

Metal-bearing capacity (Au, Sb, Te, As и Bi) of chloride oxidised heterophase fluids at temperature 700°C and pressure 109–124 MPa

A. A. Borovikov, T. A. Bul'bak, A. S. Borisenko, S. V. Palesskiy
Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk
borovik@uiggm.nsc.ru, taras@uiggm.nsc.ru

Key words: pegmatite, carbonatite, metal-bearing capacity

Citation: Borovikov, A. A., T. A. Bul'bak, A. S. Borisenko, S. V. Palesskiy (2011), Metal-bearing capacity (Au, Sb, Te, As и Bi) of chloride oxidised heterophase fluids at temperatures 700°C and pressure 109–124 MPa, *Vestn. Otd. nauk Zemle*, 3, NZ6015, doi:10.2205/2011NZ000145.

Introduction

Heterophase state of ore-forming fluids have been established for a number of hydrothermal deposits associated with the development of ore-magmatic systems of various geochemical profile such as 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, Krestovsky) deposits [Andreeva, 2000; Borisenko et al., 2006; Naumov et al., 1995; Reif et al., 2004; Zhitova et al., 2004 and many others]. Heterogenization processes are mostly expressed at the Cu-Mo(Au) porphyry deposits, that we can fix in the phase composition of fluid inclusions from the minerals of ore (Fig. 1). The specific feature of porphyry Cu-Mo (Au) deposits is the oxidized ore-forming fluids corresponding to sulphate-sulfide equilibrium.

The investigation of ore elements content in syngenetic gaseous and water-salt inclusions from minerals of ores reveals the contrast distribution of metals between the gas and water-salt phases of heterophase ore-forming fluid during formation of porphyry Cu-Mo(Au) deposits [Borisenko et al., 2006]. The study of physico-chemical conditions, which we consider responsible for the contrast distribution of ore elements between the phases of heterogenic fluids, provides insight into the understanding the reasons of formation of the associated magmatic and hydrothermal mineralization which are considered to be contemporaneous and belonging to the same geochemical profile. Experiments to synthesize fluid inclusions at P-T conditions of separation of heterophase oxidized fluid from magmatic melt allowed us to reveal the main modes in the behavior of ore-forming elements (As, Sb, Te, Au и Bi) in hydrothermal fluid.

Methods and Analytical procedure

The experiments to synthesize fluid inclusions in quartz at various pressures and temperature 700°C are carried out using autoclave technique [Balitskiy, 2008; Kotelnikova, 2008] in order to study the behavior of As, Sb, Te, Au and Bi in heterophase chloride fluid.

The initial matter is represented by colorless prismatic square-section plates of synthetic quartz (2.2–3.4 g crystals with 35–40 mm length).

Optical observations did not reveal fluid inclusions in quartz. Model aqueous solution in Au-ampoules was acidified with HCl and contained NaCl (20 wt.%), Rb- (44 ppm), Cs (430 ppm), Ba – (560 ppm), Te (150 ppm), As (100 ppm), Sb (70 ppm), and Bi (1000 ppm). In addition, Rb, Ba and Cs were introduced in the model aqueous solution as internal standards to estimate As, Sb, Bi, and Au concentrations using LA-ICP-MS. The model solution was prepared using high-purity chemical reagents $H_2TeO_4 \cdot 2H_2O$, $Bi(ClO_4)_3$, and prefabricated Sb and As solutions in HCl. The source of Au was a gold ampoule in which an experiment was carried out. In order to create an excess of silica necessary to quartz growth during an experiment, we used a mixture of ultra-pure amorphous anhydrous silicic acid (SiO_2) and ninehydrate Na metasilicate in mass proportion of 1:2. We used a hematite-magnetite mixture (1:1) of 0.50–0.25 mm fraction as a redox-potential buffer.

Quartz grains, silica and sodium metasilicate were introduced sequentially in the previously annealed Au-ampoule (\varnothing 14 x 50 x 0.5 mm). The buffer mixture was introduced directly into a gold ampoule. On the one hand, this favored to increase of the buffer action time, and on the other hand, this led to the Fe appearance in the fluid which approximated the model solution to the natural ore-

forming fluids of the porphyry ore-forming systems. The solution volume was then determined both from a free space of a container and a fill coefficient of pure water providing a necessary pressure. All ampoules were sealed off by an electric welding using liquid-nitrogen cooling in the air. Ampoule impermeability was controlled by constancy of weight before and after the experiment.

