Hydrothermal equalibria and ore formation

Akhmedzhanova G.M., Kotelnikov A.R., Suk N.I. Experimental modeling of the transport of ore components (Fe, Ni, Cu, Zn, Pb) by water and the formation of scattering halos. *UDC 550.89:550.84.092*

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Abstract. Experimental modeling of the transport of Fe, Ni, Cu, Zn, and Pb in water and aqueous NH_4Cl and KCl solutions was carried out under thermal gradient conditions at temperatures of 70-20°C (ΔT = 50°C) at atmospheric pressure. The starting material was imitation granite (Qz + Fsp mixture) with the addition of ore minerals: pentlandite $(Ni,Fe)_9S_8$, chalcopyrite $CuFeS_2$, sphalerite ZnS, galena PbS, and pyrrhotite FeS. The experiment duration was 40-45 days. After the experiments, the composition of the solutions was determined. The possibility of the formation of secondary dispersion halos of ore elements and their differential mobility during thermal gradient transport in aqueous solutions was demonstrated.

***Keywords**: dispersion halos, ore components, thermal gradient conditions, experiment*

Introduction. Geochemical halos of ore element dispersion are zones of anomalously elevated chemical element contents associated with the migration of matter from ore bodies. They serve as indicators of the presence of ore bodies and play a key role in prospecting and exploration studies. The goal of our study was to model the migration of ore elements in aqueous solutions under thermal gradient conditions and their precipitation in the upper part of the container within the soil layer.

Experimental method. Initial materials. The initial material was imitation granite (Qz + Fsp mixture) with the following composition (100 wt%): SiO_2 – 83.25, Al_2O_3 – 9.09, FeO – 0.10, MgO – 0.05, CaO – 0.04, Na_2O – 2.39, K_2O – 5.17. So, there was the addition of ore minerals: in the first variant – pyrrhotite FeS, sphalerite ZnS, galenite PbS; in the second – pentlandite $(Fe_{3.56}Co_{0.23}Ni_{5.12})_{8.91}S_{8.09}$. Distilled water, as well as 0.1 M NH_4Cl and KCl solutions, were used as transport media in the experiments. Model granite and ore minerals (0.5–1.0 mm fraction) were mixed until a homogeneous mass was obtained.

Equipment. Experiments were carried out in 150 ml glass cylinders. A granite mixture (weight ~10 g) supplemented with ore minerals (weight ~3 g) was loaded into the lower portion of the cylinder. A mesh container containing quartz sand (8 g) was placed in the middle, and approximately 10 g of soil (sandy loam) was placed in the upper portion. A filter separated the soil and sand in the container. The sand was fairly pure; except for SiO_2 and Al_2O_3, it contained the following elements (wt%): Fe_2O_3 – 0.18 MgO – 0.1; Na_2O – 0.26; K_2O – 6.21. Elements such as Ca, Ni, Zn, Cu, and Pb were not detected. These elements are also absent in the soil.

Conducting the experiments. The required amount of water (NH_4Cl or KCl solution) was added to a glass cylinder approximately 30 cm long and 30 mm in diameter, so that the container with the soil was in a semi-submerged state. The lower part of the cylinder was heated in a sand bath to 70°C. Entering the experimental mode took approximately 2 hours. The thermal gradient during the experiments was approximately 50°C. The amount of water (solution) in the cylinder decreased due to evaporation. Therefore, the required amount of water was periodically added. The duration of the experiments was 40 days. For control, samples were taken 20 days after the start of the experiments for solution analysis.

Analytical methods. After the experiments, the composition of the solutions was determined. The solid products of the experiments (soil) were washed with ~100 ml of distilled water, and the filtrate was quantitatively analyzed for the content of Na, K, Mg, Ca, Fe, Ni, Zn, Cu, and Pb. The analysis was performed on a KVANT-4M atomic absorption spectrograph. Solid experimental products were analyzed by microprobe and X-ray diffraction.

Experimental results. The experimental conditions and phase composition of the experimental products are presented in Table 1. Table 1 shows that the phase composition of the experience products almost always matched the initial mineral load. Analyses of the solutions obtained by sampling during the experiments are presented in Table 2.

The data presented in Table 2 allow us to estimate the migration of elements in the solutions. For this purpose, the mole fractions of K, Fe, Zn, Ni, and Cu in the initial "granite" mixtures with the addition of ore minerals were calculated: $X_K^{Gr1,2}=K/(Na+K)$; $X_{Fe}^{Gr1,2}=Fe/(Fe+Zn+Pb+Ni+Cu)$. The same was true for other elements. The mole fractions of the components in the solutions after sampling were calculated using the same method. The partition coefficients of the elements between the liquid phase (fl) and the solid phase (Gr1,2) were then calculated: $Kp=X_i^{fl}/X_i^{Gr1,2}$. The values of these quantities are given in Table 3.

Table 3 shows that the solution composition significantly affects the extraction of elements from the model "granite." Potassium actively passed into solution in the presence of NH_4Cl (K_p = 1.62), while for water K_p = 0.66, i.e., K was redistributed into the solid phase ("granite"). Fe enriches the KCl solution,

while in water and in 0.1 M NH_4Cl, iron prefers the solid phase. Zn is redistributed into the liquid phase in water and in 0.1 M NH_4Cl, Pb behaves similarly. Ni has the highest K_p – from 3.014 (water) to 3.328 (0.1 M NH_4Cl), the lowest K_p are for Cu – 0.239 - 0.393 (for water).

Table 1. Experimental conditions for studying the transport and precipitation of ore elements.

№	Loading, bottom	Loading, middle	Loading top	Solution	Experience products
1	10g «granite» +1.2g Gln+ 1g Shl+1g Pyr*	8g sand	10 g soil	50 ml distilled H_2O	Fsp+Qz+Gln+Shl
2	-"-"-	-"-	-"-	50 ml 1M KCl	Fsp+Qz+Gln+Shl
3	10g «granite» +1.0g Gln+ 1g Shl + 1g Pyr	10g sand	10 g soil	50 ml 1M NH_4Cl	Fsp+Qz+Gln+Shl+Pyr
4	10 g «granite» + 1 g Pln + 2 g Chp	8g sand	10 g soil	50 ml distilled H_2O	Fsp+Qz+Pln+Chp
5	-"-	-"-	10 g soil	50 ml 1M KCl	Fsp+Qz+Pln+Chp
6	10 g «granite» +1 g Pln +2 g Chp	8g sand	-"-	50 ml 1M NH_4Cl	Fsp+Qz+Pln+Chp

* Mineral indices: Chp – chalcopyrite; Fsp – feldspar; Gln – galenite; Pln – pentlandite; Pyr – pyrrhotite; Qz – quartz; Shl – sphalerite. "Granite" with additions of pyrrhotite, sphalerite, and galenite is Gr1; with additions of pentlandite and chalcopyrite is Gr2.

Table 2. Compositions of solutions (in μg/ml) from experiments (taken during sampling)

№	Initial solution	K	Na	Ca	Mg	Fe	Zn	Pb	Ni	Cu
1	H_2O	12.9	8.9	6.2	21.0	0.12	0.84	2.07	-	-
2	KCl	n.d.	39.5	154.2	234	64.8	0.85	9.81	-	-
3	NH_4Cl	9610	60.1	556.0	237.6	18.9	118.0	117.9	-	-
4	H_2O	13.4	18.4	19.9	18.8	0.6	-	-	1.34	0.31
5	KCl	n.d.	38.6	151.2	43.2	0.84	-	-	1.77	0.24
6	NH_4Cl	7362	52.8	695.6	38.4	0.56	-	-	1.56	0.25

Table 3. Partition coefficients $Kp= X_i^{fl}/X_i^{Gr1,2}$ of a series of elements between "granite" and solution

№ sample	Solution	Kp-(K)	Kp-(Fe)	Kp-(Zn)	Kp-(Pb)	Kp-(Ni)	Kp-(Cu)
1+4 average	H_2O	0.665	0.397	1.343	2.138	3.014	0.393
2+5 average	KCl	0.000	1.432	0.028	0.207	3.125	0.239
3+6 average	NH_4Cl	1.621	0.408	1.738	1.122	3.328	0.301

Table 4 shows the concentrations of ore elements in soil and sand. It is clear that the contents of elements such as Fe, Zn, Pb, Ni, and Cu are slightly higher in soil than in sand. This largely depends on the composition of the transport medium. For example, in soil, Fe concentrations are lowest with an NH_4Cl solution, while the opposite is true for sand. The presence of a KCl solution increases the Fe concentration. For nickel, an increase in solid phase concentrations is observed in the presence of an NH_4Cl solution. For Pb, maximum concentrations in soils and sand are typical with water as the transport medium.

