

Nickel isotope behavior during sorption to birnessite with and without vacancies: implications for the marine nickel budget

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Nickel is a bioessential element in enzymes that regulate the C, N, and O cycles¹. Despite Ni's biogeochemical importance, we have a poor grasp on modern marine Ni cycling. Attempts at constructing a balanced Ni budget indicate that outputs far exceed inputs, but marine sediments record no such deviation from steady state^{2,3}. Recent efforts to resolve the apparent imbalance proposed Ni isotopes as an additional mass balance constraint^{3,4}. To apply this approach, we must know the Ni isotope compositions ($\delta^{60/58}\text{Ni}$) of major sources and sinks. The largest sink for Ni likely comprises various types of Mn-rich sediments to which Ni sorbs during precipitation, but thus far those sediments show a very wide and puzzling range of $\delta^{60/58}\text{Ni}$ values: hydrogenetic crusts are generally heavier than seawater², while Mn-rich abyssal-plain sediments are considerably lighter⁴. Nickel sorption to Mn oxyhydroxides appears not to have one simple isotope effect. What can explain the wide variation among the Ni isotope compositions of Mn-rich sediments?

One hypothesis is that Mn oxyhydroxides have multiple sorption sites for Ni, including on [001] surfaces, on edges, and in structural vacancies, and these sorption mechanisms may have distinct isotope fractionations. To constrain their isotope fractionations, we sorbed Ni to triclinic birnessite (all or mostly surface and edge sites) and to pseudo hexagonal birnessite (surface, edge, and incorporation sites). We observed a smaller (yet still surprisingly large) fractionation ($\delta^{60/58}\text{Ni}_{\text{solution}} - \delta^{60/58}\text{Ni}_{\text{solid}} = \sim 1.4\text{‰}$) and a seemingly faster approach to equilibrium for triclinic birnessite, compared with a larger fractionation ($\sim 3.5\text{‰}$) and a very long-lasting kinetic effect for pseudo hexagonal birnessite. Our results suggest we must consider coordination environment and equilibration time when attempting to use experimental data to interpret the Ni isotope compositions of natural sediments.

[1] Ragsdale (2009), *Journal of Biological Chemistry* 284, 18571–18575

[2] Gall et al. (2013), *Earth and Planetary Science Letters* 375, 148–155

[3] Ciscato et al. (2018), *Earth and Planetary Science Letters* 494, 239–250

[4] Little et al. (2020), *Earth and Planetary Science Letters* 547, 116461