

**EXPERIMENTAL STUDY OF CONCENTRATION DEPENDENCE
OF PYROCHLORE AND COLUMBITE SOLUBILITY IN NaOH SOLUTIONS
AT T=550°C AND P=1000 BAR**

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To estimate quantitatively a possible role of postmagmatic processes in genesis of rare metal deposits of tantalum and niobium, genetically connected with alkaline granites, alkaline sienites and carbonatites, experimental investigations on solubility of tantalum and niobium minerals in alkaline solutions are necessary.

Earlier we investigated experimentally the dependence of pyrochlore and columbite solubility on concentration of sodium carbonate solutions Na_2CO_3 and $\text{Na}_2\text{CO}_3 + \text{NaF}$ at $T = 550^\circ\text{C}$ and $P = 1000$ bar under reduction conditions (buffer Co-CoO) [1]. It was emphasized that these two minerals are dissolved incongruently. Pyrochlore solubility is 1-1.5 orders higher than that of columbite. The presence in the solution of small numbers of F ions increases solubility of these minerals in carbonate solutions [1]. In this respect we continued investigating minerals of Ta and Nb in alkaline sodium solutions: $\text{NaOH} + \text{H}_2\text{O}$.

Concentration dependence of solubility of natural minerals of pyrochlore $(\text{Ca}, \text{Na})_2(\text{Nb}, \text{Ta})_2\text{O}_6(\text{O}, \text{OH}, \text{F})$ and columbite $(\text{Mn}, \text{Fe})(\text{Nb}, \text{Ta})_2\text{O}_6$ on concentration of NaOH solutions at $T = 550^\circ\text{C}$, $P = 1000$ bar under the conditions of different oxygen fugacity (buffers Co-CoO and Ni-NiO) has been studied. Some experiments were done in the solutions $\text{NaOH} + \text{NaF}$. The runs with NaF were caused by a positive influence of fluorine on solubility of tantalum-niobates in acidic, neutral and carbonate solutions. Fluorine participation in mineral formation processes on the deposits of Ta and Nb of an alkaline type is proved by the presence of fluorite, criolite, villiomite in the ores of these deposits, as well as its entering the micas, amphiboles, pyrochlores, apatites and other minerals.

In the runs we used pyrochlore monocrystals from the weathering crusts of the carbonatite deposit Tatarka (composition on microprobe definitions: $\text{Na}_2\text{O}-7,61\%$; $\text{CaO}-14,28\%$; $\text{Nb}_2\text{O}_5-71,61\%$; $\text{TiO}_2-0,83\%$; $\text{Ta}_2\text{O}_5 \leq 1\%$ wt.) and columbite deposit Ulug Tanzek (Eastern Sayans) (composition on microprobe definitions: $\text{MnO}-10,5\%$; $\text{FeO}-10,4\%$; $\text{Nb}_2\text{O}_5-76,5\%$; $\text{Ta}_2\text{O}_5-3,0\%$; $\text{TiO}_2-0,3\%$ wt.). For the runs we took the cut fragments of 2-3 mm in size and 0.1 – 0.2 gram in weight. The concentration of the solutions of NaOH and $\text{NaOH} + \text{NaF}$ varied in the limits 0.01-2m. The preliminarily weighed mineral monocrystal was placed into the bottom of the platinum capsule of $8 \times 0.2 \times 50$ mm in size, was watered by the solution of 1ml. The runs with the duration of 1-20 days were done in the welded platinum capsules at the hydrothermal exoclave high pressure vessel. The quenched solution was analyzed by ICP/MS and ICP/AES (mass-spectral and atomic-spectral) methods for the elements (Nb, Ta, Ca, Mn, Fe, Ti, etc.). Solid phases analyzed by microprobe and x-ray diffraction methods.

The runs have shown that columbite and pyrochlore under the chosen parameters in the presence of the redox buffers Co-CoO and Ni-NiO dissolve in NaOH and $\text{NaOH} + \text{NaF}$ solutions incongruently. The study of natural columbite crystals after the runs by microprobe and x-ray diffraction methods has shown that columbite dissolves with microlite formation. The presence of the impurities of phosphorus, calcium and silicon in a natural columbite is favourable to form tephroite (Mn_2SiO_4) with calcium impurity and partially apatite - $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$.

