2 or H_2S , (van Kerkhof, 1990) besides the CO_2 . The lowest homogenization temperatures are between -48.2 and -27.8°C in the Barombi xenoliths, and between -50.9 and -30.1°C in the Nyos xenoliths. Based on the density of CO_2 -rich inclusions in both pyroxenes ($1.12\text{--}1.03\text{ g/cm}^3$), the estimated minimum trapping pressure conditions correspond to a range between $8.4\text{--}11\text{ kbar}$ (after Holloway, 1981).

Raman microspectroscopy at room temperature indicates that beside the CO_2 a small amount of H_2S is also present in the fluid inclusions in both xenoliths series. The H_2S can cause at the decrease of the melting temperatures. Furthermore, Raman spectroscopy also reveals the presence of H_2O as dissolved component in the CO_2 -rich phase in studied xenoliths (Fig. 2).

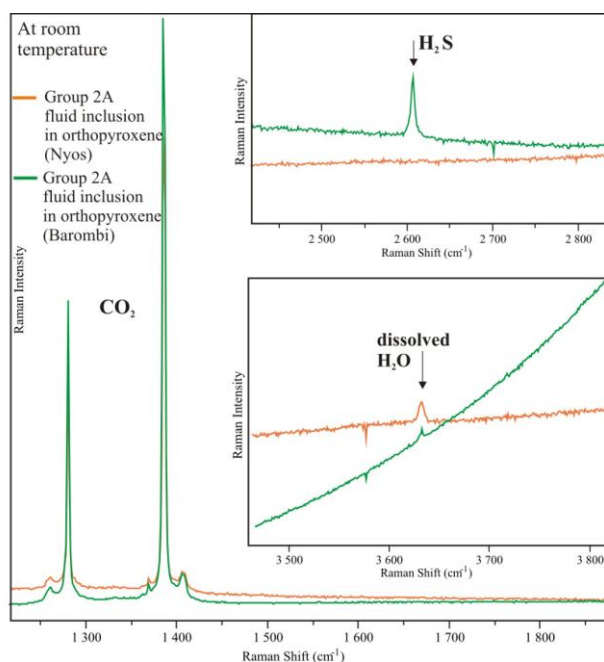


Figure 2. Representative Raman spectra of the CO_2 -rich generation 2A fluid inclusions.

Conclusions

Our results suggest that the CO_2 -rich fluid inclusions, occurring in both Barombi and Nyos upper mantle xenoliths, trapped at lithospheric mantle condition in the mantle silicates. Our study provides additional information on the composition (CO_2 , H_2O and H_2S) of mantle fluids that can be indeed a potential source of volcanic hazards along the CVL, especially in maar lakes such as Nyos.

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MELT INCLUSIONS IN OLIVINE FROM BASANITES OF WEST KAMCHATKA

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Alkaline and subalkaline volcanism was described within large West Kamchatka structural zone during Palaeogene and Neogene. This zone was in the rare arc geotectonic setting at that time (Volynets et al., 1987; Volynets, 1993). Volcanism of this zone was related to magma generation in post-subduction geodynamic settings (Perepelov et al., 2003). It is important, that rare subvolcanic trachybasaltic and basanitic rocks were also described within West-Kamchatkan zone. Their age was estimated as 8-17 Ma. Fresh and olivine-rich basanitic rocks were sampled near the Bystraya river valley (Huhch Mountain). Petrography and geochemistry of these rocks was described in details (Perepelov et al., 2007). Here we present results of the study of melt inclusions in olivine of the Huhch Mountain basanites.

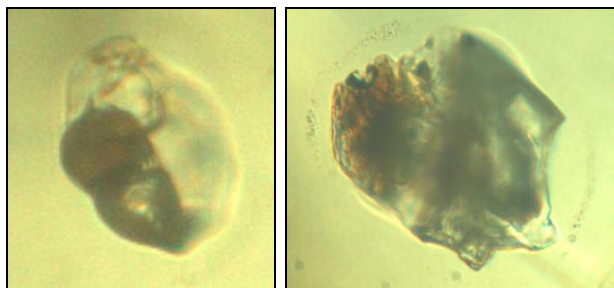


Figure 1. Crystallized melt inclusions in olivine, sample PK-02-12.

Note: diameters of the left and right inclusions are ~25 µm and 35 µm respectively.

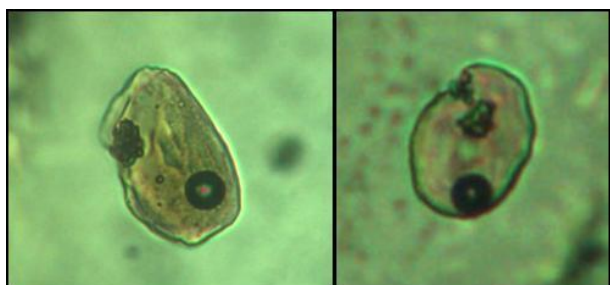


Figure 2. Heated and then quenched melt inclusions in olivine after thermometric heating experiments, sample PK-07-12.

Note: size of inclusions corresponds to Figure 1.

Samples for melt inclusion study were collected by authors in June 2007. Most well-preserved melt inclusions occurred in samples PK-07-12 and PK-07-13 among all 19 collected samples.

Figure 1 shows typical melt inclusions in olivine from investigated basanites. They are fully crystallized and contain clinopyroxene, plagioclase

and Cr-spinel as daughter phases.

Thermometric experiments and analytical methods

Twenty four thermometric experiments with visual control were carried out with melt inclusions in olivines from samples PK-07-12 and PK-07-13. We used the Sobolev-Slutsky heating stage with helium atmosphere in University of Tasmania (Hobart, Australia). During heating the melting of the groundmass around and inside olivine grains occurred at the temperature 1120-1140°C. We saw only melt, small gas bubble and small hercynite crystal at the 1060-1080°C (Fig. 2). During further heating (1080-1090°C) a gas bubble in some inclusions started to move to upper part of the inclusion. Hercynite crystal and gas bubble was not dissolved in one inclusion, which we heated up to 1315°C. Repeated experiments with experimentally quenched inclusions show same temperatures of phases melting and same volume proportion between bubble and melt. We heated and quenched inclusions for further analysis in the same heating stage. We used quick mode of heating (time with temperature above 500°C was not more than 6 min for each experiment) and all inclusions were quenched at 1200°C.

Glass composition of quenched melt inclusions and host olivines were obtained with Cameca-SX100 microprobe (Hobart, Australia). Trace elements were analyzed by LA-ICP-MS (Agilent HP 4500, with Merchantek laser beam 213nm and 266nm). Glass compositions were recalculated for olivine-melt equilibrium by reverse crystallization method with taking into account Fe-loss effect. These calculations were produced with Petrolog-III software.

Bulk rocks compositions were defined with SRM-25 (XRF), Plasma Quad 2+ and Element 2 (ICP-MS) equipment in Institute of geochemistry of SB RAS (Irkutsk). Description of bulk methods is given in (Perepelov et al., 2007).

Results

As a result of the study the early magmatic assemblage was determined. It comprises melt, olivine and Cr-spinel.

Averaged compositions of glasses and host olivines are given in the Table 1. Melt compositions were estimated by calculations to follow the

method of Danyushevsky et al. (2000). Comparison of melt composition with bulk rock compositions shows that rocks have a significant excess of olivine and depleted in feldspar or/and foid component. Possibly, it is due to cumulative processes of minerals in transitional magma chambers.

Composition of olivine, which contained melt inclusions, lies in narrow range from Fo_{83.9} to Fo_{86.5} and most of them are within Fo_{85.3-85.9}. In the rock we noted wider variations of olivine composition (up to Fo_{87.6}) (Perepelov et al., 2007). Most magnesian olivine grains in the rock could represent xenocrysts because: 1) these grains do not contain melt inclusions; 2) has low CaO concentrations (~0.05 wt.%); 3) has deformation elements like mantle olivines.

Table 1. Compositions of basanite of the Huhch Mountain and early magmatic phases in this basanite.

Phase	Glass	Melt	Rock	Olivine	Spinel
n	9	9	16	33	24
SiO ₂	42.40	41.23	44.15	38.75	
TiO ₂	2.42	2.31	1.89	-	1.22
Cr ₂ O ₃	0.04	0.04	-	0.03	17.37
Al ₂ O ₃	17.77	17.07	14.43	-	37.64
Fe ₂ O ₃	-	1.24	12.40	-	-
FeO	6.88	10.08	-	14.55	26.97
MnO	0.08	0.08	0.19	0.27	0.22
MgO	9.67	8.05	10.49	44.48	14.09
CaO	12.42	11.75	9.90	0.26	0.01
Na ₂ O	4.56	4.38	3.46	-	-
K ₂ O	2.95	2.81	1.89	-	-
P ₂ O ₅	0.99	0.82	0.65	-	-
Total	100.16	98.36	99.97	98.55	98.20

Note: n – analyses for averaging, melt composition is calculated from melt inclusion glasses. All values are in wt.%.

Cr-spinel grains (see tabl.1) were measured in the same olivine grains which contain measured melt inclusions and were trapped simultaneously with melt inclusions. Cr-number of spinels (Cr/Cr+Al) in early magmatic assemblage varies in the range of 0.22-0.25. This corresponds to lherzolitic mantle source.

Crystallization conditions

Temperature of crystallization of the considered assemblage could be estimated by olivine-melt equilibrium in melt inclusions. Such estimations give range 1230-1260°C (average is 1251°C). Oxygen fugacity was calculated from olivine-spinel equilibrium (Ballhaus et al., 1991) and corresponds to QFM oxygen buffer with shift of +1.3-2.3 log units.

Conclusion

Measured melt inclusion compositions are in a good agreement with bulk rock compositions and support classification of the Huhch basanites (Perepelov et al., 2007) as a product of fractionation of K-Na alkaline magma. Determined compositions of melts and coexisting mineral assemblages could be used for discussion about genesis of Ne-normative magmas in rare arc and back arc settings.

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VOLATILES IN PRIMITIVE MAGMAS OF KAMCHATKA AND THEIR LONG-TERM FLUXES

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Introduction

Evaluation of short and long-term effects of volcanism on the global climate requires quantitative estimates for the volcanic emission of volatiles. One cannot directly measure the amount of volatiles emitted by volcanoes in the past but can estimate it using petrologic methods based on study of melt inclusions. In this work we report new data on concentrations of volatiles in primitive magmas of Kamchatka and estimate emission of volatiles resulted from basaltic volcanism in Kamchatka since the last glacial period.

We studied about 900 glassy (Fig. 1) and experimentally homogenized olivine-hosted (Fo₉₂₋₆₅) melt inclusions from 10 volcanic centers representative for 3 volcanic zones of the Eastern Volcanic Belt of Kamchatka: volcanic front (EVF: Ksudach, Zheltovsky, Vysoky, Krashenninnikov, Karymsky and Zhupanovsky volcanoes), rear-arc (Zavaritsky volcano and Tolmachev Dol) and the southern segment of the Central Kamchatka Depression (SCKD: Klyuchevskoy volcano and Tolbachinskiy Dol). The compositions of rocks studied range from low- to high-K basalts and basaltic andesites and are representative for major magma types of the Eastern Volcanic Belt.

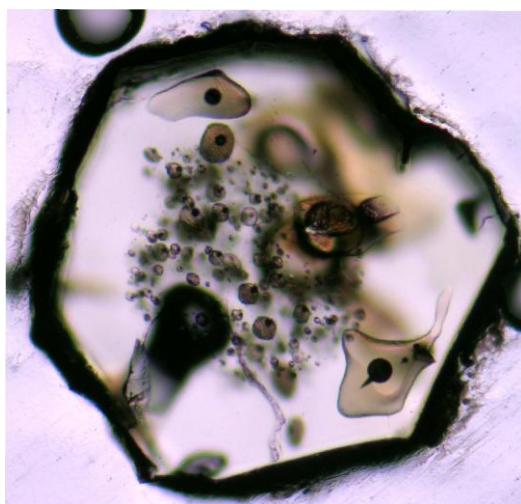


Figure 1. Glassy melt inclusions in olivine from the Klyuchevskoy volcano.

Inclusions were analyzed for volatiles (S, Cl, H₂O, F), major and trace elements using electron and ion microprobes. The data for S, H₂O and Cl including previously published results (Portnyagin et al., 2007; Churikova et al., 2007) are shown on Figure 2.

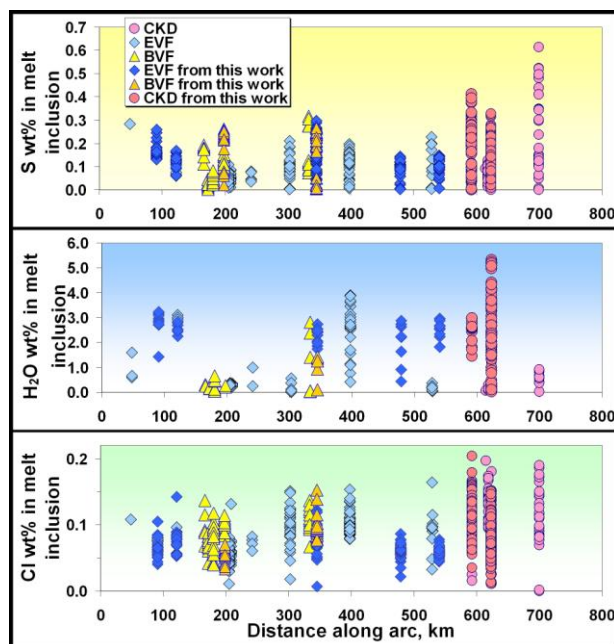


Figure 2. Volatiles in olivine-hosted melt inclusions from Kamchatka.

Volatiles in melt inclusions

The sulfur content in high-magnesian (Fo₈₈₋₈₀) olivines is 2500-3000 ppm from Zheltovsky and Zhupanovsky volcanoes from EVF, Zavaritsky and Tolmachev Dol from rear-arc zone and slightly less in olivines Fo₈₁₋₇₃ from Ksudach (1700 ppm), and in olivines Fo₇₈₋₇₅ from Vysoky and Krashenninnikova (1500 ppm). The SCKD melts also have high S concentrations ranging from 1700 to 4000 ppm. Sulfur content correlates inversely with K₂O in all samples and decreases to less than 200 ppm in groundmass glasses. Fast depletion of fractionating melts in sulfur and high proportion of sulfate species (measured S^{6+}/S^{Total} is 0.40 ± 0.16 on average) dissolved in melts suggest that sulfur preferentially partitions into fluid phases during magmatic evolution. We estimate that magmas in Kamchatka lose more than 90% of sulfur after 70% crystallization.

The H₂O content in the most primitive inclusions is 2-3.5 wt.% for EVF, 2.5-3.5 wt.% for the SCKD volcanoes and ~1.5 wt.% for the rear-arc Zavaritsky volcano. This difference in water content between frontal and rear-arc EVF volcanoes can be explained by decreasing water concentrations in parental melts and their sources with increasing depth from volcano to the subducting plate (Portnyagin et al., 2007). The H₂O

concentrations in the EVF melts decrease with increasing K_2O and indicate degassing of water during crystallization. The rate of water degassing is much slower than that of sulfur. No more than ~50% of the initial water content is lost from magmas at 70% of crystallization. The H_2O content in the SCKD melts increases up to 5-5.5 wt.% during first 30-35 % of fractionation ($F_{0.82-83}$) and then decreases due to degassing at shallow pressure.

Average chlorine and fluorine content in primitive magmas of Kamchatka volcanoes are shown at Table 1. Concentrations of these components slightly increase during crystallization but Cl/K_2O and F/K_2O ratios decrease that indicates partial loss of chlorine and fluorine into fluid phase.

Volcanic fluxes

Volcanic fluxes of volatiles to the exosphere (total flux to atmosphere, crust and hydrosphere) were estimated from published data on productivity of all EVF volcanoes during the Holocene (80×10^6 t/y) and CKD (Klyuchevskoy-Tolbachik: 10^7 t/y, Ponomareva et al., 2007) and our data on volatile content in parental melts. The total magmatic volatile flux can be higher if appropriate amount of cumulates and intrusives is taken into account (Sadofsky et al., 2008).

Minimum total and normalized to the length of the arc segments volatile fluxes are shown in Table 1. Larger fluxes of volatiles from SCKD volcanoes reflect higher volcanic productivity of this region. The estimated long-term sulfur flux for Kamchatka is at least 5 times higher than COSPEC measurements for this region (Hilton et al., 2002). The difference indicates that results of short period measurements cannot be representative for the long-term flux. Large eruption occurred during the period of satellite monitoring of gas emission from volcanic area can in turn lead to large overestimate of the long-term flux.

Table 1. Volatile content of initial magmas of Kamchatka and minimum volcanic fluxes of volatiles to the exosphere.

	EVF	BVF	SCKD
H_2O , wt. %	2.6	1.5	2.8
S, wt. %	0.25	0.3	0.35
Cl, wt. %	0.05	0.08	0.09
F, wt. %	0.01	0.01	0.034
H_2O , (t/year)/(t/km/year)	$2.0 \times 10^6 / 3.7 \times 10^3$		$2.7 \times 10^6 / 2.7 \times 10^4$
S, (t/year)/(t/km/year)	$2.0 \times 10^5 / 3.7 \times 10^2$		$3.4 \times 10^5 / 3.4 \times 10^3$
Cl, (t/year)/(t/km/year)	$4.1 \times 10^4 / 75$		$8.7 \times 10^4 / 8.7 \times 10^2$
F, (t/year)/(t/km/year)	$8.0 \times 10^3 / 14.5$		$3.3 \times 10^4 / 3.3 \times 10^2$

magmas of Kamchatka are very rich in volatiles and particularly in sulfur which concentrations in primitive Kamchatka magmas are among the highest measured so far in island arcs (3000-6000 ppm). Given the large productivity of Kamchatka volcanism during the last post-glacial period its contribution to volcanic forcing of the Earth climate should be discernable on global scale.

Acknowledgements

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In summary, we conclude that primitive

WATER-RICH MELT INCLUSIONS IN OLIVINE FROM SILICIC ICELANDIC ROCKS

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Icelandic magmas are widely believed to have low water content and evolve by tholeiitic trend of differentiation in contrast to calc-alkaline water-rich island-arc magmas. Here we report new data on composition of melt inclusions in minerals from evolved Icelandic rocks and show that concentrations of pre-eruptive water were unexpectedly high in these magmas and well comparable to those in island-arcs.

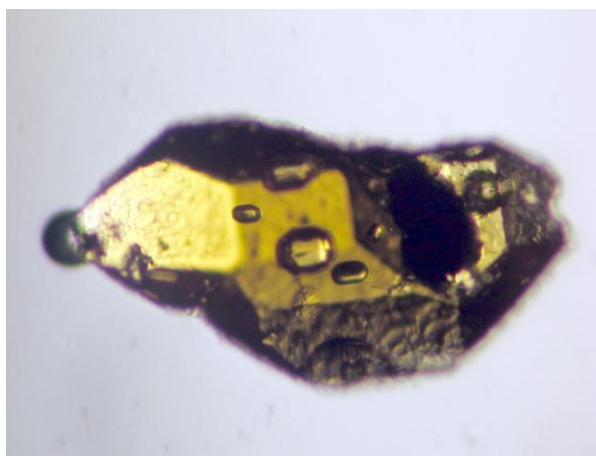


Figure 1. Typical crystal of olivine (Fo₅) with melt inclusions from the Hekla rhyolite. The crystal size is ~ 1 mm.

We studied glassy melt inclusions in Fe-rich olivines (Fo₂₋₄₀) from silicic pyroclastic deposits of the Hekla volcano (Hekla 3 and Hekla 4 eruptions) (Fig. 1). These inclusions have composition ranging from Fe-rich andesite (icelandite) to rhyolite and contain 3-7 wt.% H₂O (SIMS and FTIR data), being the most hydrous melts from oceanic setting reported to date. Water content in melt inclusions increases with decreasing Fo-number of olivine and strongly correlates with SiO₂ and concentrations of highly incompatible elements (e.g. K₂O) (Fig. 2). Silicic and primitive basaltic melt inclusions from the Hekla rocks have nearly constant H₂O/K₂O ~ 2.3 and can be related by ~90% closed-system fractional crystallization from basalts to rhyolites. Crystallization took place within the temperature interval 1200-800°C, at pressure ~200 MPa and *f*O₂ close to QFM equilibria as estimated from composition of melt inclusions and coexisting magnetite and ilmenite. Olivine, plagioclase and Ca-rich pyroxene were liquidus phases of the Hekla magmas over the entire interval of crystallization recorded in melt inclusions. Magnetite and ilmenite appeared at ~1100°C (Fo₇₀) and were joined by F-

apatite and zircon on liquidus of more evolved melts at ~1000°C (Fo₆₀). Pyrrhotite inclusions in olivine indicate saturation of all Hekla magmas with immiscible sulfide phase in agreement with the low estimated *f*O₂.

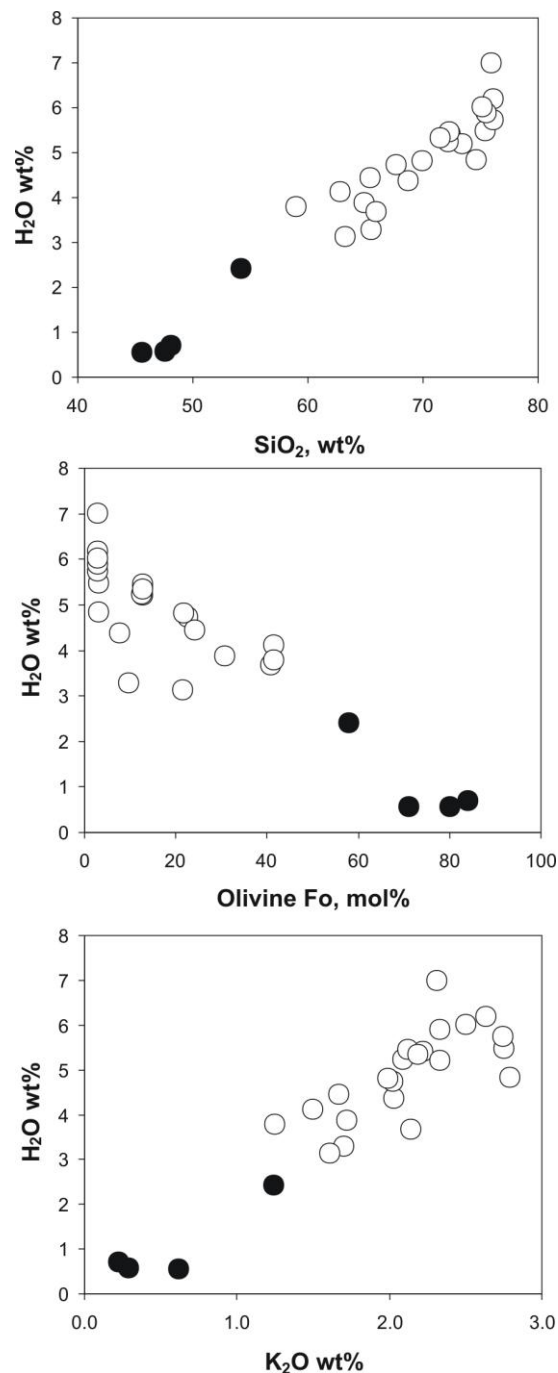


Figure 2. Composition of melt inclusions in olivine from rocks of the Hekla volcano. Open circles – this work, closed circles – data on olivine- and plagioclase-hosted inclusions from Moune et al. (2007, EPSL).

There are several implications from these new data, which are relevant to our understanding of explosive Icelandic volcanism and magma fractionation in different geodynamic settings.

1) High pre-eruptive water content in the Hekla rhyolites can explain explosive character of this volcano without invoking magma interaction with meteoric waters and/or ice. Dramatic decrease of magma viscosity in presence of water provides explanation for rapid transport of silicic magmas from magma chamber to the surface and violent eruptions of the Hekla volcano, which are known to have very short seismic precursors.

2) Similar amount of water in silicic Hekla and island-arc magmas indicates no principle difference between oceanic and island-arc settings with respect to the partial water pressure in silicic magma chambers. There is however a fundamental difference between initial water content in parental basaltic magmas of these geodynamic settings. Whereas parental island-arc magmas are water-rich and approach water saturation shortly after beginning of crystallization, parental Hekla melts contained only ~0.6 wt.% H₂O (Fig. 2) and evolved in closed system where partial water pressure increased during crystallization.

3) Distinctive features of Icelandic magmas are an expanded stability of olivine, which is present in all rock varieties, and absence of amphibole. In contrast, orthopyroxene and amphibole are typically present in silicic island-arc magmas. Possible explanation for the enhanced olivine stability in Icelandic magmas can be a low oxygen fugacity (~QFM) and high H₂O pressure at crystallization, which are known to reduce silica activity in melts and stabilize olivine on liquidus. Olivine is less stable and replaced by orthopyroxene in water-rich but strongly oxidized (>>QFM) silicic island-arc magmas. Stability of amphibole in magmas appears to be independent from oxygen fugacity. Its absence in Icelandic rhyolites with ~6 wt.% H₂O is most likely related to very low MgO (<0.1 wt.%) and Mg# (<5 mol.%) in these melts.

In general, an assemblage of anhydrous minerals crystallizing from reduced tholeiitic magmas can only seemingly imply dry conditions of crystallization. The presence of iron-rich olivine, however, can be an indicator of hydrous nature of tholeiitic magmas such as, for example, parental for the Skaergaard-type layered intrusives.

COMPOSITION AND EVOLUTION OF PARENTAL MELTS OF THE 1996 ERUPTION IN THE ACADEMY NAUK CALDERA (KARYMSKY VOLCANIC CENTER, KAMCHATKA)

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A strong freatomagmatic eruption in the Akademy Nauk Caldera on the 2nd January of 1996 marked the onset of the new phase of activity of the Karymsky volcano and became a prominent event in the latest history of volcanism in Kamchatka. In this paper we report new data on major, volatile and trace element composition of about 200 glassy melt inclusions (Fig. 1) in olivine (Fo_{82-72}), plagioclase (An_{92-73}) and clinopyroxene ($Mg\#$ 80-73) phenocrysts from basalts erupted in 1996 in the Akademy Nauk Caldera (Table 1). The data on melt inclusions is used to reconstruct the composition of parental melts, physical and chemical conditions of their evolution preceding the eruption.

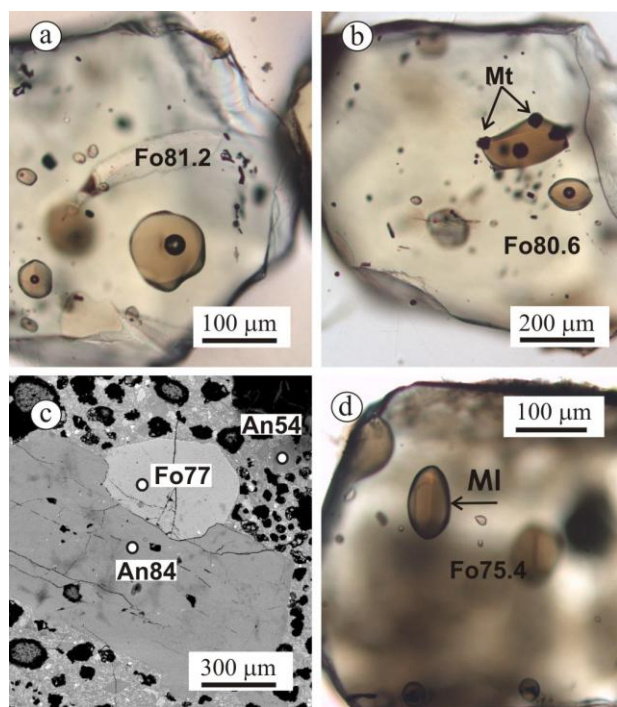


Figure 1. Micrographs of studied samples. (a), (b), (d) - melt inclusions in olivine; (c) - intergrowth of plagioclase and olivine phenocrysts from 1996 basalt.

The parental melt of the 1996 eruption, inferred from data on the most primitive melt inclusions in olivine, had a low-Mg high-Al basaltic composition ($SiO_2 = 50.2$ wt.%, $MgO = 5.6$ wt.%, $Al_2O_3 = 17$ wt.%) of the middle-K type ($K_2O = 0.56$ wt.%) (Table 1). The parental melt contained significant amount of dissolved volatile components ($H_2O = 2.8$ wt.%, $S = 0.17$ wt.%, $Cl = 0.11$ wt.%). The composition of parental melt is overall similar with bulk rocks. Somewhat higher

Al_2O_3 and lower TiO_2 and FeO in bulk rocks are explained by the presence of cumulate plagioclase phenocrysts in the rocks.

Table 1. Average compositions of parental melt (PM) estimated from the most primitive inclusions in olivine and melt inclusions in olivine (Ol), clinopyroxene (Cpx), plagioclase (Pl) and groundmass glasses (Gl).

Comp. n	PM 5	Ol 92	Cpx 25	Pl 87	Gl 2
SiO_2	50.22	53.22	54.86	54.51	58.20
TiO_2	0.90	1.02	1.15	1.15	1.40
Al_2O_3	17.04	16.25	16.17	16.02	15.07
FeO	9.91	9.55	9.43	9.40	9.52
MnO	0.15	0.18	0.20	0.19	0.09
MgO	5.59	4.44	3.55	3.93	2.57
CaO	9.43	8.01	7.40	7.35	6.08
Na_2O	2.98	3.31	3.67	3.73	3.96
K_2O	0.56	0.82	0.89	1.04	1.50
P_2O_5	0.13	0.18	0.17	0.15	0.30
H_2O	2.81	2.79	2.29	2.29	1.14
S	0.20	0.13	0.09	0.10	0.03
Cl	0.084	0.10	0.13	0.14	0.14
Total	100.00	100.00	100.00	100.00	100.00

Melt inclusions in olivine, plagioclase and pyroxene have close compositions ranging from basalts to andesites and originating by cotectic crystallization of these crystalline phases from the parental melt that took place prior eruption at magma ascent. Crystallization started at ~5 km depth and continued in polybaric but nearly isothermal ($1040 \pm 20^\circ C$) regime until the near surface depths. The decompression-driven crystallization was caused by H_2O degassing at pressure less than 1 kbar. The extent of fractional crystallization of parental melt approached immediately before eruption is estimated as ~55%.

The magma degassing took place under open-vent conditions and resulted in the loss of ~82% H_2O , 93% S and 24% Cl from magmas into fluid phase. The emission of volatiles to the atmosphere during the 18 h long eruption is estimated as high as 1.7×10^6 t H_2O , 1.4×10^5 t S and 1.5×10^4 t Cl .

Concentrations of most incompatible trace elements in melt inclusions are similar to those in

the host rocks and follow expected trend of increasing concentrations at fractional crystallization (Fig. 2). Selective Li enrichment was, however, found in plagioclase-hosted melt inclusions (Fig. 2b), which have Li concentrations 2-3 times higher than melt inclusions in olivine and pyroxene at similar concentrations of major and trace elements. It is suggested that Li enriched plagioclase phenocrysts with melt inclusions originate from early formed cumulates in magma feeding system beneath Karymsky volcano. The plagioclase phenocrysts could interact and diffusively re-equilibrate with Li-rich melts or brines and were mobilized by ascending magmas during eruption in 1996.

The results were submitted for publication in *Geochemistry International (Geokhimiya)* in March, 2010. This work was supported by the Russian Foundation for Basic Research (projects No 09-05-01234 and 10-05-00209) and the Russian-German KALMAR project.

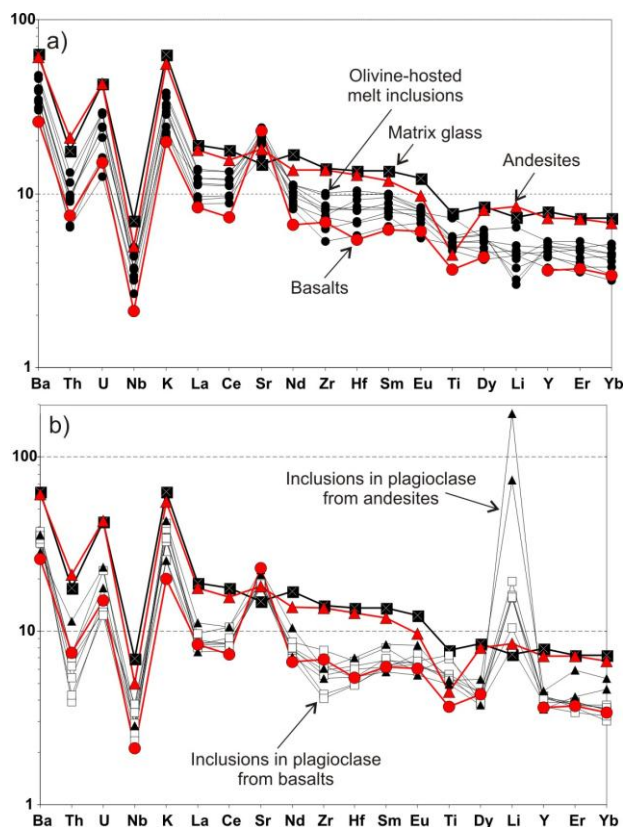


Figure 2. Trace element composition of olivine- (a) and plagioclase-hosted (b) melt inclusions. Average compositions of the Karymsky basalts (1996 year eruption) and andesites (1963-1999) and matrix glass from groundmass of basalt are shown for comparison. Melt inclusions in plagioclase from andesites are shown after Tolstykh et al. (2001, *Geochem. Inter.*). All compositions are normalized to the primitive mantle values.

MICROTHERMOMETRIC STUDY OF FLUID INCLUSIONS FROM VEIN QUARTZ OF THE UDEREI GOLD-ANTIMONY DEPOSIT, KRASNOYARSK TERRITORY, RUSSIA

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Introduction

Currently 24 Sb provinces and 20,000 deposits and occurrences are known in the world. In Russia, gold-antimony deposits are located in the Krasnoyarsk territory, Yakutia, Chukotka, and some other regions.

In the Krasnoyarsk territory, there are the Razdol'ninsk gold-containing Sb deposit; Au-Sb deposits Uderei, Veduga, Poputninskii, and Bogolyubovo; and large gold deposit Olympiada enriched in Sb.

The Uderey Au-Sb deposit discovered in 1966 is located 100 km north of settlement Motygino.

For the first time, fluid inclusions (FI) from vein quartz at the deposit were studied in the mid 1970th (Distanov et al., 1977).

This study presents some new data on fluid inclusions and supports the previous results.

Formation. Quartz, calcite, feldspar, chlorite, muscovite, rutile, pyrite, and organic matter are the major constituents of the host rocks. The orebodies are numerous quartz veins and veinlets of variable thickness (up to 1 m) and length (up to 100 m).

Two types of wall-rock alteration were identified at Uderei: (1) early beresite (quartz + muscovite + carbonate ± chlorite ± pyrite ± arsenopyrite) and (2) late argillic.

The first type altered rock accompanies gold mineralization, whereas the second type, antimony mineralization. Frequently, antimony mineralization spatially overlaps the gold ore. According to Nevol'ko and Borisenko (2009), the gold ore is of ~712 Ma age, whereas antimony mineralization, ~670 Ma.

In addition to quartz, muscovite (sericite) and siderite are gangue minerals of the gold ore stage. The ore minerals of the stage are pyrite-I enriched in As, arsenopyrite, Fe-rich sphalerite-I, gersdorffite, tetrahedrite, chalcopryite, and native gold as nanoinclusions in arsenopyrite. The ore minerals of the antimony stage are stibnite, berthierite, zinkenite, ulmanite, chalcostibite, and rare free native gold probably remobilized from early arsenopyrite.

Fluid inclusions

Petrographic and microthermometric study of FI was carried out with double side polished sections. The FI are negative crystals or irregular shaped and 2 to 25 microns in size. The primary FI are evenly distributed in crystal body; pseudosecondary inclusions heal fractures within crystal, and secondary FI heal fractures rising at the crystal surface. At room temperature on the basis of phase composition, the following types of FI are recognized (Fig. 1): (1) two- or three-phase CO₂-H₂O with large (20-30 vol.%) gas bubble; (2) two- or three-phase gas-dominated inclusions with small CO₂ gas bubble and water rim; and (3) two-phase inclusions aqueous solutions. Types 1 and 2 FI are primary, type 3 FI are secondary.

Microthermometry was performed for 305 FI. Homogenization temperature of primary and pseudosecondary CO₂-H₂O inclusions (type 1) ranges from 228 to 338°C. Salinity varies from 4.1 to 7.1 wt.% equiv NaCl. Concentrations of CO₂ and methane are 1.8-6.3 and 0.5-1.2 mole/kg of

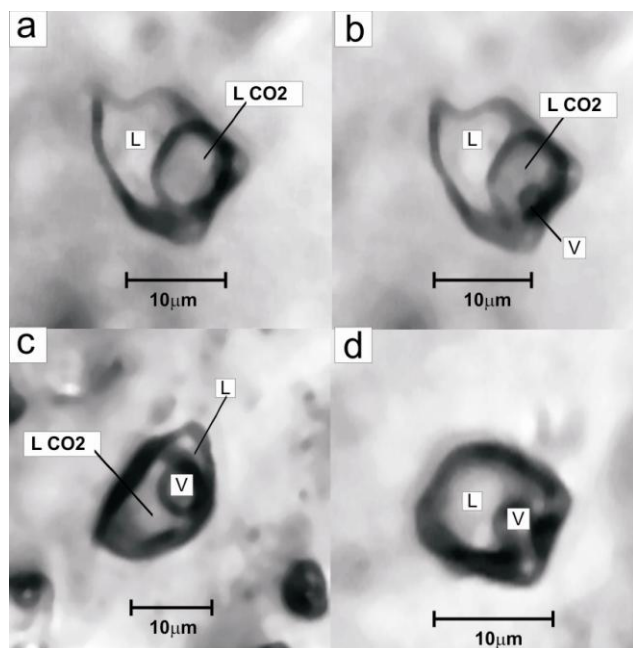


Figure 1. (a-c) Primary FI: (a, b) type 1 CO₂-H₂O (a - +24°C, b - +15°C); (c) type 2 gas dominated CO₂; (d) type 3 secondary two-phase FI of aqueous solution.

Geological setting and mineralogy

The Uderei Au-Sb deposit located in the central Enisei Ridge within zone of the Ishimba large fault is hosted in the NE trending shear zone. Ore bodies of the deposit are hosted in metamorphosed (green schist facies) siltstone and carbonate-clay rocks of the Late Proterozoic Uderei

solution. According to eutectic temperature (-37 to -30°C), the mineralizing fluid were dominated by sodium and magnesium chlorides. The density of CO₂-H₂O fluid ranges from 0.75 to 1.03 g/cm³.

Gas-dominated CO₂ FI (type 2) homogenize into liquid at +1.1 to +24.7°C and its melting temperature ranging from -58.7 to -57°C differs from melting temperature of pure CO₂ (-56.6°C) indicating an admixture of gases boiling at low temperature. CO₂ density varies from 0.63 to 0.86 g/cm³. The pressure estimated from these simultaneous FI is 77 to 250 MPa. The P_{tot}/P_{H₂O} ratio ranges from 14.1 to 46.9.

Two-phase FI of type 3 homogenize into liquid at 136-194°C and contain aqueous solution with salinity of 2.9 to 6.9 wt.% equiv NaCl. The density varies from 0.92 to 0.98 g/cm³. The fluid of these inclusions is also dominated by sodium and magnesium chlorides (eutectic temperature -31 to -29°C).

According to Distanov et al. (1977) gold ore was deposited at 200-350°C, whereas temperature of antimony mineralization is 120-180°C.

Thus, the secondary fluid inclusions studied here probably correspond to the antimony stage of the Uderei formation.

In general, ore-forming fluids are moderately saline and CO₂-rich and by many parameters correspond to fluids responsible for the formation of orogenic gold deposits (Ridley, Diamond, 2000).

The P_{tot}/P_{H₂O} values of fluids of the Uderei deposit indicate the shallow (hypabyssal) formation of the deposit in closed system with tectonic activity. Tectonic activity was expressed as local opening and closing fractures resulting in boiled gas-saturated fluid (Prokof'ev, 1998).

According to Prokof'ev et al. (1995) gold ores of the Olympiada deposit were formed at 140-450°C and 57-215 MPa from CO₂-, CH₄-, and N₂-rich fluids of salinity ranging from 2.4 to 25 wt.% equiv NaCl. Stibnite was deposited at lower temperature and pressure 125-235°C and 19-106 MPa from fluids of salinity varying from 1.9 to 9.5 wt.% equiv. NaCl.

At the Veduga deposit, ore bodies were formed also during two stages, gold (230-330°C) and antimony (120-170°C) (Prokof'ev, Krylova, 2001; Nevol'ko, Borisenko, 2009).

Thus, the fluids responsible for the gold mineralization at the Au and Au-Sb deposits of the Enisei Ridge are similar to those of orogenic gold deposits (Ridley, Diamond, 2000).

Acknowledgements

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ORIGIN AND VERTICAL FLUID ZONING OF FLUID-MAGMATIC GOLD ORE-FORMING SYSTEMS OF EASTERN TRANSBAIKALIA (RUSSIA)

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Introduction

Gold deposits of Transbaikalia have the long-term study history. The characteristic for Transbaikalia large Darasun deposit for a long time was considered as a typical mesothermal gold deposit (Timofeyevsky, 1972; Safonov, 1997; Bortnikov, 2006; and others). However there are other opinions about the Darasun deposit origin in literature. Yakubchuk et al. (2005) have classified the Darasun deposit as an orogenic gold deposit. Some authors (Gosselin, Dube, 2005) have classified the Darasun deposit as a greenstone-hosted quartz-carbonate Au vein deposit. But other researchers, based on several indicators, have demonstrated that this deposit differs from the typical mesothermal deposits and are similar to porphyry copper deposits or fluid-magmatic systems associated with the shallow granitoid intrusions (Prokofiev et al., 2000). The consideration of the Transbaikalian gold deposits as the products of the homotypic fluid ore-forming systems at different levels allows us to obtain the new arguments for the last point of view.

Geological background

The Talatuy, Darasun and Baley gold deposits represent the basic types of gold deposits of Transbaikalia.

The Talatuy deposit comprises complex shaped mineralized zones. These zones contain dikes of diorite porphyry, lamprophyre, granodiorite-porphyry, quartz-porphyry, and granite-porphyry (J_2 - K_1). Ore stage minerals compose veinlets and impregnation. Pyrite, chalcopyrite, magnetite, hematite, ilmenite, native gold, scheelite, and pyrrhotite (the latter mainly intergrown in pyrite and chalcopyrite) are the major ore minerals. Tourmaline, epidote, titanite, chlorite, quartz, carbonates, biotite, orthoclase, and chalcedony are gangue minerals.

The large gold deposit Darasun includes more than 200 steeply dipping gold-mineralized quartz-tourmaline-sulfide veins spatially related to the K-rich granodiorite porphyry intrusion of the Amudzhikansky complex (J_2 - K_1). Intense propylitic alteration predates ore formation, whereas a sericite-chlorite-quartz-pyrite-carbonate alteration coeval with ore deposition is observed close to the veins. Pipe-like bodies of hydrothermal explosive

breccias cemented with quartz, tourmaline and sulfide minerals occur within the endocontact zone of this intrusion and are considered to be feeders (Timofeyevsky, 1972). Ores of this deposit are enriched in sulfides (40-60%) and in Bi- and Te-bearing minerals. Pyrite, arsenopyrite, chalcopyrite, pyrrhotite, fahlore, sphalerite, galena, sulfosalts, tellurides and native gold are the major ore minerals. A large amount of arsenopyrite in veins is a specific feature of the Darasun deposit. Quartz, tourmaline, calcite, gypsum, and anhydrite are gangue minerals.

The large gold deposit Baley is formed by multitude of quartz-adularia veins with high contents of native gold. These veins occur both in sedimentary and igneous rocks.

Fluid inclusion study

Bottom level. The highest and widest range of homogenization temperature (610–120°C), pressure (3370–150 bar), and salinity (56.3–0.4 wt.% equiv NaCl) are observed in gangue minerals of the Talatui deposit. The distribution of fluid salinity at Talatui is bimodal as fluid decoupling into gas and brine at these temperature and pressure conditions. The K/Rb ratio of the fluid is minimum compared to magmatic fluids (Irber, 1999). The range of Br/Cl ratios in the fluid inclusions of Talatui is very narrow, and similar to the magmatic ratios (Böhlke, Irwin, 1992). The major characteristic features of the Talatui ores are: gold of very high fineness (997–777‰), the high concentration of Au, Te and Bi in pyrite, and the presence of two minerals of tellurium; pilsenite Bi_4Te_3 and hessite Ag_2Te .

Intermediate level. Moderate temperature (430–120°C), pressure (1560–60 bar), and salinity (44.8–0.7 wt.% equiv NaCl) are characteristics of the Darasun ores, which form the middle level of the fluid-magmatic system. At the Darasun deposits, the fluid density is around the boiling area and salinity distribution has only one peak K/Rb ratios increase as temperature decreases. Large variations in the Br/Cl ratio are observed in the fluid of the Darasun deposit. These effects can be caused by the evolution of a convection system and the involvement of non-magmatic water (formation or meteoric) or by Br fractionation between gas and liquid phases upon fluid boiling (Liebscher et al., 2006). The ore veins of the Darasun deposit also

contain Te minerals. In addition to sulphotellurides, Bi and Ag tellurides, alexite, volynskite, and petzite were also found. The Au fineness of the Darasun deposit is 896–590‰. Whereas the concentration of Au, Te, and Bi in pyrite of the Darasun deposit are of intermediate value

Top level. The lowest homogenization temperature (353–131°C), pressure (150–30 bar) and salinity (7.6–0.5 wt.% equiv NaCl) are characteristic of the Baley deposit. These deposits contain only small quantities of sulfides and tellurides, the lowest fineness of gold (750–385‰), and the lowest concentration of Au, Te, and Bi in ore pyrites.

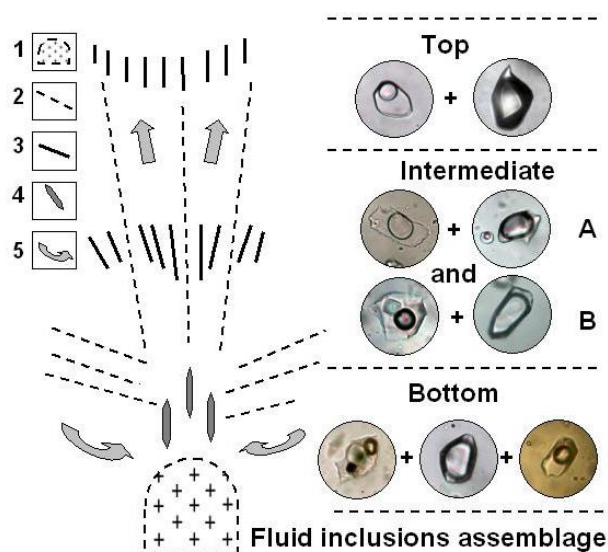


Figure 1. Model of gold fluid-magmatic ore-forming system in Transbaikalia with vertical zoning: Bottom level – metasomatic gold tourmaline-pyrite-magnetite ore bodies (Talatui deposit, assemblages of chloride brines, vapor and gas-liquid fluid inclusions); Intermediate level – gold tourmaline-quartz-sulfide ore vein (Darasun deposits, two type of fluid inclusions assemblages: A - chloride brines and vapor fluid inclusions, and B – two-phase gas-liquid and vapor fluid inclusions); Top level – epithermal gold adularic-quartz veins (Baley deposits, assemblages of gas-liquid and vapor fluid inclusions).

1 – subvolcanic granodiorite-porphyre, 2 – faults, 3 – gold ore vein, 4 – metasomatic gold tourmaline-pyrite-magnetite ore bodies, 5 – directions of fluids movements.

Conclusions

Recent studies of East Transbaikalia ore gold deposits have showed that specific character of fluid regimes for different East Transbaikalia gold deposits can be explained by their different position in monotype porphyritic epithermal fluid-igneous ore-forming systems (fig. 1). Ores of epithermal deposits (Baley, Taseevskoye and others) are formed under near-surface conditions from low-mineralized solutions, which were heterogeneous by early stages at relatively low temperatures (up to 300–370°C) and pressures (up to 200 bars). Vein ores of intermediate deposits (Darasun, Teremkyn, Sredne-Golgotayskoye and others) are formed in

subvolcanic situation from heterogeneous fluids with wide varieties of salt concentrations up to high concentrated chloride brines at higher temperatures (the process started at 430–470°C) and pressures (up to 2 kbar). The magnetite-containing vein impregnated ore of gold-porphyric deposits from Bottom level (Talatui, Kariyskoye and others) is crystallized at high temperatures (higher then 600°C) and pressures (up to 3 kbar) from heterogenic fluid with the participation of high-mineralized chloride brines. The data of fluid inclusions research can be used for the rating of depth grades of studied gold deposits, even at visual stage of fluid inclusions study. The composition of ore-forming fluids of the East Transbaikalian gold deposits differed strongly from ones for typical fluids of orogenic gold deposits (Ridley, Diamond, 2000), for which the presence of slightly mineralized solutions, containing big quantities of dissolved gases is typical.

