Fundamental study on DFO complexation of Zr : Application to the behavior of geochemical pairs in aquatic environment

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The zirconium (Zr)-hafnium (Hf) pair is known as a "geochemical twin"[1] with Zr/Hf ratios in various systems being theoretically the same as that of the chondrite meteorite. However, owing to the ongoing development of analytical techniques, significant fractionation of the two elements between seawater (Zr/Hf $\sim$ 180–350)[2] and ferromanganese crusts (FMCs) (Zr/Hf $\sim$57–87)[3] has been observed. In addition, these elements are found to undergo fractionation between crustal rock and seawater. [4]

To clarify the fractionation of Zr and Hf at the water-rock interface, the behavior of the siderophore complexes of these elements has been studied, given that these refractory elements are thought to exist as siderophore complexes in environmental water.[4] However, even the complexation formation constants of siderophore-Zr/Hf have not been established owing to experimental difficulties. In this research, we have attempted to devise a method for obtaining such complexation formation constants.

To gain an improved understanding of the behaviour of Zr, first, a radiochemical tracer was used in laboratory experiments. ^{88}Zr (T$_{1/2}$ = 83.4 day) was produced in the reaction ^{89}Y(d, 3n)^{88}Zr by using the AVF cyclotron at RIKEN. ^{88}Zr was chemically separated from an Y foil [5] and mixed with stable Zr to produce a radiotracer solution with a total Zr concentration of 12.5 μM.

About 40 μL of tracer solution was added to 50 mL of 0.01 M NaCl solution, and ^{88}Zr γ-ray (393 keV) in the solution was assayed using a Ge detector. The pH value of this solution was adjusted to pH 8 using HCl and NaOH solutions to obtain hydrolysed Zr. The solution was filtered using a membrane filter (pore size of 0.2 μm) after stirring for 30 min. The ^{88}Zr in the filtered solution was determined, and the amount of hydrolysed Zr on the filter was estimated.

The hydrolysed Zr was transferred to 50 mL of 0.01 M NaCl solution containing 100 nM of siderophore, and the resulting solution was stirred for 90 h. As an analogous ligand to the siderophore, desferrioxamine B (DFO) was employed for this experiment. A portion of the solution was sub-sampled at t = 1, 4, 9, 16, 27, 66, and 90 h, and the sub-samples were filtered using a membrane filter (GTBP01300, Merck Millipore). The ^{88}Zr γ-ray intensities in the filtered solutions were measured using a Ge detector. The amount of filtered Zr was considered to represent the concentration of the DFO-Zr complexes.

The chemical yield of ^{88}Zr from the Y foil was found to be very low, a few percent, in the first experiment. This low yield might have been caused by Zr fixation at the bottom of the PFA vial owing to complete evaporation of the solution in the first step of the procedure. Subsequently, in the first step, evaporation to dryness was avoided, and the sample solution was carefully treated to prepare the chloride complex, ZrCl$_6^{2-}$.[6] Thus, a high chemical yield of 95% was realized.

The amount of hydrolysed Zr on the filter was estimated to be 59%, and the absolute amount was 295 pmol. The remainder of the Zr (41%) had passed through the membrane filter in the form of dissolved species and/or colloidal material.
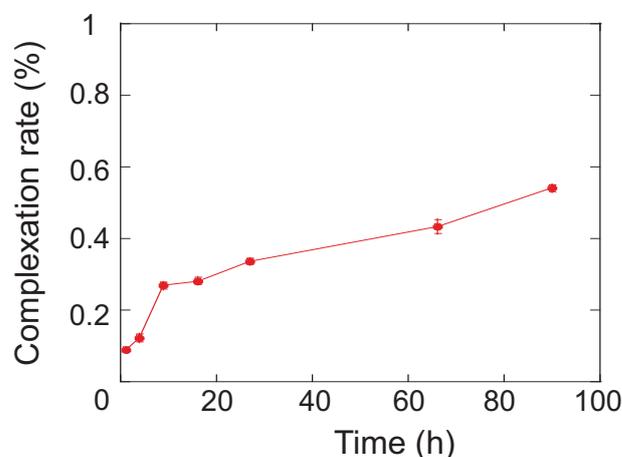
Fig. 1. DFO-Zr complexation rate as a function of stirring time.

The complexation rate of Zr with DFO is outlined as a function of stirring time in Fig. 1. As can be seen, the complexation rate of Zr with DFO increased with time, and an equilibrium condition was not established. Moreover, the percent complexation rate was quite low. Here, the ratio between Zr and DFO (in moles) was about 20 and the competitive reaction between OH$^-$ and DFO did not seem to have been operating. Thus, for future experiments, the concentration of DFO should be increased to study more precisely the complexation of Zr with DFO. An additional work is definitely needed to clarify the complexation behavior of Zr and Hf.

References
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