Foto 1 represents crystals formed at columbite dissolution in 0.1mNaOH solution at $T = 550^\circ\text{C}$, $P = 1000$ bar in the buffer Co-CoO. Pyrochlore dissolves in NaOH solutions with sodium niobate formation NaNbO_3 , needle-like crystals of a compound composition and crystals CaMgSiO_4 .

Foto 2 shows crystals formed at pyrochlore dissolution in 0.1m NaOH solution in the presence of the buffer Co-CoO.

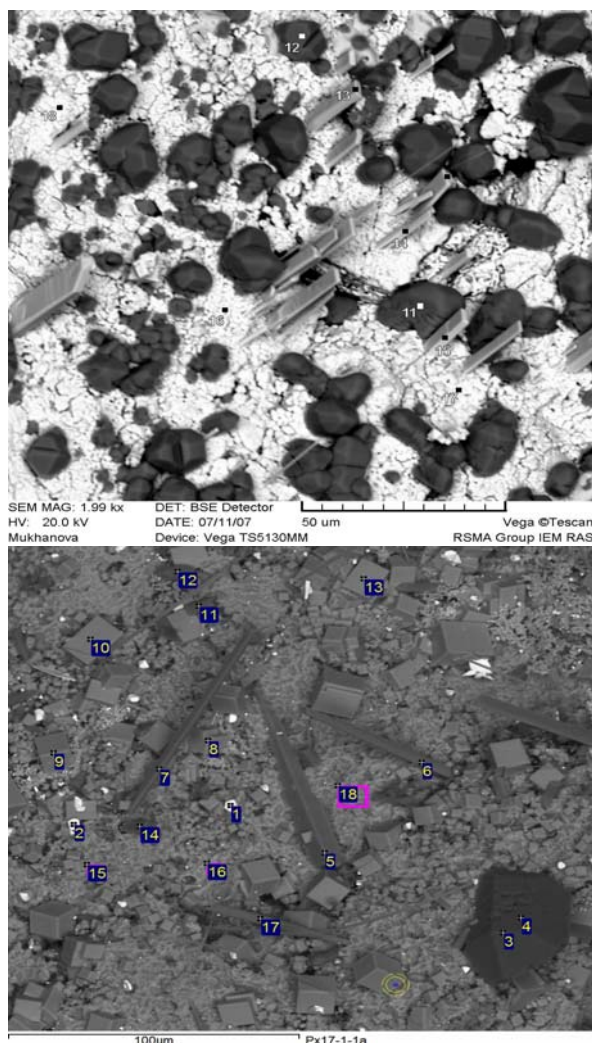


Foto 1. Products of incongruent columbite dissolution $(\text{Mn,Fe})_2(\text{Nb,Ta})_2\text{O}_6$ in the solution 0,1m NaOH, $T = 550^\circ\text{C}$, $P = 1000$ bar, buffer Co-CoO. Dark crystals represent tephroite mineral Mn_2SiO_4 with a small Ca impurity; grey plate-like crystals in the form of “boards” represent Mn-columbite; white mass represents microlite mineral (pyrochlore) with $\text{Ta} > \text{Nb}$ content)

Foto 2. Products of incongruent pyrochlore dissolution $(\text{Ca,Na})_2(\text{Nb,Ta})_2\text{O}_6(\text{O,OH,F})$ in the solution 0,1m NaOH, $T = 550^\circ\text{C}$, $P = 1000$ bar, buffer Co-CoO (3,4 - CaMgSiO_4 ; 5,6,7 - needle-like crystals of a compound composition: Na_2O -1,58%; CaO -43,97%; SrO -1,39%; Nb_2O_5 -21,08%; Ta_2O_5 -3,15%; SiO_2 -25,82%; F -2,52%; MgO -0,24%; 8,9,10,13 – crystals of a cubic shape – NaNbO_3)

For columbite mNb with NaOH concentration rise remains practically the same and is: for 0.01m NaOH $-7.21 \cdot 10^{-7}$, for 1m NaOH $-1.51 \cdot 10^{-6}$ mol/kg H_2O .

