Experimental Study of the Solubility of Natural Tantalite and Pyrochlore and Tantalum and Niobium Oxides in Hydrothermal Fluoride–Chloride Solutions

N. P. Kotova*, V. S. Korzhinskaya*, and Corresponding Member of the RAS Yu. B. Shapovalov*

Received March 25, 2022; revised April 5, 2022; accepted April 5, 2022

Abstract—The concentration and temperature dependences of the solubility of tantalite, pyrochlore, and tantalum and niobium oxides in fluoride–chloride aqueous (mHF + mHCl) solutions at 300–550°C and 100 MPa (Co–CoO buffer) were studied experimentally. The initial concentration of HF varied from 0.01 m to 2 m, while the HCl concentration remained constant and was 0.5 m. A comparative analysis of the equilibrium contents of Nb and Ta upon dissolution of tantalum and niobium oxides and natural tantalite and pyrochlore in fluoride, chloride, and mixed (mHF + mHCl) solutions was carried out.

Keywords: experiment, tantalite, pyrochlore, tantalum and niobium oxides, solubility, fluoride–chloride fluid

DOI: 10.1134/S1028334X22070108

INTRODUCTION

The development of scientific criteria for prediction and the search for deposits of economically important metals requires a clearer understanding of the conditions of their formation, the forms of transport of ore elements, and their behavior in various physicochemical environments. It is well known that rare-metal granite is a promising object for tantalum–niobium mineralization. The geological data (mineralogical, structural, geophysical, etc.) on a particular deposit undoubtedly provide the fundamental basis for the study of the genesis of rare-metal deposits. Over the past several years, researchers have accumulated a huge amount of material on their geological structure, petrology, geochemistry, mineralogy, geo-dynamic position, and genesis. However, despite the great achievements of geologists in the field of the study of ore-bearing granite and related greisen, albitite, and other genetic types of rare metals, many fundamental problems of their genesis still remain unclear.

The most generally accepted genetic ideas of V.I. Kovalenko [5] suggest that rare-metal lithium–fluorine granite hosting tantalum ores is formed by crystallization fractionation of ordinary granite magma under the specific conditions that ensure the gradual accumulation of F, Li, Ta, Nb, and other rare metals in the residual granite melt. However, it is also necessary to take into account the role of hydrothermal–metasomatic processes in order to model the physicochemical conditions of the formation of greisen and albitite deposits of W, Mo, Sn, Ta, Nb, and Li associated with standard calc-alkaline granite, including the lithium–fluoride variety [2, 15]. The papers [3, 4, 6, 7] showed the decisive role of metasomatic processes in the genesis of granite, as well as in the distribution of accessory minerals of rare metals. The role of these processes in the formation of Ta and Nb deposits is one of the most important issues of modern geochemistry.

In this regard, experimental studies of the solubility of ore minerals under controlled physicochemical parameters are of key importance, since their results are necessary for the creation of reliable databases of experimental data applied for definition of the predominant forms of transfer of ore elements, assessment of their thermodynamic properties, and subsequent creation of quantitative models of fractionation of ore elements in the natural environment. They are also used for study of the conditions of the formation of large and industrially significant rare-metal deposits associated with granite of various alkalinity, including Li–F granites, and for validation of the existing genetic hypotheses of their origin.

At present, the data on the solubility of Ta and Nb minerals under the T–P–X–f(O2) conditions corresponding to magmatic and hydrothermal processes of mineral and ore formation available at the world level

---

GEOCHEMISTRY
are clearly insufficient for understanding the role of hydrothermal–metasomatic processes in the genesis of rare-metal deposits. Therefore, the assessment of the limiting concentrations of ore elements in hydrothermal solutions in a wide range of \( T-P-X \) parameters necessary for construction of a quantitative model of ore formation is an important problem of ore genesis.

