

Effect of physico-chemical conditions on pyrochlore solubility in fluoride solutions at $T = 300\text{--}550^\circ\text{C}$ and $P = 500\text{--}1000$ bar

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Experimental studies on pyrochlore solubility in HF and KF solutions are continued. It is determined that pyrochlore has a weakly marked temperature dependence in HF and a strongly marked one in KF solutions. The dependence of mineral solubility on HF and KF concentrations is strong, positive. The influence of redox conditions in the limits of Ni–NiO and Co–CoO buffers is almost negligible. The role of temperature, pressure and redox conditions for this type of deposits is secondary.

Key words: experiment, pyrochlore, columbite, solubility, buffer, fluorine

Citation: Korzhinskaya, V. S. (2012), Effect of physico-chemical conditions on pyrochlore solubility in fluoride solutions at $T=300\text{--}550^\circ\text{C}$ and $P=500\text{--}1000$ bar, *Vestn. Otd. nauk Zemle*, 4, NZ9001, doi:10.2205/2012NZ_ASEMPG.

We carry out systematic investigations of solubility of mineral phases of tantal-niobates of a complicated composition stable under natural conditions (columbite, pyrochlore etc.). Earlier we studied the behavior of columbite-tantalite in fluoride and chloride solutions what is important for tantal and niobium deposits, connected with lime-alkaline, including lithium-fluorine granites (“apogranites”). [Zaraisky G.P., Korzhinskaya V., Kotova N., 2010]. It has been shown that participation of acidic fluoride solutions of high concentration (1.0m and higher) and redox situation are favourable for a hydrothermal transfer of Ta and Nb. For the first time established a strong increase of tantal-columbite solubility (by 1.5–2 orders of magnitude) with the decrease of oxygen fugacity from the Ni–NiO level to the Co–CoO buffer can be extremely important to form this type of deposits in “apogranites” due to high reduction of high-temperature magmatogeneous aqueous fluids, generated by the maternal granites of the “ilmenite type”. A subsequent increase of oxygen fugacity on the postmagmatic stage in the domes of rare-metal granites can serve one of the main reasons of tantal-niobate deposition here. Experimental investigations of the behavior of pyrochlore $(\text{Ca},\text{Na})_2(\text{Nb},\text{Ta})_2\text{O}_6$ (O,OH,F) and columbite $(\text{Mn},\text{Fe})(\text{Nb},\text{Ta})_2\text{O}_6$ in sodium carbonate and alkaline solutions typical for the deposits of these metals genetically connected with alkaline granites, alkaline sienites and carbonatites are also carried out [Korzhinskaya V. S., Zaraisky G. P., 2008a; Korzhinskaya V. S., Zaraisky G. P., 2009].

These data are a continuation of the experimental study on the solubility of natural pyrochlore $(\text{Ca},\text{Na})_2(\text{Nb},\text{Ta})_2\text{O}_6(\text{O},\text{OH},\text{F})$ in HF and KF solutions. Temperature dependence of pyrochlore solubility for 300, 400, 500 and 550°C is obtained at pressures 500 - 1000 bar and oxygen fugacity corresponding to the buffers Ni–NiO and Co–CoO. Thus, the whole spectrum of the conditions of formation of tantal-niobium deposits in different solutions within a wide range of change of concentration, temperature, pressure and oxygen fugacity will be involved into the runs.

A monocrystal of pyrochlore was selected from was selected from weathering crusts of carbonatite deposit Tatarka of the following composition: Na_2O – 7.61%; CaO – 14.28%; Nb_2O_5 – 71.61%; F – 5.18%; TiO_2 – 0.83%; $\text{Ta}_2\text{O}_5 \leq 1\%$ wt. The concentration of the solutions HF and KF varied in the limits 0.01–2m. The preliminarily weighed fragment of the monocrystal was placed at the bottom of the platinum capsule of $10 \times 0,2 \times 60$ mm in size, was flooded by the solution of 1 ml. The run duration was 15 to -20 days. The experiments were carried out in platinum capsules of the hydrothermal exclave high pressure vessel in the presence of containers with solid-phase oxygen buffers (Ni–NiO, Co–Co) isolated from the charge. A quenching solution was analyzed by ICP/MS and ICP/AES (mass-spectral and atomic-emission) methods for a row of elements (Nb, Ta, Na, Ca, Mn, Fe, Ti etc.). A solid charge was analyzed by the x-ray and microprobe methods.

