Hydrothermal equalibria and ore formation

Dadze T.P., Kashirtseva G.A., Novikov M.P., Plyasunov A.V. Experimental study of solubility of powellite CaMoO$_4$ in weakly acidic solutions at 573 K.

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Abstract: Solubility of powellite CaMoO$_4$ was studied in dilute HCl or HClO$_4$ solutions (from 10^{-4} to ∼ 0.03 m) at 573 K and ∼ 100 bars. The obtained experimental data for CaMoO$_4$ are satisfactorily reproduced with species HMoO$_4^-$ and H$_2$MoO$_4$(aq), which Gibbs energies were calculated earlier (Dadze et. al., 2017) from data on solubility of MoO$_3$ in acid solution, demonstrating an internal agreement of solubility values for these phases.

Keywords: powellite CaMoO$_4$, solubility, acidic solutions, modeling

Solubility of powellite CaMoO$_4$ was studied in dilute HCl or HClO$_4$ solutions (from 10^{-4} to ∼ 0.03 m) at 573 K and ∼ 100 bars. Crystalline CaMoO$_4$ is obtained by sintering CaCO$_3$ and MoO$_3$ in equivalent proportions. The Ca:Mo atomic ratio based on 4 microprobe (Tescan VEGA TS 5130MM) analyses in the synthesized phase is equal to (0.981±0.014):1.0. Experiments were performed in titanic autoclaves from VT-8 alloy, passivated by 20% nitric acid at 673 K within a day. Autoclaves were placed into a vertical cylindrical furnace. Temperature was controlled by the regulator Miniterm-300. Fluctuations of temperature during runs were within ±2 K. Pressure in autoclaves was set by a degree of filling based on PVT – data of water. Duration of experiments was 4-7 days. A weighed quantity of CaMoO$_4$ was loaded into a titanic container that was suspended the upper part of the autoclave. The solid phase before and after experiments was controlled by X-ray diffraction, confirming that CaMoO$_4$ was the only phase present. The Mo concentration in solutions was determined by a colorimetric method (Marchenko, 1971) on Specol-11 at λ=453 nm and controlled by the weight loss method. Solubility of powellite increases with concentrations of acids, see Fig. 1.
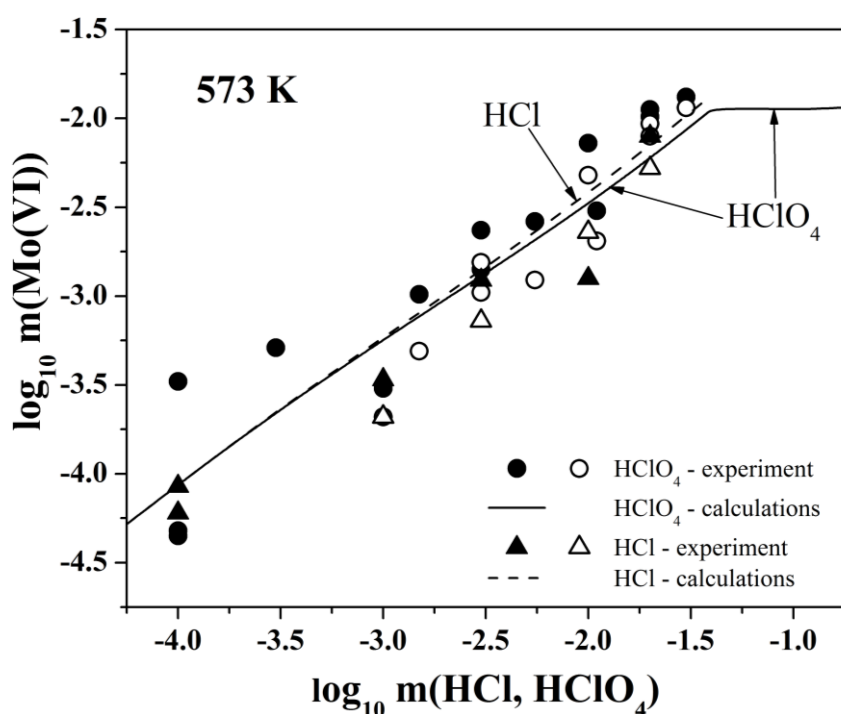

Fig. 1. Experimental (symbols) and calculated (lines) values of solubility of CaMoO$_4$ in solutions of acids. The filled symbols represent data of the chemical analysis, open symbols – the weight loss data.

