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Benthic flux of isotopically heavy Ni from sediments helps to resolve mass balance of nickel in the modern ocean

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Nickel (Ni) is a bio-essential trace metal for phytoplankton, and understanding its biogeochemistry in the modern ocean is crucial. However, the lack of a clear Ni mass balance in the ocean has puzzled scientists for decades: the estimated flux of Ni sinks is greater than the flux of Ni sources; furthermore, the isotopic composition of modern seawater is heavier than all known Ni sources. Recently, it has been hypothesized that benthic Ni from sediments may supply heavy Ni isotopes to the ocean to resolve the Ni mass balance issue. In this study, we tested this hypothesis by analyzing trace metal concentrations and Ni isotope ratios in sediment porewaters from two sites in the Southern California Borderland. Our results show that porewaters have much higher Ni concentrations than the overlying waters, and the calculated diffusive inputs indicate that similar fluxes from less than 5% of the seafloor area are needed to provide enough benthic Ni for the elemental Ni mass balance in the ocean. Furthermore, the porewater δ^{60}Ni at the sediment-water interface is +2.66‰, much heavier than deep seawater δ^{60}Ni (~+1.33‰), implicating the important role of benthic Ni flux in supplying heavy Ni isotopes to the modern ocean. We found that Ni is released to porewaters through the dissolution of Mn oxides in the Mn-reducing zone and then removed by newly precipitated Mn oxides as Ni moves towards the oxygenated zone. A Rayleigh distillation model suggests a Ni isotope fractionation factor of -0.612‰, with lighter Ni preferentially removed from porewater.

We have also reexamined previously estimated Ni fluxes in the modern ocean. We suggest a much smaller Ni sink flux in Fe-Mn crusts/nodules than previously estimated, while our Ni sink flux in authigenic clays is consistent with recent estimates. Our findings suggest that the Ni mass balance in the modern ocean is in steady-state, both elementally and isotopically, and that benthic Ni flux is an important process in ocean Ni cycling.