

**EXPERIMENTAL STUDY OF CONCENTRATION DEPENDENCE
OF Ta₂O₅ SOLUBILITY IN THE ALKALINE SOLUTIONS AT T=550°C,
P=1000 BAR AND LOW OXYGEN FUGACITY (Co-CoO BUFFER)**

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To estimate quantitatively a possible role of postmagmatic processes in genesis of rare-metal deposits of tantalum and niobium we performed systematic experimental investigations on mineral solubility of Ta and Nb under hydrothermal conditions, because the available experimental data are not enough to solve this problem. Earlier we investigated Ta oxide solubility in fluoride and chloride solutions what is actual for Ta deposits related to lime-alkaline, including lithium-fluoric granites ("apogranites") [1, 2]. This study is devoted to study of tantalum in alkaline solutions, typical for Ta deposits, generally connected with alkaline granites, alkaline sienites and carbonates. The tantalum oxide- chemical reagent Ta₂O₅, being the analogue of tantite, seldom occurring in nature, was used as initial material in the runs. The choice of simple Ta oxide is related to the fact, that its solubility restricts the upper limit of concentration of this element in hydrothermal solutions, since stable under natural conditions phases of Ta-niobates of more complex compositions (columbite, pyrochloride and others) have less solubility than oxides. The concentration dependence of Ta oxide solubility (Ta₂O₅) at T=550°C, P=1000 bar in the solutions of Na₂CO₃, NaOH with the concentration (0.01; 0.1; 0.5, 1.0 и 2.0 моль/кг H₂O) and in the solutions of NaF+NaOH, NaF+Na₂CO₃ with the concentration (0.01; 0.1; 0.5, 1.0 моль/кг H₂O) in the presence of oxygen buffer Co-CoO was studied. Run duration was 21 days. As have been shown earlier [1], it is enough to establish equilibrium. A sealed-capsule quench technique was employed. Experiments were performed on high pressure hydrothermal apparatuses. The capsules and the container with buffer were sealed into cold-seal pressure vessel of Tuttle type with big working volume that gives possibility to isolate the capsules from the container with buffer. The same technique was used to study Ta₂O₅ solubility in fluoride and chloride solutions. Solid run products were separated from the solutions by centrifugation method. After that the quenched aqueous solutions were analyzed by ICP/MS (Inductively Coupled Plasma Mass Spectrometry) and ICP/AES (Atomic Emission Spectroscopy) procedures for Nb, Ta, Mn, and Fe and admixture elements: Ti, W, Sn, K, and Na. To control congruent or incongruent dissolution of Ta oxide and to determine chemical composition of newly-formed phases (in case of their manifestation) the initial materials and solid run products were studied by X-ray phase and micro-probe analysis method (Cam Scan MV2300(VE GA TS5130MM).

It was discovered during the runs that in all studied alkaline and carbonate solutions both at low concentrations (less than 10⁻² mol/kg H₂O) and high (above 1,0 mol/kg H₂O) Ta oxide solubility is very low and within the limits n·10⁻⁷-n·10⁻⁵. In a logarithmic scale Ta content has a reverse linear dependence on NaOH and Na₂CO₃ concentration. Participation of fluorine in the runs, introduced as NaF (equimolar solutions NaF+NaOH and NaF+ Na₂CO₃) influences positively on Ta oxide solubility. The similar effect was observed in acidic and neutral solutions. However, Ta solubility only increased by the order of 1, remaining very low. In a logarithmic scale it has maximum (10⁻⁴ mol/kg H₂O) in the solutions of 0.1m NaF+NaOH and NaF+ Na₂CO₃. With the increase of fluoride concentration Ta content decreases, reaching minimum (10⁻⁷ mol/kg H₂O) in the solutions of 1m NaF+NaOH and NaF+ Na₂CO₃. (fig. 1). At addition of 0,01m, 0,1m and 0,5m solutions of NaF to 1m NaOH, the Ta₂O₅ solubility increases. In contrast to equimolar solutions of NaF+NaOH, a positive concentration dependence of Ta₂O₅ on NaF concentration can be markedly seen. Ta concentration increases from 10⁻⁷ mol/kg H₂O in the solution of 0,01mNaF+1mNaOH up to 10⁻⁶mol/kg H₂O in the solution of 0,5mNaF+1mNaOH (fig. 2). In all studied alkaline and carbonate solutions Ta₂O₅ dissolves incongruently, i.e. with the change of a composition. As solid phases wonderfully cut crystals of Na-tantite Na₂Ta₄O₁₁ with the hexaoctahedric form typical for pyrochloride are formed, as well as crystals of Na-Ta oxide NaTaO₃, referring to pseudocubic syngony (fig. 3 and 4).

