

The chemistry of Hf and Zr in chloride hydrothermal fluids studied by X-ray absorption spectroscopy

A.L.Trigub(National Research Centre “Kurchatov Institute”, Moscow, Russia; Institute of Geology of Ore Deposits, Petrography), B.R.Tagirov(Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Moscow, Russia), K.O.Kvashnina(ESRF - The European Synchrotron, CS40220, 38043 Grenoble Cedex 9, France; Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Institute of Resource Ecology, P.O. Box 510119, 01314 Dresden, Germany), O.N.Filimonova(Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Moscow, Russia) alexander.trigub@gmail.com

Zirconium and hafnium belong to group of high field strength elements (HFSE: Ta, Nb, Ti, Zr, Hf). These elements are widely used for tracing mass transfer in geological processes, as well as in geochronology. Field observations, confirmed by experimental modeling, indicate that Zr and Hf can be effectively mobilized in some geological environments. In particular, they become relatively mobile in fluoride-, chloride-, and silica-bearing fluids due to the formation of dissolved aqueous complexes whose composition is still a subject of controversial models (Migdisov et al., 2011; Wilke et al., 2012; Louvel et al., 2013). The aim of this study is to build reliable speciation model for Zr and Hf in chloride-rich hydrothermal fluids by means of X-ray absorption spectroscopy (XAS).

XAS experiments in fluorescence mode at Zr K-edge and Hf L₁,L₃-edges were performed at BM20 beamline of ESRF. The HfO_{2(cr)} and ZrO_{2(cr)} solubility experiments with in situ record of these spectra were carried out at $t = 340^{\circ}\text{C}$ - 480°C , $P = 500$ - 2200 bar using silica glass capillaries. Interpretation of the results of XAS experiments were performed using *ab initio* molecular dynamics (AIMD) calculations with the aid of CP2K program (J. Hutter, 2014). EXAFS and XANES spectra were simulated for AIMD atomic configurations by FEFF8.5 (A.L. Ankudinov et al., 1998; J.J. Rehr et al., 1990) and FDMNES (O. Bunao and Y. Joly, 2009; S.A. Guda et al., 2015) codes, respectively, and compared with the experimental spectra. EXAFS spectra were fitted using IFEFIT program (M. Newville, 2001) and evolutionary algorithms based on the Monte-Carlo procedures (J. Timoshenko, 2014) to extract structural information. Charge states of Zr and Hf were studied using XANES spectra.

Concentration of alkaline metals has no effect on the spectra and, therefore, formation of complexes with alkaline metals in the second coordination sphere is ruled out. This conclusion is important for hydrothermal chemistry of Zr and Hf as formally their solubility is

best described by negatively charged complexes whose formation is unusual for acidic high-temperature

fluids, but is confirmed by our experimental data. EXAFS spectra analysis showed that the best agreement of experimental and calculated spectra is achieved for mixed hydroxide-chloride complexes which contain oxygen atoms at three different distances, which correspond to O, OH and H₂O. Two types of XANES spectra with different white line shapes depending on the total chloride concentration were detected. This implies that at least two types of complexes of different composition presented in the experimental solutions.

Our experiments showed that Zr and Hf form strong hydroxide-chloride, complexes with stability sufficient to enable effective transport of these metals in acidic chloride fluids.

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