into concentrated brine and weakly concentrated aqueous fluid occurs. The existence of such immiscible fluid phases has been proven by studies of melt and fluid inclusions in the ore-generating granitoids of the Orot and Ermakov beryllium deposits (Damdinov et al., 2023). The transport of matter at the post-magmatic stage is carried out by fluids of complex composition, characterized by alkaline specificity. Their composition is determined by the following salts: $NaCl + KCl + Na_2CO_3 + K_2CO_3 + NH_4Cl \pm NaF \pm KF \pm (Na,K)_2SO_4$. The total salt concentration reaches 30-40 wt%. Under conditions of tectono-magmatic activation, such fluids at a temperature of 450-650℃ and a pressure of 2-4 kbar can simultaneously transport ore and silicate substances, forming ore deposits of various types.

Conclusions

1. The fundamental role of fluids in the processes of differentiation of the earth's crust has been determined.

2. Four processes are presented that determine the concentration of ore components: (1) melting of the lower crustal substrate under the influence of mantle fluids; (2) heterogenization of fluid-magmatic systems during decompression (ascent of magmas) with the separation of elements between phases and their accumulation; (3) the stage of crystallization of the magmatic melt in the presence of fluid phases and active acid-base interaction in the system, with the formation of residual melts enriched in ore elements; (4) extraction and redeposition of ore elements by hydrothermal solutions. Combinations of these processes at different PTX-parameters determine the variety of ore deposits.

3. The possibility of experimental modeling of the above processes is shown. Modeling requires accurate knowledge of boundary conditions (parameters of processes in the earth's crust).

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Kotelnikov A.R.[1], Suk N.I.[1], Damdinov B.B.[2], Damdinova L.B.[3] Experimental modeling of ore matter transport and formation of ore paragenesis. *UDC 553.062: 550.89*

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Abstract. Exploratory experiments were carried out to model ore parageneses of the Ozernoye deposit. The experiments were carried out in gold ampoules, into which mixtures of initial aluminosilicate materials with zinc and iron sulfide reagents were loaded, simulating chemogenic precipitation (the lower part of the ampoule). Calcite was loaded into the upper part of the ampoule. The initial solutions (salt concentration up to 45 wt%) were set with chlorides (NaCl, KCl, NH_4Cl) and carbonates (Na_2CO_3 and K_2CO_3). In addition, a small amount of 1M alkali solutions (NaOH, KOH) was added. Solutions of sodium and

potassium specificity were used. The experiments were carried out under thermogradient conditions: bottom – 510℃, top – 470℃ and a pressure of 3.5 kbar on an HGPV 10000 installation designed by the IEM RAS. The experimental products were studied using the microprobe method. Using the method of counter-temperature diffusion of components, parageneses similar to natural ones at the Ozernoye deposit were obtained.

Polymetallic (Pb-Zn ± Ag, Cu) sulfide deposits in volcanogenic, terrigenous and carbonate strata provide a significant share of humanity's needs for metals: the predominant quantities, sometimes up to 95%, of Zn, Pb, Ag, Cd, In, Tl, and also significant proportions of Cu, Au, Co, Ni, Se, Te, Ge and Ga (Bortnikov et al., 2016).

Fig. 1. The layout of ore clusters and minerals of the Kurbino-Eravninsky mineragenic zone and the position of the Eravninsky ore district, according to (Gordienko, Nefediev, 2015) with minor changes.

1 – boundaries of the mineragenic zone; 2–4 – remnants of host rocks among the granitoids of the Angara-Vitim batholith: 2 – Neoproterozoic sedimentary-metamorphic, 3 – Lower Cambrian predominantly carbonate-volcanogenic, 4 – Lower Cambrian and Devonian-Carboniferous terrigenous and essentially carbonate; 5 – Late Paleozoic gabbroid intrusions and xenoliths of mafic rocks among the granitoids of the batholith; 6 – faults; 7 – ore nodes; 8–14 – deposits: 8 – iron, 9 – gold, 10 – manganese, 11 – polymetals (Pb, Zn), 12 – copper, 13 – molybdenum, 14 – fluorite (a), boron (b) and aluminum (c). The white dotted line shows the boundaries of the Eravninsky ore district. The numbers in the circles are ore nodes: 1 – Atkhinsky, 2 – Abaginsky, 3 – Turkinsky (Yambuysky), 4 – Kurbinsky, 5 – Myldylgensky, 6 – Verkhne-Oninsky, 7 – Ozerninsky, 8 – Sosnovo-Ozersky, 9 – Kharasansky, 10 – Kondinsky, 11 – Egitinsky, 12 – Kydzhimitsky, 13 – Khiagdinsky, 14 – Nizhneburulzaysky.

