EXPERIMENTAL ESTIMATION OF HYDROTHERMAL TRANSPORT OF Ta and Nb IN CONNECTION WITH THE PROBLEM OF TANTALUM DEPOSITS GENESIS IN "APOGRANITES"

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Experimental studies on columbite solubility and direct modelling of masstransfer and deposition of Ta and Nb during experimental greisenization of granite were fullfiled. The experiments were conducteded to estimate of a probable role of hydrotermal-metasomatic processes in genesis of tantalic deposits of "apogranite" type in cupolas of rare-metal lithium-fluoric granites.

Experiments on solubility of natural columbite (Nb_2O_5-58,99 %, Ta_2O_5-17.70 %) carried out in fluorine NaF, KF and HF solutions with concentration of 0,01-2,0 mol/kg H_2O and carbonic solutions $NaHCO_3$ and Na_2CO_3 0.01-1,0 m at temperatures 300, 400 and 500°C, pressure 500 and 1000 bar at the presence of oxygen buffers Ni-NiO and Co-CoO.

Preliminary weighed monocrystal columbite (0.1-0.2 g.) was placed on a bottom of a platinum capsule 7x0.2x50 mm in the size, filled in solutions of 1 ml. The sealed capsule was placed in cold-seal pressute vessel of Tuttle type for 15-20 daies. All capseles were weighed before and after runs to ensure that no leaks occurred during the experiments. Total columbite solubility was determined on weight loss of the monocrystal by weighing on electronic microweights “Mettler-H54” with accuracy ±0.01 mg. A quenched solution was analyzed at spectrophotometer “Specol-11” for Nb and in parallel by ICP-MS and ICP-AES methods for Nb, Ta, Mn, Fe and admixture elements: Ti, W, Sn, K, Na.

Strong negative effect of oxygen fugacity increasing on columbite solubility is revealed. At more oxidation conditions (Ni-NiO buffer) concentration both Ta, and Nb in solutions appears on 1.5-2 order below, than at reduced their (Co-CoO buffer). Dependence of Ta and Nb solubility from the solution composition, temperature and pressure was investigated (Fig.1-3). The Ta and Nb concentration have the highest values in HF solutions at reduced conditions - up to 10^{-3}-10^{-2} mol/kg H_2O in 1.0 m HF solution (Fig. 1 & 2). In the 1.0 m NaF solution concentration of Nb appears of 2.5 order and Ta one appears of 3 order lower, than in the solution of 1.0 m HF. Solubility of Ta and Nb in solutions KF has intermediate values. It is established, that in NaF and KF solutions dependence of solubility from pressure distinctly negative (Fig. 3). At 500 bar the concentration of Nb and Ta in the solutions after experiments appears on 1-2 order above, than at P = 1000 bar. In the 1.0 m HF solution negative dependence of solubility on pressure is well expressed only for Ta and for Nb it is vague. It was revealed that columbite, both on Ta, and on Nb, under all investigated conditions has well expressed negative temperature solubility in HF, NaF and $NaHCO_3$ solutions and positive one in KF.

Dependence of solubility on concentration HF positive, and from concentration NaF feebly marked. In sodium carbonic and hydrocarbonate solutions the solubility of columbite is insignificant. Even in 1.0 m $NaHCO_3$ and Na_2CO_3 solutions it is on 10^{-5} mol/kg H_2O level for Nb and10^{-8} mol/kg H_2O for Ta.

Experiments on modelling of hydrothermal transport and precepitation of Ta, Nb and other metals (Li, W, Mo, Sn, Be, Pb, Zn) in the diffusion metasomatic columns of quartz-topaz greisen and tswitter are carried out at T=400 and 500°C, P=1,0 кбар and effect of acid fluorine solutions on the powder of a granite compacted in an open Pt capsule. Experiments by duration of 2 weeks carried out in autoclaves in sealed big gold capsules (V = 21 sm^3) in which placed a small open Pt capsula (5x50 mm) with a compacted granite powder, a solution and ore minerals in separate open containers. In result of metasomatic interaction with a solution by diffusuion the granite in small open capsule was transformed in Qtz-Toz-Zin greisen (tswitter). The metasomatic column received in the small capsula took and studied on a microprobe and on its length selected portions of substance for the ICP/MS-AES analysis on rock-forming and trace (ore, etc.) elements. A quenching solution was, also, analyzed.

Experimentally were reproduced quartz-topaz and quartz-zinnwaldite greisen and tswitter facies. Presence at a hydrothermal solution even low concentration of lithium strongly reduces area of stability of quartz-topaz greisen and expands the area of quarts-Li-mica greisen. Simultaneously precepitation of Ta and other ore metals in metasomatic zones of greisen column was reproduced. It is shown, that Ta and Nb in conditions of experiments can be gained in a column by HF solutions and be precepitated in a rear zone of greisen in the forms of own minerals (tantalite-columbite and microlitepirochlore) in small amounts and not further than 1 mm from contact with solution. New-forming Ta-Nb minerals are localized in quartz-zinnwaldite greisen near open end of capsule. Their crystals have round-isometric forms and the sizes no more than 5 micron (Fig. 4). Thay have more high content of Ta than Nb. In close accretions with individes of Ta-Nb minerals the smallest manifestations of fluorides (cryolite, elpasolite, chiolite and fluorite) are frequently found out allocation. That can testify to solubility and transfer of Ta and Nb in solutions as compound F-complexes. A little bit more deeply from the beginning of a column (3 mm) it is transported W and is much farther - up to 27 mm - Pb and Zn. Other ore metals (Sn, Mo, Cu), which were added to solution in a separate open container, do not find out appreciable transport and precipitation in the column during greisenization of granite under action of acid fluorine solutions. Contents of Sn, Mo and Cu in all zones greisen columns remains at an initial level of their contents in a granite.

