=== **GEOCHEMISTRY** ===

Experimental Study of the Solubility of Columbite, Pyrochlore, and Ta and Nb Oxides in Alkaline Hydrothermal Fluids at 300–550°C and 50 and 100 MPa

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Abstract—The concentration and temperature dependences of the solubility of natural pyrochlore and columbite and Ta and Nb oxides are experimentally studied in NaOH and (mNaF + mNaOH) alkaline aqueous solutions at 300–550°C and 50 and 100 MPa and low oxygen fugacity (Co–CoO and Ni–NiO buffers). The initial NaOH and NaF concentrations varied in the range of 0.01–2 m and 0.01–1 m, respectively. It is established that the Nb content in alkaline solutions within the entire concentration range is higher than the Ta content by approximately two and half orders of magnitude. The solubility of pyrochlore in alkaline Na solutions is significantly higher than that of columbite allowing us to consider that Nb forms complexes in alkaline fluids, whereas the Ta complexes are suppressed. The solubility of pyrochlore and columbite with increasing temperature decreases, and the presence of an F ion in form of low NaF content positively affects the solubility of Ta and Nb minerals and oxides at high temperatures (500–550°C). It is established that the lower oxygen fugacity (Co–CoO buffer) is favorable for the precipitation of Nb in NaOH fluids. The study of the pressure effect at 50 and 100 MPa on the solubility of pyrochlore, columbite, and Na and Nb oxides in alkaline Na solutions showed that the solubility of pyrochlore increases with increasing pressure, whereas that of columbite remains almost unchanged. Thus, the decrease in pressure favors the Nb precipitation in form of tantaloniobates at the dissolution of pyrochlore. No this correlation is observed for columbite.

Keywords: experiment, columbite, pyrochlore, Ta and Nb oxides, solubility, alkaline solutions, redox buffers, pressure, alkali-fluoride fluid

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INTRODUCTION

The relevance of the genesis of rare metal Ta and Nb deposits requires the necessary attraction of experimental methods for the quantitative estimations of possible Ta and Nb hydrothermal transport and deposition under physicochemical conditions typical of the formation of the main types of endogenous deposits of these metals: associated with "apogranites," pegmatites, alkali metasomatites, alkali syenites, and carbonatites. Columbite $(Mn,Fe)(Nb,Ta)_2O_6$ and pyrochlore $(Ca,Na)_2(Nb,Ta)_2O_6(O,OH,F)$ are the main Ta and Nb minerals of both magmatic and metasomatic genesis. Columbite is more typical of near-neutral and weakly alkaline conditions of mineral formation, whereas pyrochlore is deposited under strongly alkaline conditions, especially in carbonatites.

Of more than 150 hypogene Ta and Nb minerals, almost all of them belong to complex oxides. There are few experimental studies on the solubility of both natural tantaloniobates (tantalite–columbite, microlite–pyrochlore, etc.) and chemical Ta and Nb compounds (oxides, hydroxides, etc.). It is known that the Ta and Nb compounds are weakly soluble in water and aqueous solutions in comparison with other metals. It is noteworthy that tantaloniobates are dissolved only under unreal (for natural hydrothermal processes) aqueous solutions such as high-concentrated HF and KOH solutions, which are used for industrial hydrometallurgical recovery of Ta and Nb from ores [11]. Most foreign researchers traditionally consider that Ta and Nb are almost immobile in metamorphic and hydrothermal–metasomatic processes and that their endogenic deposits (pegmatites, "apogranites," associated with stratified ultra-alkaline intrusions, layered ultra-alkaline intrusions, carbonatites, etc.) have magmatic origin, where the economic mineralization formed as a result of direct crystallization of Ta and Nb minerals from alumosilicate or carbonate melts.

The data from various types of rare metal deposits, however, allow us to emphasize a special role of metasomatic processes among numerous geological

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and geochemical factors, which are responsible for the formation of economic concentrations of Ta, Nb, Zr, etc. Note the fact that there are no significant post-magmatic deposits of these elements on Earth, the formation of which would not be related to the evolution of various metasomatic processes. It can thus be suggested that the concentration of rare metals up to the economic level probably occurs by hydrothermal–metasomatic processes [1].

It can be concluded that the available data on possible transport of Ta and Nb by aqueous fluids are fragmentary and insufficient. The solution of this problem required the specific experimental studies under temperatures, pressures, oxygen fugacity, and fluid composition corresponding to the physicochemical parameters of postmagmatic processes.

In recent years, we yielded new experimental results on the solubility of natural tantaloniobates and Ta and Nb oxides in fluoride, chloride, mixed fluoride–chloride, and carbonate aqueous solutions [2, 3, 4, 8–10], which allowed us to establish for the first time that Ta and Nb can be transported by hydrothermal acid fluoride fluids and precipitated as Ta and Nb minerals in amounts sufficient to form the economic Ta and Nb deposits related to calc-alkaline (including Li–F) granites ("apogranites"), which is indicated by high Ta and Nb concentrations in 1 m HF fluids reaching $10^{-3}-10^{-2}$ m.

