

three-phase (taking into account the SB phase - four-phase) state. At 322°C, the phase of liquid hydrocarbons disappears (dissolves), and the fluid passes into a two-phase gas-liquid state. A further increase in temperature to 385°C leads to complete homogenization of the fluid with the disappearance of the gas (mainly methane) phase. Inclusion formation condition: 10 wt. % NaHCO_3 , temperature 385/405 °C, pressure 120 MPa, duration 20 days.

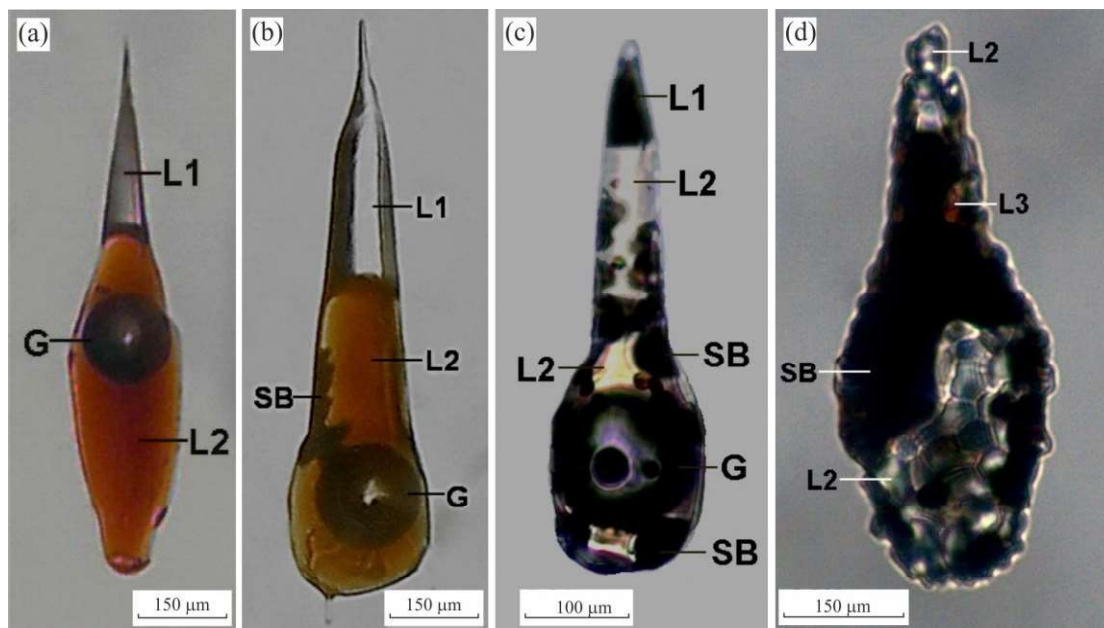


Fig. 5. Predominantly oil water-hydrocarbon inclusion after autoclave treatment at (a) – 300 °C, (b) – 320 °C, (c) – 350 °C, (d) – 380 °C and 100 MPa for 14 days. Up to 300 °C, no changes are observed in water-hydrocarbon fluids. At 320 °C and above, solid bitumen (SB) appears in them, the proportions of methane, CO_2 and light liquid hydrocarbons (L2) increase, reaching a maximum at 350 °C; above 380°C, liquid hydrocarbons almost completely disappear, turning into solid bitumen, gaseous hydrocarbons, and CO_2 . Conditions for the formation of inclusions: aqueous solution of 7.5 wt. % Na_2CO_3 + 10 vol. % oil, temperature 280/310 °C, pressure 12 MPa.

Thus, the analysis of microthermograms with the determination of the phase composition and states of trapped inclusions convincingly proves the existence of various types of water-hydrocarbon fluids in the earth's interior. The main ones are:

- heterogeneous three-phase fluids with volumetric phase ratios: $\text{L1} > \text{G} \gg \text{L2}$;
- heterogeneous two-phase liquid aqueous-hydrocarbon fluids with a phase ratio $\text{L2} \gg \text{L1}$ with a completely dissolved gas phase G;
- homogeneous liquid predominantly aqueous fluids L1_{hom} with completely dissolved gaseous and liquid hydrocarbons;
- homogeneous gas fluids G_{hom} with completely dissolved phases of liquid hydrocarbons and water;
- homogeneous hydrocarbon fluids L2_{hom} with completely dissolved aqueous (L1) and gas (G) phases.

