

Experimental modeling of possibility of hydrothermal transferring niobium by fluoride

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Concentration dependence of Nb₂O₅ and natural columbite and pyrochlore solubility is studied in HF and KF solutions in a wide range of concentrations 0.01m–2m at T = 550°C, P = 1000bar and under Co-CoO oxidizing conditions. It is determined that in HF and KF solutions a positive concentration dependence of Nb solubility both for natural minerals of columbite and pyrochlore and for Nb₂O₅ is observed, attaining $n \cdot 10^{-0.5}$ m for Nb₂O₅ and pyrochlore and $n \cdot 10^{-2}$ m – for columbite. The similar picture is observed in KF solutions. The obtained data confirm the thesis that solubility of simple oxides (Ta₂O₅ and Nb₂O₅) restricts the upper limit of concentration of these elements in the hydrothermal solutions.

Key words: experiment, pyrochlore, columbite, Ta and Nb oxides, solubility, fluoride solutions

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Metasomatic origin of W, Mo, Sn, Be and Bi greisen deposits connected with both leucocrate and lithium-fluoride granites is practically not disputed by anybody. However, with respect to Ta, Nb, Li and other rare metals associating with them many geologists consequently prove the ideas on a magmatic origin of rare-metal Li-F granites and the leading role of magmatic processes of crystallization differentiation of the melt in concentrating Ta, Nb, Li, Rb, Be, Zr, Th and other rare elements. Modern ideas on belonging “apogranites” to Li-F type of granite rocks are connected with the works of V.I. Kovalenko et al, proving their magmatic genesis for many years [Kovalenko, 1977]. It has been determined that in the process of deep fractioning of granite magma up to the level of ongonites and lithium-fluorine granites in the residual melts there occurs a considerable accumulation of F, Li, Ta, Nb and some other rare metals which minerals get a chance to be crystallized from the melt in the form of a fine accessory embedding. At present this viewpoint has become dominant in the world science. However, the appearance of even a poor accessory embedding and other tantal-niobates in the intergrain space of Li-F granites has principal importance since it makes possible a subsequent mobilization, transfer and redeposition of Ta and Nb by a hydrothermal fluid. Further concentration of Ta and Nb up to the economically significant quantities seems to occur by a hydrothermal-metasomatic way during greisenization and albitization of granites by flows of postmagmatic fluoride fluids with the redeposition of tantal-niobates in the upper part of domes of Li-F granites under the screen of metamorphosed to hornfels schisted roof. So far such a possibility has never been proved experimentally by anybody. In literature reliable data on the behavior of Ta and Nb under hydrothermal conditions have been absent. The solution of this problem needed special experimental investigations under the conditions of temperatures, pressures and compositions of the solutions corresponding to physico-chemical parameters of postmagmatic processes in the domes of lithium-fluorine granites.

Earlier we have carried out the experiments on determination of the behavior of columbite-tantalite and tantalum oxide in fluoride, chloride and carbonate solutions. It has been proved for the first time that Ta and Nb can be transferred by a hydrothermal way and be deposited in the form of proper minerals. However, in carbonate and chloride fluids the Ta and Nb solubility is negligible. So one can say about a real transfer of Ta and Nb by high concentrated fluoride solutions only, mainly by HF and KF [Zaraisky G.P., Korzhinskaya V., Kotova N., 2010].

We have studied the effect of the presence of small amounts of F⁻ ions to be introduced as NaF, the solubility of pyrochlore and niobium oxide solubility in the solutions of Na₂CO₃+NaF and NaOH+NaF. Here we determined its positive influence on solubility of tantal-niobates in neutral and carbonate solutions. The participation of fluorine in the processes of mineral formation on Ta and Nb

deposits of alkaline type is proved by the presence in ores of these deposits of fluorite, cryolite, villiomite as well as its entering micas, amphiboles, pyrochlores, apatites and other minerals.

This study is a continuation of systematic experimental investigations on solubility, transfer and deposit of minerals of Ta and Nb by hydrothermal fluids. This study gives experimental investigations of behavior of pyrochlore ((Ca, Na)₂(Nb, Ta)₂O₆(O, OH, F), columbite (Mn, Fe)(Nb, Ta)₂O₆ and Nb oxide (Nb₂O₅) – the analogue of natural mineral of nioboxide in fluoride solutions: HF and KF.

Concentration dependence of natural columbite, pyrochlore and Nb oxide solubility is studied in HF and KF solutions in a wide range of concentrations 0.01–2 m at T = 550C, P = 1000 bar and low oxygen fugacity (Co–CoO buffer). The experiments have shown that within the wide range of concentrations HF and KF pyrochlore and niobium oxide dissolve incongruently with the formation of new phases. Congruent solubility in HF is observed for columbite and the incongruent one can be seen in KF solutions [Zaraisky G.P., Korzhinskaya V., Kotova N., 2010].