The investigations have shown that at such low concentrations of Ta (10⁻⁶ - 10⁻⁷mol/kg H₂O), close to the limit of detection, it is difficult to speak about possibility of Ta hydrothermal transport by alkaline and carbonate solutions.

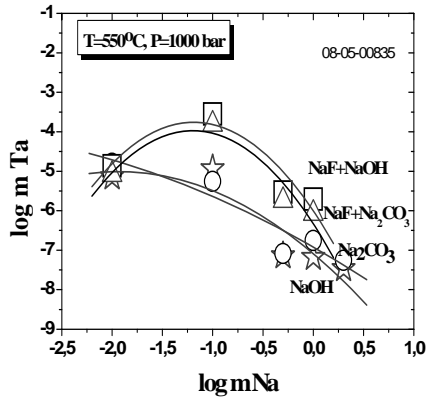


Fig.1. Concentration dependence of Ta₂O₅ solubility at T=550°C, P=1000 bar in solutions of NaOH, Na₂CO₃, NaF+NaOH, NaF+Na₂CO₃ (buffer Co-CoO)

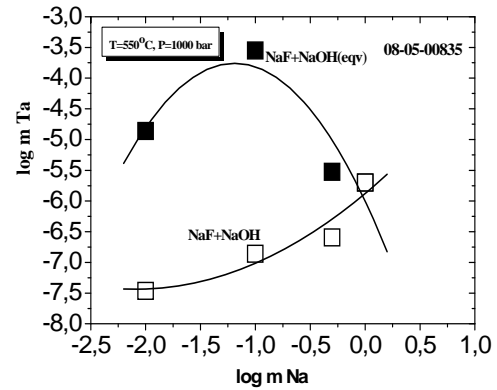


Fig.2. Concentration dependence of Ta₂O₅ solubility at T=550°C, P=1000 bar in solutions of NaF+NaOH (buffer Co-CoO) (shaded symbols-equmolal solutions)

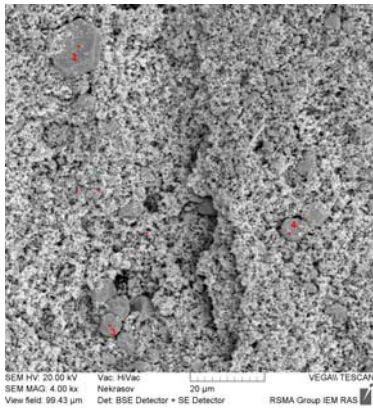


Fig.3. Crystals of Na-tantite Na₂Ta₄O₁₁ grown in 0.01 m NaOH at T=550°C, P=1000 bar (buffer Co-CoO)

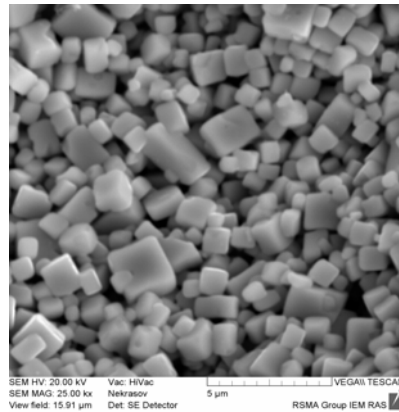


Fig.4. Crystals of Na-Ta oxide NaTaO₃ grown in 0.5 m NaOH at T=550°C, P=1000 bar (buffer Co-CoO)

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