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Experimental study of dependence of pyrochlore solubility in HF and KF solution at T = 400°, 550°C and P = 1000 bar

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Earlier we studied the effect of presence of minor amount of fluorine ions in the form of NaF on niobium behavior at pyrochlore solubility in $NaCO_3$+NaF and NaOH+NaF solutions [*Korzhinskaya and Zaraisky,* 2008]. We determined its positive influence on tantal-niobate solubility in acidic, neutral and carbonate solutions. Fluorine participation in the mineral formation processes on Ta and Nb deposits of the alkaline type is proved by the presence in ores of these deposits of fluorite, cryolite, willyamite as well as by its entering micas, amphiboles, pyrochlores, apathites and other minerals. So, we studied the behavior of pyrochlore $(Ca, Na)_2$ $(Nb, Ta)_2O_6(O, OH, F)$ in HF and KF solutions of different concentration under room and T-P conditions. The time dependent experiments were structured based on experiments on pyrochlore solubility in HF solutions under room conditions (t = 25C). The run duration was from 1 to 8 months. The results of these series are shown in Fig. 1. It follows from the diagram that for the chosen concentrations HF (0.01, 0.1 and 1m) equilibrium is attained for 4 months.

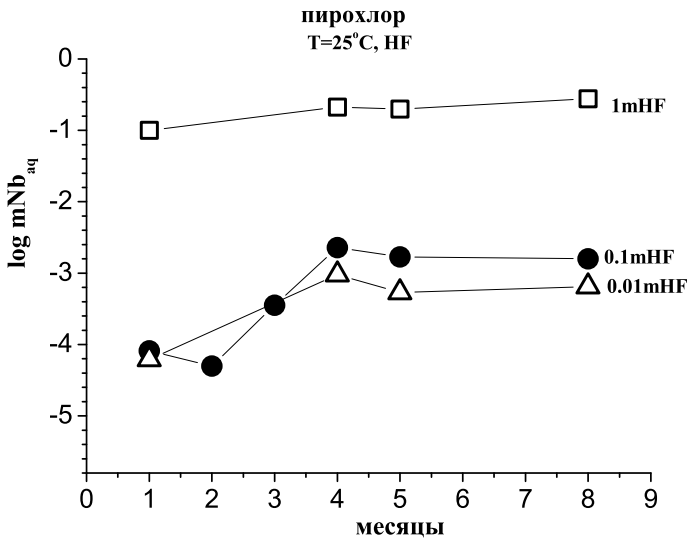


Fig.1 Kinetic dependence of Nb content at pyrochlore solubility in solutions HF (T=25C)

Niobium content in the solution increases significantly with increasing concentration of HF. At the duration of the runs for 1 month the niobium content is $n*10^{-4}$ mol/kg H_2O for 0.01 and 0.1m HF and $n*10^{-1}$ mol/kg H_2O for 1m HF. The niobium content for low concentrations of HF remains in the limits $n*10^{-3}$ m, but it increases by 3 orders and reaches high values - 0.212 mol/kg H_2O with the growth of HF concentration from 0.01m to 1m.

Experimental study of natural pyrochlore $(Ca, Na)_2$ $(Nb, Ta)_2O_6(O, OH, F)$ solubility were also carried out in aqueous HF and KF solutions with concentrations from 0.01 to 2 m at 400° C and 550° C and 1000 bar under Co-CoO oxidizing conditions. Fragments of pyrochlore monocrystal $(Ca, Na)_2(Nb, Ta)_2O_6(O, OH, F)$ from weathering crusts of carbonatite deposit Tatarka were used in the experiments.