Experimental data are shown in Figs. 1–6. The data showed that pyrochlore dissolves in HF and KF incongruently [Korzhinskaya V.S., 2011]. Fig.1 shows temperature dependence of pyrochlore

solubility in HF solutions. According to our experimental data over all investigated range of temperatures and concentrations the temperature dependence of the solubility of pyrochlore is weakly expressed. Here concentration dependence is positive. With the growth of HF concentration from 0.10 m to 2m the niobium content in the solution increases from $n \cdot 10^{-6}$ mol/kg H_2O for 0.01m solution to $n \cdot 10^{-1}$ mol/kg H_2O —for 2m HF. For KF solutions temperature dependence is positive (Fig.3) but concentration dependence (Fig.2) is expressed less markedly than for HF solutions. With the growth of KF concentration from 0.01m to 1 m the Nb content increases only by 1–1.5 orders.

Fig.2 shows concentration dependence of pyrochlore solubility in HF and KF solutions at $P=0.5$ and 1 kbar. It is determined that in HF and KF solutions the dependence of pyrochlore solubility on pressure is positive. At high concentrations of fluoride (1 and 2 m) and $P = 1000$ bar the Nb content is half an order higher than at $P = 500$ bar. At low concentrations of HF and KF (0.01m–0.5m) no pressure effect can be seen.

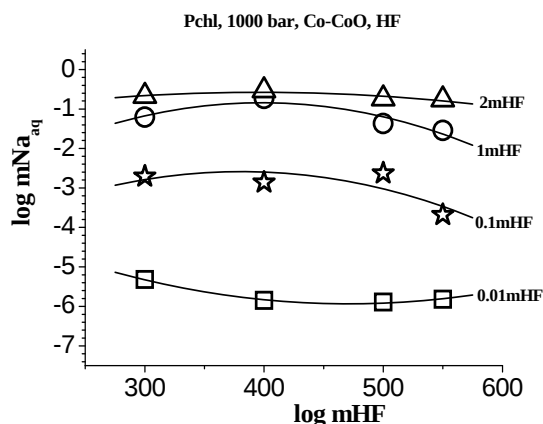


Fig. 1. Temperature dependence of pyrochlore solubility in HF solutions at $P = 1000$ bar (Co–CoO buffer)

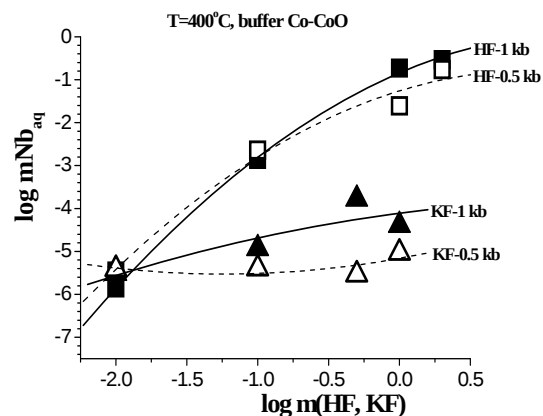


Fig. 2. Concentration dependence of pressure effect on pyrochlore solubility in HF and KF solutions at $T = 400^\circ\text{C}$ (Co–CoO buffer)

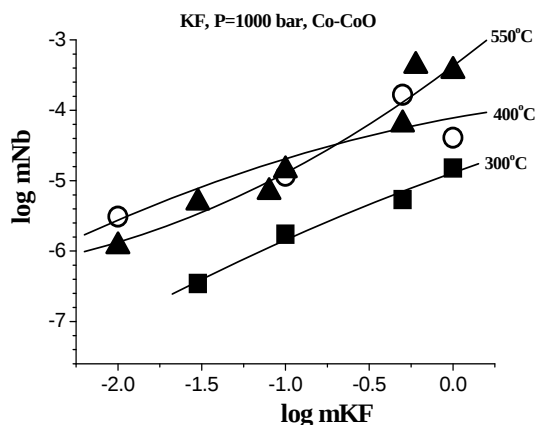


Fig. 3. Concentration dependence of pyrochlore solubility in KF solutions at $T=300, 400$ and 550°C and $P = 1000\text{bar}$ (Co–CoO buffer)

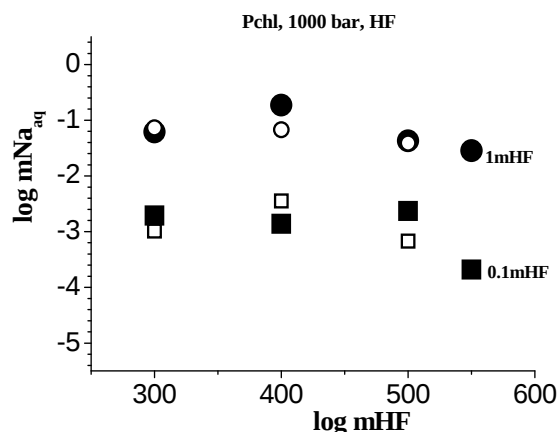


Fig. 4. Temperature dependence of pyrochlore solubility in HF solutions for different redox conditions (white symbols - Ni–NiO buffer; - dark symbols Co–CoO buffer)