**EXPERIMENTAL METHODS AND TECHNIQUES**

This work is related to long-term complex experimental studies of the processes of concentration, forms of transfer, and precipitation of ore components (Ta, Nb, W, U, etc.) \[8, 13, 14, 16\]. The method of ore-mineral solubility based on analysis of the behavior of the ore element (component, mineral) content depending on the bulk concentration of the solvent was selected as the main research instrument. All experiments were carried out on a high-pressure hydrothermal apparatus (with limiting parameters of \( 600 \pm 5^\circ \) C and \( 200 \) MPa). The redox conditions in the experiments were set with the Co–CoO buffer pair. To achieve equilibrium more rapidly, platinum test tubes that are easily permeable to hydrogen were used in the experiments. The study of the solubility of niobium oxide (an analogue of the natural mineral nioboxide) and tantalum oxide (an analogue of the natural mineral tantite) was carried out using chemical reagents preliminarily purified by hydrothermal recrystallization in a 0.1 M HF solution at \( 550 \pm 5^\circ \) C and 100 MPa, namely, pure tantalum oxide (\( \beta \)-Ta\(_2\)O\(_5\)) grade and ultrapure niobium oxide (\( \beta \)-Nb\(_2\)O\(_5\)). To study the solubility of pyrochlore (\( \text{Ca,Na}_{2}(\text{Nb,Ta})_{2}$$\text{O}_{6}(\text{O,OH,F}) $$ and tantalite (\( \text{Mn,Fe})_{2}(\text{Ta,Nb})_{2}$$\text{O}_{6} $$, natural single crystals of pyrochlore were taken from the weathering crust of the Tatarka carbonatite deposit (the composition obtained by EMPA is the following, wt \%: 7.61 Na\(_2\)O, 14.28 CaO, 71.61 Nb\(_2\)O\(_5\), 5.18 F, 0.83 TiO\(_2\), \( \leq 1 \) Ta\(_2\)O\(_5\)), and tantalite from quartz–amazonite–mica pegmatoids of the Etyka tantalum deposit, which had the following composition according to the analysis on a CamScan MV2300 (VEGA TS 5130MM) electron microprobe (wt \%, mean of seven analyses): 58.99 Nb\(_2\)O\(_5\), 17.70 Ta\(_2\)O\(_5\), 13.51 MnO, 4.42 FeO, 2.59 TiO\(_2\), 1.54 SnO\(_2\), and 1.24 WO\(_3\). In the experiments, we used their fragments with a size of \( \sim 2-3 \) mm weight of \( \sim 0.1-0.05 \) g, which were preliminarily treated with 0.1 M HF solution, washed with water, and dried. Fluoride–chloride solutions were prepared from the corresponding HF and HCl reagents of high purity grade based on twice-distilled water. The concentrations of the initial HF solutions varied from 0.01\( m \) to 2\( m \), while the HCl concentration remained constant and amounted to 0.5\( m \). It should be noted that the selected range of HF concentrations corresponds to the real range of fluoride concentrations in natural postmagmatic fluids in deposits associated with granite.

According to the data [1] obtained on the basis of an experimentally developed mica geofluorimeter, the concentration of HF in aqueous fluids separated from the granite melt at the transitional magmatic–hydrothermal stage of the evolution of ore–magmatic systems is \( \sim 0.01 \) mol/kg H\(_2\)O for copper–molybdenum porphyry deposits. It is higher by one order of magnitude in the Akchatau-type greisen deposits of W, Mo, Sn, Be, and Bi (0.1 mol/kg H\(_2\)O) and reaches the maximum values of 1.0 mol/kg H\(_2\)O in rare-metal tantalum deposits from lithium–fluorine “apogranite” of the Orlovskoe and Etyka types of rare–metal massifs. In our experiments, 2.0 mol/kg H\(_2\)O solutions were used as the limiting concentrations of HF.