The experiments were carried out in autoclaves of 10 to 20 cm³ volume made of Ni-based high-temperature alloy. Distilled water was used as a medium providing pressure on gold ampoules. An autoclave was heated in a vertical resistance furnace with current control using high-precision PIT-3B thermoregulators. The temperature during the experiment was measured by the chromel-alumel thermocouples introduced in a near-bottom channel and in a lock inside autoclave atop. An accuracy of temperature measurement was $\pm 2^{\circ}\text{C}$, while that of temperature control using thermoregulator was $\pm 6^{\circ}\text{C}$.

The synthesis of fluid and melt inclusions in quartz which crystallized from heterophase medium (aqueous solution-gas phase, silicate melt-aqueous solution-gas phase) was carried out during 5 days in an oxidized alkaline medium at temperature 700°C and pressure varied from 100 to 130 MPa. The temperature gradient along a quartz grain was 1.71°C/cm at temperature 700°C. The pH value indicates an alkaline medium, that is supported by aegirine presence among new phases. The stable experimental conditions were attained during 4 hours and 15 minutes while cooling to room temperature took approximately 12 hours. During the experiments we synthesized two-phase essentially gaseous, three-phase with halite fluid inclusions and melt inclusions which compositionally correspond to supercritical, gaseous and water-salt fluid phases as well as to silicate melt phase of the hydrothermal-magmatic system (Fig. 1).

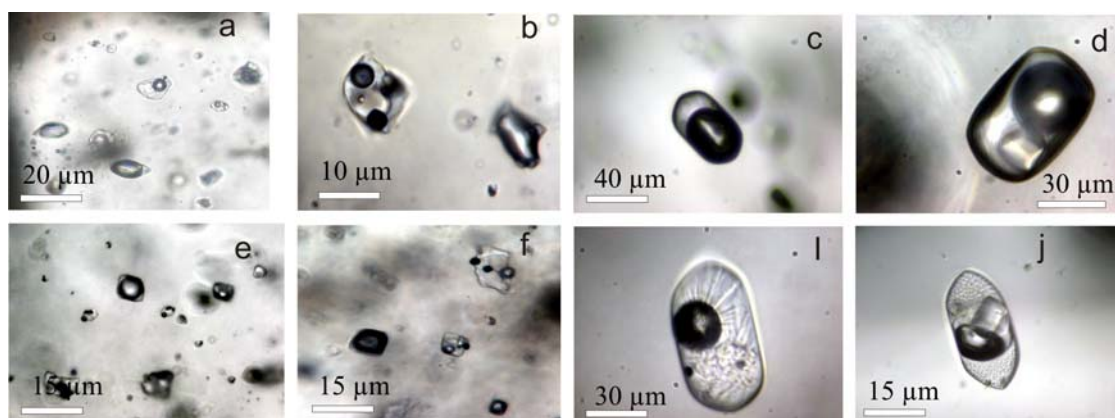


Fig. 1. The examples of trapping of coexisting gaseous and highly-concentrated phases into fluid inclusions in quartz of porphyry Cu-Mo deposits Zhireken (a, b) and Kal'makyr (c, d) and synthesized inclusions: two-phase essentially gaseous (e), three-phase with halite (f), melt partly crystallized (i) inclusions and combined trapping inclusion (j).

Synthetic inclusions study

Solution concentrations in synthesized two- and three-phase fluid inclusions were determined by the ice melting temperature and dissolution temperature of the NaCl crystals in inclusions using cryometry and thermometry techniques (Table 1). Three-phase inclusions trapped in quartz during experiments with low autoclave fill coefficient decrepitated before full dissolution of NaCl crystal. For such inclusions characterized by highest solution concentrations we measured volumes of individual phases. Based on these measurements, we calculated the volumes of solutions and NaCl crystals and then, using concentration values for saturated NaCl solution at 20°C as well as NaCl densities, we calculated NaCl content in such inclusions. The calculated NaCl concentrations showed a tolerable agreement with concentrations obtained by thermometric and extrapolation methods using Sourirajan and Kennedy data, although they have a range of values (Table 1).