Earlier, it has been shown that the solubility of columbite-tantalite is 1.5 to 2 orders of magnitude higher under more reducing conditions (buffer Co–CoO) than under more oxidizing conditions (buffer Ni–NiO) [Korzhinskaya V.S., Zaraisky G.P. 2008b]. To clarify the effect of redox conditions on natural pyrochlore $(Ca, Na)_2(Nb, Ta)_2O_6(O, OH, F)$ solubility in HF and KF solutions we performed a series of the experiments with the concentrations 0,1 and 1,0 mol/kg H_2O at $T = 300–550^\circ\text{C}$, $P = 1000$ bar in the presence of the Co–CoO and Ni–NiO oxygen fugacity buffers. Fig.4 and Fig.5 show

temperature dependence of pyrochlore solubility in HF and KF solutions with the concentrations 0.1m and 1m buffered either to the Ni–NiO or Co–CoO oxygen fugacity buffer. The effect of the redox conditions in the limits of the Ni–NiO and Co–CoO buffers is practically not seen in HF solutions. For KF solutions the picture is somewhat different (Fig.5). At $T = 400^{\circ}\text{C}$ the Nb concentration in 1m KF buffered to the Ni–NiO oxygen fugacity buffer is a bit lower and in 0.1m KF more than by 0.5 order lower. At $T = 500^{\circ}\text{C}$, on the contrary, the Nb content under Ni–NiO oxidizing conditions is half an order higher than under Co–CoO reducing conditions. Fig.6 shows the comparative data of Nb content in HF solutions for natural minerals of pyrochlore and columbite. As we see the columbite solubility under reducing conditions (Co–CoO buffer) is more than by 2 orders of magnitude than that under Ni–NiO oxidizing conditions. Metals Mn and Fe changing their valence with changing redox conditions enter columbite composition.

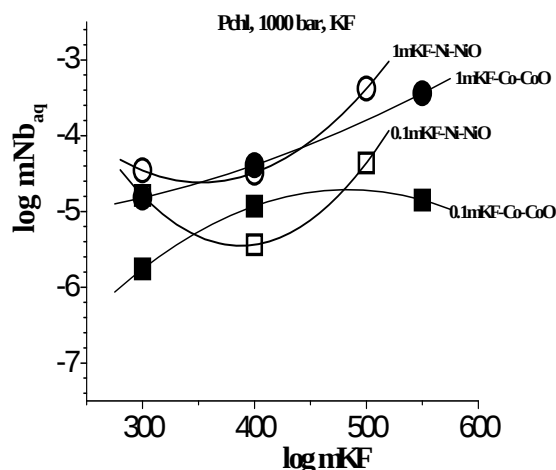


Fig. 5. Temperature dependence of pyrochlore solubility in KF solutions for different redox conditions (white symbols — Ni–NiO buffer; dark symbols – Co–CoO buffer).

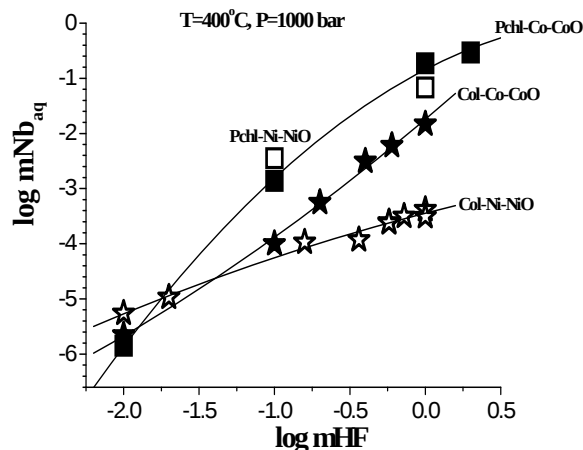


Fig. 6. Concentration dependence of columbite and pyrochlore solubility in HF solutions under different redox conditions (white symbols – Ni–NiO buffer; dark symbols – Co–CoO buffer)

On the basis of the obtained experimental data one can conclude that pyrochlore and columbite solubility in fluoride solutions is rather high. That allows us to speak about a possibility of real Nb transfer via concentrated fluoride solutions (HF and KF). It is concluded that the deposition of niobium favors reducing the concentration of fluoride. The role of temperature, pressure and redox conditions for this type of deposits is secondary.

Financial support by RFBR, project 10-05-00292-a.

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