During the preparation of experiments, 50 mg of the investigated solid material was added to a platinum test tube \( 8 \times 0.2 \times 50 \text{ mm}^3 \) in size, the solution was poured in an amount corresponding to the \( T-P-X \) parameters of the experiment, and then the tube was sealed by electric arc welding. Equipped test tubes and special containers made of stainless steel with an oxygen buffer of Co–CoO were placed in the reactors of a high-pressure hydrothermal apparatus, the working zones of which provided isolation of test tubes made of noble metals from buffer devices. The duration of the experiments was 15–30 days depending on the parameters selected. After the experiment, the test tubes were removed from the reactor, weighed, and opened. Weighing was carried out on an AP250D electronic balance (Ohaus) with an accuracy of \( \pm 0.01 \) mg. The solution from the test tube was separated from the sample by centrifugation (an adjustable rotation speed up to 10 000 rpm) and taken for analysis. The sample was thoroughly washed and dried at \( 100^\circ \) C in an oven. Analysis of quenched solutions for the concentration of Ta, Nb, and impurities of other elements (Mn, Fe, Ti, W, Sn, etc.) was carried out using the most precise and modern methods of inductively coupled plasma ICP/MS and ICP/AES. The phase composition of run solid products was studied by powder X-ray diffraction (XRD), and the composition of the crystals was analyzed on a CamScan MV2300 scanning electron microscope (VEGA, 130 mm).

**RESULTS OF EXPERIMENTS AND DISCUSSION**

Using modern research methods, the first data on the solubility of niobium (\( \beta \)-Nb\(_2\)O\(_5\)) and tantalum (\( \beta \)-Ta\(_2\)O\(_5\)) oxides, as well as natural pyrochlore (\( \text{Ca,Na}_{2}(\text{Nb,Ta})_{2}$$\text{O}_{6}(\text{O,OH,F}) $$ and tantalite (\( \text{Mn,Fe})_{2}(\text{Ta,Nb})_{2}$$\text{O}_{6} $$, were added to a platinum test tube \( 8 \times 0.2 \times 50 \text{ mm}^3 \) in size, the solution was poured in an amount corresponding to the \( T-P-X \) parameters of the experiment, and then the tube was sealed by electric arc welding. Equipped test tubes and special containers made of stainless steel with an oxygen buffer of Co–CoO were placed in the reactors of a high-pressure hydrothermal apparatus, the working zones of which provided isolation of test tubes made of noble metals from buffer devices. The duration of the experiments was 15–30 days depending on the parameters selected. After the experiment, the test tubes were removed from the reactor, weighed, and opened. Weighing was carried out on an AP250D electronic balance (Ohaus) with an accuracy of \( \pm 0.01 \) mg. The solution from the test tube was separated from the sample by centrifugation (an adjustable rotation speed up to 10 000 rpm) and taken for analysis. The sample was thoroughly washed and dried at \( 100^\circ \) C in an oven. Analysis of quenched solutions for the concentration of Ta, Nb, and impurities of other elements (Mn, Fe, Ti, W, Sn, etc.) was carried out using the most precise and modern methods of inductively coupled plasma ICP/MS and ICP/AES. The phase composition of run solid products was studied by powder X-ray diffraction (XRD), and the composition of the crystals was analyzed on a CamScan MV2300 scanning electron microscope (VEGA, 130 mm).

Figure 1a shows the results of experiments studying the concentration dependences of the equilibrium
The equilibrium Ta content practically does not change with increasing HF concentration, remaining at a low level of $10^{-6}m$ upon dissolution of tantalite in fluoride–chloride fluids at 550°C and 100 MPa. It is established that, similarly to pyrochlore, tantalite dissolves incongruently in high-temperature fluids of complex composition ($m$HF + $0.5m$HCl) with the formation of new phases. This may be explained by the presence of Mn and Fe in tantalite, which form easily soluble complexes with the Cl ion. The contents of Mn and Fe in mixed ($m$HF + $0.5m$HCl) solutions are much higher than for tantalum [9]. Thus, the equilibrium content of Mn in $0.01m$HF + $0.5m$HCl is $3.93 \times 10^{-3}$, while the content of Fe is $7.70 \times 10^{-4}m$. The manganese content at 550°C and 100 MPa in the area of high HF concentrations is $n \times 10^{-2}m$, while the Fe content almost does not change.