References

- Balitsky V.S., Balitskaya L.V., Bublikova T.M., Borkov F.P. Water-hydrocarbon inclusions in synthetic quartz, calcite, and fluorite crystals grown from oil-bearing hydrothermal solutions (experimental data)// *Doklady Earth Sciences*. 2005. Vol. 404. No7. P.1050–1053.
- Balitsky V.S., Penteley S.V., Pironon J., Barres O., Balitskaya L.V., Setkova T.V. Phase states of hydrous–hydrocarbon fluids at elevated and high temperatures and pressures: Study of the forms and maximal depths of oil occurrence in the earth's interior// *Doklady Earth Sciences*. 2016. Vol. 466 No 2. P.130–134.
- Ermakov N.P., Dolgov Yu.A. Thermobarogeochemistry. Publishing House Nedra, M.1979, 271 p. (in russian).
- Redder E. Fluid inclusions. The nature of inclusions and methods for their study. Volume 1. M.: Mir, 1987. 560 p. (in russian)

Kotelnikov A.R.¹, Damdinov B.B.², Suk N.I.¹, Damdinova L.B.², Kotelnikova Z.A.^{1,3}, Akhmedzhanova G.M.¹ Transport of matter under the Earth's crust conditions and the genesis of ore deposits (experimental studies).
UDC: 553.21/.24

This study was funded by RFBR according to the research project No 21-55-15010 and Research Program № FMUF-2022-0003 of the Korzhinskii Institute of Experimental Mineralogy RAS.

¹IEM RAS, Chernogolovka Moscow district, (kotelnik@iem.ac.ru); GI SB RAS, Ulan-Ude (damdinov@mail.ru); ³IGPMG RAS, Moscow (kotelnik@igem.ru)

Abstract. Model experiments have been carried out to study the transport of matter under the conditions of the lithosphere. The experiments were carried out at $T=500\text{--}680^\circ\text{C}$ and a pressure of 1.5-5 kbar in concentrated water-salt solutions under a temperature gradient in a high gas pressure vessel. The temperature gradient in the experiments was $0.5^\circ\text{C}/\text{mm}$, the duration of the experiments was 14 days. It is shown that intensive recrystallization and precipitation of sulfide minerals (sphalerite, galena, chalcopyrite, pyrite, cooperite, etc.) occur at a temperature of $680\text{--}650^\circ\text{C}$ together with feldspars, micas and quartz. The data obtained make it possible to explain the Krauskopf paradox and show the possibility of quantitative modeling of ore genesis processes.

Keywords: *experiment, ore genesis, water-salt solutions, sulfide minerals*

To understand the mechanism of transport of ore matter under the conditions of the earth's crust, it is necessary to study the chemical and phase composition of fluids in the presence of silicate matter. The main problems of transport and ore deposition are as follows.

(1) What is the source of the ore substance, what processes lead to the concentration of ore elements.

(2) Conditions for the transport of matter – at what temperatures and pressures is the transport of matter carried out in the conditions of the earth's crust? What is the phase and chemical composition of the transport fluids? The role of fluid heterogenization in the transfer of matter.

(3) Krauskopf's paradox – many deposits were formed in post-magmatic (hydrothermal) conditions, however, the solubility of ore elements in water-salt solutions is low and volumes of solutions are required by 3-5 orders of magnitude greater in mass than the mass of ore. Then we should see signs of hydrothermal reworking of host rocks. Where are the traces of these metasomatic processes?

(4) Nests of ore minerals occur in quartz veins (polymetal sulfides of Sadon, Caucasus); the famous "apogranites" of Transbaikalia – with accumulations of tantalum-niobate crystals in altered granites. According to a number of features (study of fluid inclusions), both ores and host rocks are syngenetic. How did they form at the same time? What solutions are needed so that they simultaneously transport both the silicate substance and ore components?

(5) Albitization, K-feldspathization, silicification – its mechanism, significance and role in the formation of ore deposits.

The answer to the first question may be the preliminary concentration of the ore substance in the process of differentiation of silicate melts. In the process of crystallization 1, incompatible elements enrich the residual melt, or in the form of a high-

density liquidus crystalline phase, being precipitated, are separated from the silicate melt (chromites). A very important mechanism for concentrating ore matter is liquid immiscibility: (1) separation of sulfide droplets from the silicate melt; (2) layering of the silicate melt in the presence of fluid into two liquids, with enrichment of one of the phases in ore elements; (3) layering of the silicate melt - salt melt type, etc. The primary accumulation of sulfide minerals may be submarine deposits of "black smokers".