Acknowledgements

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COMPOSITION OF ORE-FORMING FLUIDS OF FE-F-TR CARBONATITE DEPOSITS OF THE KARASUG AND ULATAI-CHEZSK GROUP (TUVA)

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LA-ICP-MS technique, the scanning electron microscopy (LEO 1430VP, detector OXFORD), and Raman spectroscopy (spectrometer Ramanor U-1000 and detector Horiba DU420E-OE-323 Jobin Yvon, laser, Millennia Pro, 532 nm, power 2 w, Spectra-Physics) have been used to analyze the composition of multiphase fluid inclusions in quartz and fluorite from the Fe-F-TR carbonatite deposits of the Karasug and Ulatai-Chezk group (Tuva).

Multiphase fluid inclusions are found in idiomorphic colorless quartz or morion crystals and violet to green fluorite cubic crystals which occur among ankerite-calcite or siderite matrix of carbonatite ores. Inclusions in quartz contain a large cubic halite crystal with violet shade occupying a large volume of vacuole, a small sylvite crystal, as well as 3-4 anisotropic crystalline phases, and frequently small opaque ore phases (Fig. 1). Gas phase contains liquid CO₂. Multiphase inclusions in fluorite have similar phase composition but differ in the absence of CO₂ in gas phase. Raman spectroscopy revealed ancylite, anhydrite, Fe-copiapite among solid phases in multiphase inclusions (Fig. 1).

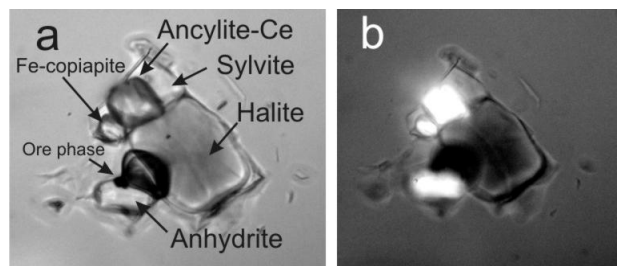


Figure 1. Multiphase fluid inclusion in morion in ordinary (a) and polarized (b) light.

Using scanning electron microscopy we established TR-carbonate, galena, barite, anhydrite in uncovered vacuoles of multiphase inclusions (Fig. 2). There is a liquid CO₂ at 200°C in multiphase inclusions in the idiomorphic quartz crystals. Raman spectroscopy showed the predominance of CO₂ with minor N₂ admixture in the composition of gas phase inclusions in quartz. The gas phase of inclusions in fluorite is of low density and characterized by the predominance of N₂ (86.7-72.6 mol.%) over CO₂ (27.4-13.3 mol.%). Thermometric study of quartz-hosted inclusions indicate that sylvite melts at temperature 220-260°C and about 9/10 of halite volume dissolves at

480-500°C with subsequent decrepitating of inclusions.

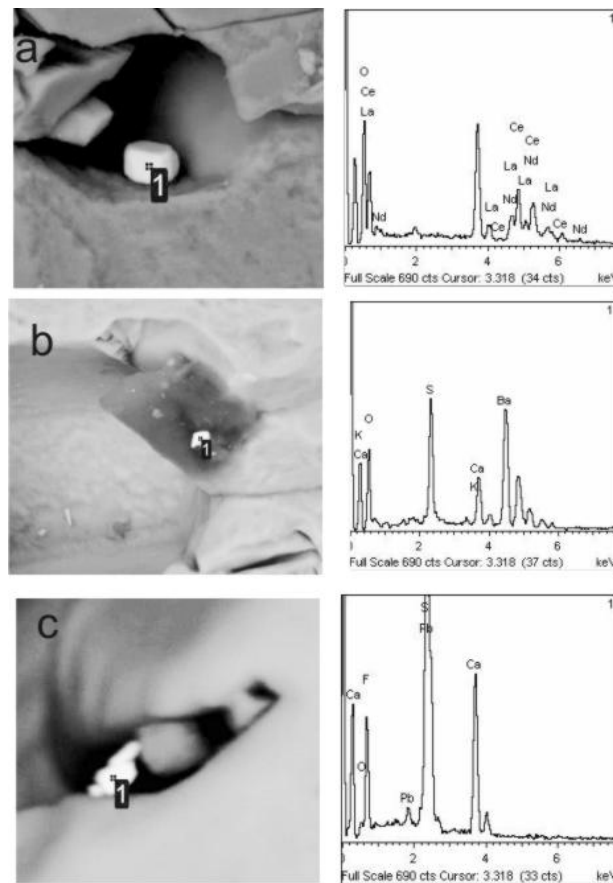


Figure 2. BSE images and EDS for daughter phases in exposed multiphase inclusions in quartz: TR-carbonate (a), barite (b); and in fluorite - galena (c).

Thus, total salt concentration in inclusion solutions may be approximately estimated to be no less than 78 wt.%. Concentration of NaCl was determined to be not less than 48 wt.%, whereas KCl was 30-27 wt.%. Analysis of multiphase inclusions by LA-ICP-MS technique revealed high Fe, Sr, Ba, Mn, Pb, Zn concentrations from 0.1 to 1 wt.%. The amounts of Cu, Mo, As, Sb, Hg, Bi and rare-earth elements such as Y, Cs, La, Ce, Nd appeared to be from 100 ppm to 1 ppm (Table 1, Fig. 3).

According to the inclusion study, ore-forming fluids of the Karasug and Ulatai-Chezk ore fields were represented by highly concentrated (more than 78 wt.%) water-salt solutions-melts of chloride-carbonate composition. The main salt components were NaCl and KCl with minor amounts of TR-carbonates and Fe- and Ca-sulphates. The presence

of sulphate daughter phases (barite, anhydrite and Fe-copiapite) and predominance of CO₂ and N₂ in the gas phase in the absence of reduced gases point to the oxidized state of fluids involved in the formation of carbonatite ores.

We acknowledge the financial support from RFBR (grants 08-05-00915, 10-05-00720 and 10-05-00730).

Table 1. Concentration of elements in the multiphase fluid inclusions according to LA-ICP-MS.

	Concentration (in ppm).		Concentration (in ppm).
Na	181000*	Ag	0.04
Ca	3200-140	Sn	0
K	156000-140000*	Sb	0.4-0.3
Mn	11000-1300	Cs	0.5-0.0
Fe	36600-38600	Ba	8000-7000
Zn	2300-1300	La	60-30
Cu	30-7	Ce	130-70
As	1-0.1	Nd	50-30
Rb	12-0.7	W	0.3-0.1
Sr	6970-2800	Hg	50-0.0
Y	7-3	Pb	760-200
Mo	8-1	Bi	15-0.5

* - according to the thermometric data.

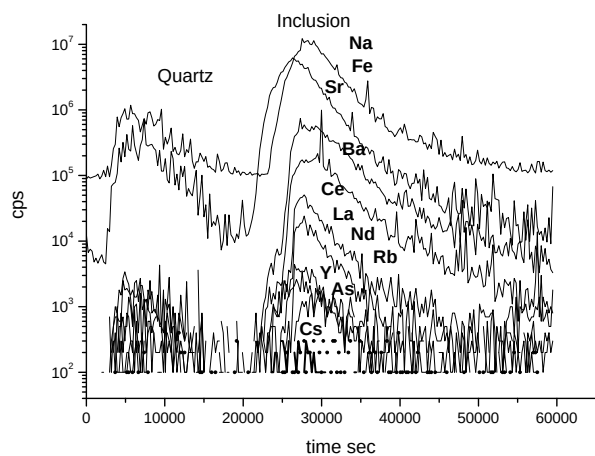


Figure 3. LA-ICP-MS signal of a multiphase inclusion.

SILICATE-CARBONATE-SALT IMMISCIBILITY DURING CRYSTALLIZATION OF SHONKINITES FROM THE RYABINOVYI MASSIF (CENTRAL ALDAN, RUSSIA)

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Introduction

The Ryabinovyi massif is an intricate volcano-plutonic structure (Kochetkov et al., 1981, Kim, 1981, Kostyuk et al., 1990). It consists of volcanic and vein rocks varied from ultrabasic to more siliceous compositions. The common feature of these rocks is their high alkalinity at pronounced potassium specialization. Micaceous shonkinites are the highest-magnesian Si-undersaturated rocks of the massif with the age - K_1 - K_2 . They contain clinopyroxene, Fe-Mg mica, potassium feldspar, albite, apatite, magnetite, sphene and rutile. The rock texture is hypidiomorphic-granular.

Petrography of melt inclusions

Clinopyroxenes is represented mainly by aegirine, less often by subcalcium diopside and subcalcium salite. Completely crystallized melt inclusions are observed in clinopyroxenes. Silicate, silicate-carbonate, carbonate salt and carbonate inclusions were found among them.

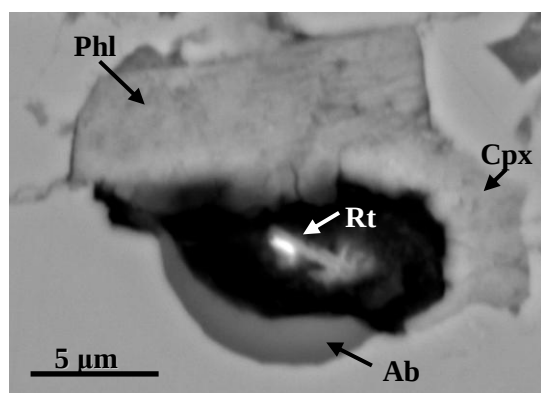


Figure 1. Silicate-rich inclusion. Cpx – clinopyroxene; Phl – phlogopite; Ab – albite; Rt – rutile.

Table 1. Composition of daughter phases from inclusions, wt.%.

Component	Cpx	Phl	Ab
SiO ₂	54.81	41.94	69.04
Al ₂ O ₃	0.91	12.24	19.50
FeO	12.00	11.74	0.28
MgO	10.16	20.14	-
CaO	18.88	0.19	0.12
Na ₂ O	3.26	0,1	11.33
K ₂ O	-	10.09	-
Total	100.02	96.44	100.27

Silicate-rich crystallized inclusions (Fig. 1) contain clinopyroxene, phlogopite, albite (Table 1),

and rutile (99.3 wt.% TiO₂).

Silicate-carbonate inclusions (Fig. 2) are represented by clinopyroxene, phlogopite (Table 1), and calcite (in wt.% - 53.48 CaO; 4.25 SrO; 0.52 FeO; 0.11 MnO; 0.12 MgO).

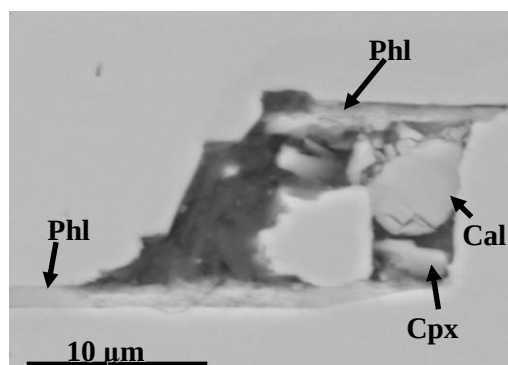


Figure 2. Silicate-carbonate inclusion. Cal – calcite.

Carbonate-salt inclusions (Fig. 3) consist of crystals of calcite, alkaline chlorides (wt.% - 50.59 Cl; 18.48 Na; 9.54 K; 2.28 Ca) and sulfates (wt.% - 31.4 SO₃; 29.35 SrO; 48.24 CaO), and sphene (wt.% - 38.17 TiO₂; 30.20 SiO₂; 0.45 Al₂O₃; 27.02 CaO; 2.44 Fe₂O₃; 0.14 Na₂O; 0.03 MgO; 0.12 SrO).

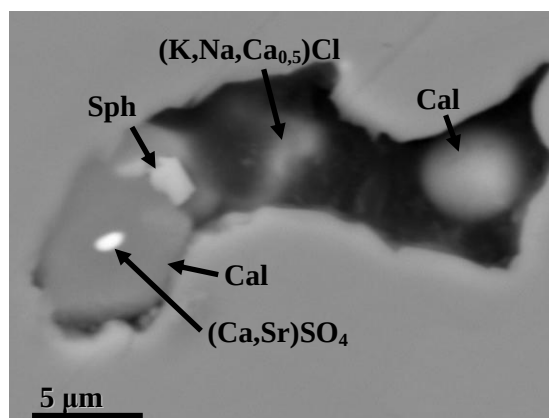


Figure 3. Carbonate-salt inclusion. Sph – sphene.

Carbonate inclusions (Fig. 4) are represented by calcite, in places with portlandite (wt.% - 73.64 CaO; 0.41 SrO; 0.6 FeO; 0.04 MnO; 0.09 MgO).

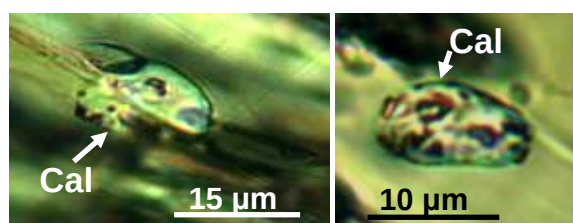


Figure 4. Carbonate inclusions.

Heating experiments

In silicate-rich inclusions daughter phases started to melt at above 1000°C and a gas bubble appeared and at 1050-1070°C daughter phases melted completely and the gas bubble disappeared. The composition of quenched homogenized glass of inclusion is as follows (wt.% - 45.22 SiO₂; 2.48 TiO₂; 3.37 Al₂O₃; 13.93 FeO; 0.41 MnO; 5.62 MgO; 19.23 CaO; 3.84 Na₂O; 1.19 K₂O; 0.4 SrO; 0.84 P₂O₅). In carbonate-salt inclusions salt phases partly melted at 390-420°C but above 450-460°C the inclusions decrepitated even at slow increasing of temperature. We failed to completely homogenize such inclusions

Chromatographic analysis showed that fluid in clinopyroxene of shonkinites at 1000°C contains mainly CO₂ (3400 mg/kg) and H₂O (2500 mg/kg).

Conclusions

1. Shonkinites crystallized from magmatic melt enriched in CO₂ - H₂O fluid.

2. At the crystallization stage of clinopyroxenes the melt was heterogeneous and consisted of immiscible silicate, silicate-carbonate, carbonate-salt, and carbonate fractions. The carbonate-salt and carbonate melts separated from silicate magma were enriched in Ca, alkalies, CO₂, S, Cl and were, undoubtedly, an immiscible fraction of carbonatite melt. Panina and Motorina (2008) reported that the carbonatite melts separated from silicate magma under nonequilibrium conditions separated into immiscible fractions of carbonate, alkaline-chloride, alkaline-sulfate, and alkaline-phosphate compositions.

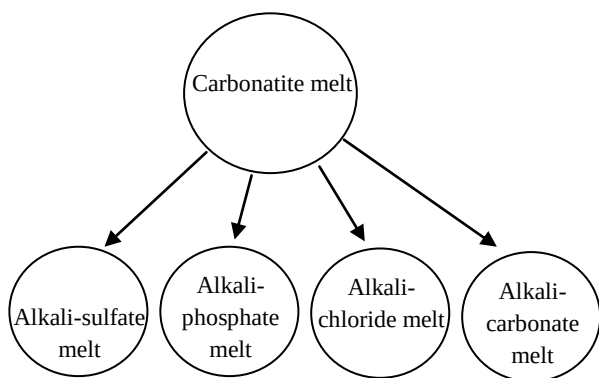


Figure 5. Polyphase carbonate-salt liquid immiscibility in deeply derived magmas (Panina, Motorina, 2008).

3. Homogenization temperature of silicate inclusions was 1050-1070°C, and that of carbonate-salt melts was much higher than 650°C.

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THERMOBAROGEOCHEMICAL PREDICTION OF INDUSTRIAL PARAMETERS OF DEPOSITS

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Introduction

Despite a large amount of works in the field of thermobarogeochemistry, one can see its inefficiency in solving practical issues of prediction and industrial evaluation of deposits, whereas it is prediction of deposits that is regarded as the principal and final target of scientific researches of natural ore genesis. The main reason of the low efficiency of thermobarogeochemistry in solving practical issues is the poor level of the existing theory of fluid ore genesis. This theory, developed more than 70 years ago, is not capable of answering the most important questions of fluid ore genesis.

The mentioned significant problems were solved by the new theory of fluid ore genesis (Royzenman, 2004, 2008) developed on the basis of complex researches of 35 deposits of 17 minerals of various genetic types (skarns, pegmatites, metasomatites, hydrothermalites). The new theory establishes that repeated crystallization, dissolving and crystal rejuvenation of ore minerals at decrease of the temperature of solutions were regulated by undulating alteration of CO_2 concentration (C_{CO_2}) which is referred to as “carbon-dioxide wave phenomenon”. Whereas, *lean mineralization is featured with decrepitation temperatures of 480-320°C and low C_{CO_2} (1-4 mole/kg H_2O), and prolific mineralization is featured with decrepitation temperatures of 320-100°C and much higher C_{CO_2} (6-12 mole/kg H_2O). It is established that prolific mineralization took place in closed ore-fluid systems.*

On the basis of the “carbon-dioxide wave” new search-evaluating criteria of ore content were developed. These criteria were included as an important component into the system of quantitative local prediction of ore bodies (Royzenman, 2004).

Prediction of location and magnitude of ore bodies

With this aim “decreptometric search factor” was developed:

$$Kd = C(100-300^\circ) : C(100-800^\circ) \times 100\%$$

where $C(100-300^\circ)$ and $C(100-800^\circ)$ are total quantities of micro-explosions of gaseous-liquid inclusions at heating samples in temperature ranges of 100-300°C and 100-800°C.

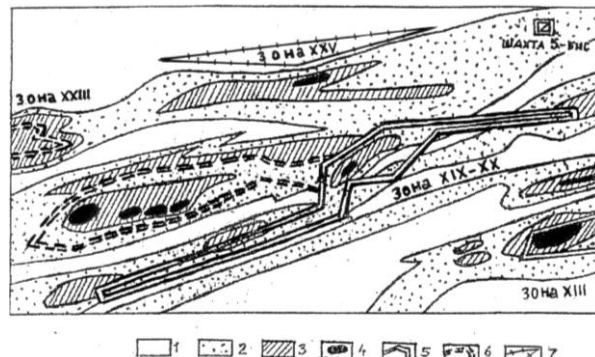


Figure 1. Schematic map of decreptometric anomalies and location of industrial phlogopite-containing bodies on the 1130 m horizon of the 5-bis mine of the Yuzhnoye deposit (Aldan). 1-4 – zones with Kd values: 1 – 0-7%; 2 – 7-20%; 3 – 20-35%; 4 – >35%; 5 – 6 – industrial phlogopite zones: 5 – on 1130 m horizon, 6 – projection on the 1130 m horizon from the 1089 m horizon. 7 – contour of phlogopite zone XXV on the 1089 m horizon discovered by the decreptometric anomaly.

Figure 1 is the illustration of the map of Kd anomalies on the 1130 m horizon of the Yuzhnoye phlogopite deposit (Aldan schield, Russia). On this map we can see that Kd anomalies coincide with industrial phlogopite zones XIII, XIX-XX and XXIII. In the northern part of this horizon, the Kd anomaly was detected which was not associated with the known phlogopite zones. Predicted reserves of phlogopite in the area below this anomaly were estimated as 5000 tons. By means of wells drilled by our recommendation under this anomaly to the depth of 50 m, a new phlogopite zone XXV was discovered and surveyed, and afterwards completely worked out (see Fig. 1) with reserves of industrial phlogopite as high as 5400 tons. It is worth noting that the illustrated the phlogopite zones XIX-XX of the Yuzhnoye deposit, the largest in the world (at the moment of discovery thereof) with reserves of phlogopite of 40000 tons, was also discovered with using of Kd factor anomaly.

Prediction of the mineral content

The exact correlation is established between contents of surveyed minerals, on the one hand, and Kd factor and C_{CO_2} , on the other hand. These relations were established for deposits of phlogopite, muscovite, graphite, lithium, tantalum, cesium and other raw marterials.

Prediction of reserves of ore bodies is performed to use thermobarogeochemical data of

predicted magnitudes of ore bodies and contents of minerals.

Prediction of quality of mineral raw materials, being especially important for non-metallic minerals, is established by Kd factor and by C_{CO_2} for phlogopite, muscovite, quartz, diopside and feldspar raw materials, graphite, rare metals and other raw materials. There are some preliminary prerequisites of using these prediction criteria for gold, copper, nickel and raw materials.

High veracity of the prediction is supported by complexing the geologic formally one-valued mapping and the developed thermobarogeochemical criteria. Here it was managed to achieve prediction veracity up to the level of over 80%, that is, 6-8 times higher than for conventional predicting.

Supposed technique of growing coarse crystals

It is sensible to use the “carbon-dioxide wave” for synthesis of coarse crystals.

Conclusions

1. The new theory of fluid ore genesis permits to develop much more efficient searching and evaluating criteria of predicting industrial parameters of ore bodies: their location, amount and reserves, as well as contents and quality of minerals.

2. Approbation of the new prediction techniques led to discovery of 16 industrial ore bodies of 10 minerals, with the value of mineral ore materials as high as 2 billion dollars, which confirmed high efficiency of the new prediction techniques.

3. Further development of the new theory of fluid ore genesis and use of new methods of predicting deposits of various minerals on the basis thereof may be regarded as prospective. It may give a tremendous economic effect.

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NEW THEORY OF FLUID ORE GENESIS UNDER INFLUENCE OF “CARBON-DIOXIDE WAVE”

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The theory of fluid ore genesis developed more than 70 years ago is not able to solve the most important problems of fluid ore genesis. *Solution of these most important problems can be found in the new theory of fluid ore genesis under influence of “carbon-dioxide wave”* (Royzenman, 2004, 2008) developed on the basis of formally one-valued geological mapping and complex researches of 35 deposits of 17 minerals of various genetic types (scarns, pegmatites, metasomatites, hydrothermalites). The complex of thermobarogeochemical researches included: 1) separate research of lean and prolific ores by methods of homogenization, thermoacoustic and thermovacuum decrepitation; 2) detailed gas-chromatographic analysis via each 40°C of heating samples in the temperature range of 100-800°C; 3) detailed decrepitemetric charting of deposits. As a result of these complex researches, it was found that, regardless of the genetic type and genera of a mineral (phlogopite, muscovite, lithium, rubidium, cesium, graphite, copper, nickel, quartz raw material, etc.), *prolific ore genesis under 600°C took place in all examined objects in monotype way, on the background of fluctuating undulating alteration of CO₂ (C_{CO2}) concentration in cooling down post-magmatic solutions – that is referred to as “carbon-dioxide wave” phenomenon*. Whereas, *lean ore genesis is featured with decrepitation temperatures of 480-320° and low concentrations of CO₂ (1-4 mole/kg H₂O), while prolific ore genesis is featured with decrepitation temperatures of 320-100°C and very high C_{CO2} – up to 12 mole/kg H₂O*. Due to the fact that adding CO₂ may significantly (up to hundredfold) increase solubility of ore-genetic components, the “carbon-dioxide wave” shall actively regulate consequent repeated crystallization, solution and crystal rejuvenation of ore minerals as the solution temperature decreases.

Fluid ore genesis model

Concerning the “carbon-dioxide wave” and data of solubility of components, 5 stages (see Fig. 1) may be selected in the process of ore genesis.

At the 1st stage (550-380°C) at low concentrations of CO₂ (1-4 mole/kg H₂O), in conditions of significant oversaturation of the

solution from significantly aqueous solution, crystallization of minerals (including ore minerals) took place with formation of scattered, lean ores (the stage of lean ore genesis).

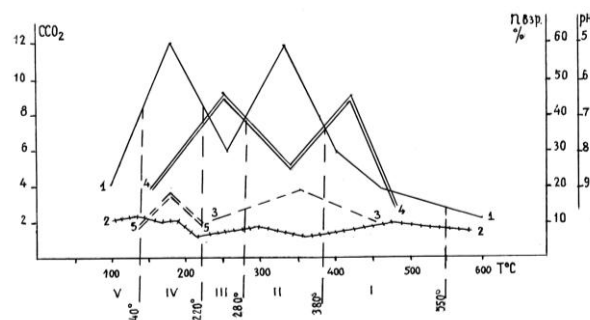


Figure 1. Fluid ore genesis model. 1 – curve of C_{CO2} variance in prolific ores, 2 – the same in lean ores, 3 – C_{CO2} variance in the H₂O-CO₂-NaCl system (Takenouchi, Kennedy, 1968), 4 – decrepitation curve, 5 – curve of variance of “salting-out factor” Ksh. I, II, III, IV, V – stages of mineral and ore genesis.

At the 2nd stage (380-280°C), due to abrupt increase of concentration of CO₂ – up to 12 mole/kg H₂O, despite the temperature decrease, solubility of ore components increased, and they were transferred back to the solution (the first stage of ore components dissolving).

At the 3rd stage (280-220°C) significant decrease of concentration of CO₂ took place – down to 5-6 mole/kg H₂O. Due to decrease of solubility of ore components at comparatively low temperatures, crystallization of minerals took place at insignificant oversaturations of the solution. In these conditions, forming of concentrated, prolific, including coarse-crystalline ores took place (the first stage of prolific mineralization).

The 4th stage (220-140°C) is marked with repeated abrupt increase of concentration of CO₂ – up to 12 mole/kg H₂O and, consequently, with new increase of solubility of some components of the first group which were transferred back to the solution (the second stage of dissolving).

At the 5th stage (below 140°C), on the background of further decrease of temperature and concentration of CO₂ (down to 4 mole/kg H₂O), genesis of prolific ores of uranium, mercury and a number of other minerals took place (the second stage of prolific mineralization).

Due to the fact that the peak of concentration

of CO₂ at 340°C in natural orogenic systems with prolific mineralization coincides with the maximum of concentration of CO₂ in the H₂O – CO₂ – NaCl experimental system, one may conclude that *genesis of prolific mineralization took place in closed ore-fluid systems*.

Detection of the “carbon-dioxide wave” and its regulating role in repeated solution and crystallization of minerals allowed solving the most important problems of fluid oreogenesis, including: 1) *“ore columns”* were formed in closed ore-fluid systems wherein lean mineralization under influence of the “carbon-dioxide wave” (the 1st stage), solving the ore substance (the 2nd and 4th stages) and prolific mineralization (the 3rd and 5th stages) were taking place; 2) *absence of prolific deposits in large splits* is explained by the fact that their fluid system losses CO₂ and due to it, the “carbon-dioxide wave” and related to it prolific mineralization are absent; 3) *growth of coarse crystals* was possible in closed ore-fluid systems only where the “carbon-dioxide wave” was determining the genesis of fine crystals at first (the 1st stage), their dissolving (the 2nd and 4th stages) and rejuvenation of their crystals, with genesis of coarse crystals (the 3rd and 5th stages).

The new theory permits to develop, for the first time, efficient searching and evaluating criteria of prediction (including those for use in depth) of industrial parameters of ore bodies: their location, amount and reserves, as well as contents and quality of minerals. Approbation of the new prediction techniques led to discovery of 16 deposits of 10 minerals, with the value of mineral ore materials as high as 2 billion dollars. It confirmed high efficiency of search-evaluating methods based on the new theory of fluid ore genesis. Further development of the new theory of fluid ore genesis and use of new methods of predicting deposits of various minerals on the basis thereof may be regarded as prospective.

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CONDITIONS OF SEAFLOOR FORMATION AND ALTERATION OF ORE FACIES OF THE SAF'YANOVKA MASSIVE SULFIDE DEPOSIT, THE MIDDLE URALS

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Introduction

The Saf'yanovka massive sulfide deposit located in the Middle Urals, Rezh ore district, was formed in the Devonian – Early Carboniferous back-arc basin during a short-time break of rhyolite-dacite-andesite-basalt volcanism (Yazeva et al., 1991). The deposit is quite uniquely in comparison with other Ural massive sulfide deposits because of the low grade of metamorphism and high safety degree of the mound-like sulfide edifice formed following the black smoker model (Maslennikov, 2006).

Research of the deposit is based on ore-facies analysis which allows determining ore facies being the mineral accumulations with similar structural and textural features peculiar to similar processes of mineral formation (Maslennikov, Zaykov, 2006). The central part of the reconstructed Saf'yanovka mound is composed of massive Cu-Zn-Fe sulfides of hydrothermal facies with quartz-sphalerite-chalcopyrite black smoker chimneys and colloform pyrite ores on the top of the mound.

Ore facies analysis of the deposit showed the domination of clastic sulfide facies over hydrothermal sulfides (Safina, Maslennikov, 2009). Clastic facies with clasts of massive and colloform sulfides, and black smoker chimneys are located on the flanks of the mound. The structural mapping of the mound displayed lateral and stratigraphic transitions of partly brecciated sulfides into strongly disintegrated colluvial breccia and sulfide sandstone with graded bedding. These facies transit to the barite-galena-tennantite-sphalerite and barite layers (diagenites) interbedded with siliceous sandstone and carboniferous siltstone at the distance of about 300 m from the sulfide mound. Barite-bearing diagenite lost features of their clastic origin and were intensely transformed during submarine alteration of fine-clastic sulfides.

The aim of the study was an establishment of evolution of physicochemical parameters of hydrothermal solutions formed massive sulfides of hydrothermal (seafloor crusts and plates), clastic (colluvial breccia), and seafloor alteration (sulfide diagenite) facies.

The following barite from the three ore facies was studied: (1) interstitial barite from colloform FeS₂ aggregates; (2) barite from the cement of the colluvial breccia composed of colloform FeS₂ clasts; and (3) barite from nests in barite-galena-

tennantite-sphalerite diagenite. In all cases barite is a late mineral in respect to sulfides.

Analytical methods

Fluid inclusions were studied in Laboratory of Thermobarogeochemistry at Geological Faculty of the South-Urals State University (Miass, Chelyabinsk oblast) using a THMSG-600 (LINKAM) equipment with Olympus microscope and LinkSys 32 computer program. An accuracy of measurements is $\pm 0.1^\circ\text{C}$ in temperature interval of $-20\dots+80^\circ\text{C}$ and $\pm 1^\circ\text{C}$ out this interval. Eighty measurements in thin polished sections were used based on standard methods (Borisenko, 1977; Bodnar, Vityk, 1994).

Aqueous fluid inclusions in barite, comprised a liquid and a vapor phases or a liquid phase only, are clustered as groups of 3–7 inclusions, and do not related to the cracks that confirms their primary origin. Inclusions are up to 10 μm in size and have euhedral, sometimes angled, morphology. Negative crystal facing of fluid inclusions was observed in barite-1.

Results

First melting temperatures of fluid inclusions in barite-1 and -3 range from -21.0 to -22.3°C indicating the domination of NaCl in solution. These temperatures for barite-2 (-21.7 – -22.0°C) suggested the presence of NaCl+Na₂SO₄ in the system.

Melting temperatures of ice range from -1.7 to -3.3°C for barite-1, from -1.5 to -2.3°C for barite-2, and from -0.9 to -1.8°C for barite-3. The salinities obtained vary from 3–5.5, 2.6–3.8, and 1.5–3 wt.% NaCl-equiv. for fluid inclusions in barite-1, -2, and -3, respectively. Temperatures of homogenization are 130–165, 165–180, and 190–215 $^\circ\text{C}$ for barite-1, -2, and -3, respectively.

Discussion

Results of study showed that salinity of fluid inclusions in barite-1 and -2 is close to seawater salinity (~ 3.5 wt % NaCl-equiv.) (Fig. 1, fields 1 and 2). But temperatures of their homogenization are lower than the average interval of temperatures of seafloor hydrothermal sulfide formation in some modern (Bortnikov, Vikent'ev, 2005) and ancient (Simonov et al., 2006) oceanic structures (Fig. 1, fields I, III–VI). In our case it is probably related

(1) to the association of barite with relatively low temperature iron disulfides that was also described for barite of the Semyenov-1 hydrothermal sulfide field, Mid-Atlantic Ridge (Fig. 1, field II) (Melekestseva et al., 2010) and (2) to the absence of high temperature Cu sulfides or pyrrhotite in association with barite that is observed, e.g., at the Vai Lili and Semyenov-4 hydrothermal sulfide fields (Fig. 1, fields I and VI) (Herzig et al., 1993; Melekestseva, Ankusheva, 2009).

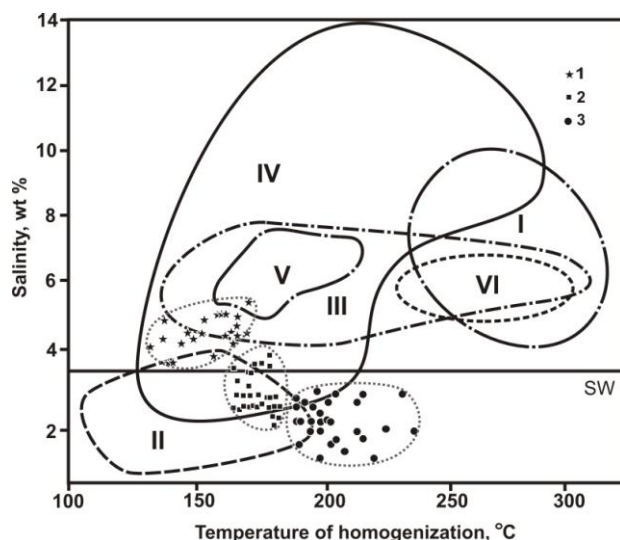


Figure 1. Salinity vs. homogenization temperature for studied fluid inclusions.

Barite, Saf'yanovka massive sulfide deposit, from: 1 – colloform ore, 2 – cement of colluvial breccia, 3 – barite-polymetallic diagenite. Barite from: I – clastic ore of the Semyenov-4 hydrothermal sulfide field, Mid-Atlantic Ridge (Melekestseva, Ankusheva, 2009); II – fine-grained pyrite ore of the Semyenov-1 hydrothermal sulfide field (Melekestseva et al., 2010); III – barite-sulfide chimneys of the Manus back-arc basin, Pacific ocean (Bortnikov et al., 2004); IV – the mineralized near-hydrothermal fauna of the Yaman-Kasy massive sulfide deposit, South Urals (Simonov et al., 2006); V – barite-silica-sulfide chimney of the Franklin Seamount, Woodlark back-arc basin, Pacific ocean (Bortnikov et al., 2004); VI – barite-sulfide chimneys of the Vai Lili hydrothermal field, Lau back-arc basin, Pacific ocean (Herzig et al., 1993).

The grains of barite-3 were precipitated from more diluted and high temperature solutions (Fig. 1, field 3) that could be explained by catagenetic alteration of the mineral composition and structure of the primary sediment at the higher temperature (up to 200°C) and presence of porous solutions (Yapaskurt, 1999).

Conclusions

Fluid inclusion study of barite from the Saf'yanovka massive sulfide deposit showed the clear dependence of decreasing in salinity of ore-forming solutions and increasing in temperature from hydrothermal ore (barite-1) through colluvial breccia (barite-2) to sulfide diagenite (barite-3) that is in agreement with increasing in degree of their postsedimentation alteration.

Acknowledgements

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FLUID INCLUSION CHARACTERISTICS FOR DIFFERENT ZONES OF PORPHYRY-TYPE ALTERATION IN THE ERZURUM-OLTU-İNANMIS BASIC ROCKS, TURKEY

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Introduction

The studied area, located in the eastern part of Pontides, covers an area of about 20 km². It comprises various Jurassic-Cretaceous units, some of which bears a continuous succession lasting until Upper Paleocene, bordered by about NE-SW trending structural lineaments.

Exhibiting distinct litho-stratigraphical characteristics, these units are categorized by Konak et al. (2001) as four groups: Hopa-Borçka zone, Artvin-Yusufeli zone, Olur-Tortum zone and Erzurum-Kars ophiolite zone, respectively from north to south, taking into consideration similarities between them.

Of these belts, the southernmost Olur-Tortum zone is distinguished as “Olur, Aksu and Çardaklı Units” from north to south, and these units are chaotically overthrust between İnanmış and Balkaya, constituting “Oltu Overthrust Zone” (OOZ) (Konak et al., 2001). Enclosing this zone in the south, Tertiary successions are composed of Eocene marine clastic and volcanic rocks at the bottom and Oligo-Miocene continental evaporitic and clastic rocks with andesitic-basaltic volcanic rocks. The youngest units in the region are various Late Miocene volcanic rocks and Plio-Quaternary deposits.

The İnanmış locality, situated within Oltu Overthrust Zone, is 25 km W distant from the Erzurum-Oltu district, between the Çamlıbel and İnanmış villages. In the locality, there are observed outcrops of Jurassic-Cretaceous basic volcanics (Konak et al., 2001), coeval with the Meydantepe limestone, clastic rocks of Eocene together with acidic and basic rocks, intruding all these rocks. Basic volcanic rocks of Jurassic-Cretaceous often show porphyritic texture, intruded by acidic, intermediate and basic rocks and so subjected to a widespread alteration.

Alterations, which are observed in the field, are argillitization, limonitization, hematitization, pyritization, chloritization and epidotization. Besides these, it is observed that basic volcanic and acidic intrusive rocks contain quartz, calcite and

pyrite veins/veinlets.

The alterations, which are observed in the field, is associated with tectonic lineaments and dykes, which developed oblique to NE-SW line, which is the main tectonic trend in the region.

Fluid inclusions

It may be estimated that there have been fluid inclusions, which are trapped within a magmatic-hydrothermal system during the crystallization of magma. Therefore, we can obtain all data related with ore genesis and follow ore mineralization. In order to do so, fluid inclusion types were determined in both laterally and vertically on alterations occurred in porphyry copper deposits (Bodnar, 1982).

Zones of alteration and particularly ore mineralization may be easily determined using this general assumption. Fluid inclusions observed in porphyry copper deposits vary in distribution and type with their deeper emplacement.

For instance, deeper-occurring oldest fluid inclusions include chalcopyrite-bearing daughter minerals with milder salinity as liquid-rich three-phase fluid inclusions, while shallower-occurring younger fluid inclusions represented as chalcopyrite-bearing gas-rich three-phase fluid inclusions, and finally the shallowest fluid inclusion assemblages, built from higher salinity magmatic liquids with co-existing halite- and vapour-rich fluid inclusions.

Fluid inclusion assemblages (FIA), observed in the porphyry copper deposits, as well as systematic variations occurred in time and place during the formation of deposits, allow using FIAs to seek these deposits efficiently.

Results

For this reason, it is discussed that 65 samples were taken from alteration zones observed within the study area to examine petrographically in both alterations and fluid inclusions. Characterizing a phyllic zone, a mineral assemblage of quartz, pyrite, muscovite-illite, chlorite, hematite and

anhydrite was detected by means of alteration petrography.

A table is both laterally and vertically given by determining of fluid inclusion assemblages in samples obtained from these altered zones, especially those on quartz samples.

It is determined that altered samples taken from this locality characterize a phyllic alteration zone and contain its related fluid inclusion assemblages except those representing an ore mineralization zone.

MELT INCLUSIONS IN MINERALS OF THE SHIBANOVSKY GRANITE MASSIF**Shabanova Y.A., Pakhomova V.A., Zalishchak B.L., Ushkova M.A.**

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Introduction

While solving problems of ore genesis, thermobarogeochemical approach is well-founded and effectively used for investigation of tungsten, molybdenum-tungsten, molybdenum, tin, and complex deposits of greisen, quartz vein, and stockwork types allocated in greisen-vein-ore formation (GVO) of the Transbaikalian region, Kazakhstan and North Caucasus (Reiff, 2009). The Far East deposits of different metals are less studied. Thermobarogeochemical results still have no wide application for solving problems of ore-forming process.

Geological setting

The Shibansky Mining Centre is located within the limits of granite massif of the same name and its near-intrusive zone. Here, two tin-tungsten manifestations of cassiterite-wolframite-quartz type are known, as well as industrial placers of cassiterite and wolframite. Endogenous mineralization is confined to pegmatitic and quartz veins and greisen zones in granites of the Shibansky massif and is undoubtedly genetically connected with them. Industrial mineralization is supposed to present at depth. Beside cassiterite and wolframite, the placer contains xenotime, orthite, fergusonite, zircon, and arsenopyrite at significant amount. Exploratory works in the Shibansky granite massif revealed crystal-bearing pegmatites with morion and beryl, and alluvial placers with morion, topaz and beryl.

The Verkhne-Shibansky deposit is represented by three magmatic complexes of different age: Middle Palaeozoic (γP_2), Late Permian (γP_2), and Late Cretaceous (γK_2). The Shibansky massif is situated in the Srednekhankaisky fault zone in the basin of the brook of the same name. It has rough oval form.

Formation of the Shibansky massif granites occurred during 4 phases. The first phase is represented by coarse-grained and medium-grained corniferous-biotite and biotite granites, the second one – by medium-grained biotite granites, the third one – by fine-grained granites (and small amount of pegmatite and greisen), and the fourth phase – by porphyry-like biotite granites. Endocontact zones of the Shibansky massif granites are represented by fine-grained biotite granites in the west, north-west, and north-east of the massif, and quartz-feldspathic

porphyry along its southern border. Fine-grained biotite granites of the endocontact facies are similar by their composition and structure to the granites of the third intrusive phase of the massif.

In addition to the mentioned and known from the literature data on the massif's structure, the deposit is characterized by rare-metal mineralization as we discovered in zone of aegirine and hastingsite alkaline syenites. The latter are represented by coarse-grained and medium-grained massive rocks composed of albite, orthoclase-perthite, aegirine, arfvedsonitic amphibole, hastingsite and accessory apatite, zircon, monazite, xenotime, delite, cheralite, brabantite and Nb-ilmenite. Geological situation of the discovered alkaline syenite is not clear enough, as they are not mentioned previously in the known fund literature. In the observed native outcrops, boundaries between syenites and anisometric granites are smooth and evidently occur mostly in the edge parts of the massif, though forming no continuous endocontact zone. Syenites are most likely dike-shape apophyses having no distinct contacts with surrounding granites.

Thermobarogeochemical data

We examined melt inclusions in rock-forming quartz of granite, syenite and pegmatite. As a rule, inclusions have size of 5-10 μm and consist of silicate and fluid phases. Thermometric experiments on inclusion homogenization revealed temperature range of homogenization in granite within 850-900°C, in syenites - within 650-700°C, in pegmatites – within 400-600°C, and in hydrothermal quartz of druse voids within 350-400°C. After the experiment, part of melt inclusions in pegmatites was totally homogenized to get transparent glass. Quenched glasses of melt inclusions in quartz of granites contain from 65 to 70 wt.% SiO_2 . It should be noted that high SiO_2 in melt inclusions is not result of SiO_2 dissolution of from host quartz, as SiO_2 content in the rock is 77 wt.%. Alkali content reaches totally 10 wt.%, Al_2O_3 - 13-14 wt.%. The relics of solid phases in the homogenized melt inclusions are identified as feldspar and amphibole.

Composition of glass in granites and syenites is distinctively different: melts have content of SiO_2 equal to 54-56 wt.%, total alkali in the rock is up to 10 wt.%, whereas glasses of melt inclusions contain

up to 5 wt.%. Unlike the rock, glasses are virtually free in K_2O . Syenite melts show significant scatter and high CaO (36-37 wt.%), as well as the presence of F (2.5-3 wt.%). Amphibole and wollastonite are found among relics of daughter phases in some homogenized inclusions in the rock-forming quartz of syenites.

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APPLYING PETROLEUM INCLUSIONS MICROTHERMOMETRY IN RECONSTRUCTING THE OIL TYPES IN ASMARI-JAHNUM FORMATION, IRAN

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Introduction

Kuh-i Mond located at the east of the Zagros Basin represents over 482 million cu/m³ barrels of conventional heavy oil resources. Oil is trapped in the Oligocene to Miocene fractured carbonates of the Asmari-Jahrum reservoirs. Thermal recovery processes produced oil successfully. Original geochemical signatures overprinted by the post accumulation processes, characteristics of the heavy oil produced from Lower Oligocene-Miocene reservoirs, are not easily identifiable. Furthermore, oil after migration has mixed with the other hydrocarbon fluids which consequently produced heterogeneous fluid in which the viscosity is changing gradually in the different reservoir depths. Seems biodegradation processes affected on the increasing heavy molecules source. So we need a powerful method could identify the geochemical circumstances of the reservoir. Petroleum inclusions are effective tools will provide us the history of the hydrocarbon fluids migrated. They are assumed well-preserved packages, which protected and maintained and left

the inclusions contents pristine from the time of deposition. They could give trustful information about the oil charged to reservoir.

According to petrographic observations the applications of the method are useful to determine the original composition of the oil migrated to the petroleum reservoirs in Southern Iran, Kuh-i Mond are producing conventional heavy oils.

This paper tried to find the circumstances that hydrocarbon fluids had in time of migration based on the results of the petrography and microthermometry of petroleum inclusions in the Asmari-Jahrum reservoir, Kuh-i Mond oilfield, SE Zagros Basin, Southern Iran.

Geology and stratigraphy

The heavy oil in the Mond oilfield has accumulated, sourced possibly from the Hanifa/Tuwaiq (Oxfordian, Callovian) and other sources, and then later migrated from potential shaly source rocks located in Arabian Parts (Figure 1) (Bordenave, 2008).

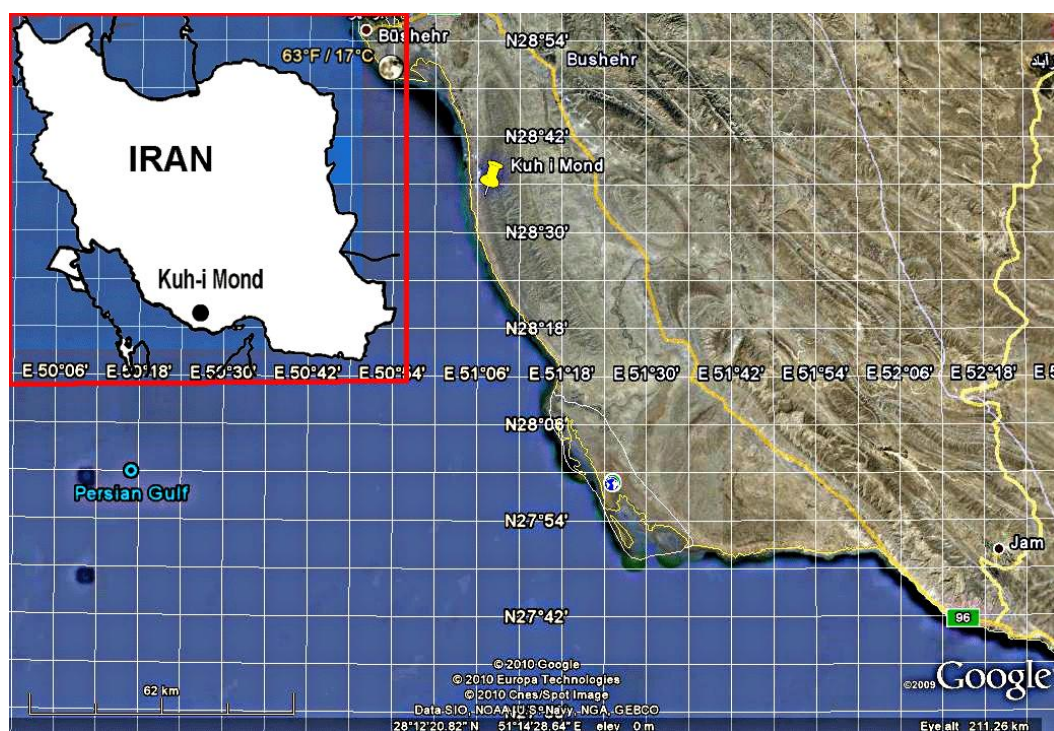


Figure 1. Kuh-i Mond is located in Iranian offshore. The field is a part of the N-trending Qatar Arch structural feature that is bounded by the Zagros fold belt to the north and northeast.

The Asmari Formation of Oligocene-Miocene age in the Zagros Basin is characterized by that carbonate microfacies that have been attributed to supratidal carbonate ramp depositional settings which are secondarily influenced by regional fracturing. It is mainly composed of carbonates petrofacies related to the restricted marine which is widely dolomitized; has interbedded shales, dolomites and sparse anhydrite units. Fracturing and channel porosities considerably improved the reservoir quality which has made the traps for oil.

In the history of the geology of ancient Zagros Basin, while the ancient geochemical conditions have been unsteadily change, this effect reflected in the form of on the fabrics modifications of the carbonate reservoirs of the Asmari-Jahrum Formations, and composition of oils already accumulated. This is responsible for retarding the original composition of the oil after accumulating. This meant that every new fluid flow regime with particular geochemical signatures when moves on through porous media, causes the original signatures achieves another characteristics.

Petroleum inclusion microthermometry

The microscopic investigations were performed with the wafers of carbonate samples shown that petroleum inclusions occurred as trails of primary inclusions in dolomite overgrowths and through calcite vein cements as secondary inclusions. Microthermometry of inclusions revealed that hydrocarbon fluids had the homogenization temperatures (Th) around 100 to 120°C for primary inclusions. Th in anhydrite-hosted inclusions varies between 32.4 and 38.7°C. Secondary inclusions in the anhydrite fracture-cements show Th at 54.2, 57.2 and 49.7°C.