Table 4. Ore element concentrations (ppm) in model soil and sand (based on experimental results)

Initial	Soil					Sand				
Solution	Fe	Zn	Pb	Ni	Cu	Fe	Zn	Pb	Ni	Cu
H_2O	25.76	0.58	1.65	3.2	0.14	0.15	0.31	0.91	0.51	0.14
KCl	22.67	0.56	0.64	0.56	0.11	3.40	0.06	0.85	0.233	0.12
NH_4Cl	0.411	0.44	0.79	29.41	0.09	1.20	1.50	0.846	0.92	0.06

Conclusions

1. Modeling of the transport and precipitation of various ore elements (Fe, Zn, Pb, Ni, and Cu) into the soil layer was conducted. It was shown that active transport and precipitation of the substance occurs under thermal gradient conditions $\Delta T°C = 70 \rightarrow 30°C$.

2. The influence of solution composition on the transport of the substance was demonstrated. In general, the extraction of elements into the liquid phase is highly dependent on the solution composition. Salt additions (KCl, NH_4Cl) facilitate the transfer of metals into solution.

3. The ore metal contents in the soil increased over 40 days (ppm (g/t)): 1.5 (Zn), 1.7 (Pb), 26 (Fe),

and 29 (Ni). Cu behaved most inertly.

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Korzhinskaya V.S., Kotova N.P. Study of concentration dependence of Nb_2O_5, pyrochlore, and columbite solubility in HF and KF solutions. *UDC-550.814*

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Abstract. The concentration dependence of the solubility of Nb_2O_5 and the natural minerals columbite and pyrochlore in HF and KF solutions was studied over a wide concentration range of 0.01-2 m at T = 550°C, P = 100 MPa, and low oxygen fugacity (Co-CoO buffer). The experiments showed that pyrochlore dissolves incongruently over the entire studied range of HF and KF concentrations, forming new phases. Columbite exhibits congruent solubility in HF and incongruent solubility in KF solutions. Niobium oxide exhibits congruent solubility at low HF concentrations, while niobium oxyfluorides are formed in 1 m and 2 m HF. It was established that in HF and KF solutions a positive concentration dependence of the niobium content is observed, both for natural minerals columbite, pyrochlore, and for Nb_2O_5.

***Keywords**: experiment, solubility, pyrochlore, niobium oxide, columbite, fluoride solutions, niobium, physicochemical conditions*

To confirm the possible transport of ore matter during the postmagmatic stage of the development of fluid-magmatic systems, the solubility of the natural mineral pyrochlore and niobium oxide in fluoride solutions was studied under various T-P-fO_2 conditions. We previously studied the solubility of the natural mineral columbite and tantalum and niobium oxides (Zaraisky et al., 2010), which allowed us to compare the results obtained for them.

This paper presents the results of a study of the concentration dependence of the solubility of the natural minerals columbite (Mn, Fe)(Nb, Ta)$_2O_6$, pyrochlore (Na, Ca)$_2Nb_2O_6$(O, OH, F), and Nb_2O_5 in HF and KF solutions over a wide concentration range of 0.01 - 2 m at T = 550°C, P = 100 MPa, and low oxygen fugacity (Co-CoO buffer). The experiments lasted 15 days. The experiments were conducted in a high-pressure hydrothermal setup in welded platinum tubes using an ampoule technique that allows the use of an oxygen buffer isolated from the reagents. The solutions were analyzed for niobium and a number of trace elements (Ta, Ti, Mn, Fe, Zr, Na, Ca, etc.) using the most precise and modern methods of inductively coupled plasma (ICP/MS) and ICP/AES. The solid products of the experiments were studied using X-ray diffraction and analysis on a CamScan MV2300(VE GA TS5130MM electron X-ray microanalyzer (microprobe).

The following were used in the experiments: Nb_2O_5 – (analogue of the natural mineral nioboxide) in the form of a chemical reagent (special purity grade); single crystals of pyrochlore (Na, Ca)$_2$(Nb, Ta)$_2O_6$(O, OH, F) from weathering crusts of the Tatarka carbonatite deposit (composition according to microprobe determinations: Na_2O-7.61%; CaO-14.28%; Nb_2O_5-71.61%; F-5.18%; TiO_2-0.83%; Ta_2O_5≤1% by weight). For the experiments, cut fragments of 2-3 mm in size and weighing 0.1–0.2 grams were taken. For the experiments, columbite single crystals were selected from quartz-amazonite-mica pegmatites of the Etykinskoye tantalum deposit, having the following composition, according to the CamScan microprobe data: Ta_2O_5 - 17.70%; Nb_2O_5 - 58.99%; MnO - 13.51%; FeO - 4.42%; TiO_2 -2.59%; SnO_2 – 1.54%; WO_3 – 1.24% by weight (average of seven analyses).

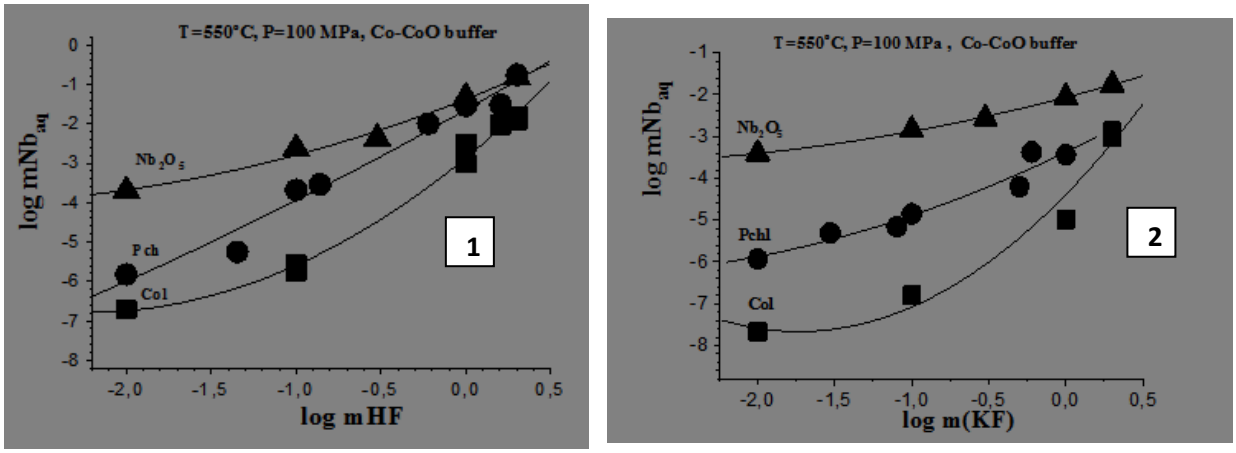

Fig. 1. Concentration dependence of the solubility of niobium oxide, pyrochlore and columbite in HF solutions at T = 550°C, P = 100 MPa (Co-CoO buffer)
Fig. 2. Concentration dependence of the solubility of niobium oxide, pyrochlore and columbite in HF solutions at T = 550°C, P = 100 MPa (Co-CoO buffer)

Table 1. Experimental data on the niobium content during the dissolution of pyrochlore, Nb_2O_5 and columbite in fluoride solutions of HF, KF at T = 550 °C and P = 100 MPa