A comparative analysis of experimental data on the study of the concentration dependence of the equilibrium contents of niobium and tantalum upon dissolution of niobium and tantalum oxides, pyrochlore and tantalite in fluoride [16, 17], chloride [8], and mixed fluoride–chloride solutions was performed. It was shown (Figs. 2a, 2b) that at $T = 550°C$ and $P = 100$ MPa, the addition of the CI ion to fluoride solutions reduces the solubility of niobium and tantalum upon dissolution of Nb$_2$O$_5$ and Ta$_2$O$_5$ by $1–1.5$ orders of magnitude. The trends in the concentration dependence of the solubility of Nb$_2$O$_5$ and Ta$_2$O$_5$ on the concentration of the F ion in fluoride–chloride solutions occupy an intermediate position between the trends in the solubility of oxides in pure fluoride and chloride solutions. However, at high contents of the F ion in solutions ($1m$HF + $0.5m$HCl) and ($2m$HF + $0.5m$HCl), the equilibrium contents of Nb and Ta upon dissolution of oxides in fluoride and mixed solutions become comparable and reach $10^{-1}$ and $10^{-2}$ mol/kg H$_2$O, respectively.

Comparison of the data on the study of the concentration dependences of the solubility of pyrochlore and tantalite in HF, HCl, and $m$HF + $0.5m$HCl solutions...
Table 1. Experimental data on the solubility of pyrochlore, tantalite, and oxides of tantalum and niobium in $m$HF + 0.5$m$HCl fluids

