Ionic strength strongly affects Ni isotope fractionation between solution and Mn oxyhydroxide

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Recent stable isotope analyses of nickel in river water, in seawater, and in ferromanganese crusts pose a conundrum regarding isotopic mass balance for Ni in the oceans. Seawater, at $\delta^{60/58}$Ni = +1.44 ‰, is considerably heavier than the flux-weighted average of major rivers (+0.80 ‰) [1]. Hence, a significant, isotopically light sink must be present somewhere, unless the ocean is far from steady state. Athough isotopically light Ni in sulfide-rich Black Sea sediments recently suggested an answer [2], another study reported $\delta^{60/58}$Ni of organic- and sulfide-rich Peru Margin sediments nearly the same as seawater [3]. Meanwhile, in ferromanganese sediments, $\delta^{60/58}$Ni was found to be *heavier* than seawater [4], thus worsening the observed imbalance.

In an experimental study aimed at understanding this last result, we sorbed Ni to synthetic K-birnessite. Surprisingly, we observed *light* Ni isotopes preferentially sorbed, with an average $\Delta^{60/58}$Ni of 1.4 ‰, at low ionic strength. Next, in simplified seawater with I = 0.7 m, we observed *extremely light* Ni sorbed to the Mn oxyhydroxide, with $\Delta^{60/58}$Ni as large as 4.0 ‰! The fractionation diminishes significantly over ~1 month, suggesting a kinetic effect.

Ni EXAFS spectra of solids from low and high ionic strength experiments strongly suggest that the mechanism of sorption (and presumably the mechanism of Ni isotope fractionation) differs between our I = ~0 m and I = 0.7 m experiments. All samples can be fit with linear combinations of a tridentate corner-sharing site on {0 0 1} and a structurally incorporated site, but the fraction of Ni that is structurally incorporated is significantly higher at high ionic strength, likely because other cations occupy the {0 0 1} sites and drive the Ni into Mn vacancies at a faster rate than observed at low ionic strength.

[1] Cameron & Vance 2014, *GCA* [2] Vance et al., 2015 *Phil Trans R Soc A;* [3] Ciscato et al. 2018, *EPSL;* [4] Gall et al., 2013, *EPSL.*