It's composition is Na_2O-7,61%; CaO-14,28%; Nb_2O_5-71,61%; F-5,18%; TiO_2-0,83%; $Ta_2O_5 \leq 1\%$wt. The run duration was 15-20 days. We did the runs at a hydrohermal high pressure vessel in welded platinum tubes capsule technique allowing us to use oxygen buffer Co-CoO, isolated from the reagents. The analysis of the solutions for niobium and the whole row of elements –impurities (Ta, Ti, Mn, Fe, Zr, Na, Ca etc.) was made by the most modern methods of the inductionally bound plasma of ICP/MS and ICP/AES. The composition of the solid product was characterized using an x-ray phase and microprobe (Cam Scan MV2300(VE GA TS5130MM) methods of the analysis. Experimental data on the solubility of pyrochlore as a function of the total concentrations of HF and KF are shown in Fig. 2 and Fig. 3.

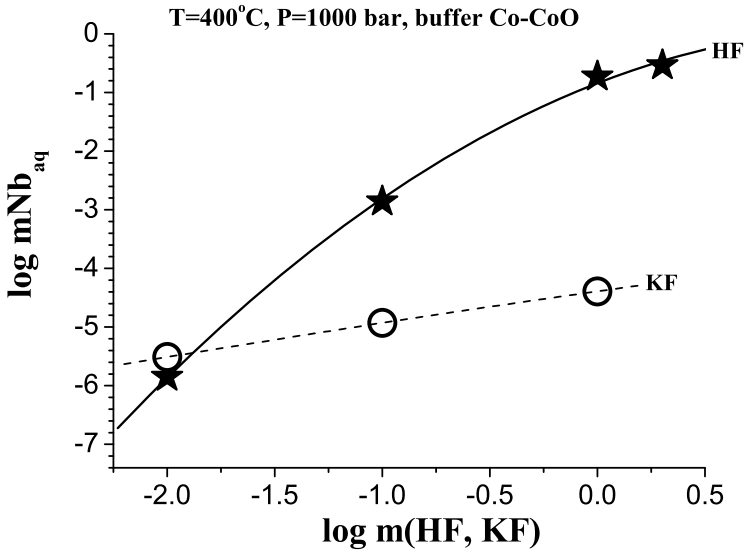


Fig.2 Concentration dependence of niobium content at natural pyrochlore solubility in HF and KF solutions (T = 400°C, P = 1000 bar, buffer Co-CoO)

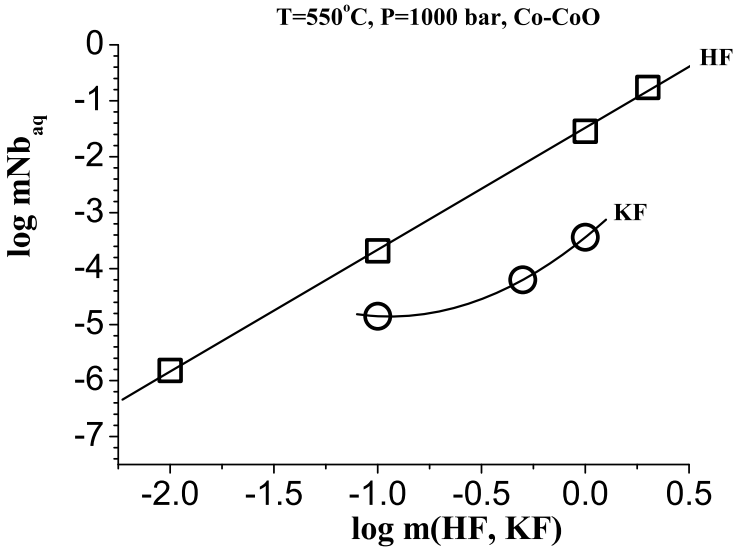
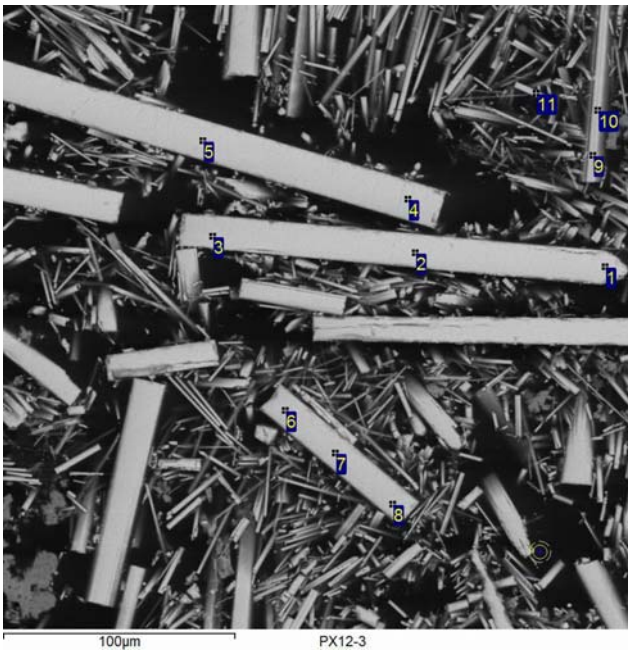