| Starting material | Starting solution, mol/kg H$_2$O | Nb, mol/kg | Na, mol/kg | Ca, mol/kg | Ta, mol/kg | Mn, mol/kg | Fe, mol/kg |
|-------------------|----------------------------------|------------|------------|------------|------------|------------|------------|
|                   | $T = 550^\circ$C, $P = 100$ MPa, Co–CoO buffer |            |            |            |            |            |            |
| Pyrochlore         | 0.01$m$HF + 0.5$m$HCl             | 1.66E–04   | 6.21E–02   | 2.73E–02   |            |            |            |
|                   | 0.1$m$HF + 0.5$m$HCl              | 1.55E–03   | 1.43E–01   | 4.80E–02   |            |            |            |
|                   | 0.5$m$HF + 0.5$m$HCl              | 1.78E–03   | 2.93E–01   | 2.75E–02   |            |            |            |
|                   | 1$m$HF + 0.5$m$HCl                | 2.54E–03   | 2.97E–01   | 2.07E–02   |            |            |            |
|                   | 2$m$HF + 0.5$m$HCl                | 1.33E–02   | 2.94E–01   | 1.02E–02   |            |            |            |
| Tantalite          | 0.01$m$HF + 0.5$m$HCl             | 3.77E–05   | 1.44E–07   | 7.74E–03   | 3.94E–03   |            |            |
|                   | 0.1$m$HF + 0.5$m$HCl              | 7.10E–05   | 4.42E–07   | 2.04E–02   | 1.73E–02   |            |            |
|                   | 0.5$m$HF + 0.5$m$HCl              | 1.52E–04   | 7.18E–07   | 1.26E–02   | 1.22E–02   |            |            |
|                   | 1$m$HF + 0.5$m$HCl                | 1.83E–05   | 2.76E–07   | 6.53E–03   | 2.51E–04   |            |            |
|                   | 2$m$HF + 0.5$m$HCl                | 4.06E–04   | 9.45E–07   | 7.90E–03   | 1.04E–02   |            |            |
| $Ta_2O_5$          | 0.01$m$HF + 0.5$m$HCl             |            | 2.98E–07   |            |            |            |            |
|                   | 0.1$m$HF + 0.5$m$HCl              |            | 1.11E–05   |            |            |            |            |
|                   | 0.5$m$HF + 0.5$m$HCl              |            | 4.03E–04   |            |            |            |            |
|                   | 1$m$HF + 0.5$m$HCl                |            | 2.84E–03   |            |            |            |            |
|                   | 2$m$HF + 0.5$m$HCl                |            | 9.93E–03   |            |            |            |            |
| $Nb_2O_5$          | 0.01$m$HF + 0.5$m$HCl             | 8.61E–06   |            |            |            |            |            |
|                   | 0.1$m$HF + 0.5$m$HCl              | 2.64E–04   |            |            |            |            |            |
|                   | 0.5$m$HF + 0.5$m$HCl              | 6.44E–04   |            |            |            |            |            |
|                   | 1$m$HF + 0.5$m$HCl                | 6.10E–03   |            |            |            |            |            |
|                   | 2$m$HF + 0.5$m$HCl                | 5.60E–02   |            |            |            |            |            |
|                   | $T = 500^\circ$C, $P = 100$ MPa, Co–CoO buffer |            |            |            |            |            |            |
| Pyrochlore         | 0.01$m$HF + 0.5$m$HCl             | 2.46E–04   | 0.154      | 0.093      |            |            |            |
|                   | 0.1$m$HF + 0.5$m$HCl              | 1.83E–04   | 0.119      | 0.0895     |            |            |            |
|                   | 0.5$m$HF + 0.5$m$HCl              | 2.14E–03   | 0.286      | 0.0542     |            |            |            |
|                   | 1$m$HF + 0.5$m$HCl                | 4.16E–03   | 0.267      | 0.0217     |            |            |            |
|                   | 2$m$HF + 0.5$m$HCl                | 3.24E–02   | 0.436      | 0.0025     |            |            |            |
| Tantalite          | 0.01$m$HF + 0.5$m$HCl             | 2.26E–06   | 8.84E–08   | 0.113      | 7.23E–03   |            |            |
|                   | 0.1$m$HF + 0.5$m$HCl              | 5.70E–06   | 3.92E–07   | 0.115      | 5.50E–03   |            |            |
|                   | 1$m$HF + 0.5$m$HCl                | 2.32E–04   | 4.14E–04   | 0.126      | 1.65E–02   |            |            |
|                   | 2$m$HF + 0.5$m$HCl                | 3.79E–03   | 8.27E–03   | 0.185      | 6.05E–03   |            |            |
|                   | 0.5$m$HF + 0.5$m$HCl              | 2.26E–05   | 1.38E–06   | 7.26E–02   | 3.94E–03   |            |            |
| $Ta_2O_5$          | 0.01$m$HF + 0.5$m$HCl             |            | 1.60E–07   |            |            |            |            |
|                   | 0.1$m$HF + 0.5$m$HCl              |            | 6.08E–06   |            |            |            |            |
|                   | 0.5$m$HF + 0.5$m$HCl              |            | 2.80E–04   |            |            |            |            |
|                   | 1$m$HF + 0.5$m$HCl                |            | 2.00E–03   |            |            |            |            |
|                   | 2$m$HF + 0.5$m$HCl                |            | 4.00E–03   |            |            |            |            |
| $Nb_2O_5$          | 0.01$m$HF + 0.5$m$HCl             | 8.07E–06   |            |            |            |            |            |
|                   | 0.1$m$HF + 0.5$m$HCl              | 8.93E–05   |            |            |            |            |            |
|                   | 0.5$m$HF + 0.5$m$HCl              | 6.73E–04   |            |            |            |            |            |
|                   | 1$m$HF + 0.5$m$HCl                | 1.32E–02   |            |            |            |            |            |
|                   | 2$m$HF + 0.5$m$HCl                | 3.90E–02   |            |            |            |            |            |
**Table 1. (Contd.)**