The conditions of substance transfer require an accurate assessment of the TP-parameters of the processes, for which we have a complex of mineral thermometers and barometers that allow us to estimate the parameters with an accuracy of $\pm 30^\circ\text{C}$ and $\pm 0.5 \div 1$ kbar. To assess the compositions of ore-forming fluids, studies of the compositions of fluid inclusions are widely used. It can be concluded that the following salt composition (per 100% dry salt) of ore fluids is: $(\text{NaCl}+\text{KCl}) \sim 40\text{--}50$ wt%, $(\text{Na}_2\text{CO}_3+\text{K}_2\text{CO}_3) \sim 30\text{--}40$ wt%, $\text{NH}_4\text{Cl} \sim 10$ wt%. In some cases (alkaline magmatic rocks, lithium-fluorine granites), fluorides ($\text{NaF}+\text{KF}$) begin to play an important role in the composition of fluid salts. The presence of carbon dioxide is almost always noted. The phase composition of the fluid is determined by the PTX-parameters. The salt load of the ore-bearing fluid is (on average) $15\div 50$ wt%. Fluid heterogenization by the salt hydrolysis reaction $\text{NaCl} + \text{H}_2\text{O} = \text{NaOH} + \text{HCl}$ produces acidic and alkaline components. This reaction in a homogeneous fluid is reversible; in the presence of a two-phase system, an interphase redistribution of alkaline and acidic components occurs: acids enrich the less dense phase, and alkalis enrich the denser one. This mechanism of reactions in heterophase systems allowed D.S. Korzhinsky put forward the position on the waves of acidic and alkaline fluids. Moreover, the later, alkaline fluid was considered ore-bearing. Therefore, we set the task of studying the transport of matter in the ore (alkaline) phase of the fluid.

To overcome the "Krauskopf paradox", sufficiently high concentrations of ore metals in the mineral-forming fluid are required. In addition, such a fluid must simultaneously transport both silicate and ore matter.

Experiments to study the transport of ore matter were carried out at a temperature of $500\text{--}650^\circ\text{C}$ and a pressure of 3–5 kbar. It is these values of PT-parameters that were obtained for a number of deposits using mineral thermometers and barometers and the results of studying fluid inclusions. The total salt concentration in the model fluid was 37–41 wt%. The experiments were carried out in the temperature gradient mode of $30\text{--}40^\circ\text{C}$. All experiments were performed using the ampoule method in high gas

pressure vessel designed by IEM RAS. The accuracy of temperature regulation and control was no worse than $\pm 2^{\circ}\text{C}$, pressure ± 50 bar. Gold and platinum ampoules 7 mm in diameter and 70 mm long were used. The duration of the experiments was 14 days. The initial sample was placed in the lower part of the ampoule and transported to the upper part. Table 1 shows the conditions of experiments on the transport of marine sediment material (basalts and black smokers), in order to simulate the formation of the Zun-Kholbinsk polymetal and gold deposit.

Experiments 7368 and 7369 are characterized by the formation of parageneses of the Fsp + Qz + sulfides type in the upper part of the ampullae (Fig. 1a).

We have carried out experiments on the joint transfer of a number of ore elements Fe, Ni, Cu, Zn,

As, Cd, Hg, Bi, Au under gradient conditions at a temperature $T_{\text{bottom}}=680^{\circ}\text{C}$; $T_{\text{top}}=650^{\circ}\text{C}$; $P=5$ kbar, with the duration of the experiment 14 days. Loading of gold ampoule with a diameter of 7 mm is shown in table 2.

As a result of the experiment, it was shown that a number of elements form their own minerals, while others are present in the form of isomorphic elements: Fe, Ni, Cu are included in pyrite, pyrrhotite; Pb, Au, As, Bi, Zn are present in galena; sphalerite includes Zn, Cd, Fe, Mn, Cu; As is included in galena, orpiment, realgar, gold; Hg is present in gold. Figure 1b shows intergrowths of minerals from run 7387. Thus, it is shown that ore and silicate matter can be transported together by a relatively simple fluid and form ore parageneses.

Table 1. Experiments on the transport of substances from submarine marine sediments ($T_{\text{bottom}}=680^{\circ}\text{C}$; $T_{\text{top}}=650^{\circ}\text{C}$; $P=4$ kbar; experiment duration 14 days).