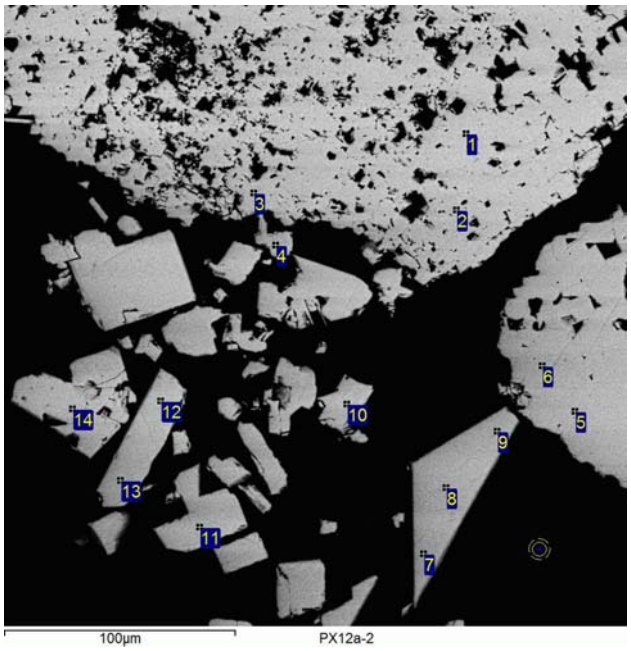
Fig.3 Concentration dependence of niobium content at natural pyrochlore solubility in HF and KF solutions (T = 550°C, P = 1000 bar, buffer Co-CoO)

A study of pyrochlore crystals after the runs by microprobe and x-ray phase methods has shown that in 1m HF pyrochlore dissolves incongruently with the formation of new phases of two kinds: a) white needle-like crystals with the formula $Na_2Nb_4O_{11}$, where niobium is partially substituted for

titanium (up to 1,45% wt.Ti), but oxygen is substituted for fluorine (up to 4,24 %wt.F) (picture 1a); b) Nb_2O_5 crystals, containing titanium (up to 0.56%wt.) and fluorine (up to 3.88 %wt.) (picture 1b). At dissolution in KF solutions the presence of iron impurities in natural pyrochlore is favourable to form black crystals (picture 2) having the formula $K_3(Nb_3O_6)(Si_2O_7)$, where oxygen is partially substituted for fluorine which content reaches more than 4 wt.%. A porous mass in the centre of the crystal represents iron niobate that contains more than 2 wt.% of Ti and F.