| Starting material | Starting solution, mol/kg H₂O | Nb, mol/kg | Na, mol/kg | Ca, mol/kg | Ta, mol/kg | Mn, mol/kg | Fe, mol/kg |
|-------------------|--------------------------------|------------|------------|------------|------------|------------|------------|
|                   |                               |            |            |            |            |            |            |
|                   | **T = 400°C, P = 100 MPa, Co–CoO buffer** |            |            |            |            |            |            |
| Pyrochlore         | 0.01mHF + 0.5mHCl              | 2.05E–05   | 0.108      | 7.59E–02   |            |            |            |
|                   | 0.1mHF + 0.5mHCl               | 2.26E–05   | 0.142      | 8.18E–02   |            |            |            |
|                   | 1mHF + 0.5mHCl                 | 6.12E–03   | 0.201      | 2.37E–02   |            |            |            |
|                   | 2mHF + 0.5mHCl                 | 2.52E–02   | 0.351      | 4.14E–04   |            |            |            |
| Tantalite          | 0.01mHF + 0.5mHCl              | 1.51E–07   |            |            | 2.21E–09   | 3.93E–03   | 7.70E–04   |
|                   | 0.1mHF + 0.5mHCl               | 2.15E–07   |            |            | 9.39E–09   | 4.1E–03    | 8.55E–04   |
|                   | 1mHF + 0.5mHCl                 | 1.06E–04   |            |            | 1.44E–04   | 8.46E–03   | 7.25E–04   |
|                   | 2mHF + 0.5mHCl                 | 3.69E–04   |            |            | 9.06E–04   | 1.08E–02   | 6.41E–04   |
| Ta₂O₅              | 0.01mHF + 0.5mHCl              |            |            |            | 9.35E–08   |            |            |
|                   | 0.1mHF + 0.5mHCl               |            |            |            | 1.22E–05   |            |            |
|                   | 0.5mHF + 0.5mHCl               |            |            |            | 2.03E–04   |            |            |
|                   | 1mHF + 0.5mHCl                 |            |            |            | 3.00E–03   |            |            |
|                   | 2mHF + 0.5mHCl                 |            |            |            | 1.50E–02   |            |            |
| Nb₂O₅              | 0.01mHF + 0.5mHCl              | 7.64E–06   |            |            |            |            |            |
|                   | 0.1mHF + 0.5mHCl               | 8.93E–05   |            |            |            |            |            |
|                   | 0.5mHF + 0.5mHCl               | 1.03E–03   |            |            |            |            |            |
|                   | 1mHF + 0.5mHCl                 | 6.08E–03   |            |            |            |            |            |
|                   | 2mHF + 0.5mHCl                 | 4.78E–02   |            |            |            |            |            |
|                   | **T = 300°C, P = 100 MPa, Co–CoO buffer** |            |            |            |            |            |            |
| Pyrochlore         | 0.01mHF + 0.5mHCl              | 3.60E–06   | 0.196      | 0.108      |            |            |            |
|                   | 0.1mHF + 0.5mHCl               | 6.67E–06   | 0.229      | 7.41E–02   |            |            |            |
|                   | 0.5mHF + 0.5mHCl               | 1.16E–05   | 0.366      | 1.55E–02   |            |            |            |
|                   | 1mHF + 0.5mHCl                 | 4.61E–03   | 0.4405     | 8.76E–04   |            |            |            |
|                   | 2mHF + 0.5mHCl                 | 3.39E–02   | 0.394      | 2.99E–03   |            |            |            |
| Tantalite          | 0.01mHF + 0.5mHCl              | 9.90E–06   |            |            | 1.33E–07   | 1.85E–02   | 1.42E–03   |
|                   | 0.1mHF + 0.5mHCl               | 1.11E–04   |            |            | 2.54E–07   | 4.09E–02   | 1.97E–03   |
|                   | 0.5mHF + 0.5mHCl               | 3.35E–04   |            |            | 3.45E–04   | 3.70E–02   | 2.33E–03   |
|                   | 1mHF + 0.5mHCl                 | 4.74E–03   |            |            | 5.23E–03   | 4.19E–02   | 1.67E–03   |
| Ta₂O₅              | 0.01mHF + 0.5mHCl              |            |            |            |            |            |            |
|                   | 0.1mHF + 0.5mHCl               |            |            |            | 2.43E–06   |            |            |
|                   | 0.5mHF + 0.5mHCl               |            |            |            | 2.63E–04   |            |            |
|                   | 1mHF + 0.5mHCl                 |            |            |            | 5.24E–03   |            |            |
|                   | 2mHF + 0.5mHCl                 |            |            |            | 4.97E–02   |            |            |
| Nb₂O₅              | 0.01mHF + 0.5mHCl              | 5.71E–06   |            |            |            |            |            |
|                   | 0.1mHF + 0.5mHCl               | 1.79E–06   |            |            |            |            |            |
|                   | 0.5mHF + 0.5mHCl               | 1.44E–03   |            |            |            |            |            |
|                   | 1mHF + 0.5mHCl                 | 1.30E–02   |            |            |            |            |            |
|                   | 2mHF + 0.5mHCl                 | 7.41E–02   |            |            |            |            |            |
tions at \( T = 300^\circ \text{C} \) and \( P = 100 \text{ MPa} \) (Figs. 3a, 3b) shows that, at low concentrations of the initial solutions (0.01\text{mHF}, 0.01\text{mHCl}, and 0.01\text{mHF} + 0.5\text{mHCl}), the equilibrium contents of niobium are practically the same and are \( \times 10^{-5} \text{ mol/kg } \text{H}_2\text{O} \). However, with an increasing concentration of the initial solutions, the Nb content in HF solutions increases sharply and becomes higher than that in mixed (\text{mHF} + 0.5\text{mHCl}) and HCl solutions by two orders of magnitude (Fig. 3a).