Initial solution	mNb_{aq}, mol/kgH_2O	-lgm
Source material: Pch; T: 550°C ; P: 100 MPa		
2m HF	0.173	0.76
1.6m HF	3.02E-02	1.52
1m HF	2.85E-02	1.545
0.6m HF	9.96E-03	2.00
0.138 HF	2.92E-04	3.54
0.1m HF	2.08E-04	3.68
0.045m HF	3.55E-06	5.45
0.01m HF	1.51E-06	5.82
1m KF	3.65E-04	3.44
0.6m KF	4.29E-04	3.37
0.5m KF	6.36E-05	4.20
0.1m KF	1.40E-05	4.85
0.08m KF	7.00E-06	5.16
0.03m KF	4.84E-06	5.31
0.01m KF	1.18E-06	5.93
Source material: Nb_2O_5 ; T: 550°C ; P: 100 MPa		
2m HF	1.99E-01	0.70
1m HF	6.64E-02	1.18
0.3m HF	1.09E-02	1.96
0.1m HF	62E-03	2.33
0.01m HF	2.28E-04	3.64
2m KF	1.74E-02	1.76
1m KF	8.73E-03	2.06
0.3m KF	2.72E-03	2.57
0.1m KF	1.43E-03	2.84
0.01m KF	3.90E-04	3.41
Source material: Col ; T: 550°C ; P: 100 MPa		
2m HF	1.26E-02	1.90
1.6m HF	9.33E-03	2.03
1m HF	9.81E-04	3.01
0.1m HF	2.82E-06	5.55
0.1m HF	1.82E-06	5.74
0.01m HF	1.95E-07	6.71
2m KF	9.55E-04	3.02
2m KF	1.32E-03	2.88
1m KF	1.02E-05	4.99
0.1m KF	1.58E-07	6.80
0.01m KF	2.14E-08	7.67

Table 1 shows experimental data on the niobium content during the dissolution of pyrochlore (Pch), Nb_2O_5 and columbite (Col) in fluoride solutions of HF, KF of different concentrations at T = 550°C; P = 100 MPa (Co-CoO buffer).

The experiments showed that pyrochlore dissolves incongruently over the entire studied range of HF and KF concentrations, forming new phases: $NaNb_4O_{11}$, where niobium is partially replaced by titanium (up to 1.45 wt.% Ti) and oxygen by fluorine (up to 4.24 wt.% F), and Nb_2O_5 crystals containing titanium (up to 0.56 wt.%) and fluorine (up to 3.88 wt.%). Columbite exhibits congruent solubility in HF and incongruent solubility in KF solutions (Zaraisky et al., 2010). Congruent solubility is observed for niobium oxide in the region of low HF concentrations, while niobium oxyfluorides are formed in 1m and 2m HF solutions.

Fig. 1 shows the results of experiments on studying the concentration dependences of the equilibrium contents of Nb during the dissolution of pyrochlore, columbite and niobium oxide in aqueous solutions of HF at T = 550 ^{O}C, P = 100 MPa in the presence of an oxygen buffer Co-CoO.

It was found that in the region of low HF concentrations (0.01 m), the niobium content in the solution is maximum for Nb_2O_5 and amounts to $2.28*10^{-4}$ mol/kg H_2O. For pyrochlore, the niobium content in 0.01 m HF is $1.51*10^{-6}$ mol/kg H_2O and increases to $1.73*10^{-1}$ mol/kg H_2O in 2 m HF, and for columbite – $1.95*10^{-7}$ mol/kg H_2O. In the region of high HF concentrations (1.0 m and higher), the niobium content during columbite dissolution reaches values of $n*10^{-2}$ mol/kg H_2O, and for Nb_2O_5 and pyrochlore **(Fig. 1 and Table 1)** it increases, reaching values of $n*10^{-0.5}$ mol/kg H_2O.

Fig. 2 shows the results of experiments on studying the concentration dependences of the equilibrium content of niobium during the dissolution of pyrochlore, columbite and Nb2O5 in KF hydrothermal fluids.

Analysis of the obtained data shows that in the region of low KF concentrations (0.01 m), the niobium content in the solution is maximum for Nb2O5 and is n*10-3.5 m; for pyrochlore it is n*10-6 m, and for columbite – n*10-7.5 m. In the region of high KF concentrations (1.0 m and higher), the niobium content is maximum for Nb2O5 (n*10-2 m), and for pyrochlore and columbite it has similar values and is n*10-3.5 m. Our experimental results confirm the thesis that the solubility of simple oxides (Ta2O5 and Nb2O5) limits the upper limit of the concentration of these elements in hydrothermal solutions.

Conclusions. The solubilities of the natural minerals pyrochlore, columbite and niobium oxide in fluoride solutions of HF and KF were studied in the concentration range of 0.01–2.0 mol/kg H_2O. It should be noted that the chosen concentration range corresponds to the actual range of fluoride concentrations in natural postmagmatic fluids at

granite-associated deposits. According to A.M. Aksyuk's data, obtained using an experimentally developed mica geofluorimeter (Aksyuk A.M., 2002), the HF concentration in aqueous fluids separating from granite melt reaches maximum values of 1.0–2.0 mol/kg H_2O at rare-metal Ta deposits in lithium-fluoride "apogranites" such as the Orlovsky and Etykinsky rare-metal massifs.

It has been established that the composition and concentration of the solution have the greatest impact on the solubility of Ta and Nb. A comparative analysis of experimental data on the solubility of natural minerals columbite, pyrochlore, and tantalum and niobium oxides in HF and KF fluoride solutions suggests that Nb dissolves significantly better than Ta in both HF and KF solutions.

Our experimental results can serve as an objective basis for assessing the potential for tantalum and niobium mass transfer by hydrothermal solutions in natural environments. The obtained concentration curves allow us to estimate the maximum possible concentration of Ta and Nb in aqueous fluid during the early postmagmatic stage after its separation from crystallizing granite melt. These data clearly indicate that the solubility and transport of Ta and Nb by aqueous fluids are facilitated by the presence of acidic fluoride solutions and a high fluorine concentration. The deposition of Nb minerals from solutions can occur as a result of: neutralization of acidic fluoride solutions; and a decrease in fluorine concentration.

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Kotelnikov A.R., Suk N.I. Experimental study of tungsten transport by water-salt fluids at increased PT-parameters. *UDC 550.89:549.761.6*

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Abstract. Experimental modeling of tungsten transport by postmagmatic hydrothermal solutions under thermal gradient conditions was performed. Two series of experiments were carried out for Na- and K-specific solutions. 1) P=4.5 kbar, T_{low}= 680°C, T_{up}= 640°C. Granite imitation (Qz + Fsp mixture) with the addition of $Na_2WO_4*2H_2O$ crystals was used as the starting material. A mixture of (Qz + FeO + MnO + Sid) was placed in the upper part of the ampoule. In these experiments, the synthesis of wolframite on a geochemical "barrier" was modeled—during the interaction of sodium tungstate with an iron-containing substrate. 2) P=3.5 kbar, T_{low}=680°C, T_{up}=620°C. Imitation granite (Qz + Fsp mixture) with added wolframite $(Fe_{0.16}Mn_{0.84})WO_4$ crystals was used as the starting material. The (Qz + Fsp) mixture was placed in the upper part of the ampoule. Transfer of the substance to the upper part of the ampoule was observed in both Na- and K-solutions. It can be concluded that wolframite is transported quite well by alkaline (Na, K)- solutions. The experimental studies confirm the possibility of tungsten concentration and accumulation in the postmagmatic process with the formation of vein and stockwork greisen ores.