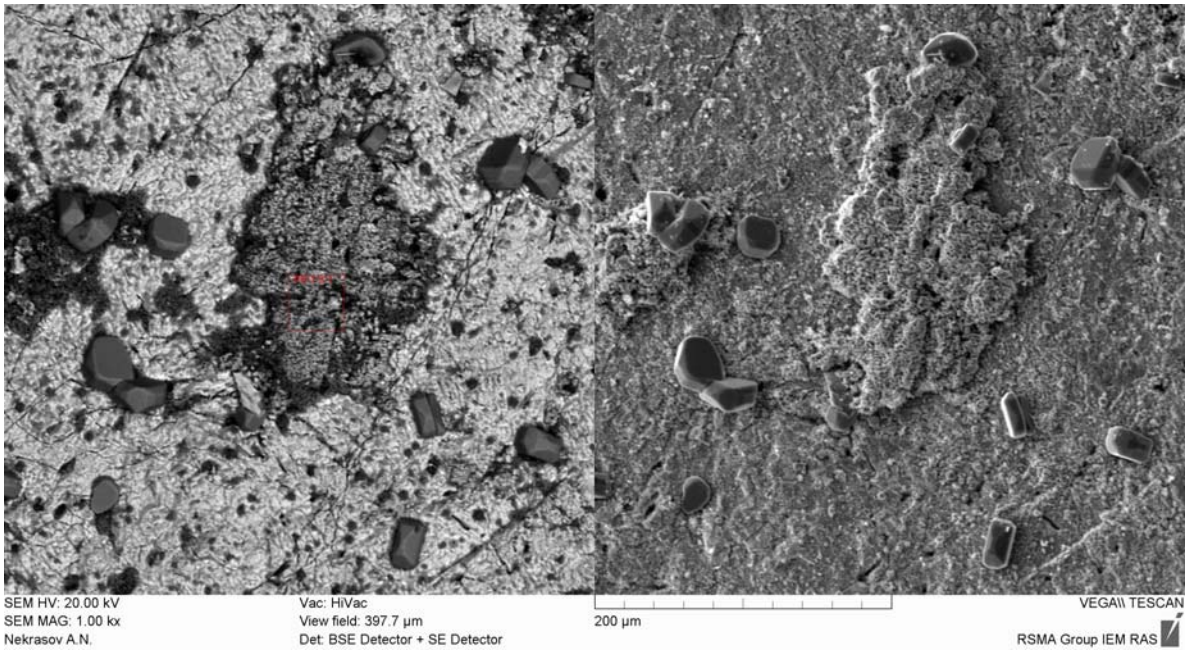
Picture 1a Crystals of $Na_2Nb_4O_{11}$, formed at pyrochlore dissolution in 1m HF (T=400°C, 1kb, buffer Co-CoO)



Picture 1b Crystals of Nb_2O_5, formed at pyrochlore dissolution in 1m HF (T=400°C, 1kb, buffer Co-CoO)

It can be seen from the obtained experimental data that niobium content increases with increasing HF and KF concentration in spite of the incongruent mineral solubility, although this pattern for KF is not as distinct. The niobium content increases with increasing HF concentration and reaches values $1.40*10^{-6}$ mol/kg H_2O in 0.01m HF and 0.291 mol/ kg H_2O in 2m HF at 400°C. At T = 550°C concentration dependence looks the same, but with temperature growth the niobium content

decreases a bit and is $1.51*10^{-6}$ in 0.01m HF and 0.172 mol/kg H_2O in 2m HF. In KF solutions pyrochlore solubility is much lower, but with temperature growth it increases and reaches values $4.06*10^{-5}$mol/kg H_2O at 400°C and $3.65*10^{-4}$mol/kg H_2O at 550°C for 1m KF.



Picture 2 Crystals formed at pyrochlore dissolution in 1m KF (T=400°C, 1 kb, buffer Co-CoO) (black crystals - $K_3(Nb_3O_6)(Si_2O_7)$;porous mass in the centre-$Fe_4Nb_7O_{14}$)

On the basis of the obtained experimental data we can conclude that solubility of both pyrochlore and columbite in fluoride solutions is rather high what allows us to speak about the possibility of real Nb transfer by highly concentrated (0.1mol/kg H_2O and higher) fluoride solutions HF and KF.

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Reference

Korzhinskaya, V. S., G. P. Zaraisky (2008), Experimental study of concentration dependence pyrochlore and columbite solubility in carbonate solutions at T = 550°C and P = 1000 bar. *Vestn. Otd. nauk Zemle RAN*, N 1(28)'2008, Moscow, IPE RAS.
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