

SOLUBILITY OF NATURAL TANTALITE-COLUMBITE IN FLUORINE SOLUTIONS AT $T = 300\text{--}500^\circ\text{C}$ AND $P = 1000$ BARS

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The solubility of natural tantalite-columbite (Mn, Fe) $(\text{Ta, Nb})_2\text{O}_6$ was investigated in water solutions of HF, KF, NaF in the concentration ranges 0.01 – 2.0 mol/kg H_2O at temperatures 300, 400, 500°C and pressure 1000 bars. The goal of the study is a quantitative estimation of the contribution of hydrothermal transport to the processes of Ta and Nb gain during the albitite and greisen formation in cupola of Li-F granite. The experiments were performed by using monocrystal of natural tantalite-columbite from quartz-amazonite-zinnwaldite pegmatoids of the Etyka tantalum deposit, Transbaikalia. The crystal has the next composition (weight %): Nb_2O_5 – 58.99, Ta_2O_5 – 17.70, MnO – 13.51, FeO – 4.42, TiO_2 – 2.59, SnO_2 – 1.54, WO_3 – 1.24. The runs were carried out in sealed platinum capsules by using high-pressure vessel [1]. The red-ox run conditions were controlled by buffers: Ni-NiO, Co-CoO, Q-Mt-Fa. At $T = 500^\circ\text{C}$ a part of runs were carried out without oxygen buffers, but their red-ox condition were close to Ni-NiO buffer because the walls of high pressure vessel is composed from nickel bearing alloy. The duration of the runs was 15-20 day. Bulk solubility of tantalite-columbite was defined using loss weight method by weighting a crystal before and after the runs. Accuracy of weighing is 0.02 mg. In several experiments the contents Nb and Ta were analyzed in a quenched solution by using ICP-MS/AES methods.

The researches have shown, at all temperatures columbite in HF solutions is dissolved by congruently. Its solubility increases with the raising of HF concentration in a solution from below 10^{-5} mole Nb_{aq} per kg H_2O in 10^{-2} mole HF solution up to near 10^{-3} mole Nb_{aq} at 1.0 m HF concentration. The concentration dependence of columbite solubility in NaF solutions is expressed weakly (Fig. 1). The $\lg m(\text{Nb}_{\text{aq}})$ varies from -5.25 to -4.5 in the 0.01-1 m NaF solutions. The crystals of NaF were observed in the products of the runs at the concentration of NaF more than 1-2 m and their appearance hindered to definition of true solubility of the mineral.

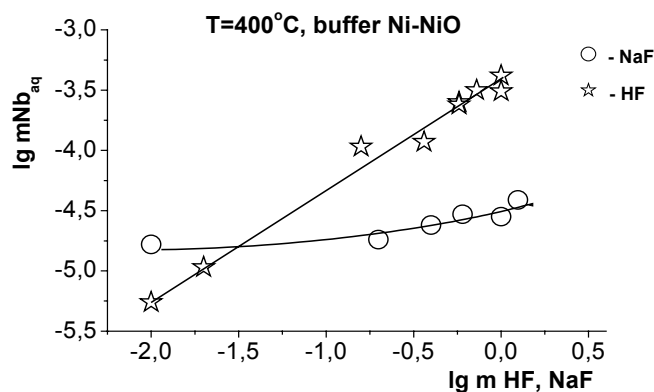


Fig. 1. Equilibrium contents of niobium in solution depending from HF and NaF concentration at $T = 400^\circ\text{C}$ and $P = 1000$ bars

A reactionary interaction columbite to formation of white needle crystals of K-Nb oxifluoride in KF solutions was observed. The amount of this compound was the maximum in the runs without using of the oxygen buffer. At presence of the Q-Mt-Fa buffer such crystals are absent. By means of x-ray and microprobe analyses are established, the structure of these crystals corresponds to: $\text{K}_x\text{NbO}_{2+x}\text{F}_{1-x}$ where x is in limits from 0.42 up to 0.6, in which niobium partially replaced by tantalum.

The equilibrium contents of Ta and Nb in HF solutions decrease with growth of temperature (Fig. 2 and 3). At presence of KF the increase of temperature is resulted in growth of the equilibrium contents of Ta and Nb, however their concentration at temperatures 300°C and 400°C are on 2-3 order lower

than in HF solution. The contents Nb and Ta in HF and KF solutions are close one to other at the temperature 500°C.

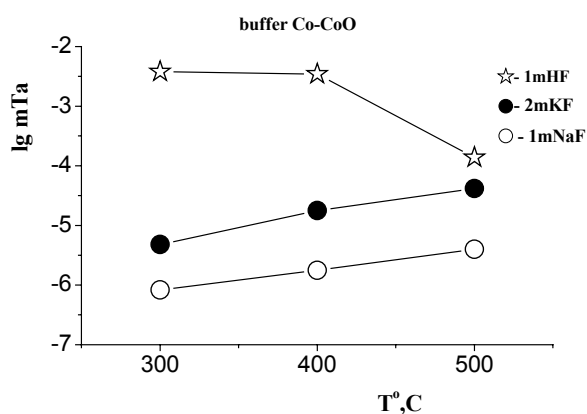


Fig. 2. Temperature dependence of the contents tantalum in HF, KF, and NaF solutions.

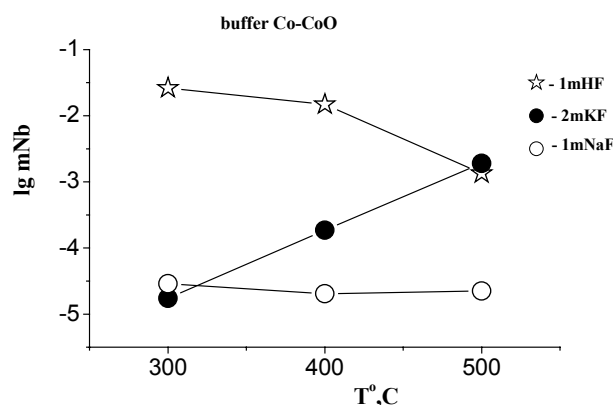


Fig. 3. Temperature dependence of the contents niobium in HF, KF, and NaF solutions.

The increase of the contents Ta in NaF solutions with growth of temperature is observed, while the concentration of Nb remains practically constant. The influence of oxygen fugacity in HF and NaF solutions at investigated T-P parameters is insignificant. However for KF solutions this influence is appreciable, as the formation of a new phase take place under more oxidizing conditions.

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Reference:

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