***Keywords**: wolframite, aluminosilicate melt, postmagmatic hydrothermal solutions, experiment*

The W ore deposits owe their origin to the evolution of granite melts, most often involving complex fluids. G.P. Zaraisky (2004) substantiated a 2-step scheme for the concentration of rare metals, which we supplemented. This is the following scheme: (1) stage – crystallization of granite intrusions (batholiths), under conditions of preservation of fluids present in the granite melt – H_2O + CO_2 + salts (NaCl, KCl, NaF, KF, Na_2CO_3, K_2CO_3, NH_4Cl, etc.) with the formation of residual melts enriched with a fluid-salt component and incompatible elements (ore); (2) stage – concentration and accumulation of ore elements in the postmagmatic process (due to their extraction by water-salt fluids of alkaline specificity) with the formation of vein and stockwork greisen ores.

This work is devoted to the experimental study of the second stage of concentration and accumulation of tungsten in the postmagmatic process due to extraction with alkaline-specific water-salt fluids.

Previously, we conducted experimental modeling of the transport of sulfide ore components in the presence of basalt glass and a fluid phase represented by water-salt systems of different compositions containing NaCl, KCl, NH_4Cl, $FeCl_2$, Na_2S, NaCNS, Na_2CO_3, K_2CO_3, as well as sodium and potassium hydroxides (Damdinov et al., 2022, 2023) at P=4-5 kbar under thermogradient conditions (T= 680-580°C). This served as the basis for an experimental study of the transfer of tungsten by hydrothermal solutions with the formation of ore parageneses.

Experimental results and discussion. The first series of experiments was conducted to test the formation of wolframite during the interaction of

aqueous solutions of Na_2WO_4 with silicate rocks containing FeO, MnO. The experiments were carried out under thermogradient conditions at a pressure of 4.5 kbar; at the same time, the temperature in the lower part of the ampoule was T_{low} = 680 ℃, in the upper part of the ampoule T_{up}= 640℃. The duration of the experiment was 14 days. Experiments were conducted for two types of solutions: Na- and K-specific. Imitation granite (a mixture of Qz + Fsp) with the addition of Na_2WO_4*$2H_2O$ crystals was used as the starting material. A mixture (Qz + FeO + MnO + Sid) was placed in the upper part of the ampoule.

The following phases were found in the products of experiments with Na-specific fluid in the upper part of the ampoule: quartz, clinopyroxene $(Na_{0.82}Mg_{0.06}Ca_{0.02}Fe_{0.97}Al_{0.03})_{1.90}Si_{2.13}O_6$, albite, wolframite containing Fe and Mn, the average formula is $(Fe_{0.32}Mn_{0.67}Mg_{0.01})WO_4$, with X_{Fe} =0.32±0.1 (Fig. 1a).

In experiments with K-specificity, the following phases were encountered: quartz, potassium feldspar, ferryanite: $K_{1.02}(Mg_{0.20}Fe_{2.03}Ni_{0.21}Mn_{0.59})_{3.03}(Al_{0.06}Fe^{3+}_{1.06}Si_{2.83})_{3.95}O_{10}[OH]_{1.6}$, wolframite $(Fe_{0.53}Mn_{0.49}Mg_{0.01})_{1.03}W_{0.96}O_4$, the molar fraction of iron X_{Fe} =0.49-0.52. Wolframite grains up to 50 microns in size. The remaining phases (Qz, Fsp, Cpx, Bt) are much larger, on the order of 100-1000 microns. In addition, scheelite was found in the products of the experiment. Drop-shaped precipitates of an alkaline melt with an agpaity coefficient (K_{agp}) of ~6 are also observed (Fig. 1b). The composition of the glass is as follows: SiO_2 – 65.45; Al_2O_3 – 2.08; FeO – 9.90; MnO – 3.23; Na_2O – 1.46; K_2O – 9.67.

It follows from the experimental results that the mechanism of postmagmatic hydrothermal transport of tungsten in the form of aqueous solutions of Na_2WO_4, followed by their interaction with iron, manganese and the formation of wolframite may well work in natural conditions by reactions:

$$Na_2WO_4+FeO_s+H_2O=FeWO_4\downarrow+2NaOH_{aq}$$

$$Na_2WO_4+Fe(HCO_3)_2= FeWO_4\downarrow+2Na(HCO_3)_2$$

In the oxidation zones, divalent iron is oxidized and replaced by calcium to form scheelite ($CaWO_4$).

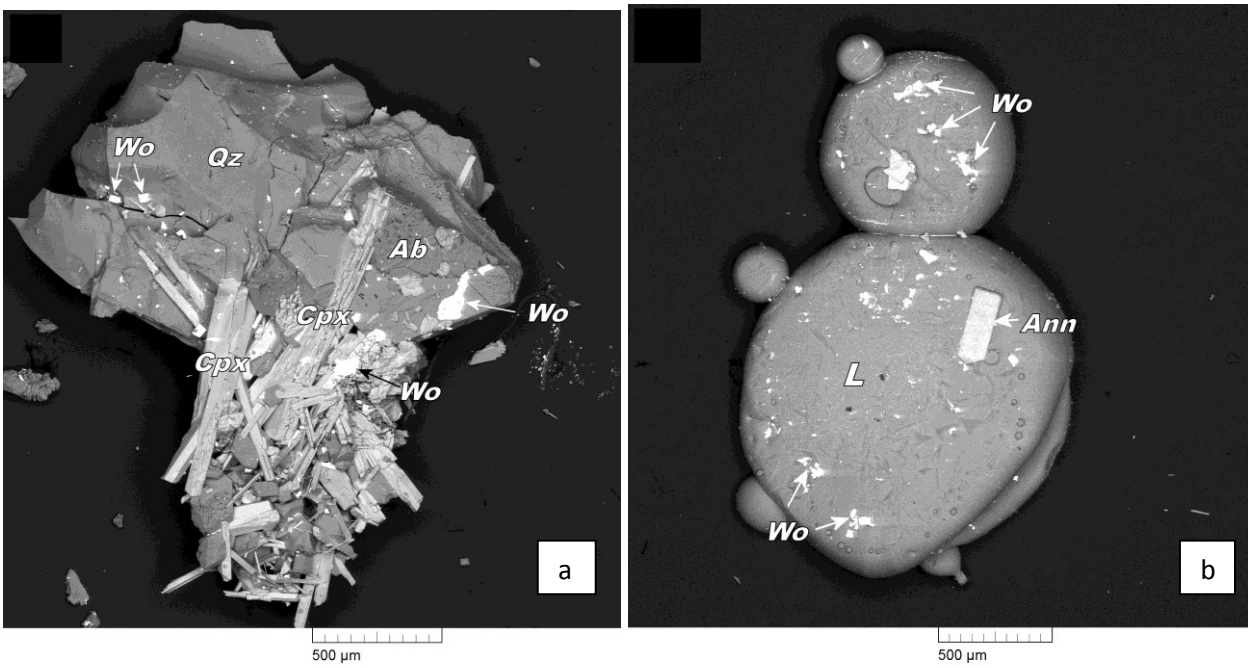

Fig. 1. Crystals of synthesized wolframite in association with Ab+Cpx+Qz. Na-specific fluid (sample7489) (a); b – synthesized wolframite in glass. K-specific fluid (sample 7490). *Ab* is albite, *Cpx* is clinopyroxene, *Qz* is quartz, and *Wo* is wolframite**.**