At the same time, the involvement of acid fluoride fluids in the formation of Ta–Nb deposits related to alkali granites of the Nigerian type (Jos Plateau, Zashikha, Ulug-Tanzek), alkali metasomatites of deep fault zones (Katugin, Taikeu, etc.), and alkali syenites and carbonatites (Ilmenogorsk–Vishnevogorsk group of deposits in the South Urals) is unlikely. It is evident that these fluids must be alkaline. Based on our experimental data, however, it was established that the solubility of tantalite–columbite in alkaline carbonate and bicarbonate Na solutions with a concentration of 1–2 m is negligible: $10^{-7}-10^{-5}$ m (by the Ta and Nb concentrations) [10]. At the same time, the mass transport and deposition of Ta and Nb by hydrothermal deposits with the formation of significant ore concentrations at the deposits of alkali metasomatites is a reliable fact. It is clear that the fluids in this case were alkaline because of the related formation of alkali albitites and riebekite and aegirine metasomatites. In addition, it can be suggested that, similarly to acid and neutral solutions, the mass transfer of Ta and Nb in alkaline hydrothermal fluids could occur in the presence of F [9, 10]. The involvement of F in mineral formation processes at Ta and Nb deposits of the alkaline type is confirmed by the presence of fluorite, cryolite, and villiaumite in ores of these deposits, as well as the incorporation of F in mica, amphiboles, pyrochlore, apatite, and other minerals. The experimental studies on the solubility of tantaloniobates in alkaline and mixed fluoride-alkaline aqueous solutions is thus of paramount importance. Note that a link between Ta–Nb mineralization and F-bearing solutions in early carbonatites is unlikely, because the calcite carbonatites in this case should be replaced by fluorite-bearing rocks, which is not observed in reality. In carbonatite deposits, F is involved at the stage of the formation of later dolomite and ankerite carbonatites, where fluorite is a typical mineral, and the role of hydrothermal fluids in their formation is undoubted.

To cover almost the entire spectrum of the formation conditions of Ta–Nb deposits, we thus expanded the area of studies of the solubility of Ta and Nb minerals in alkaline solutions and therefore involved the experimental results on rare metal deposits, which are genetically related to alkali granites, alkali metasomatites, nepheline syenites, and carbonatites. In particular, the most available objects include the Taikeu group of Ta deposits in the Polar Urals localized in alkali Na metasomatites [6] and the Ilmenogorsk–Vishnevogorsk group of Nb deposits in the South Urals genetically related to an eponymous nepheline–syenite–carbonatite complex. It is concluded on the basis of the study of rocks that the rare metal-bearing rocks of the Polar Urals, as well as the apogranites of Eastern Transbaikalia, were formed from a fluid enriched with alkalis (K–Na) and volatile (F) components. The rocks of Eastern Transbaikalia and the Polar Urals, however, differ in other specific features.

EXPERIMENTAL METHODS AND TECHNIQUES

The solubility of ore minerals in the hydrothermal fluid is an important characteristic of the geochemical behavior of elements: conditions of their mobilization, transport, and deposition. The solubility of minerals first of all defines the upper limit of the saturation of ore elements in natural processes and allows the estimation of modes of their transportation under the given conditions. The main experimental method thus included the dissolution of minerals at $T-P-X-f(O_2)$ conditions corresponding to hydrothermal-metasomatic processes of mineral and ore formation. To study the solubility of pyrochlore $(Ca,Na)_2(Nb,Ta)_2O_6(O,OH,F)$ and columbite $(Mn,Fe)(Nb,Ta)_2O_6$, we used the natural monocrystals of pyrochlore from the weathering crust mantle of the Tatarka carbonatite deposit (the microprobe composition, wt % (CamScan MV2300 (VEGA TS 5130MM) microprobe): 7.61 Na_2O, 14.28 CaO, 71.61 Nb_2O_5, 5.18 F, 0.83 TiO_2, ≤1 Ta_2O_5) and columbite from the Ulug Tanzek deposit (East Sayan) (the microprobe composition, wt %: 10.5 MnO, 10.4 FeO, 76.5 Nb_2O_5, 3.0 Ta_2O_5, 0.3 TiO_2). For the experiments, the fragments 2–3 mm in size and 0.02–0.10 g in weight were cut from the crystals, treated by 0.1 M HF solution, washed, and dried.

Using columbite and pyrochlore in experiments has its advantages, which include the direct application of experimental data for the estimation of natural ore formation conditions due to identical Ta and Nb minerals in both cases. The disadvantage of this choice for the study of Ta and Nb behavior in hydrothermal fluids is related to the relatively complex compositions of minerals, which makes difficult thermodynamic description of the experimental results. Therefore, to increase the informativity of experiments, we studied the solubility of Ta and Nb oxides (pure chemical reagents cleaned by hydrothermal recrystallization in 0.1 M HF solution at 550°C and 100 MPa) parallel to the study of the solubility of natural minerals. The alkaline and fluoride-alkaline solutions were prepared from the corresponding especially pure NaOH and NaF reagents based on twice-distilled water.

The experimental redox conditions were given by a Co−CoO buffer couple with low oxygen fugacity $f(O_2)$. This choice is related to a strongly negative influence of higher oxygen fugacity on the solubility of columbite−tantalite in HF, HCl, and Na_2CO_3 solutions established before [8, 10]. To identify the influence of redox conditions on the solubility of natural pyrochlore in alkaline NaOH solutions with the concentration of 0.01−2 m, we conducted a series of experiments at 300−550°C and 100 MPa in the presence of Co−CoO and Ni−NiO oxygen buffers.

It is established that, in an area of low NaOH concentrations (0.01−0.1 m), the equilibrium Nb content in the presence of the Co−CoO buffer is higher by 1−2 orders of magnitude than in the presence of the Ni−NiO buffer. The equilibrium Nb content in the presence of both buffers with an increasing initial NaOH content up to 1 m becomes almost equal. All further experimental studies of the solubility of minerals were conducted under reduced conditions in the presence of the Co−CoO buffer.

Experiments 15−30 days long were conducted in Pt tubes 8 × 0.2 × 50 mm in size soldered by electric arc welding. The weight of the solid sampling was 50 mg. The volume of the solutions introduced in the tube was calculated according to the experimental $T−P−X−f(O_2)$ parameters. To control the possible weight loss during the experiments, the tubes were weighed before and after runs on the Ohaus ANALYTICAL Plus Series balances with an error of ±0.01 mg. The tubes with solutions were placed into a reactor of an UVD-2000 exoclave hydrothermal high-pressure device. A cylindrical nonhermetic container with a buffer mixture was placed into the reactor beneath the Pt tubes. After the runs, the reactors were cooled for 3−5 min by the aqueous−air capillary mixture to room temperature. The run products were transported to the polypropylene tubes, and the solution was separated from solid phases by centrifugation at 6000 vortices/min. The Ta, Nb, and trace element composition in quenching solutions was analyzed by the most precise current method of inductively couple plasma (ICP-MS and ICP/AES). The solid run products dried at 100°C were studied using X-ray powder diffraction (XRD) and VEGA-TESCAN and Cam Scan MV2300 scanning electron microscopes to control the congruent and incongruent dissolution of Ta and Nb minerals and to determine the chemical composition of the newly formed phases (in case of their formation).