Conclusions

The results of petroleum inclusions petrography are shown that primary hydrocarbons inclusions occurred as trails in dolomite overgrowths and secondary inclusions inside calcite vein cements. The homogenization temperatures (Th) of first group of inclusions obtained around 100 to 120°C. The Th data are from primary inclusions in anhydrite varies between 32.4 and 38.7°C. Also Th data for secondary inclusions in the anhydrite fracture-cements obtained of 54.2, 57.2 and 49.7°C. The inclusions data seems follows a decreasing temperature upward the Asmari Formation and represent following uplifting happened during migration in the Cenozoic.

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FLUID INCLUSIONS IN MINERALS OF GOLD-BEARING PEGMATOID FORMATIONS OF GABBRO-NORITE COMPLEXES OF THE CENTRAL ALDAN

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Introduction

Fluid inclusions in minerals are the source of small but valuable evidence for deciphering the geological processes of the past. These inclusions are relics of the primary fluid/melt, gas and liquids, which were trapped by mineral during crystallization process, as well as secondary gas-liquid vacuoles formed during healing of cracks in minerals and as a result of metamorphic and metasomatic alterations.

One of the most actual problems is to identify the primary origin of stratified gabbro-norites for addressing critical issues of stratification and metallogeny of Archean crystalline formations of the Aldan Shield. Although there are supporters of its primary sedimentary origin, according to the most modern researchers these formations are considered as primary magmatic.

Geological peculiarities of the Pinigin deposit

The Pinigin deposit is situated in the Upper Lyubkayskoe ore field in the central part of the Aldan Shield near the border between the Amginskaya collision zone and Nimnyrskiy granulite-ortogneiss terrain among rocks of the Nimnyrskaya suite (AR^1_{1mn}) in its contact area with the Fedorovskaya suite (AR^2_{1fd}).

Gold mineralization is localized in the basic rocks, which belong to the Medvedevskiy magmatic complex. Ore bodies have tabular or lenticular form and concordance with the host gabbro-norite rocks.

They are composed of zonal lenticular segregations of sulphide-pyroxene-plagioclase-quartz. Thickness of segregations varies from the first centimeters to 0.8-1.0 m. Gold isolations have zonal, coarse-grained structure and quartz composition of the central parts of the lenses, presence of sulphides, whose number is usually 5-12% but can reach 50-60%. Visually they differ sufficiently sharply from the surrounding rocks.

The outer zone, contacting with gabbro-norite, is composed of large (1.0-1.5 cm) grains of orthorhombic and monoclinic pyroxenes, in the interstices of which are a variable number of xenomorphic isolations of sulfides.

The next zone, from the first centimeters to 12-15 cm thick, is composed of prismatic crystals of oligoclase-andesine, among which idiomorphic pyroxene grains in subordinate amounts are found.

The central part of segregations composed of big grains of quartz, where idiomorphic grains and aggregate accumulation of pyroxene and plagioclase are scattered as well as a variable number of large xenomorphic sulphide precipitates. Thickness of the nuclear part ranges from the first centimeters to a few meters.

Fluid inclusions in minerals of gold-bearing bodies

In the pyroxene zone there are species with two- and three-phase composition (gas bubble; solidified melt - in transmitted light the substance is colorless, the refractive index is close to the host mineral; in crossed nicols the substance is isotropic, what is typical for glass). Rarely sulphide blebs occur in the inclusions (Fig. 1).

Primary - secondary (subsynchronous) vacuoles is attributed to the most prevailing kind - syngenetic inclusions in healing cracks of the crystals during their growing. The inclusions are irregular and oval shape. Along with much gas vacuoles the crystal-fluid inclusions are found.

Secondary inclusions are associated to numerous cracks crossing the border of adjoining grains. The inclusions are irregular and oval shape. They belong to the two-phase species (aqueous solution and gas bubble, liquid carbon dioxide and gas bubble), but often to the three-phase species (aqueous solution, liquid carbon dioxide and gas bubble).

In the plagioclase area primary inclusions were observed by the location along the crystallographic mineral grains, as well as the phase composition of vacuoles. Most inclusions are oval; sometimes there are vacuoles with elongated shape (Fig. 1). They are related to three-phase composition species (gas bubble; solidified melt-glass, small prismatic crystals, probably silicates). The presence of sulfide melt inclusions suggests that the temperature of homogenization is more than 1000°C.

Primary-secondary and secondary inclusions are also present in plagioclase. The morphology of these inclusions and phase composition is usually the same as in the pyroxenes.

Three types of inclusions were found in the quartz core of pegmatoid bodies: gas, gas-liquid, multiphase (Fig. 1). Primary and primary-secondary inclusions are mostly gas and multiphase vacuoles. Shape of inclusions is non-isometric, their size

rarely exceeds 0.03 mm.

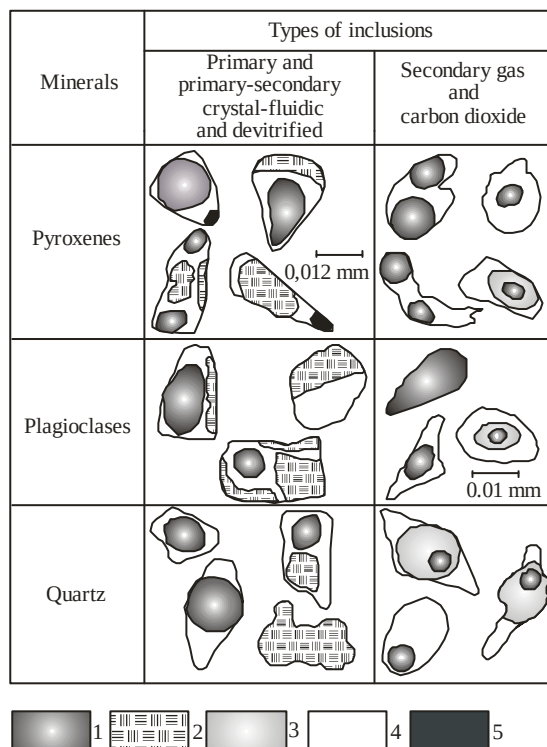


Figure 1. Morphogenetic types of fluid inclusions in minerals of gold-bearing pegmatites.

Explanation: 1 – gas bubble, 2 – solid substance, 3 – liquid carbon dioxide, 4 – aqueous solution, 5 – melt.

Mostly gas inclusions in the 95-98% of the volume are filled with gas. They are homogenized in the gas phase at a temperature of 500-530°C. In melt-gas inclusions volume of fluids varies from 25 to 40%, and their homogenization in the gas phase occurred in the temperature range of 350-500°C. Multi-phase inclusions are composed of gas (20-25), liquid (25-30 vol.%) and daughter minerals.

Secondary inclusions in quartz are the gas-liquid vacuoles. The amount of gas inside the inclusions does not exceed 30-35 vol.%. In some inclusions, except for gas and aqueous solution, there is a small amount (less than 15%) of liquid carbon dioxide. Homogenization of gas-liquid inclusions in quartz nuclei occurs in the interval from 100 to 380°C.

Conclusion

The presence of melt inclusions, the phase composition of the inclusions, partially crystallized glass and the presence of silicate crystals in the vacuoles in gabbro-norite studied indicates primary-magmatic nature of their generation.

SULFIDES IN MELT INCLUSIONS FROM PERIDOTITE XENOLITHS, UDACHNAYA KIMBERLITE PIPE, YAKUTIA, RUSSIA

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Introduction

Melt and fluid inclusions, enclosed within mantle minerals, as well as interstitial melt pockets and veins in mantle xenoliths, are samples of actual mantle melts or fluids available for study. Investigation of these objects provides significant information on processes within the subcontinental lithospheric mantle and during host magma ascent. Unfortunately the existing data on melt inclusions from kimberlite-hosted mantle xenoliths is very scarce because in most cases kimberlites and their xenoliths are modified by post-magmatic alteration. Here we present preliminary results from the study of melt inclusions in unaltered peridotite xenoliths from kimberlites.

Sample description

We have studied 25 unaltered sheared peridotite xenoliths from uniquely fresh kimberlite of the Udachnaya-East pipe (Siberian craton, Russia). The sheared xenoliths show porphyroclastic to fluidal-mosaic-porphyroclastic textures based on the classification of Harte (1977). The primary mineral assemblage of these xenoliths is composed of olivine, orthopyroxene, garnet and $\pm$ clinopyroxene. Their P-T formation conditions based on geothermobarometer (Brey, Köhler, 1990) can be estimated as $P=60-75$ kb and $T=1200-1400^{\circ}\text{C}$. Primary sulfide assemblage is represented by monosulfide solid solution (exsolution to pentlandite and pyrrhotite) chalcopyrite, pentlandite and pyrrhotite. Melt inclusions in primary minerals were recognized in all of the studied xenoliths. Melt pockets also occur in the studied samples.

Methods

The chemical composition of sulfide minerals in melt inclusions was determined on a CAMEBAX electron microprobe at the V.S. Sobolev Institute of Geology and Mineralogy SB RAS (Novosibirsk, Russia) using standard techniques. EDS, BSE images and X-ray elemental mapping were carried out using a LEO electron scanning microscope at the Institute of Geology and Mineralogy SB RAS.

Melt inclusion petrography

Melt inclusions occur as clusters in differently oriented healed cracks (Fig. 1), some of which transect entire grains of host minerals, and hence, can be considered as secondary melt inclusions.

They consist of fine-grained aggregate of carbonates, sulphates and chlorides, some translucent crystals (olivine, clinopyroxene, phlogopite, tetraferriphlogopite, apatite, perovskite, halite, sylvite, various carbonates and sulfates), opaque minerals (magnetite and sulfides) and a bubble.

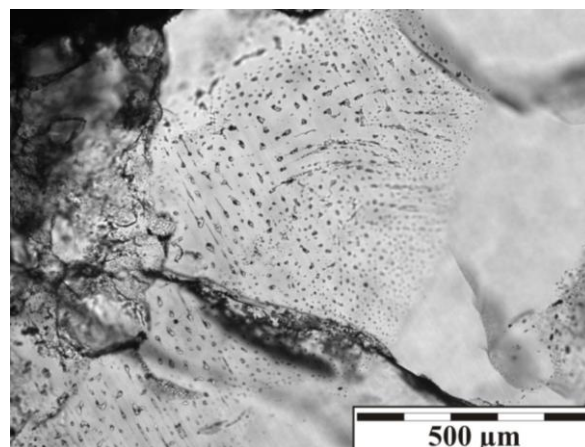


Figure 1. Photomicrograph of secondary melt inclusions in olivine from a sheared peridotite xenolith from the Udachnaya-East pipe.

Various carbonates and sulfates were recognized with the laser Raman spectroscopy (Golovin et al., this volume). In general, the main phases are Ca-, Na- and K-bearing carbonates, chlorides and sulphates, whereas silicate minerals occupy <15 vol.% of the inclusion volume. Thus, these inclusions have composition close to alkaline-carbonatite magmas. Sulfide assemblage of melt inclusions is represented by pentlandite, pyrrhotite, djerfisherite and rasvumite (Fig. 2).

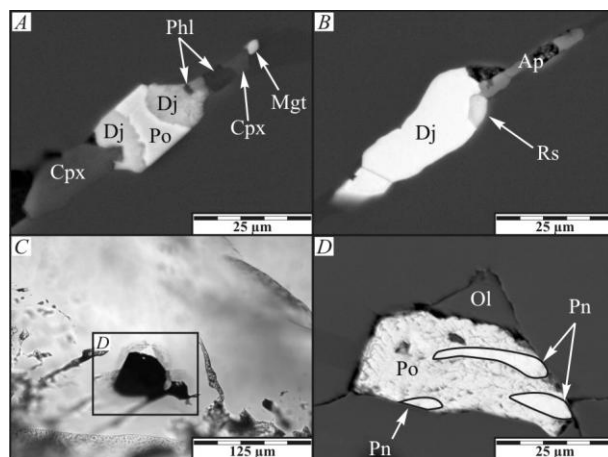


Figure 2. Individual melt inclusions with sulfide minerals. (D) – Mss exsolution texture (Pn + Po). Note: Ol – olivine; Cpx – clinopyroxene; Phl – phlogopite; Ap – apatite; Mgt – magnetite.

Results

Pentlandite (Pn) forms lamellas in pyrrhotite (Po). The composition of Pn varies within the following ranges (in wt.%): Fe 29.3-37.3; Ni 27.5-37.3; Co 0.1-1.5; Cu <0.2; S 32.9-33.7. Pn has $Ni/(Ni+Fe)=0.43-0.55$ and $Me/S=1.1-1.15$ and close to ideal $Fe_{4.5}Ni_{4.5}S_8$.

Pyrrhotite (Po) occurs together with Pn and as single grains. The composition of Po is (in wt.%): Fe 58.9-63.1; Ni <2.0; Co <0.8; Cu <0.7; S 35.9-40.5. The Me/S ratio of Po is 0.84-1.00.

Monosulfide solid solution (Mss) is an unstable phase under standard conditions, but presence of Mss in melt inclusions are recognized by exsolution texture by Pn and Po (Fig. 2D). The composition of Mss before exsolution was calculated using modal proportions of Pn and Po and their compositions. Calculated composition of Mss varies within the following ranges (in wt.%): Fe 51.9-57.3; Ni 3.3-9.5; Co < 0.5; Cu <0.3; S 36.2-38.3.

Djerfisherite (Dj), chlorine-bearing potassium sulfide (ideally, $K_6Na_{0.1}(Fe,Ni,Co)_{24}S_{26}Cl$), is a dominant sulfide phase in melt inclusions. Dj has the following compositional variations (in wt.%): Fe 38.6-47.9; Ni 4.2-14.6; Co <0.3; Cu 0.1-10.3; K 9.0-9.5; Na <0.6; S 32.1-34.9; Cl 1.3-1.6.

Rasvumite (Rs, ideally KFe_2S_3) is rare in melt inclusions and forms small subhedral grains. This potassium sulfide was identified by EDS signature (peaks of Ni, Cu and Cl are absent instead of those in djerfisherite spectra) and X-ray elemental mapping.

Discussion

Thus, sulfide assemblage of secondary melt inclusion is represented of monosulfide solid solution (exsolution to pentlandite and pyrrhotite), pyrrhotite, djerfisherite and rasvumite. The mineralogy of daughter phases in secondary melt inclusions of sheared peridotite xenoliths resembles that of the melt inclusion in olivine phenocrysts from unaltered kimberlites of the Udachnaya-East pipe (Golovin et al., 2007). Moreover, composition of djerfisherite is similar to this mineral in melt inclusion in olivine phenocrysts and groundmass of host kimberlites (Sharygin et al., 2007). We suppose the following crystallization sequence of sulfide minerals in melt inclusions: Mss or Po → Rs → Dj, similar (excluding Mss) to that observed in host kimberlites (Sharygin et al., 2007, 2008) and reflecting an increase in activity of Cl in melt. These results suggest that the melt inclusions are crystallization products of infiltrating host kimberlite melt. The compositions of Mss, Pn and Po plotted in the experimental phase diagrams in the Fe-Ni-S system (Raghavan, 2004) show that

Mss was exsolved between 500 and 600°C. Therefore, melt inclusions were entrapped at temperature above 600°C. This agrees with homogenization temperature of melt inclusions (700-780°C).

The occurrence of djerfisherite is not rare in mantle xenoliths and diamonds from the Siberian kimberlites (e.g., Bulanova et al., 1990). However, the literature is very unspecific about the origin of djerfisherite in kimberlite-hosted rocks, and a metasomatic reaction with hypothetical K-Cl-rich fluid or melt is assumed. Based on the presence of djerfisherite as a daughter phase in secondary melt inclusions in sheared peridotite xenoliths, we can suggest that all djerfisherite in kimberlite-hosted mantle rocks and diamonds may be result of infiltration of kimberlitic magma. If this previously statement is correct we can speculate that the protokimberlite magma was enrichment in Cl because the presence of djerfisherite indicates high activity of Cl in the magma.

Acknowledgments

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SILICATE-CARBONATE LIQUID IMMISCIBILITY IN PERALKALINE NEPHELINITE MELT: THE OLDOINYO LENGAI CASE, TANZANIA

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Introduction

Abundant silicate melt inclusions with silicate-carbonate immiscibility have been found in nepheline phenocrysts of peralkaline nephelinite lava of the 1917 eruption at the Oldoinyo Lengai volcano, Tanzania. The host rock is porphyritic and contains abundant euhedral phenocrysts (>1-5 mm) of nepheline and clinopyroxene, and rarer euhedral combeite, titanite, Ti-andradite and apatite. The groundmass consists of microphenocrysts (<1 mm) of the above mentioned minerals and green to brown glass. Delhayelite, perovskite, magnetite, wollastonite with combeite corona, pyrrhotite, K-feldspar, Sr-bearing barite and calcite are minor or accessory minerals in the groundmass. In general, the studied rock is similar to wollastonite-combeite nephelinite previously described by Dawson (1998) and Dawson and Hill (1998). In addition to nepheline, rare melt inclusions were found in apatite, wollastonite and clinopyroxene.

Melt inclusions in nepheline phenocrysts

Primary silicate melt inclusions together with crystal inclusions outline the growth zones in host nepheline phenocrysts. Other inclusion types (fluid, carbonate, sulfide and chloride) are scarce. Diopside is abundant among crystallites in nepheline, whereas other crystallites (apatite, titanite, Ti-andradite, magnetite and perovskite) occur occasionally.

Silicate melt inclusions (10-100 µm) in nepheline are very specific in phase composition: green glass ± gas-carbonate globules ± daughter crystals + trapped crystals + fluorite ± other salts (Fig. 1). The most typical inclusions contain glass and one gas-carbonate globule. In some inclusions gas and carbonate components are separated into individual phases, and gas bubble always contains some amounts of salt crystals on the walls. According to optical observations, SEM and EMPA, trapped crystals are diopside, apatite, Ti-andradite and titanite, whereas daughter phases are Na-Fe-rich clinopyroxene, Fe-rich leucite and delhayelite, Na-Mg-Ti-rich tetraferriannite, fluorite, wollastonite and K-feldspar. Fluorite occurs both in carbonate globule and in silicate glass. Carbonate globule is commonly fine-devitrified and some individual phases (calcite, nyerereite, Na-carbonate, fluorite) are sometimes fixed in it, like in

gregoryite-hosted inclusions from the Oldoinyo natrocarbonatite (Mitchell, Belton, 2004). Same immiscible inclusions in nepheline were previously described in rocks of the Oldoinyo 2007-2008 eruptions (Mitchell, 2009) and nephelinite lavas of other carbonatite-related volcanoes of the Gregory rift (Romanchev, 1972; Bazarova et al., 1975).

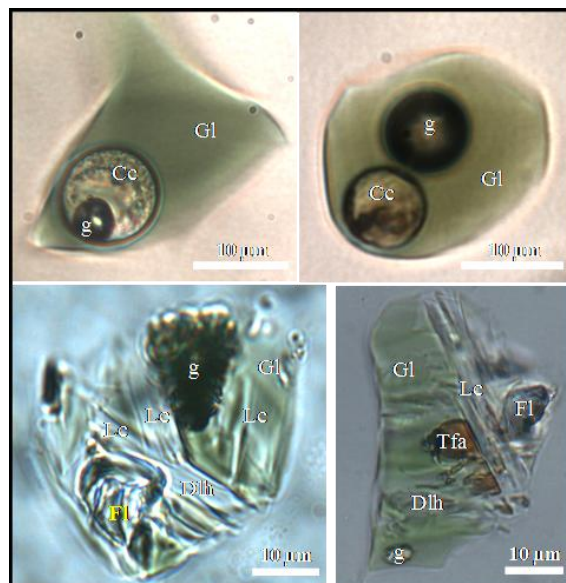


Figure 1. Primary melt nepheline-hosted inclusions, nephelinite of the 1917 eruption. Cc - natrocarbonatite composition, Gl - silicate glass, g - gas, Fl - fluorite, Dlh - Fe-rich delhayelite, Lc - Fe-rich leucite, Tfa - Na-Mg-Ti-rich tetraferriannite.

Heating experiments

Heating experiments with the Oldoinyo nepheline-hosted inclusions were provided for the 20-900°C range (Fig. 2-3). First changes within inclusions are observed in a gas-carbonate globule at 470-510°C and assigned to recrystallization of phases. The carbonate component of gas-carbonate globules melts instantaneously at 550-570°C. Silicate glass melts at 600-670°C. In partly crystallized inclusions delhayelite and mica and then leucite melted in the temperature range of 650-750°C. The appearance and then disappearance of blebs of different salt liquids or phases (fluoride, chloride or sulfate) occur in both silicate and carbonate melts at 670-840°C (Fig. 3). The salt and carbonate blebs then amalgamate into one large globule, which gradually decreases in size and gas bubble in it also decreased in size at 800-900°C. The gas-carbonate melt globule homogenizes at 900-940°C (Fig. 2-3) and phase composition of the

melt inclusions is silicate melt + carbonate melt. Quenching of inclusions led to the initial phase composition (Fig. 2).

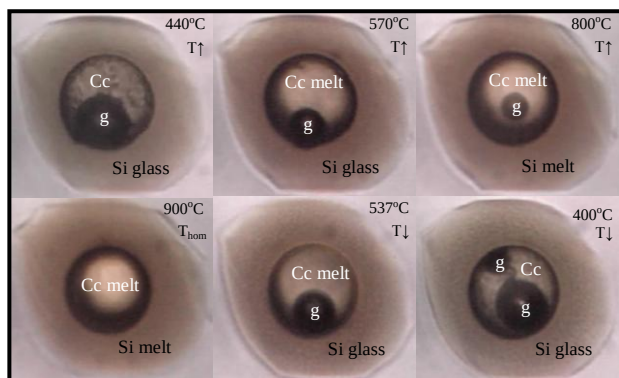


Figure 2. Heating experiment with a nepheline-hosted inclusion, nepheline of the 1917 eruption. Size of inclusion is 40 μm . Initial phase composition is similar to that on photo at 440°C. Cc - natrocarbonatite. Rate of heating was $\approx 100^\circ\text{C}/\text{min}$.

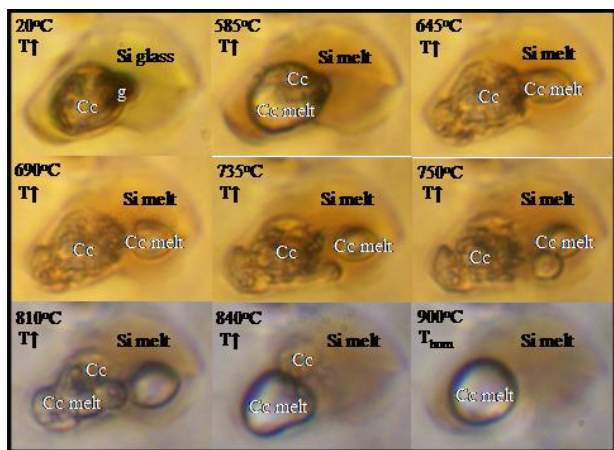


Figure 3. Heating experiment with a nepheline-hosted inclusion, nepheline of the 1917 eruption. Size of inclusion is 35 μm . Rate of heating was $\approx 50^\circ\text{C}/\text{min}$.

Chemical composition

The silicate glass is peralkaline and strongly varies in SiO_2 (43.6-53.0), FeO_t (7.5-18.6), CaO (1.0-7.2), alkalis (16.5-24.5) and $\text{SO}_3+\text{F}+\text{Cl}$ (1.0-4.3 wt.%). This glass is poor in H_2O (0.1-0.6 wt.%), Cr and Ta (<10 ppm) and rich in Ba (1720-6490), Sr (1880-6700), Zr (1440-2200), REE (520-1040), Nb (450-980), Rb (250-460) and Li (240-390 ppm). The most Si-undersaturated compositions in partly crystallized inclusions approach the groundmass glasses. The EDS and EMPA data have show that the carbonate globules are natrocarbonatite in composition and Na, Ca, K, C, Cl, F, S and P are major components, like in the Oldoinyo natrocarbonatites (Zaitsev, 2010). We were unable to fully quantify major composition of carbonate globules due to their rapid decomposition after exposing at the surface to form Na-water-bearing carbonate (trona?), apthitalite and Na-K-chlorides. LA-ICP-MS data for non-opened carbonate globules in the inclusions are shown that chondrite-normalized pattern for REE and abundance of other

trace elements are similar for those of the Oldoinyo fresh natrocarbonatites (Zaitsev, 2010).

Conclusions

Our study of nepheline-hosted inclusions in nepheline lavas advocates very complicated history during cooling of initial silicate melt as suggested by Dawson (1998). The silicate-natrocarbonatite immiscibility took place at temperature above 900°C and nepheline phenocrysts crystallized from immiscible liquids in an intermediate chamber. In the 900-600°C range the gas phase and salt liquids of different compositions may be separated from natrocarbonatite melt. The carbonate-carbonate immiscibility (Mitchell, 1997) and reaction between carbonate and silicate liquids cannot be excluded. The enrichment of peralkaline silicate melt in Fe and alkalis was favorable to crystallization of minerals rich in these components and poor in Al. Unlike inclusions (closed system), during crystallization of nepheline lavas (open system) the silicate-natrocarbonatite immiscibility is commonly hidden, owing to degassing of silicate melt, separation of carbonate melt from silicate melt and/or reaction of carbonate melt with primary silicate minerals. Evidences of immiscibility were observed only in the Oldoinyo hybrid rocks intermediate between silicate rocks and natrocarbonatites (Church, Jones, 1995).

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SILICATE-MELT INCLUSIONS IN MINERALS OF IJOLITE XENOLITHS, OLDOINYO LENGAI VOLCANO, TANZANIA

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Introduction

Xenoliths of magmatic plutonic rocks (ijolite, jacupirangite, pyroxenite, etc.) occur mainly in the Oldoinyo Lengai pyroclastics. They are cumulate rocks crystallizing in an intermediate chamber and consist of nepheline, clinopyroxene, Ti-andradite, Fe-rich spinel, fluorapatite, titanite, perovskite, mica, wollastonite, sulfides, glass and K-feldspar, most of which are strongly zoned (Dawson et al., 1995). We selected one sample of ijolite xenolith to study melt and fluid inclusions in minerals. This rock is equigranular, most grains are 0.5-3 mm in size. Some micas reach 10-15 mm. The studied ijolite contains abundant zoned clinopyroxene, nepheline, phlogopite and Ti-andradite; other phases (titanite, fluorapatite, perovskite, Ti-magnetite and glass) are minor. Here we present preliminary data on petrography and chemistry of melt inclusions in ijolite minerals.

Melt inclusions in ijolite minerals

Primary melt inclusions were found in nepheline, fluorapatite, clinopyroxene and Ti-andradite (Fig. 1-2).

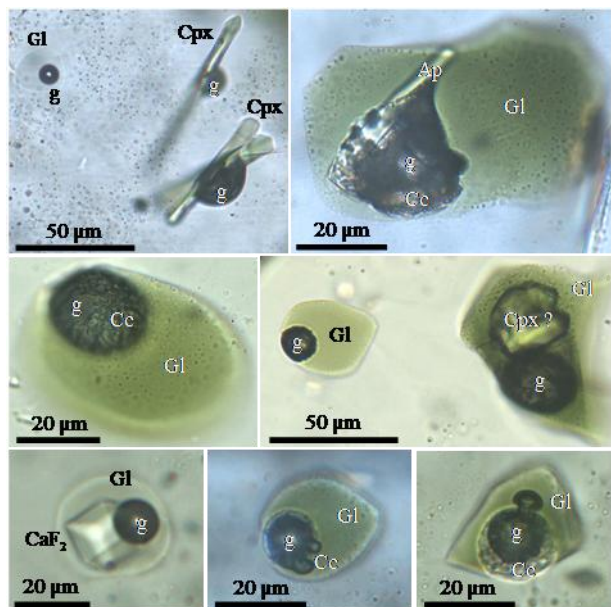


Figure 1. Primary melt inclusions in nepheline, ijolite xenolith, sample Ol-006-05, ordinary light.

Gl - silicate glass, Cc - salt (carbonate) phases, g - gas, Cpx - clinopyroxene, Ap - fluorapatite.

Abundant silicate melt inclusions together with crystal inclusions outline the growth zones in nepheline like in nepheline from the Oldoinyo

nephelinite lavas (Sharygin et al., 2010). Fluid and sulfide inclusions are scarce. Myriads of submicron inclusions are sometimes localized around one large (>10-20 μm) melt inclusion (Fig. 1). Diopside and fluorapatite are abundant among crystallites in nepheline. Silicate melt inclusions (10-100 μm) in nepheline are various in phase composition: green glass ± gas or gas-carbonate bubble ± daughter crystals ± trapped crystals ± salts phases (Fig. 1). The most typical inclusions contain green glass and gas bubble. Daughter/trapped crystals are represented by clinopyroxene, fluorapatite, perovskite, titanite and cubic phase (possibly, fluorite CaF₂). Unlike nepheline-hosted inclusions in nephelinite lavas (Sharygin et al., 2010), gas-carbonate globules in melt inclusions in ijolitic nepheline are scarce. Nevertheless, precipitation of salt (carbonate ?) phases in the vacuole of gas bubble is common of many inclusions. In addition, separation of abundant submicron globules is observed in large melt inclusions (Fig. 1).

Melt inclusions also occur in fluorapatite, clinopyroxene and Ti-andradite (Fig. 2). In clinopyroxene and Ti-andradite they are two-phase in composition: colorless glass + gas. Such inclusions in clinopyroxene are commonly confined to the central green zone (Fig. 2).

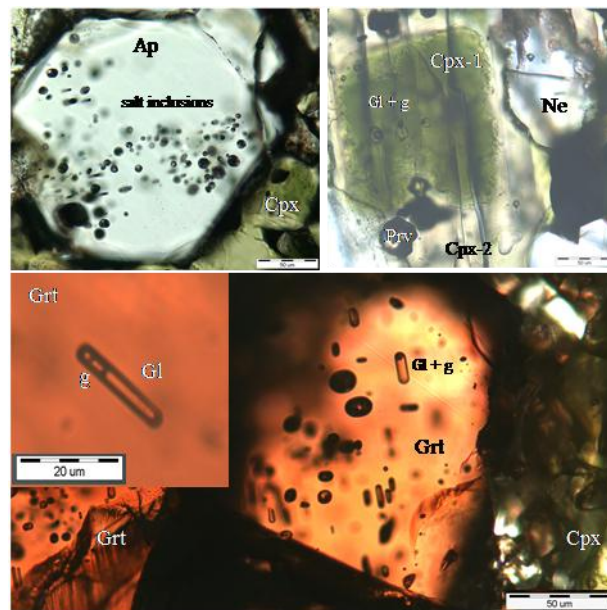


Figure 2. Primary melt inclusions in fluorapatite, clinopyroxene and Ti-andradite, ijolite xenolith, sample Ol-006-05, ordinary light.

Cpx-1, -2 - different zones of clinopyroxene, Ap - fluorapatite, Grt - Ti-andradite, Prv - perovskite, Ne - nepheline.

Melt inclusions in apatite are completely crystallized and seem to be salt-silicate in composition. They are localized mainly in the central parts of the host (Fig. 2).

Chemical composition of melt inclusions

The silicate glasses from melt inclusions in the Oldoinyo ijolitic minerals are peralkaline and strongly vary in composition (Table 1). Glasses from inclusions in nepheline are characterized by more drastic variations (in wt.%): SiO₂ - 42.5-53.0, TiO₂ - 0.1-2.6; Al₂O₃ - 3.2-12.6; FeO_t - 5.9-15.0; MnO - 0.4-0.8; Mg - 1.1-2.5; CaO - 2.7-7.5; BaO - 0.0-0.7; Na₂O - 4.8-8.0; K₂O - 5.1-7.0; P₂O₅ - 0.1-1.2; F - 0.2-1.9; Cl - 0.2-0.4; SO₃ - 0.3-2.7. However, most glasses correspond to siliceous compositions (SiO₂ - > 50 wt.%) depleted in mafic components and are related to inclusions with simple phase composition (glass + gas). The most Si-undersaturated and peralkaline glasses in partly crystallized inclusions approach the groundmass glasses (Table 1). Such compositional variations are also common of glasses in nepheline-hosted inclusions in the Oldoinyo nephelinites (Sharygin et al., 2010).

Table 1. Representative analyses of glasses from nepheline- and clinopyroxene-hosted inclusions and groundmass, ijolite, Oldoinyo Lengai.

n	Nepheline				Cpx			Gm
	1	1	2	4	3	1	2	2
SiO ₂	42.45	48.84	50.09	51.58	52.42	51.08	51.41	44.51
TiO ₂	2.61	1.47	1.12	1.55	0.30	1.27	1.57	3.23
Al ₂ O ₃	3.19	8.37	9.82	10.17	10.64	13.60	17.99	5.77
FeO	14.98	14.06	11.95	10.10	11.16	10.99	5.74	16.98
MnO	0.76	0.65	0.52	0.59	0.45	0.54	0.30	0.73
MgO	2.00	2.04	1.83	2.46	1.55	0.37	0.41	1.37
CaO	7.45	4.01	4.25	4.38	3.43	2.68	1.48	6.45
BaO	0.38	0.03	0.16	0.00	0.19	0.25	0.15	0.46
Na ₂ O	7.24	4.77	6.40	5.92	6.91	5.13	4.69	6.49
K ₂ O	5.09	5.45	5.53	5.85	6.43	5.96	9.68	4.76
P ₂ O ₅	1.16	0.57	0.62	0.81	0.13	0.29	0.08	0.88
F	1.90	0.92	0.66	0.94	0.59	0.49	0.50	0.78
Cl	0.40	0.37	0.33	0.32	0.20	0.28	0.22	0.75
SO ₃	2.72	2.80	1.66	1.63	0.69	0.39	0.18	2.47
Sum	92.33	94.35	94.92	96.30	95.10	93.32	94.37	95.63
O/F,Cl ₂	0.89	0.47	0.35	0.47	0.29	0.27	0.26	0.50
Sum	91.44	93.88	94.57	95.83	94.81	93.05	94.11	95.13

Note. Cpx - clinopyroxene; Gm - rock groundmass.

The glasses from clinopyroxene-hosted inclusions are approximately similar to those from nepheline, but they differ in higher Al₂O₃ and TiO₂. Glasses from inclusions in apatite and Ti-andradite are not yet analyzed by EMPA.

In general, low analytical sums for all glasses possibly point to significant concentration of

dissolved volatiles (mainly CO₂) in magma parent for the Oldoinyo ijolites as suggested by Dawson et al. (1995). The abundance of phlogopite with low fluorine concentration (< 1.1 wt.%) strongly assumes that H₂O was a dominant volatile in parent magma. Moreover, low sums for glasses also possibly indicate high concentrations of trace elements (Sr, Zr, REE, Nb, Rb, Li) like in glasses from the Oldoinyo nephelinites (Sharygin et al., 2010).

Conclusions

Our study of mineral-hosted inclusions in ijolite xenoliths advocates very complicated history of initial silicate melt for Oldoinyo Lengai as suggested by Dawson (1998). In first order, melt inclusions in ijolitic minerals indicate local P-T-X-conditions for evolved magma in an intermediate chamber before eruptions.

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APPLICATION OF ACOUSTIC DECREPITATION METHOD TO EXPLORING DEEP-LEVEL GOLD ORES IN THE SHANDONG PENNINSULA, EASTERN CHINA

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Fluid inclusion decrepitation method was used in Russia and China in the 1970's to help mineral exploration (Yermakov, 1967). This method can be used in combination with other measurements in mineral exploration (Burlinson, 2007; Rankin, 2007).

The Shandong Peninsula holds many large-sized gold deposits and is the most important area for gold production in China. With continued mining gold reserves decrease rapidly and programs of searching for blind gold ores at deep level in the area have been carried out in recent years. In the area two types of hydrothermal gold deposits, i.e. disseminated ores in altered rocks (the Jiaojia type) and auriferous quartz veins (the Linglong type), occur in granitic country rocks with well-developed alteration zones of pyritization, silicification, sericitization and K-feldspathization, which are distributed, in turn, from the mineralization center (i.e. ore deposit) outwards to unaltered granites.

Samples from drill cores of the Jiaojia gold deposit, including gold ores and surrounding wallrocks from alteration zones and granites were collected and then crushed for mineral separation and quartz was picked out from separates of each sample under binocular microscope. These quartz samples were analyzed by acoustic decrepitation using the model DT-4 decrepitemeter developed by Prof. Xie Yihan in the Institute of Geology and Geophysics, CAS in Beijing. Meanwhile, doubly-polished thin sections of representative samples were prepared for petrographic study of fluid inclusions in granites, alteration rocks, quartz veins and gold ores. Aqueous (H₂O) and mixed H₂O-CO₂ inclusions are the two major types in the all samples although their size, morphology,

abundance and occurrence vary that have caused distinct features of decrepigrams (decrepitation curves) among different lithologies.

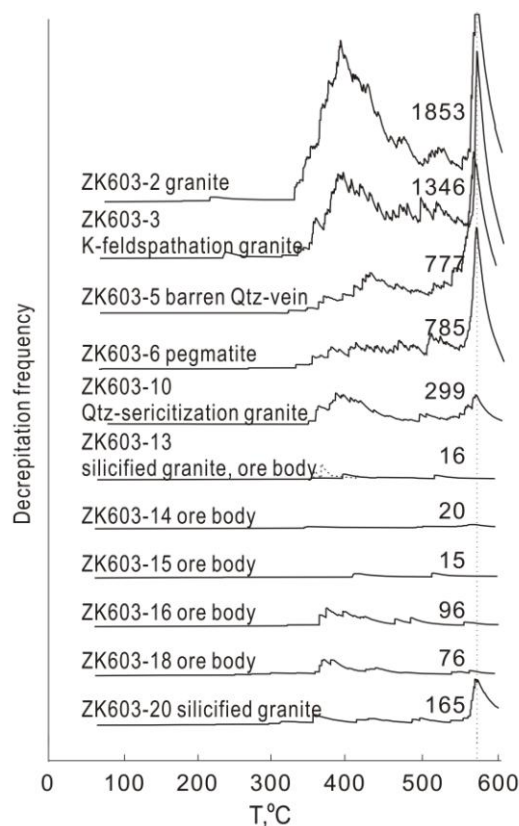


Figure 1. Decrepigrams of different lithologies (granite, alteration rocks and ores) from a drillhole in the Jiaojia gold deposit, Shandong peninsula. Figures on the right side are decrepitation frequencies.

The results have shown that the decrepigrams from unaltered granites, through altered rocks of K-feldspathization, sericitization, silicification, pyritization, quartz veins towards gold ores vary regularly and have its own features (Fig. 1). The samples of unaltered granites begin to decrepitate at about 300°C and their decrepigrams have a pronounced peak with normal distribution in the

temperature interval 360-450°C and a sharp peak at 573°C which is the phase transition temperature of α/β -quartz. On the other hand, the decrepigrams of alteration rocks are characterized by lowering of decrepitation peaks and occurring of one or more small peaks at lower temperature intervals. With the increase in alteration intensity the decrepitation frequencies are decreased from samples of K-feldspathization zone, through beresitization (pyritization-sericitization-silicification) zone, to gold ores. The decrepigrams of gold ores in the mineralization center become weak-waved curves or near horizontal lines with very low decrepitation frequencies and negative steam aureoles occur around gold deposits. Hence the unique decrepigrams and negative steam aureoles can be used to delineate gold ores in the peninsula.

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FLUID INCLUSIONS - SOURCE OF INFORMATION ON «BLACK SMOKER'S» HYDROTHERMAL SYSTEMS: A CASE STUDY OF THE ASHADZE AND LOGATCHEV FIELDS

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Introduction

A direct study by means of deep-water submersibles allow to measure temperature and chemistry of hydrothermal fluids venting onto sea floor in the limited site and for very local period of time, whereas «black smokers» have a complex structure and are formed for the period from several to thousand years. Fluid inclusions study allows to obtain the direct information on conditions of minerals crystallization at various times and in different parts of sulphide constructions, and by that there is a possibility to reconstruct character features of evolution of physico-chemical parameters of hydrothermal ore-forming systems of «black smokers».

During last years authors carry out researches of fluid inclusions in minerals from sulphide ores of «black smokers» of the Atlantic and Pacific Oceans (Simonov et al., 1997; Bortnikov et al., 2004, 2005; Bortnikov, Simonov, 2008, 2009).

This report is based on original results of fluid inclusion researches in minerals of sulphide ores from modern hydrothermal fields at the Mid-Atlantic Ridge. The samples were collected with the help of ROV «Victor» at the Ashadze and Logatchev field during the French-Russian Serpentine cruise of the R/V Pourquoi Pas in 2007 fields have been studied. The major objective of the Serpentine cruise was to study the geological, geochemical and biological processes on the hydrothermal fields, associated with mantle derived ultramafic rocks (Fouquet et al., 2008).

Physico-chemical parameters of the ore-forming systems on the hydrothermal fields have been defined by means of the analysis of fluid inclusions in anhydrite. Inclusions were studied with the help of thermometry and cryometry methods (Ermakov, Dolgov, 1979; Roedder, 1984).

Ashadze-1 hydrothermal field

Primary fluid inclusions (5-40 microns) settle down in regular intervals in anhydrite. Two-phase inclusions, with the forms of correct tubules, are prevailed. Presence of sulphide phases in inclusions (Fig. 1) is characteristic and testifies to capture by growing anhydrite an ore-forming fluid, from which simultaneously a crystallization of sulphide ore took place.

Cryometric study of fluid inclusions in anhydrite from sulphide ores of the Ashadze-1 field

has shown that solutions of inclusions are sharply frozen at temperatures from -35°C to -40°C. Eutectic temperatures are from -24.5 to -26.5°C prevail. Thus, NaCl is mainly presented in the compositions of solutions of fluid inclusions, KCl is minor. Judging by melting temperatures of the last ice chips (from -3.2 to -5.1°C), salinity of the trapped solutions was 5-7 wt.% of NaCl equivalent.

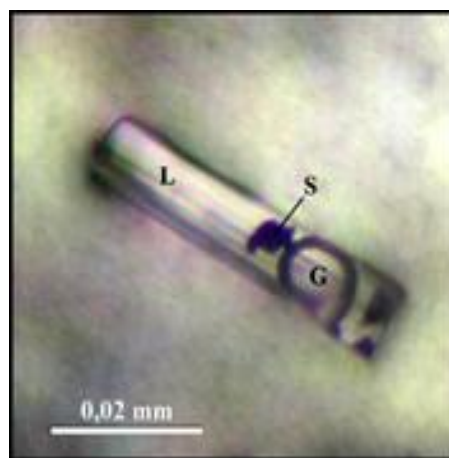


Figure 1. Fluid inclusion in anhydrite from «black smokers» of the Ashadze-1 field.

Note: L – liquid. G – gas bubble. S – sulphide crystals.

According to microthermometry fluid inclusions in anhydrite from the sample SE-DV 03-03, with homogenization temperatures varying from 265 to 310°C, form one group. For the sample SE-DV 04-20 it is possible to allocate two groups of inclusions with homogenization temperatures correspondingly from 210 to 250°C and from 260 to 320°C. Taking into account amendment on pressure, according to the depth of ocean in the sampling place (4088 m), intervals of temperatures of anhydrite crystallization on the Ashadze-1 hydrothermal field constitute nearby 235-300°C and 340-355°C. Maximum temperatures obtained by us well coincide with data of direct measurements of temperature of fluid streaming from the crater of «Long Chimney» - 353-355°C (Fouquet et al., 2008).

Thus, the carried out researches of fluid inclusions have shown, that sulphide ores of the Ashadze-1 field were formed from solutions with temperatures from 210 to 355°C and salinity 5-7 wt.%. This data considerably expand an interval of physical and chemical conditions of deposition of sulphide ores, than it has been established by means

of direct measurements. Salinity of fluid, higher in comparison with salinity of sea water, possibly is caused by phase separation of fluid that was confirmed by periodically observed segregations of gas bubbles.

Logatchev-1 hydrothermal field

Experiments with fluid inclusions in freezing stage have shown that solutions of inclusions in anhydrite from the sample DV-7-29 are sharply frozen at temperatures -36.5 - -41.0°C and have following eutectic temperatures: -25 - -28°C . Thus, in the compositions of inclusion solution system $\text{NaCl-H}_2\text{O}$ dominate with additive KCl . Judging by melting temperatures of the last ice chips (-3.7 - -5.2°C), salinity of the trapped solutions was 5.8-7.9 wt.% of NaCl equivalent. The values of concentration of salts for inclusions in anhydrite are essentially above salinity of sea water.

Experiments in heating stage have allowed defining temperatures of homogenization of fluid inclusions. According to thermometry of inclusions in anhydrite from the sample DV-7-29 three main intervals of homogenization temperatures are established: 150 - 180°C , 190 - 220°C and 230 - 260°C . Taking into account correction for pressure, according to the depth of sulphide ores location on the bottom of the ocean (nearby 3000 m), real temperatures of hydrothermal solutions have been estimated: 170 - 200°C , 210 - 240°C , 250 - 280°C . Thermometric researches of inclusions in anhydrite from the sample DV-6-8 testify to two intervals of homogenization temperatures: 190 - 240°C and 250 - 260°C . Taking into account the amendment on pressure, intervals of temperatures of anhydrite crystallization constitute nearby 210 - 260°C and 270 - 280°C .

According to correlation of homogenization temperatures of fluid inclusions in anhydrite with contents of salts in their solutions, it is clearly visible that the data on two studied samples is overlapped. The absence of dependence of solutions concentration from temperatures can testify to an openness of hydrothermal system, as in case of the closed conditions at temperature decrease accordingly there would be also changes of concentration of solutions.

Comparison with data from other fields

The considered hydrothermal fields are dated to the low-spreading Mid-Atlantic Ridge and naturally there is a necessity to compare to the data on high-spreading mid-oceanic ridges. During the comparative analysis the data of authors on fluid inclusions in anhydrite from sulphide ores of hydrothermal fields of the East Pacific Rise (EPR) was used: 9°N field (speed of spreading - 10.6

cm/year) and 21°N field - rift valley of a mid-oceanic ridge with speed of spreading 6.2 cm/year . It is found out that compositions of solutions at the hydrothermal field with the maximum speed of spreading (9°N EPR, NaCl with additive MgCl_2) obviously differ from hydrothermal systems of the Ashadze-1 and Logatchev-1 fields, where KCl is present. Salinity of solutions of the Ashadze-1 and Logatchev-1 is close to the data on 21° EPR and it is essential below the contents of salts in solutions of 9°N EPR, reaching 13 wt.%.

Temperatures of hydrothermal solutions of the Ashadze-1 and Logatchev-1 fields correspond to the data on rather low temperature inclusions in anhydrite of 21°N EPR field. In general for hydrothermal systems of high-spreading mid-oceanic ridges considerably more high temperatures (to 370°C), than established by us for the Ashadze-1 and Logatchev-1 field, are characteristic.

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MELT INCLUSIONS IN CR-SPINELS – IMPORTANT SOURCE OF DATA ON FORMATION OF ULTRAMAFIC ROCKS

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Introduction

Conditions of the ultrabasic rocks formation draw attention of many researchers. One of the main genetic questions is related to a role of melts during crystallization of ultramafic rocks. As a decision of this problem can be study of primary melt inclusions, which reserve the direct information on magmatic systems. Recently, we obtain the new data on melt inclusions in Cr-spinels from ultrabasic rocks. In this report results of melt inclusions study in Cr-spinels from dunites of the South Tuva ophiolites (South Siberia) and of the Konder platinum-bearing ultrabasic massif (Aldan Shield, Far East) are given.

Since Cr-spinel is virtually opaque and it is impossible to check the inclusions during heating, we created a special experimental technique and heating stage. Graphite microcontainers (few millimeters in size) were made to provide reducing conditions. Inclusions were heated to 1250-1270°C and quenched in order to reach complete homogenization (Simonov et al., 2009). Glasses of quenched inclusions were analyzed on a Camebax-Micro microprobe at the Institute of Geology and Mineralogy SB RAS, Novosibirsk. Contents of trace elements, rare-earth elements (REE), and water in the inclusion glasses were determined on IMS-4f ion microprobe using the technique of Sobolev (1996).

Ultramafic rocks from the South Tuva ophiolites (South Siberia, Russia)

Primary melt inclusions in Cr-spinels from the Karashat massif dunites settle down in regular intervals in the grain of a mineral and contain some dark and light phases (Fig. 1). Glasses of heated-up inclusions according to SiO₂ content (46-59 wt.%) correspond with gabbro-diorite series, which are well presented in this Agardag ophiolite zone. Inclusions contain small amount of alkalis and correspond to rocks of normal alkalinity. On the FeO/MgO-SiO₂ diagram inclusions settle down in the field of tholeiitic series in the association with gabbro and dikes of the South Tuva ophiolites. It is possible to allocate on the TiO₂-SiO₂ diagram two trends - inclusions with maximum TiO₂ correspond to data on dikes and inclusions with higher SiO₂ are coordinated with diorites. Inclusions with increased FeO values correspond to residual melts.