№ sample	Weight, mg	Salts, mg	H ₂ O, μl	Experience Products
7368	184 powder VTP bas ¹⁾ , 111 ZnS+176 BS +135Qz(gl)+202Ab+284 Qz	50 NH ₄ Cl + 100 NaCl + 100 Na ₂ CO ₃	460	Ab +Cpx+ Qz + ZnS + PtS
7369	150 powder VTP bas, 100 ZnS+200 BS +100Qz(gl)+10 FeO+10 grp+ 100Mic+243 Qz	200 K ₂ CO ₃ + 200 KCl + 100 NH ₄ Cl	720	Ksp+Qz+ZnS+PbS+ PtS+ CuFeS ₂

1) powder VTP – basalt, BS – black smoker substance (base ZnS+ a little PbS); Qz – quartz, Qz(gl) – quartz glass; Ab – albite, grp – graphite, Cpx – clinopyroxene; Ksp – potassium feldspar.

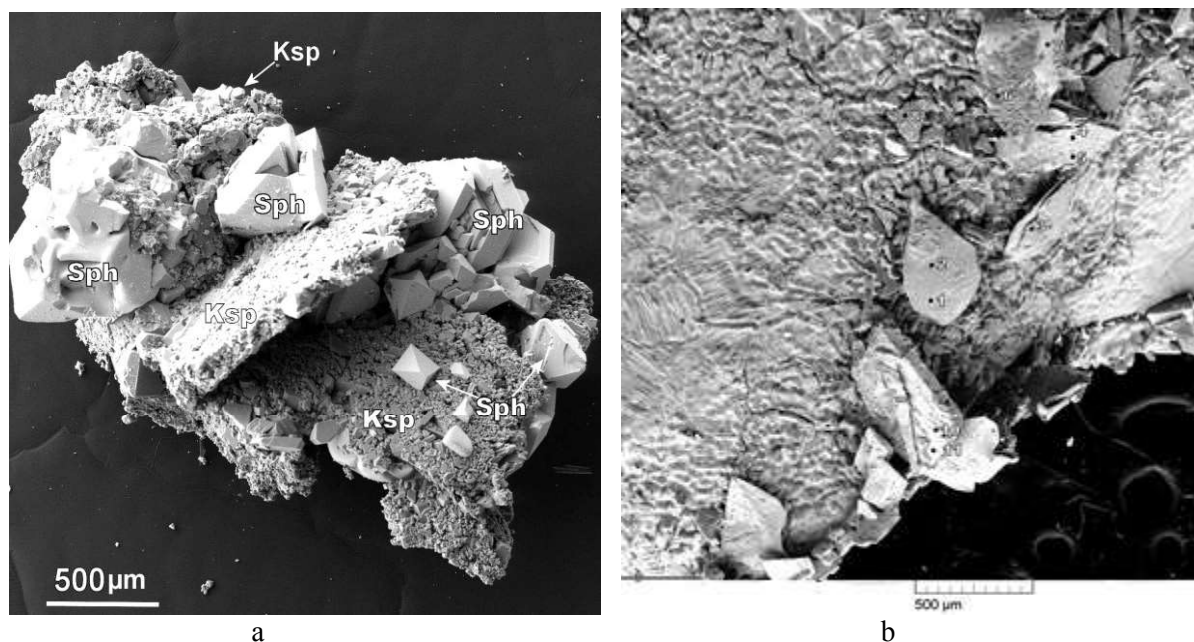


Fig. 1. Paragenesis of Ksp + Sph (experiment 7369) – a; 1,2 – orpiment; 3,5 – realgar?; 4,7 – Au (with As, Hg); 6 – Sph (with Mn, Fe, Cd, Cu, As); 8 – (PbS+As₂S₃); 9, 10 – Gn (with As, Cd). Ksp – potassium feldspar, Sph – sphalerite, Gn – galena – b.

Table 2. Experiment in the joint transport of ore elements

№ sample	Weight, mg	Solution, salts, mg	H ₂ O, µl	Products of experience (top of the ampoule)
7387	260 powder VTP bas ¹⁾ , + 210 BS+ 72 CPy+ 44 Pentl + 14 AsPy+ 24 CdS + 10 HgS +10 Bi ₂ O ₃ +28 Au +135 Qz(gl)+202 Ab +284 Qz	120 NH ₄ Cl+ 50 NaCl+90 Na ₂ CO ₃ + 100 µl 20% NaOH + 20 C + 20 S	360	Qz + Ab + Cpx + Sph + Py + Pyr + Wrz + Gn + <u>orpiment</u> + realgar + Au

1) powder VTP – basalt, BS – black smoker substance (base ZnS+ a little PbS); Qz – quartz, Qz(gl) – quartz glass; Ab – albite, grp – graphite, Cpx – clinopyroxene; AsPy – arsenopyrite; Cpy – chalcopyrite; Gn – galena; Py – pyrite; Pyr – pyrrhotite; Wrz – wurtzite; Sph – sphalerite.

