Experimental study of concentration dependence of niobium oxide solubility in fluoride solutions at T=550ºC, P=500 bar and low oxygen fugacity (Co–CoO buffer)

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The dependence of Nb_2O_5 solubility as a function of fluoride concentration was investigated in HF, KF solutions with concentrations from 0.01 to 2 m at 550 °C and 1000 bar under Co–CoO oxidizing conditions. It is found that at low concentrations of fluoride (less than 10^{-2} m) the niobium concentration is at 10^{-4}–$10^{-3.5}$ m. Nb_2O_5 solubility strongly increases with increasing fluoride concentration and achieves significant values on the order of 10^{-2} to $10^{-1.5}$ m in aqueous solutions with high fluoride concentrations of 1 m and greater. Under such conditions hydrothermal mass transfer of Nb is really possible.

Key words: experiment, oxide tantalum, oxide niobium, hydrothermal solubility, fluoride solutions, concentration dependence

The peculiarity of the ore-bearing granites and associated greisenized and albitized deposits of rare metals is that their formation along with magmatic, it is necessary to consider the role of hydrothermal-metasomatic factors. However, the published data on the behavior of tantalum and niobium minerals in hydrothermal solutions of different compositions in a wide range of concentrations, temperatures, pressures and oxygen fugacity are insufficient to understand the role of hydrothermal-metasomatic processes in the genesis of rare metal deposits of tantalum and niobium and estimate the reliability of the genetic hypothesis. Therefore, we carry out a systematic experimental study on the solubility of natural columbite and pyrochlore [*Korzhinskaya, Kotova., 2011; Kotova., 2011*]**.** The use of columbite and pyrochlore experiments has its advantages, consisting in the possibility of direct application of experimental data to estimate the natural conditions of ore formation in connection with the identity in both cases, the main carrier minerals of tantalum and niobium. The disadvantage of the choice of columbite and pyrochlore to study the behavior of Ta and Nb in hydrothermal solutions is the relative complexity of their composition. This makes the thermodynamic interpretation of the experimental data more difficult. Therefore, to increase the reliability of experiments in parallel with the solubility of natural minerals was investigated under the same conditions the solubility of the tantalum and niobium oxides, which have been used as a pure chemical reagents. The solubility of simple Ta and Nb oxides, restricts the upper concentration limit of these elements under hydrothermal conditions. Stable under natural conditions, the mineral phase of tantalum-niobates of a more complex structure (columbite, pyrochlore, etc.) are less soluble than the oxides.

The study is aimed at solving a specific problem: the experimental determination of the solubility of niobium oxide in aqueous fluoride solutions at high temperatures and pressures for a quantitative estimation of the possibility of hydrothermal transport and precipitation of niobium at formation of commercially viable ore deposits.

The dependence of Nb_2O_5 solubility as a function of fluoride concentration was investigated in HF, KF solutions with concentrations from 0.01 to 2 m at 550 °C and 1000 bar under Co–CoO oxidizing conditions. 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). Consequently, the experiments were carried out at low oxygen fugacity (buffer Co–CoO). Experiments were performed on a hydrothermal line. The chemical reagent Nb_2O_5 (>99.99% purity) was used as the starting material. Fifty mg of Nb_2O_5 and 1 ml of the fluoride

solution were sealed into Pt capsules (80 mm long, 8 mm diameter, 0.2 mm wall thickness) using arc welding. The run duration was 15–20 days. Before and after the experiments all capsules were weighed on electronic balances with an accuracy of ± 0.01 mg to check for leaks during the run.

After the run, the quenched aqueous solutions were 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).

The experimental results are shown in (Fig. 1). The data show similarities in Nb_2O_5 solubility in fluoride solutions. The dependence of Nb_2O_5 solubility on fluoride concentrations follows linear trends in HF and KF solutions. The experiments indicate that at low concentrations of fluoride (less than 10^{-2} m) the niobium concentration is at 10^{-4}–$10^{-3.5}$ m. However, Nb_2O_5 solubility strongly increases with increasing fluoride concentration and achieves significant values on the order of $10^{-1.5}$ to $10^{-0.5}$ m in aqueous solutions with high fluoride concentrations of 1 m and greater. Under such conditions significant hydrothermal mass transfer of Nb is really possible. At high fluoride concentrations (1 and 2 m) the highest Nb_2O_5 concentrations ($10^{-0.5}$ m) were detected in HF solutions. Nb_2O_5 is less soluble in KF solutions than in HF solutions (up to $10^{-1.5}$ m in 2 m KF).