Calculation by program PLUTON (Lavrenchuk, 2004) on the basis of the data on inclusions has shown that initial for the stratified series melts have a picrite-basalt composition with the MgO contents nearby 18 wt.%.

The REE patterns in melt inclusions have a positive inclination with growth of heavy lanthanides and positive Eu anomaly. A series of subparallel graphs with synchronous increase of REE, reflecting evolution of melts during crystallization of the stratified ophiolite complexes, are established. Spectrums of inclusions with diorite composition (SiO₂ 56-59 wt.%) differ in the higher role of light lanthanides.

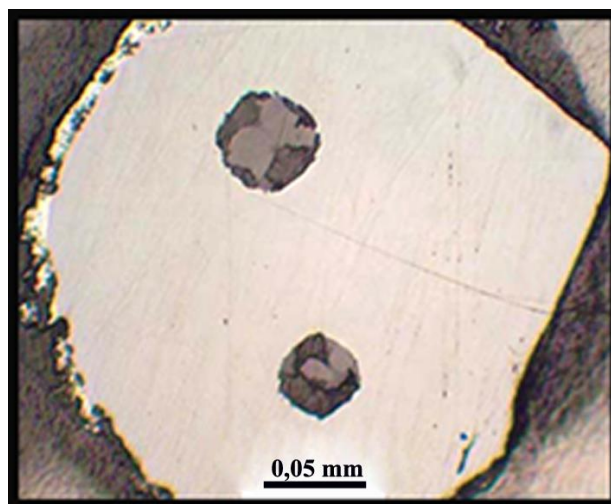


Figure 1. Melt inclusions in Cr-spinel from dunite of the South Tuva ophiolites.

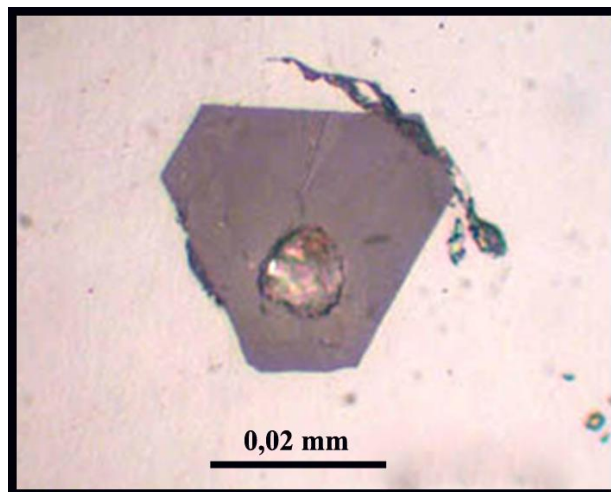


Figure 2. Heated melt inclusion in Cr-spinel from dunite of the Konder massif.

As a whole, data on melt inclusions in Cr-spinel from dunite-vehlrite-pyroxenite association in the South Tuva ophiolites characterize processes of layered complex crystallization in magmatic chamber. Inclusions also correspond to melts, which form gabbro-diorite series and are responsible for dyke complex formation. The computation on the basis of inclusion composition has shown, that crystallization of ultramafic rocks took place at higher temperatures (dunite - 1380-1250°C, wehlrite - 1250-1220°C), than gabbro (1220-1140°C) and gabbro-diorite series (1220-1120-1020°C).

Ultramafic rocks from the Konder massif (Far East, Russia)

Primary melt inclusions in Cr-spinel from the Konder massif dunites settle down in regular intervals in the grains of mineral and contain light silicate crystals, dark phases and gas bubble. Initial multiphase content of inclusions have been completely melted during heating experiments, and in the quenched inclusions glass and a gas bubble are observed only (Fig. 2).

Glasses of inclusions, possessing the high sums of alkalis (5.3-9.3 wt. %) at the rather low values of SiO₂, settle down in the field of alkaline series. On ratio MgO-SiO₂ inclusions are divided on two groups. Inclusions with high values of MgO (20.9-29.8 wt.%) and the minimum SiO₂ contents (39.2-42.3 wt.%) coincide with the data on picrite rocks. Inclusions with lower MgO are close to picrite-basalts and olivine basalts. As a whole, Inclusions high MgO completely coincide with the data on biotite-pyroxene alkaline picrites.

On the Harker diagram evolution of melts with increase CaO, TiO₂, K₂O and falling MgO on the background of SiO₂ growth is established. On the diagram CaO-Al₂O₃-MgO a part of inclusions closely associated with the ultrabasic cumulates, and another is actually in the field of cumulates of the basic composition. On low values FeO/MgO (close to 1) the studied inclusions correspond to ultramafic rocks from the stratified ophiolite series. With decreasing of MgO such components as chlorine, sulphur and phosphorus were accumulated in melts.

The ion probe analysis of inclusion glasses has shown low H₂O content (0.45-0.54 wt.%) in the Konder melts. Inclusions with maximum water (0.54 wt.%) also are enriched in copper (356 ppm).

On the Nb/Y - Zr/Y ratio inclusions is located in area of melts with plume source. The REE patterns for melt inclusions are characterized by negative inclination with sharp enrichment of light lanthanides in relation to heavy REE that is typical for the data on plume magmatic systems.

Calculation by program PETROLOG (Danyushevsky, 2001) on the basis of the data on inclusions has shown that the minimum temperatures of melts containing H₂O 0.54 wt.% are nearby 1230°C.

As a whole, researches of melt inclusions in Cr-spinels directly testify to active participation of the ultrabasic (picrite) alkaline, water-containing, magmatic systems in formation of the Konder massif dunites.

Conclusions

The carried out researches have shown that, despite every possible difficulties of the ultrabasic rocks study, there are the methods, allowing receiving the direct information on genesis conditions of ultramafites. It has been found out that during the secondary alteration, often transforming olivine rocks into the serpentinites, Cr-spinels not only preserve their characteristics, but also protect melt inclusions from external influence. These melt inclusions contain direct information on magmatic systems, at which participation ultrabasic rocks were crystallized. Results of researches testify that melt inclusions in the Cr-spinels give the data on parameters of magmatic processes of ultramafites formation independently of their belonging to various types of the ultrabasic associations.

Acknowledgements

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CONDITIONS OF MAGMATIC CRYSTALLIZATION OF ZIRCON FROM THE DAK NONG GEM CORUNDUM PLACER (CENTRAL VIETNAM): MELT INCLUSION STUDY

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Introduction

The Dak Nong placer is situated in the Central Vietnam, Dak Lac province. It is a part of the laterite crust developed over the alkali basalt volcanic center.

The placer contains megacrystic minerals (clinopyroxene, garnet, K-Na feldspar, ilmenite), minerals of mantle xenoliths (olivine, clino- and orthopyroxene, spinel), blue sapphire and zircon.

Zircon- and sapphire-bearing placers related to Tertiary-Quaternary basaltic terrains are typical of South-East Asia. Age, mineralogy and stable isotope composition data indicate that sapphire and zircon from those placers are products of the deep-seated source, related to basaltic mantle magmatism.

Zircon composition

The Dak Nong zircons are represented by variously rounded crystals about 3-5 mm in size. The HfO₂ content varies from 0.7 to 1.7 wt.%. Generally Th and U contents do not exceed 100 ppm. However, in several crystals concentrations of ThO₂ up to 0.5 wt.% and UO₂ - up to 0.11 wt.% were measured. Placer zircon differ strongly in composition from zircon inclusions in sapphire, which are much higher in HfO₂ (up to 2.6 wt.%), ThO₂ (up to 0.93 wt.%) and UO₂ (up to 0.76 wt.%).

Inclusions in zircon

The placer zircons contain primary and secondary silicate melt inclusions (Fig. 1). Neither primary nor secondary fluid inclusions were found on examination of hundreds of grains. Primary melt inclusions at room temperature are composed of transparent glass, fluid bubble and sometimes daughter crystalline phases. The latter are represented by crystals of hornblende amphibole, Fe-oxide and Cu-spinel. Secondary inclusions are similar in appearance to the primary ones.

All primary inclusions are surrounded by a fissure halo. Tiny fissures are healed and contain vitreous melt inclusions. It is noteworthy that the largest Fe-oxide crystals are in inclusions that show the more intensive fracturing.

Fluid bubbles of melt inclusions at room temperature consist of the CO₂ with various densities. Most of the bubbles homogenize into liquid between +4.8 and +28.2°C. Volume fraction of inclusions varies strongly depending on the density of fracturing around inclusions.

The healing of fractures around melt inclusions by melt, relatively high density of CO₂ in fluid bubble, dependence of the fluid bubble size on fracturing suggest that the melt inclusions decrepitated at high temperature and pressure after entrapment.

The composition of glass of inclusions, which were less subjected to decrepitation, is close to

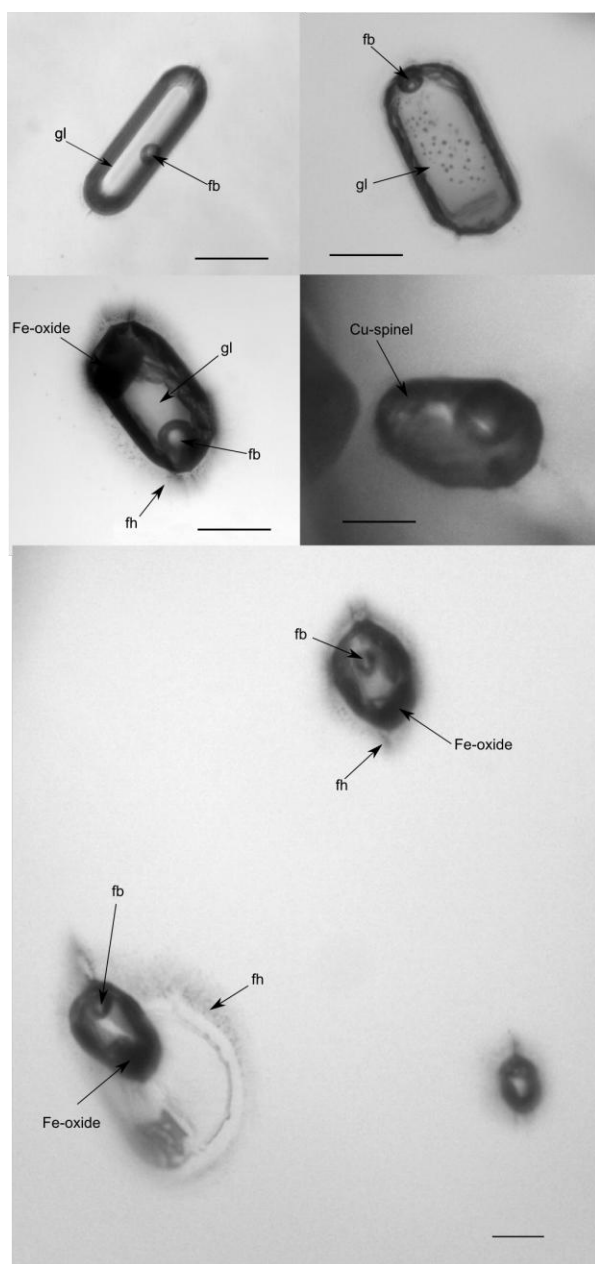


Figure 1. Silicate melt inclusions in zircon from the Dak Nong placer (Central Vietnam). gl - glass; fb - fluid bubble; fh - fissure halo. Scale bar is 20 μ m.

nepheline syenites with SiO_2 55.6-63.1 wt.% and $\text{ASI} \sim 1$. Total alkali content varies from 10 to 14 wt.%; $\text{FeO}/(\text{FeO}+\text{MgO}) \sim 0.9$. The studied glasses contain elevated amounts of P_2O_5 (0.05-0.3 wt.%), Cl (0.18-0.43 wt.%) and SO_3 (0.07-0.19 wt.%). Previously studied sapphires from the Dak Nong placer also contain melt inclusions, but their compositions differ from those in the zircon by higher Al_2O_3 , lower MgO and higher TiO_2 . Moreover, sapphires frequently contain CO_2 and $\text{H}_2\text{O}-\text{CO}_2$ fluid inclusions.

Along with the melt inclusions the placer zircon contains inclusions of baddeleyite, anorthoclase and inclusion of jadeite was identified once by EMPA. Composition of anorthoclase allows estimation of the zircon crystallization temperature at about 750°C.

Assuming that melt inclusions in zircon owed their fluid bubbles to decrepitation, which could occur in the course of transportation of host-mineral by basaltic melts with temperature $\sim 1200^\circ\text{C}$ one can estimate that the pressure of decrepitation ~ 4 -6 kbar. In that case the crystallization of zircon should occur at depths where pressure exceeded 4-6 kbar.

Discussion

On the basis of the data obtained we conclude that zircon of the Dak Nong placer crystallized from the salic melt with compositions close to nepheline syenite. This melt was enriched in volatiles CO_2 , SO_3 , Cl . CO_2 is probably dominating fluid component. In spite of the high concentration of CO_2 the melt was not saturated in fluid components and thus no fluid phase co-existed with the melt at the time of entrapment. This can evidence for the crystallization at the deep crustal levels under high pressure.

The reported differences in compositions of the placer zircon and sapphire-hosted zircon inclusions, and compositions of the melt and fluid inclusions in zircon and sapphire from Dak Nong suggest that zircon and sapphire have syenitic magmatic sources that differ in composition and fluid regime.

Conclusions

Taking into consideration all the data on thermobarometry of megacrystal minerals from the placer (Izokh et al., 2009), geology and age of the Dak Nong volcanic center (Garnier et al., 2005) and data on mineral, melt and fluid inclusions in sapphire and zircon (van Long et al., 2004; Smirnov et al., 2006; this paper) we propose the model of magmatic corundum and zircon formation in the course of basaltic magma influence on the mature intraplate Earth crust. This model suggests

the formation of the salic (syenitic) melts under thermal and fluid influence of basaltic magma chambers resided at the Moho margin depths under the studied area (Izokh et al., 2009). Fractionation of the salic melts results in formation of syenitic and nepheline syenitic melts sources enriched in volatiles, predominantly CO_2 . Carbonic fluid should play an important role in formation of high-alumina magmas, which produced sapphire. Percolation of CO_2 -rich fluids through the aluminosilicate melts could result in bonding of Na and K in alkali carbonate species and thus excess of Al_2O_3 could crystallize in the form of corundum. Carbonic fluid can originate either from mantle source, parental to alkali basaltic magma, or through decompression of the deep seated alkali-syenitic magma.

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MELT INCLUSIONS IN MINERALS AND PROCESSES IN THE EARTH MANTLE: MILESTONES, PROBLEMS AND PERSPECTIVES

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Knowledge of the composition of Earth's deep interior, and in particular its largest portion, the "convecting mantle", depends to a large extent on analysis of mantle-derived melts delivered to the surface by volcanoes. Unfortunately, "primary" melts, which retain the maximum amount of information about their source rocks, generally do not reach the surface, because they are modified *en route* by multiple processes of crystallization, contamination, and mixing. Although a significant compositional range does exist in published datasets of MORB rocks and glasses and nearby abyssal peridotites (e.g. Johnson et al., JGR, 1991), the only melt compositions actually "matching" equilibrium with abyssal peridotites can occasionally be found among melt inclusions in the most primitive olivine (Sobolev, Shimizu, Nature, 1993; Sobolev, Petrology, 1996) or spinel (Portnyagin et al., EPSL, 2009) phenocrysts. Such a "mismatch" between the compositions of erupted magmas and mantle restites suggests that the latest partial melts (namely those equilibrated with the abyssal peridotites) are effectively mixed during transport into earlier melt fractions residing in the plumbing systems. Several recent authors (e.g. Sobolev, Shimizu, Nature, 1993; Gurenko, Chaussidon, GCA 1995; Sobolev, Petrology, 1996) have therefore investigated melts trapped as inclusions in early-formed phenocrysts and found that the compositional range of melt inclusions dramatically increases when host olivine composition approaches the most primitive one. These authors interpret this as a strong evidence for early mixing of primary melts. Saal et al. (Science, 1998) identified an enormous range of Pb-isotopic compositions in melt inclusions in olivines from Polynesia and interpreted them to reflect mantle-source heterogeneity. Similarly, Sobolev et al. (Nature, 2000) interpreted trace element patterns showing extreme, positive Sr anomalies in a small number of exotic melt inclusions in olivines from Mauna Loa volcano to be generated by melting of ancient recycled gabbros. One important implication of these studies has been that the **melt inclusions are actually representative of the source rocks** in the mantle rather than being products of crustal interactions within the magma chamber. Another implicit assumption has been that such **melt inclusions can preserve chemical**

characteristics of parental melts formed in the mantle, thus delivering information about the chemical (and isotopic) composition of magma sources in the mantle.

Both of the above assumptions have recently been challenged.

(1) Danyushevsky et al. (J. Petrology, 2005) have interpreted the diversity of melt inclusion compositions as being caused by "side reactions" with the idea that crystallization in a magma chamber occurs preferentially in the temperature gradient near the relatively cool chamber wall. As a result, the composition of crustal wall rocks and their compositional heterogeneity would be significantly and systematically overrepresented in the melt inclusions. If this is the case, then the melt inclusions are not representative of the bulk melts existing in the magma chamber. More important, they cannot be good representatives of the mantle source(s) of the melts.

The other process, which can potentially compromise representativeness of melt inclusions for the primary melt composition is the boundary layer trapping. If operates this process can create irrelevant melt inclusions compositions.

(2) Spandler et al. (Nature, 2007, CMP, 2010) have challenged the assumption of the "perfect container." They measured unexpectedly high diffusivities of rare-earth elements in olivine. When coupled with the appropriate partition coefficients, these results indicate a potential level of REE mobility in olivine that appears to undermine the assumed "immobility" of REE (and perhaps other incompatible elements) in olivine during magmatic time scales. As a result, Spandler et al. concluded that some of the more unusual melt inclusion compositions are actually introduced by interaction of magma chamber with their crustal wall rocks. Both of these studies, and especially any combination of the effects proposed by their authors would, if justified, seriously undermine the usefulness of melt inclusion studies for any assessment of mantle compositions and their heterogeneity.

In this talk, I will assess both of these challenges, using new data and published results.

The representativeness of exotic melt inclusions for compositions of parental (or even primary) melts I will discuss on the base of

numerous data for melt inclusions in olivine from Hawaiian lavas. In particular, I will demonstrate that the “exotic”, Sr-rich end member of all Mauna Loa melt inclusions contributes fully 18% to the bulk melt found in erupted lavas and does not represent assimilated wall-rock gabbro, but rather indicates source composition signature. I will also show that boundary layer trapping in olivine hosted melt inclusions, if present, would be easily recognised by unusual enrichment by slow diffusion elements incompatible with olivine (e.g. Al).

I will also demonstrate that in some highly unusual melt inclusions from Iceland diffusion through the host olivine has not affected the abundances of most of the incompatible trace elements, with the exception of the heaviest REE which do show signs of slight post-incorporation modification as predicted by the high diffusion coefficients for these elements in olivine. The compositional heterogeneities of the “middle” and light REE, as well as those of all highly incompatible trace elements are fully preserved.

In addition, I will discuss potential of new analytical methods in melt inclusions study. In particular, I will demonstrate how *in-situ* LA-ICP MS isotopic studies of Sr and Pb in melt inclusions in early olivine from Hawaiian lavas can date recycled component in the Hawaiian mantle source.

I conclude that:

(1) Time scales in the magmatic system are commonly short enough to preserve the abundances of highly and moderately incompatible elements inherited from primary melts.

(2) There is no evidence that wall-rock interaction has contributed significantly to the incompatible-element composition of Hawaiian melt inclusions.

(3) Available data for basalts and picrites show no evidence for boundary layer trapping affect in the melt inclusions of more than 20 micrometers in size.

(4) New *in-situ* analytical methods significantly increase importance of melt inclusions study in addressing processes in the Earth mantle.

CONDITIONS OF VEIN QUARTZ FORMATION OF MANITANYRD REGION

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The Manitanyrd ore region is now characterized by the presence of several gold deposits. We have investigated samples from two deposits: Verkhneniyayuskoye-1 and Verkhneniyayuskoye-2. Ore zones are represented by the elongated areas of schistose rocks where quartz-sulphide, quartz and quartz-chlorite veins and veinlets are concentrated. In the surrounding rocks mineralization is very poor and presented by sulphides diffused on the schistosity.

In order to determine mineral-forming conditions we have studied gas-liquid inclusions in such transparent minerals as quartz, calcite, epidote and axinite occurred in the gold-bearing and barren veins (Fig. 1).

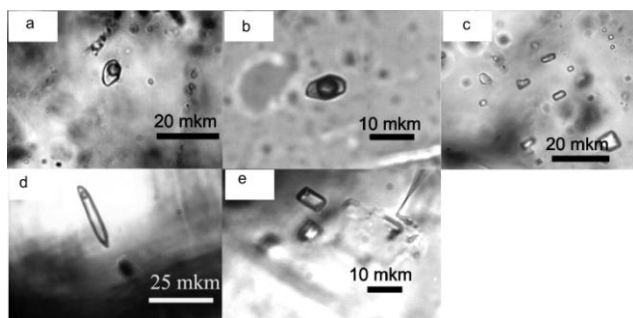


Figure 1. Typical fluid inclusions: a, b, c – in quartz, d – in epidote, e – in calcite.

It was established that the gold-bearing and barren quartz from these veins has no differences. Monophase water inclusions are typical of them; homogenization temperatures of most two-phase inclusions are about 100-400°C (Fig. 2). Design pressure is about 1-200 technical atmosphere. Gas-liquid inclusions in the gold-bearing and barren quartz have almost equal salinity (0-17 and 4-16.5 wt.% NaCl equiv. respectively). Salt composition of the inclusions is also similar. Eutectic temperature of the inclusions is about -23 и -35°C that is corresponding to water-salt systems NaCl-KCl-H₂O and NaCl-MgCl₂-H₂O. Isotope compositions of inclusions in quartz are the evidence of two sources for mineral formation – pallial and crustal (Table 1).

Homogenization temperatures of inclusions in rock crystal are equal to 130-350°C. Inclusion salinity is 2 wt.% (NaCl equiv.). Eutectic temperature of the inclusions is -23°C that is corresponding to water-salt system NaCl-KCl-H₂O.

Homogenization temperatures of inclusions in calcite are 80-300°C. Inclusion salinity is 15 wt.%

(NaCl equiv.). Eutectic temperature of the inclusions is about -35°C that is corresponding to water-salt system NaCl-MgCl₂-H₂O. Isotope composition of O and C in calcite is the evidence of its hydrothermal-metamorphogenetic origin (Table 2).

Table 1. The results of isotopic mass-spectrometric research for gas-liquid inclusions.

№	Isotopic composition, ‰			
	$\delta^{13}\text{C}(\text{CO}_2)^{**}$	$\delta^{18}\text{O}(\text{CO}_2)^*$	$\delta^{18}\text{O}(\text{CO}_2)^{**}$	$\delta\text{D}(\text{H}_2\text{O})^*$
545	-			
550	-4.3	+10.0	-20.5	-106
533	-4.2	+10.1	-20.4	-105
531	-4.2	+10.2	-20.3	-102

Note: * – SMOW, ** – PDB

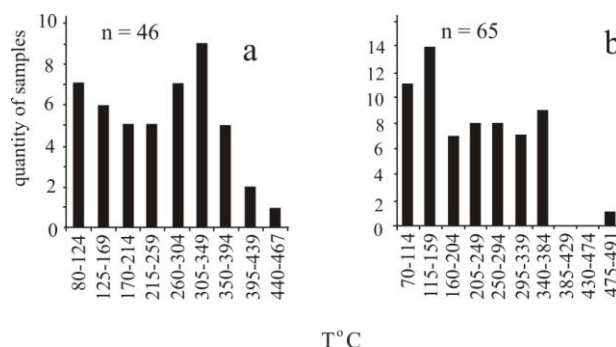


Figure 2. The distribution histogram of homogenization temperature: a – for barren quartz, b – for gold-bearing quartz.

Table 2. The results of isotopic mass-spectrometric research for calcite.

№	Isotopic composition, ‰	
	$\delta^{13}\text{C}^{**}$	$\delta^{18}\text{O}^*$
CH 1	-15.8	+11.5
CH 14	-13.0	+11.4
CH 50	-11.0	+12.2
CH 99	-10.9	+11.8

Note: * – SMOW, ** – PDB

Homogenization temperatures of inclusions in epidote are 120-220°C. Inclusion salinity is 6-11 wt.% (NaCl equiv.). Eutectic temperature of the inclusions is about -35°C that is corresponding to water-salt system NaCl-MgCl₂-H₂O. We haven't found inclusions representative for gold-bearing process that is testifying to the absence of any

connection between quartz and ore-forming process (gold mineralization).

Rare earth elements (REE) in the gas-liquid inclusions were determined by ISP-MS method. Increasing of Eu concentration and relatively high REE content in some quartz samples are probably the evidence of relations between mineral formation in this region and basic dikes and deep fault where hydrothermal solutions circulated (Fig. 3).

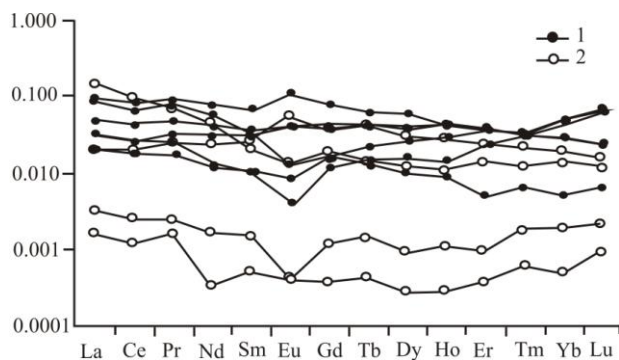


Figure 3. The distribution of REE in the gas-liquid inclusions: 1 – in gold-bearing quartz, 2 - in barren quartz.

Acknowledgement

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FLUID REGIME IN THE CARBON-SATURATED REDUCED MANTLE

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Ferric-ferrous iron equilibria reconstructed from peridotite and eclogite xenoliths evidence a decrease in fO_2 with depth in subcratonic mantle (Woodland, Koch, 2003). In vicinity of lithosphere and asthenosphere boundary fO_2 in the mantle rocks is estimated at the level of FMQ -4 log units. At depth of >250 km the mantle may be (Fe, Ni)-metal saturated owing to the high solubility of ferric iron in pyroxenes and garnets in equilibrium with Fe metal (Rohrbach et al., 2007).

Thermodynamic modeling shows that, at mantle fO_2 , the composition of fluid phases equilibrated with graphite/diamond-bearing rocks might vary from CO_2 to a mixture of CH_4 , H_2O , and H_2 (Saxena, 1989). The molecular composition of a reduced fluid phase at mantle P-T conditions has been poorly studied experimentally. At P-T conditions of the lower lithosphere and asthenosphere and at low fO_2 thermodynamic calculations predicts CH_4 -rich compositions (Saxena, 1989). The dominance of CH_4 -rich fluids in the reduced areas of the mantle was challenged by a number of studies. In experiments using diamond anvil cells it was established *in-situ* that at 2-10 GPa and 800-2000°C methane dissociates to form carbon, hydrogen, and unsaturated hydrocarbons (Kolesnikov et al., 2009). Theoretical studies in the C-H system predict high concentrations of hydrocarbons heavier than methane at pressures above 3 GPa and high temperatures. An additional evidence for the stability of hydrocarbons is derived from their presence in some diamonds.

Experimental procedures

We present the results of high-pressure experiments in the C-O-H systems at 6.3 GPa, 1200-1600°C. Experiments were carried out in a multi-anvil high-pressure apparatus of the “split-sphere” type. To buffer the fH_2 in the experiments, we modified the double-capsule technique by substituting the outer noble metal capsule with a thick-walled capsule made of molybdenum or iron (Sokol et al., 2009). In this case the outer capsule (Mo or Fe) acts as a container and a buffer. Two Pt capsules containing the sample assemblages were inserted into the single outer capsule. The inner capsules were isolated from the outer one by talc. At experimental P-T conditions, the talc

decomposed to form a mixture of enstatite + coesite + H_2O . Distilled water, stearic acid ($C_{18}H_{36}O_2$), anthracene ($C_{14}H_{10}$), docosane ($C_{22}H_{46}$), and graphite powder were used for generation of reduced C-O-H fluid. Initial concentrations of components were calculated from equilibrium composition of the fluid at the fO_2 corresponding to the Mo-MoO₂ and Fe-FeO buffers. Several experiments have been conducted without buffering of the fO_2 .

Experimental results

Chromatographic analysis of the quenched fluid shows that the composition of the fluids coexisting with graphite/diamond in the buffered experiments varied from $H_2O > H_2 > CH_4$ (at fO_2 somewhat lower than the “water maximum”) to $H_2 > CH_4 > (C_2H_4 + C_2H_6) > C_3H_8$ (in C-H system). In the C-H system the maximum concentrations of major species in the synthesized fluid were: $H_2 = 79$ mol.% and $CH_4 = 21$ mol.%. The composition of the H_2 -rich fluids, which were synthesized at 6.3 GPa and 1400–1600°C for the first time, differs considerably from that of the ultra-reduced CH_4 -rich fluids stable at 2.0–3.5 GPa and 1000–1300°C.

The results obtained in the C-O-H system demonstrate the stability of fluid rich in hydrogen, water and light hydrocarbons ($H_2 > CH_4$, $H_2O > \text{light hydrocarbons}$) in the reduced regions of the Earth's mantle. Synthesis of such fluid was realized in buffered experiments as a result of reactions between carbon and hydrogen and pyrolysis of heavy hydrocarbons. At high P-T conditions, the degree of decomposition of the heavy hydrocarbons added to the charge was >99.9%. Thermodynamic calculations at P-T- fO_2 conditions of the present study do not permit the adequate modeling of the concentrations of the main components of the fluid. The most likely reason for rather low concentrations of CH_4 in the reduced fluids is dissociation of CH_4 and formation of carbon and unsaturated hydrocarbons. The quenching rate of 200°/sec ensures reliable data on the molecular composition of fluids at the P-T conditions of experiments. While at lower quenching rates the reverse reactions of light hydrocarbons formation were established.

In the C-O-H system diamond crystallization had a maximum intensity in the pure aqueous fluids, while in the H_2 -rich fluids no diamond

formation was observed. Only metastable graphite precipitated from the ultra-reduced fluids.

Due to buoyancy, reduced fluids could migrate upwards through cratonic peridotites and generate multiple redox-fronts (Arculus, Delano, 1987). The probable reason for the oxidation of fluids within these fronts is the interaction with the less reduced environments (Arculus, Delano, 1987). Moreover, a drastic increase in fO_2 and auto-oxidation of fluid is possible at $P < 7$ GPa as a result of fluid reaction with Fe_2O_3 , which can be formed by the breakdown of majorite (Rohrbach et al., 2007). The oxidation of H_2 and hydrocarbons within these multiple redox-fronts could lead to the formation of an essentially aqueous fluid and a drastic reduction of total carbon content in this fluid. At fO_2 , close to the so-called “water maximum”, the fluid consists of 95 mol.% water. Thus, multiple redox-fronts would probably be an impassable boundary for further ascent of hydrocarbons to the surface. Carbon in methane and other hydrocarbons would be released in the form of C^0 upon oxidation and be consumed for saturation with the aqueous fluid. Subsequently this C^0 could be involved in diamond crystallization.

Conclusions

Fluids rich in hydrogen, water and light hydrocarbons ($H_2 > CH_4$, $H_2O > \text{light hydrocarbons}$) are likely to predominate in the reduced regions of the Earth's mantle.

Aqueous fluid with H_2 and CH_4 admixtures is the most probable medium for diamond crystallization in the reduced mantle. Catalytic ability of C-O-H fluids with respect to diamond formation slows down with the decreasing of both oxygen fugacity and temperature.

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CRYSTALLIZATION CONDITIONS OF RARE-METAL ROCKS OF THE EAST KALGUTINSKY DIKE BELT (SOUTHERN ALTAY, RUSSIA)

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The East Kalgutinsky dike belt is spatially and genetically related to the Kalgutinsky rare-metal granite massif and hydrothermal W-Mo deposit. Dikes are composed of rare-metal (RM) and ultra-rare-metal (URM) ongonites and elvanites. Ultra-rare-metal here means very high concentrations of rare lithophile elements. Geochemical mapping showed that URM rocks form a group of bodies, which are situated on the straight line striking to the North-East in the axial part of the belt. Contents of Li, Rb, Cs, Be, Ta and Nb in those bodies are by the order of magnitude higher than those of earlier granitoids of the Kalgutinsky massif and are comparable with those of commercial RM pegmatite deposits. The Ar-Ar and U-Pb dating along with geological observations indicate that the dike ages are close to ages of W-Mo hydrothermal veins. Thus, the Kalgutinsky granite massif, East Kalgutinsky dike belt and ore deposit are considered as a single ore-magmatic system (Annikova et al., 2006; Potseluev et al., 2008).

The rocks of the East Kalgutinsky belt differ from ongonites and elvanites from around the world by higher P₂O₅ (up to 0.5-0.7 wt.%) and lower F contents (up to 0.2-1 wt.%).

PT-parameters and fluid regime of crystallization of ongonites and elvanites were determined on the basis of study of cogenetic melt (MI) and fluid (FI) inclusions (Fig. 1) in quartz.

The MIs are composed of crystallized aggregate of silicate daughter phases (mostly muscovite). This means that the host quartz grew in magmatic chamber under slow cooling conditions. Fluid segregations sometimes are observed. Meanwhile, most of the inclusions are surrounded by a halo of radiating fissures, which are healed and contain fluid inclusions. This feature suggests that the host quartz was formed under high fluid pressure at some depth, while decrepitation of inclusions occurred in the course of their ascent with magma to shallower horizons.

The MIs, which are not associated with fissure halos, were chosen for homogenization. In order to avoid decrepitation quartz grains with MIs were heated in H₂O filled autoclave under confining pressure 1-2.5 kbar.

The MIs in quartz from different dikes homogenize within 635-695°C. However, regarding the data on quartz thermal expansion and compression under pressure the measured

temperatures are about 25-35°C higher than entrapment temperature. Thus, quartz crystallization temperatures should be about 600-670°C. Notably, the lowest temperatures are recorded for quartz from URM ongonites in axial part of the East Kalgutinsky belt.

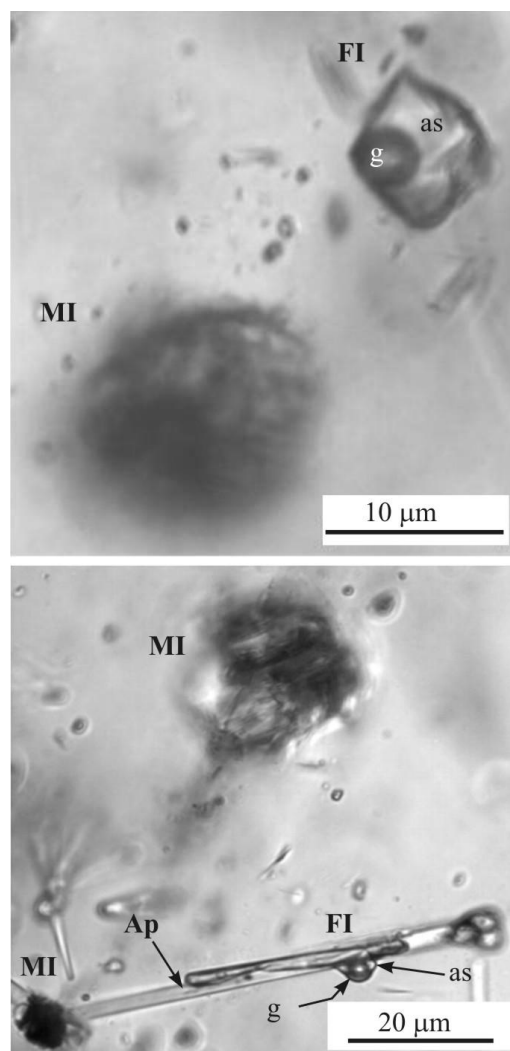


Figure 1. Inclusions in quartz: a – cogenetic silicate melt (MI) and fluid (FI) inclusions; b – fluid inclusion (FI), combined with magmatic apatite crystal (Ap) and co-genetic with silicate melt inclusions (MI). g – gaseous phase, as – aqueous solution.

Compositions of quenched glasses of the heated MIs determined by EMPA are in general close to bulk rock compositions of the dikes. The MIs differ from bulk rock by lower P₂O₅. The appearance of apatite and unidentified fluorophosphate of Al in MIs lead to conclusion that parent melt was richer in phosphorus in the course of quartz crystallization.

Quartz phenocrysts in elvanites and ongonites contain abundant FIs. Most of them are secondary. The FIs, which occur in the single groups with MIs (Fig. 1a) and combined with magmatic crystalline phases (Fig. 1b), were considered to be primary and cogenetic with MIs. The FIs are composed of aqueous salt solutions and gaseous bubble. Quartz phenocrysts of several dikes contain FIs with liquid CO₂. The FIs homogenize into liquid at 130-200°C. Eutectic temperature of most inclusions is between -24°C and -19°C. Thus, volumetric properties of inclusions can be modeled by the system NaCl-H₂O. Salt concentration is estimated as 4-8 wt.% NaCl eq.

According to the data reported above quartz phenocrysts of ongonites and elvanites of the East Kalgutinsky belt crystallized from H₂O-saturated magma at 600-670°C and 4-6 kbar.

The determined conditions can be verified by the phenocryst mineralogy. The presence of magmatic muscovite phenocrysts with elevated F content (up to 1-2 wt.%) suggests its formation from F-rich magma at pressures greater than 3 kbar. The coexistence of K-feldspar and acid plagioclase points to their crystallization below 700°C. Regarding difference in Na content in K-feldspar and Ti content in magmatic muscovite, elvanite phenocrysts crystallized at higher temperatures than phenocrysts of ongonites.

The increase of concentrations of Rb in K-feldspar and muscovite from elvanites through RM ongonites to URM ongonites indicates that URM rocks were formed from more differentiated melts than RM rocks.

One of the major features of the East Kalgutinsky dike belt rocks is elevated concentration of phosphorus. In addition to main mineral concentrator – apatite, elevated P₂O₅ contents were found in K-feldspar. Content of P₂O₅ in K-feldspar correlates positively with Rb and Rb/Sr in the bulk rock and inversely with bulk rock K/Rb. It means that elevated phosphorus in ongonites and elvanites resulted from differentiation of parental magma.

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FORMATION OF HEAVY FLUID AND PECULIAR LIQUID IMMISCIBILITY IN THE PERALKALINE MAGMAS OF THE ISLAND OF PANTELLERIA, ITALY

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Introduction

This contribution reports a study of pantellerites from the Island of Pantelleria, which is situated in the zone of the Sicilian continental rift. The rocks are a classic occurrence of strongly evolved peralkaline silicic volcanics (220–100 ka) strongly enriched in iron and chlorine.

Formation conditions of heavy fluid

Melt inclusions in anorthoclase phenocrysts were investigated using a Linkam TS1500 heating stage. During cyclic heating-cooling experiments, the formation of a transparent isotropic phase was observed near a gas bubble at temperatures of 400–600°C (Fig. 1). Its boundary with silicate glass was always meniscus-like.

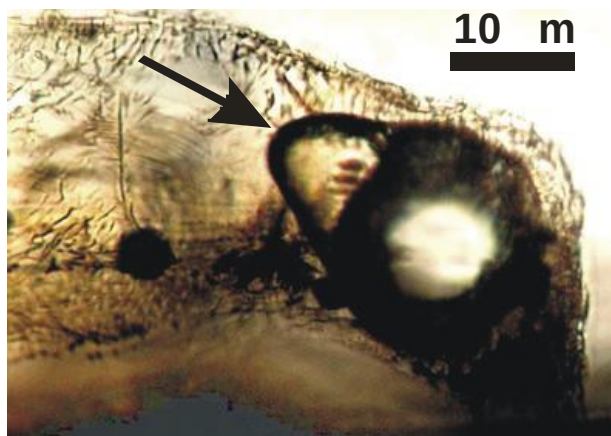


Figure 1. Fragment of an inclusion with heavy fluid at the contact with a gas bubble (indicated by the arrow).

The interpretation of the observations is not straightforward, because we could not determine the composition of the new-formed phase. Its behavior during heating indicates that its physical properties are significantly different from those of the adjacent gas phase and silicate melt (glass). On the other hand, it is not an aqueous solution, which is indicated by the absence of apparent effects during cooling to -180°C. Visual observations suggest that its properties are intermediate between those of aqueous solutions and silicate melts. In our opinion, this material can be a heavy fluid, which has been described during the investigations of interactions in silicate systems with volatile components (e.g., Anfilogov et al., 1972; Smirnov et al., 2003; Kotelnikova et al., 2003). Its formation is related to the specific features of the behavior of

water-silicate systems of the P-Q type.

What is the process that could provide the increase of water content in the fluid? It was noted that gas (fluid) bubbles were extensively formed in the inclusions at 500–650°C, which is in agreement with the decrease of H₂O solubility in silicic melts at increasing temperature and constant pressure. The number and sizes of gas bubbles in inclusions decreased above 650°C up to their complete disappearance. This phenomenon is related to the microautoclave effect, i.e., an increase in pressure and H₂O solubility in the melt within the inclusion under near isochoric conditions. The formation of heavy fluid must have accompanied the effect of H₂O solubility decrease. High-temperature experiments showed that this phase retained in inclusions up to 750°C. The high peralkalinity of the melts promoted the separation of excess alkalis into an individual heavy fluid phase.

Anomalous liquid immiscibility

In addition to daughter anorthoclase, residual glass, salt (NaCl–NaF–Ca₂F) aggregates, and gas bubbles (Solovova et al., 2010), the unheated inclusions contain areas of vermicular aggregates of two isotropic phases (Fig. 2) with different birefringence. Sometimes, they surround salt aggregates (Fig. 2a).

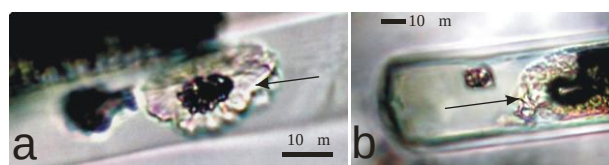


Figure 2. Fragments of melt inclusions containing immiscible melts (arrows) and salt globules.

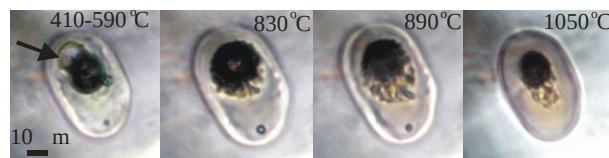


Figure 3. Formation and dissolution of two immiscible melts. The arrow indicates heavy fluid.

Similar aggregates were obtained in experiments. During heating of inclusions with heavy fluid up to 700–750°C, the shape of this phase changed and it migrated along the boundary of the gas bubble. The homogeneous phase was replaced above 750°C by two immiscible melts,

whose total volume increased gradually up to 900°C (Fig. 3). A further temperature increase resulted in their dissolution in the silicate melt of the inclusions and complete disappearance at 1050–1080°C.

The observations can be interpreted in the following manner. As the inclusions were heated, heavy fluid dissolved in silicate melt, but the compositions of melt remained nonuniform owing to the high viscosity of the melt, and areas near fluid bubbles appeared to be enriched in those components that were concentrated in the heavy fluid. The analyses of glasses suggest that among such components could be alkalis and, probably, iron. The local disturbance of melt composition near the fluid phase could lead to the unmixing into two silicate liquids with strong fractionation of Si, Fe, Na, and K, which is probably a kinetic phenomenon.

Chemical compositions of melts

The analyses of residual glasses from the inclusions, immiscible melts, and defocused-beam compositions of two-phase areas are given in the Table 1.

Table 1. Compositions of glasses from inclusions.

	SiO ₂	Al ₂ O ₃	FeO	Na ₂ O	K ₂ O
1	74.73	1.68	10.70	3.28	2.10
2	87.29	1.37	3.69	1.18	1.19
3	53.96	2.95	22.88	8.15	3.51

Note. 1–mixture of two immiscible melts, 2 and 3 –coexisting melts.

The two liquids that are formed owing to heavy fluid–silicate melt interaction differ most significantly in SiO₂ and alkali contents. The low-SiO₂ liquid (54–68 wt.% SiO₂) is enriched in FeO (up to 23 wt.%) and alkalis (10.7–16.5 wt.%) with molar Na/K ratios of up to 6.7. The Al₂O₃ content is no higher than 3 wt.%. The high-SiO₂ (85–89 wt.%) liquid contains no more than 6 wt.% of total alkalis. The maximum FeO content is 5 wt.%, which is four times lower than in the low-SiO₂ melt. The contents of Cl and F are similar in the two melts: up to 2 wt.% Cl and 0.9 wt.% F.

Zirconium and Sm preferentially are partitioned into the low-SiO₂ melt: up to 7000 ppm Sm and 5400 ppm Zr, whereas only traces of these elements were detected in the more silicic melt. Homogenized inclusions from the same samples showed 2400–2800 ppm Zr and 32.7 ppm Sm.

The peculiar character of the immiscibility in the inclusions is clearly seen in the SiO₂–Na₂O+K₂O diagram (Fig. 4). All the available data from the literature on liquid immiscibility in natural and experimental systems indicate a significant enrichment of the more silicic melt in alkalis and

alumina (dashed lines in Fig. 4). In the products of liquid unmixing described here, alkalis are concentrated in the more basic melt (solid lines in Fig. 4). The anomalous behavior of components during liquid immiscibility could be a kinetic phenomenon, although variations in experimental duration did not result in any significant redistribution of Na and K.

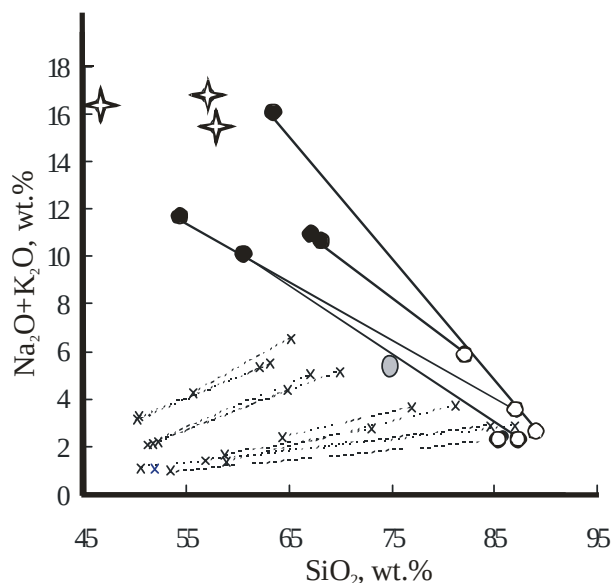


Figure 4. Compositions of silicate melts at anomalous (circles) and normal (crosses) liquid immiscibility, the stars are the data of Smirnov et al. (2003).

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NOBLE GAS STUDY OF INCLUSIONS IN DIAMONDS AND OLIVINES IN UDACHNAYA KIMBERLITE, SIBERIA

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Introduction

Noble gas isotopes trapped in fluid/melt inclusions in diamonds and kimberlitic olivines can constrain the origin of such deep-mantle-derived materials because they show completely different values between the more primordial source, which contributes OIBs and which is possibly stored in the deep mantle, and the depleted MORB source in the convecting mantle. In contrast, *in situ* radiogenic/cosmogenic noble gas isotopes might be distributed homogeneously in the mineral lattices. *In vacuo* sequential dynamic crushing extraction - by which sample grains are crushed mechanically in vacuum (Kurz, 1986) - and laser microprobes (Burnard et al., 1994) are powerful tools for selective noble gas extraction from the inclusions.

This report presents a noble gas study, conducted using a combination of several non-destructive micro-spectroscopic methods, of inclusions in diamonds and olivines in the Udachnaya kimberlite (Siberia). The examinations revealed the original isotopic signature and their trapping sites of noble gases.

Primordial noble gas in the kimberlite magma

Fresh olivine phenocrysts in kimberlite collected from deep levels (ca. 500 m) of the Udachnaya kimberlite pipe have been revealed to preserve magmatic noble gases in low-density CO₂ fluid inclusions associated with carbonate-chloride inclusions (Golovin et al., 2003; Kamenetsky et al., 2008). Noble gases in the olivine separates (ca. 1 g) were extracted using *in vacuo* sequential dynamic crushing.

The ³He/⁴He ratios decreased from 5.7–1.2 *R*_A (where *R*_A denotes the atmospheric ³He/⁴He = 1.4 × 10⁻⁶) with progress of crushing, indicating that the original ³He/⁴He ratio of the magma resembles that of subcontinental lithospheric mantle (SCLM) and that ⁴He produced *in-situ* after the kimberlite emplacement (ca. 350 Ma, Maas et al., 2005) was released from olivine lattice and/or solid phase of inclusions because the olivine particle size was getting smaller with progress of crushing. Neon isotope ratios indicate a less-nucleogenic feature in the kimberlite magma than in the MORB source. The He–Ne systematics revealed that helium and

neon in the Udachnaya kimberlite magma are explainable by a mixing between a plume-like component, which would be the original characteristic of the source of kimberlite magma, and the SCLM-like one, which would be acquired from surrounding materials in the SCLM and/or crust during magma ascent. The results indicate that the source of the Udachnaya kimberlite has similar noble gas characteristics to those of OIBs, and constrain a depth of its origin to be deeper than the upper mantle (Sumino et al., 2006).

