# Fractionation of Zr-Hf in ferromanganese crusts

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Ferromanganese crusts (FMCs) are abyssobenthic chemical sediments that consist mainly of Fe and Mn oxide and hydroxide minerals, and are enriched with trace and precious metals.[1] As a result of their similar physicochemical properties, the elements zirconium (Zr) and hafnium (Hf), which are concentrated in FMCs, have a theoretically uniform ratio (Zr/Hf), and this ratio is found in numerous systems. However, recent developments in analytical techniques have allowed observation of significant fractionation of these elements between seawater (Zr/Hf$\sim$45–350)[2] and FMCs (Zr/Hf$\sim$57–88).[1] In this study, we conducted adsorption experiments to clarify the concentrations and fractionation mechanisms of Zr-Hf in FMCs using synthesized minerals (ferrihydrite and $\delta$-MnO$_2$) and radio-Zr and Hf tracers.

Radiotracers of $^{88}$Zr (T$_{1/2}$ = 83.4 d), $^{89}$Zr (T$_{1/2}$ = 78.4 h), and $^{175}$Hf (T$_{1/2}$ = 70.0 d) were produced in $^{89}$Y(d, 3n)$^{88}$Zr, $^{89}$Y(p, n)$^{89}$Zr, $^{175}$Lu(d, 2n)$^{175}$Hf, and $^{175}$Lu(p, n)$^{175}$Hf rections using the RIKEN Azimuthally Varying Field cyclotron. The $^{88}$Zr, $^{89}$Zr, and $^{175}$Hf were radiochemically purified following Haba *et al.* (2001),[3] and mixed with stable Zr or Hf in 1-M HCl solutions.

Appropriate amounts of these solutions were added to 5 mL/0.7 M NaCl solutions containing organic chelate desferrioxamine B (DFOB) to obtain 0 $\mu$M, 5 $\mu$M, 1 $\mu$M, 100 nM, 10 nM and 1 nM solutions. The pH values of these solutions were all adjusted to 8. DFOB, a kind of siderophore present in the environment, has been reported to affect the fractionation of Zr-Hf between crustal rock and seawater.[4] The speciations of these elements in the solutions were confirmed as [Zr(DFOB)]$^+$ and [Hf(DFOB)]$^+$ via electron spray ionization time-of-flight mass spectrometry. The activities of $^{88}$Zr, $^{89}$Zr, and $^{175}$Hf were measured using a Ge detector after stirring for 1 h. Synthesized ferrihydrite or $\delta$-MnO$_2$ (2.50 mg) was added to the solutions and stirred for 3 h at a pH of 8. Note that this stirring time was previously confirmed to be sufficient to achieve the equilibrium condition required for the adsorption reactions. The activities of the $^{88}$Zr, $^{89}$Zr, and $^{175}$Hf in the filtered solutions were measured using a Ge detector. The adsorption amounts to the solid phase were calculated using the differences in the solution radioactivity before and after filtration.

The Zr and Hf adsorption amounts are shown in Fig. 1. Hf to $\delta$-MnO$_2$ yielded the largest adsorption rate, with Zr to $\delta$-MnO$_2$, Hf to ferrihydrite, and Zr to ferrihydrite following in order. The partition coefficients ($K_D$ values) were calculated using the Zr and Hf concentration ranges of in seawater, and it was clear that the
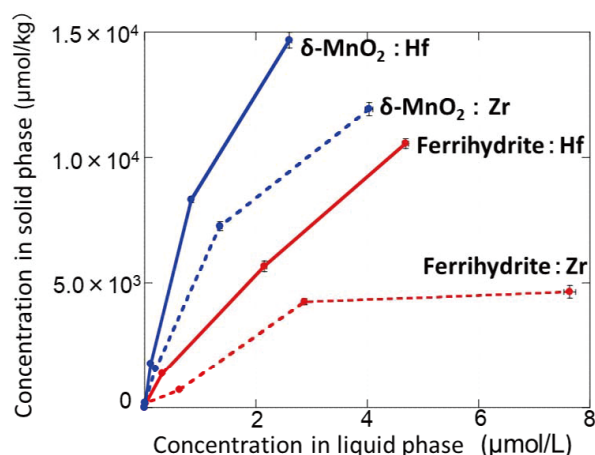


Fig. 1. Adsorption behavior of Zr (dashed line) and Hf (solid line) on ferrihydrite (red) and $\delta$-MnO$_2$ (blue).

Table 1. Partition coefficients $K_D$ for Zr and Hf.

| Elements | Minerals | Partition coefficients $K_D$ |
|---|---|---|
| Zr | Ferrihydrite | $5.73 \times 10^4$ |
| | $\delta$-MnO$_2$ | $1.83 \times 10^5$ |
| Hf | Ferrihydrite | $2.75 \times 10^5$ |
| | $\delta$-MnO$_2$ | $5.01 \times 10^5$ |

Hf underwent greater adsorption on both minerals than the Zr, and that the Zr and Hf had greater adsorption on $\delta$-MnO$_2$ than ferrihydrite, as apparent from Table 1.

Even though the complexation rates estimated through radioactive isotope thin-layer chromatography (87% for Zr and 79% for Hf) were considered, the adsorption behaviors of these experiments did not change. Furthermore, the ferrihydrite (232 m$^2$/g) and $\delta$-MnO$_2$ (135 m$^2$/g) surface areas obtained from Brunauer-Emmett-Teller measurements did not affect the results. It is predicted that the fractionation of Zr and Hf can be caused by differences in the stabilities of the adsorption processes. The binding energy differences between these elements and DFOB/minerals are now being calculated using density functional theory to observe their adsorption stabilities. This knowledge will allow us to discuss the results of Zr-Hf fractionation results obtained from our experimental systems.

References
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