A similar pattern is typical of tantalum as well: the Ta content upon dissolution of tantalite in HF solutions is higher than that in chloride and mixed (\text{mHF} + 0.5\text{mHCl}) solutions by several orders of magnitude (Fig. 3b).

The temperature dependences of the equilibrium contents of niobium and tantalum upon dissolution of Nb\(_2\)O\(_5\), Ta\(_2\)O\(_5\), pyrochlore, and tantalite in m\text{HF} + 0.5\text{mHCl} solutions are shown in Figs. 4a and 4b. The experimental studies did not reveal clearly expressed unambiguous dependences of the effect of temperature on the solubility of Nb and Ta compounds in solutions (m\text{HF} + 0.5\text{mHCl}) of different concentrations. It has been established that when Nb\(_2\)O\(_5\) was dissolved in (0.1\text{m} + 0.5\text{mHCl}) solutions with a low HF concentration at 300\(^\circ\)C and 100 MPa, the equilibrium content of niobium is 1.5 orders of magnitude higher than that of pyrochlore and 3.5 orders of magnitude higher than that of tantalite and is \( \times 10^{-4} \text{ mol/kg } \text{H}_2\text{O} \) (Fig. 4a).

A change in temperature does not affect the solubility of niobium oxide in (0.1\text{mHF} + 0.5\text{mHCl}) solutions significantly, while a positive temperature dependence is observed for pyrochlore and tantalite. At 550\(^\circ\)C and 100 MPa, the content of niobium for pyrochlore increases by one order of magnitude and amounts to \( \times 10^{-3} \text{ mol/kg } \text{H}_2\text{O} \). The equilibrium content of niobium for tantalite is \( \times 10^{-5} \text{ mol/kg } \text{H}_2\text{O} \).

The solubility of niobium oxide increases by 1.5 orders of magnitude and amounts to \( \times 10^{-5} \text{ mol/kg } \text{H}_2\text{O} \) in solutions with a high content of the F ion (1\text{mHF} + 0.5\text{mHCl}) (Fig. 4b), which is almost identical to the content of niobium upon the dissolution of pyrochlore at the same parameters [9]. An increase in tempera-
The equilibrium content of niobium is significantly higher than that for Ta₂O₅. The equilibrium concentration of tantalum and niobium deposits is the experimental fact that only fluorine-bearing solutions, with an insignificant role of chloride solutions, favor the hydrothermal transport of Ta and Nb with the contents necessary to form commercial concentrations.

