

Experimental study of concentration dependence of Ta₂O₅ and Nb₂O₅ solubility in the alkaline and carbonate solutions at T=550°C, P=500 bar and low oxygen fugacity (Co-CoO buffer)

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This study is a continuation of long-term work to build a quantitative model of genesis of deposits of Ta, Nb and Li, connected with granites. Importance of the problem is the need to use the available experimental data to estimate quantitatively a possible role of hydrothermal transport and redeposition of tantalum and niobium under physical-chemical conditions typical for Ta and Nb deposits, generally connected with alkaline rocks. Earlier we investigated concentration and temperature dependence of the tantalum and niobium oxides solubility in the sodium alkaline and carbonate solutions in a wide range of temperature, compositions and concentrations of solutions at $P=1000$ bar [Kotova and Zاراisky, 2009; Zاراisky et al., 2009]. The choice of sodium specificity of the solutions is related to the fact, that Ta-Nb mineralization in lithium-fluoric granites ("apogranites"), alkaline granites, alkaline metasomatites, sienites and carbonates is closely associated with sodium metasomatism (albitization, ribektization, egrinization). In order to practically cover the entire range of conditions for the formation of Ta-Nb deposits the experimental studies of Ta₂O₅ and Nb₂O₅ solubility were carried out in aqueous alkaline solutions at $P=500$ bar. The tantalum and niobium oxides- chemical reagents Ta₂O₅ and Nb₂O₅, being the analogues of tantite and nioboxide, seldom occurring in nature, were used as initial material in the runs.

The concentration dependence of the Ta₂O₅ and Nb₂O₅ solubility at $T=550^{\circ}\text{C}$, $P=500$ bar in the solutions of Na₂CO₃ and NaOH with the concentration (0.01; 0.1; 0.5, 1.0 и 2.0 m) in the presence of oxygen buffer Co-CoO was studied. Run duration was 21 days. Experiments were performed on a hydrothermal line. 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. After the run, the quenched aqueous solutions and the solid products were separated using a centrifuge. The solutions were then analyzed using ICP/MS (Inductively Coupled Plasma Mass Spectrometry) and ICP/AES (Atomic Emission Spectroscopy) for Nb, Ta, Mn, and Fe and admixture elements Ti, W, and Sn. The composition of the solid product was characterized using optical microscopy, X-ray diffraction, and electron microprobe analysis (Cam Scan MV 2300 (VEGA TS5130MM)).

Experimental data are shown in fig. 1, 2, 3 and 4. The Ta₂O₅ solubility isotherms was found to have a negative trend in all studied alkaline and carbonate solutions at $P=1000$ bar. The concentration dependence of the Ta₂O₅ was found to be more complicated at $P=500$ bar. In NaOH solutions a pressure decrease from 1000 bar to 500 leads to a decrease of tantalum content by a factor of 1 between 0.01 and 0.05 m NaOH. However, the Ta₂O₅ solubility increases by a factor of 1 in aqueous solutions with NaOH concentrations of 1 m and greater (fig. 1). In the Na₂CO₃ solutions with decreasing pressure from 1000 bar to 500 the tantalum content decreases by a factor of 1 (fig. 2).

Experimentally established fact of the weak solubility of tantalum oxide in aqueous alkaline and carbonate solutions is fundamentally important for understanding of genesis of Ta deposits. The experimental data show that, for the range of concentrations, temperatures and pressures considered in this study, the Ta₂O₅ solubility is very low with concentrations on the order of 10^{-5} to 10^{-7} m in aqueous alkaline and carbonate solutions. The investigations have shown that at such low concentrations it is difficult to speak about possibility of Ta hydrothermal transport by alkaline and carbonate solutions. In NaOH and Na₂CO₃ solutions oxide tantalum has incongruent solubility. As solid phases wonderfully cut crystals of Na-tantite Na₂Ta₄O₁₁ with the hexaoctahedric form typical for pyrochloride are formed in 0.01 and 0.1m NaOH and

Na₂CO₃ solutions. In aqueous solutions with NaOH and Na₂CO₃ concentrations of 0.5 m and greater the crystals of Na-Ta oxide NaTaO₃, referring to pseudocubic syngony, are formed.

The investigations have shown that no distinct patterns of the effect of concentration and fluid pressure on the Nb₂O₅ solubility was observed in alkaline and carbonate solutions. The curves obtained have extreme, and difficult to interpret (fig. 3). But independently of this, we can confidently conclude that in all studied alkaline solutions as with low concentrations (0.1 m NaOH) so with high ones (1 m NaOH) oxide tantalum solubility is very low with concentrations on the order of 10⁻⁴ to 10⁻⁷ m.

