

Fractionation of Hafnium-Zirconium in ferromanganese crusts

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The couples of High Field Strength elements (HFS elements), e.g. Zirconium (Zr)-Hafnium (Hf) and Niobium (Nb)-Tantalum (Ta), are called Twin-element due to the consistency of their valences and ionic-radii in the environment. As a consequence, these couples must show uniform ratio, which is theoretically same as that of chondrite meteorite. However, the significant fractionations among HFS elements in natural samples have been found, and it was proposed as enigma of Zr-Hf and Nb-Ta fractionation (Niu et al. 2012). The large fractionation of these elemental couples has also been found in the ferromanganese crust (FMC) (Bau 1996). In this study, we attempted to clarify the accumulation mechanism of HFS elements in FMCs with some methods including X-ray absorption fine structure (XAFS) technique for synthesised and natural samples to serve as an aid to approach to this enigma.

Six FMC samples were collected from the Takuyo-Daigo and Ryusei seamounts, from 950 m (summit) to 3000 m water depth, with hyper-dolphin (remotely operated vehicle) equipped with live video camera and manipulators. Near urface layer (less than 1 mm) of all FMC was analysed with XRD and XAFS to confirm the mineral composition and speciation of Zr together with chemical reagents, Zr minerals and rock samples as standard materials. The concentrations of Zr and Hf in these samples were also measured by ICP-MS after appropriate treatments. Furthermore, to serve as an aid to clarify the fractionation mechanism between Zr and Hf in FMCs, distribution coefficients (Kd) and chemical states were determined through the co-precipitation experiments of Hf and Zr with ferrihydrite and δ -MnO₂. To analyse the chemical states on the solid phase, XAFS was employed.

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 that in the seawater (Firdaus et al., 2011). For all samples, Hf was enriched in FMC compared to Zr. The chemical state of Zr in FMCs through the depth showed, 1) coprecipitation with ferrihydrite, 2) coprecipitation with δ -MnO₂, and 3) basalt-like composition, and the rate of basalt-like composition of Zr was increased with water depth. The concentrations of Zr in the fraction between ferrihydrite and δ -MnO₂ were uniform through with the depth. Furthermore, the concentration of Zr in these fraction was also uniform, that is, the increased-concentration of Zr in the samples from deeper seamounts could be explained by the increase in basalt-like fraction. From the results of co-precipitation experiments of Zr and Hf with ferrihydrite and δ -MnO₂, it was found that the Hf-DFO was more precipitated compared with Zr-DFO. In this case, the bond length of Hf-O was significantly shorter than that of Zr-O.

Keywords: Zirconium, Hafnium, Ferromanganese crust