Experimental study of Zr- and Hf-OH-Cl complexing in supercritical fluids by solubility method

N. D. SHIKINA[1], B. R. TAGIROV[1]*, V. A. VOLCHENKOVA[2] AND YA. V. BYCHKOVA[1]

[1]Institute of Geology of Ore Deposits RAS, Staromonetnyi per. 35, Moscow, 119017 Russia (*correspondence: tagir@igem.ru)

[2]Institute of Metallurgy and Matherial Science RAS,Leninskii pr. 49, Moscow, 119991 Russia)

The aim of this study is to characterize the speciation of Zr and Hf in supercritical chloride fluids, and to evaluate concentration of these metals and Zr/Hf ratio in equilibrium with baddeleyite $(Zr,Hf)O_2$ and zircon $(Zr,Hf)SiO_4$. For this purpose we chose to study the solubility of baddeleyite (0.74 wt.% Hf) as a function of HCl (to 1.5 *m*) and NaCl (to 3 *m*) concentration. The solubility experiments were performed at t = 450, P = 0.5 – 1 kbar using gold-lined Ti alloy autoclaves. Solid phase (several baddeleyite crystals ~ 1 mm in size) was placed in small gold containers, which were mounted in the upper part of autoclave. At the end of the experiment (~ 1-2 months), autoclaves were quenched in running water, opened, experimental solutions were extracted and the walls of the autoclaves were washed with EDTA solution in 2 M HCl. The obtained solutions (experimental + washing) were analyzed for Zr and Hf with ICP-MS and ACP-AES.

It was found that the concentdration of both Zr and Hf increased sharply with increase in the concentration of HCl and NaCl. The solubility of baddeleyite in 0.5 *m* HCl + 3 *m* NaCl was as high as 4 ppm and 70 ppb for Zr and Hf, respectively (P = 1 kbar). As follows from the experimental data, $ZrOHCl_3°$, $HfOHCl_3°$, and $HfCl_4°$ are predominant complexes in pure HCl solutions. Addition of NaCl results in the formation of $NaZrOHCl_4°$, $NaHfOHCl_4°$, and $NaHfCl_5°$ (as was suggested in [1]). These complexes probably are analogues of outer-sphere zircono-silicate clusters formed in alkaline Na-Si solutions (c.f. [2]). Decrease of pressure results in decrease of both Zr and Hf concentration that reflects strong hydratation of these metals. The Zr/Hf concentration ratio in fluid decreased with increrase of fluid acidity which is generally in agreement with the hard-soft acid-base theory and can stand for separation of these metals in geological systems.

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[1] Shikina N. *et al.* (2015) *Petrology*, № 1, 93-101. Wilke M. *et al.* (2012) *Earth Planet. Sci. Lett.* **349-350,** 15-25.