

Fractionation of zirconium-hafnium in ferromanganese crusts

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The zirconium(Zr)-hafnium(Hf) pair is known as a “geochemical twin”, and Zr/Hf ratios in various systems are theoretically the same as that of the chondrite meteorite. However, significant fractionation of the two elements between seawater and ferromanganese crusts (FMCs) has been reported (Bau, 1996). In this study, we have attempted to clarify the accumulation mechanisms of Zr and Hf in FMCs by performing sequential extraction and desferrioxamine (DFO) complexed radio-Zr and radio-Hf (DFO-Zr and DFO-Hf) adsorption experiments with X-ray absorption fine structure analysis for synthesised and natural samples obtained from the Ryusei and Takuyou seamounts. The Zr and Hf partition coefficient K_d between natural FMCs and seawater were around 10^8 , and their ratios were fractionated compared to that of seawater (Firdaus et al., 2011). The observed Zr chemical states in FMCs resembled that for coprecipitation with ferrihydrite, coprecipitation with δ -MnO₂ and a basalt-like composition, although the results of sequential extraction showed that Zr and Hf were found predominantly in the Fe fraction. In the case of the adsorption experiments for DFO-Zr and DFO-Hf to ferrihydrite and δ -MnO₂, it was found that the Hf-DFO had larger K_d values for both minerals than Zr-DFO. In this case, the observed bond length of Hf-O was slightly shorter than that of Zr-O in the synthesized minerals.