RESULTS AND DISCUSSION

Using the present-day analytical studies, we obtained the first data on the solubility of oxides of Nb (β-Nb_2O_5) and Ta (β-Ta_2O_5), as well as natural pyrochlore $(Ca,Na)_2(Nb,Ta)_2O_6(O,OH,F)$ and columbite $(Mn,Fe)_2(Nb,Ta)_2O_6$ in aqueous NaOH and (mNaOH + mNaF) solutions at 300−550°C and a pressure of 50 and 100 MPa and oxygen fugacity corresponding to the Co−CoO and Ni−NiO buffers.

Figures 1a and 1b show the results of experiments of the study of the concentration dependences of equilibrium Nb and Ta contents during the dissolution of pyrochlore, columbite, and Nb and Ta oxides in NaOH solutions in a concentration range from 0.01 to 2 m at temperature of 550°C and pressure 100 MPa in the presence of the Co−CoO buffer. The analysis of our data showed that the equilibrium Nb content of the solution decreases from $n \times 10^{-4}$ m in 0.01 m NaOH to $n \times 10^{-7}$ m in 2 m NaOH with an increasing NaOH concentration during the dissolution of pyrochlore. During the dissolution of columbite, the equilibrium Nb content remains almost unchanged ($n \times 10^{-6}$ m in 0.01 m and 1 m NaOH solutions) with increasing NaOH concentration. During the dissolution of Nb oxide, the maximum Nb concentrations ($n \times 10^{-4}$ m) are observed in 0.1 m NaOH solutions. The equilibrium Nb content with increasing NaOH concentration decreases, is only $n \times 10^{-7.5}$ m in 1 m NaOH solution, and then again increases. In the logarithmic scale, the dependence of the solubility of Nb oxide on the concentration of alkali has the form of a broken line, which is probably due to the abrupt change of the complex compounds formed.

The data in Fig. 1b show that the maximum equilibrium Ta content ($n \times 10^{-5}$ m) during the dissolution of Ta oxide in alkaline solutions is observed in 0.01 m NaOH solution and that the minimum content ($n \times 10^{-8}$ m) is typical of the 2 m NaOH solution. On the logarithmic scale, the equilibrium Ta content has a reverse linear correlation with the NaOH concentration. During the dissolution of pyrochlore, the equilibrium Ta content in NaOH solutions is very low, almost does not depend on the NaOH content, and is at the level of $n \times 10^{-8}$ m.

The involvement of F in experiments, which was introduced in the alkaline solution in form of NaF,
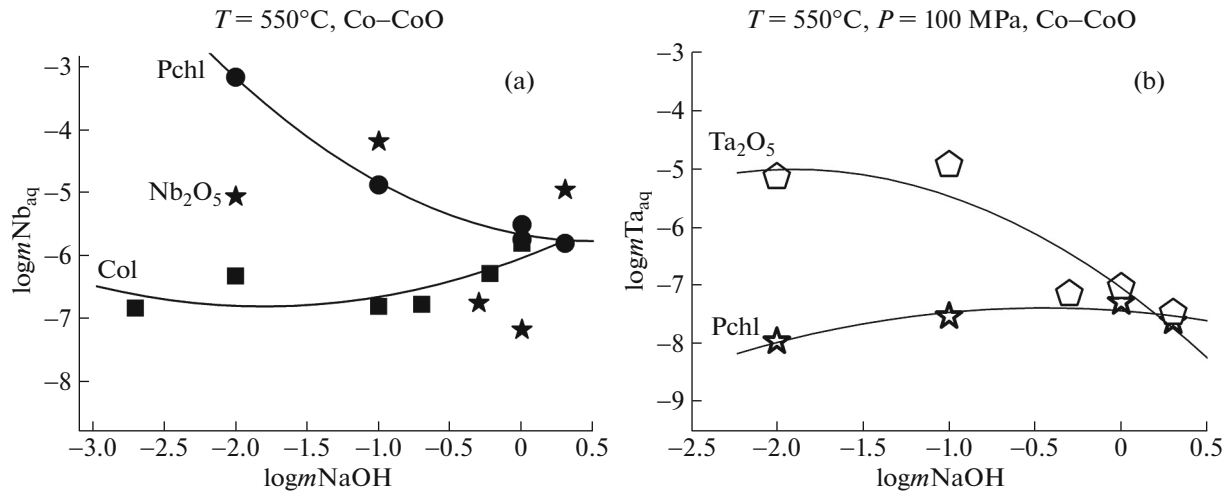
Fig. 1. Concentration dependences of the (a) Nb equilibrium content upon the dissolution of pyrochlore (Pchl), columbite (Col), and Nb_2O_5 in NaOH solution and (b) Ta upon the dissolution of pyrochlore (Pchl), and Ta_2O_5 in NaOH solution (T = 550°C, P = 100 MPa, Co−CoO buffer).
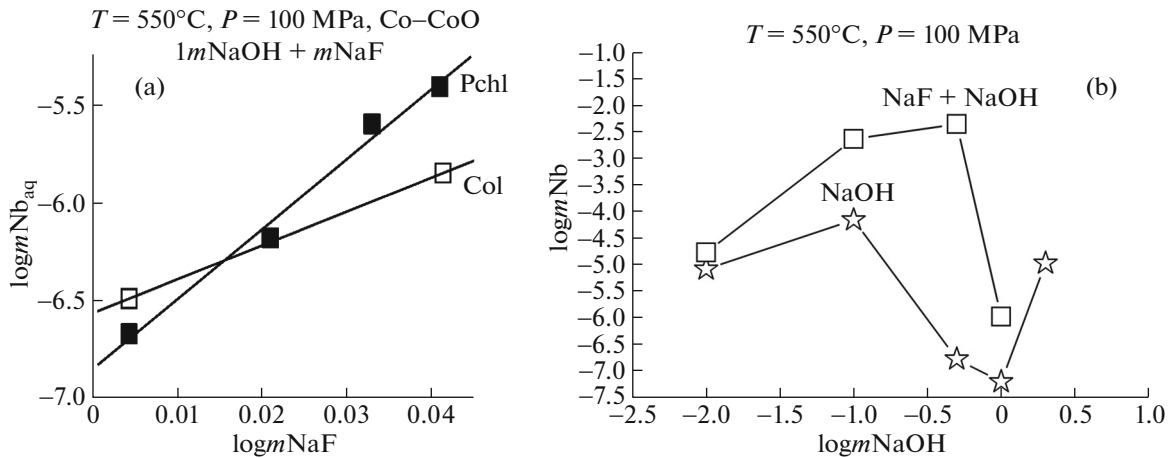
Fig. 2. Concentration dependences of the Nb equilibrium content upon the dissolution (a) of pyrochlore (Pchl) and columbite (Col) in ($1m$ NaOH + m NaF) solution (b) and Nb_2O_5 in NaOH and (mNaOH + mNaF) solution with equimolal NaOH and NaF contents (T = 550°C, P = 100 MPa, Co−CoO buffer).

