

## Fractionation of Zirconium-Hafnium in ferromanganese crusts

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Pair of Zirconium (Zr) and Hafnium (Hf) is called "Geochemical twins" due to the consistencies of their ionic valences and radii. As a consequence, this elemental pair shows same behaviour and uniform Zr/Hf ratio, which is theoretically same as that of chondrite meteorite, in the environment. However, the significant fractionation between these elements in natural samples has been found, and it has been proposed as enigma of Zr-Hf fractionation (Niu et al. 2012). The large fractionation of these elemental couple has also been found in the ferromanganese crust (FMC) (Bau 1996). In this study, we attempted to clarify the accumulation mechanism of Zr and Hf in FMCs with some methods including X-ray absorption fine structure (XAFS) technique for synthesised and natural samples.

Six FMC samples were collected from the Takuyo-Daigo and Ryusei seamounts, from 950 m to 3000 m water depth, with hyper-dolphin (remotely operated vehicle) equipped with live video camera and manipulators. Near surface layers (less than 1 mm) of all FMCs were analysed with XRD, and measured elemental concentrations by ICP-MS after the total decomposition of samples. Sequential extraction was conducted by following Koschinsky et al. (1995) to confirm the existence phase of Zr and Hf in FMC. XAFS analysis was also conducted to confirm the mineral composition and speciation of Zr together with chemical reagents, Zr minerals and rock samples as standard materials. Furthermore, distribution coefficients ( $K_d$ ) and chemical states were determined through the adsorption experiments of Zr and Hf DFO complexes with ferrihydrite and d-MnO<sub>2</sub>.

The major mineral composition of Fe and Mn had no significant variation with the water depth of these seamounts. The concentrations of Zr and Hf were increased with depth, and their ratios were varied without showing any trends. However, these ratios were totally fractionated from those of the seawater (Firdaus et al., 2011), and Hf was more enriched in all FMCs than Zr. The observed Zr chemical states in FMCs were 1) coprecipitation with ferrihydrite, 2) coprecipitation with d-MnO<sub>2</sub>, and 3) basalt-like composition, although the results of sequential extraction showed that Zr and Hf dominantly exist in Fe fraction. From the results of adsorption experiments of Zr and Hf with ferrihydrite and d-MnO<sub>2</sub>, it was found that the Hf-DFO was more adsorbed compared with Zr-DFO. In this case, the observed bond length of Hf-O was significantly shorter than that of Zr-O in the synthesised minerals.

Keywords: ferromanganese crusts, Zirconium, Hafnium