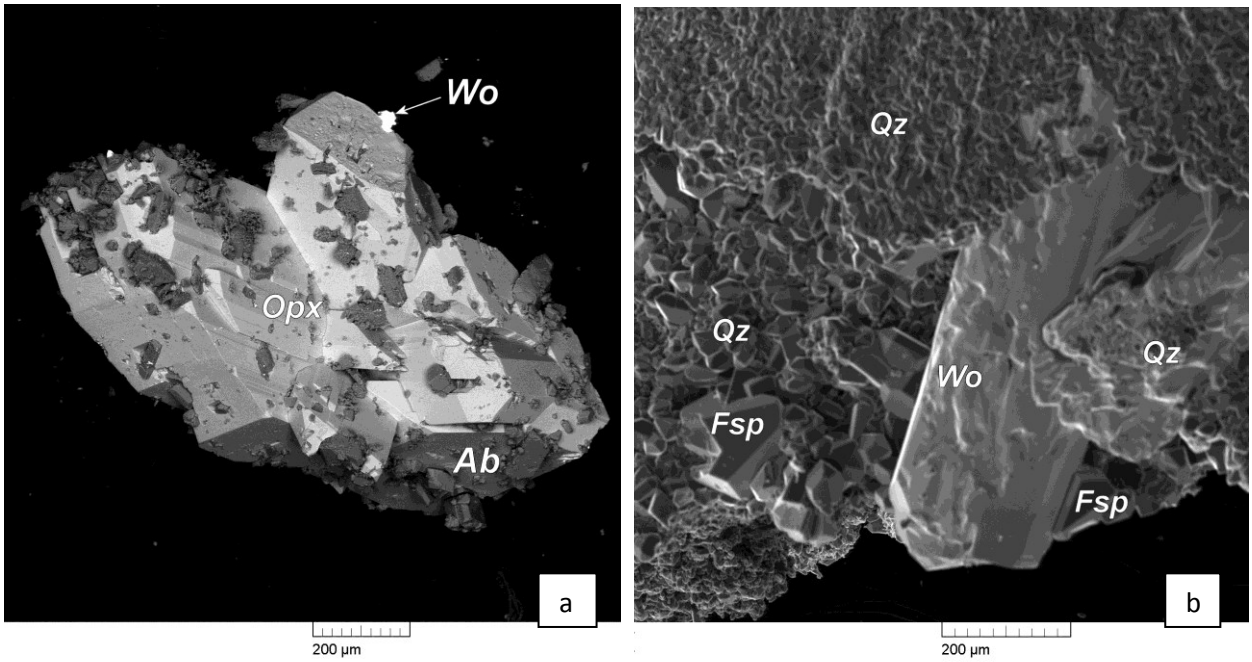

Fig. 2. Wolframite intergrowths with feldspar and orthopyroxene (a) – sample 7646, Na-specific solution; b – wolframite crystals in an intergrowth with quartz and potassium feldspar – sample 7647, K-specific solution. *Ab* – albite, *Qz* – quartz, *Fsp* – potassium feldspar, *Opx* – orthopyroxene, *Wo* – wolframite**.**

The second series of experiments was conducted to study the possibility of wolframite recrystallization and transport in postmagmatic conditions. The experiments were also conducted under thermal gradient conditions at a pressure of 3.5 kbar; the temperature at the bottom of the ampoule was T_{low} = 680°C, and at the top, T_{up} = 620°C. The experiment lasted 14 days.

Experiments were carried out for two types of solutions: Na- and K-specific. Imitation granite (Qz + Fsp mixture) with the addition of wolframite crystals $(Fe_{0.16}Mn_{0.84})WO_4$ was used as the starting material. The (Qz + Fsp) mixture was placed in the upper part of the ampoule. Substance transfer to the upper part of the ampoule was observed in both Na- and K-solutions. More intense transfer was observed in potassium-specific solutions. The following phases were found in the products of Na-specific experiments in the upper part of the ampoule: orthopyroxene, crystals from 20 μm to 2 mm (Fig. 2a), formula: $(Ca_{0.03}Mg_{0.01}Fe_{0.20}Mn_{1.80})_{2.04}Si_{1.98}O_6$, X_{Fe}^{Opx} = 0.098; rare crystals of olivine – tephroite, sizes up to 200 microns, formula $(Ca_{0.04}Mg_{0.03}Fe_{0.16}Mn_{1.57})_{1.80}Si_{1.11}O_4$, X_{Fe}^{Ol} = 0.09; feldspar $(Na_{0.80}K_{0.14})_{0.94}Al_{0.97}Si_{3.06}O_8$, X_K^{Fsp} = 0.15; wolframite (crystals up to 100 μm), formula $(Fe_{0.12}Mn_{0.86}Mg_{0.02})WO_4$, X_{Fe}^{Wo} = 0.12. Minerals often form intergrowths.

In the products of K-specific experiments, the set of phases (in the upper part of the ampoule) is as follows: orthopyroxene $(Ca_{0.04}Mg_{0.02}Fe_{0.30}Mn_{1.82})_{2.18}Si_{1.91}O_6$, X_{Fe}^{Opx}=0.14, crystallite sizes up to 30 μm; feldspar $(Na_{0.04}K_{1.03})_{1.07}Al_{0.96}Si_{3.01}O_8$, X_K^{Fsp} = 0.96; it forms crystals up to 300 microns; wolframite, formula $(Fe_{0.13}Mn_{0.85}Mg_{0.02})WO_4$, X_{Fe}^{Wo} = 0.13, sizes up to 1.5 mm (Fig. 2 b). The composition of the transferred wolframite is almost identical to the original. In addition, scheelite was found in the experimental products $(Fe_{0.01}Mn_{0.01}Ca_{0.94}Al_{0.02})WO_4$.

Based on the experimental results, it can be concluded that wolframite is transported quite well by (Na, K)-solutions of alkaline nature. During crystallization from transporting alkaline fluids with the participation of $(Na,K)_2WO_4$, parageneses of the type Qz ± Fsp + Wo are formed during interaction with Fe, Mn-bearing rocks of the endo- and exocontact zones. In addition, we have shown that wolframite can be relatively easily transported in alkaline hydrothermal fluids, practically preserving its composition (relative to the Fe/Mn ratio). This fact testifies in favor of the transport of wolframite in the form of a complex, in which the complexing agent is the molecule of the original $(Fe,Mn)WO_4$ itself, and the ligands are anions of the type (NH_4^+, Cl^-, CO_3^{2-}, OH^-). A similar mechanism is discussed in the work (Damdinov et al., 2023). The results of our experimental studies support the two-stage formation scheme of rare metal ore deposits proposed by G.P. Zaraysky (Zaraysky, 2004). W concentration occurs in residual melts of increased alkalinity, with subsequent hydrothermal processing during the separation of heterophase fluids and the formation of greisen parageneses (Qz ± Fsp + Wo), which are the source of tungsten ores.

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Kotelnikov A.R.[1], Suk N.I.[1], Kotelnikova Z.A.[2], Damdinov B.B.[3], Damdinova L.B.[4], Akhmedzhanova G.M.[1] Hydrothermal natural fluids, transport and accumulation of ore and rare elements. *UDC 550.89:550.46*

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Abstract. Based on literature and original data, the TPX parameters of ore-forming fluids in the Earth's crust were determined. They are shown to have a complex composition, a relatively high concentration (up to 35 wt%), and to be aqueous solutions of type I and II salts. This fact implies the presence of heterophase states of hydrothermal solutions. Experiments were conducted under thermal gradient conditions at T = 500-680°C and P = 3-5 kbar to assess the influence of TPX parameters of fluids on the transport of ore components. The transport of various elements (rare elements – Nb, Ta, W; ore elements – Ni, Cu, Zn, Cd, Pb) and the formation of various ore minerals in parageneses with silicate minerals, simulating natural ore associations, were experimentally studied.