Based on the data obtained in this study, it is possible to propose geochemical models for the transport and precipitation of Ta and Nb in natural conditions and to specify the physicochemical parameters of ore-bearing fluids, such as the temperatures, pressures, brine composition, and the concentrations of rare elements in the fluid.

**FUNDING**

This study was conducted as part of the theme FMUF-2022-0003 and was supported by the Russian Foundation for Basic Research, project no. 20-05-00307.

**CONFLICT OF INTEREST**

The authors declare that they have no conflicts of interest.

**OPEN ACCESS**

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.
REFERENCES

1. A. M. Aksyuk, Petrology 10 (6), 557–570 (2002).
2. A. A. Beus, E. A. Severov, F. F. Sitnin, and K. D. Subbotin, *Albitized and Greisenized Granites (Apogranites)* (USSR Acad. Sci., Moscow, 1962) [in Russian].
3. G. P. Zaraisky, Petrology 7 (4), 440 (1999).
4. G. P. Zaraiskii, in *Smirnov Coll. Sci. Works* (Foundation after the Name of Acad. V. I. Smirnov, Moscow, 2004), pp. 105–192 [in Russian].
5. V. I. Kovalenko, *Rare Earth Granitoids: Petrology and Geochemistry* (Nauka, Novosibirsk, 1977) [in Russian].
6. P. V. Koval’, in *Metasomatism and Ore Formation* (Nauka, Moscow, 1974), pp. 215–225 [in Russian].
7. P. V. Koval’, *Albitized Granites: Petrology and Geochemistry* (Nauka, Novosibirsk, 1975) [in Russian].
8. V. S. Korzhinskaya, N. P. Kotova, and Yu. B. Shapovalov, Dokl. Earth Sci. 459 (1), 1409–1413 (2014).
9. V. S. Korzhinskaya and N. P. Kotova, in *Proc. All-Russ. Annu. Sem. Experiment. Mineral., Petrol., Geochem.* (VESEMPG-2016), Ed. by A. A. Kadik (Vernadsky Inst. Geochem. Anal. Chem., RAS, Moscow, 2016), pp. 132–133.
10. V. S. Korzhinskaya, N. P. Kotova, and Yu. B. Shapovalov, Dokl. Earth Sci. 475 (1), 793–797 (2017).
11. V. S. Korzhinskaya, in *Proc. All-Russ. Annu. Sem. Experiment. Mineral., Petrol., Geochem.* (VESEMPG-2017), Ed. by O. A. Lukhanin (Vernadsky Inst. Geochem. Anal. Chem., RAS, Moscow, 2017), pp. 120–121.
12. N. P. Kotova, in *Proc. All-Russ. Annu. Sem. Experiment. Mineral., Petrol., Geochem.* (VESEMPG-2017), Ed. by O. A. Lukhanin (Vernadsky Inst. Geochem. Anal. Chem., RAS, Moscow, 2017), pp. 132–133.
13. E. V. Lukyanova, N. N. Akinfiev, A. V. Zotov, I. T. Rass, N. P. Kotova, and V. S. Korzhinskaya, Geol. Ore Deposits 59 (4), 305–315 (2017).
14. N. Akinfiev, V. Korzhinskaya, N. Kotova, A. Redkin, and A. Zotov, Geochim. Cosmochim. Acta 280, 102–105 (2020).
15. A. A. Beus and N. Y. Zhalashkova, Int. Geol. Rev. 6, 668–681 (1964).
16. V. S. Korzhinskaya and N. P. Kotova, Exp. GeoSci. 18, 119–121 (2012).
17. G. P. Zaraisky, V. S. Korzhinskaya, and N. P. Kotova, J. Mineral. Petrol. 99 (3/4), 287–300 (2010).

*Translated by A. Bobrov*