Trapping sites of the noble gases in olivines: Laser-microprobe analysis

Some single olivine grains were doubly polished into thin slabs (approximately 200–300 μm thick). First, major element compositions of the polished olivine slabs were analyzed using SEM–EDX to distinguish their phenocryst/xenocryst-like origin in terms of Fo zoning (Kamenetsky et al., 2008). Then distributions of carbonate and water were investigated using micro-FTIR spectrometry with an aperture of 60×60 μm. Composite inclusions of carbonate, chloride, sulfate, and fluid (Golovin et al., 2003; Kamenetsky et al., 2008) were investigated in detail using micro-Raman spectroscopy with resolution of several microns. After these non-destructive analyses, noble gases were extracted by drilling and carving out a sample area of approximately several hundreds of microns using an ultraviolet laser beam (213 nm wavelength) in an ultrahigh-vacuum chamber. Ablated volumes of each laser pit were about 10⁻⁵ cm³, corresponding to several tens of micrograms of olivine.

Amounts of ⁴He and ⁴⁰Ar extracted from each laser pit vary by more than an order of magnitude (0.6–16 × 10⁻¹⁰ cm³ STP for ⁴He and 0.5–9 × 10⁻¹⁰ cm³ STP for ⁴⁰Ar) and are heterogeneous, even in a single crystal. Based on their homogeneous Fo content (Kamenetsky et al., 2008), the xenocryst-like olivines systematically show low noble gas concentrations. The ⁴He/³He ranging from 1.1 × 10⁵ to 2.6 × 10⁶ (corresponding to ³He/⁴He of 6.5 and 0.3 *R*_A) are also heterogeneous in a single crystal. Based on the He–Ar isotope systematics, two components are recognizable. The first resembles

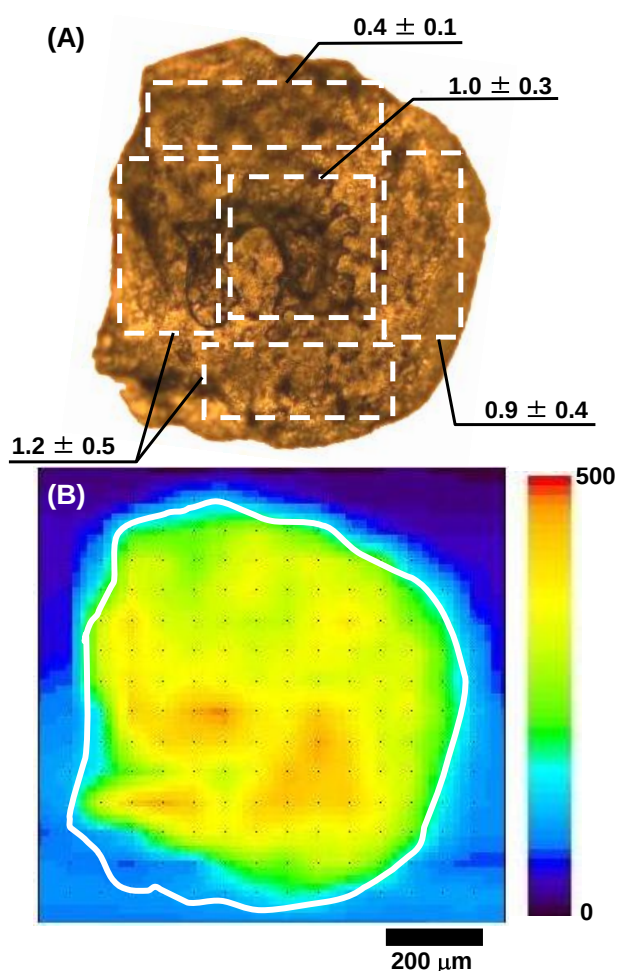


Figure 1. (A) An optical microscope image of a thin olivine slab analyzed in this study. Boxes indicate laser-ablated areas for noble gas extraction. Numbers are $^4\text{He}/^3\text{He}$ (in unit of 10^6 with 1σ errors) observed for each laser pit. (B) A color map of CO_3^{2-} content (ppm) of the same slab obtained by micro-FTIR spectrometer.

$^4\text{He}/^3\text{He}$ and $^4\text{He}/^{40}\text{Ar}^*$, where $^{40}\text{Ar}^*$ is non-atmospheric ^{40}Ar , to those obtained using the bulk *in vacuo* crushing of phenocrystic olivines, suggesting its residence in the fluid phase of inclusions. The other component has higher $^4\text{He}/^{40}\text{Ar}^*$ and $^4\text{He}/^3\text{He}$ than the fluid inclusion-hosted component, implying that a significant part of ^4He in the second component is of *in-situ* radiogenic origin. A rough correlation between CO_3^{2-} content determined using micro FT-IR analysis and $^4\text{He}/^3\text{He}$ in a single crystal (Fig. 1) suggests that the radiogenic component is enriched in the carbonate phase in inclusions, which is consistent with the high concentration of U in carbonates.

Noble gases in diamonds

Diamond crystals of cubic habit with abundant micro-inclusions and of 1–3 mm were collected from the Udachnaya kimberlite pipe. The individual micro-inclusions are usually smaller than several micrometers, with some exceptions reaching 10–15

μm (Zedgenizov et al., 2004). According to the distribution of carbonates (i.e., inclusions) obtained by FTIR investigation, doubly polished plates of the samples were cut into several pieces. Noble gases in the sample pieces (less 0.5–1 mg each) were extracted using *in vacuo* stepwise heating or crushing. Although the samples released helium that was dominated by radiogenic ^4He at their graphitization (2000°C) during stepwise heating, the crush-released helium exhibited $^3\text{He}/^4\text{He}$ of 6.2 R_A , indicating that the inclusion-hosted helium has similar $^3\text{He}/^4\text{He}$ to that of the host kimberlite magma. This similarity implies diamond formation in a SCLM environment. A correlation between CO_3^{2-} content and ^3He suggests that mantle-derived noble gases are trapped in the carbonate-rich inclusions. In contrast, diamond-lattice-hosted helium is dominated by radiogenic ^4He , possibly produced *in situ* from trace amounts of U and Th after diamond formation. Because of the scarcity of neon released through stepwise heating and crushing, it remains unclear whether the inclusion-hosted noble gas contains a primordial component, as it does in the case of the kimberlitic olivines. Therefore, we are conducting further investigations into noble gases in the Udachnaya diamonds using larger samples.

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ORE-FORMING FLUID GEOCHEMISTRY AND METALLOGENIC MECHANISM OF BANGBU LARGE-SCALE OROGENIC GOLD DEPOSIT IN SOUTHERN TIBET, CHINA

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The Bangbu gold deposit is located to the south of the east section of the Yarlung Zangbo tectonic suture zone in the southern Tibet. The gold ore bodies are controlled by the secondary brittle fractures in the large-scale brittle-ductile shear zone (Lv et al., 2005). It is the largest proved primary gold deposit in Tibet before present. Microthermometric measurements and laser Raman analysis show that auriferous quartz veins of the Bangbu gold deposit contain three types of fluid inclusions: liquid aqueous inclusions (type I); CO₂ brine inclusions (type II), which can be subdivided into two-phase (type IIa) and three-phase (type IIb) inclusions; pure gaseous hydrocarbon inclusions (type III) (Fig.1). The CO₂ brine inclusions have salinity values of 2.20-9.45 wt.% NaCl eq., with a peak of 6.0-7.0 wt.% NaCl eq. and an average of 6.25 wt.% NaCl eq., homogenization temperature values of 166.7-335.8°C, with a peak of 210-250°C and an average of 235.4°C, and density values of 0.63-0.96 g/cm³, with a peak of 0.85-0.95 g/cm³ and average of 0.87 g/cm³, suggesting that the ore-forming fluids of the Bangbu gold deposit is characteristics by high content of CO₂, lower salinity, medium to lower homogenization temperature and lower density, which are similar to those of typical orogenic gold deposits (Goldfarb et al., 2004). Oxygen and hydrogen isotopic analyses show that δD and $\delta^{18}O$ of the ore-forming fluids in the Bangbu gold deposit are -44.4 ~ -105.5‰ and 4.7-9.0‰, respectively, indicating that the ore-forming fluids is composed mainly of metamorphic fluid, with addition of mantle-derived fluid (Table 1, Fig. 2). In addition, He-Ar-S isotopic compositions of ore-forming fluids in pyrites collected from Bangbu auriferous quartz veins were analyzed, and the results show that ³He/⁴He ratio is 0.174 to 1.010Ra, ⁴⁰Ar/³⁶Ar ranges from 311.9 to 1724.9 and $\delta^{34}S$ is 2.8-4.7‰, averaging 3.6‰, whereas pyrite collected from country rocks has ³He/⁴He ratio of 0.01137Ra, ⁴⁰Ar/³⁶Ar of 1709.7 and $\delta^{34}S$ of 6.5‰, suggesting that the ore-forming fluid of the Bangbu gold deposit was a mixture of crust fluid and mantle-derived fluid, and the former is predominant (Sun et al., 1999, 2004, 2006). The ration of mantle-derived He is 6.3-16.7%. Crust-mantle interaction and the subsequent injection of

mantle-derived fluids might have played an important role in the mineralization of the Bangbu gold deposit. During collision between the Indian plate and Asian plate, large-scale vertical lithospheric shear zones were formed, and the subsequent mantle-derived fluid went up through the shear zone, mixing with the lower crust derived CO₂-rich fluid. The mixed ore-forming fluids migrated to the secondary brittle structures in the shear zones, and finally precipitated auriferous sulfide quartz ores because of decline of temperature and pressure. Geologic and geochemical features show that the Bangbu gold deposit may be a Cenozoic orogenic gold deposit formed under continental collisional background.

Table 1. δD - $\delta^{18}O$ isotopic compositions (‰, SMOW) of fluid inclusions in auriferous quartz veins from the Bangbu gold deposit.

Sample Number	Sample name	δD	$\delta^{18}O_Q^*$	T_h^{**} (°C)	$\delta^{18}O_w^{**}$
BB003		-64.9	15.0	236.1	5.4
BB004	Auriferous	-44.4	18.2	235.4	8.5
BB010	quartz vein	-59.4	15.9	239.6	6.4
BB013		-49.7	15.6	235.4	5.9
BB014	Auriferous quartz sulfide vein	-76.0	15.3	250.3	6.4
BB019	Auriferous quartz vein	-61.8	17.7	227.9	7.6
BB020	Auriferous quartz sulfide vein	-61.0	16.0	235.4	6.3
BB025	Auriferous pyrite quartz vein	-85.2	18.7	235.4	9.0
BB027	Auriferous	-75.8	15.9	229.0	5.9
BB029	quartz vein	105.3	14.4	235.4	4.7
BB032	Barren quartz vein	-38.2	15.4	242.0	6.1

* $\delta^{18}O$ (‰) of quartz; ** T_h represents homogenization temperature of fluid inclusions; *** $\delta^{18}O$ (‰) of fluids calculated based on the measured $\delta^{18}O$ of quartz, homogenization temperature of fluid inclusions, and equilibrium oxygen isotope fractionation between quartz and water, $\Delta_{Q-H_2O}=3.38 \times 10^6/T^2-3.4$ (Clayton et al., 1972).

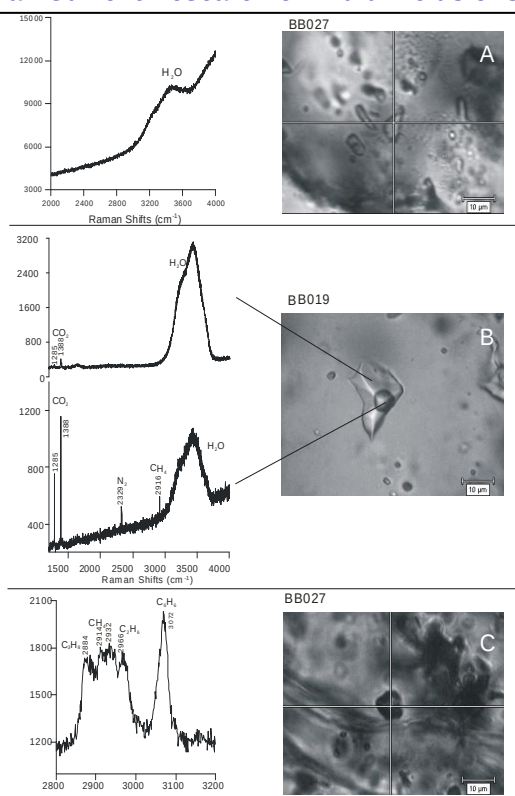


Figure 1. Laser Raman spectra of fluid inclusions from the Bangbu gold deposit.

Laser Raman spectrum of the type 1 fluid inclusion indicates that the composition is predominately H_2O (Sample BB027). B. Laser Raman analyses indicate that the gaseous phases in the type IIa fluid inclusions are composed predominantly of CO_2 and H_2O with minor N_2 and CH_4 ; and the liquid phases are composed of H_2O with a little CO_2 (Sample BB019). C. Laser Raman analysis indicates that the type III fluid inclusion is composed of C_mH_n (include CH_4 , C_2H_6 , C_3H_8 and C_6H_6 , etc.) (Sample BB027).

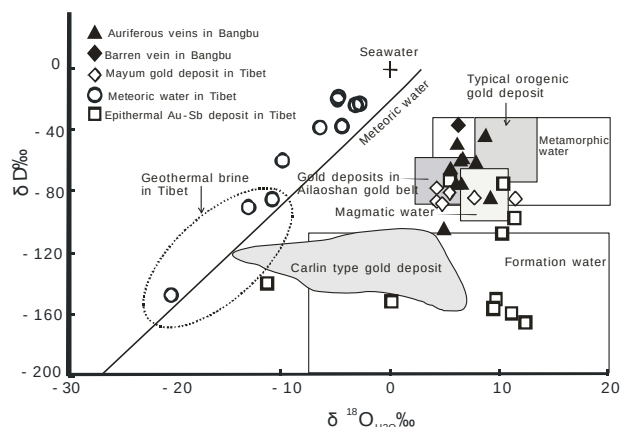


Figure 2. Plot of δD versus $\delta^{18}\text{O}$ for ore-forming fluids from the Bangbu gold deposit.

Fields of magmatic, metamorphic and formation water (e.g., devolatilization of organic matter in sediments) after Sheppard (1986); Field for typical orogenic gold deposits after Goldfarb et al. (2004); Field for the Carlin deposits after Field et al. (1985); Field for gold deposit in the Ailaoshan gold belt after Sun et al. (2009); Values for geothermal brine in Tibet after Zheng et al. (1982); Values for meteoric water in Tibet after Zheng et al. (1983); Values for the Mayum gold deposit after Wen et al. (2006) and Duoqi et al. (2009); Values for antimony and gold deposits in South Tibet after Yang et al. (2006).

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CASSITERITE AND WOLFRAMITE ORE FORMATION IN HYDROTHERMAL SYSTEM ASSOCIATED WITH GRANITES (THERMODYNAMIC MODELLING)

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Thermodynamic modelling of cassiterite and wolframite deposition as a result of acting in mineral-forming solutions such processes as cooling, boiling, interaction with wall rocks and mixing of genetically different fluids has been carried out. In the study evolution of mineral forming process was described with the help of sequence of equilibrium states of the systems and total compositions were determined by dynamic relationships. The calculations of equilibrium states of heterogeneous systems were fulfilled with HCh software package (Shvarov, Bastrakov, 1999). Input data for modelling were obtained in the studies of the Iultin deposit

The Iultin deposit was formed in the hydrothermal system, associated with leucocratic granites (K₂). The groups of quartz veins with cassiterite and wolframite mineralization are located in hornfelsized sandstone-schist rocks (T₁₋₂) and in the greisenized granites of the stock. The following mineral associations were subsequently formed: 1 - quartz-muscovite-albite-fluorite; 2 - quartz-muscovite-cassiterite-wolframite; 3 - sulfide; 4 - quartz-fluorite-calcite.

The formation of the productive association took place from sodium chloride boiling solutions enriched in CO₂ and CH₄ at T 270-350⁰ C ,P 0,5-1,0 kbar as it followed from fluid inclusion data (Table 1).

The results of the calculations showed that in ore-forming solutions of the Iultin deposit tin was transported mainly in the form of SnOHCl, while tungsten in the form of H₃WO₄F(aq). This difference determined the ways and causes of the cassiterite and wolframite deposition.

Cooling of the hydrothermal fluid leads to the deposition of these two minerals but in a broader temperature interval (450-150°C) than it took place during the formation of the deposit (Fig. 1a, 1b).

Boiling gives rise to the formation of cassiterite and, to less extent, of wolframite, but it cannot account in full measure for the occurrence of tin and tungsten mineralization in the Iultin ore-forming system (Fig. 2a, 2b)

Results of the calculations, which take into account **mixing** of the ore-forming fluid with the exogenic one and equilibration of this mixed fluid with the wall rocks, correspond to the natural situation to a greater extent (Fig. 3a, 3b). This

process reproduces mineral zonality of the deposit quite well and may be accepted as the main factor of the ore deposition.

Table 1. Mineral-forming solutions of the Iultin deposit (microthermometric and cryometric data).

	T, °C	P, bars	S, wt. %	Chemical type
Magmatogeneous fluid				
Primary melt inclusions and secondary fluid inclusions in quartz from the Iultin stock	700 - 650	5000 - 4500	6.5 - 10.5	NaCl - H ₂ O
Fluid from recrystallisation zones in granites of the Iultin stock				
Fluid inclusions in quartz	370 - 300	900 - 400	10.3 - 4.8	NaCl - H ₂ O - CO ₂
Fluid from zones of greisenization				
Fluid inclusions in quartz	350 - 300	1200 - 900	10.4 - 9.8	NaCl - H ₂ O - CO ₂
Exogenic fluid				
Fluid inclusions in preore quartz from wall rocks (hornfels, shales, argillites)	350 - 300	1100 - 200	3.9 - 1.9	CO ₂ - CH ₄ - H ₂ O - NaCl
Fluid of productive stage				
Primary fluid inclusions in quartz, beryl, cassiterite, fluorite from quartz veins:	350 - 300	1000 - 200	9.0 - 3.3	H ₂ O - NaCl - CO ₂ - CH ₄
a) homogenization in liquid phase	350 - 300	250 - 120	3.6 - 0.7	
b) homogenization in gaseous phase				
Postproductive fluid (a)				
Fluid inclusions in quartz, calcite, fluorite	290 - 210		6.6 - 1.4	H ₂ O - NaCl - CO ₂
Postproductive fluid (b)				
Fluid inclusions in quartz, calcite, fluorite	200 - 100		5.0 - 1.2	H ₂ O - NaHCO ₃

Note: Boiling was found to be intensive during the productive stage, so deposition of Sn-W ores took place from heterogeneous fluid

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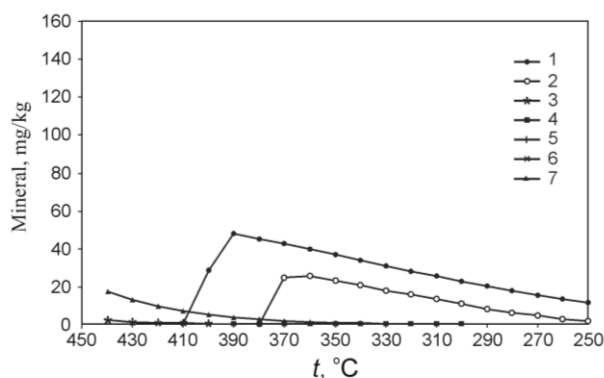


Figure 1a. Calculation results of model of ore-forming fluid cooling: deposition of minerals from 1 kg of fluid.

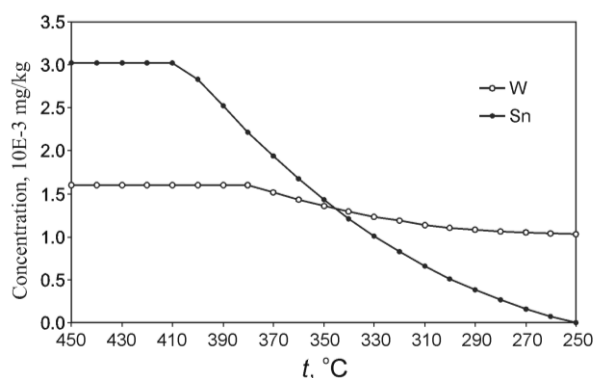


Figure 1b. Calculation results of model of ore-forming fluid cooling: Sn and W concentrations.

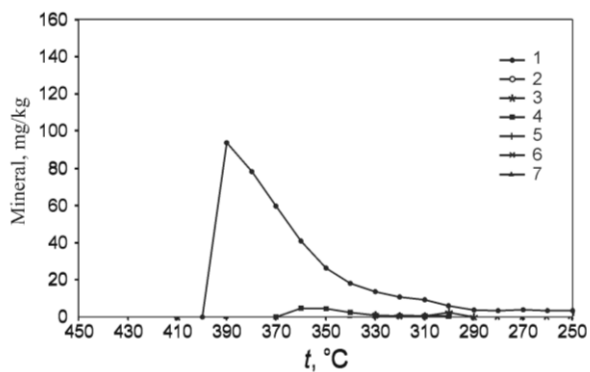


Figure 2a. Calculation results of model of ore-forming fluid boiling: deposition of minerals.

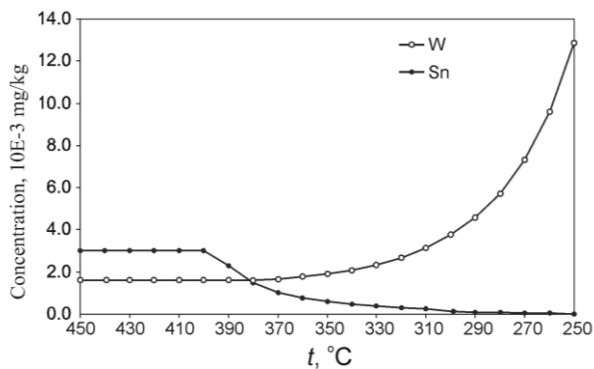


Figure 2b. Calculation results of model of ore-forming fluid boiling: concentrations of Sn and W.

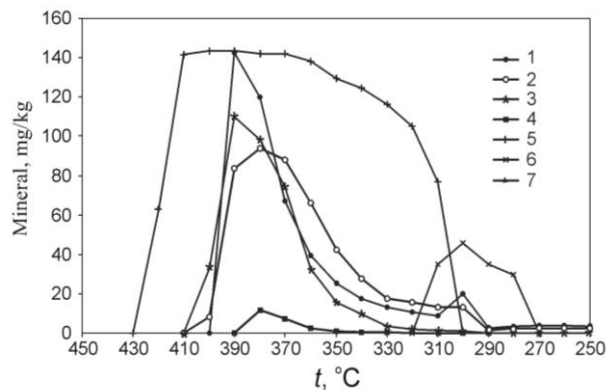


Figure 3a. Calculation results of model of fluid mixing: deposition of minerals

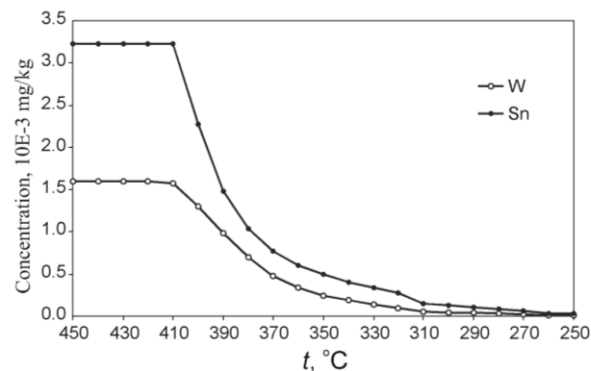


Figure 3b. Calculation results of model of fluid mixing: Concentration of Sn and W.

Notes for all the figures - minerals: 1 - cassiterite, 2 - wolframite, 3 - arsenopyrite, 4 - fluorite, 5 - muscovite, 6 - microcline, 7 - topaz.

SILICATE MELT INCLUSIONS IN UPPER MANTLE XENOLITHS FROM THE PANNONIAN BASIN (HUNGARY)

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Introduction

In mantle environments mostly silicate, sulfide and carbonatite melts can be found as accidentally trapped melt phases. Among these, the silicate melts show the highest abundance, although sulfide and carbonatite melts also provide valuable information on melt/fluid percolation related to metasomatic processes that are associated with transporting and concentrating incompatible elements and volatiles in the mantle.

Silicate melt accumulations occurring as inclusions, melt pockets, interstitial glass patches and veins in ultramafic xenoliths have been described from several localities all over the world. Whereas the interstitial glass patches or veins in xenoliths significantly re-equilibrated and their chemical composition usually reflects low-pressure conditions, the primary silicate melt inclusions from deep lithospheric environments are generally considered to be mantle melts/fluids that were trapped at high pressure and temperature in equilibrium with the peridotitic assemblages.

Therefore, the most important conclusion of melt inclusion studies of mantle xenoliths is that they may preserve the original composition of melts that were entrapped at mantle pressures and temperatures. Similarly, silicate melt inclusions are key materials to reveal post-entrapment processes, such as crystallization on the wall or in situ immiscibility of volatiles and silicates within the inclusions.

Geodynamic settings

The Carpathian-Pannonian region is located in Central Europe and includes the Pannonian Basin which is surrounded by the Carpathian fold and thrust belt. The driving force of the evolution of the region that is associated with displacement of tectonic units and subsequent extension of the subcontinental lithosphere is considered to be the collision between the Adrian indenter and the stable European platform. The formation of the Pannonian Basin was accompanied by intensive asthenospheric upwelling and, therefore, the area is characterized by an anomalously thin lithosphere (~60 km).

Goals

As a result of the special geodynamic evolution of the Carpathian-Pannonian region,

silicate, carbonatite and sulfide melt accumulations are abundant metasomatic phases in mantle xenoliths outcropped in Neogene alkaline basalts of the region. In this work we will focus on silicate melts preserved in Type-1 peridotitic and Type-2 pyroxenitic mantle xenoliths from the northern (Nógrád-Gömör Volcanic Field: NGVF) and central (Bakony-Balaton Highland Volcanic Field: BBHVF) part of the Carpathian-Pannonian region, with the aim of showing how the silicate melt inclusion studies contributed to the revelation of the different types of metasomatism in the subcontinental lithospheric mantle associated with the geodynamic evolution of the region.

Results and conclusions

In the NGVF metasomatized Type-1 upper mantle xenoliths contain andesitic and basaltic silicate melt inclusions hosted mainly in olivines. Besides, melt pockets occur interstitial to mantle phases. Petrographic and geochemical data suggest a common source for these distinctly different occurrences. Of these possible origins for the melt inclusions and melt pockets the one that is most consistent with the available data is a subduction-related, volatile-rich silicate melt that infiltrated through and interacted with mantle phases, causing cryptic and modal metasomatism in the peridotitic wall-rock and a progressive evolution of the melt composition to produce residual melts. Formation of melt pockets and multiphase silicate melt inclusions with basaltic composition was associated with the less residual melts. Conversely, more evolved melts percolated through the shallow lithospheric mantle with little or no interaction and were trapped as andesitic silicate melt inclusions. Similar results were obtained from the Type-2 mantle xenoliths, crystallized as cumulates from underplating of mafic alkaline magmas in the upper mantle near the Moho, that contain abundant silicate melt inclusions. The parental melt of the host cumulates was a basanite formed by low degree (~2%) partial melting of a garnet peridotite source. The compositional trend of the silicate melt inclusions show that the parental melt evolved by major clinopyroxene and minor olivine crystallization followed by the appearance of amphibole simultaneously with significant resorption of the earlier clinopyroxene and olivine. The residual melt was highly enriched in the most

incompatible major and trace elements. This type of melt is likely to infiltrate and react with surrounding mantle peridotite as a metasomatic agent. It might also form high-pressure pegmatite-like bodies in the mantle that might be the source of the amphibole and sanidine megacrysts also found in the alkali basalts of the NGVF.

In the BBHVF unusual Type-2 quartz-bearing orthopyroxene-rich websterite xenolith has been found that contain primary and secondary silicate melt inclusions enclosed in ortho- and clinopyroxenes. The melt inclusions are silica rich and show enriched LREE and LILE composition with negative Nb, Ta and Sr, as well as positive Pb anomalies. The xenolith is interpreted to represent a fragment of an orthopyroxene-rich body that crystallized in the upper mantle from a hybrid melt that formed by interaction of mantle peridotite with a quartz-saturated silicate melt that was released from a subducted oceanic slab. Evidence for the percolation of silica enriched melts has been also found in the Type-1 xenoliths containing either isolated fluid inclusions or coexisting silicate melt and fluid inclusion from other sites of the same volcanic field. Petrographic and geochemical results indicate that coexisting carbonic fluid inclusions and silicate melt inclusions are trapped as primary inclusions in clinopyroxene rims and as secondary inclusions along healed fractures in orthopyroxene suggesting that these inclusions were entrapped from a silicate melt saturated in volatiles at mantle P-T conditions. The entrapment of silicate melt inclusions happened after partial melting and subsequent crystallization of clinopyroxenes, most probably due to an interaction between hot volatile-saturated evolved melt and mantle wall-rock.

TRANSPRESSIONAL DUCTILE SHEARING AND PALEOFLUID CIRCULATION ALONG THE OBLIQUE CONVERGENT MARGIN OF EASTERN GONDWANA: FLUID INCLUSION DATA FROM THE NORTH-WESTERN MARGIN OF THE LUT BLOCK, CENTRAL IRAN

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Introduction

Definition of the geological history of the pre-Tertiary crystalline basement in central Iran has been so far hampered by lack of firm constraints on its polyphase tectono-metamorphic evolution.

The Zeber-Kuh-Saharangi metamorphic zone (Fig. 1) is exposed at the north-western margin of the Lut block in Central Iran and is considered to be part of the Pan-African (Neoproterozoic) active margin during the terminal assembly of the Eastern Gondwana (Ramezani, Tucker, 2003). It consists of the Precambrian and Lower Paleozoic rock sequences arranged to form a major NE-SW trending high strain zone made of orthogneisses, garnet-bearing mica schists and low-grade phyllonites. The Mesozoic-Cenozoic sediments and volcanics unconformably cover the metamorphic domain.

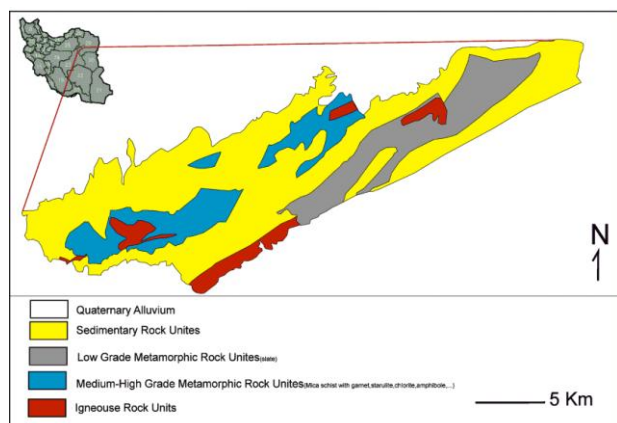


Figure 1. Simplified geological sketch of the studied area.

In this contribution we reconstruct the structural architecture of the Pre-Cambrian phyllites forming the axial zone of the Saharangi Range as controlled by a major ductile-to-brittle episode of left-lateral transpressional tectonics.

Fluid inclusion study

Quartz vein arrays incrementally developed during the progressive left-lateral shearing. The quartz veins form a sub-vertical giant, NNE-SSW striking array. In the high shear strain domains, the veins are transposed into parallelism with the NE-SW mylonitic foliation and axial-planar crenulation cleavage.

Quartz crystals contain very abundant fluid

inclusions that occur isolated (rare), along grain boundaries and along intra- and inter-grain planes.

Fluid inclusion study will help to reconstruct the deformation history and the paleo-fluid circulation during oblique convergence at the active margin of East Gondwana.

Sample petrography and preliminary fluid inclusion microthermometry were carried out from two dm-thick quartz veins (784s and 784b), sampled within a m-wide left-lateral shear zone. Sample 784s corresponds to a shear vein, while sample 784b is from a tension-gash like array. Both veins show the presence of an early fluid $\text{H}_2\text{O}-\text{CO}_2 \pm$ other gases as indicated from the high (around -58°C) TmCO_2 value, trapped under conditions of immiscibility. The inclusions contain high (784b sample) to very high (784s sample) X_{CO_2} (Diamond, 2001). At room temperature they all occur as two phase inclusions, V-rich inclusions; during microthermometric freezing runs a small bubble of carbonic vapor appears and disappears on heating (Fig. 2).

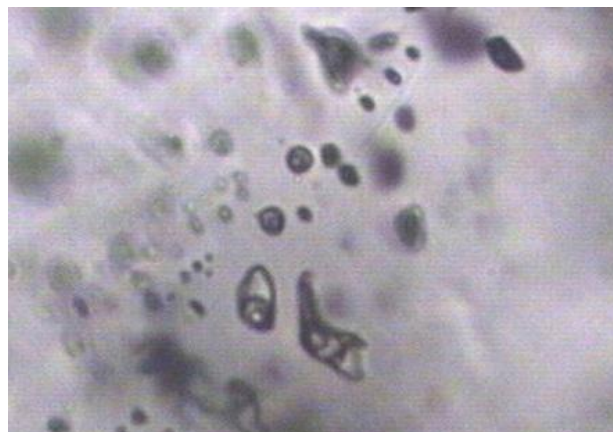


Figure 2. Fluid inclusions containing $\text{H}_2\text{O}+\text{CO}_{2\text{L}}+\text{CO}_{2\text{V}}$ at 8°C , they homogenize at -0.5°C .

The homogenization temperature values (always to carbonic liquid) group are around $+7^\circ\text{C}$ for 784s and around -1°C and $+11^\circ\text{C}$ for 784b samples (Fig. 3) indicating a quite dense fluid, from $0.76-0.89 \text{ g/cm}^3$ to $0.90-0.97 \text{ g/cm}^3$ for sample 784s and 784b, respectively (Bakker, 2003).

In 784b samples, a later saline aqueous fluid has been trapped as intragrain planes. Fluid inclusions are all L-rich, some show a very small cubic crystal which melt at about 200°C (Fig. 4).

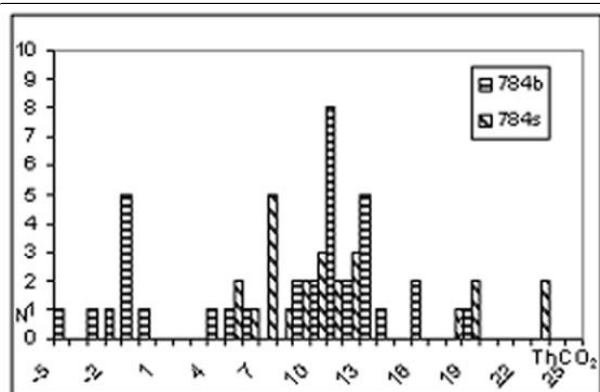


Figure 3. Th of the carbonic fraction.

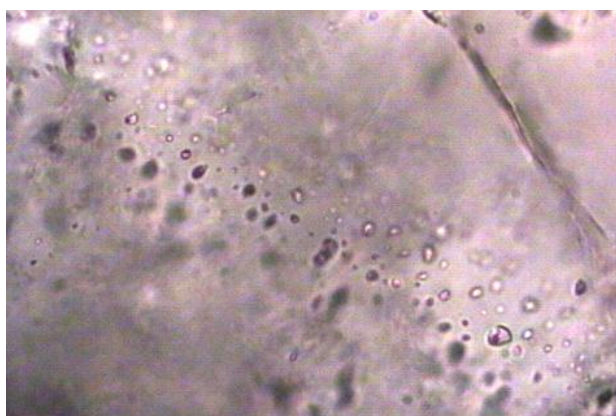


Figure 4. Plane of late L-rich fluid inclusions; inclusion on the right (7 μ long) contains a small cubic mineral.

Such fluid seems to be characterized by a salinity up to 30 wt.% NaCl equivalent (Sterner et al., 1988); it possibly contains also Ca^{++} (low eutectic temperature) and no carbonic component. First microthermometric data indicate total homogenization temperature of about 200°C for this later fluid and a possible hydrothermal origin.

Conclusions

Collectively, these preliminary data suggest control exerted by the strike-slip shearing onto the regional hydrothermal circulation, and advocate an intimate linkage between arc magmatism and strike-slip tectonics during the final assembly of the Gondwana supercontinent in central Iran.

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FORMATION OF HYDROSILICATE LIQUIDS IN THE SYSTEM $\text{Na}_2\text{O} (\pm \text{K}_2\text{O}) - \text{SiO}_2 (\pm \text{Al}_2\text{O}_3) - \text{H}_2\text{O}$ AND THEIR ABILITY TO CONCENTRATE SOME ELEMENTS (ON THE BASIS OF EXPERIMENTAL DATA)

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Introduction

The study of root parts of quartz crystals from miaroles and mineral assemblages surrounding miaroles (near miarolitic assemblages) of granitic pegmatites revealed inclusions of unusual media. Those inclusions represent magmatic-hydrothermal transition in pegmatitic crystallization. At room temperature inclusions consist of aggregate silicate minerals, which after homogenization quench into glass. Such behavior is similar to typical melt inclusions. However, in contrast to inclusions of silicate melts those found in miarolitic and near-miarolitic quartz homogenize at temperatures down to 500°C. Besides unusually low temperatures the inclusions have very high water content ~15 wt% (Smirnov et al., 2003; Peretyazhko et al., 2004; Thomas et al., 2006). Concentrations of H_2O in these inclusions exceed its solidus solubility in granitic melts and hereby we will call those media hydrosilicate liquids (HSL). It is important to note that inclusions with HSL sometimes have very high concentrations of Cs, Ta, Nb, Be, B and F. This suggests that they can play important role at late and postmagmatic ore formation.

Liquids with similar $\text{SiO}_2/\text{H}_2\text{O}$ ratios easily form in hydrothermal experiments when quartz-feldspar compositions react to aqueous solutions, containing NaOH, Na_3BO_3 , Na_2CO_3 , Na_2SiO_3 (Butuzov, Bryatov, 1957; Anfilogov et al., 1972; Valyashko, Kravchuk, 1979; Smirnov et al., 2005) at temperatures 300-600°C and pressures up to 2 kbar. Smirnov et al. (2005) showed that vitreous phases that were formed on quench of the HSL in the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ have properties of typical ultradisperse colloidal solutions, such as reversible dehydration and ion exchange.

Experimental results

This study was aimed to understand how HSL forms under hydrothermal conditions in the systems $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ and rare-element granite- H_2O at 600°C and 1.5 kbar and their ability to concentrate some elements, which are important at postmagmatic ore formation. Our experiments showed that formation of HSL occurs through dissolution of SiO_2 (and Al_2O_3 in granitic charge) in alkaline supercritical aqueous fluid and following polymerization of silicate and aluminosilicate species. Polymerization results in formation of HSL

droplets in the aqueous fluid and their deposition on the fluid-charge interface. Quench experiments showed that dissolution-polymerization stage almost completely finishes in 3 days. When HSL was formed major amounts of Si and Na in the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ and Si, Al, Na and K in the system granite- H_2O are concentrated in HSL. Polymerization continues within the deposited HSL. This results in increase of its density and decrease of water content down to 12-15 wt.%.

Addition of F, Ta, Sn, Zn, Mo and W to the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ resulted in their distribution between supercritical alkaline aqueous fluid and HSL. Fluorine, Ta, Sn and Zn are almost completely concentrated by HSL. Concentrations of Sn and Zn exceed those in aqueous fluid by 20 and 50 times. W and Mo are concentrated in HSL in a lesser degree. Their concentrations in HSL exceed those in aqueous fluid by 5.1 and 3.6 times respectively. Experiments with Ta, which behaves similarly to Sn and Zn showed strongly inhomogeneous distribution of Ta concentrations within HSL. Boundaries between enriched and depleted domains of HSL quenched products are frequently sharp, showing no evidence of diffusion smoothing between them after 9 days experiment. Distribution of Ta remains inhomogeneous even after 18 days experiments. This suggests that diffusion coefficients for Ta in HSL are much higher than in ionic aqueous solutions, and in our experiments equilibrium was not reached.

If experimental products were cooled at 50°/hr, skeletal crystals of quartz and albite grew within HSL. Addition of F resulted in formation of NaF skeletal crystals. Crystal growth in HSL has much in common with crystal growth in gels (Henisch, 1996). It is important to note that cooling lead to nucleation of second generation of HSL droplets and their deposition on the surface of earlier formed HSL. The newly formed HSL at room temperature transforms into low-viscosity plastic substance, with concentration of H_2O about 50 wt.%. Thus with decreasing T and P hydrothermal HSL becomes more enriched in H_2O , while Al, Si and alkalis are deposited in the form of silicate minerals and quartz. After long exposure at room temperature the system HSL + aqueous solution becomes unstable. HSL breaks apart with formation of zeolites and kaolinite.

Conclusions

The HSL similar in $\text{SiO}_2/\text{H}_2\text{O}$ ratio to inclusions in miarolitic and near-miarolitic quartz of some granitic pegmatites can be formed in nature when alkaline aqueous fluid reacts with silicate rock-forming minerals or even the latest portions of magmatic silicate melts. Some elements, which play important role in postmagmatic mineral and ore formation, can be effectively transported by hydrosilicate liquids. Thus, those liquids can also be important mineral-forming media in the typically hydrothermal processes. It is suggested that the transported elements can be extracted from HSL at geochemical barriers through the ion-exchange mechanism. Based on our data, we can also suspect the smectites and zeolites, which often fill voids in various hydrothermal veins and pegmatites were originated from the HSL low-temperature ageing process rather than from the low-temperature hydrolysis of the earlier formed silicate minerals.

Acknowledgements

This study was supported by RFBR grant 09-05-01153 and by the CODES Initiative Grant P2.N1 "Phase and chemical composition of high-temperature hydrothermal systems undergoing interaction between silicate rocks/magmas and aqueous fluid", and the Australian Research Council Professorial Fellowship and Discovery Grant to V. Kamenetsky.

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COMPOSITION OF MELT AND FLUID INCLUSIONS IN SPINEL OF PERIDOTITE XENOLITHS FROM AVACHA VOLCANO (KAMCHATKA, RUSSIA)

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Introduction

The main purpose of this paper is a reconstruction of different transformation stages for primary peridotites. In our opinion, the term “primary peridotites” means the initial mineral composition of peridotites which was prior to their recrystallization affected by the fluids. Our research is based on the study of melt and fluid inclusions in spinel of various harzburgite xenoliths from the Avacha volcano (Kamchatka, Russia).

Geological background and sample descriptions

The Avacha volcano (53°15'N, 158°51'E) is one of the most active stratovolcanoes in southern Kamchatka. The Avacha height is 2743 m above sea level (Active volcanoes..., 1991). The volcanic activity started in the late Pleistocene and is still going.

The Avacha volcanic rocks are represented by basalts, andesite-basalts, andesites, containing peridotite xenoliths. Spinel harzburgites are dominant type among the Avacha ultramafic xenoliths. Lherzolites, wehrlites, websterites and clinopyroxenites occur rarely and represented derivatives of primary harzburgites. Detailed petrography of xenoliths is given by Koloskov (1999).

We studied harzburgite samples affected by processes of recrystallization and melting in different degrees and samples of primary harzburgites. Most peridotite xenoliths contain spinel as omnipresent mineral which chemical composition varies broadly. Composition of spinel and presence of different types of inclusions in this mineral reflect the evolution stages of initial rocks.

Changing of spinel chemistry and phase composition of spinel-hosted inclusions are able to identify the sequence and intensity of transformation processes for peridotites.

Fluid and melt inclusions in spinel

Three type of spinel were subdivided in chemical features and presence of inclusions.

The first type-I is “primary” spinel, occurs as small crystals (up to 5-10 µm) in olivine grains of harzburgites. This spinel has the highest magnesian number $Mg\# = Mg/(Mg+Fe^{2+}) = 0.69-0.71$. It also contains high of Al_2O_3 (26.2-27.1 wt.%) and relatively low Cr_2O_3 (37.5-38.5 wt.%, Table 1). This spinel does not contain inclusions.

Spinel of the second type (II) has lower magnesian number $Mg\# = 0.61-0.64$ and contains lower Al_2O_3 (18-19 wt.%) and higher Cr_2O_3 (45.3-47.2 wt.%) than “primary” spinel (Table 1). This spinel forms large grains and contain abundant crystal-fluid inclusions (Fig. 1).

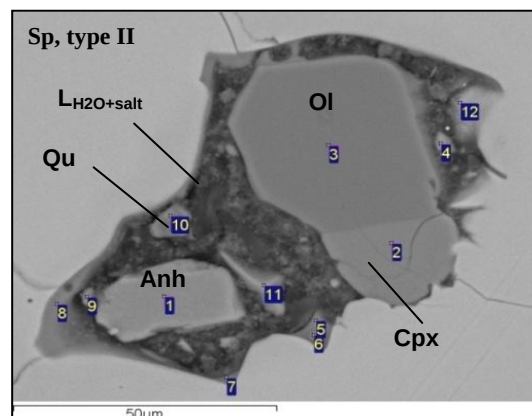


Figure 1. BSE image of primary combined crystal-fluid inclusions in recrystallized type-II spinel. Qu – quartz, Anh – anhydrite, Ol – olivine, Cpx – clinopyroxene, L – fluid inclusion.

The phase composition of these inclusions is crystal phases and carbonate-water-salt fluid separation. The trapped phases are represented by orthopyroxene, clinopyroxene, olivine and amphibole. The daughter phases are calcite, albite, quartz and anhydrite.

Table 1. Chemical composition (wt.%) of different type spinels and glasses of primary melt inclusions in the type-III spinel from peridotite xenoliths of the Avacha volcano.

	Type I	Type II	Type III	Incl. *	Incl. heated
SiO ₂	n.d.	n.d.	n.d.	63.92	51.42
TiO ₂	0.03	0.06	0.05	0.10	0.41
Al ₂ O ₃	27.07	18.90	13.06	15.25	15.80
Cr ₂ O ₃	37.53	47.24	55.41	0.73	1.22
FeO	18.07	19.47	17.86	0.47	1.62
MgO	15.83	13.62	12.62	0.10	3.86
MnO	0.13	0.25	0.05	0.01	n.d.
CaO	0.00	0.02	0.00	3.44	8.60
NiO	0.25	0.15	0.08	n.d.	n.d.
Na ₂ O	n.d.	n.d.	n.d.	3.30	9.71
K ₂ O	n.d.	n.d.	n.d.	0.34	0.34
SO ₃	n.d.	n.d.	n.d.	0.03	n.d.
Cl	n.d.	n.d.	n.d.	0.01	0.04
Total	98.92	99.71	99.67	87.70	93.37

Note: Incl.* - unheated primary inclusion in type III spinel. Incl. heated – primary inclusion in type III spinel heated at 1050°C, n.d. – not detected.

The third type-III of spinel has the highest contents of Cr_2O_3 – 46.2-55.4 wt.% and lowest contents of Al_2O_3 – 13.6-19.2 wt.% (Table 1). This spinel is represented by the large anhedral grains with primary melt and fluid inclusions and seems to crystallize directly from melt.

All melt inclusions in this spinel we can subdivide into three types: normal, anomalous and combined melt inclusions. The phase composition of normal inclusions is glass + fluid bubble + daughter amphibole $\pm$ sulfide globule (Fig. 2).

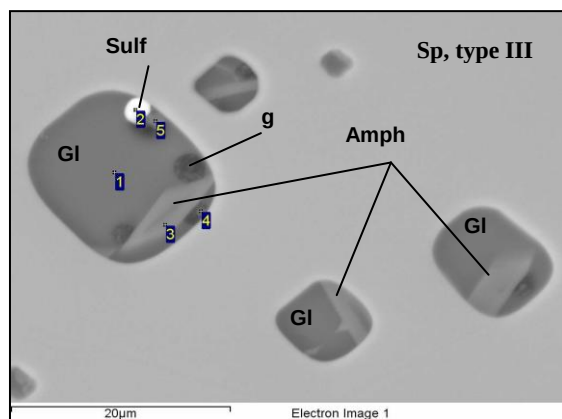


Figure 2. BSE image of primary normal melt inclusions in spinel. Gl – glass, g – gas bubble, Amph – amphibole, Sulf – sulfide.

In primary anomalous melt inclusions the fluid occupies most part of their volume. The small glass edgings are to be observed around fluid (Fig. 3). The sizes of such inclusions vary from 20 to 100 μm . The following phases were identified inside fluid isolation: calcite, anorthite, albite, quartz, fluorite, Cl-enriched phase, anhydrite.

