

Fractionation of Zirconium-Hafnium in ferromanganese crusts

*Aya Sakaguchi¹, Junpei Inagaki¹, Minami Inoue², Akira Usui³, Hiromitsu Haba⁴, Masashi Kaneko⁵, Shinya Yamasaki¹, Keisuke Sueki¹, Yoshio Takahashi⁶

1. Faculty of Pure and Applied Science, 2. Graduate School of Science, Hiroshima University, 3. Center for Advanced Marine Core Research, Kochi University, 4. Nishina Center, Riken, 5. Nuclear Science and Engineering Center, Japan Atomic Energy Agency, 6. Graduate School of Science, The University of Tokyo

Ferromanganese crusts (FMCs) are abyssal benthic chemical sediments that consist mainly of Fe and Mn oxide and hydroxide minerals, enriched with trace and precious metals. Due to their similar physicochemical properties, the elements zirconium (Zr) and hafnium (Hf), which are concentrated in FMCs, have a theoretically uniform ratio (Zr/Hf), which ratio is found in numerous systems. However, recent advances in analytical techniques have allowed observation of significant differences in the fractionation of these elements between seawater (Zr/Hf \sim 45-350; Firdaus et al. 2011) and FMCs (Zr/Hf \sim 57-88; Schmidt et al., 2014). In this study, we conducted adsorption experiments and XAFS analyses to clarify the concentrations and fractionation mechanisms of Zr-Hf in FMCs using synthesized minerals (Ferrihydrite and δ -MnO₂), radio-Zr and Hf tracers, and natural samples.

Six FMCs were collected from the Takuyo-Daigo and Ryusei seamounts, at water depths of from 950 m to 3000 m, using a ROV equipped with a live video camera and manipulators. The near surface layers (less than 1 mm) of all the FMCs were analyzed with XAFS and ICP-MS for Zr, Hf and other elements, and with XRD for mineral composition. Radiotracers were produced using the RIKEN AVF cyclotron for adsorption and co-precipitation experiments. Appropriate amounts of these tracers were added to 0.7 M NaCl solutions containing desferrioxamine B (DFOB) to obtain some Zr and Hf concentrations of solutions. The speciations of these elements in said solutions were confirmed by ESI-TOF-MS. Synthesized Ferrihydrite or δ -MnO₂ was added to the solutions and stirred for three hours at a pH of 8. In addition, Ferrihydrite or δ -MnO₂ was synthesized in said solutions. The activities of radio tracers in the filtered solutions were measured using a Ge detector. The adsorption/co-precipitation amounts to the solid phase were calculated using the differences in the radioactivity of the solution before and after filtration.

The major mineral composition of Fe and Mn in the FMCs did not vary significantly with the water depth of these seamounts. The concentrations of Zr and Hf increased with depth, and their ratios were totally fractionated from those of the seawater (Firdaus et al., 2011). Hf was more enriched in all FMCs than was Zr. The observed Zr chemical states in the FMCs were mainly coprecipitation with Ferrihydrite and coprecipitation with δ -MnO₂. In our adsorption experiments, the largest adsorption rate was observed in Hf to δ -MnO₂, followed in order by Zr to δ -MnO₂, Hf to Ferrihydrite and Zr to Ferrihydrite. The partition coefficients (K_D values) were calculated using the concentration ranges of Zr and Hf in seawater, where it was clear that Hf adsorbed more on both. Even though complexation rates estimated by RI-TLC were considered, there was no change in the adsorption behaviors in these experiments. For these samples, we found that the bond lengths between Zr-O and Hf-O in the first shells were shortened when they were incorporated into the oxides, with Hf-O becoming more shortened compared to Zr-O. The DFT calculations showed that Zr and Hf adsorb on Fe and Mn oxides as bidentate-mono nuclear and bidentate-binuclear structures. The calculation results for the binding energies and bond orders of Zr and Hf to minerals gave a reasonable explanation of the fractionation mechanism for Zr-Hf pairs in FMCs.

Keywords: Ferromanganese crusts, Zirconium, Hafnium