positively affects the solubility of pyrochlore and columbite. Figure 2 shows the results of experiments on the study of the concentration dependences of the equilibrium Nb content in the dissolution of pyrochlore and columbite in hydrothermal fluids of complex composition ($1m$ NaOH + m NaF), where the NaF concentration varies from 0.01 to 0.1 m.

The analysis of our data showed that, during the addition of low NaF concentrations (up to $0.1m$) to alkaline NaOH solutions, the equilibrium Nb content linearly increases for both pyrochlore and columbite. The positive influence of the F ion on the solubility of pyrochlore is however stronger than for columbite.

The curves resulting from the study of the concentration dependence of the solubility of Nb oxide in

alkaline solutions are characterized by extremes and are difficult to interpret (Fig. 2b). The introduction of NaF to the alkaline solution with the concentrations of 0.1, 0.5, and $1m$NaOH in equimolal proportion significantly increases the solubility of Nb oxide: by two, four, and one orders of magnitude, respectively. At the same time, with the addition of NaF to NaOH solution of low concentration ($0.01m$), the equilibrium Nb concentration remains almost unchanged ($n \times 10^{-5}m$).

It has been established during the experiments on the solubility of Ta oxides in mixed ($1m$ NaOH + m NaF) solutions (Fig. 3) that the addition of 0.01, 0.1, 0.5, and $1m$ of NaF solutions to $1m$ NaOH solution leads to an increase in the equilibrium Ta content. A
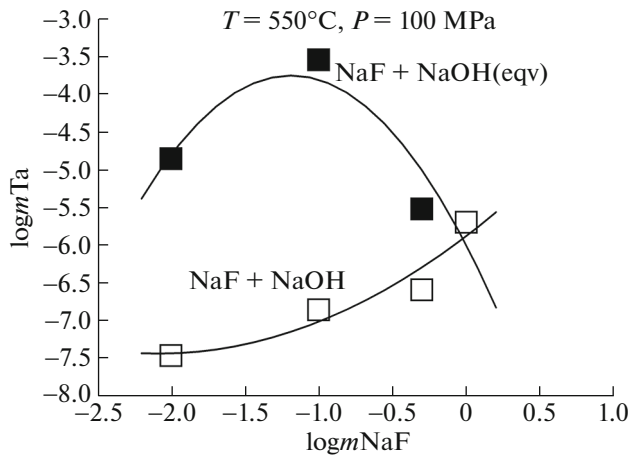
Fig. 3. Concentration dependence of Ta_2O_5 solubility in (mNaOH + mNaF) solution: (black squares) ($1m$NaOH + mNaF) and (white squares) (mNaOH + mNaF) solutions with equimolal NaOH and NaF contents (T = 550°C, P = 100 MPa, Co–CoO buffer).

similar effect was observed in acid and neutral solutions [4]. It is found that the Ta oxide in fluoride-alkaline solutions ($1m$NaOH + mNaF) at 550°C and 100 MPa exhibits a clear positive correlation between the solubility and F ion concentration. However, the equilibrium Ta content in solutions ($1m$ NaOH + mNaF) with increasing NaF concentration increases only by an order of magnitude: from $n \times 10^{-7}$ m in solution ($1m$ NaOH + $0.01m$ NaF) to $n \times 10^{-6}$ m in solution ($1m$ NaOH + $1m$ NaF) remaining at a low level.

The addition of NaF in alkaline solution with concentrations of 0.01, 0.1, 0.5, and 1 m NaOH in equimolal proportions (Fig. 3) leads to an increase in the equilibrium Ta content by an order, two orders, and an

order of magnitude in (0.1 m NaOH + $0.1m$ NaF), ($0.5m$ NaF + $0.5m$ NaOH), and ($1m$ NaOH + $1m$ NaF) solutions, respectively. The addition of $0.01m$ NaF to 0.01 m NaOH solution does not change the Ta concentration. The equilibrium Ta content remains at the level of $n \times 10^{-5}m$.

The experimental data on the study of temperature dependences of the equilibrium Nb and Ta content during the dissolution of Nb_2O_5, Ta_2O_5, pyrochlore, and columbite in alkaline aqueous NaOH solutions with a concentration of 0.1 and 1 m and in hydrothermal fluids of complex composition of ($1m$NaOH + $0.1m$NaF) and ($1m$NaOH + $0.5m$NaF) in the temperature range of 300–550°C and pressure of 100 MPa (Co–CoO buffer) are shown in Figs. 4a, 4b, 5a, and 5b.