Table 3. Experiments on the transport of tantalite under gradient conditions: T_{bottom}=700°C; T_{top}=650°C; pressure 3.5 kbar. The duration of the experiments was 14 days.

№ sample	Weight, (bottom of ampule)	Solution	Total salinity	Experience Products
7399	Tnt +Fsp+ Qz	NaF+NaCl+Na ₂ CO ₃ +NH ₄ Cl	25 wt%	Tnt+ Ab +Qz+gl
7400	Tnt +Fsp +Qz	KF+KCl+K ₂ CO ₃ +NH ₄ Cl	31 wt%	TnT+Mcl+Ksp+Rip+Qz+gl

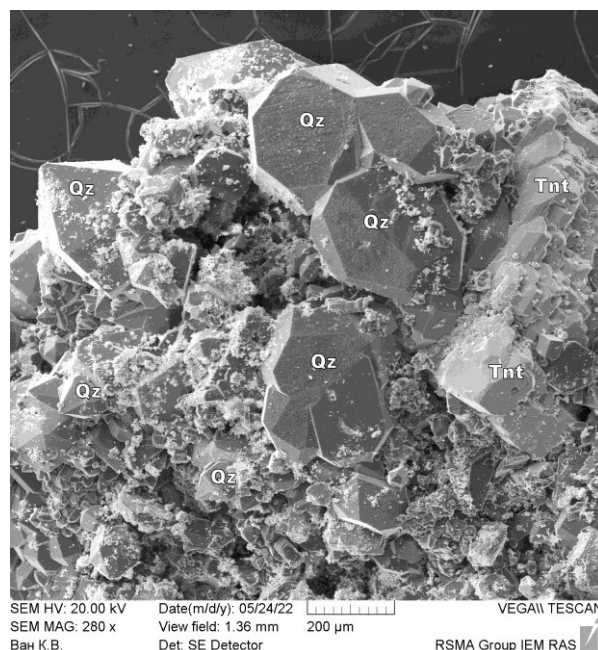
1) mineral indices: Ab – albite; Fsp – alkaline feldspar; gl – silicate glass; Ksp – potassium feldspar; Mcl – microlite; Qz – quartz; Rip – rippit; Tnt – tantalite.

Experiments were carried out to study the transport of tantalite together with a silicate substance. These experiments were carried out in order to test the hypothesis of a possible hydrothermal origin of ore apogranites in Transbaikalia. For the Orlovsky deposit, the TP-parameters for the formation of apogranites were determined: temperature is about 600-650°C, pressure is ~3.5 kbar. These parameters were estimated for the formation of Orlovka apogranites from the structural state of feldspars and from the study of the densities of carbon dioxide in fluid inclusions. The conditions for conducting experiments on the transfer of tantalite and silicates are given in Table 3. Figure 2 shows parageneses of tantalite with silicate minerals of the experimental products.

Based on our experiments, we can conclude that it is possible to transport and concentrate the substance of tantalum-niobate ores at the hydrothermal, post-magmatic stage of the evolution of lithium-fluoric granites. Most likely, this mechanism could be implemented during the formation of ore apogranites in Transbaikalia.

Conclusions

It is shown that ore components are able to migrate at relatively high parameters due to concentrated water-salt fluids. Mineralizers are solutions of chlorides, alkali metal carbonates and ammonium salts. In some cases, alkali metal fluorides may be present in the salt composition. These model solutions are distinguished by increased alkalinity and can serve as a model for solutions of the alkaline ore stage of mineral genesis (according to D.S. Korzhinsky).

**Fig. 2.** Crystals formed as a result of the transfer of a substance to the upper part of the ampoule. Qz – quartz, Tnt – tantalite.

Along with the ore components, a silicate substance is transported in water-salt solutions, which gives to these water-salt systems the properties of II (P-Q) type solutions, characterized by a number of features: high solubility of both silicate and ore minerals, the presence of a lower (liquid-vapor) and the upper (liquid1-liquid2) regions of heterogenization, where separation into two fluids

occurs – a highly concentrated brine and a weakly concentrated aqueous fluid.

