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Experimental investigation of stable Nd isotope fractionation during adsorption on acid mine drainage-related solids

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Acidic coal mine drainage (AMD) is considered a potential source of critical metals, including rare earth elements (REE). In passive treatment systems involving flow through limestone beds, the REE are attenuated during AMD neutralization, likely by adsorption on precipitated oxyhydroxides of Fe, Al and Mn. To better understand the adsorption processes of REE on AMD precipitates, we investigated the mass-dependent isotope fractionation of Nd during adsorption-titration experiments on Mn and Al oxyhydroxides. Because acidity in coal mine drainage is generated by pyrite oxidation, we varied sulfate concentrations from 0 to 30 mM to explore possible adsorption effects from sulfate complexation of REE and mineral surfaces.

Fluids containing Nd were interacted with birnessite or Al hydroxides/hydroxysulfates [1] under pH conditions ranging from 4 to 8. The addition of sulfate shifted the Nd adsorption edge for both Mn and Al solids to lower pH by 1-2 units. The stable Nd isotope composition ($^{146}Nd/^{144}Nd$) was measured in the residual fluids and is reported as the permil deviation from the JNdi-1 Nd standard ($\partial^{146}Nd$). In every case, the lighter isotopes of Nd were adsorbed onto mineral surfaces, leaving the residual fluid higher in $\partial^{146}Nd$ by up to 0.15‰ (Mn solids) or 0.13‰ (Al solids), with measurement uncertainty <0.02‰. The measured $\partial^{146}Nd$ of the experiment fluid was linearly correlated with fraction Nd adsorbed in all cases. For the Mn solids, there was no discernible effect of sulfate levels on the Nd adsorption-$\partial^{146}Nd$ slope. For the Al experiments, the adsorbing solid in zero sulfate conditions was Al-hydroxide, whereas the adsorbing solid in the 10-30 mM sulfate experiments was Al hydroxysulfate. The hydroxide experiments yielded a greater magnitude of fractionation (by ~2x) than the hydroxysulfate experiments, but solution sulfate concentrations (10 vs. 30 mM) did not affect the fractionation. Despite evidence that sulfate pushes adsorption of Nd to lower pH values, these data indicate that the adsorption mechanism associated with isotope fractionation is largely unaffected. Stable Nd isotopes could be a robust indicator of REE attenuation mechanisms in mixed-solids AMD treatment systems.

[1] Boothe-Lordon, Cravotta, Tasker, Stewart, Capo & Hedin (accepted 2026), *Chemosphere*.