It is established that a clear negative almost linear correlation between the solubility of pyrochlore and the temperature is observed during the dissolution of pyrochlore in 0.1 m NaOH solution (Fig. 4a). In other words, with increasing temperature, the equilibrium Nb content decreases linearly from $n \times 10^{-5}m$ at 300°C to $n \times 10^{-6.5}$ m at 550°C, which is related to the formation of weakly soluble Nb phases. During the dissolution of pyrochlore in $1m$ NaOH solution with increasing temperature, the equilibrium Nb content (mNb) remains almost the same ($n \times 10^{-5.5}$–$10^{-5.8}$ m). The addition of a low NaF content ($0.1m$ NaF) to a NaOH solution at low temperatures (300–400°C) has a negligible influence on the solubility of pyrochlore and increase the solubility of the mineral by 0.5–1.5 orders of magnitude at high temperatures (500–550°C).

No clear correlations between the Nb content and the temperature were found during the dissolution of columbite in NaOH solution and hydrothermal fluids of complex composition ($1m$NaOH + mNaF).
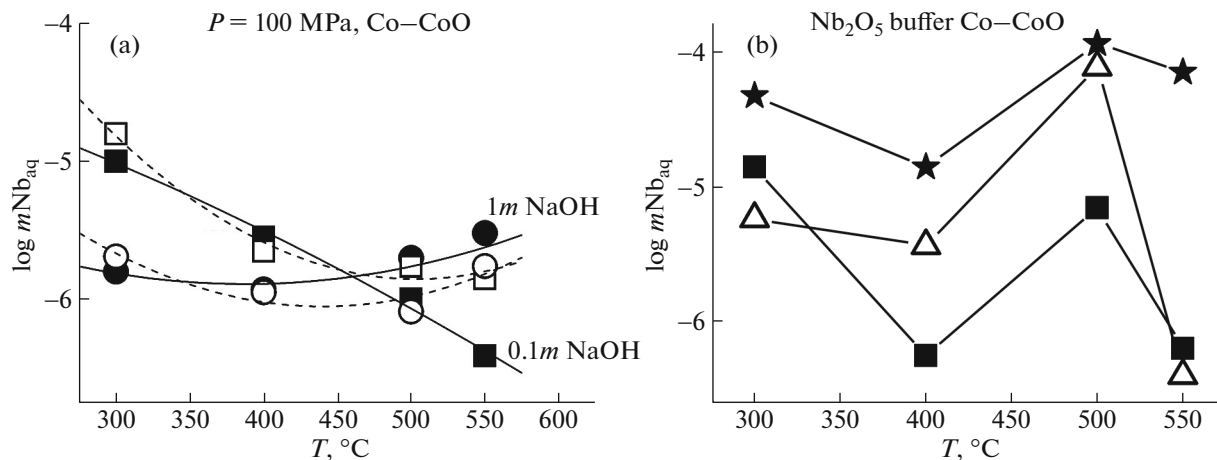
Fig. 4. Temperature dependences of the Nb equilibrium content in NaOH and (mNaOH + mNaF) solutions at 100 MPa. (a) For pyrochlore, 0.1 and $1m$ NaOH solution (black figures) and (mNaOH + $0.1m$ NaF) solution (white figures); (b) for Nb_2O_5: $0.1m$ NaOH solution (stars), $1m$ NaOH solution (squares), ($1m$ NaOH + $0.5m$ NaF) solution (triangles).
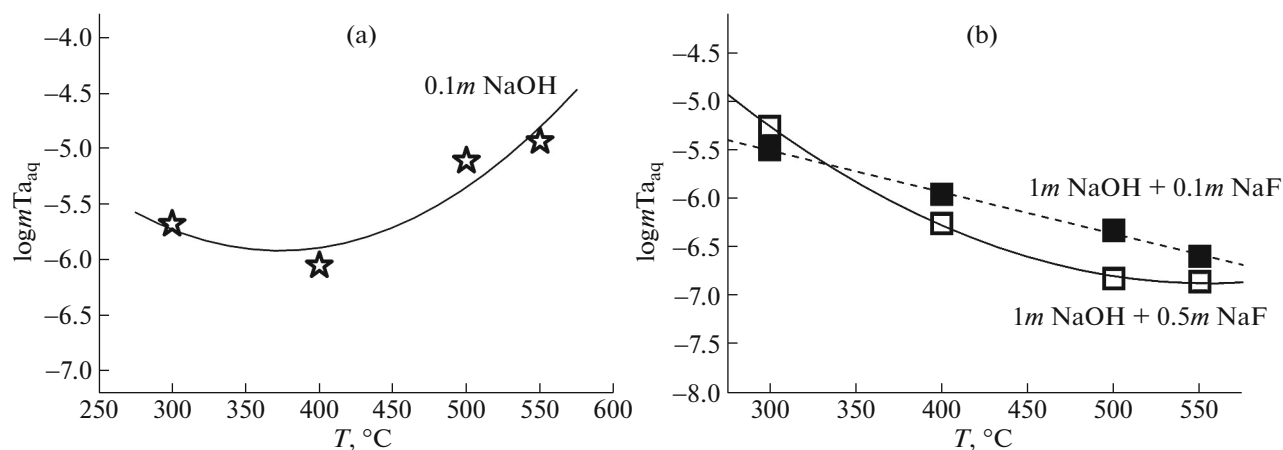
Fig. 5. Temperature dependences of the Ta_2O_5 solubility: in 0.1 m NaOH (a) and (mNaOH + mNaF) solutions (b) (P = 100 MPa, Co−CoO buffer).