During experiments, the ambient pressure was estimated based on calculated NaCl concentrations in gaseous and water-salt phases existed in autoclave at the trapping time together with Sourirajan and Kennedy data for the H₂O-NaCl system at high pressures and temperatures [Sourirajan and Kennedy, 1962]. According to obtained solution concentrations for gaseous and water-salt inclusions, the range of trapping temperatures could be 700–690°C, and pressure during experiments was similar to 109, 113, 117 и 123.5 MPa (Fig. 2, Table 1).

Table 1. Results of measurements of NaCl concentration in the synthetic fluid inclusions trapped at 700–690°C and pressure 109–124 MPa

Trapping pressure(MPa)	Temperature of melting (°C)		Concentration based on thermo-cryometric data (wt.%)		Concentration of three-phase inclusions (wt.%)	
	Ice	NaCl B	Two-phase	Three-phase	Extrapolation	Volumetry
109	-4.0 – -2,9	No data*	6.4 – 4.7	No data	53.5–48.5	56.1–49
113	-6.4 – -4.8	No data *	9.2 – 6.4	No data	49–43	53.0–37.0
117	-7.5 – -5.2	335-385	10.5–7.8	45.1 – 41	46 – 41.7	46.5–36.6
124	-	+4.3 –+3.9**	-	26.3	-	-

Note: *- partial melting of NaCl and decrepitation of inclusions at 550–600°C

** - gas inclusions representing supercritical fluid

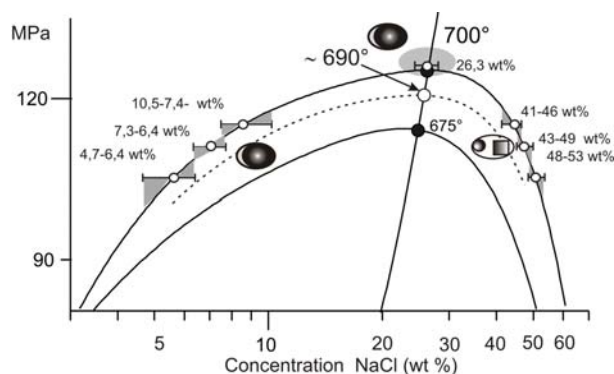


Fig. 2. Part of the diagram of the aqueous-saline NaCl-H₂O system at 700°C [Sourirajan and Kennedy, 1962] showing the results of measurements (mean values) of solution concentration of two-phase and three-phase inclusions plotted on the isotherm 700°C.

Fluid inclusions with no signs of the combined trapping were used to determine the content of As, Sb, Te, Au and Bi in fluid phase during the experiment. The LA-ICP-MS technique was used to analyse individual inclusions (FINNIGAN MAT with NAWA 213 laser device). We used NIST-612 glass as a standard. To analyze the composition of fluid and melt inclusions we used Na as an internal standard. To calculate ore element concentration in fluid inclusions we used Na concentration values determined by extrapolation and thermometry methods. Na content in melt inclusions was analyzed by X-ray microprobe CAMECA.

Experiment results show that distribution of As, Sb, Te, Au and Bi in gas and water-salt phases at 700°C depends on pressure values (Fig. 3). Thus, in supercritical fluid existing at 124 MPa and in equilibrium with silicate melt, ore elements concentration can reach (in average, ppm): As 180, Sb 2250, Au 66, Te 1.4, Bi 340. At pressure drop lower than critical (117 MPa) the gas phase contained (in average, ppm): As 45, Sb 5.5, Te 1.9, Au 0.2 and Bi 6, while aqueous-salt phase contained 440 ppm As, 690 ppm Sb, 640 ppm Au, 2.7 ppm Te, 70 ppm Bi. Further pressure drop down to 110 MPa resulted in the enrichment of gas phase by ore elements whose content increased by two orders of magnitude, and on the contrary, concentration of ore elements in water-salt phase are lower by an order of magnitude: As 90 ppm, Sb 53 ppm and Au 22 ppm. A decrease of Te and Bi concentration at increased pressures in both gas and water-salt phases during our experiments we explain by the reaction of these metals with the substance of gold ampoule. According to X-ray microprobe analysis, silicate melt which occurred during the experiment had content of SiO₂ from 73.2 to 67.6, FeO from 16.2 up to 4, NaO from 6.1 to 0.5, and Cl ranging from 1.1 to 0.4 wt%. The concentration of ore elements in silicate melt did not undergo significant changes at increased pressures.