***Keywords**: hydrothermal fluid, ore and rare elements, experiment*

Fluids in the Earth's crust have various origins. Several main sources of fluid supply to the Earth's crust are distinguished: (1) migration from the upper mantle due to the mechanism of plume ascent and their degassing during pressure reduction. The supply of mantle fluids occurs to the greatest extent in structures where mantle melts rise to the lower boundary of the crust, that is, in zones of tectonic-magmatic activation; (2) bound water is drawn into the upper mantle due to the mechanism of plate tectonics in the subduction zone, while with increasing temperature dehydration and separation of the fluid phase from the oceanic plate plunging into the mantle occurs – "subduction fluid"; (3) the formation of fluids directly in the deep crust as a result of metamorphic dehydration of minerals; this also includes bound water in sedimentary rocks that are submerged in deep crustal zones and dehydrated; (4) atmospheric precipitation and seawater play a certain role (diffusion and infiltration of water into mineralogenesis zones). Understanding mineralogenesis processes requires knowledge of the boundary TPX parameters. Sources of this information include various mineral geothermometers and the study of fluid inclusions in minerals. A comprehensive study of mineral parageneses allows us to obtain fairly accurate data on the processes: 1) temperatures of endogenous mineral and ore genesis vary from 700 to ~250°C; pressure – from 5 to 0.5-1 kbar; 2) mineral and ore-forming solutions are complex in composition and contain (in addition to H_2O, CO_2, CH_4, CO, H_2, N_2, SO_2, H_2S, NH_3) the following cations: Na^+, K^+, Ca^{2+}, NH_4^+, Mg^{2+}, Fe^{2+}, Fe^{3+}, Li^+, Rb^+; anions: Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, SiO_3^{2-}, NO_3^-, F^-, Br^-, BO_3^{3-}, PO_4^{3-} and others; 3) the concentration of salts in ore-generating solutions is quite high and varies from ~5 to 70 wt% (Moiseenko, Sorokin, 1988; Damdinov et al., 2023); 4) fluids enriched in salts actively dissolve silicate matter (at high TP-parameters), forming type II (PQ) solutions. Binary water-salt systems containing silica or silicates belong to type II (PQ), complicated by a metastable region of stratification of saturated solutions (Ravich, 1974; Valyashko, 1990). Such systems are characterized by anomalous solubility at elevated PT-parameters, whereas at low parameters, the solubility of metals decreases to a certain point with increasing temperature. Studies of water-salt systems of the 2nd type (Kotelnikova, Kotelnikov, 2008, etc.) have shown that in the upper region of heterogenization, separation occurs into concentrated brine and low concentrated aqueous fluid. The existence of such immiscible fluid phases has been demonstrated by studies of melt and fluid inclusions in ore-generating granitoids of the Orotskoye and Ermakovskoye beryllium deposits (Reif, 2008). In water-silicate systems with elevated parameters, heterophase fluid phases (layering of the $L_1 + L_2$ or V + L types) are often encountered – for both type I and type II systems. Such heterophase systems are characterized by hydrolysis processes with interphase separation of the hydrolytic reaction products. For example, in the H_2O – NaCl system in the liquid + vapor region: $NaCl + H_2O = HCl\uparrow + NaOH\downarrow$. Acids enrich the vapor, and alkalis enrich the liquid. Consequently, the liquid, highly saline phase will be alkaline, while the less dense vapor phase will be acidic. When moving through a porous medium,

these phases will separate spatially. The less dense, acidic phase will move ahead of the alkaline phase. The acidic and alkaline phases differ markedly in their effects on the mineral substance. The acidic phase has a destructive effect on the main rock-forming minerals, transferring their cations into an aqueous acidic solution, leaving only porous silica. This process is called acid leaching. The acidic phase decomposes sulfide minerals into salts and hydrogen sulfide: $ZnS+2HCl(aq) \rightarrow ZnCl_2(aq) + H_2S\uparrow$. And subsequently, they can migrate separately from each other – hydrogen sulfide can be oxidized to oxygen compounds. Zinc precipitation can occur at a "geochemical barrier," in a different environment, through interaction with anions CO_3^{2-}: $Zn^{2+} + CO_3^{2-} = ZnCO_3\downarrow$. Alkaline solutions interact with minerals in a different way, converting silica and alumina into soluble (in alkaline media) salts such as $(Na,K)SiO_3$ and $(Na,K)AlO_2$. Alkaline solutions form hydroxy complexes with sulfide minerals and transport the sulfide minerals, precipitating them as the temperature or alkali concentration decreases. The goal of our work was to experimentally study the transport of matter by alkaline aqueous salt solutions. Furthermore, it was necessary to explain the following problems:

1) the so-called Krauskopf paradox: many granite-related deposits formed in postmagmatic (hydrothermal) conditions, but the solubility of ore elements in aqueous salt solutions is low, requiring solution volumes 3-5 orders of magnitude greater in mass than the ore. Therefore, we should see evidence of hydrothermal reworking of the host rocks. Where are the traces of these metasomatic processes?

2) ore minerals are found in quartz veins and greisenized rocks (Sadon polymetallic sulfides, Caucasus); the famous "apogranites" of Transbaikalia with clusters of tantalum-niobate crystals in altered granites. A number of indicators (fluid inclusion studies) indicate that both the ores and host rocks are syngenetic. How did they form synchronously? What solutions and PT-parameters are required for them to simultaneously transport both silicate matter and ore components?

EXPERIMENTAL METOD

Starting materials. For experiments on the transport of sulfide minerals, we used basaltic glass from the East Pacific Rise, 3894 – a submarine sulfide ore composed primarily of sphalerite with minor amounts of galenite (Table 1). Basaltic glass composition (wt%): SiO_2 – 47.65; TiO_2 – 2.05; Al_2O_3 – 13.04; FeO – 11.26; MnO – 0.10; CaO – 10.51; MgO – 6.02; Na_2O – 2.79; K_2O – 0.05; SO_3 – 0.52; sum 93.98. The composition of the solutions was determined by various salts: NaCl, KCl, NH_4Cl, Na_2CO_3, K_2CO_3; sodium and potassium hydroxides were also added. The total salt concentration reached 30-40 wt%. To create reducing conditions, a small amount of graphite powder (10-40 mg) was added to the sample. A buffer mixture was used in some experiments (Fe-FeO-FeS-FeS_2).

Equipment. Experiments were carried out using high gas pressure vessel designed by the Institute of Experimental Mineralogy of the Russian Academy of Sciences. The experiments were conducted under gradient conditions in ampoules of quite large in size (ø7x0.2x60 mm). Temperature regulation and control accuracy was ±1°C, and pressure ±50 bar. The gradient in the experiments was 30-45°C.

Experimental Procedure. Experiments were carried out in gold (5x0.2x50 mm or 8x0.2x70 mm) and platinum (7x0.2x70 mm) ampoules. The ampoules were loaded with salts, the initial sample, and the required amount of solution. The ampoule was sealed, weighed, placed in a HGPV reactor, and were kept in experimental regime for 14-15 days.

The compositions of the experimental products were studied using X-ray microanalysis using a Tescan Vega II XMU electron microscope (Czech Republic), equipped with energy-dispersive (INCAx-sight) and crystal diffraction (INCA wave) X-ray spectrometers (Oxford, England).

Experimental results

Experiments on the transport of sulfide material (Table 1) demonstrated intense material transport to the upper (cooler) part of the capsule. The co-formation of sulfide ore mineral and silicate assemblages was demonstrated (Fig. 1 a, b).

We also studied the transport of tantalite under hydrothermal conditions (Table 2). It was shown that under gradient conditions at a pressure of 3.5 kbar, tantalite intensively recrystallizes and forms co-associations with feldspar and quartz (Fig. 2).

Table 1. Experiments on the transport of sulfide substances. T_{low} = 680 °C; T_{up} = 650°C; P=4 kbar; gradT=30 °C; 14 days

№ exp	Starting material	Solution	Experimental products
7368	200 mg basalt VTP+ sm3894 +100 mg ZnS + Fsp + Qz	50 mg NH_4Cl +100 mg NaCl+ 100 mg Na_2CO_3 +460 mkl H_2O	Ab + Cpx+Qz +Sph
7369	-"-	100 mg NH_4Cl +200 mg KCl + 200 mg K_2CO_3 +720 mkl H_2O	Ksp +Qz + Sph + Gn

Note: Ab – albite, Cpx – clinopyroxene, Qz – quartz, Sph – sphalerite, Ksp – potassium feldspar, Gn – galenite.

Table 2. Experiments on tantalite transport under gradient conditions: T_{low}=700 °C; T_{up}=650 °C; P=3.5 kbar. Duration of experiments is 14 days.