The experiments indicate that in carbonate solutions Nb₂O₅ solubility is also very low with concentrations on the order of 10⁻⁶ m and changes very little with the increase of carbonate concentration. But contrast to the alkaline solutions, in carbonate solutions Nb₂O₅ has clearly expressed concentration dependence close to linear (fig. 4). The effect of fluid pressure is only observed at low concentrations of Na₂CO₃ (0.01; 0.1 m) and a pressure decrease from 1000 bar to 500 leads to a decrease of niobium content by a factor of 1. At greater concentrations of Na₂CO₃ niobium oxide solubility does not change with a pressure decrease. Similar to Ta₂O₅, niobium oxide dissolves congruently. Under all condition studied as solid phases crystals of Na-niobate–Na₂Nb₄O₁₁ are formed in 0.01 and 0.1m NaOH and Na₂CO₃ solutions. In all other cases both in alkaline and carbonate solutions the crystals of Na-Nb oxide–NaNbO₃ are formed.

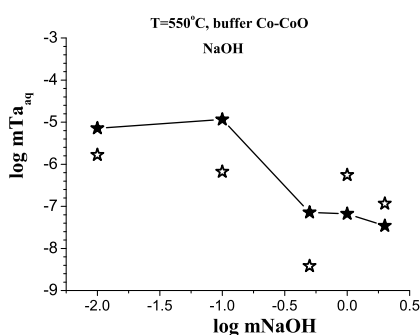


Fig.1 The solubility of Ta₂O₅ as a function of NaOH concentration and fluid pressure at $T=550^{\circ}\text{C}$ Na₂CO₃ concentration and fluid pressure at $T=550^{\circ}\text{C}$

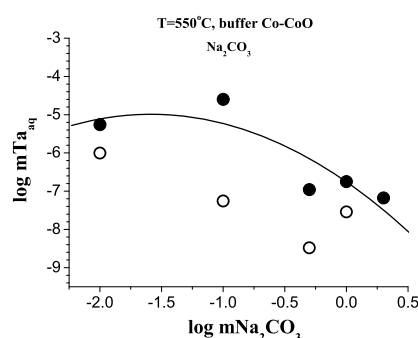


Fig.2 The solubility of Ta₂O₅ as a function of (stars-at $P=0.5$ kb; shaded stars-at $P=1$ kb) (circles-at $P=0.5$ kb; shaded circles at $P=1$ kb)

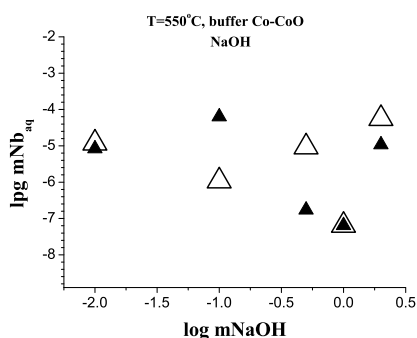


Fig.3 The solubility of Nb₂O₅ as a function of NaOH concentration and fluid pressure at $T=550^{\circ}\text{C}$ (triangles-at $P=0.5$ kb; shaded triangles –at $P=1$ kb)

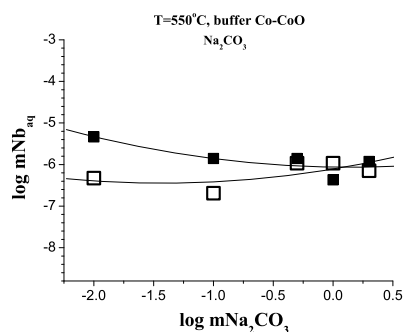


Fig.4 The solubility of Nb₂O₅ as a function of Na₂CO₃ concentration and fluid pressure at $T=550^{\circ}\text{C}$ (squares-at $P=0.5$ kb; shaded squares at $P=1$ kb)

A basic conclusion from our experiments is that in all studied alkaline and carbonate solutions for the range of temperatures, pressures and concentrations considered in this study the tantalum and niobium oxides solubility is low with concentrations on the order of 10⁻⁵ to 10⁻⁷ m for Ta and 10⁻⁴ to 10⁻⁷ for Nb. At such low concentrations close to the detection limits is hard judge any appreciated role of the complex of Ta and Nb in alkaline and carbonate solutions in natural conditions.

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References

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