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Future models of the marine Ni budget should account for months-long equilibration time and smaller Ni isotope fractionations during sorption to birnessite

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For nearly 50 years, researchers have puzzled over the apparent imbalance between fluxes of Ni into the oceans and fluxes out into marine sediments[1-5]. Published flux estimates imply extreme deviation from steady state (outputs far exceed inputs), but marine sediments record no exponential decline in seawater [Ni]. Fluxes are difficult to measure, so recent studies have turned to Ni stable isotopes to help identify poorly estimated or unrecognized fluxes[3-5]. These studies established that seawater is isotopically heavier than inputs (riverine[6]) and certain outputs (organic matter[4] and sulfides[3]). Thus, balancing the budget requires an additional isotopically light output or a heavy input to seawater.

Little et al.[5] proposed a new input: a benthic flux from abyssal plain sediments. Ni sorbs to Mn oxyhydroxides during deposition, and, upon burial, reductive dissolution of Mn oxyhydroxides releases Ni into porewater that may diffuse back to seawater. Using available flux estimates and isotopic compositions for other inputs and outputs, they calculated the magnitude and $d^{60/58}$Ni of benthic flux needed to balance the budget. The heavy isotopic composition of the benthic flux (+3.0‰) compared to the light Ni remaining in sediments (-0.8 to -0.2‰) implied a very large equilibrium fractionation between dissolved Ni and sorbed Ni.

Recent short-duration experiments displayed a similar fractionation[7-8], but in longer experiments[8] fractionation decreased over time and was therefore at least partially kinetic. Here, we performed very long-duration experiments, some spiked with ^{62}Ni to monitor extent of isotope exchange. The fractionation was ~3.5‰ early on but decreased to ~2.5‰ over 90 days and still did not reach steady state. Because abyssal sediments accumulate very slowly, and porewater-sediment contact times are long, we expect that fractionation between porewater Ni and Ni sorbed to Mn oxyhydroxides in sediments is likely ≤ 2.5‰, such that an adjustment to the Little et al. model is necessary.

[1] Sclater et al. 1976, *EPSL*; [2] Gall et al. 2013, *EPSL*; [3] Vance et al. 2016, *PhilTranRSocA*; [4] Ciscato et al. 2018, *EPSL*; [5] Little et al. 2020, *EPSL*; [6] Cameron and Vance 2014, *GCA* [7] Sorensen et al. 2020, *Chem.Geol;* [8] Wasylenki et al. 2019, *Goldschmidt*.