The studies showed that the temperature dependence of the Nb_2O_5 solubility in 0.1 and 1m NaOH solutions, as well as a mixed (1m NaOH + 0.5m NaF) solution, is of a similar extreme type (Fig. 4b). At 300°C and 100 MPa, the equilibrium Nb content is $n \times 10^{-4.8}$ and $n \times 10^{-4.2}$ in 1m and 0.1m NaOH solutions, respectively, and $n \times 10^{-5.2}$ in mixed (1m NaOH + 0.5m NaF) solution. At 400°C and 100 MPa, the equilibrium Nb content is minimal: $n \times 10^{-6.2}$ and $n \times 10^{-4.6}$ in 1 and 0.1m NaOH solutions, respectively, and $n \times 10^{-5.4}$ in the mixed (1 m NaOH + 0.5 m NaF) solution. At 500°C and 100 MPa, the equilibrium Nb content increases approximately by an order of magnitude: $n \times 10^{-5}$ and $n \times 10^{-4}$ in 1 and 0.1 m NaOH solutions, respectively, and $n \times 10^{-3.8}$ in mixed (1m NaOH + 0.5m NaF) solution. Upon increasing the temperature up to 550°C, the equilibrium Nb content again decreases indicating an ambiguous temperature effect on the solubility of Nb oxide in alkaline solutions.

It was found during the experiment that the solubility of Ta oxide in alkaline solutions at 300−550°C is very low ($n \times 10^{-7}-10^{-5}m$) both at low (0.1$m$) and high (1 m) NaOH concentrations. Upon an increase in temperature from 300 to 550°C, the Ta content in NaOH solutions weakly increases reaching the value of $10^{-5}m$, which exceeds the Ta concentration at 300°C by less than one order of magnitude (Fig. 5a). The involvement of F in experiments in the form of low NaF contents (0.1m and 0.5m) in NaOH solutions has a negligible influence on the Ta_2O_5 solubility. The character of correlation between the Ta_2O_5 solubility and the temperature changes. On the logarithmic scale, the Ta oxide exhibits the opposite temperature dependence of the solubility. The equilibrium Ta content in (1 m NaOH + 0.5 m NaF) solutions is $n \times 10^{-5} m$ at 300°C and 100 MPa and $n \times 10^{-6.5} m$ at 550°C (Fig. 5b).

We studied the concentration and temperature dependences of the solubility of natural columbite and pyrochlore and Ta and Nb oxides in aqueous NaOH and (mNaF + mNaOH) solutions at 300−550°C and a pressure of 50 MPa and low oxygen fugacity (Co−CoO buffer).

It has been established that the solubility of pyrochlore in NaOH solutions increases with increasing pressure within the entire temperature and pressure range (Fig. 6a). Upon the dissolution of pyrochlore in 0.1 m NaOH solution, the equilibrium Nb content at 100 MPa is higher by almost an order of magnitude than at 50 MPa. At 300°C and 100 MPa, mNb is $n \times 10^{-6} m$ ($n \times 10^{-7} m$ at 50 MPa) and $n \times 10^{-7} m$ at 400°C and 100 MPa. Upon increasing the temperature, the correlation between the equilibrium Nb content and the pressure decreases. In more concentrated solutions (1m NaOH), the correlation between the solubility of pyrochlore and the pressure is negative: the equilibrium Nb content at 300°C is almost the same for both pressure values ($n \times 10^{-6} m$). Upon increasing the temperature from 400 to 550°C, the increase in the fluid pressure from 50 to 100 MPa leads to an increase in the solubility of pyrochlore by almost an order of magnitude.

Figure 6b shows the concentration dependence of the solubility of columbite and pyrochrore in NaOH solutions at 550°C and 100 MPa. The influence of fluid pressure is observed only at low NaOH concentrations (0.01 and 0.1m), where the decreasing fluid pressure from 100 to 50 MPa leads to decreasing solubility of columbite. At higher NaOH concentrations, the solubility of columbite remains the same for the decreasing fluid pressure. In other words, relatively to pyrochlore, the change in pressure during the dissolution of columbite has almost no effect on the solubility of the mineral.
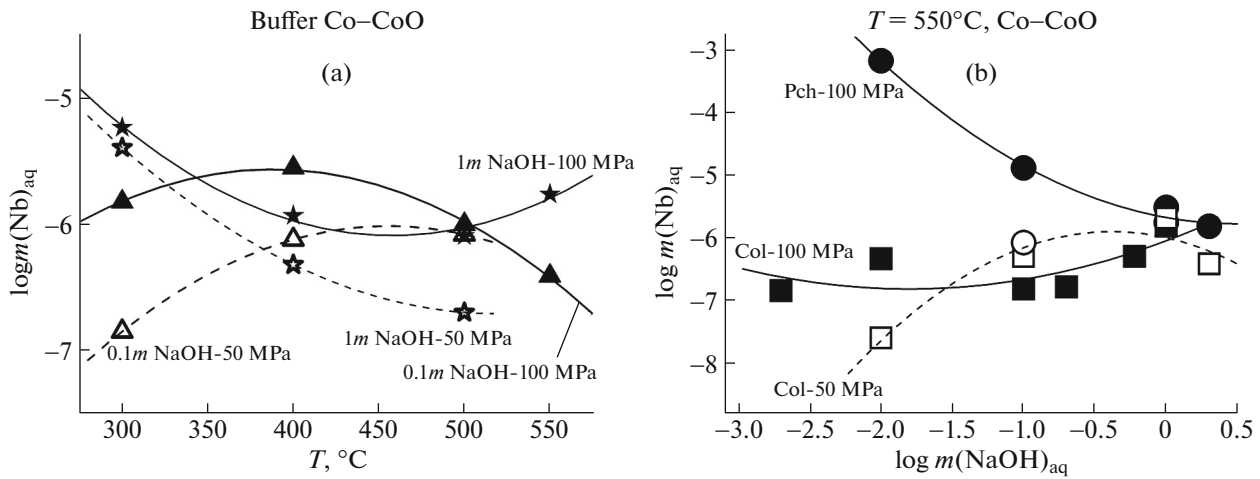
Fig. 6. (a) Temperature dependences of the Nb equilibrium content upon the dissolution of pyrochlore in 1 and 0.1m NaOH at different pressure (black figures at 100 MPa, white figures at 50 MPa); (b) concentration dependence of Nb equilibrium content upon the dissolution of columbite and pyrochlore in NaOH solution at different pressures (black figures at 100 MPa, white figures at 50 MPa) (T = 550°C, Co−CoO buffer).
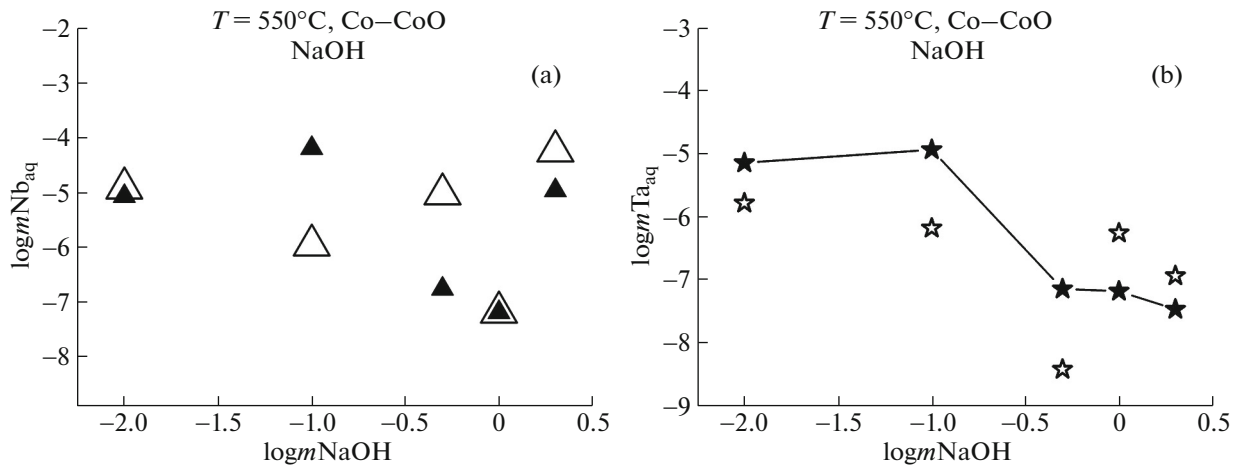
Fig. 7. Influence of NaOH concentration and fluid pressure on the solubility of Nb_2O_5 (a) and Ta_2O_5 (b) at different pressures (black figures at 100 MPa, white figures at 50 MPa) (T = 550°C, Co−CoO buffer).

