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Nickel isotope fractionation during uptake into marine phytoplankton

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Nickel (Ni) is a bio-essential trace metal for phytoplankton, serving as the metal cofactor for various enzymes that influence carbon and nitrogen cycling. Nickel stable isotopes (δ^{60}Ni) provide a powerful tool to study Ni biogeochemistry and have great potential to become a proxy to study marine redox conditions, climate change, and biogeochemistry in the geological past. Analysis of seawater δ^{60}Ni in the modern ocean indicates that lighter Ni isotopes are preferentially used by phytoplankton. However, direct analysis of Ni isotope fractionation during biological uptake is lacking. In this study, we explore Ni isotope fractionation during biological uptake by conducting three different culturing experiments. We began with culturing phytoplankton in EDTA-buffered Aquil medium for metal quota and δ^{60}Ni analysis. Nickel isotope analysis of the cells and culture medium reveals that all cellular δ^{60}Ni are 2‰ to 5‰ higher than the culture medium, and δ^{60}Ni of culturing medium decreases as phytoplankton grow. These results indicate preferential assimilation of heavy Ni isotopes by phytoplankton in the EDTA-buttered culture medium—in contrast to what is suggested by natural seawater and particulate δ^{60}Ni results. Realizing this discrepancy, we conducted a second culturing experiment using non-EDTA-buffered natural seawater. We monitored seawater Ni concentration (dNi) and δ^{60}Ni during phytoplankton growth and two of the three phytoplankton (*E. huxleyi* and *Trichodesmium*) decreased dNi and increased seawater δ^{60}Ni. In particular, *Trichodesmium* drew down seawater dNi from 4 nM to 1 nM—a concentration even lower than the typical 2 nM dNi in the oligotrophic ocean—and increased seawater δ^{60}Ni from +1.3‰ to +1.8‰. These results indicate lighter Ni isotopes are preferentially used during phytoplankton growth in natural seawater—in line with field observations—and that natural seawater is a better culture medium to study biologically driven Ni isotope fractionation. Finally, we analyzed seawater and particulate δ^{60}Ni of samples collected from a mesocosm incubation experiment conducted in Hawaii to investigate Ni isotope fractionation by natural microbial community in the oligotrophic North Pacific. This study fills the gap of Ni isotope fractionation during biological uptake and improves our understanding of Ni biogeochemistry.