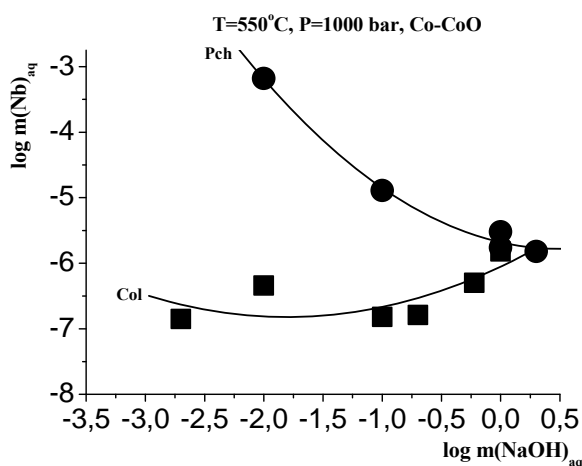


Fig.1. Concentration dependence of niobium equilibrium content at pyrochlore and columbite solubility in NaOH solutions at $T = 550^\circ\text{C}$, $P = 1000$ bar, buffer Co-CoO

Fig.1 shows concentration dependence of equilibrium content of Nb at pyrochlore and columbite solubility in NaOH solutions of a different concentration for $T = 550^\circ\text{C}$, $P = 1000$ bar. Pyrochlore and columbite solubility has an incongruent character. For pyrochlore Nb equilibrium content in the solution with NaOH concentration rise decreases: in 0.01m NaOH concentration $m(\text{Nb})$ has a maximum value and is $(6.60 \cdot 10^{-4} \text{ mol/kg } \text{H}_2\text{O})$, but in 2m NaOH- has a minimum concentration $((4.37 \cdot 10^{-7} \text{ mol/kg } \text{H}_2\text{O})$.

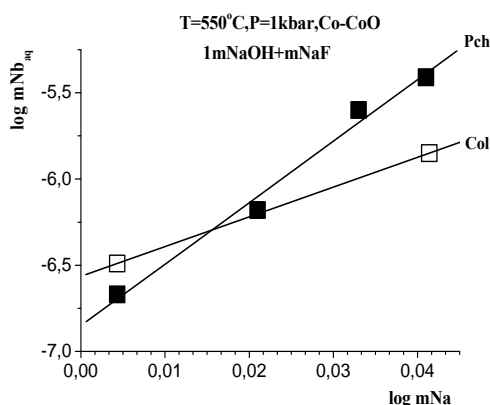


Fig.2. Dependence of niobium equilibrium concentration change on NaF content in the solution for pyrochlore and columbite

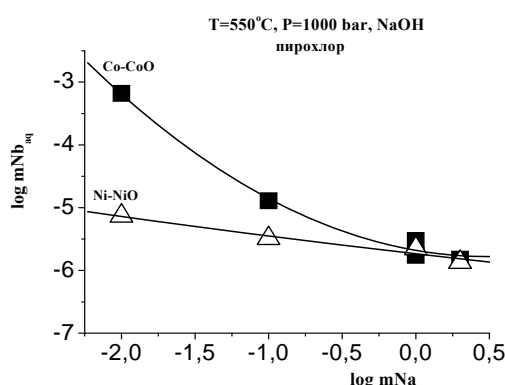


Fig.3. Concentration dependence of Nb equilibrium content at pyrochlore solubility in NaOH solutions under different redox conditions. T = 550°C, P = 1000 bar (buffers Co-CoO and Ni-NiO)

Fig. 2 shows the diagram of dependence of niobium equilibrium content in the alkaline solution, containing 1m NaOH and mNaF where NaF concentration was 0.01; 0.05; 0.08; 1 mol/kg H₂O.

Fig. 3 represents concentration dependence of Nb equilibrium content at pyrochlore solubility in alkaline solutions for different redox conditions: for buffers Co-CoO and Ni-NiO. As seen, at T = 550°C in the buffer presence Co-CoO niobium equilibrium content is 2 orders higher in the region of low concentrations NaOH (0.01m) than in the presence of buffer Ni-NiO. As the NaOH initial concentration rises, this difference disappears.

From the obtained experimental data on solubility of natural pyrochlore and columbite in carbonate-alkaline solutions for T = 550°C and P = 1000 bar one can say that pyrochlore dissolves much better than columbite in both carbonate and NaOH solutions. The presence of F-ion in the form of low concentrations NaF influences positively the solubility of both minerals, for pyrochlore it is more marked. A more reduction situation is more favourable for solubility of these minerals.

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