The experimental studies revealed no clear unambiguous correlations between the fluid pressure and the solubility of Nb oxide in alkaline solutions of various concentrations (Fig. 7a). Irrespective of this fact, however, it can surely be concluded that the solubility of Nb oxide is low ($n \times 10^{-7}-10^{-4}$ m) in all alkaline solutions studied at both low (0.1m NaOH) and high (1 m NaOH) concentrations.

As was noted above, Ta oxide has a negative concentration dependence of the solubility in NaOH solutions of various concentrations at 550°C and 100 MPa. It was found experimentally that the concentration dependence of the solubility of Ta oxide in NaOH solutions and a fluid pressure of 50 MPa is more complex. The decrease in the fluid pressure from 100 to 50 MPa with increasing NaOH concentration

from 0.01 to 0.5 m leads to a decrease in the solubility of Ta_2O_5 by one order of magnitude (Fig. 7b). At higher NaOH concentrations, the Ta content in the solution increases approximately by one order of magnitude with decreasing pressure from 100 to 50 MPa. The solubility of Ta oxide in alkaline solutions, however, remains low ($n \times 10^{-7}-10^{-5}$ m).

It can be concluded on the basis of our data that the increase in pressure leads to an increase in the solubility of pyrochlore, whereas the pressure plays a subordinate role in the solubility of columbite and Ta and Nb oxides.

The experiments have shown that natural columbite and tantalite, as well as Ta oxide, are incongruently dissolved with the formation of new phases at all run parameters and the entire range of NaOH concen-
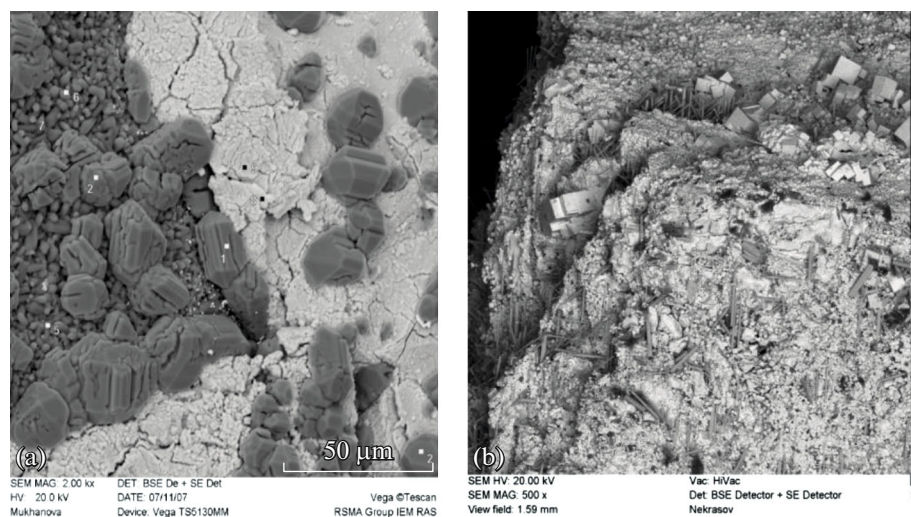
Fig. 8. Crystals formed upon the dissolution: (a) of columbite in 0.1*m* NaOH solution and (b) pyrochlore in 0.1*m* NaOH solution (*T* = 550°C, *P* = 100 MPa, Co−CoO buffer).
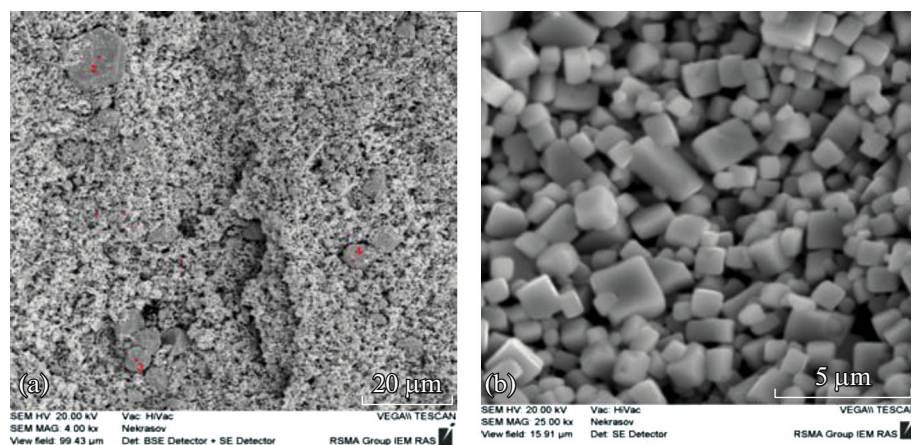
Fig. 9. (a) Crystals of natrotantite $Na_2Ta_4O_{11}$ formed upon the dissolution of Ta_2O_5 in 0.01 *m* NaOH solution; (b) crystals of $NaTaO_3$, formed upon the dissolution of Ta_2O_5 in 0.5*m* NaOH (b) (*T* = 550°C, *P* = 100 MPa, Co−CoO buffer).