Modeling of experimental results was carried out with the HCh program (Shvarov, 2008). The Gibbs energies of aqueous species H$^+$, OH$^-$, Cl$^-$, HCl(aq), ClO$_4^-$, Ca^{2+}, CaOH$^+$ are calculated the HKF model, CaCl$^+$, CaCl$_2$(aq) – taken from (Arcis et al., 2014), HMoO$_4^-$, H$_2$MoO$_4$(aq) – taken from (Dadze et al., 2017). Thermodynamic properties of powellite CaMoO$_4$ at 298.15 K are recommended recently (Gamsjäger and Morishita, 2015), the temperature dependence of the heat capacity to 1200 K is calculated based on data of (Zhidikova and Khodakovsky, 1984). According to calculations, powellite is stable up to concentrations of acids ∼ 0.04 m, at greater acid concentrations the stable phase is molybdenum trioxide MoO$_3$. The obtained experimental data for CaMoO$_4$ are satisfactorily reproduced with species HMoO$_4^-$ and H$_2$MoO$_4$(aq), which Gibbs energies were calculated earlier from data on solubility of MoO$_3$ in acid solutions, demonstrating an internal agreement of solubility values for these phases.

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Korzhinskaya V.S. Effect of the fluid composition (Hf + HCl) on the behavior of metals (Ta, Nb, Mn, Fe) at dissolution of tantalite at T = 550°C, P = 1000 bar (Co-CoO buffer) UDC: 550.8.014

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Abstract. We present new data on the solubility of natural tantalite $(Mn,Fe)(Nb,Ta)_2O_6$ in mixed fluids (HF + HCl), which allowed estimating the equilibrium metal contents (Ta, Nb, Mn, Fe) in solutions at T = 550 °C, P = 1000 bar in the presence of an oxygen buffer Co-CoO. The initial HF concentration varied from 0.01 m to 2 m, and the HCl concentration remained constant and was 0.5 m. It is concluded that in (HF + HCl) solutions, tantalite dissolves incongruently with a predominant release into a solution of Mn and Fe in comparison with Ta and Nb. The comparison is made on content of tantalum in pure solutions of HF, HCl in the concentration range of 0.01 - 2 m and in mixed solutions (HF + 0.5m HCl).

Key words: experiment, tantalite, solubility, mixed fluoride-chloride solutions

To determine a quantitative estimate of the role of postmagmatic processes in the formation of rare-metal deposits of tantale and niobium, we do systematic experimental investigations on mineral solubility of Ta and Nb (columbite, tantalite, pyrochlore) under hydrothermal conditions, since the experimental data available in literature are not quite enough to solve this problem. Earlier we investigated tantalite solubility in fluoride and chloride solutions what is valid for the tantalum deposits connected with lime-alkaline, including lithium-fluoride granites (apogranites) [Zaraisky et al, 2010; Korzhinskaya et al, 2014].This paper describes the investigation of the behavior of Ta, Nb, Mn and Fe at tantalite dissolution in the fluids of the mixed composition (HF + HCl).

We got new data on solubility of tantalite natural mineral $(Mn, Fe)_2(Ta, Nb)_2O_6$ in mixed fluids (HF + HCl) at T = 550°C and P = 1000 bar in the presence of oxygen buffer Co-CoO. For the experiments we chose tantalite mono crystals from quartz-amazonite-mica pegmatites of the Etyka tantalum deposit, having composition according to the data of the microprobe CamScan:Ta_2O_5-17,70%; Nb_2O_5-58,99%; MnO-13,51%; FeO-4,42%; TiO_2-2,59%; SnO_2-1.54%; WO_3-1,24wt.% (the average values from seven analyses). The initial concentration HF varied from 0.01 m to 2m, but HCl concentration remained constant and was 0.5 m. Experiments were carried out on hydrothermal apparatus of high pressure in sealed platinum capsules using the ampoule technique. The quenched aqueous solutions were analyzed using ICP / MS and ICP / AES (mass spectrometry and atomic emission) methods. The composition of the solid product was characterized using X-ray diffraction and electron microprobe analysis.

Figs.1 and 2 show the obtained results on the behavior of metals of Ta, Nb, Mn and Fe at tantalite dissolution.Fig.1 shows concentration dependence of equilibrium content of Ta in (HF + HCl) solutions. Here the data of tantalum content in pure HF and HCL solutions are given for comparison. As seen from the diagram, concentration curve has a weakly marked positive dependence. It is determined that in the region of low initial concentrations in (0.01m HF + 0.5 m HCl) solution tantalum equilibrium concentration is very low, attains the values $1.44*10^{-7}$ mol./ kg H_2O what is an order of magnitude lower than that in pure 0.01m HF [Zaraisky et al, 2010] and coincides with tantalum content in pure HCl. As HF concentration grows, tantalum content in equilibrium solution rises in essentially and attains the values $n*10^{-6}$ in the solution (2m HF + 0.5m HCl). In this case Ta content is 4 orders of magnitude lower than that in 2m HF and only by one order higher than that in HCl [Korzhinskaya et al, 2014].