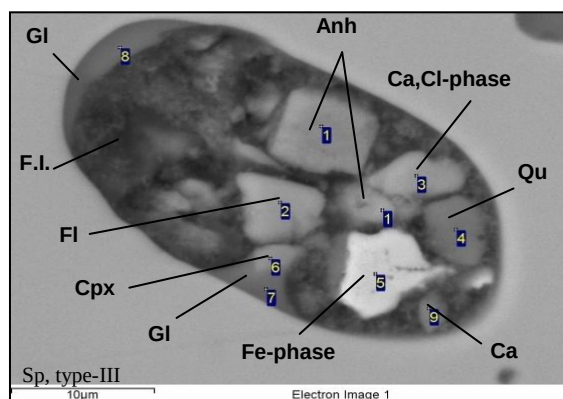


Figure 3. BSE image of primary anomalous melt inclusion in spinel. Gl – glass, F.I. – fluid isolation, Cpx – clinopyroxene, Ca – calcite, Fl – fluorite, Qu – quartz, Anh – anhydrite.

The phase composition of combined melt inclusions is glass + fluid + trapped crystals (orthopyroxene, amphibole). The fluid isolations of these inclusions also contain quartz and calcite.

Thermometry

A lot of individual type-III spinel grains with

primary melt inclusions were selected from several samples of peridotite xenoliths for thermometric experiments. These spinels were heated in a heating stage by “blind” method at three different temperatures. The grains were quenched rapidly after heating. The relicts of daughter amphibole were observed in melt inclusions heated at 1000°C. Phase composition of melt inclusions heated at 1050°C is glass + fluid. The decay structures were fixed in spinel heated at 1100°C (overheated grains). Thus, the crystallization of “magmatic” spinel and trapping of melt inclusions occurred at temperatures near 1050°C.

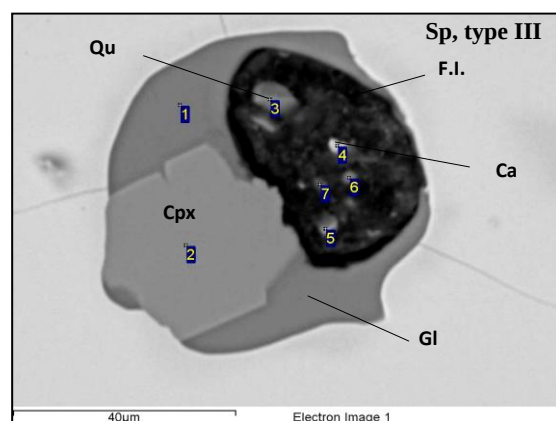


Figure 4. BSE image of primary combined melt inclusion in spinel. Gl – glass, F.I. – fluid isolation, Cpx – clinopyroxene, Ca – calcite, Qu – quartz.

Discussion

Metasomatism involving Si, Al, Ca, H_2O and salt-enriched fluids led to the appearance of local recrystallization zones in primary peridotites.

Recrystallization of the spinel began in interstitials between olivine grains. The secondary orthopyroxene forms due to olivine expense. First grains of clinopyroxene and amphibole without inclusions also appear. Spinel grains become larger during recrystallization and the crystal-fluid inclusions are trapping (Fig. 2). The further metasomatism resulted to appearance of local partial melting zones. It is indicated by formation of orthopyroxene, spinel and interstitial glasses along the grain edges. Moreover, thin edges of glass are generated around the fluid isolation of primary anomalous inclusions in spinel (Fig. 3). The process of intensive metasomatism resulted to active melting of peridotites, what was favorable for trapping of melt inclusions by spinel.

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T-P-X FORMATION CONDITIONS OF STOCKWORK-TYPE AURIFEROUS GIANT DEPOSITS: MURUNTAU (UZBEKISTAN) AND VASILKOVSKOE (KAZAKHSTAN)

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Introduction

Reasoning from the newest mineral processing technology, huge auriferous stockworks correspond to the cost-effective type of ore concentration (Rafailovich, 2009). The gold-sulphide-quartziferous Vasilkovskoe field is related to this type. This gold field with production of more than 380 tons Au is located in northern Kazakhstan, 25 km away from Kokchetav. This field is confined to the igneous rocks, which are placed in the strongly faulted metamorphic complex from Pre-Cambrian to Palaeozoic age. The second field, which is related to auriferous stockwork type is the Muruntau gold field with production of about 4000 tons. It is located in western Uzbekistan within the Navoy region. The Muruntau field is confined to the turbidite host rocks.

The main purpose of the work is to identify T-P-X parameters of ore-forming and barren fluids, which participate in the stockwork formation, and to compare these two giant deposits.

Fluid inclusion characteristics

In the Muruntau gold field, representative samples of primary fluid inclusions hosted in quartz were selected for investigation of ore vein-forming fluids. Secondary fluid inclusions, hosted in carbonates and quartz, were selected to study the conditions, under which veinlets were formed at the last stage of the Muruntau formation.

The common feature of the Vasilkovskoe gold field is simultaneous presence of white and grey quartz (Rafailovich, Los, 2007). Grey quartz considered to be ore quartz, as it is associated with ore minerals and high gold content, and was formed at the ore stage of the Vasilkovskoe formation. Fluid inclusions in grey (ore) quartz were selected to investigate ore vein-forming fluids. Fluid inclusions hosted in white quartz were selected to study the fluids at the last stage of stockwork formation.

Fluid inclusions hosted in quartz of the Muruntau and Vasilkovskoe gold stockworks have similar features. Therefore, the following classification combines fluid inclusions from both gold fields.

Six main types of fluid inclusions have been identified at room temperature on the basis of phases, phase proportions, composition and genetic variety.

Type I: One-phase, liquid rich $(\text{CO}_2)_L$ fluid inclusions hosted by “ore” quartz in the Muruntau gold field and one-phase, liquid rich $(\text{CO}_2 \pm \text{CH}_4 \pm \text{N}_2 \pm \text{H}_2\text{S})_L$ in grey quartz from the Vasilkovskoe. Inclusions range in diameter from 3 to 12 μm .

Type II: Two-phase, vapor rich $(\text{H}_2\text{O})_L + (\text{CO}_2 \pm \text{CH}_4)_V$ fluid inclusions hosted by “ore” quartz in Muruntau gold field and two-phase, vapor rich $(\text{H}_2\text{O})_L + (\text{CO}_2 \pm \text{CH}_4 \pm \text{N}_2 \pm \text{H}_2\text{S})_V$ in “ore” grey quartz from the Vasilkovskoe. Inclusions vary in the $\text{CO}_2/\text{H}_2\text{O}$ ratio of 50/50 to 90/10. Sizes of inclusions are from 3 to 10 μm .

Type III: Two-phase, liquid rich $(\text{CO}_2)_V + (\text{H}_2\text{O})_L$ fluid inclusions hosted by “ore” quartz from the Muruntau and Vasilkovskoe. Inclusions vary in the $\text{CO}_2/\text{H}_2\text{O}$ ratio of 10/90 to 30/70. Inclusions range in size from 2 to 10 μm .

Type IV: three-phase, carbon-dioxide $(\text{H}_2\text{O})_L + (\text{CO}_2)_L + (\text{CO}_2 \pm \text{CH}_4)_V$ fluid inclusions hosted in “ore” quartz in the Muruntau gold field and three-phase, carbon-dioxide $(\text{H}_2\text{O})_L + (\text{CO}_2)_L + (\text{CO}_2 \pm \text{CH}_4 \pm \text{N}_2 \pm \text{H}_2\text{S})_V$ in “ore” grey quartz from the Vasilkovskoe field. Inclusions range in size from 3 to 15 μm .

Type V: Multiphase, liquid rich $(\text{CO}_2)_V + (\text{H}_2\text{O})_L + (\text{one or more daughter crystals}) + (\text{xenomorphic organic matter})$ fluid inclusions hosted by “ore” quartz from the Muruntau and Vasilkovskoe. The daughter crystals were identified as chlorides on the basis of habit and the eutectic temperature of liquid phase. Xenomorphic organic matter was determined as graphite, the particles of which are also present in the host mineral. Inclusions range in diameter from 3 to 8 μm .

Type VI: Two-phase, liquid rich $(\text{CO}_2)_V + (\text{H}_2\text{O})_L$ secondary fluid inclusions hosted in quartz from the Muruntau and in white quartz, calcite and fluorite in the Vasilkovskoe gold field. Inclusions vary in $\text{CO}_2/\text{H}_2\text{O}$ ratio of 10/90 to 30/70; sizes are from 2 to 7 μm .

Results

Muruntau gold stockwork

Two-phase fluid inclusions of type II and IV either homogenized into liquid or tended to the critical point. The Type III inclusions are homogenized into vapor. Homogenization temperatures show a wide spread ranging from 140°C to 365°C (n=145) (Table 1). Final melting

temperature of solid CO₂ ranges from -57°C to -64°C (n = 340) for depths (from 0 to 633 m). These temperatures essentially vary within each sample. The Type I, II and IV inclusions have CO₂ triple point below -56.6°C, indicating the presence of significant amounts of CH₄, which has been confirmed by Raman spectroscopic analyses (n=16). The Type III fluid inclusions have eutectic temperatures ranged from -24.3°C to -26.4°C, indicating the presence of chlorides Na-K-Mg-Fe-rich in aqueous phase. Final melting temperature of ice ranged from -1°C to -15°C. Salinities vary from 2 to 19 wt percent NaCl equiv (n=30). The Type V fluid inclusions have salinities of about 30-40 wt.% NaCl equiv. Fluid densities of the Type I, II and IV were calculated using the CO₂ partial homogenization temperatures (from -5 to + 5.5°C) (n=310) according to (Ely et al., 1987). Bulk densities were from 0.71 to 0.96 g/cm³. Estimated trapping pressures for fluid inclusions, which were trapped at the ore stage of formation show a range from 0.87 to 2 kbar in depth. The Type VI secondary fluid inclusions are homogenized into liquid at the temperature from 100 to 200°C.

Table 1. Comparison of ore fluid characteristics of the Muruntau and Vasilkovskoe gold fields.

	Muruntau	Vasilkovskoe
Au, t	4000	380
ore-bearing fluid characteristics		
TmCO ₂ , °C	-57 to -64	-56.6 to -67
Teut, °C	-24.3 to -26.4	-20.7 to -38
Salinity, wt.% NaCl equiv.	2 to 19 (to 30-40)	2 to 22.5 (to 30 - 40)
Density, g/cm ³	0.71 to 0.96	0.6 to 1.12
Th, °C	160 to 365	150 to 550
P, kbar	0.87 to 2	0.4 to 2.5

Vasilkovskoe gold field

Two-phase fluid inclusions of the type II and IV either homogenized into liquid or tended to the critical point. The Type III inclusions homogenized to vapor. Homogenization temperatures range from 130°C to 550°C (n=600). Triple point for CO₂ is from -56.6°C to -67°C (n=400) for depths from 400 to 765 m. The Type I, II and IV inclusions have CO₂ final melting temperature below -56.6°C, indicating the presence of significant amounts of CH₄, and other gases, which have lower triple point. Raman analyses of individual fluid inclusions (n=73) show presence CO₂, CH₄ and small amounts of N₂ and H₂S in vapor phase of several inclusions. The Type III fluid inclusions have eutectic

temperatures ranged from -20.7°C to -38°C, indicating the presence of Na-K-Mg-Fe chlorides in aqueous phase. Final melting temperature of ice ranged from -1°C to -20°C. Salinities vary from 2 to 22.5 wt.% NaCl equiv. (n=300). The Type V fluid inclusions have salinities of about 30-40 wt.% NaCl equiv. Fluid densities of the Type I, II and IV were calculated using the CO₂ partial homogenization temperatures (from -40 to + 30°C) (n=400). Bulk densities were from 0.6 to 1.12 g/cm³. Estimated trapping pressures for fluid inclusions, which were trapped at the ore stage of formation vary from 0.44 to 2.5 kbar in depth.

The Type VI fluid inclusions trapped by white quartz, calcite and fluorite, homogenized into liquid at the temperature range from 125°C to 215°C. Eutectic temperatures ranged from -42°C to -49°C, indicating the presence of Na-K-Mg-Fe-Ca chlorides in aqueous phase. Final melting temperature of ice varies from -2°C to -12°C. Salinity is from 4.5 to 16.5 wt.% NaCl equiv. (n=100). It should be noted that white quartz does not appear to host the type V multiphase fluid inclusions with salinities of about 30-40 wt.% NaCl equiv.

Conclusions

Fluids responsible for gold mineralization in Au-bearing quartz veins at the Muruntau and Vasilkovskoe stockworks are in the CO₂-CH₄-H₂O-NaCl (±N₂±H₂S±KCl±FeCl, etc.) system, whereas those of barren veins of post-mineral stage of formation are characterized by CO₂-H₂O-NaCl (±KCl±MgCl±FeCl±CaCl, etc.) system. Gold mineralization occurred at temperatures of 300°C to 500°C, pressures of 0.4 to 2.5 kbar. Fluid, participating in the formation of ore zones of stockwork, is characterized by salinity, equal to 2 - 20 wt.% NaCl equiv. Some portions of the fluid are richer in salinity (30-40 wt.% NaCl equiv.). Fluid inclusions from white quartz in barren veins were trapped under low temperature and pressure. Our results allow the obtained T-P-X fluid properties to be used as prospecting evaluation features for gold stockwork fields.

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FLUID IMMISCIBILITY AND GOLD MINERALIZATION, GURHAR PAHAR GOLD PROSPECT, SIDHI DISTRICT, M.P., INDIA

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Introduction

The Gurhar Pahar gold prospect forming a part of the Son Valley greenstone belt is important gold prospect in the area situated in the Sidhi district of M.P. Fluid inclusion systematic of the samples collected from mineralized and non-mineralized zones intersected in bore holes, was carried out to understand the physico-chemical process involved in the ore genesis and also to create a database related to fluid characteristics associated with gold mineralization.

The mode of mineralization is of mainly two types, viz. (a) quartz/quartz-carbonate $\pm$ sulphide veins, and (b) disseminated specks of galena, pyrite and arsenopyrite rich bands of sheared phyllonite or sheared quartzite. The mineralized quartz veins are white to smoky grey in colour with or without foliation parallel veins of sulphides (<1 cm to 2 cm thick).

Fluid inclusion petrography

Detailed fluid inclusion petrography (FIP) reveals the presence of the five types of primary inclusion populations: Type-I - multiphase solid + liquid + vapour S+L+V (Fig. 1); Type-II - immiscible aqueous-carbonic inclusion $H_2O + CO_2(L) + CO_2(V)$, Type-III - immiscible aqueous-carbonic inclusion $H_2O + CO_2(L)$ - without $CO_2(V)$; Type-IV - aqueous biphasic inclusion $H_2O + NaCl$; and Type-V - aqueous-carbonic monophasic inclusion $H_2O(L)$ or $CO_2(L)$.



Figure 1. Multiphase inclusion in sample-26, GDB-1 Bore Hole, Mineralized zone, Gurhar Pahar.

FIP of the samples from mineralized zones

indicate wide range of variations (0.42 to 1.0) in the liquid vapour-ratio (degree of fill) of the primary biphasic inclusions or group of synchronous inclusions (GSI), indicating heterogeneous trapping of the fluid. Furthermore, presence of opaque as trapped/daughter phases in the aqueous carbonic biphasic and irregular shaped large carbonic monophasic inclusions, indicate that mineralization was introduced by carbonic fluid. Daughter phases are absent in the aqueous inclusions. Based on these observations, it is possible to conclude that carbonic-aqueous immiscibility played an important role in the mineralization related fluid processes. Fluid immiscibility causes volatile species such as CO_2 and H_2S to be lost from liquid, thus triggering ore deposition by increasing the fluid pH and decreasing the availability of complexing ligands (Garba, Akande, 1992). A commonly used criterion for fluid immiscibility is the coexistence cogenetic and coeval inclusions that correspond to two immiscible phases (Ramboz et al., 1982).

Monophasic CO_2 -rich inclusions commonly coexist with aqueous two phase inclusions either in groups, or along the same healed fracture. This phenomenon is generally regarded as convincing evidence of fluid immiscibility (Roedder, 1984). At room temperature, the inclusions range with increasing CO_2 content from two-phase aqueous, through three-phase in which the CO_2 homogenizing to vapour, to three phase with CO_2 homogenizing to liquid. This wide range of inclusion compositions is interpreted as evidence for fluid immiscibility, where most inclusions being accidental mixtures of two end-members immiscible fluids (Craw et al., 1993).

Given that the solubility of the most metals increases with the chlorine content in solutions (Barnes, 1979), the highly saline fluids related to mineralization have much stronger capabilities to carry metals as chloride complexes than the dilute fluids related to barren veining.

There are three most common processes in gold deposition:

- I. Mixing of gold bearing fluid with cooler and more dilute fluid like meteoric water has been involved in some deposits (Craw, Koons, 1989).
- II. Boiling of rising hydrothermal fluid is commonly responsible for gold precipitation as epithermal gold deposits (Haneley, 1984).

III. Fluid immiscibility has been reported in many mesothermal deposits (Naden, Shepherd, 1989) and it is quite possible that this process may have operated in the present area also.

The presence of methane in some samples is very significant as it facilitates fluid immiscibility because of its addition to pure H₂O that a separate gas and liquid phase can coexist, if CH₄ is present (Goldstein, Reynold, 1994). Carbonic fluids are poorly miscible with aqueous fluids, particularly at high temperature and low pressure, so that the presence of CO₂ can induce immiscibility both within the magmatic volatile phase and in hydrothermal systems. Because gold is more volatile in vapour phase than coexisting liquids, the presence of CO₂ may directly aid the process of metallogenesis by inducing phase separation. Various mechanisms have been proposed to explain transport and deposition of the gold (Shenberger, Barnes, 1989; Powel et al., 1991). In many environments, sulphide complexes are the most effective agent for gold transport. This might be the case in the Gurhar Pahar gold prospect.

Conclusions

Fluid immiscibility has been reported in many mesothermal deposits and it is quite possible that this process may have operated in the present area also. Furthermore, the close association of gold with sulphide minerals like pyrite, arsenopyrite, chalcopyrite, galena, pyrrhotite, sphalerite and others in the area indicates that gold might have transported as sulphur complex.

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EVOLUTION OF T-P-CONDITIONS DURING THE CRYSTALLIZATION OF YUSTYD GRANITIC PLUTON (GORNÝ ALTAI) USING DATA ON MELT AND FLUID INCLUSIONS

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Introduction

The Yustyd granitic pluton (south-east of Gorný Altai) was intruded into Middle-Upper Devonian terrigenous sandstone-aleurolite succession of the Yustyd formation. Metasomatic zoning is well exposed in the north-west part of the pluton. Internal zone is represented by unaltered biotite-bearing leucogranite with large (4-6 cm) microcline phenocrysts. Transitional zone is composed of medium-grained leucocratic granite, slightly altered by metasomatic process (~10-15% in volume). External zone is represented by intensively altered (up to 40% in volume) biotite-bearing leucogranite in a result of postmagmatic greisenization.

Thermobarogeochemical study was aimed at evaluation of TP-condition of early magmatic, late magmatic and postmagmatic stages of the pluton crystallization. For this purpose melt and fluid inclusions of granites from the three zones listed above were studied. Homogenization temperature (T_{hom}) was measured using the Leica stage accurate to $\pm 10^\circ\text{C}$.

Melt and fluid inclusions

Granite porphyry is composed of large deformed phenocrysts of microcline and not deformed medium grained matrix of leucogranitic composition. Deformation manifests itself in phenocryst jointing and cataclasis exposed along fractures and periphery of phenocrysts, and in a destruction of the great majority of melt inclusions and complete destruction of all fluid inclusions. Just few small (1-6 μm) melt inclusions are preserved. They are composed of silicate phases and visible fluid phase evidencing for high fluid saturation of the original melt. Silicate phases begin to melt at 900-920 $^\circ\text{C}$, and gas bubble separates at 990 $^\circ\text{C}$. Further heating almost at once led to complete homogenization, or to exposure of melt inclusion. Consequently microcline crystallized at a temperature of 990-995 $^\circ\text{C}$.

Primary fluid inclusions hosted in microcline phenocrysts are completely destroyed. But there are numerous chains of secondary fluid inclusions represented by high concentrated salt-aqueous solutions, distributed along fractures and intersertal space.

Quartz grains in matrix of granite porphyry are not deformed, and host primary syngenetic melt

and fluid inclusions evidencing for quartz crystallization at the stage of melt degassing. Fluid phase in melt inclusions is not visible. Homogenization temperature is in the range of 970-980 $^\circ\text{C}$. Primary fluid inclusions hosted in quartz are analogous to secondary inclusions hosted in phenocrysts, and are composed of salts (NaCl, KCl and not identified phases), high concentrated (up to 75-85 wt.% in the NaCl equivalent) solution, and gas bubble. These inclusions were trapped at pressure of 2.3-2.5 kbar.

Intensive phenocryst deformation, undeformed minerals from matrix, and different grade of preservation of fluid and melt inclusions from phenocrysts and matrix as well evidence for protoclastic origin of granite porphyry. Phenocrysts crystallized from fluid-saturated melt in magmatic camera before melt degassing (1 stage). Medium-grained granites crystallized from residual liquid at pressure about of 2.3-2.5 kbar because of significant magma elevation (stage 2) resulting to melt degassing and phenocryst protoclast. There are traces of fluid migration to intersertal space in quartz grains. Final stage of quartz crystallization was attended with crystallization of biotite, minor hornblende, and ore minerals, which proceeded with the participation of mentioned fluid.

Quartz from medium-grained granite of transitional zone hosts numerous well preserved primary melt and fluid inclusions. Fluid inclusions (FI) are represented by two generations: FI₁ - are syngenetic with melt inclusions, FI₂ - were trapped later. Melt inclusions from medium-grained granite and from granite porphyry matrix are similar. Their T_{hom} is in a range of 970-975 $^\circ\text{C}$. The FI₁ are composed of salts (NaCl, KCl), high concentrated (50-70 wt.% in the NaCl equivalent) aqueous solution, gas bubble, and often – ore mineral. They occur as small groups or separate inclusions associated with melt inclusions. The FI₂ occur as separate chains and are mostly represented by aqueous-salt (about 50 wt.% in the NaCl equivalent) inclusions with rare CO₂ bubble. Study of these inclusions allowed an evaluation of pressure of their capture: 2-2.2 kbar for FI₁ and 1.8-1.9 kbar for FI₂ respectively.

Quartz from medium-grained granite hosts two generation of postmagmatic secondary fluid inclusions. The first generation is represented by H₂O-NaCl-CO₂ inclusions (salinity about 25-27

wt.%). Their T_{hom} is in a range of 320-355°C, pressure of their capture – 0.8-1.2 kbar. Inclusions of the second generation are more common, and are represented by inclusions of “boiling fluid” with varying proportion of gas and liquid. Sometimes these inclusions host submicron NaCl crystal. Migration of secondary postmagmatic fluid along fractures and grain borders resulted to partial quartz leaching (acidization) and consequently to growth interstices and fractures in volume, and to oversaturation of fluid in SiO_2 . Postmagmatic quartz associated with mica precipitates in interstices from the oversaturated fluid, depleting fluid in SiO_2 . Depleted fluid interacts with rock leaching quartz, and this process repeats giving start to postmagmatic greisenization. Isometric quartz grains of the late generation host just single primary low-concentrated fluid inclusions homogenized at 150-295°C, and primary aqueous inclusions. Liquid-gas proportion varies in a wide range evidencing for “boiling” of postmagmatic fluid.

Conclusions

It is found that microcline phenocrysts crystallized during early magmatic stage at $T=990-995^\circ\text{C}$ and $P \gg 2.5$ kbar (more precise pressure evaluation is impossible because of complete destructure of fluid inclusions trapped during this stage). After that magma with phenocrysts was significantly elevated. This elevation was responsible for phenocryst protoclase, magma degassing and medium-grained granite crystallization at $T=970-980^\circ\text{C}$, $P=2.3-2.5$ kbar in the internal zone, and $T=970-975^\circ\text{C}$, $P=1-1.9$ kbar in the transitional and external zones respectively. Postmagmatic greisenization resulted from boiling fluid interaction with medium-grained granite at $T=150-355^\circ\text{C}$ and $P=0.8-1.2$ kbar.

CHEMICAL COMPOSITION AND EVOLUTION OF VOLCANIC CENTER GORELY (SOUTHERN KAMCHATKA): EVIDENCE FROM MELT INCLUSIONS

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The Gorely volcano is known as a large long-living volcanic center at Southern Kamchatka persisting its eruptive activity in recent time. This volcano is composed of two different volcanic structures; one of them being ancient and other is recent. The ancient structure (pra-Gorely) has a shield-like shape, its center is presented with a caldera of 12x13 km in diameter, the latter being formed along with enormous ignimbrite eruptions. The recent structure (Young Gorely) occupies the central part of the caldera and is comprised of three conjoined cones.

We studied samples of ignimbrites (caldera-forming stage), dacites (post-caldera stage), andesites and andesitic basalts of the Young Gorely

structure as well as olivine basalts presumably formed at the pra-Gorely stage. The bulk chemical and mineral composition, glass of melt inclusion composition in phenocrysts was studied. The melt inclusions in olivines and plagioclases were heated up to two phase (melt + gas) state and then chilled. The homogeneous glasses were analyzed by use of electron microprobe (Cameca SX-100, Moscow) and ion microprobe (Cameca IMS-4f, Yaroslavl).

Melts of the Gorely volcano are characterized by rather broad compositional range (Fig. 1). Melt inclusions in basalt were found to have basic composition with the following content of the major oxides (in wt.%): 45-49 SiO₂; 0.3-2.0 TiO₂; 6.4-9.2 MgO; 0.6-5.6 K₂O.

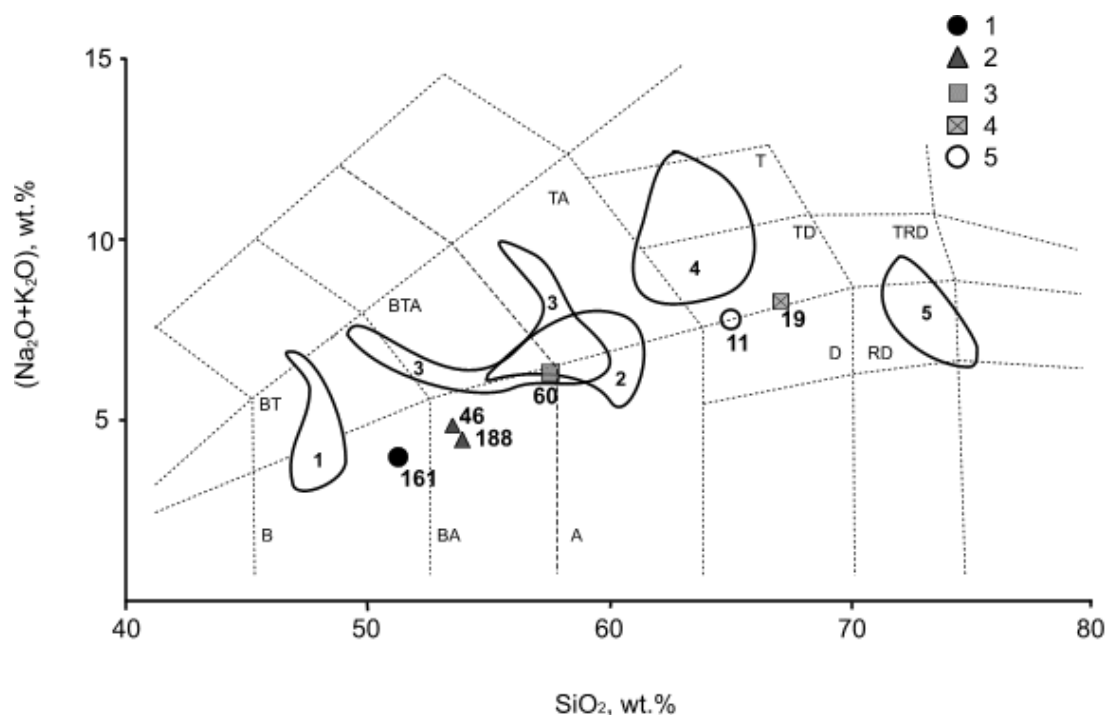


Figure 1. TAS-diagram for the melt inclusions and the rocks of the Gorely volcanic center.

1-5 – samples (1 – basalt, 2 – andesitic basalt, 3 – andesite, 4 – ignimbrite, 5 – dacite). Fields – melt inclusion compositions.

Melt inclusions in andesitic basalts differ in sufficiently higher SiO₂ (54-60) and TiO₂ (1.1-3.1) concentration, lower MgO (1.6-3.3) and analogous K₂O (1.6-3.7 wt.%). Melt inclusions in andesite are characterized by mostly broad SiO₂ (49-60) compositional range, rather high TiO₂ (0.6-2.6) and K₂O (2.4-6.1 wt.%). Melt inclusions in ignimbrite have a trachyte-trachydacitic composition: 57-69 SiO₂, 2.6-8.2 K₂O and comparatively high TiO₂

content (up to 1.8 wt.%). Melt inclusions in dacite are mostly enriched in SiO₂ (70-74) with low TiO₂, FeO, MgO and CaO content and moderate K₂O (3.4-4.3 wt.%). It is emphasized that in all melt types the high potassium varieties are established (Table 1).

All melt types of the Gorely volcanic center are enriched in trace elements. LILE elements were found in highest concentrations excluding Sr as its

behavior is related with the plagioclase fractionation; HFSE elements are also sufficiently high excluding Nb-minimum, being typical for the island-arc rocks. The melts of the Gorely volcano are specific in comparatively low Ti and Th concentration even in low differentiated melts as well as in high HREE elements.

The analogous distribution pattern of all trace elements, regular increase of incompatible element content from basic to acidic melts, Sr and Eu-minima in most acidic types could be interpreted as criteria of the Gorely volcano melts to comprise a single magmatic series.

Table 1. Chemical composition (wt.%) of various melt types from the Gorely volcanic center.

Component	Types of melt					
	I	II	III	IV	V	VI
SiO ₂	46.51	47.19	50.69	58.66	57.90	70.46
TiO ₂	1.11	1.10	2.54	0.79	1.47	0.70
Al ₂ O ₃	16.80	16.62	14.87	18.52	15.60	13.75
FeO	11.65	8.66	10.39	2.99	7.45	2.82
MnO	0.20	0.13	0.22	0.08	0.15	0.10
MgO	8.45	8.54	2.77	1.89	2.08	0.65
CaO	8.68	11.44	7.21	4.28	5.75	1.81
Na ₂ O	0.92	3.20	3.73	3.99	3.87	3.93
K ₂ O	3.22	1.08	2.48	6.28	2.96	3.54
P ₂ O ₅	0.13	0.40	1.47	0.41	0.47	0.15
Cl	0.00	0.05	0.08	0.02	0.08	0.17
S	0.02	0.06	0.04	0.01	0.02	0.02
Total	97.69	98.47	96.49	97.92	97.80	98.10
Host mineral	Ol	Ol	Pl	Pl	Pl	Pl
<i>n</i>	6	4	4	9	32	8

Note. I-III – basaltic melts (I – high-potassium, II – sodium, III – potassium-sodium with high content of TiO₂ and P₂O₅); IV, V – andesitic melts (IV – high-potassium, V – sodium); VI – dacitic potassium-sodium melts; *n* is the number of melt inclusion analyses.

METASOMATIC RECRYSTALLIZATION AND MELTING OF ULTRABASIC ROCKS OF MANTLE WEDGE BENEATH AVACHA VOLCANO, KAMCHATKA

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Introduction

The study of mantle xenoliths from the Kamchatka volcanic rocks and the elucidation of the character and physicochemical conditions of their transformations make it possible to obtain important information on the emergence and evolution of magmatic melts in geodynamic setting of the ocean-continent transition zone. Harzburgites and dunites are common among xenoliths of the Avacha volcano, whereas pyroxenites, wehrlites, websterites and cortlandites are rare (Koloskov, 1999). Highly siliceous interstitial silicate glasses often occur in these xenoliths (Koloskov, 1999; Ishimaru et al., 2009). Transformation of xenoliths and appearance of highly siliceous silicate glasses are usually related to metasomatic treatment and partial melting followed by the substance introduction (Schiano et al., 1998; Ishimaru et al., 2007) or their interaction with andesite and andesite-basalt magma during the transport to the surface of the Earth (Klugel, 1998).

Analytical procedures

Fluid and melt inclusions in the minerals of xenoliths were studied by optical and scanning electron microscopy (SEM), microthermometry, electron (EMPA) and ion (SIMS) microprobes and micro-Raman spectroscopy.

Results and discussion

“Primary” harzburgites are composed of fine-grained high magnesium olivine (in wt.%: SiO₂ 41.0; FeO 8.8; MgO 49.5; NiO 0.36; MnO 0.15), orthopyroxene (SiO₂ 56.3; Al₂O₃ 1.2; FeO 5.4; Cr₂O₃ 0.4; MgO 35.4; MnO 0.14; CaO 0.36) and accessory spinel (Al₂O₃ 27.07; FeO 18.07; Cr₂O₃ 37.53; MgO 15.83; NiO 0.25). The increase of the grain size, natural change of iron content in olivine (SiO₂ 39.2-40.5; FeO 10.4-16.6; MgO 45.3-42.6; MnO 0.25-0.29; CaO 0.09-0.13; NiO 0.2-0.3) and orthopyroxene (SiO₂ 55.7; Al₂O₃ 1.7; FeO 8.8; MgO 31.7; CaO 1.1), and the decrease of alumina content associated with the increase of chromium content in spinel (Al₂O₃ 14.97; FeO 19.33; Cr₂O₃ 51.95; MgO 12.83) are typical of the recrystallized harzburgites. Orthopyroxene amount increases, and clinopyroxene (SiO₂ 53.7; Al₂O₃ 1.2; FeO 4.5; MgO 17.2; CaO 22.4; Na₂O 0.3) and amphibole (SiO₂ 46.2-48.3; TiO₂ 0.5; Al₂O₃ 11.6-9.4; FeO 3.8-6.6; MgO 2.9-1.4; CaO 11.8-4.4; Na₂O 3.1-4.5; K₂O

0.5-1.4) appear as the degree of recrystallization of the “primary” harzburgite increases. Interstitial silicate glasses different in composition (in wt.%: SiO₂ 49.7-63.1; TiO₂ 0.1-1.0; Al₂O₃ 18.1-20.0; FeO 2.6-7.7; Cr₂O₃ 0.3-1.6; MgO 18.6-19.0; CaO 11.5-11.8; Na₂O 1.9-2.2) usually occur at the boundaries between grains of orthopyroxene, olivine, clinopyroxene and amphibole in the xenoliths subjected to melting (Fig. 1).

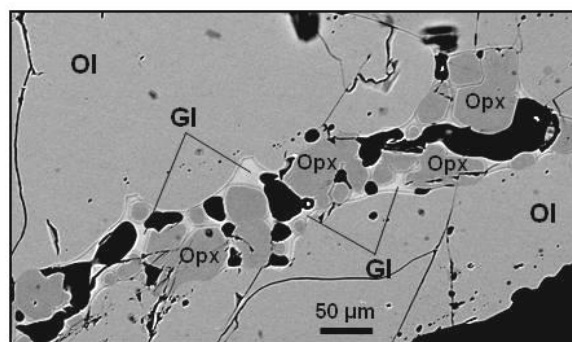


Figure 1. Microphotograph of interstitial silicate glass occurring at the boundaries between orthopyroxene and olivine grains in the recrystallized harzburgite of the Avacha volcano, Kamchatka. Gl - glass; Opx – orthopyroxene; Ol – olivine. Back-scattered electron image.

Fluid inclusions. Primary fluid inclusions were found only in the minerals of metasomatically recrystallized harzburgites. Their phase composition is represented by gas bubble, carbonate-water-salt (chloride) solution and several daughter crystalline phases (quartz, fluorite, calcite, anhydrite, albite, etc., Fig. 2).

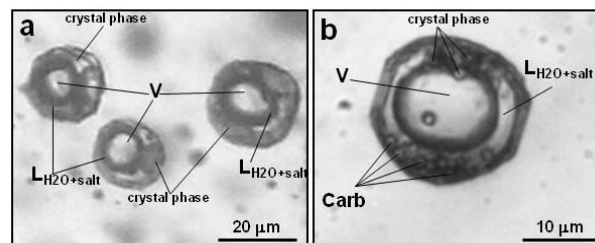


Figure 2. Microphotographs of primary carbonate-water-chloride inclusions in olivine of metasomatically recrystallized harzburgites of the Avacha volcano, Kamchatka. V – gas bubble; L_{H2O+salt} – liquid phase; Carb – carbonate.

Partial homogenization in fluid inclusions occurs into the liquid at 330-350°C. Complete homogenization is observed as a result of dissolution of last crystalline phase at about 960°C.

Melt inclusions. Primary inclusions of silicate melt were found in olivine, clinopyroxene, spinel, orthopyroxene and amphibole from the recrystallized xenoliths, subjected to partial or complete melting (Fig. 3).

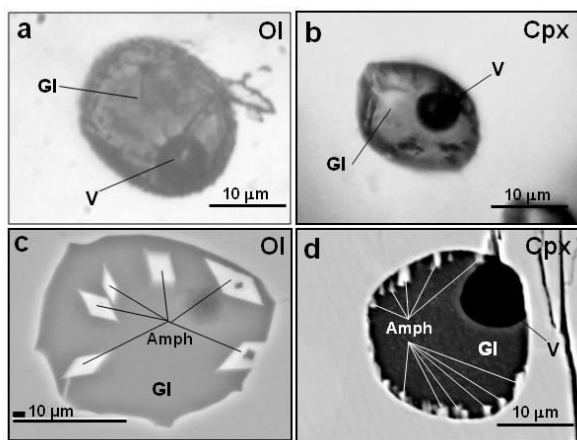


Figure 3. Microphotographs of primary silicate-melt inclusions in olivine (a, c) and clinopyroxene (b, d) from the recrystallized harzburgites of the Avacha volcano, Kamchatka. Gl - glass; V - gas bubble; Amph - daughter amphibole. a-b - ordinary light; c-d - back-scattered electron images.

Phase composition of common primary melt inclusions in olivine and clinopyroxene is represented by glass, gas bubble and one or several daughter crystalline phases (amphibole).

Homogenization temperatures for melt inclusions in clinopyroxene range from 1040 to 1170°C. We were unable to reliably determine homogenization temperature for melt inclusions in olivine because the gas phase did not disappear up to 1300°C. According to the microprobe data (EPMA), the composition of glasses in the heated and quenched melt inclusions in olivine is (in wt.%): SiO₂ 55.1; TiO₂ 0.7; Al₂O₃ 17.7; FeO 7.5; MgO 3.8; CaO 7.8; Na₂O 5.1; K₂O 0.6, and in clinopyroxene is: SiO₂ 60.1-59.0; TiO₂ 0.5-0.12; Al₂O₃ 19.6-16.4; FeO 3.3-1.2; MgO 2.8-0.6; CaO 3.8-5.1; Na₂O 1.7-3.1; K₂O 0.9-1.1.

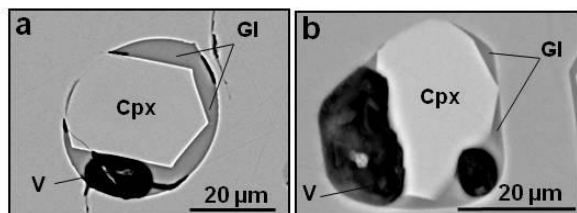


Figure 4. Microphotographs of primary combined inclusions of silicate melt in olivine (a) and orthopyroxene (b) from the recrystallized harzburgites of the Avacha volcano, Kamchatka. Gl - glass; V - gas bubble; Cpx - trapped clinopyroxene. Back-scattered electron images.

water content in the unheated melt inclusions in olivine is 2.8 wt.% and in clinopyroxene it ranges from 2.7 to 4.1 wt.%. Interstitial xenolith glasses are considerably more “dry”, that seems to be the result of melt degassing during the vitrification.

In addition to normal melt inclusions primary combined melt inclusions were found. Their phase composition is glass, gas bubble, daughter amphibole and trapped crystalline phases (olivine, orthopyroxene and clinopyroxene, Fig. 4).

Our data indicates that all transformations of the ultrabasic xenoliths of the over mantle wedge beneath the Avacha volcano, Kamchatka, have occurred before they have been trapped by andesite or andesite-basalt melt. Two main stages can be distinguished in the observed sequence of changes of mineral phases during the transformation of xenoliths of “primary” harzburgites. First, the intensive metasomatic treatment with the active role of high-temperature and high-concentrated carbonate-water-chloride fluids. Second, partial or complete melting of metasomatized harzburgites with the formation of silicate melts from which the newly formed clinopyroxene, orthopyroxene, spinel, olivine and amphibole have crystallized. Melting of the primary harzburgites is preceded by the addition of Si, Al, Ti, Ca, Fe, Na, K, S, P, etc. We believe that metasomatism and complete melting of primary harzburgites of the over mantle wedge beneath the Avacha volcano could cause the formation of such rocks as pyroxenites, wehrlites, websterites and occurrence of andesite melts.

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According to ion microprobe analysis (SIMS),

MOLECULAR THERMOBAROGEOCHEMISTRY OF NATURAL SYSTEMS "MINERAL-ROCK-FLUID"**Trufanov V.N., Trufanov A.V.***Southern Federal University, Rostov-on-Don, Russia (trufanov_v37@mail.ru; smaf207@mail.ru).*

Molecular thermobarogeochemistry - a new direction of fundamental and applied researches in the field of Earth sciences which study the phase interactions in "mineral-rock-fluid" systems at molecular and upmolecular levels at high thermobarogradient parameters, which are accompanied by destruction of these systems and the effects of gas evolution, influencing practically on all physical, chemical and technological properties of geological objects. Unlike the classical thermobarogeochemistry, investigating rather large optically visible fluid inclusions for the purpose of reconstruction of physical and chemical conditions of their preservation, the field of activity of a molecular thermobarogeochemistry extends also on ultramicroscopic, molecular and upmolecular fluid inclusions that predetermines the new approach to understanding the nature of mineral-generated fluids and to their interaction with a firm litobasis in the Earth crust.

The current experimental material on electronic microscopy of "mineral-rock-fluid" systems shows, those high dispersed fluid inclusions are presented as satellite systems with the sizes from 1-2 micron to 100 Å, clathrate compound inclusions, which are upmolecular fluid associates, and also free fluid-generated radicals, entering in structural heterogeneities of a crystal lattice of minerals.

Molecular thermobarogeochemistry represents in fact transition to nanotechnological methods of research of geological objects. Such transition is actual and inevitable in connection with necessity of forecasting and opening of the new deposits, situated on the big depths, where firm and fluid components make uniform high dispersed systems. Appreciably it concerns to superficial, exogenous objects, which are quite often composed by the high dispersed mineral units, containing fluid inclusions of different degree of dispersion.

Thus, the main purpose of the researches is the establishment of physical and chemical parameters of formation the mineral deposits arising in the conditions of molecular interaction of firm and fluid phases in earth crust, working out of criteria of forecasting and an estimation of the industrial importance of geological objects, including objects on the big depths, creation of economically effective geotechnological methods of development of georesources of bowels the interior.

The basic methods of researches are: the geological-structural analysis of various scale geological objects for definition of possible PTC-parameters of occurrence of "mineral-rock-fluid" systems; high resolution optical and electronic microscopy of fluid inclusions; vacuum decriptometry of minerals, rocks and ores; methods of electromagnetic influence; thermic, mass spectrometer and gaseous chromatographic analyses of high dispersed, molecular and upmolecular fluid systems; gemological research methods of precious stone mineral raw materials.

For realization of these methods the available equipment and devices of the "Gertehprognoz" and "Kameya" laboratories and analytical laboratory of geology-geographical faculty of SFU was used. They are vacuum decriptometer type VD, a scanning electronic microscope, derivatograph STA 449C.

Objects of researches were ore deposits, nonmetallic and combustible minerals of Southern federal district and other regions of Russia, including coal-bed methane and gold deposits of East Donbass, ore and nonmetallic deposits of the Big Caucasus, oil and gas deposits of Western Siberia, diamond deposits of Yakutia, coal deposits of Kuzbass and Primorski Krai. For the studied deposits PTC-parameters of progressive, extreme and regressive stages of their formation were established, optimum thermodynamic barriers of mineral and ore formation were defined.

The basic results of the researches are the further development of fundamental positions of a thermobarogeochemistry about the leading part of geofluid systems and processes of hydrocarbonic fluid influence in formation of mineral deposits, modernization on a computer basis of modern methods, devices for research of high dispersed "mineral-rock-fluid" systems, monitoring of fluid components in fossil coals and products of their processing, working out the scientific bases of geotechnological methods of the forecast, an estimation and development of new and nonconventional kinds of mineral raw materials.

Investigations in the field of molecular thermobarogeochemistry establish the laws of formation of ore, non-metalliferous and combustible mineral deposits. The PTC-parameters of phase transitions in natural systems "mineral-rock-fluid", the optimal thermodynamic barriers for

localization of the ore bodies and oil-gas pools, the particular features of fluid regime for rock massives and the reasons of the mineral crystallization stages was determined.

The processes of hydrocarbonic fluidization have been of special interest, because they have been accompanied by formation of dangerous gas-dynamic effects, anomaly concentrations of methane and strategically important elements in coal beds.

Actual problems of molecular thermo-barogeochemistry, which have been discussed in this paper, are to determine the necessity of continuation of the investigations in that direction.

THERMOBAROGEOCHEMICAL CONDITIONS OF NORTH-WEST CAUCASUS LISTVENITE FORMATION

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Introduction

Listvenite is metasomatic rock, consisting of carbonates (more frequently it is ankerite), quartz and muscovite or fuchsite (chromic mica) mixed with various minerals (talc, chlorite, albite, schorl, rutile, grothite and others). Listvenites have bright green (from fuchsite) or grey (at colourless muscovite) colour. They are resulted from listvenitization. They generally occur in the shape of lenses and vein bodies among schistosity rocks. They can form casing around gold-bearing quartz veins. For the first time listvenites have been discovered in Ural Mountains and described by the German geologist G. Roze (1842).

Listvenites are known to be in all serpentinite mountain mass of North-West Caucasus Front Range. There are particularly numerous on the Dahovsky, Thachsky and Malo-Labinsk massifs. To study listvenite body have been chosen from listvenite lenses of North-West Caucasus, situated within the Dahovsky crystal massif. Listvenites are rather extended within the studied area. They are presented by grey, green, brown, dark grey granular-crystalline rocks of solid composition, but occasionally stripe and jasperoid variety can be observed there. Its principal mineral composition is carbonates and quartz, therefore in the publications of North-West Caucasus they are known as quartz-carbonate strata. According to conclusion of technical and art council of stone-cutting factory, listvenites are quite suitable for manufacturing of various stone-cutting products and can be used as qualitative semi-precious and a facing stone.

Thermobarogeochemical researches

To define thermobarogeochemical conditions of the North-West Caucasus listvenite formation vacuum-decryptometric researches have been carried out at decrepigrapher VD-5 (technique of V.N. Trufanov et. al, in laboratory "Geotechprognos" of geology-geography faculty SFU). Vacuum-decrepigraphic method developed by scientists of "Mineral deposit" department of RSU, is based on registration of gas release effects, arising during destruction of "mineral-fluid" systems in vacuole, as a result of sharp increase of pressure in vacuoles of inclusions after reaching of homogenization temperature.

According to morphological and mineralogic-petrographic features three types of listvenites,

characterized by decreptogram structures and temperature of fluid inclusions decrepitation has been picked out.

The first type is characterized by presence of two effects of fluid components extraction. The first maximum of gas release is marked at temperatures in the range from 40 to 100°C with F-datum of fluid activity being from 102 to 105 relative units. The second effect of fluid components extraction is registered at 360-500°C, with F-datum value of fluid activity being in the range from 28 to 32 relative units.

The second type has three peaks of gas release. The first effect of fluid components extraction is registered at 40-60°C with F-datum of fluid activity being 9-12 relative units. The second maximum of gas release is attributed to average temperature interval, which is at 320-400°C, datum value of fluid activity makes up 4-7 relative units. The high-temperature effect of fluids extraction occur at interval 420-520°C, with F-datum of fluid activity equaling 58-60 relative units, the relative value of this gas release effect in F_{general} makes up 50 %.

The third type is characterized by presence of four peaks of fluid components extraction. The first and second effects are registered in low temperature intervals 20-40°C and 80-120°C with F-datum of fluid activity 2-4 and 1-2 relative units respectively. The third effect is attributed to medium temperature interval and occurs in the range from 340 to 420°C, with F-datum value of fluid activity making up 5-8 relative units. The fourth maximum of gas release is in interval of temperatures 440-520°C with F-datum of fluid activity 66-70 relative units, the relative value of this gas release effect in F_{general} makes more than 50 %.

Vacuum-decrepigraphic researches show, that DCM listvenites have undergone considerable transformations in process of their geological evolution. Consequences of various fluid influences have led to big variety of thermobarogeochemical features, which energy F-datum value of "mineral-fluid" systems fluid activity, kind and structure of decreptogram with different temperature decrepitation peak may be attributed to. The analysis of received decreptogram of most representative samples is represented below.