For HF and KF solutions we see positive concentration dependence of the Nb solubility both for natural minerals of columbite, pyrochlore and for Nb₂O₅ (Figs. 1, 2).

Fig. 1 shows concentration dependence of solubility of pyrochlore, columbite and Nb₂O₅ in HF solutions.

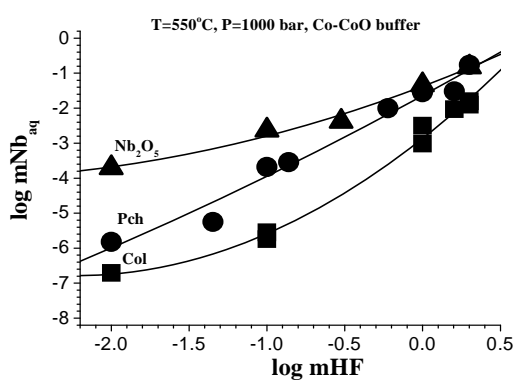


Fig. 1 Concentration dependence of niobium oxide, pyrochlore and columbite solubility in HF solutions at T = 550°C, P = 1000 bar (Co-CoO buffer)

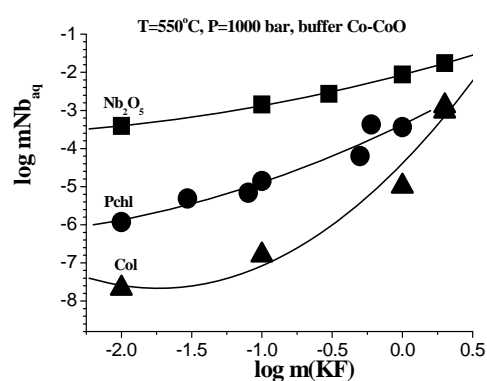


Fig. 2 Concentration dependence of niobium oxide, pyrochlore and columbite solubility in KF solutions at T = 550°C, P = 1000 bar (Co-CoO buffer)

It is found that in HF solutions at low concentrations (0.01m) the niobium content is maximum for Nb₂O₅ and is $n \cdot 10^{-4}$ m; for pyrochlore it is $n \cdot 10^{-6}$ m, but for columbite it is $n \cdot 10^{-7}$ m. At high concentrations of HF (1.0 m and higher) the niobium content increases, reaching $n \cdot 10^{-0.5}$ m for Nb₂O₅ and pyrochlore and $n \cdot 10^{-2}$ m – for columbite.

Fig. 2 shows concentration dependence of pyrochlore, columbite and Nb₂O₅ solubility in KF solutions. It can be seen from Fig. 2 that at low concentrations of KF (0,01 m) the niobium content is maximum for Nb₂O₅ and is $n \cdot 10^{-3.5}$ m; for pyrochlore it is $n \cdot 10^{-6}$ m, but for columbite it is $n \cdot 10^{-7.5}$ m. At high concentration of KF the niobium content is maximum for Nb₂O₅ ($n \cdot 10^{-2}$ m), but for pyrochlore and columbite it has the similar values and is $n \cdot 10^{-3.5}$ m. The obtained data confirm the thesis that solubility of simple oxides (Ta₂O₅ and Nb₂O₅) restricts the upper limit of concentration of these elements in hydrothermal solutions.

From the obtained data on solubility of natural columbite, pyrochlore and Nb oxide solubility in fluoride solutions consisting of HF and KF at T=550C, P=1000bar we can conclude that pyrochlore dissolves much better than columbite in both HF and KF solutions. Its solubility is 1–1.5 orders of magnitude higher at of low fluoride concentrations. Solubility of Nb oxide in HF solutions at low concentrations is approximately an order and a half higher than that of natural minerals, but in KF solutions the niobium content for Nb oxide is 2.5–3.5 orders of magnitude higher than for pyrochlore and columbite. At fluoride concentrations of 1-2m the niobium and natural minerals solubility increase markedly and become approximately comparable.

Experimental results can serve an objective basis to estimate the possibility of Nb mass transfer by hydrothermal solutions in natural conditions since on the basis of the obtained concentration curves we can judge about the maximum possible value of the Nb concentration in an aqueous fluid at the

early postmagmatic stage after its separation from the crystallizing granite melt. The obtained data clearly show that participation of acidic fluoride solutions, high concentration of fluorine and redox conditions are favourable for Nb solubility and transfer (as well as for Ta) by aqueous fluids. The sedimentation of Ta and Nb minerals from the solutions with the formation of their deposits can take place as a result of (1) neutralization of acidic fluoride solutions (2) the decrease of fluorine concentration and (3) the increase of oxygen fugacity.

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