№ exp	Sample (low)	Solution	Concentration wt%	Experimental products
7399	Tnt + Fsp + Qz	NaF+NaCl+Na_2CO_3+NH_4Cl+H_2O	25	Tnt+Fsp+Qz+gl
7400	Tnt + Fsp + Qz	KF+KCl+K_2CO_3+NH_4Cl+H_2O	30	Tnt +Mcl+Fsp+Rip+Qz+gl

Note: Qz – quartz, Ksp – potassium feldspar, Tnt – tantalite, Mcl – microlite, Rip – rippite, gl – glass.

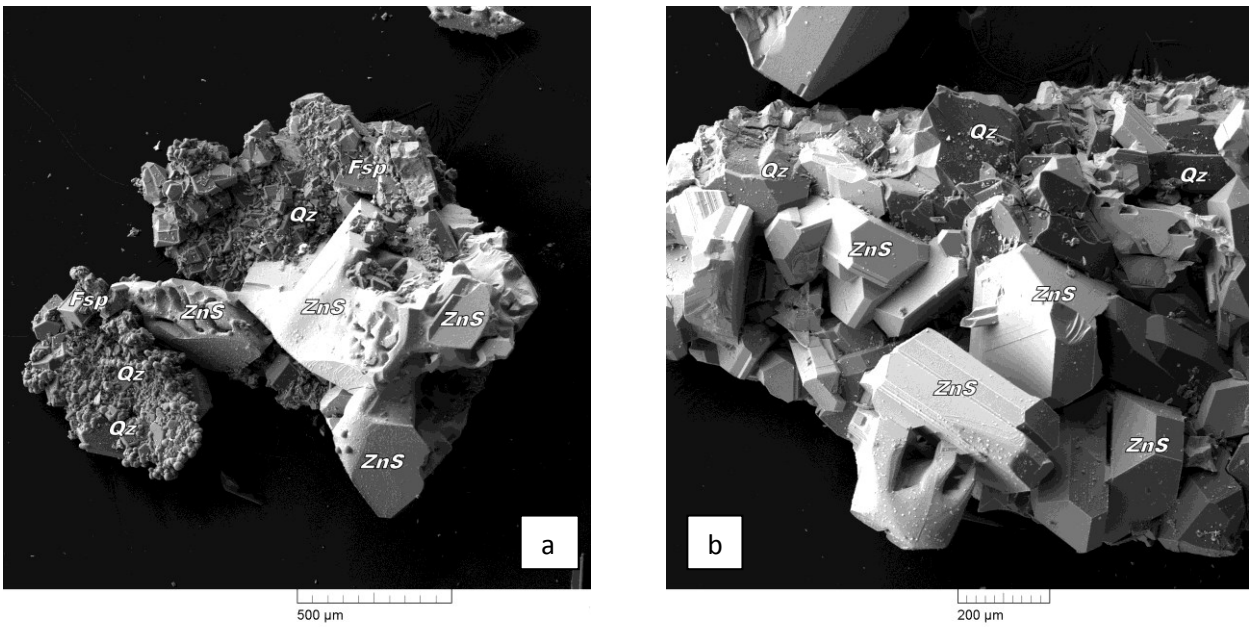

Fig. 1. Association of sphalerite, feldspar and quartz formed in the upper part of ampoule. Sample 7368. *Qz* – quartz, *ZnS* – sphalerite, *Fsp* – feldspar.

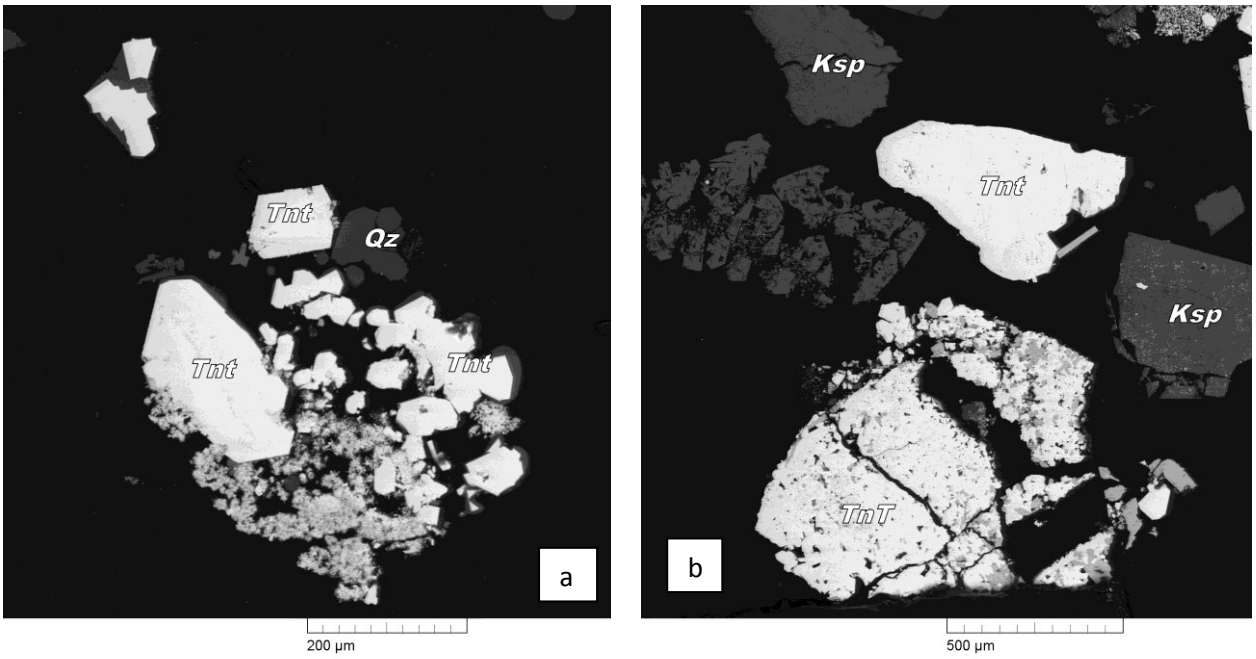

Fig. 2. Synthesized tantalite crystals with feldspar and quartz. *Tnt* – tantalite, *Qz* – quartz, *Ksp* – potassium feldspar

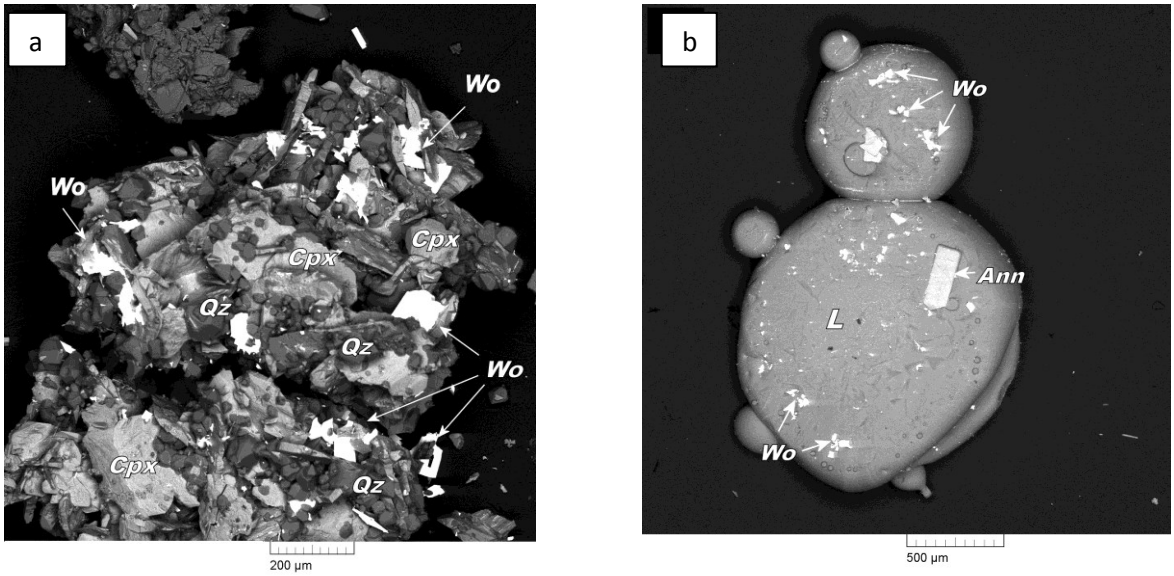

Fig. 3. Photographs of synthetic wolframite-containing parageneses. *Ab* – albite, *Cpx* – clinopyroxene, *Qz* – quartz, *Wo* – wolframite, *Ann* – ferri-annite, *L* – mel**t.**

Using thermal gradient experiments and supercritical fluids with high salt contents, we were able to model the transport and formation of tungsten ore assemblages in association with quartz and feldspar (Fig. 3). Thus, the experiments showed that at high concentrations of ore-forming fluid, pressures of ~3 kbar, and temperatures of 600-700°C, intense transport of ore minerals (polymetallic sulfides, rare-metal minerals such as tantalite and wolframite) occurs along with silicate material. This results in the formation of assemblages similar to those found in nature.

