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Yttrium and rare earth element adsorption onto freshly precipitated hydroxides of Fe(III), Al, Ga, and In

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Yttrium and rare earth element (YREE) concentrations in the ocean are controlled by a competition between surface and solution complexation. While YREE solution speciation has been well characterized, surface complexation effects have not been thoroughly investigated. To improve the model of YREE oceanic distributions, experiments have been performed to study YREE adsorption onto freshly precipitated hydroxides of the trivalent metals Fe, Al, Ga, and In. The results are expressed in terms of the distribution coefficient: $\log K_s = [\text{MS}_i][\text{M}^{3+}]^{-1}[\text{S}_i]^{-1}$, where $[\text{MS}_i]$ is the concentration of adsorbed YREEs, $[\text{M}^{3+}]$ is the concentration of free hydrated YREE ions, and $[\text{S}_i]$ is the concentration of adsorptive solid substrate.

YREE adsorption onto Fe(III) hydroxide precipitates was studied over a range of pH (4-7) and ionic strength (0.01M-0.09M). The $\log K_s$ values show a linear dependence on pH although the overall shape of the $\log K_s$ pattern is relatively independent of pH. No significant dependence on ionic strength was observed. The $\log K_s$ values for the Al and Ga hydroxide precipitates, which were studied over a smaller pH range ($\Delta\text{pH}<1$), also show a linear dependence on pH.

Observed $\log K_s$ patterns have been compared to the patterns of solution stability constants for YREE hydroxides ($\log \text{OH}\beta_1$) and fluorides ($\log \text{F}\beta_1$). Linear free-energy relationships between $\log K_s$ and $\log \text{OH}\beta_1$ show an excellent correlation for Al hydroxide precipitates, a good correlation for Ga and In hydroxide precipitates, and a relatively poor correlation for Fe(III) hydroxide precipitates. The correlation between $\log K_s$ and $\log \text{F}\beta_1$ is generally poor for all the trivalent metals, but the patterns for $\log K_s$ and $\log \text{F}\beta_1$ display a similar sequence of inflections along the YREE series. While the $\log K_s$ pattern for Fe(III) hydroxide precipitates is distinct from the $\log K_s$ patterns for Al, Ga, and In hydroxide precipitates, it is similar to modeled $\log K_s$ patterns for natural marine particles, which are based on shale-normalized oceanic YREE concentrations and YREE solution speciation.

Surface and solution complexation behaviors of the YREEs are typically investigated either separately in simple systems, or together in systems that are very challenging to model. We are currently performing experiments to study the adsorption of YREEs onto Fe(III) hydroxides in the presence of a single solution ligand, carbonate, which is the dominant YREE ligand in seawater and many alkaline fresh waters.

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$^{231}\text{Pa}/^{230}\text{Th}$ as a tracer of ocean circulation in the Indian Ocean?

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After formation in the water column by decay of U, ^{231}Pa is removed to the sediment on timescales of ≈ 120 years, while ^{230}Th is removed more quickly in ≈ 30 years. This difference in residence time has led to $^{231}\text{Pa}/^{230}\text{Th}$ ratios in marine sediments being used as a proxy for ocean circulation in the Atlantic, productivity in the Southern Ocean, and boundary scavenging in the Pacific. No water-column profiles of ^{231}Pa or ^{230}Th have been published for the Indian Ocean so that the possible use of this nuclide pair is not known for that ocean.

In this study we present the first 5 water-column profiles for the Indian Ocean, measured along a transect to the east of Madagascar which samples the deep-western boundary current as it flows northwards. Measurements of total ^{231}Pa , ^{230}Th , and ^{232}Th have been made on 5 litre samples using a new MC-ICP-MS technique [1]. The typical precision being 3% for ^{230}Th , and 4% for ^{231}Pa (2 standard errors). Results indicate that ^{230}Th concentration profiles, 10-15gf/kg at 2000m, are similar to those typical of the open ocean and do not show the high ^{230}Th concentrations characteristic of the Southern Ocean from where these waters have recently been transported. ^{231}Pa , on the other hand, is found at higher concentrations, 1-1.5fg/kg at 2000m, than is typical for the open ocean, and this concentration decreases northwards along the flow path. We interpret this data as reflecting an evolution from initially high ^{230}Th and ^{231}Pa in the Southern Ocean towards a new steady state condition. At our locations, ^{230}Th , with its shorter residence time, has already decreased to typical values while ^{231}Pa is still adjusting.

The continued decrease of ^{231}Pa suggests that its concentration contains information about ocean circulation rates in a way analogous (but opposite) to the increasing Pa and Th concentrations seen in waters flowing south in the deep North Atlantic. A simple model of expected $^{231}\text{Pa}/^{230}\text{Th}$ ratio in the sediments underlying this evolving water mass is presently being tested by the measurement of core-top sediments underlying the profiles. This work is accompanied by an assessment of productivity in the area from modern measurements and sedimentary Ba concentrations. Our hope is that, as understanding of ^{231}Pa and ^{230}Th behaviour in this region develops, the nuclide ratio will provide a proxy for the flow rate of waters in the western boundary current which fills the deep Indian Ocean. Recently collected waters and sediments from offshore South Africa will help to develop understanding of ^{231}Pa and ^{230}Th behaviour and may allow extension of the use of sedimentary $^{231}\text{Pa}/^{230}\text{Th}$ to this more complex oceanographic region.

Reference

[1] Robinson, L.F. et al. (In Press) *GCA*.