ORE ELEMENTS DISTRIBUTION IN HETEROGENOUS FLUIDS OF RARE METAL DEPOSITS

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Concentrations of ore elements have been determined in ore-forming solutions of Sn-W, Cu-Mo, Ag-Sb and Ag-Pb deposits using LA-ICP-MS and PIXE as quantitative techniques for the analysis of fluid inclusions (Heinrich et al., 1992, 1999; Audétat et al., 1997, 2000; Ulrich et al., 1999; Borisenko et al., 1997, 1999). Detailed studies have shown that part of ore elements is concentrated in the water-salt phase, and other elements are separated in the gas phase. In Sn-W deposits related to the Mole granite, the gaseous phase of inclusions is rich in Cu, Cs and As. In Cu-porphyry deposits the concentration of Cu, Au and As in the gas phase is 50-100 times higher than in the inclusion solution. The phenomenon is very important for the study of ore element behavior in ore-forming processes.

The distribution pattern of ore elements in heterogeneous fluids, as shown by thermodynamic analysis, between gas and water-salt phases depends on the p-T-parameters of fluids and their composition and redox-potential (CO_2/CH_4, Fe^{2+}/Fe^{3+} ratio).

Studies of fluid inclusion composition have been carried out on the Deputatsky Sn-W deposit, which is one of the superlarge deposits in Russia. The deposit sampled down to 1200 m allowed us to trace the change in p-T-parameters, composition and concentration of fluids, and the evolution of the fluid regime from deep horizons up to surface (Borisenko et al 1997, 1999). Microthermometric studies of fluid inclusions in quartz and fluorite from the Deputatskoye deposit allowed the recognition of three consecutively forming mineral parageneses: cassiterite-arsenopyrite-quartz (± wolframite, fluorite, topaz), sulfide (quartz, pyrrhotite, chalcopyrite, stannite, sphalerite) and sulfide-carbonate (siderite, galena, chalcopyrite, Ag-tetrahedrite, sulfosalts). Several types of inclusions occur in quartz and fluorite: multiphase (liquid+gas+ 1-4 solid phases), 2-phase (essentially liquid L>G and essentially gaseous L<G), and 3-phase inclusions containing $L+CO_{2\ liq.}+G$. Multiphase water-salt inclusions consist of solution, gas bubble, NaCl and KCl crystals, an anisotropic phase - likely siderite, and an isometric crystal of an opaque ore mineral. The anisotropic crystal dissolves at temperature ≥400°C.

The characteristic feature of the ore-forming fluids is their heterogeneity, manifest by the presence of water-salt inclusions with concentrations up to 55 wt% and gas inclusions, containing solutions of variable concentrations from 5 up to 27 wt%, mostly in the range 5-8 wt%. Variations in solution concentrations of gas inclusions are determined by variable Fe contents in the solutions.

Table. Results of LA-ICP-MS analysis of gas and water-salt inclusions in quartz of the Deputatsky deposit

NaCl concentration (cryometry), wt%		2.0	2.1	12
Inclusion type		vapour	vapour	water-salt
Na	wt. %	0,79	0,83	4,72
Mg	wt. %	0,058	0,082	3,07
K	wt. %	0,015	0,038	2,58
Ca	wt. %	0,0028	0,0028	1,35
Mn	wt. %	0,032	0,015	0,10
Fe	wt. %	2,08	1,42594	33,09
Co	ppm.	0	0	3,2
Ni	ppm.	205	88	577
Cu	ppm.	206	29	166
As	ppm.	470	146	128
Rb	ppm.	280	208	787
Sr	ppm.	9,2	125	843
Ag	ppm.	15	21	7,3
Sn	ppm.	-	878	1575
Sb	ppm.	325	18	129
Cs	ppm.	70	40	65
W	ppm.	-	-	0,03779
Bi	ppm.	855	-	65

To study ore elements behavior in heterogeneous fluids, LA-ICP-MS analyses of gas and water-salt phases were carried out in quartz from ore veins and magmatic rocks (granite-porphyry and ongonite dikes) (UIGGM, Novosibirsk). Gas components in such inclusions are CH_4, CO_2 and N_2. Methane prevails in deep horizons, and nearer the surface CO_2 and N_2 became predominant in the inclusions. Quantities of nitrogen and carbon dioxide in the inclusions increase from the central part of hydrothermal system to the periphery and upper levels. The appearance of N_2 in significant quantities is probably related to oxidation of the reduced nitrogen species (NH_4^+, CN^-, etc.). The presence of NH_4^+ in the solutions of inclusion was detected using water leaching in several Sn-W deposits, including Deputatsky. The increase in the CO_2/CH_4 ratio indicates a redox-potential increase. In gas inclusions carbon dioxide predominates with minor methane and nitrogen.

Results of LA-ICP-MS analysis has shown that the major components of water-salt inclusions are Fe (up to 33 wt%), Na, Mg, K, and Ca. The prevailing microcomponents are: Zn (0.28), Sr (0.16), Sn (0.16), Ba (0.07), W (0.04), Pb (0.03) wt%, etc. (Table). In the solutions of gas inclusions Na and Fe are also predominant, but in contrast to water-salt inclusions higher concentrations of Cu, As, Sb, Cs and Bi are determined. In addition, Ni, Rb, Cs and Ag occur in significant concentrations. Accumulation of As, Sb, and Bi in gas phase can be explained by the presence of their volatile Cl- and F- forms such as $AsCl_3$ and $SbCl_3$.

All these facts suggests that complex distributions of ore elements in heterophase fluids between gas and water-salt phases under their separated migration could lead to the formation of different compositional types of mineralization.

Computer modeling of the distribution of ore elements between gas and water-salt phases in fluids, similar in composition to those founded at the Deputatsky deposit, indicates that Hg, Sb and As are concentrated in the gas phase, and Ag, Zn, Pb, Fe in the water-salt phase. The main Ag and Sb species in acidic (pH 3) highly concentrated 5 M chloride solutions are $AgCl_4^{3-}$, $AgCl_3^{2-}$, $AgCl_2^-$, $SbCl^{2+}$, $SbCl_2^+$, $SbCl_3$, $SbCl_4^-$. Thermodynamic calculations have shown the high metal-bearing capacity of concentrated chloride solutions. Such solutions are able to transport up to 10^{-2} M Ag and Sb at temperature 250°C. At a temperature of 350°C and a pressure of 1000 bars the Ag solubility increases up to 47 g/kg H_2O. At temperature above 250°C Sb can be transported in the gas phase of a boiling fluid as $SbCl_{3\ (gas)}$. In heterogeneous fluids (250°C, 40 bar) Ag is concentrated only in the liquid phase, and Sb is present both in liquid and in gas phase as $SbCl_{3gas}$ (up to 10^{-2} m), together with CO_2, CH_4, H_2S, and HCl.

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