CONCLUSIONS

1. Conditions for the concentration and transport of ore matter under hydrothermal conditions are shown.

2. Ore-forming solutions are represented by salts that form type 2 solutions, which are characterized by liquid immiscibility.

3. Salt concentrations in ore-forming solutions vary from 10 to 70 wt.%.

4. Ore matter transport and the formation of ore parageneses are experimentally modeled.

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Kotova N.P. Experimental studies of Nb_2O_5 solubility in HCl solutions at 550°C and 50 TO 500 MPa.

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Abstract. Experimental data on the solubility of niobium oxide in HCl solutions with a concentration of 0.1 and 1m at T = 550 °C and P = 50, 100, 200 and 500 MPa were obtained. It was found that. with an increase in pressure from 50 to 100 MPa, the Nb content in 0.1m HCl solutions remains virtually unchanged, remaining at the level of 10^{-5} mol/kg H_2O. With a further increase in pressure from 100 to 500 MPa, the niobium content decreases and is 10^{-6} mol/kg H_2O. In 1 m HCl solutions, with a change in pressure from 50 to 100 MPa, the Nb content increases from 10^{-5} mol/kg H_2O to 10^{-4} mol/kg H_2O and remains at this level with a further increase in pressure to 500 MPa. A comparison of experimental results on the solubility of

niobium oxide in HCl solutions showed that at T = 550°C, the trends in the dependence of niobium oxide solubility on Cl - ion concentration and fluid pressure are identical.

Keywords: *experiment, niobium oxide, hydrothermal solubility, pressure, chloride solutions*

The data available in the literature on the behavior of tantalum and niobium minerals in hydrothermal solutions of various compositions over a wide range of changes in concentration, temperature, pressure, and oxygen fugacity are insufficient to understand the role of hydrothermal-metasomatic processes in the genesis of rare metal deposits in granites and to assess the degree of reliability of a particular genetic hypothesis. Therefore, the assessment of the maximum concentrations of ore elements in hydrothermal solutions in a wide range of T-P-X parameters necessary for constructing a quantitative model of the ore formation process is a pressing problem of ore genesis. For this purpose, we are conducting systematic experimental studies of the solubility of mineral phases of tantalum-niobates of complex composition (columbite, pyrochlore, etc.), stable in natural conditions, as well as simple oxides of Ta and Nb (Korzhinskaya, Zaraysky, 2003; Zaraysky et al., 2008; Kotova, Zaraysky, 2009; Kotova, 2014, 2015). The choice of simple oxides of Ta and Nb is due to the fact that their solubility limits the upper limit of the concentration of these elements in hydrothermal solutions, since the more complex composition of natural minerals with lower solubility complicates the thermodynamic interpretation of the results.

New data have been obtained on the study of the solubility of niobium oxide (Nb_2O_5), an analogue of the rarely occurring in nature mineral nioboxide, in model water-salt fluids HCl with a concentration of 0.1 and 1m at T = 550 °C, P = 50, 100, 200 and 500 MPa and the oxygen fugacity corresponding to the reducing buffer Co-CoO. In the experiments, Nb_2O_5 was used as the starting material in the form of a chemical reagent (high purity grade) previously purified by recrystallization. The duration of the experiments was 10–21 days. Experiments at 550°C and 50, 100 MPa were carried out on a high-pressure hydrothermal unit (UVD-1000) in welded platinum test tubes using a double ampoule technique, which allows the use of solid-phase oxygen buffers isolated from reagents. Experiments at 550°C and 200, 500 MPa were carried out on a high gas pressure installation UVGD-10000 with internal heating (gas bomb). It allows reaching pressures up to 1000 MPa and temperatures up to 1400°C. The temperature control accuracy is ±5°C, pressure ±5MPa.

To control congruent or incongruent dissolution and to determine the chemical composition of newly formed phases (if they appeared), the solid products of the experiments were studied using X-ray phase and microprobe analysis methods (Cam Scan MV2300(VE GA TS5130MM. The analysis of quenching solutions to determine the concentration of Nb and impurity elements was carried out using the most precise and modern methods of inductively coupled plasma ICP/MS and ICP/AES.

The results of the experiments are presented in Fig. 1. Analysis of the obtained data showed that with an increase in pressure from 50 to 100 MPa, the equilibrium content of Nb in 0.1m HCl solutions remains virtually unchanged, remaining at the level of $n*10^{-5}$ mol/kg H_2O. With a further increase in pressure from 100 to 500 MPa, the niobium content decreases and is $n*10^{-6}$ mol/kg H_2O.

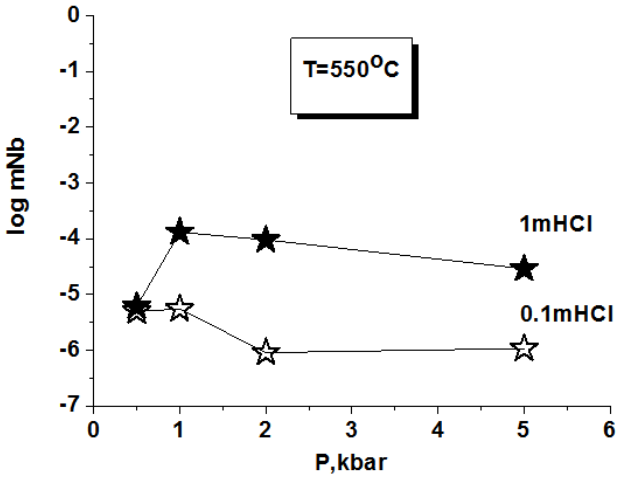

Fig 1. The effect of HC1 concentration and fluid pressure on the solubility of Nb_2O_5 at T=550°C, Co - CoO buffer (asterisks - 1 m HC1, shaded asterisks - 1 m HC1)

In 1 m HCl solutions, with a change in pressure from 50 to 100 MPa, the Nb content increases from $n*10^{-5}$ mol/kg H_2O to $n*10^{-4}$ mol/kg H_2O and practically remains at this level with a further increase in pressure to 500 MPa. A comparison of the experimental results on the solubility of niobium oxide in HCl solutions showed that at T = 550°C, the trends in the dependence of niobium oxide solubility on the concentration of the Cl - ion and fluid pressure are identical.

The results of the X-ray phase analysis of solid experimental products showed that in a 0.1 m HCl solution at T = 550°C and P = 100 MPa, niobium oxide dissolves congruently without changing the composition. In 1 m HCl solution at T = 550°C and P = 100 MPa, niobium oxide is replaced by the β-Nb_2O_5 modification of the monoclinic syngony c2./c.

The experimental studies of the concentration and pressure dependence of the solubility of niobium oxide (Nb_2O_5) in aqueous solutions of 0.1m and 1m HCl at T = 550°C, P = 50–500 MPa and low oxygen fugacity (Co-CoO buffer)

showed that over the entire range of conditions studied, niobium oxide has a clearly expressed positive dependence of solubility on the concentration of chlorides, and the pressure dependence is practically absent.

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