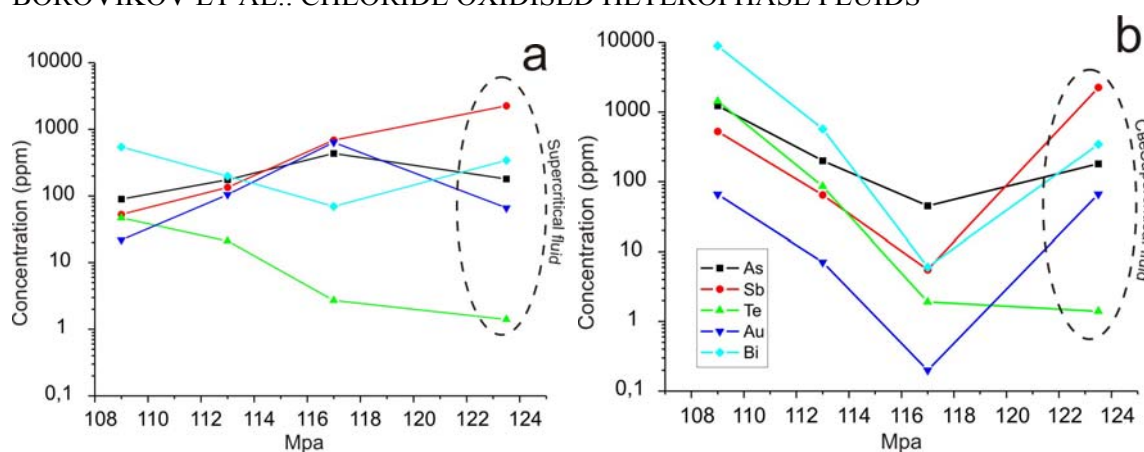


Fig. 3. Average values of As, Sb, Te, Au and Bi concentration in water-salt (a) and gas phases (b) at 700°C and pressure 118–108 MPa. A dashed line denotes the compositions for supercritical fluid.

Results of our experiments show that

- 1) Supercritical oxidized chloride-water fluid coexisting with silicate melt is a powerful extractor for As, Sb, Te, Au, and Bi elements.
- 2) Water-salt chloride phase of oxidized heterophase fluid has the highest concentrations of ore-forming elements such as As, Sb, Te, Au, and Bi at P-T conditions close to subcritical.
- 3) Pressure decrease results in the formation of gas fluids with high metal contents due to the strong re-distribution of As, Sb, Te, Au, and Bi between water-salt and gaseous phases.

Conclusion

The experiments confirmed a high metal-bearing capacity of oxidized fluids and a significant role of heterogenization process responsible for the geochemical specialization of its individual phases. A separate migration of water-salt and gaseous phases towards the surface could explain the spatial association of porphyry Cu-Mo mineralization formed with the participation of highly concentrated chloride fluids and epithermal Au ores formed from the low-concentrated chloride solutions.

This work was supported by RFBR (grants 08-05-00915 and 10-05-00730).

References

- Andreeva, I. A. (2000) *Silicate, silicate-salt and salt magmas of the Mushugai-Khuduk alkaline carbonatite-bearing complex, Southern Mongolia (data on melt inclusion study)*: Abstract of Ph.D thesis M., IGEM, 27 p.
- Borisenko, A. S., A. A. Borovikov, L. V. Zhitova, G. G. Pavlova (2006) Composition of magmatogenic fluids, factors of their geochemical specialization and metal content, *Geology and Geophysics, Vol. 47, № 12*, pp. 1308-1325.
- Reif, F. G., L. V. Damdinova, Y. M. Ishkov, N. S. Karmanov (2004) Diverse specialization of ore-forming fluid flow simultaneously produced by a single granite intrusion. The Yermakov Fe-Be deposit, Transbaikalia, Russia, *Metallogeny of the Pacific Northwest: tectonics, magmatism and metallogeny of active continental margins: Proc. Interim IAGOD Conf. Vladivostok, Dalnauka*, pp. 314-317.
- Zhitova, L. V., I. F. Rakhmenkulova, A. S. Borisenko et al. (2004) The factors of precious metal concentrations in sulfide ores of the Chineisky Massif (Transbaikalia Region, Russia), *Abstracts of Geoscience Africa, University of the Witwatersrand. Johannesburg, South Africa, Vol. 2*, pp. 740-741.