The analysis of listvenites vacuum-decreptograms shows they to be characterized by enough difficult structure, containing from two to

four effects of fluid components extraction, major of which are three maximums of fluids extraction. They are obviously linked to three inclusions systems of mineral formation environment – low-temperature, medium-temperature and high-temperature.

Genesis

Thermobarogeochemical researches have also allowed revealing laws of listvenite genesis. Listvenite genesis is represented below. Listvenites were believed to appear at magmatic contact between granites and serpentinites. Such position doesn't correspond to the facts because listvenites often occur without any links with magmatic contacts. In addition, listvenites not always originate in response to serpentinite changing. Listvenites of the DCM are proved to be resulted from crystal shale and granites, and at the area of the Malaya Laba river – from greenstone metamorphic shales. In Thachsky Serpentine Mountain massif there are listvenites arisen at for account for limestones. Therefore, it is more correctly to consider that listvenite genesis of this area as hydrothermal. However, listvenites usually occur both down and on the contacts with serpentinites, or among other rocks, but close to serpentinite massifs. Hence, listvenite formation is linked partly with serpentinites.

Plentiful carbonate and quartz-carbonate hydroterms during their movement penetrated in the cracks, being among other crystal rocks and serpentinites. Circulating in serpentinites, hydroterms actively interacted with them and dissolved nickel minerals, always being in serpentinites, in result of chemical reactions. Solution occurred with formation of green nickel silicate – garnierite. During the further movement in various crystal rocks carbonate hydroterms enriched by garnierite changed these rocks, deposited in them ferriferous carbonates and garnierite, and formed, thus, listvenites. The spatial listvenite arrangement relative to serpentinite massifs is quite coordinated with such explanation of their genesis.

Conclusions

Based on facts of thermobarogeochemical researches three stages of rocks temperature conditions formation have been allocated (high-temperature, medium-temperature and low-temperature). The high-temperature stage is linked with processes of regional and contact metamorphism (serpentinization). Medium-temperature stage is connected with imposing of hydrothermal metasomatic processes (listvenitization). Nature of the effect in low-

temperature interval can be linked with epigene processes and with conclusive listvenite transformation.

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FLUID INCLUSIONS IN WOLFRAMITE-BEARING VEINS AT DEGANA AND BALDA GREISEN TUNGSTEN DEPOSITS, RAJASTHAN, INDIA

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Introduction

Fluid inclusion (FI) studies were conducted to characterize the fluids responsible for greisen-type wolframite deposits at Degana and Balda in Rajasthan, India. Quartz samples from three types of wolframite-containing veins in Degana, namely granite-hosted lode, stockwork ore in phyllite and breccia ore in granite, and W-mineralized vein at Balda were studied.

Geology of Degana and Balda W deposits

The Degana and Balda tungsten deposits are associated with Late Proterozoic granites occurring along the western margin of the Mid-Proterozoic Delhi fold belt in the Aravalli craton, NW India.

In the Degana tungsten deposit, granite magmatism has produced three successive intrusions of porphyritic granites and a large number of aplite dykes, emplaced within phyllite. Intrusion-centred hydrothermal activity has resulted in extensive fracturing of the granitic rocks and the development of greisen veinlets, greisen-bordered lodes, and breccia fillings, consisting of quartz, zinnwaldite, topaz, fluorite and wolframite. Field relationship shows that there were two consecutive cycles of magmatic and hydrothermal events, which produced granite, aplite, greisen veinlet and wolframite mineralized lode/breccia fill during each cycle. The granitic rocks are greisenized adjacent to the lodes, the width of alteration zone varying from few cm to several m, and composed of grey quartz, dark green zinnwaldite and minor topaz, fluorite and wolframite. The lodes commonly show crustification with zinnwaldite/muscovite lining the vein walls and quartz occupying bulk of the veins along with disseminated topaz, fluorite and wolframite of ferberitic composition (Mn/Fe ratio - from 0.02 to 0.33) (Pandian, Varma, 2001).

In the Balda tungsten deposit, a tourmaline leucogranite (Balda granite) is emplaced within phyllite, and the intrusive contact is generally sheared. These shear zones are occupied by wolframite-bearing quartz veins. Wolframite is ferberitic in composition with Mn/Fe ratio varying from 0.08 to 0.12. Greisenization of wall-rock phyllite and granite adjoining the W-mineralized quartz veins is prominent (Chattopadhyay et al., 1982).

Fluid inclusion petrography

Four distinct types of primary FI in the size range of 2 to 20 μm (Fig. 1a-d) were trapped by quartz from both W deposits. The Type I is aqueous biphas containing a liquid and vapor; the Type II is aqueous-carbonic containing liquid CO_2 rimmed by liquid H_2O ; the Type III is multiphase aqueous containing aqueous liquid, vapor and solid daughter phases; and the Type IV is monophas carbonic FI containing CO_2 liquid. On cooling below 20°C a CO_2 vapor phase develops in the Type IV fluid inclusions.

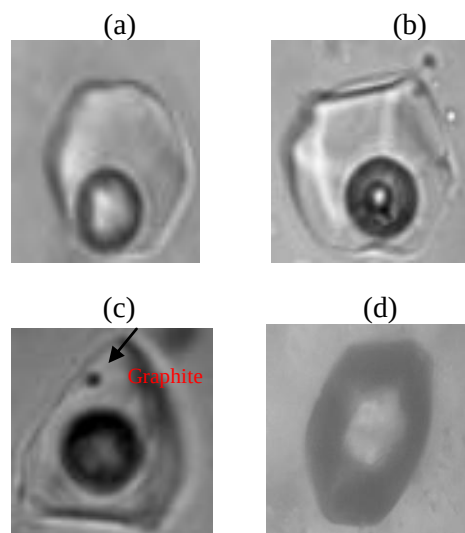


Figure 1. (a) Aqueous biphas and (b) aqueous-carbonic inclusions in the Balda quartz, (c) multiphase (graphite-bearing) and (d) carbonic monophas inclusions in the Degana quartz.

Microthermometry

In both deposits, in most of Type I aqueous bi phase FI eutectic T is observed at -29°C to -15°C (H_2O - NaCl - KCl) and in some inclusions from -57°C to -42.5°C (H_2O - CaCl_2 - MgCl_2). Final ice melting T varies from -13°C to -1.6°C corresponding to salinity of 13.5 to 8.81 wt.% NaCl eq. (Goldstein, Reynolds, 1994). These FI homogenized into liquid between 120°C and 380°C ($\text{L}+\text{V}\rightarrow\text{L}$). In the Type II aqueous-carbonic FI $T_{\text{m-}\text{CO}_2}$ was recorded to lie between -59.0°C and -56.5°C . The $T_{\text{h-}\text{CO}_2}$ in these inclusions varies between 10°C to 29°C ($\text{L}+\text{V}\rightarrow\text{L}$). In the Type III multiphase inclusions disappearance of solid crystal occurred between 110°C and 337°C (28 to 41 wt.% NaCl eq.). EDS spectra of the Type III inclusions

(Fig. 2) show presence of K, Na and Cl. It allows suggesting NaCl and KCl solid composition. The total T_h of multiphase inclusions occurs between 150°C and 450°C. The main component of Type IV inclusions is high density liquid CO_2 with a small admixture of, probably CH_4 ($T_{m-\text{CO}_2} = -60$ to -58°C , T_h V→L between 5 and 19°C). Phase changes in many gaseous FI were not observed by microthermometry, which indicate a low density vapor. Different CO_2 density in monophasic FI indicates wide pressure variations.

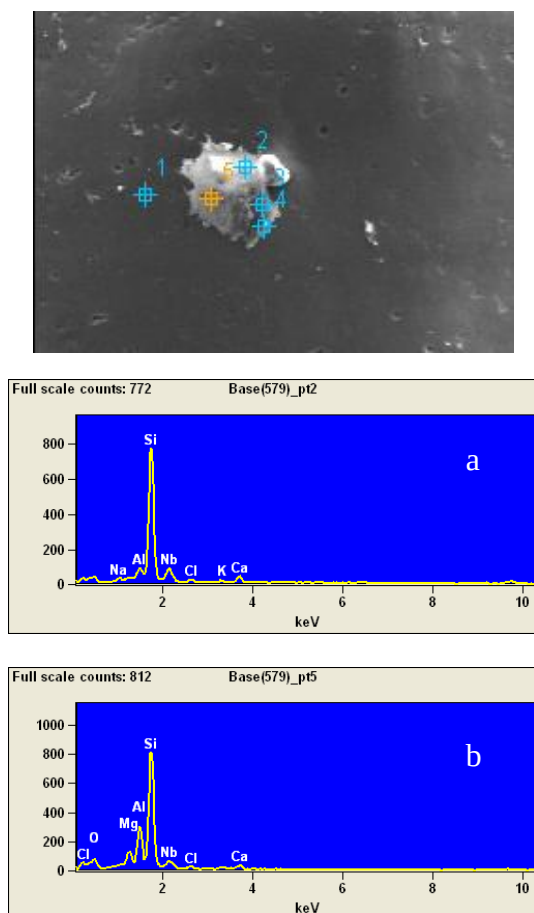


Figure 2. EDS for a multiphase fluid inclusion (a) and enclosing quartz (b) from the Degana deposit.

Laser Raman Microspectroscopy

Raman spectra (Fig. 3) obtained on the Type III multiphase FI (Fig. 2c) show presence of small amount of CH_4 ($\sim 2911 \text{ cm}^{-1}$), along with CO_2 (1151 cm^{-1} and 1380 cm^{-1}) and graphite (1602 cm^{-1}).

Conclusion

The wolframite-containing veins in the Degana and Balda tungsten deposits were deposited in temperature interval of 450-150°C. No pressure correction was made on homogenization temperatures in this work. Given temperatures should be taken as the minimum temperature of mineral formation. Ore-forming fluids had Na-K-chloride composition. Graphite-containing FI and

CO_2 -rich FI with small CH_4 admixture indicates wide range of Eh, which may be the possible reason for ore deposition.

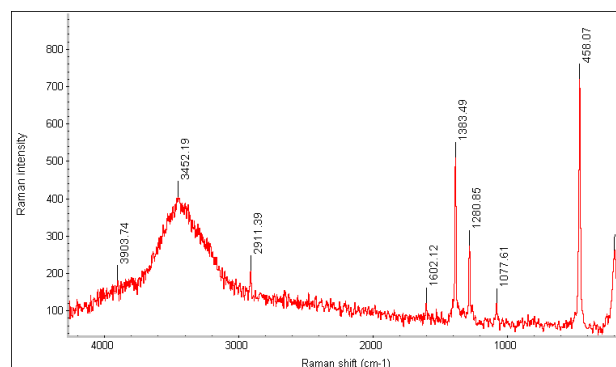


Figure 3. Raman spectra of multiphase inclusion in the Degana quartz.

Acknowledgements

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POPIGAI SUEVITE MEGABRECCIA: DENSE WATER INCLUSIONS IN MONO-MINERAL GLASSES AND THEIR PETROLOGIC SIGNIFICANCE

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Introduction

The results presented below complete the series of our studies devoted to the features of fluid inclusions in mono-mineral impact glasses from the main Popigai vitro-clastic formations. Based upon fluid inclusions studies, important origin conditions of the impactites are found, including the fluid regime specificity on the initial stages of cratering at high pressure-temperature conditions. Suevites and bottom megabreccia were characterized earlier in this aspect (Vishnevsky et al., 2010a; 2010b). Below, there is a similar description of the Popigai suevite mega-breccia (Smb). It should be noted, that high-pressure water inclusions in the glasses from the rocks mentioned above, are the unique feature of the Popigai (Vishnevsky, Gibsher, 2008) and are still not known in other terrestrial astroblemes.

Rock description

The Smb (mixed colliding deposits of the Popigai explosion cloud) occupy the top of the suevite column in the crater (Vishnevsky, 2007). The Smb is the chaotic mixture of the large, 1 to 80 m across, mainly Mesozoic, low-shocked target rock lumps cemented by tuff-like matter. The glasses from the cement are derived from the target gneisses affected to III–IV stages of shock metamorphism ($P \sim 45 \div 90$ GPa, $T \sim 900\text{--}3000^\circ\text{C}$, see Stöffler, 1971). In addition to the mixed apogneiss glasses (GGs), the mono-mineral melt glasses (MMGs) are common here. Their study is the subject of our paper. The Popigai Smb is paradoxical to a certain extent as far as its origin, location, composition, etc. are concerned (see for details in Vishnevsky, Montanari, 1999; Vishnevsky, 2007).

Glass description

The MMGs are present as schlieren in the shocked gneiss fragments and the Smb cement. Lechatelierite (Lch, SiO_2 96.5–99.5 wt.%) and K-Na feldspar glasses (FGs, in wt.%: SiO_2 62.54–63.0; Al_2O_3 19.9–20; K_2O 6.5–7.14; Na_2O 2.61–3.01; CaO 0.6–1.64) are known here. To this one can add the high-silica glasses (HS, SiO_2 76.3–93.4 wt.%) resulted from the partial homogenization of Lch with GGs on the “early” stages of the shock melting (Vishnevsky et al., 2010a). Microprobe totals are 92.74–94.89 wt.% for FGs and 95.58–97.88 wt.% for HS-glasses.

After (Vishnevsky et al., 2010a; 2010b) the total deficits observed may be related to the presence of H_2O (up to 6.27 wt.% in FGs, and up to 4.12 wt.% in HS-glasses). All the MMGs show often the complex dynamic interaction with the GGs, but no homogenization is observed here exhibiting a “later” stage of interaction. All the MMGs studied are fresh, clean and transparent.

Fluid inclusions in the glasses

The inclusions were studied in 4 Lch and in 2 FGs samples. Like for the similar glasses from other Popigai impactites, the samples contain a number of coexisting/cogenetic fluid inclusions of various densities at 20°C : entirely-liquid (L), gas+liquid (G+L) with various phase proportions between, and entirely gaseous (G) ones (**Fig. 1-2**). All the inclusions have a regular rounded form typical for the fluid drops in the melt and show irregular distribution in the schlieren, up to the origin of highly-porous and pumice-like glasses.



Figure 1. Fluid inclusions of various phase composition in the lechatelierite from the Popigai Smb. Plane polarized light. Note: Indicated in numbers, there are the fluid inclusions investigated (see the text for details).

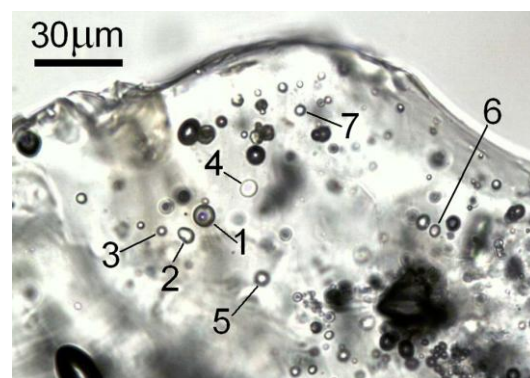


Figure 2. Fluid inclusions of various phase composition in K-Na FG from the Popigai Smb. Plane polarized light. Note: Indicated in numbers, there are the fluid inclusions investigated (see the text for details).

Cryometric investigations

Following to cryometry, the liquid phase in the inclusions is made up of low-salt water (**Fig. 3**). 9 L bubbles (eutectic temperature, t_e , is $-19.3 \div -21.3^\circ\text{C}$; ice fusion temperature, t_f , is $-0.1 \div -0.7^\circ\text{C}$; H_2O salinity is $0.1 \div 1.5$ wt.%) and 8 G+L bubbles (t_e is $-18.9 \div -21.4^\circ\text{C}$; t_f is $-0.1 \div -0.7^\circ\text{C}$; H_2O salinity is $0.1 \div 1.5$ wt.%) were studied in Lch. For the bubbles on **Fig. 1** these data are the next (bubble # and its phase composition $\rightarrow t_e, ^\circ\text{C}/t_f, ^\circ\text{C} \rightarrow$ salinity, wt.%, respectively): #1 (L+G), $-19.0/-0.3$, 0.5; #2 (L+G), $-18.9/-0.5$, 1.0; #3 (L+G), $-19.4/-0.7$, 1.5; #4 (L), $-21.0/-0.6$, 1.4; #5 (L), $-20.8/-0.4$, 0.6; #6 (L), $-19.3/-0.6$, 1.4; #7 (L), $-20.5/-0.7$, 1.5. 10 L bubbles (t_e is $-19.3 \div -21.3^\circ\text{C}$; t_f is $-0.1 \div -0.7^\circ\text{C}$; salinity is $0.1 \div 1.5$ mass %) and 9 G+L bubbles (t_e is $-19.3 \div -21.3^\circ\text{C}$; t_f is $-0.1 \div -0.7^\circ\text{C}$; salinity is $0.1 \div 1.5$ wt.%) were studied in FGs. For the bubbles on **Fig. 2** these data are the next: #1 (L+G), $-19.3/-0.7$, 1.5; #2 (L), $-20.9/-0.9$, 1.8; #3 (L), $-20.4/-0.8$, 1.7; #4 (L), $-19.9/-0.8$, 1.7; #5 (L), $-21.3/-0.9$, 1.8; #6 (L), $-21.5/-0.7$, 1.5; #7 (L), $-21.5/-0.7$, 1.5.

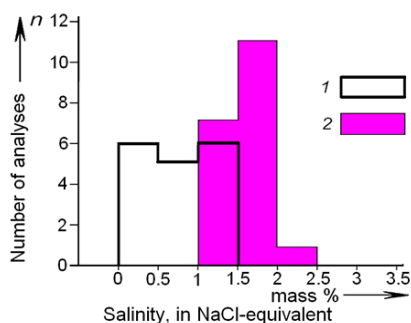


Figure 3. Salinity of water fluid in the inclusions from the lechatelierite (1) and K-Na fused glasses (2).

Discussion

The dense (0.5 to 1 g/cm^3) liquid water inclusions in the glasses investigated are of a great petrologic concern. Following to high temperature of the corresponding melts, $>1700^\circ\text{C}$ for Lch, and 700 to 1200°C for FGs ("wet" and "dry" melting points), the bubbles' trapping pressures are estimated to be up to $0.8 \div 3.3 \text{ GPa}$ in Lch and from ~ 0.2 – 0.5 to 1.5 – 2.6 GPa in FGs (**Fig. 4**). Such high pressures rule out any lithostatic variant and are related to the origin and evolution specificity of the glasses. Earlier it was discussed on the example of other Popigai rocks (Vishnevsky, Gibsher, 2006; 2008; Vishnevsky et al., 2010a; 2010b). This specificity includes initially complex thermal micro-structure of the host melts, quenching at residual shock pressures and prolonged shock pressure release under the water buffer action. At this, the dense fluid drops have time to be trapped in "cold" parts of the melt whereas the "hot" parts of the melt can trap the fluid drops of a decreasing density.

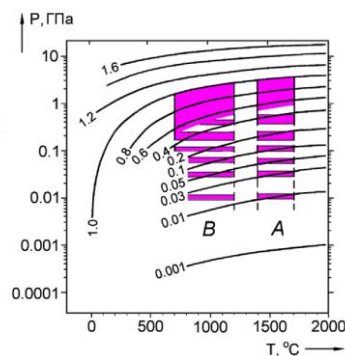


Figure 4. Trapping pressures for dense (0.5 – 1 g/cm^3) water inclusions in lechatelierite (A) and K-Na feldspar glasses (B).

Conclusion

Unique high-pressure water inclusions in the SMb glasses are similar to those found in some other Popigai impactites (suevites, mega-breccia and impact fluidizites). Prolonged shock pressure release due to the action of H_2O buffer is a dynamic aspect for the inclusions' origin. So, H_2O has an important role in the post-shock evolution of impactites in large craters. This feature of fluid regime of impactites should be taken into account at any study of terrestrial, Martian and other astroblemes originated on water-rich targets.

Acknowledgements: This study was supported by RFBR (grant #08-05-00408).

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FORMATION CONDITIONS AND COMPOSITION OF ORE-FORMING FLUIDS IN THE PROMEZHUTOCHNOE GOLD–SILVER DEPOSIT (CENTRAL CHUKOTKA, RUSSIA)

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Introduction

According to the conventional concept based on a great body of empirical data, volcanogenic or epithermal deposits do not grade into mesothermal or plutonogenic ones with depth. However, in the Maisk ore group of central Chukotka, epithermal Promezhutochnoe (Northeast), Sil'noe, and Sopka Rudnaya gold–silver deposits have been discovered in terrigenous flysch sequences at the basement of the Okhotsk–Chukot volcanogenic belt (OCVB) (Fig. 1).

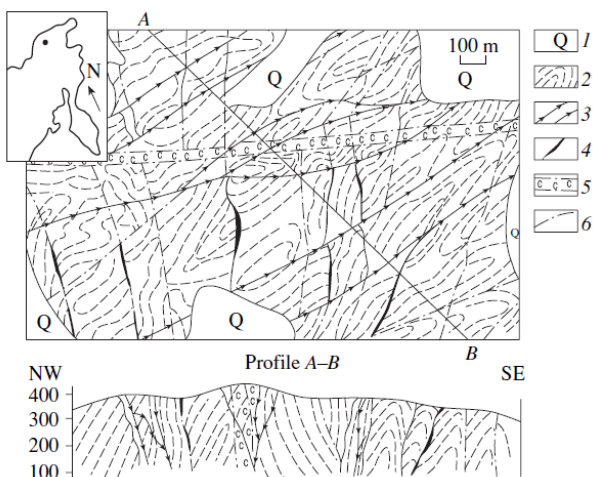


Figure 1. Schematic geostructural map and cross section of the Promezhutochnoe deposit. (1) Quaternary sediments; (2) Triassic flysch sequence; (3) basaltic andesite dikes; (4) shear and foliation zones with orebodies; (5) Major sublatitudinal fault; (6) secondary faults.

Similar epithermal ore deposits and occurrences have also been discovered in the terrigenous-sedimentary framing of intrusive domes in transmagmatic reactivation zones of the central Kolyma region (e.g., Pechal'noe and Vetvistoe deposits in the Khurchan–Orotukan zone and Rogovik deposit in the Balagychan–Sugoi zone). Analogous gold–silver deposits are also known in other regions. For example, the central Kyzyl Kum region incorporates the Vysokovol'tnoe and Kosmanyichi deposits, while the Transbaikalian region includes the Balei and Taseevka deposits. In this connection, let us recall the Hishikari deposit, Japan (Au reserve - 250 t). In terrigenous rocks of the basement beneath the volcanic cover of this deposit, geologists have discovered a second level of epithermal auriferous veins with an average grade of as much as 25–75 g/t. However, all

epithermal gold–silver orebodies (except the Hishikari, Balei and Taseevka deposits) have small and medium reserves. This phenomenon is probably related to their significant erosion.

Deposit geology

The Promezhutochnoe deposit is confined to dome uplift at the southern end of the Kukenei Pluton located 18 km from the Maisk gold–sulfide deposit of disseminated ores. Volcanic rocks are completely eroded in the ore field. Effusive rocks of the OCVB are developed at a distance of no more than 15 km. Terrigenous rocks of the deposit are composed of an intercalation of siltstones and shales with lenses of flyschoid fine-grained sandstones. The ore deposit is confined to the southwestern limb of a brachysyncline.

Orebodies of the deposit are mainly located on the southern side of the sublatitudinal belt of basaltic andesite dikes that make up nearly vertical ramified bodies with stepwise (sometimes Z-shaped) contacts (Fig. 1). The dikes are 0.5–5 m thick and more than 3 km long along the strike. They contain abundant xenoliths of sandstones, siltstones, granodiorites, and granite porphyries similar to granitoids in marginal facies of the Kukenei Pluton.

The majority of ore-bearing veins are traced along oriented debris of quartz boulders. The submeridional veins cut the sublatitudinal basaltic andesite dikes at right angles. The central area of the deposit includes an aureole of sericitized and silicified siltstones and shales.

The Promezhutochnoe deposit incorporates 11 orebodies outlined as slightly mineralized shear zones with axial quartz veins. The northern block hosts Aurich orebodies (Au/Ag = 2:1–10:1), whereas the southern block includes both Au- and Ag-rich orebodies (Au/Ag = 1:10–1:100).

Fluid inclusion study

In order to examine formation conditions of high grade ores, we investigated the quartz-hosted fluid inclusions (FI) in the orebodies 3 and 11 of the Promezhutochnoe deposit. Quartz grains have crustification, skeletal-lamellar and drusy structures.

Quartz in the orebody 3 includes primary FIs enriched in the syngenetic gaseous and gaseous–

liquid phases that testify to the heterogeneous state of the fluid. The gaseous FIs contain low-density (0.30 g/cm^3) carbon dioxide that homogenizes into the gaseous phase at $+28.5^\circ\text{C}$. The gaseous–liquid FIs contain a water solution of Na–K chlorides with a salt concentration of 4.1–3.8 wt.% NaCl equiv. They homogenize at $221\text{--}194^\circ\text{C}$ ($P = 270\text{--}230 \text{ atm}$, $P_{\text{tot}}/P = 13.4\text{--}21.3$).

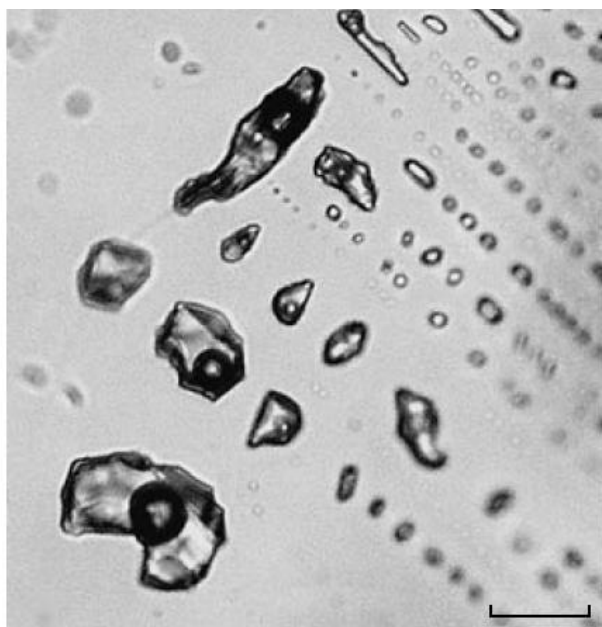


Figure 2. Primary two-phase quartz-hosted fluid inclusions in the orebody 11 of the Promezhutochnoe deposit. ($T_{\text{hom}} = 240^\circ\text{C}$; scale bar $10 \mu\text{m}$).

The quartz of the orebody 11 also includes syngenetic FIs enriched in the gaseous and gaseous–liquid phases (Fig. 2). Parallel layers of such quartz-hosted FIs represent relicts of chalcedony- and agate-type (lamellar and skeletal-lamellar) structures of silica. However, the gaseous FIs in the quartz contain only water vapor. The gaseous–liquid FIs are filled with the water solution of sodium chlorides with a salt concentration of 4.2–2.9 wt.% NaCl equiv.

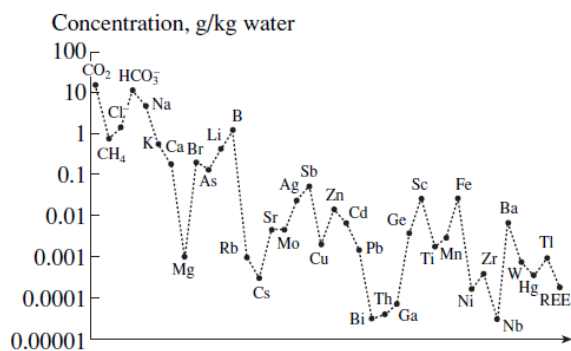


Figure 3. Composition of the ore-forming fluid in the orebody 11.

The homogenization temperature of such FIs is $247\text{--}241^\circ\text{C}$ (water vapor pressure $\sim 30 \text{ atm}$, $P_{\text{tot}}/P =$

1). In addition, the outer zone of quartz crystals contains low-temperature gaseous–liquid FIs with a salt concentration of 4.3–3.6 wt.% NaCl equiv. ($T_{\text{hom}} = 193\text{--}178^\circ\text{C}$) that are not accompanied by syngenetic gaseous FIs. Hence, the solution did not boil in the course of their entrapment. The composition of the quartz-hosted FI solution in the orebody 11 was investigated by gas chromatography, ion chromatography and ICP-MS.

Data obtained on the composition of water leachates from the vein quartz-hosted FIs (Fig. 3) allowed to estimate concentrations of many components in the FI solution (in g/kg of water, unless otherwise stated). The major components are Na (4.6) and Cl (1.4), whereas the subordinate components are K (0.5), Ca (0.2) and Mg (0.001). The FIs are also enriched in carbon dioxide (15.3), methane (0.7), (11.0), Br (0.19), As (0.13), Li (0.40) and B (1.2). The additional components are as follows (mg/kg of the solution): Rb (1.0), Cs (0.3), Sr (4.3), Mo (4.38), Ag (22.9), Sb (51), Cu (1.9), Zn (14), Cd (6.2), Pb (1.4), Bi (0.03), Th (0.04), Ga (0.07), Ge (3.7), Sc (26), Ti (1.7), Mn (2.8), Fe (26), Co (0.04), Ni (0.16), Nb (0.03), Zr (0.37), Ba (6.3), W (0.7), Hg (0.34), Tl (0.85) and REE (0.18). Ag, Sb, and Fe are the major trace elements. The trace element distribution is consistent with the geochemical profile of the deposit. The total salt concentration in the leachate is 37.5 g/kg of water. This value matches the cryometric data on the FIs.

Conclusions

Low salt concentrations and relatively low temperatures indicate the hydrosulfide mode of occurrence of Au in the solution. High B and Li concentrations in the FIs suggest the participation of granitoid-related fluids in the ore-forming process. At the same time, the high K/Rb value (556) indicates the involvement of genetically different solutions as well. Pressure estimates suggest various tectonic settings in the course of the formation of orebodies. For example, fractures were open during the formation of the orebody 11, whereas they were semienclosed and less permeable for carbon dioxide during the formation of the orebody 3. The orebody 11 could be formed near the main discharge zone of the hydrothermal system indicating a high ore potential of this part of structure of the deposit.

Acknowledgements

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INFLUENCE OF CO₂-FLUID FLOWS ON FORMING OF AZOV Zr-REE DEPOSIT (UKRAINIAN SHIELD)

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Introduction

Products of magma degassing at favourable conditions form the deposits of different useful minerals. By results of study of volatile components in the primary inclusions of magmatic rocks it is determined, that content of CO₂ in basic/ultrabasic magmas may reaches 2.4 wt.% (Naumov et al., 2000). Such magmas are potential sources of delivery of high-thermobaric CO₂-fluid flows in rocks. Influence of high thermobaric flows of CO₂-fluid on well crystalline rocks is ordinary nature phenomenon. Forming of different areas of the Ukrainian Shield, in particular, the Maiske gold deposit (Golovanivsk sutural zone), lithium pegmatites of the Kirovohrad megablock, chamber pegmatites of the Volodarsk-Volynsky pegmatitic field of the North-western megablock, show signs of its influence. High thermobaric CO₂-fluid flows caused cracking and melting of gold inclusions in quartz and formation of silicate glass in the first case (Voznyak et al., 2009), melting and cracking of pyrrhotite inclusions in quartz, sulfide appearance, carbonate and silicate melts in the second (Voznyak et al., 2000), and forming of the so-called honeycombous quartz in the third case (Voznyak et al., 2004). On the whole CO₂-fluid flows may: (a) to be the transfer mean of ore components from magma to water solutions of upper horizons of the earth's crust; (b) to change a mineral form of ore component (Voznyak et al., 2000; Voznyak, Pavlishin, 2006); (c) to lower the quality of raw materials in chamber pegmatites (Voznyak et al., 2006).

Research results

The Azov deposit of Zr and REE is located in layered intrusion (stock) of syenites. Enclosing rocks are syenites of the South-Kalchiksky massive (Eastern Priazovie, Ukraine). The upper part of stock consists of leucocratic syenites, containing annite and alkali feldspar (72 % NaAlSi₃O₈). Amphibole syenites, containing anorthoclase – micropertthite (62 % NaAlSi₃O₈), ferrohastingsite, fayalite, hedenbergite and ore minerals, are located below. Fluorite presents in all varieties of syenites. Zircon and britholite are the main ore minerals; allanite and REE-carbonates are the minor minerals. It is supposed that ferrohastingsite syenites were formed as result of fractional

crystallization of syenitic melt, and high concentration of Zr, REE and Y are related with cyclic delivering of mantle fluids (F, CO₂, H₂) in melt which originated from the outer mantle. The Azov Zr-REE deposit is a new type of accumulation of rare-metal elements in endogenic conditions with the typical association of zircon, britholite and fluorite.

Results of study of fluid inclusions in zircon crystals from the Azov deposit are given below (Melnikov et al., 2000). Average size of individuals along *L*₄ is 2–3 mm, however ~ 10 % crystals are 10–15 mm. The color of zircon is pink with a tint of violet, rarer with orange or reddish. Large crystals are usually semi-transparent because of abundance of solid inclusions and fissuring. Prism {110} prevails on crystals, and their heads form dipyrramids {111}, {331}, sometimes {221}.

Indirect and direct signs point out the influence of CO₂-fluid flows on zircon.

In the first group it is necessary to include cracking and appearance of silicate glass in the primary inclusions of magmatic origin (fig. 1). Inclusions cracking occurred as the explosive process (fluid pressure of inclusion > outer pressure) because among located near inclusions only large inclusions crack.

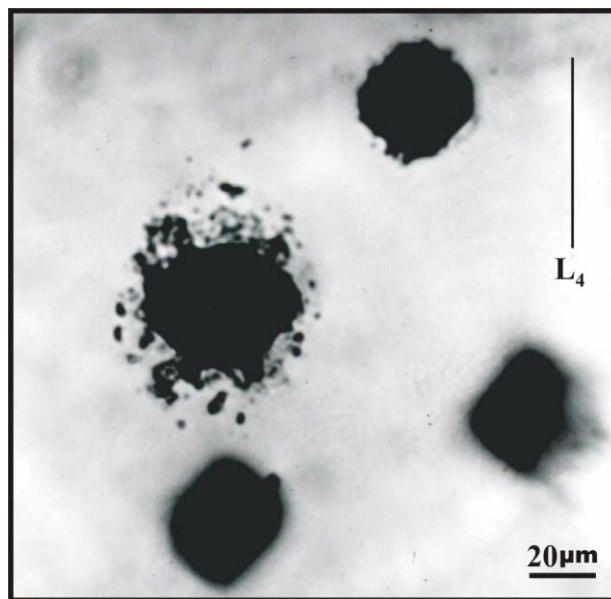


Figure 1. Cracked glass inclusion in zircon crystal. Inclusions of smaller size are not cracked.

Occurrence of CO₂-fluid in wide temperature interval of forming of the Azov deposit is the direct sign. The CO₂ phase in the secondary fluid inclusions associates both with the phase of silicate glass and liquid solution, in particular high-concentrated saline solution. Fixed inclusions with CO₂-phase indicate on the temperature change probably during relatively short time interval.

The CO₂-rich homogeneous inclusions (Kaluzhnyj, 1982) are syngenetic with melt inclusions and characterized with:

temperature of triple point of CO₂-solution

$$T_{tp} = -57.7... - 57.4 \pm 0.2^\circ\text{C};$$

temperature of homogenization of CO₂-phase

$$T_h = +17.5... + 24.7... + 27.0 \pm 0.2^\circ\text{C};$$

density of CO₂ liquid solution

$$\rho = 0.79 ... 0.67\text{--}0.70 \text{ g/cm}^3.$$

On the CO₂ *PT*-diagram pressure of 520–450 – 350–380 MPa corresponds to the temperature 1000–1200°C on the isochors of these densities.

High thermobaric flows of CO₂-fluid are presented with not pure CO₂, but different components solution, because of T_{tp} of CO₂-solution of inclusions differs from T_{tp} of pure CO₂. Value ρ corresponds to density of pure CO₂ by T_h .

The findings of inclusions of liquid saline high-concentrated solution, enriched with carbon dioxide, are very seldom. The secondary inclusion of water solution (≈ 50 volume %) and liquid CO₂ solution is characterized with:

$$T_{tp} = -58.6 \pm 0.2^\circ\text{C},$$

$$T_h = 0.0 \pm 0.2^\circ\text{C},$$

$$\rho = 0.91 \text{ g/cm}^3.$$

Pressure and temperature of inclusion of water solution with 48 wt.% CO₂ correspond approximately 300°C and 70 MPa (Kaluzhnyj, 1982).

Conclusions

Glass is an original speedometer which indicates on high speed of rock's cooling-down. Investigated zircons were taken from macrocrystalline rocks of the area, therefore it is evidently that only the small masses of matter may cool down quickly and rocks warming up to the high temperatures was also local. It caused not only content melting of already crystalline inclusions and appearance of glass in zircon crystals but also their cracking. Inclusions cracking occurred as the explosive process (fluid pressure of inclusion > outer pressure) because among located near inclusions only large inclusions crack. On the basis of findings of the secondary syngenetic melt and CO₂ fluid inclusions of homogeneous trapping it is possible to assert that, undoubtedly, high thermobaric flows of CO₂ fluid were material transporter of such high temperatures. Most

probably they are products of basal magma degassing. Within the deposit such situation could be realized during tectonic dislocations and forming of dike rock complex here.

On some areas of the deposit CO₂ fluids and water solutions enriched with CO₂ participated actively in britholite substituting with carbonate minerals (bastnasite, synchysite and others) and fluorite, and also in formation of siderite which has considerable distribution within the deposit.

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FLUID INCLUSIONS AND H-O ISOTOPES OF GUQIONG AG-AU POLYMETALLIC DEPOSIT IN SOUTHERN TIBET, CHINA

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Introduction

Located to the south of the east section of the Yarlung Zangbo suture zone in southern Tibet, China (Fig. 1), the Guqiong Ag-Au polymetallic deposit (altitude ~5200 to 5500 m; total resource ~Ag 173 t @ 272.2 g/t, Au 4 t @ 6.07 g/t, Pb 9938 t @ 1.98% & Zn 8212 t @ 1.39%) is a recent significant discovery after the large scale Mayum gold deposit in the west section of the Yarlung Zangbo suture zone (Wen et al., 2006; Duoqi et al., 2009; Jiang et al., 2009), and the Bangbu orogenic gold deposit in the east section (Sun et al., 2010). The geochemical characteristics and genesis of the Guqiong deposit is still unreported.

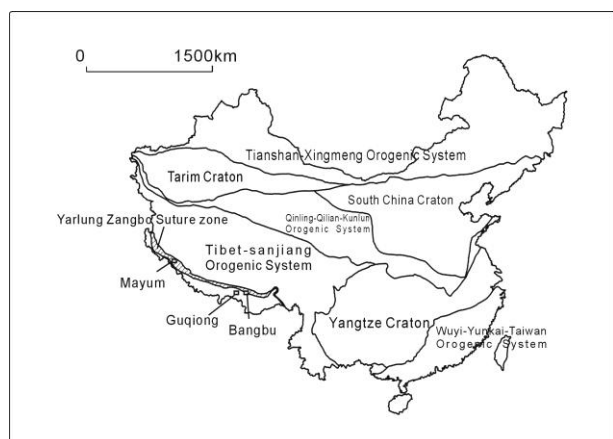


Figure 1. Tectonic setting of the Guqiong deposit (modified after Pan et al., 2009).

Geological background and deposit geology

Rocks at Guqiong are mostly made up of Triassic to Cretaceous low-grade metamorphic, intensely folded clastic sedimentary rocks, and Cretaceous diabase. The ore bodies of the Guqiong deposit are controlled by the secondary brittle fractures of a large-scale brittle-ductile shear zone. Numbers of mafic dykes cropped out along the shear zone and its secondary fractures, implying that the shear zone is a lithospheric fault.

The majority of host rocks for the mineralization at Guqiong altered Cretaceous diabase. Ore forming elements Ag, Au, Pb and Zn occur primarily within sulphide-bearing quartz veins. Ore minerals include electrum, silver-bearing tetrahedrite, pyrite, galena, sphalerite and arsenopyrite, etc.

The main alterations of the Guqiong deposit include sulfidation, sericitization and carbonatization, etc.

Fluid inclusions

Three major types of fluid inclusion were identified in the ore-bearing quartz veins of the Guqiong deposit: liquid aqueous inclusions (type I), CO₂ brine inclusions (type II) and pure gaseous hydrocarbon inclusions (type III) (Fig. 2).

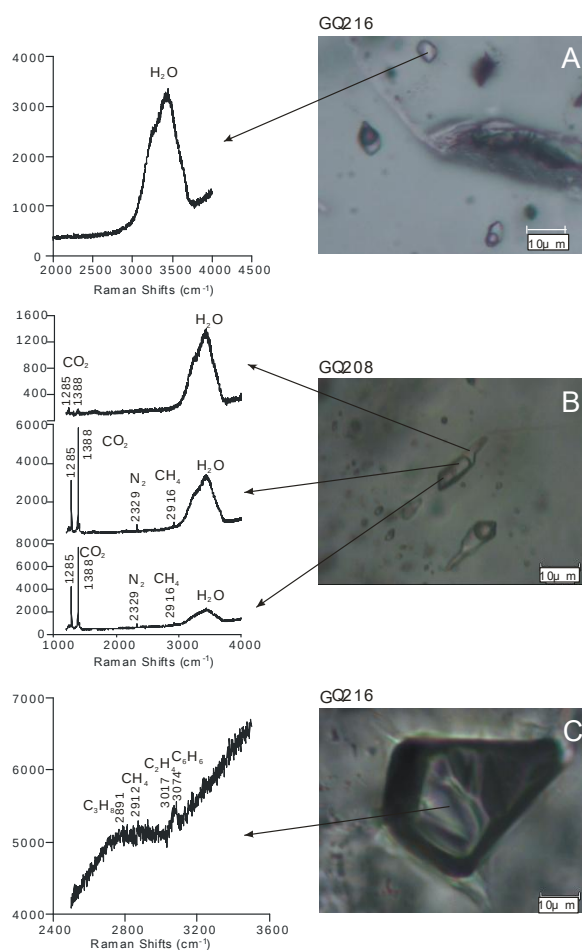


Figure 2. Laser Raman spectrum of fluid inclusions from the Guqiong deposit. A. type I fluid inclusions (H₂O), B. type II fluid inclusions (CO₂, with a little N₂, H₂O and CH₄), C. type III fluid inclusions (C_mH_n).

Microthermometric measurements and Laser Raman analyses show that the ore-forming fluids of the Guqiong deposit is featured by high content of CO₂, low salinity (4.2~6.2 wt.% NaCl_{eq}) and low to

moderate temperature (184.3–338.1°C), which are similar to those of typical orogenic gold deposits (Groves et al., 1998; Goldfarb et al., 2004).

H-O isotopes

The $\delta^{18}\text{O}$ values measured for the ore-bearing quartz from the Guqiong deposit range between 19.0 and 20.7 per mil; the estimated $\delta^{18}\text{O}$ fluid values range from 8.6 to 12.5 per mil (Tab.1). The δD of the fluid inclusions shows a broad range between –172.3 and –113.9 per mil, which suggests that the ore-forming fluid is primarily crust-derived, with a contribution from devolatilization of organic matter from the sedimentary rocks (Fig. 3). It is accordingly to the rock types in the area and the shallow formation depth of the Guqiong deposit.

Table 1. δD – $\delta^{18}\text{O}$ isotopic compositions (‰, SMOW) of fluid inclusions in ore-bearing quartz veins from the Guqiong deposit.

Sample Number	Sample Name	δD	$\delta^{18}\text{O}_\text{Q}^*$	$T_\text{h}^{**} (^\circ\text{C})$	$\delta^{18}\text{O}_\text{w}^{***}$
GQ002		–172.3	20.7	257.9	12.1
GQ003	ore-bearing quartz veins	–155.2	19.0	224.6	8.8
GQ006		–164.2	20.5	257.9	11.9
GQ008		–138.9	19.1	304.2	12.4
GQ009		–113.9	20.6	284.8	13.1

* $\delta^{18}\text{O}$ (‰) of quartz; ** T_h represents homogenization temperature of fluid inclusions; *** $\delta^{18}\text{O}_\text{w}$ (‰) of fluids calculated based on the measured $\delta^{18}\text{O}$ of quartz, homogenization temperature of fluid inclusions, and equilibrium oxygen isotope fractionation between quartz and water, $\Delta_{\text{Q-H}_2\text{O}}=3.38\times 10^6/T^2-3.4$ (Clayton, et al., 1972).

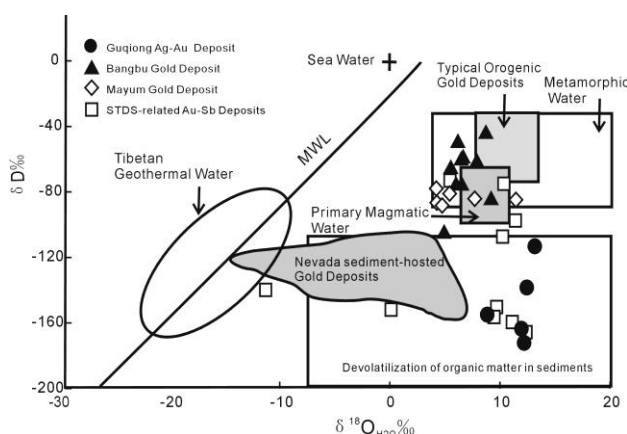


Figure 3. Plot of δD - $\delta^{18}\text{O}$ for ore forming fluids from the Guqiong Ag-Au deposit (modified after Sheppard, 1986; Goldfarb et al., 2004; Field et al., 1985; Zheng et al., 1982; Wen et al., 2006; Yang et al., 2006).

Discussion and conclusions

Geologic and geochemical features of the Guqiong deposit are basically consistent with typical orogenic gold deposits. The ore-forming elements were deposited in the shallow part of the tectonic fracture zone, which was dominated by orogenic system.

During the collision between the Indian and

Asian plate, large-scale vertical lithospheric shear zones were formed, and the lower crust derived CO_2 -rich fluid mixed with the hydrocarbon-bearing formation water derived devolatilization of organic matter in the sedimentary rocks. The mixed ore-forming fluids migrated to the secondary brittle structures in the shear zone, and finally precipitated sulfide quartz ores due to the decline of temperature and pressure.

Acknowledgements

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METAMORPHIC CARBONIC FLUIDS IN VMS DEPOSITS, KELAN VOLCANIC BASIN, ALTAIDES, NORTH XINJIANG, CHINA

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Introduction

Carbonic fluid inclusions are non-aqueous trappings in the system $\text{CO}_2\text{-CH}_4\text{-N}_2$ (van den Kerkhof, Thiery, 2001). In addition to mantle sources, pure CO_2 inclusions are commonly associated with metamorphism, and they are typically found in high-grade metamorphic rocks such as granulites (Roedder, 1984). Abundant carbonic inclusions have recently been recognized in some gold deposits such as in the Ashanti, Sarekoubu and Red Lake gold districts (Schmidt Mumm et al., 1997; Xu et al., 2005; Chi et al., 2006). Carbonic fluid inclusions are also present in metamorphosed VMS deposits. Here we give an example from southern Altaides in northwest China.

Geological setting

The southern margin of the Altai Mountains in Xinjiang is one of the most important metallogenic provinces in China with distinct mineralizing episodes related to sedimentary deposition, magmatic activity, and metamorphism. The Kelan volcano-sedimentary basin is the largest one and hosts the Tiemurte Zn-Pb(Cu) and the Dadonggou Zn-Pb VMS deposits (Fig. 1).

The Tiemurte and the Dadonggou deposits are comprised of several lensoidal banded and mineralized layers. The deposits are controlled by the Abagong-Kurti fault, occurring in the metasedimentary strata of the lower Devonian Kangbutiebao formation in the hanging-wall of the fault. The immediate host rocks to the deposit are chlorite-quartz schist, marble and banded calc-silicates. Three paragenetic stages of deposit formation and subsequent veining are recognized. The earliest stage (I) is the formation of disseminated to massive sphalerite and galena from seafloor hydrothermal activity. The second stage (II) is characterized by sulfide-quartz veins that are foliation parallel and likely formed during early regional metamorphism. The third stage (III) is characterized by much younger chalcopryrite-bearing quartz veins that cross-cut the Zn-Pb massive sulfides.

Fluid inclusions

Quartz samples from the stage II and stage III mineralization at the Tiemurte and the stage II

quartz at the Dadonggou were studied. The foliated sulfide-quartz veins (Q1) relating to synorogenic metamorphism and late chalcopryrite-bearing quartz veins (Q2) cutting the schist related to a younger metamorphic overprinting event.

