## Teasing apart kinetic and equilibrium fractionation for Ni sorbing to Mn oxyhydroxides: implications for the modern marine budget of Ni

LAURA E WASYLENKI AND EVA J BARANSKY

Northern Arizona University Presenting Author: laura.w@nau.edu

The composition of the marine ecosystem is in part a function of trace metal abundances in seawater, and shifts in these abundances have shaped ecosystem evolution in ways we know little about. Our ability to reconstruct ancient marine cycles, such as for nickel, is hampered by lack of knowledge about the modern cycle. During the Cenozoic Era, steady state has been maintained by a balance of input and output fluxes, but, even after several years of using Ni stable isotopes as an additional mass balance constraint, we cannot yet construct a balanced budget model. A significant challenge is the unusual behavior of Ni when sorbing to Mn oxyhydroxides in oxic abyssal plain sediments, which represent the largest output for Ni from seawater. In most sorbate-mineral systems, metal cations bond only to mineral surfaces. Nickel, however, can also occupy vacant Mn sites within the structure of the most common Mn oxyhydroxide, birnessite [1]. This behavior has complicated interpretation of Ni isotope signatures in natural sediments and prevented direct determination of the isotopic composition of Ni in this largest output.

Previous experimental studies examining Ni sorption to birnessite suffered from (a) inability to tease apart the two sorption mechanisms (surface adsorption versus incorporation in Mn vacancies) and (b) inability to infer isotope behavior at equilibrium, which we expect in such slowly accumulating sediments. Here, we build on our results from last year [2], which demonstrated that (1) the enormous fractionation past studies reported is a kinetic effect associated only with structural incorporation of light Ni (~3.5‰), and (2) as incorporated Ni slowly exchanges with solution, that initial fractionation decreases greatly. We show now that surface adsorption on its own equilibrates quickly, with  $\Delta^{60} Ni_{solution-surfaces orb}$  as low as 0.3‰. Therefore, Mn-rich sediment in equilibrium with solution should be fractionated by far less than previously thought, regardless of how Ni is distributed between surface sites and Mn sites in the mineral. We can revise previous models that assumed a fractionation of  $\sim 3.5\%$  as we work to balance the Ni budget.

[1] Peacock and Sherman, 2007, American Mineralogist

[2] Baransky et al., Goldschmidt 2023