The deposition of ore components occurs mainly from highly concentrated fluids, later they are displaced by weakly concentrated fluids. The latter are conserved as fluid inclusions containing low concentrations of ore elements. Nevertheless, when analyzing the FI of quartz from ore parageneses, inclusions with anomalously high concentrations of metals are encountered. Apparently, they are relics of highly concentrated – ore-forming solutions.

The work was supported by the FMUF-2022-0003 program.

Kotova N.P. Experimental study of Nb₂O₅ solubility in KF solutions at 550° C and from 50 to 500 MPa.

Institute of Experimental Mineralogy RAS, Chernogolovka
Moscow district kotova@iem.ac.ru

Abstract. Experimental data on the niobium oxide solubility in KF solutions with a concentration of 0.1 and 1.0 m at 550° C and 50, 100, 200 and 500 MPa were obtained. It was found that with an increase in pressure from 50 to 200 MPa, the Nb content in 0.1 mKF solutions increases by an order of magnitude. With a further increase in pressure to 500 MPa, the niobium content practically does not change and remains in the range of $10^{2.5}$ mol / kg H₂O.

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

For many years, we have been conducting systematic experimental and field geological studies aimed at obtaining quantitative estimates of the physico-chemical conditions for the formation of greisen and albitite deposits of W, Mo, Sn, Ta, Nb and Li associated with standard lime-alkaline, including lithium-fluoride granites. Despite the great achievements of geologists in the field of studying ore-bearing granites and related greisen, albitite and other genetic types of rare metal deposits, many fundamental questions of their genesis still remain unclear. As is known, there are various hypotheses of the genesis of these deposits - magmatic and hydrothermal-metasomatic.

The most generally accepted are the genetic concepts of V.I. Kovalenko [Kovalenko, 1977], consisting in the fact that rare-metal lithium-fluoride granites containing tantalum ores are formed as a result of crystallization fractionation of ordinary granite magma under specific conditions that ensure the gradual accumulation of F, Li, Ta, Nb and other rare metals in the residual granite melt.

However, to model the conditions for the formation of tantalum deposits, it is also necessary to take into account the role of hydrothermal-metasomatic processes [Beus et al., 1962]. The

results of our experimental studies under conditions of temperatures, pressures and compositions of solutions corresponding to the physicochemical parameters of postmagmatic processes may provide some new criteria and limitations regarding the interpretation of geological data and the assessment of the degree of reliability of a particular genetic hypothesis of the origin of rare-metal deposits in granites.

New experimental data were obtained on the solubility of niobium oxide (β -Nb₂O₅), an analogue of the mineral nioboxide, rarely found in nature, in 0.1 and 1 m KF solutions at 550 °C and 50, 100, 200 and 500 MPa. The run duration was 10 - 18 days. Experiments at 550 °C and 50 to 100 MPa were performed on a hydrothermal line. A sealed-capsule quench technique was employed.

Experiments at 550°C and 200 to 500 MPa were carried out on a high gas pressure installation with internal heating (gas bomb). It allows reaching pressures up to 6 MPa and temperatures up to 1400 °C. Run temperatures were measured with an accuracy of ± 5 °C. The pressure was regulated with a maximum uncertainty of ± 5 MPa. Regulation and maintenance of the required temperature in the working chamber of the furnace is carried out using the TRM-101 OVEN thermostat through two S-type thermocouples (Pt90Rh10-PT100). Thermocouples are mounted at the top and close to the bottom of the chamber to control the temperature gradient. The chamber system pressure is set from above by pure argon gas pressure. The lid of the working chamber is made of pyrophyllite. Aluminum oxide and kaolin wool serve as filler in the chamber with ampoules.

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.

To control congruent or incongruent dissolution of Nb oxide 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 experimental results are shown in Figures 1 and 2. Analysis of the data obtained showed that in 0.1 m KF solutions, an increase in fluid pressure from 50 to 200 MPa leads to an increase in the solubility of niobium oxide by one order of magnitude (from $n \cdot 10^{-3.5}$ to $n \cdot 10^{-2.5}$ m). With a further increase in pressure from 200 to 500 MPa, the solubility of niobium oxide does not change, remaining at the level of $n \cdot 10^{-2.5}$ m. With an increase in the concentration of F⁻ - ion (1 m KF solutions), the equilibrium content of Nb increases, reaching a significant value ($n \cdot 10^{-2}$ m.). However, in concentrated 1 m KF solutions, with an increase in