trations. According to the XRD and SEM analysis, the presence of even low amounts of Ca and P during the dissolution of columbite leads to the formation of apatite $Ca_5(PO_4)_3(OH)$, whereas the presence of Si results in the formation of tephroite Mn_2SiO_4. The presence of Ta in columbite leads to the formation of microlite. The main mass of the dissolved mineral is replaced by $NaNbO_3$. Figure 8a shows the crystals that formed upon the dissolution of columbite in 0.1 *m* NaOH at 550°C, 100 MPa, and Co−CoO redox buffer. The dark crystals are composed of $NaNbO_3$, and the white fractured overgrowths consist of microlite−pyrochlore with (wt %) 8.34 Na, 1.18 Ca, 1.29 Mn, 13.20 Nb, and 54.51 Ta. Pyrochlore dissolves in NaOH with the formation of $NaNbO_3$, acicular crystals of complex composition (wt %: 1.58 Na_2O, 43.97 CaO, 1.39 SrO,

21.08 Nb_2O_5, 3.15 Ta_2O_5, 25.82 SiO_2, 2.52 F, 0.24 MgO), and $CaMgSiO_4$ crystals (Fig. 8b).

Excellent crystals of natrotantite $Na_2Ta_4O_{11}$ with hexaoctahedral morphology typical of pyrochlore form during the dissolution of Ta oxide in 0.01 and 0.1*m* NaOH solutions. The higher concentrations of alkaline solutions lead to the formation of crystals of $NaTaO_3$, which belongs to pseudocubic syngony (Figs. 9a, 9b). The Nb oxide in the 0.01 and 0.1 *m* NaOH solutions dissolves congruently. The crystals of $NaNbO_3$ form at higher concentrations.

According to our experimental data on the solubility of natural pyrochlore and columbite, as well as Ta and Nb oxides, it is established that the Nb solubility is higher (by approximately one and a half orders of magnitude) in comparison with the solubility of Ta: $n \times 10^{-7}-10^{-4}m$ for Nb and $n \times 10^{-7}-10^{-5.5}m$ for Ta in

all alkaline Na solutions studied and the entire range of temperatures, pressures, and concentrations of the solutions. This allows us to consider that Nb is more able to form complexes with Na and Ca in alkaline solutions, whereas the formation of Ta complexes is mostly suppressed, which that is consistent with the selective affinity of Nb deposits to alkaline eruptive rocks and carbonatites.

Our previous studies showed that the Ta and Nb transport is only possible by highly concentrated fluoride, mainly, HF and KF fluids. Due to the very low solubility of tantaloniobates close to the detection limit, the chloride, carbonate, and alkaline hydrothermal fluids are unable to transport these metals in amounts necessary to form economic deposits [10]. Our new experimental data on the solubility of tantaloniobates in alkaline fluids of mixed composition (mNaOH + mNaF), however, are of primary importance and allow us to conclude that significant Ta and Nb transport by alkaline hydrothermal fluids can occur only in the presence of F.

This is also supported by the results of thermodynamic modeling of our experimental data [5, 7], which describe the solubility of Nb and Ta oxides in a wide temperature and pressure range using hydroxo- and hydroxofluoride complexes. It was established in these works that the most important factor, which controls the concentration of the dissolved Nb and Ta, is the presence of the F ion: the neutral hydroxocomplex $Me(OH)_5(aq)$ forms at low F ion concentrations, whereas the higher F ion contents result in higher concentrations of $Me(OH)_4F_2(aq)$- and $Me(OH)_3F_2(aq)$ complexes. In acid solutions, the mixed neutral complex $Me(OH)_3F_2(aq)$ is dominant. In alkaline F-bearing fluids, the solubility of Nb and Ta is defined by an oxofluoride anion $Me(OH)_5F^-$ and the stability of $Ta(OH)_5F^-$ is much higher than that of $Nb(OH)_5F^-$. The more detailed modeling of natural ore formation requires the determination of the thermodynamic properties of Na- and Ta-bearing minerals (columbite and pyrochlore).

The data on key experiments for the corresponding conditions and compositions of experimental solutions, which prevent the formation of secondary phases, will be the basis for the elaboration of an internally consistent database of the thermodynamic properties of aqueous Nb and Ta components, which is necessary for the prediction of their behavior in a wide range of compositions, temperatures, and pressures of hydrothermal fluids.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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