The results of X-ray diffraction of solid products of the experiments show that in HF solutions of low concentrations niobium oxide dissolves congruently, without changing the composition. In highly concentrated HF solutions niobium oxide has an incongruent solubility. In 1 and 2 m HF solutions the crystals of niobium oxide (Nb_3O_7), referring to orthorhombic crystal system, are formed as a solid phase

For all KF concentrations considered, niobium oxide dissolves incongruently. In 0.01 and 0.1 m KF solutions fluorides are formed with the formula $KNb_6O_{15}F$, referring to monoclinic system. In 0.3 m, 1 m and 2 m KF solutions the crystals of K-niobate-$K_2Nb_4O_{11}$, referring to tetragonal system, are formed.

The data shown in Fig. 1 show, in general, and the same kind of dependence of the Nb_2O_5 solubility on F-ion concentration in all studied fluoride solutions – HF and KF. All curves can be well approximated by straight lines having a slope. All available data correlate well. The discrepancy in the values of Nb_2O_5 solubility in HF and KF solutions does not exceed one order of magnitude.

In comparison with niobium at low concentrations of fluoride the solubility of tantalum is very small and is located at 10^{-5}–10^{-6} (Fig. 2). This indicates a low probability of hydrothermal transport of tantalum in such solutions. However, with increasing concentration of fluoride the Ta_2O_5 solubility greatly increases and at fluoride concentration 1.0 m and higher reaches 10^{-3}–10^{-2}. At such concentrations, the real mass transfer tantalum by hydrothermal solutions is possible. By analogy with niobium at low concentrations of F-ions (0.01, 0.1 m) the concentration dependence of Ta_2O_5 solubility in all fluoride solutions (HF, KF, NaF, LiF) has similar values. It was found that the Ta_2O_5 solubility isotherms have a positive trend in all studied fluoride solutions. At high fluoride concentrations (1 and 2 m) the highest Ta_2O_5 concentrations (10^{-1} m) were detected in HF solutions. The dependence of Ta_2O_5 solubility on the HF concentration in a logarithmic scale has a distinct linear. The solubility of Ta_2O_5 in 2 m KF solution is 10^{-1} m, which is the order of magnitude lower than the solubility of Ta_2O_5 in 2 m HF solution. Experiments have shown that the solubility of tantalum in fluoride solutions is approximately 1-1.5 orders of magnitude lower than the solubility of niobium.

The experimental data show that the solubility of Nb_2O_5 and Ta_2O_5 strongly depends on the fluoride concentration. Fluoride solutions with high concentrations of 1 m are the most probable for hydrothermal mass transfer and precipitation of Nb and Ta in the temperature range 400 to 550 °C. At saturation the concentration of Nb achieves values on the order of $10^{1.5}$ to $10^{-0.5}$ m and of Ta of 10^{-4} to 10^{-2} m. It also demonstrates the importance of complexing agents, such as F, in the transport of Ta and Nb. Experimental studies have allowed for the first time establish that Ta and Nb can be transported by hydrothermal acidic fluoride solutions and deposited in the form of its own minerals in quantities sufficient for the formation of commercial deposits, as evidenced by high concentrations of Ta and Nb in 1.0 m HF and KF solutions. Results of the study are important for the development of science-based prediction methods and the search for rare metal deposits of tantalum and niobium associated with granites.
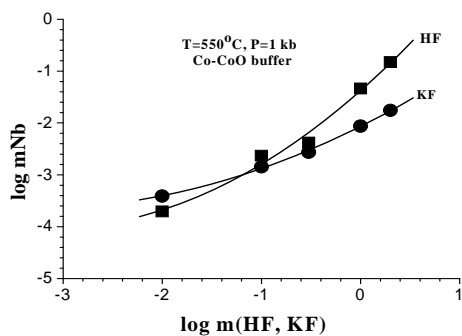
Fig. 1 The solubility of Nb_2O_5 as a function of HF and KF concentration at T=550° C and P= 1 kbar (Co–CoO buffer)

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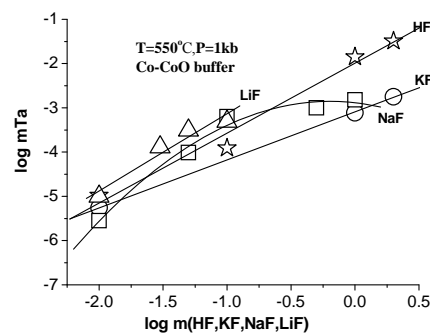
Fig. 2 The solubility of Ta_2O_5 as a function of HF, KF, NaF and LiF concentration at T=550° C and P= 1 kbar (Co–CoO buffer)

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