Polymetallic deposits of the Ozerninsky ore cluster are characterized by a complex composition of ores: sulfide mineralization (Pb, Zn), carbonate (siderite), oxide (magnetite) ores. The main part of the ore cluster is composed of stratified Paleozoic formations, making up a remnant (roof sag) with an area of about 250 km² in the field of development of Late Paleozoic granitoids of the Angara-Vitim batholith (Fig. 1). The processes of deposit formation and sources of ore matter are still controversial. However, most authors are inclined to metasomatic genesis. Figure 2 shows the geological section of the Ozernoe deposit.

Exploratory experiments were carried out to model ore parageneses of the Ozernoye deposit. The experiments were carried out in gold ampoules, into which mixtures of initial aluminosilicate materials with zinc and iron sulfide reagents were loaded, simulating chemogenic precipitation (the lower part of the ampoule). Calcite was loaded into the upper part of the ampoule. The initial solutions (salt concentration up to 45 wt%) were set with chlorides (NaCl, KCl, NH_4Cl) and carbonates (Na_2CO_3 and K_2CO_3).

In addition, a small amount of 1M alkali solutions (NaOH, KOH) was added. Solutions of sodium and potassium specificity were used in the experiments. The experiments were carried out under

thermogradient conditions: bottom − 510℃, top − 470℃ and a pressure of 3.5 kbar. The experiments were carried out on an high gas pressure vessel (HGPV) designed by IEM RAS. The duration of the experiments was 12 days. The experimental products were studied using the microprobe method. Using the method of counter temperature diffusion of components, parageneses similar to natural ones at

the Ozernoye deposit were obtained. Of particular note is the synthesis of siderite (Fig. 3), carried out according to the reaction:

$$FeS + K_2CO_3(aq) + H_2O + 1.5O_2 \rightarrow FeCO_3 + K_2SO_4(aq).$$
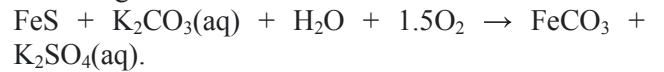
In this way, the genesis of siderite, formed under the influence of alkaline carbonate fluid at an increased oxygen potential, can be explained.
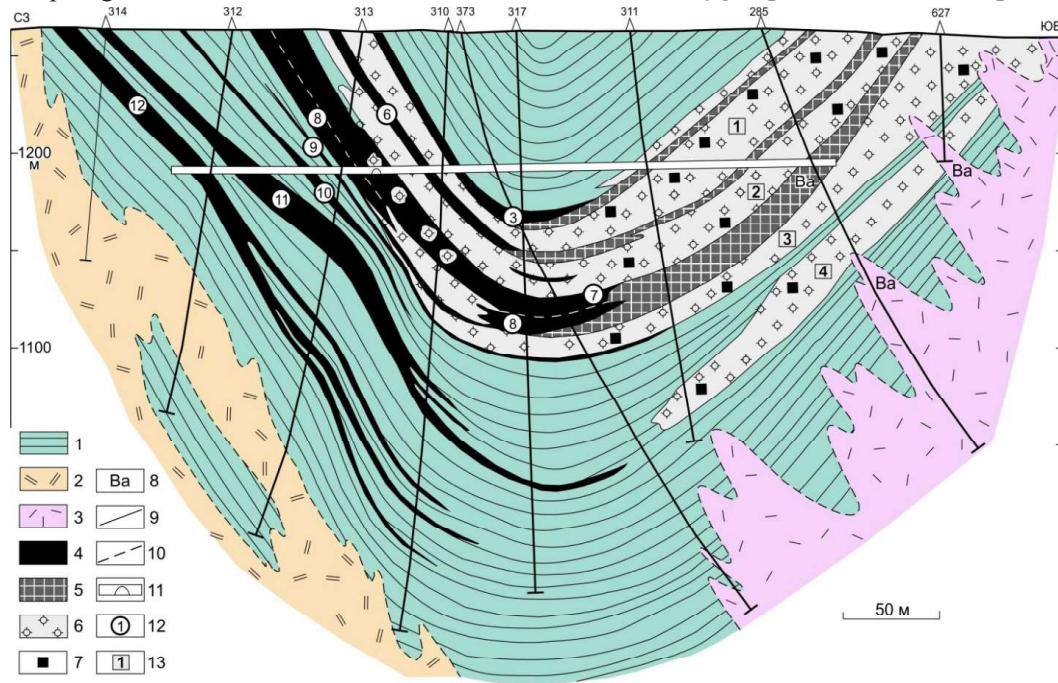
Fig. 2. Schematic geological section of the Ozernoe deposit. 1 − host carbonate-volcano-terrigenous rocks; 2,3 − automagmatic breccias of dacites and andesitodacite (2), rhyolites and rhyodacites (3); 4 − layered bodies of sulfide polymetallic ores; 5 − recrystallized sulfide polymetallic ores; 6 − siderites; 7 − veinlet-disseminated sulfide mineralization; 8 − barite mineralization; 9,10 − geological boundaries established (9) and proposed (10); 11 − mine adit and crosscut; 12,13 − numbers of layered deposits of polymetallic ores (12) and siderites (13).
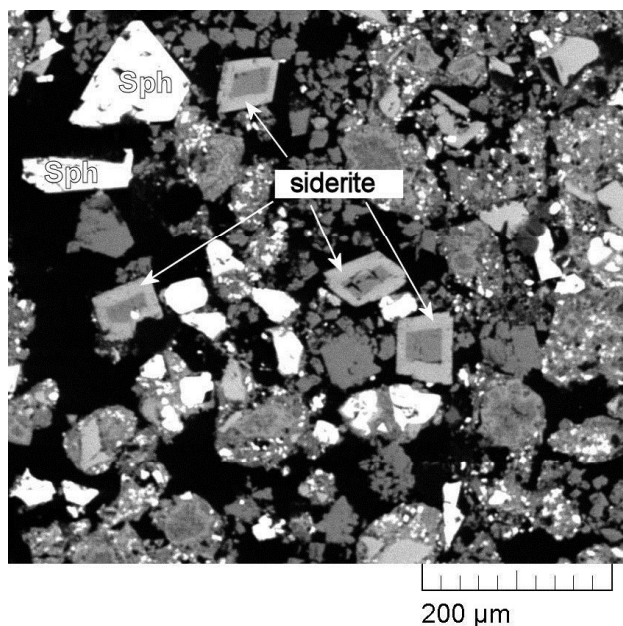
Fig. 3. Siderite (calcite rims) synthesized in experiments of ore substance transport. Sph – sphalerite.

Conclusions

1. Modeling of the formation of parageneses of the Ozernoe deposit under hydrothermal conditions was carried out using the counter-diffusion method at a temperature of 510 - 470℃ and a pressure of 3.5 kbar.

2. The possibility of recrystallization of "chemogenic sediments" enriched in ore components into ore parageneses through metasomatic reactions has been shown.

3. The process of formation of siderites from carbonate-silicate-sulfide substance under the influence of hydrothermal solutions of potassium carbonates was modeled.

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Kotova N.P., Korzhinskaya V.S. Comparative analysis of data on pyrochlore and niobium oxide solubility in aqueous fluoride solutions

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Abstract. Experimental data are presented on pyrochlore and niobium oxide solubility in HF, KF solutions in the concentration range of 0.01 - 2 m, in NaF solutions with concentrations of 0.01 - 1 m and in LiF solutions with concentrations of 0.03 - 0.1 m from 300 to 550 °C and 50 to 100 MPa at low oxygen fugacity (Co-CoO buffer). The influence of temperature and pressure on the solubility of Nb oxide and pyrochlore has been established. A comparative analysis was carried out of the niobium equilibrium contents during the dissolution of niobium oxide and natural pyrochlore in fluoride hydrothermal fluids.