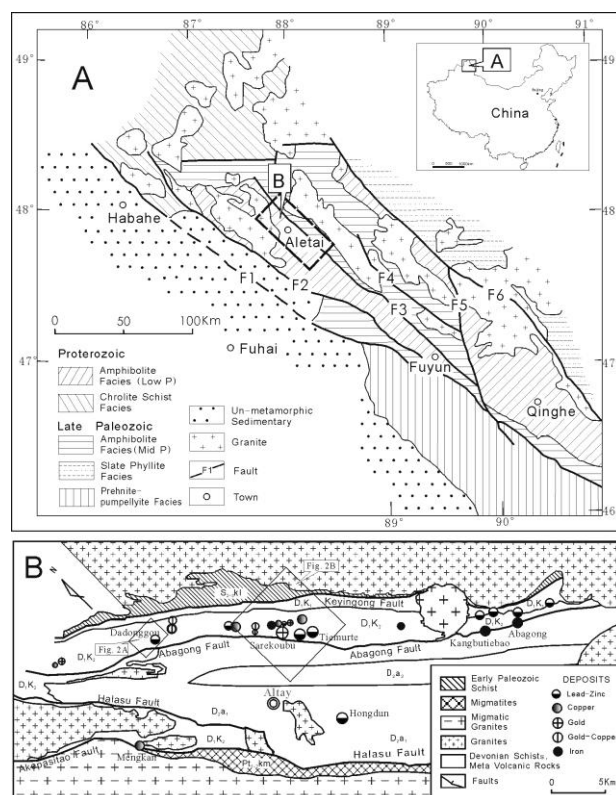


Figure 1. Regional map of the Chinese Altaides (A) and the Devonian Kelan Basin (B). Modified from: (A) - Liu et al. (2003); (B) - Yin et al. (2005).

Carbonic ($\text{CO}_2\text{-CH}_4\text{-N}_2$) fluid inclusions are ubiquitous in the Q1 and Q2 veins (Fig. 2). A few carbonic fluid inclusions may be primary and some may be pseudosecondary, whereas a large number of carbonic fluid inclusions are secondary and can be identified as two generations representing later events. A microthermometry study shows that primary carbonic fluid inclusions in Q1 and Q2 have $T_{m\text{CO}_2}$ ranging from $-64.5\sim-59.4^\circ\text{C}$ with $Th_{\text{CO}_2} = -13.4 - +18.6^\circ\text{C}$. The secondary carbonic fluid inclusions exhibit two behaviors when cooling and heating: the $T_{m\text{CO}_2}$ of the first group (L_{CO_2}) ranges from -63.3 to -57.7°C , and that of the second group ($L_{\text{CO}_2\text{-CH}_4\text{-N}_2}$) ranges from -83.4 to -61°C . The second group of carbonic fluids has much higher CH_4 and/or N_2 proportions than the first group.

More than 90 carbonic inclusions were analyzed by laser Raman microprobe. The data show that all analyzed inclusions are water-free carbonic inclusions. Most of them are CO₂-N₂ inclusions, some are pure CO₂ inclusions, and some are CH₄-N₂ inclusions.

The trapping temperatures for the carbonic inclusions have been estimated to be 243.1-412.1°C (Tiemurte) and 216-430°C (Dadonggou) based on some L_{CO2}-L_{H2O} inclusions associated with carbonic inclusions, and the trapping pressures have been estimated to be 120-340MPa, which were consistent with deformation *P-T* conditions of quartz by X-ray petrofabric (Zang et al., 2007) (Fig. 3). The isochore range calculated for the highest density carbonic inclusions is consistent with the *P-T* condition of garnet metamorphic zone (Zhang, et al., 2007), whereas that calculated for the mid-low density carbonic inclusions is consistent with the *P-T* condition of the biotite metamorphic zone (Fig.3).

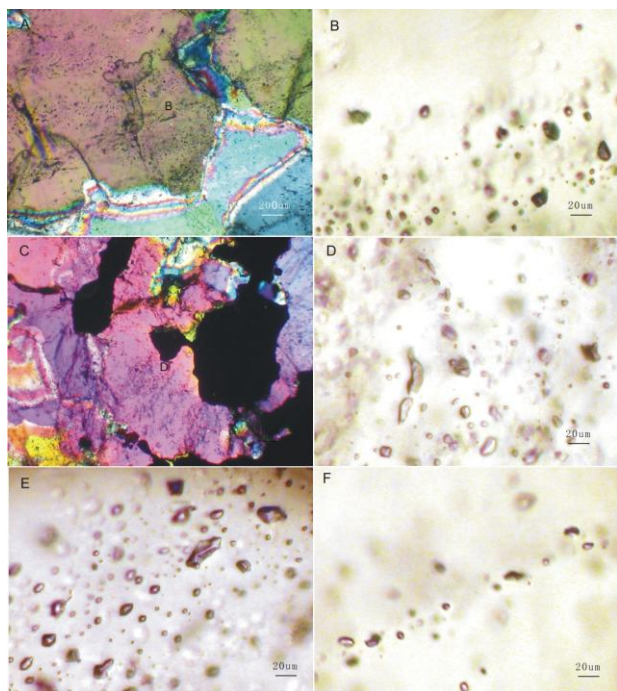


Figure 2. Carbonic fluid inclusions in vein quartz of the Tiemurte and Dadonggou deposits, Kelan Basin, Altaides, China.

A and B - Secondary carbonic inclusions cutting across quartz grains, Tiemurte, TM205; C and D - Pseudosecondary carbonic inclusions in quartz of Cp-Q vein, Tiemurte, TM204; E - Secondary carbonic inclusions in grey quartz vein, Dadonggou, DD-3; F - Secondary carbonic inclusions in striped pyrite-quartz vein, Dadonggou, DD-34.

Conclusions

The zinc-lead-(copper) VMS deposits in the Devonian Kelan Basin and enclosing rocks were subsequently metamorphosed and overprinted by synmetamorphic foliation-parallel sulfide-quartz veins and post-peak metamorphic quartz veins that cross-cut the deformed and metamorphosed ores and the schistosity. Carbonic fluid inclusions are

ubiquitous in both the synmetamorphic and post-peak metamorphic quartz veins. They were not a part of an ore producing system but represent a much younger synorogenic metamorphism which may have contributed to orogenic gold during Early Carboniferous to Early Permian.

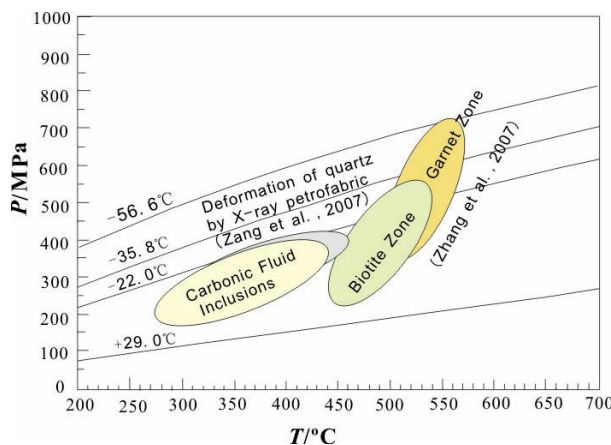


Figure 3. The *P-T* conditions of carbonic fluid trapping and metamorphic zones in the Kelan Basin.

Four curves in the diagram are isochores for the system CO₂ (after van den Kerkhof, Thiéry, 2001), and the data above the isochores are homogenization temperatures for carbonic inclusions.

Acknowledgements

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TEM-EDS STUDY OF NANO-INCLUSIONS IN CLINOPYROXENE (AUGITE) PHENOCRYST IN BASALTS, BARREN ISLAND, INDIA

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Introduction

The nanoinclusions were observed in augite phenocrysts in basalts of the Barren Island volcanic eruption. During crystallization process, the melt inclusions must have been trapped inside the host minerals as primary inclusions. During sudden cooling of magma at atmospheric/surface temperature nanoinclusions must have been got entrapped as amorphous (noncrystalline) melt inclusions (AMI) or glassy inclusions (GIs) and crystalline melt inclusions (CMIs).

Studied area

The Barren Island (BI) is a part of the Andaman and Nicobar chain of islands in the Andaman Sea, Indian Ocean. It has an aerial extent of about 10 sq km. The island rises from a depth of about 2250 m from sea floor and attains a maximum elevation of 305 m above sea level.

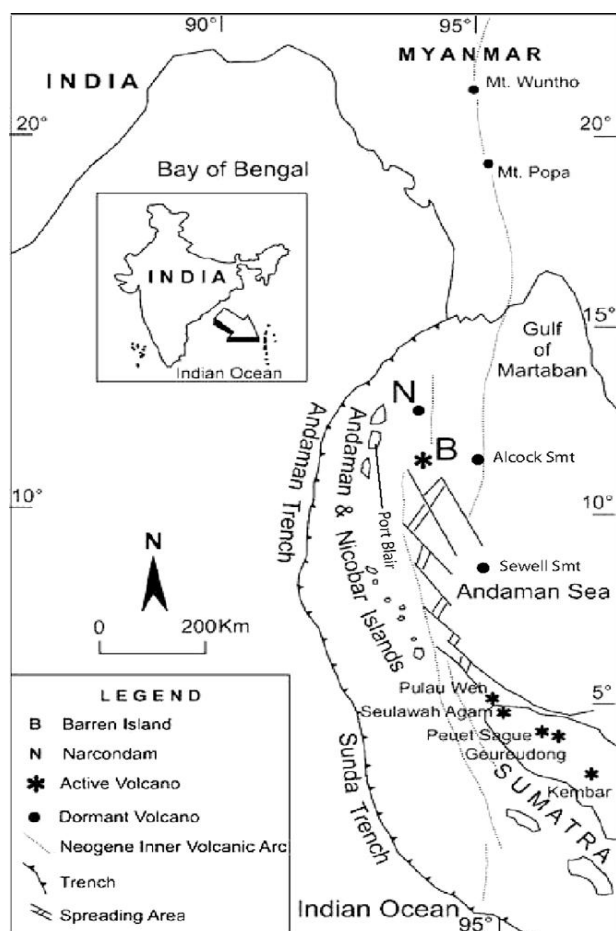


Figure 1. The Barren Island on the Myanmar-Andaman-Sumatra volcanic arc in the Andaman Sea, Indian Ocean. (modified after Rodolfo, 1969).

Methodology

TEM studies were performed using a JEOL JEM-2100F, high-resolution analytical transmission electron microscope, which has been developed to achieve the highest image quality and the highest analytical performance in the 200 kV with a probe size under 0.5 nm. This investigation was carried out in the SAIF, IIT Bombay. Here, the TEM unit is equipped with EDS and CCD-camera.

Clinopyroxene (augite) megacrysts were separated with the help of 10-x lens and washed with isopropyl alcohol (IPA) and later dried at 60-70°C in oven. These grains were then taken for the TEM study at the TEM lab, SAIF, IIT Bombay.

Petrographic study

Clinopyroxene (augite) employed for present study was exhibiting subhedral to rectangular lath shape with high relief in polarized light and anisotropism between cross nichols with first order red to oranges colours (Fig. 2). The size of selected grain ranges from 1 to 5 mm. Between cross nichols these augite phenocrysts exhibited polysynthetic twinning with parallel cleavage and extinction angle around 38-41°.

TEM study of nanoinclusions

TEM-EDS is useful analytical instrument, which provides chemical and structural information of NIs trapped within the host minerals. It also gives information about the heterogeneities in single individual mineral grain. The crystalline and amorphous natures of the nanoinclusions are confirmed by the selected area diffraction pattern (SAED). Therefore, we could use terms as crystalline nanoinclusions (CMI) and amorphous nanoinclusions (AMI) during further discussion (Fig. 3).

The studied nanoinclusions were extremely fine (70-80 nm), with variation in chemical composition (Table 1). The SAED of amorphous inclusions shows weak diffuse diffraction rings where as in crystalline inclusions shows distinct rings (Fig. 3).

Shape and size

The shape of the NIs were found to be oval, equant and some of them were irregular in nature, and size ranges from 2 nm to 80 nm.

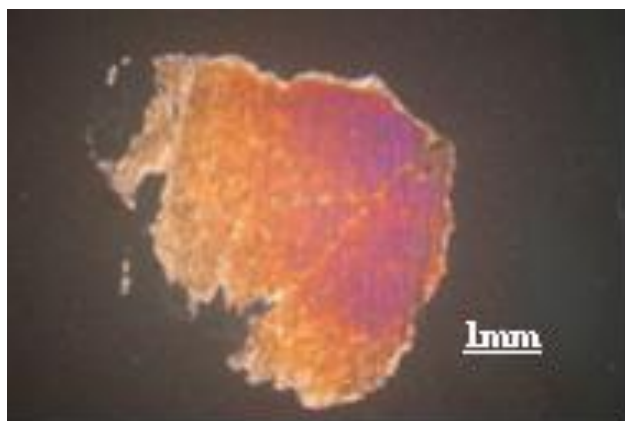


Figure 2. Separated clinopyroxene (augite) phenocryst.

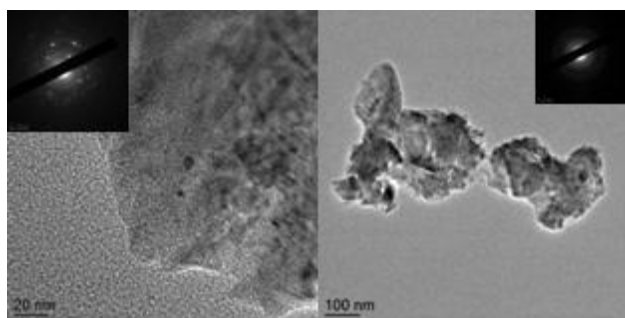


Figure 3. a) BF (Bright field) image of typical region of nanocrystalline material with (SAED) electron diffraction pattern; b) BF-TEM image of typical amorphous nanoinclusion with (SAED) electron diffraction pattern.

Table 1. Chemical composition (wt.%) of nanoinclusions by TEM-EDS.

Sample	1	2	3
SiO ₂	10.74	0.70	22.96
TiO ₂	0.10	0.00	0.00
Cr ₂ O ₃	0.31	1.74	0.13
Al ₂ O ₃	1.62	1.04	0.61
FeO	1.11	5.56	8.13
MnO	0.00	0.00	0.12
MgO	2.66	0.25	23.04
CaO	0.91	11.63	22.70
CoO	0.16	0.58	0.09
Na ₂ O	0.06	0.02	0.00
Cl	0.04	0.14	0.00
Total	20.47	10.12	55.03

Discussion

On the basis of TEM-EDS observations, nanoinclusions within host augite appeared to be associated with chlorite, Ti and Cr. A few of the NIs, there was variation in Al₂O₃, SiO₂, and MgO concentration. In addition, the presence of volatile like chlorine in NIs pointing towards the role of volcanic eruptions as well as in transportation of variety of metal ions (Table 1).

During TEM-EDS analysis of crystalline and amorphous nanoinclusions, surprisingly same

chemical composition was found with variation in NIs shapes and sizes. This compositional similarity may be because of individual crystallites in the nanocrystalline region could be the product of the Barren Island volcanic eruption.

Conclusions

This investigation of the nanoinclusions in augite was a systematic and first time approach, which can be used to study the chemical variation at nano-scale within a single crystal/grain of natural minerals occurring in the Barren Island volcanic rocks. It was confirmed that the amorphous or glassy type nanoinclusions must have been formed due to rapid cooling (quenching), where as CMIs must have been formed due to slow cooling rate of the Barren Island volcanic eruption in recent past.

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THERMODYNAMIC CONDITIONS OF EARLY SERPENTINE FORMATION WITH HYDROCARBONIC FLUID ASSOCIATION

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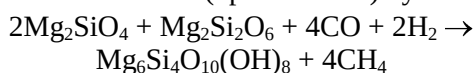
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Introduction

Research was conducted in the northwest active continental margin of the Pacific: Sakhalin, Kamchatka, Koriakskiy range, Karaginy Island, Shirshova range in the Bering Sea. Different types of ultrabasite serpentinization were studied: early pseudomorphous and multistage hydrothermal metasomatic, superimposed types. Stages and conditions of serpentinization and subsequent hydrothermal metasomatic transformation of ultrabasites in various structural tectonic positions were traced. Initial generations of serpentinite of early non-magnetitic serpentinization were studied. They are represented in apoharzburgite serpentinite common in the central non-dislocated parts of dunite-harzburgite massif of an area of 42 km², which is considered to be the most ancient mantle complex of ophiolite.

Hydrogen and methane in serpentines of ophiolite diapir

In the process of early loop-shaped serpentinization, antigorite serpentinite with elementary cell parameter $a = 35.5 \text{ \AA}$ and a natural melt of iron and nickel of taenite composition in the form of smallest inclusions (2.5 μm) in antigorite were formed at the expense of olivine. Very fine texture of antigorite zone and direct replacement of olivine by antigorite, then the antigorite in the hollow of the loop by coarse laminated lizardite and the latter in its turn by linear laminated lizardite of the second generation suggests early formation of antigorite directly by olivine. The formation of antigorite on conditions of mantle serpentinization at depths of 40–50 km (up to 100 km) by reaction



is supported by experimental, thermodynamic ($T=450\text{--}600^\circ\text{C}$, $P=13\text{--}16 \text{ kbar}$) and balance calculations (Yurkova, 1991).

The highest content of H_2 , CH_4 in harzburgite serpentinite (230 mmole/kg of rock) are characteristic of apoolivine antigorite of early generation (Table 1). Hydrogen high content in harzburgite (800 mmole/kg of rock) is associated with olivine. Hydrogen amount decreases with lizardite replacing antigorite (150 mmole/kg of rock) and in lizardite of breakings through forming large loops with long-lived ways of fluid migration in the middle (140 mmole/kg of rock) and reduces to zero in bastite lizardite (Table 1.).

Table 1. Contents of hydrogen and methane (in mmol/kg) and Fe^{2+} - Fe^{3+} in serpentinite and serpentinite.

Serpentine and Serpentinite	Mantle		Crust-pseudomorphous		
	Olv	251a	251b	251c	251d
H_2	800	230	150	140	0.0
CH_4	-	30	15	20	15
Fe^{2+}	0.19	0.22	0.00	0.00	0.44
Fe^{3+}	0.00	0.14	0.44	0.47	0.18

Olv – olivine; 251a – antigorite; 251b – lizardite of early generation; 251c – lizardite of late generation; 251d – bastite.

The association of antigorite, which contains iron in predominant bivalent state, with iron-nickel was formed in reduced conditions. Carbon oxide suggests reduced conditions of the environment where serpentinization processes went on. In these conditions hydrogen formation is impossible at the expense of partial oxidation of bivalent iron, what have been predicted by some researchers (Charlou et al., 2002). In our experiments it is supported by a lacking of correlation between FeO content in samples (improved from data of microanalysis with the use of the Mössbauer spectroscopy) and the amount of hydrogen emission.

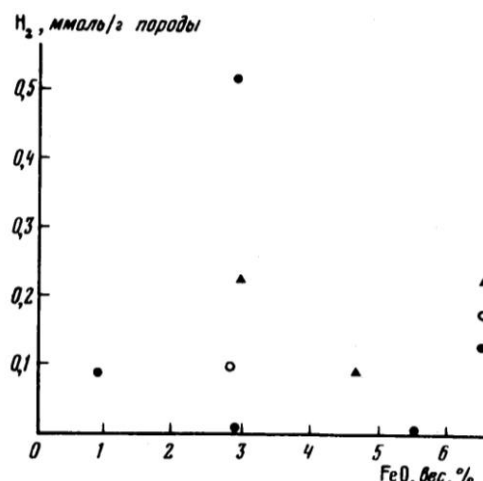


Figure 1. Correlation of FeO and H_2 in serpentinite: 1 – antigorite, 2 – lizardite, 3 – bulk serpentinite.

These data and mainly coincidence of H_2 and CH_4 emission in the process of heating samples allow us to assume that predominant part of hydrogen cannot be attributed to autooxidation of Fe^{2+} ions during serpentinite heating and was originally contained in the minerals under investigation. The rise and transformation of deep

hydrocarbon fluids in the regions under investigation are associated with the formation of ophiolite diapir in the transition zone of primitive island arc-trench above the Benioff zone (Yurkova, Voronin, 2006). Magmatism evolution is traced from abyssal facies (lherzolite, gabbro-norite) to hypabyssal (dike series of diabase and gabbro-diabase, plagiogranite intrusions) and further to effusive underwater facies (spilite, quartz keratophyre). In addition, some researchers corroborate diapir intrusions of serpentinized ultrabasites in the frontal areas of island arcs above the Benioff zone in the Japan and Mariana island arc systems (Maekawa et al., 2001; Maruyama, 1997).

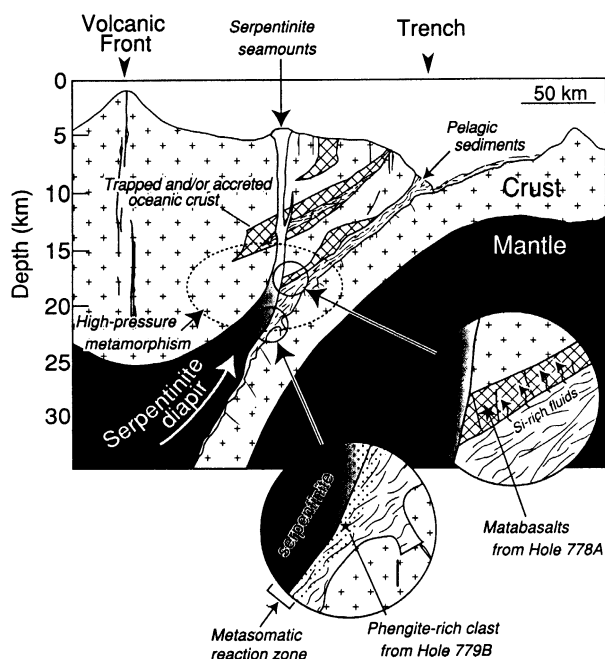


Figure 2. Schematic cross-section showing the tectonic framework of the Mariana arc-trench system. Serpentine diapir may continue to serpentinized wedge mantle at a depth of 30-25 km. It must contain trapped clastic and xenolithic fragments originally situated on the pathway of diapir and entrain them in a fault gouge rising to the seafloor.

An ophiolite diapir is exposed on the surface in the Schmidt Peninsula (Sakhalin). The continuation of the diapir or the column of diapirs in the Okhotsk Sea water area is established from zones of intense (2000 gamma) positive magnetic anomalies and gravity anomalies in Bouguer's reduction (88 mgk). The amount of methane of the order of $4 \cdot 10^{13}$ tons is taken out with the diapir. Judging from the data of fluid dynamics studies up to now the flow and discharge of deep hydrocarbon fluids go on in gravitation convection and compression conditions and with ophiolite diapir the rise of which has not been fully completed in the Sea of Okhotsk. These conditions provided the formation of gas hydrate and gas deposits in the Sea

of Okhotsk as a result of migration and transformation of hydrocarbon fluids on shear faults feathering the ophiolite diapir.

The hydrocarbon deposits formed at the final stage of ophiolite generation related with the mantle diapir uplift in the Okhotsk Sea. In increased temperature ($T \geq 350^\circ\text{C}$) and with catalytic activity of finely dispersed serpentine and iron-nickel compounds (taenite, pentlandite) serpentinized hydrocarbon fluids formed all group components of oil, such as normal alkanes, isoalkanes, naphthenes and aromatic hydrocarbons according to the scheme of Ione (2003).

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CARBONATITIC AND SILICIC GROWTH ENVIRONMENTS OF ALLUVIAL DIAMONDS FROM NORTH-EAST OF SIBERIAN PLATFORM

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Introduction

Microinclusions in natural diamonds represent a bulk sample of fluids/melts from which they crystallized (e.g. Navon et al., 1988) and provide a unique opportunity to characterize diamond-forming liquids and to understand their origin and evolution within the mantle. Worldwide comparison of microinclusions in fibrous and cloudy diamonds reveals a wide range of compositions of HDF between three end-members: (i) a silicic end-member rich in water, Si, Al, and K; (ii) a carbonatitic end-member rich in carbonate, Mg, Ca, Fe and K, and (iii) a saline end-member rich in water, Cl and K.

Here we report the composition of microinclusions in fibrous diamonds recovered from alluvial placers in the Ebelyakh area (North-East of Siberian Platform). Up to now, the primary sources of diamonds of these placers have not been established. These results are used to characterize the diamond-forming media to answer whether there is a genetic relationship with kimberlitic diamonds and their host kimberlites.

Samples and methods

Eighteen cubic and rounded crystals, almost opaque due to abundant microinclusions (Fig. 1 a, b), were selected from collections of diamonds (sieve classes -4+3) from the Holomolokh and Istok alluvial placers located in the Ebelyakh river basin. The proportion of such diamonds is high (up to 15% of the examined collections) in the diamond populations from both locations. Most of them have typical resorption features, such as rounded edges, etching channels and tetragonal etch-pits.

The samples were polished into plates along the 110 plane (Fig. 1 c). The size of individual microinclusions observed in the samples is usually less than one micron. X-ray topography (XRT) of most samples revealed “fibrous” internal texture (Fig. 1 d) which is sometimes defined by trains of microinclusions. Some diamonds display concentric zones of varying inclusion density (Fig. 1 c, f). Growth zones of primary near-cubic (cuboid) morphology have been observed in many samples (Fig. 1 c-f). The variations of carbon isotope composition in some diamonds have been studied using SIMS as shown on Fig. 1 e. The observed range of $\delta^{13}\text{C}$ is from -2.5 to -7.1 ‰.

The major-element compositions of the subsurface microinclusions have been determined using EDS. All analyses are normalized to 100% on a carbon free basis (with excess oxygen for chlorine). Major- and trace-element compositions of the bulk microinclusion populations have been quantitatively analyzed by LA-ICP-MS. The abundances of water and carbonates in the diamonds were determined by FTIR.

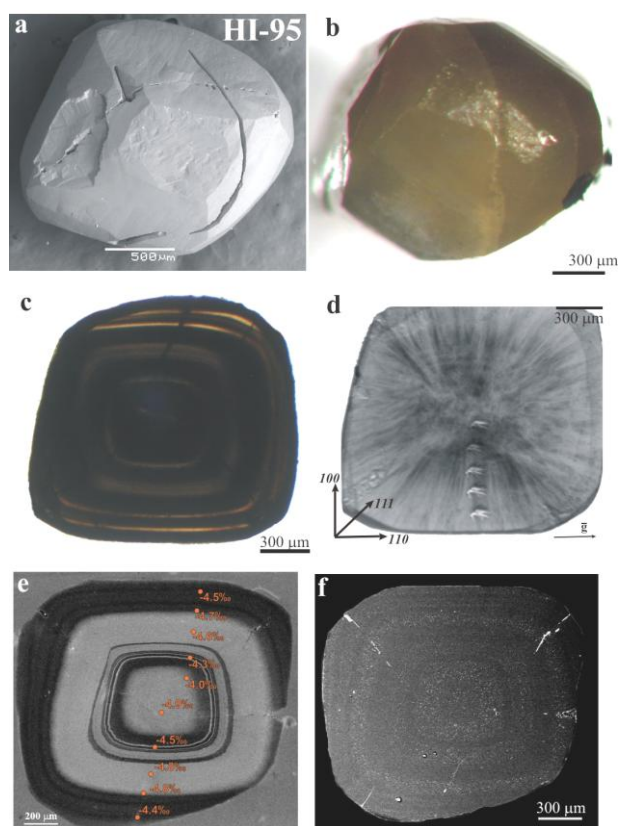


Figure 1. Photomicrographs of microinclusion-bearing diamond (sample HI-95) showing crystal morphology (a – SEM; b – RL) and internal structure (c – TL; d – XRT; e – CL; f – BSE).

Results

The major-element compositions of microinclusions in alluvial diamonds show wide variations (Table 1). Each of the studied diamonds displays some compositional variations among individual microinclusions due to their real chemical variability. However, the standard deviation (σ) of the major element values within most diamonds was usually no more than 10-15%.

Some important inter-element correlations between silica and chlorine content and the

water/carbonate ratio of microinclusions are observed. In comparison with the worldwide database, the fluids/melts in studied diamonds define two groups: (i) silicic and (ii) carbonatitic, only a few of which falls into the starting interval of the carbonatitic to saline range (Fig. 2). The silicic end-member (HI-91), constrained from combined EDS and FTIR data, carries ~80 wt.% silicates, 11 wt.% water, 6 wt.% carbonates and 3 wt.% apatite. The carbonatitic end-member (HI-111) comprises 77 wt.% carbonates, 10 wt.% silicates, 4 wt.% water, 7 wt.% apatite and 2 wt.% halides. The most saline microinclusions consisting of 69 wt.% carbonates, 5 wt.% halides, 11 wt.% silicates, 6 wt.% water and 8 wt.% apatite have been observed in the central part of sample HI-90.

Table 1. The end-members averaged composition of microinclusions in alluvial diamonds (EDS data, wt.%).

Sample	HI-91 n=21	HI-111 n=24	HI-90 center n=19
SiO ₂	64.69	6.23	7.43
TiO ₂	3.03	2.66	2.56
Cr ₂ O ₃	0.00	0.25	0.00
Al ₂ O ₃	9.55	1.72	1.19
FeO	3.01	15.03	4.96
MnO	0.00	0.03	0.00
MgO	2.45	18.84	19.29
CaO	5.67	33.06	28.13
BaO	0.00	0.80	0.29
Na ₂ O	2.62	6.74	7.74
K ₂ O	7.56	5.94	14.64
P ₂ O ₅	1.34	7.06	8.69
Cl	0.08	1.44	5.08
H ₂ O/(H ₂ O+CO ₂)*	0.44	0.06	0.08

Note: *The H₂O/(H₂O+CO₂) molar ratio is calculated from the IR spectrum. CO₂ represents the CO₂ component of carbonates.

Two of studied diamonds have revealed significant compositional differences between microinclusions in the central and peripheral growth zones (linked by arrows in Fig. 2). One of them shows the change of growth media from chloride-carbonate to predominantly carbonatitic (HI-90), and another from carbonatitic to silicic (HI-98).

The trace-element compositions of the microinclusions are generally similar to those of kimberlites and carbonatites, but there are significant differences in major elements: the bulk analyses show significantly higher abundance of alkalis (K and Na). Microinclusions have smooth PM-normalized patterns for the LILE. Some samples show enrichment in Cs and depletion in Sr. The pattern of HFSE in the microinclusions shows general enrichment in Ta and Nb relative to Ti, Zr and Hf. The REE pattern reveals overall high

abundances of the light REE. The La/Dy ratio of the microinclusion decreases from the carbonatitic to the silicic compositions. Many samples with carbonatitic composition have a negative anomaly in Y. The alluvial diamonds have low contents of transition metals and most of them are significantly depleted in Ni and Co.

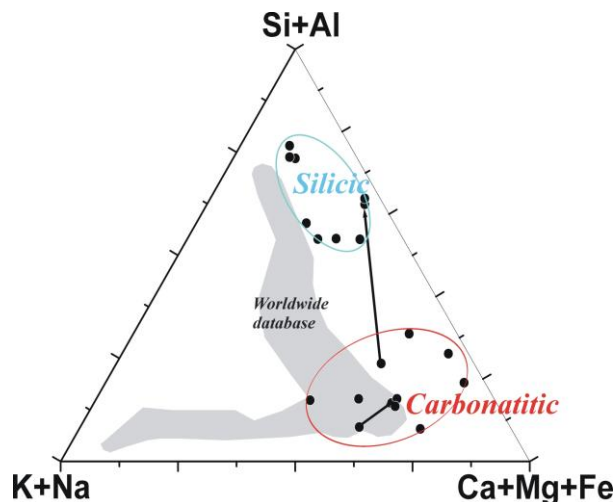


Figure 2. Compositional features (EDS data, molar ratio) of microinclusions in alluvial diamonds from NE of Siberian platform.

Remarks

The observed geochemical features are consistent with a genetic link between the diamond-forming media and ephemeral carbonatitic and silicic liquids (fluids/melts) which may be precursors of the host kimberlite. These fluids/melts may originate either from the metasomatic influx of volatile agents and/or from low-degree partial melting of eclogites and/or peridotites. A general correlation of $\delta^{13}\text{C}$ of diamonds with the relative abundance of water in the microinclusions suggests that carbon isotope compositions are related to the evolution of the parental media. Some elemental variations may be explained by the fractional crystallization of such fluids/melts, or mixing between liquids with different compositions. These processes result in diamond formation and kimberlite generation.

Acknowledgements

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MINERALOGY OF MULTIPHASE SOLID INCLUSIONS IN CHROMIUM SPINELS OF THE MERENSKY REEF, BUSHVELD COMPLEX, SOUTH AFRICA

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Introduction

Chromite in differentiated basic intrusions is associated with the platinum-group minerals (PGM), and is thus important for understanding of origin, evolution and accumulation of PGM in the reef horizons (Naldrett et al., 1986; Cawthorn, Barry, 1992; Finnigan et al., 2008). Origin of reefs and their chromite content in the Bushveld Complex is still under considerable debate. This work contributes to the on-going debate about genetic aspects of the Bushveld chromites by presenting preliminary results on compositions of chromite and chromite-hosted inclusions from the Merensky Reef.

Samples and methods

The samples of chromitites were collected from the normal Merensky Reef in the Dwars River area of the eastern Bushveld Complex. The rock and chromite samples were polished without using water to ensure preservation of water-soluble components (e.g. salts) and analyzed using electron microprobes (Camebax-Micro and JEOL JXA-8100), scanning electron microscopy (LEO 143 OVP EDX Oxford). Bulk composition of vapor components was detected using gas chromatography (LHM-80). All the analyses were carried out in V.S. Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia.

Types of chromites and chromite-hosted inclusions in the Merensky Reef

Chromium spinel in the Merensky Reef of the Bushveld Complex is represented by two morphological and compositional types that occur (1) in thin seams in the basal and upper chromitite seams among coarse-grained pyroxenites and (2) as disseminated grains in the central part of the Reef. The first type is represented by hypidiomorphic and amoeboid grains in association with plagioclase An₈₅₋₇₈. This compositionally homogeneous type contains negative-crystal shaped multiphase inclusions (already described by Li et al. 2005), composed of ortho- and clinopyroxene, K-Na-phlogopite (K₂O - 4.3, Na₂O - 3.3 wt.%), and minor ilmenite, pyrrhotite, pentlandite, chalcopyrite, rutile, zircon, sperrylite, Os-Ir-Ru alloys, native Bi (Fig. 1a-b).

Heating of such silicate-rich inclusions revealed partial melting at 850-1150°C and

formation of the spinifex-like aggregate (SiO₂ - 44.3, TiO₂ - 0.6, Cr₂O₃ - 0.5, Al₂O₃ - 2.7, FeO - 7.0, MgO - 42.5, CaO - 0.3, Na₂O - 0.3, K₂O - 0.4, Cl - 0.2 wt.%) and plagioclase-like glass (SiO₂ - 48.43, Al₂O₃ - 17.4, MgO - <0.05, CaO - 15.2, Na₂O - 2.8, K₂O - <0.05 wt.%) at subsequent quenching. Sulfide minerals melted and formed spherical globules and blebs of mss that included PGE.

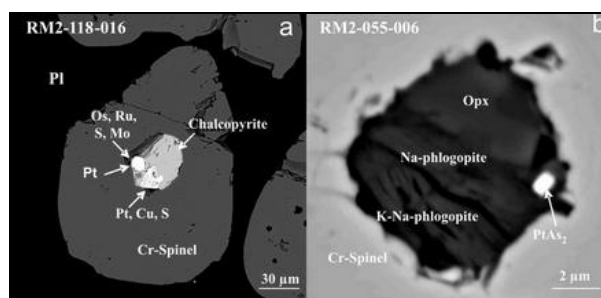


Figure 1. BSE images of (a) PGM-sulfide inclusion and (b) silicate multiphase inclusion in chromium spinel, the basal chromitite seam of the Merensky Reef.

The second type of spinel in the central zone is strongly compositionally heterogeneous, and occurs in association with orthopyroxene En₈₂₋₆₀ as euhedral grains, rims around sulfides, inclusions in sulfides and olivine, and lamellas along the orthopyroxene cleavage planes. The outmost zones of the spinel may contain sulfide inclusions, whereas the inner parts are characterized by negative-crystal shaped multiphase inclusions of carbonate-chloride composition (Fig. 2a-b).

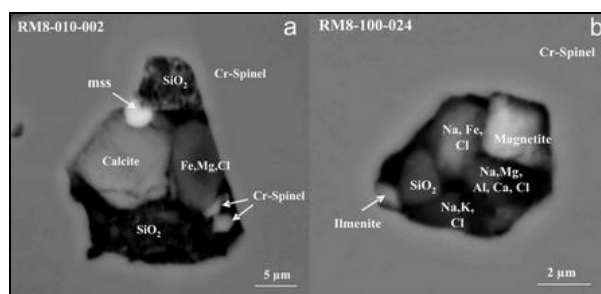


Figure 2. BSE images of (a) carbonate-chloride inclusion with mss bleb and (b) salt inclusion in chromium spinel, the central zone of the Merensky Reef.

This unusual assemblage includes calcite, dolomite, halite, sylvite, anhydrite, K-Na phlogopite, and minor chalcopyrite, pentlandite, sperrylite, Pd minerals, mss blebs, Cl- and REE-rich apatite, quartz, zircon and U-thorianite. The carbonate-chloride inclusions contain H₂O, CO₂,

H₂, N₂, CO, CH₄, C₂H₂, and trace C₃H₈, according to gas-chromatography.

Composition of chromium spinel in the Merensky Reef

Cr-spinel from various zones of the Merensky Reef is compositionally different (Fig. 3). It in the basal horizon is chromite, similar to Cr-spinel in the Upper (Eales et al., 1986), Lower and Middle Groups (Naldrett et al., 2009) of the Critical Zone in the Rustenburg Layered Suite, and does not show any variations across grains. The compositions of spinel grains in the central part of the Reef belong to continuous series from chromite-hercynite in the cores to hercynite-spinel in the rims. A large number of representative analyses (320 in total) do not show compositions that are transitional between those in the basal seam and central zone of the Merensky Reef.

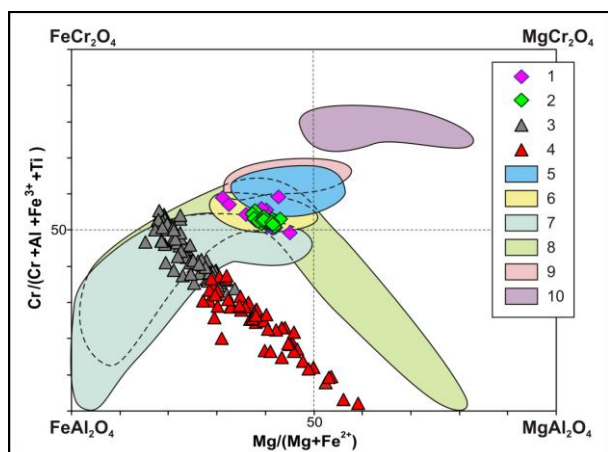


Figure 3. Composition of chromium spinel in the Merensky Reef. Our results: 1 – core and 2 – rim of chromite grains in the basal chromitite seam; 3 – core and 4 – rim of accessory chromite grains for the central zone of the Merensky Reef. Published data on chromites: 5 – Lower and Middle Groups of the Critical Zone (Naldrett et al., 2009); 6 – Upper Group of the Critical Zone (Eales et al., 1986); 7 – Norilsk type intrusions (Ryabov et al., 2000); 8 – Ioko-Dovyren pluton (Kislov, 1998); 9 – Nizhny Tagil complex (Pushkarev et al., 2007); 10 – Kempirsai pluton (Pavlov et al., 1968). Fe³⁺ and Ti are minor components in all spinels.

The compositions of studied chromite, when compared to those of chromites from other layered intrusions, appear to be unique (Fig. 3). Limited similarity is found among chromites from the Norilsk type intrusions and Ioko-Dovyren Layered Pluton, however, the Merensky Reef is still exceptional among other Pt-Cu-Ni-bearing differentiated suites.

Conclusions

Compositional variability of chromite from different parts of the Reef, and different types of spinel-hosted inclusions suggest different physical and chemical conditions of crystallization. The

chromite grains of both basal and upper seams of the Merensky Reef were possibly transported to their present-day position by a silicate liquid from a deep-seated magma chamber like other chromitite horizons in the Critical Zone of the Rustenburg Layered Suite, and as such are “xenocrysts”. The accessory chromite-hercynitic zoned crystals in the central part of the Merensky Reef crystallized *in-situ* from a residual volatile-rich liquid that evolved towards enrichment in carbonate-chloride components.

Acknowledgements

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COMPOSITION, METAL CONTENT AND AGE OF MAGMATOGENE FLUIDS OF THE PLATREEF: FLUID INCLUSION DATA, BUSHVELD COMPLEX, SOUTH AFRICA

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Introduction

Felsitic veins composed of quartz-feldspar simplexes cross-cut ultramafic rocks of the Platreef (Armitage et al., 2002). These veins contain a number of accessory minerals included in quartz: sulphides, REE-bearing Ir-Os-alloys, cooperite (PtS), native silver, zircon, monazite, U-Th- and Nb-Ti-bearing phases (Hutchinson, Kinnaird, 2005). According to ICP-MS and XRF analyses the veins are enriched in metals: 230 ppb Au, 1440 ppb Pt, 1665 ppb Pd, 2826 ppm Cu and 2063 ppm Ni. It has been considered that felsitic liquids originated from prolonged crystallization of magmas and/or contamination of a mafic melt by the sedimentary country rocks or the basement granitic gneiss (Kinnaird et al., 2005). The formation of the felsitic veins, defined by a zircon age of 2053.7 ± 3.2 Ma, corresponded to the age of main magmatic activity at the Bushveld Complex (Kinnaird et al., 2005). The felsitic liquids and related fluids, while percolating through the Platreef rocks, are thought to be responsible for redistribution of initial magmatic sulphides and PGM (Armitage et al., 2002; Kinnaird et al., 2005; Hutchinson, Kinnaird, 2005).

This idea was tested in our study of fluid and sulphide inclusions hosted in quartz and calcite from the Platreef felsitic veins. We used the methods of thermometric studies, Raman-spectroscopy, scanning electron microscopy and laser ablation ICP-MS.

Sample description

The samples of the felsitic veins with quartz-feldspar symplectites were collected from the Sandsloot open-pit mine and Malatzane Stream, as well as the borehole cores of the Tweefontein Section of the Platreef. Most quartz grains are characterized by disseminated sulphides, REE-phosphates and numerous small fluid inclusions (< 5 µm), unsuitable for detailed studies.

Samples of quartz from a large miarolitic cavity in the pegmatitic quartz-feldspar vein (SS2) in the Sandsloot open-pit mine were found most informative to our study. Quartz SS2 is formed by large (10x8 cm) prismatic, semi-transparent and zoned Brazilian twin crystals of the first generation, overgrown by clear small crystals (up to 1-3 cm).

Fluid inclusion study

Primary multiphase inclusions (L+V+H+1-4S) and coeval vapour-rich inclusions with liquid CO₂ are present in the inner zones of the first generation quartz and form clusters that subparallel twinning. Primary two or three-phase inclusions and syngenetic CO₂-CH₄ gaseous inclusions decorate outer growth zones of this quartz. The second generation quartz hosts aqueous saline inclusions and CH₄-bearing vapour inclusions at the base of the crystals only, so other parts of grains are very clear in appearance. Most fluid inclusions are 10-20 µm, and some are up to 30-50 µm.

The multiphase inclusions usually decrepitated at 250-300°C, before complete homogenization. Similar inclusions have been described in miarolitic and symplectitic quartz of the Merensky Reef (Borisenko et al., 2006). We succeeded in dissolving vapour bubble at 220-200°C in the smaller size multiphase inclusions, however, melting of solid phases were not observed before decrepitation, except partial dissolution of halite at 550°C. If all solid minerals in these inclusions belong to daughter phases, then the total salinity of their parental fluid would be extremely high (~80 wt.% NaCl eq.), which seems unlikely. Scanning electron microscopy of opened multiphase inclusions recorded a number of minerals, such as NaCl, KCl, CaCl₂, MnCl₂, CaCO₃, BaSO₄, REE-aluminosilicate and REE-phosphate.

Syngenetic fluid inclusions with liquid CO₂ are represented by a type L+LCO₂+V. The temperatures of CO₂ melting and homogenization are -57.8/-59.6 and +29.6/+31.0°C, respectively. Homogenization occurred in the vapour phase in most cases, and sometimes a critical behaviour was observed. The pressure of 0.74 kbar was estimated using the average CO₂ density of 0.34 g/cm³ and inferred trapping temperature of 650°C. Complete homogenization of these inclusions occurred at 240-235°C.

The results of the Raman-spectroscopic studies of fluid inclusions suggest the evolution of gaseous phase from essentially CO₂ (first generation quartz) to essentially CH₄ (second generation quartz). The bulk fluid composition evolved from high-temperature oxidized brines with CH₄-CO₂ vapour towards cooler and more reduced saline aqueous solutions with CH₄-rich vapour.

Composition and metal content of fluids

The composition of fluid inclusions in the SS2 quartz (first generation) was studied in the University of Tasmania using LA-ICPMS (New Wave UP-183 laser and AGILENT 7500 mass-spectrometer). Among different types of analyzed inclusions (multiphase L+V+H+1-4S with 29-36% salinity, four-phase L+V+H+S with 30-32% salinity and three-phase L+V+H with 21-23% salinity) the most saline multiphase inclusions are characteristically more metal-enriched. They contain elevated Mn, Fe, Pb, and also Co, Ni, Cu, As, Mo, Sn, Sb, Bi (Fig. 1). The PGE (Pt and Pd) are not present in the contents above the detection limits. All compositions have a deficit of Cl relative to major cations (Na, K and Ca), which suggests presence of other anions (e.g. carbonate). These data confirm the possibility of metal redistribution by the late magmatic fluids.

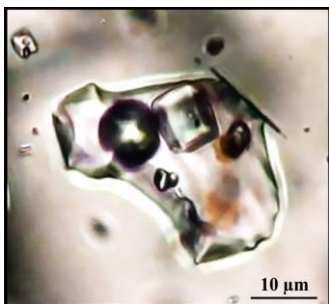


Figure 1. Typical multiphase inclusion in quartz SS2, available for both detailed LA-ICPMS study of metal content and Pb isotope composition of fluids.

High Pb abundances (1000 ppm) in the fluid inclusions permitted quantification of Pb isotope composition, including minor isotope ^{204}Pb . For example, Fig. 2 and 3 demonstrates a typical pattern of the LA-ICPMS signal produced by ablation of numerous fluid inclusions over analysis time. Comparison of Pb isotope ratios in the fluid inclusions with the crustal Pb growth trend produced an age estimate of 2000 ± 70 Ma (c.f. 2054 ± 22 Ma age of the Bushveld Complex, Kinnaird et al., 2005; Hutchinson, Kinnaird, 2005).

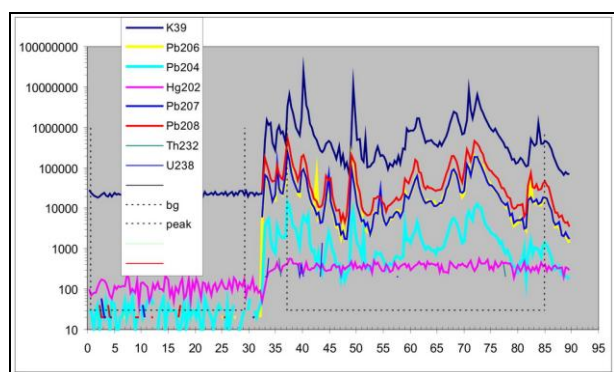


Figure 2. Pb isotope composition of fluid inclusions in quartz SS2 from the Platreef by LA-ICP-MS data.

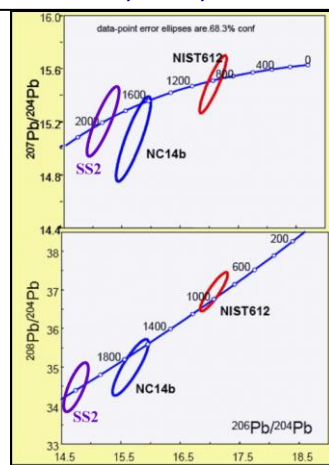


Figure 3. Comparison of Pb isotope ratios in the fluid inclusions of quartz SS2 with the crustal Pb growth trend.

Conclusions

The study of fluid inclusions in quartz from the miarolitic cavity of the pegmatite symplectitic vein resulted in new estimates of physical and chemical characteristics of magma-related fluids at a postcumulus stage of the Platreef formation. The most primitive fluids were trapped by quartz at 600-650°C and >2 kbar. They were represented by heterogeneous oxidized carbonate-chloride solutions (20-80 % salinity) with the methane-carbon dioxide gaseous phase. These fluids evolved into lower temperature, more reduced aqueous solutions with less salinity (< 25%) and the methane gaseous phase. All the above fluid components were immiscible with each other. High-temperature brines carried metals, including high concentrations of Pb, which isotope composition corresponded to crustal Pb at the time of formation of the Platreef symplectitic veins and the Bushveld Complex. High concentrations of metals in quartz-hosted fluid inclusions indicate significant role of carbonate-chloride aqueous fluids in the redistribution of metallic elements, including the PGE, primarily deposited in the magmatic process.

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