The obtained results for the first time have allowed to conclude, that Ta and Nb can be transferred by hydrothermal way in acid fluorine solutions and be precipitated as own minerals in amounts, which are sufficient for formation of commercial deposits as demonstrated by high concentration of Ta and Nb in 1,0 m HF solution achieving 10^{-3}-10^{-2} mol/kg H_2O. Solubility and hydrothermal transfer of Ta and Nb is favored with participation of acid fluorine solutions of high concentration and reduce conditions. Precipitation of Ta and Nb from solution with formation of their deposits can occur as a result of (1) neutralization acid fluorine solutions, (2) decrease of fluorine concentration, (3) increase of chemical potential of oxygen. Usual for many other metals the factor of decrease of temperature and pressure cannot serve as the reason of deposition of Ta and Nb from hydrothermal solutions in investigated T-P a range of conditions 500-300°C and 1000-500 bar.

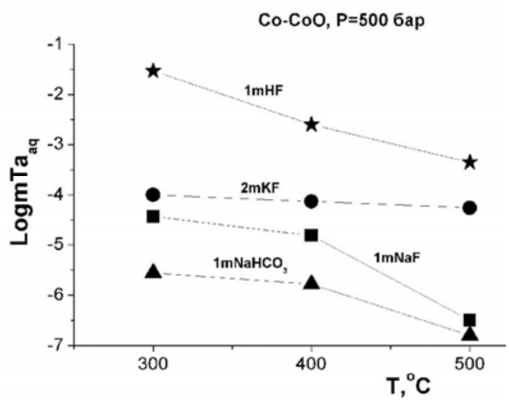

Fig. 1. Temperature dependence of tantalum concentration in the solutions

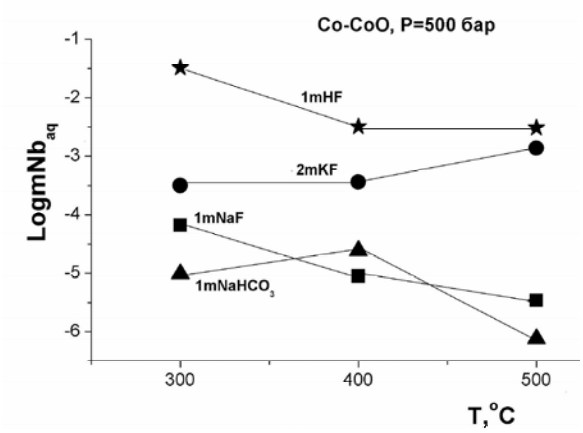

Fig. 2. Temperature dependence of niobium concentration in the solutions

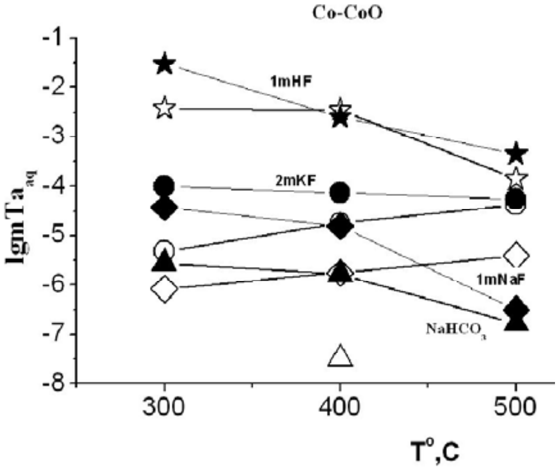

Fig. 3. Temperature dependence of Ta concentration in the solutions at 500 bars (dark figures) and at 1000 bars (light figures)

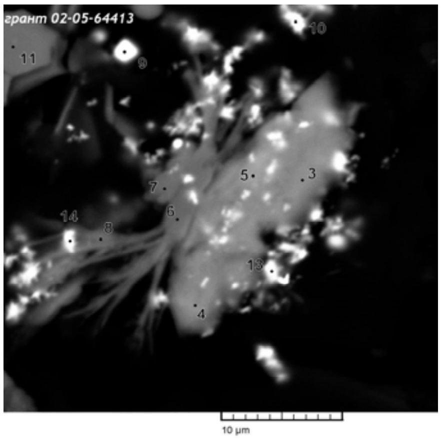

Рис. 4. Precipitation of Ta and Nb as tantalite (10, 13, 14) and Pb-pyrochlore (9) in rear Qtz (11)-Zin (3-8) zone of experimental greisen column.

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