Keywords: experiment, pyrochlore, niobium oxide, fluid, fluoride solutions, physico-chemical conditions

To model the conditions for the formation of rare metal deposits (Ta, Nb, Be, etc.), in addition to the magmatic factor, it is also necessary to take into account the role of hydrothermal-metasomatic processes. Therefore, we are conducting experimental studies of the behavior of rare metals in aqueous fluids at temperatures and pressures corresponding to the physical and chemical parameters of post-magmatic processes, aimed at obtaining quantitative estimates of the physical and chemical conditions for the formation of greisen and albitite deposits of W, Mo, Sn, Ta, Nb and Li, associated with standard calc-alkaline, including lithium-fluoride granites (Korzhinskaya, Kotova, 2012; Kotova, 2014).

Experimental data on the solubility of pyrochlore $(Ca, Na)_2(Nb, Ta)_2O_6(O, OH, F)$ and niobium oxide $(\beta\text{-}Nb_2O_5)$ in HF, KF, NaF and LiF fluoride solutions are presented, since these are the components that have been established as the main components of fluid inclusions in minerals of rare metal deposits (Webster et al., 2004).

The solubilities of the natural mineral pyrochlore and niobium oxide were studied in solutions of HF, KF with a concentration of (0.01-2.0 m), NaF with a concentration of (0.01-1.0 m) and LiF with a concentration of (0.01-0 ,3 m) in a wide temperature range of $300 - 550^\circ$ C, P = 50 and 100 MPa and low oxygen fugacity (Co-CoO buffer). For the experiments we used fragments of pyrochlore single crystals from the weathering crusts of the Tatarka carbonatite deposit with the following composition: Na_2O-7,61%; CaO-14,28%; Nb_2O_5-71,61%; F-5,18%; TiO_2-0,83%; $Ta_2O_5 \leq 1\%$ wt. and niobium oxide in the form of a reagent (special purity grade), pre-purified by recrystallization in 0.1m HF at 550°C and P = 100 MPa. The experiments were carried out on a high-pressure hydrothermal installation in welded platinum tubes using the ampoule technique. Run duration was 15-30 days (Korzhinskaya et al, 2017; Kotova et al, 2022).

To control congruent or incongruent dissolution and to determine chemical composition of newly-formed phases (in case of their detection) the initial materials and solid run products were studied by X-ray diffraction, and electron microprobe analysis (Cam Scan MV 2300 (VEGA TS5130MM).

The quenched aqueous solutions were then analyzed using ICP/MS (Inductively Coupled Plasma Mass Spectrometry) and ICP/AES (Atomic Emission Spectroscopy) for Nb, Ta, Mn, and Fe and admixture elements Ti, W, and Sn.

The results of experiments to study the concentration dependences of the equilibrium niobium content during the dissolution of pyrochlore and niobium oxide HF, KF, NaF and LiF solutions at T = 550° C, P = 100 MPa (Co-CoO buffer) are presented in Fig. 1 (a, b).

Studies have shown that when pyrochlore is dissolved in HF and KF solutions, the equilibrium Nb content increases from $n*10^{-6}$ m in 0.01m HF to $n*10^{-1}$ m in 2m HF, and from $n*10^{-6}$ m in 0.01m KF to $n*10^{-4}$ m in 1m KF. In NaF solutions, the equilibrium Nb content is much lower than in HF and KF solutions, and in 1 m NaF solution it is $n*10^{-5}$ m. It has been experimentally established that the niobium content in LiF solutions is very small and in a 0.1 m LiF solution is $n*10^{-6}$ m. Moreover, with increasing LiF concentration it practically does not change.

The results of the X-ray phase method for analyzing solid experimental products showed that in fluoride solutions, pyrochlore dissolves incongruently with the formation of new phases: oxyfluoride $Na_2Nb_4O_{11}$ and crystals of Nb_2O_5 containing titanium (up to 0.56 wt.%) and fluorine (up to 3.88 wt.%).