

Experiments reveal the mechanism by which Ni isotopes fractionate in the weathering environment

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To advance understanding of Ni isotope cycling in terrestrial and marine settings and to establish a basis for interpreting signatures in nature, we are combining simple-system experiments with analysis of natural samples to quantify Ni isotope fractionation during key abiotic reactions governing the distribution of Ni near the earth's surface.

Samples from a laterite profile in Democrat, North Carolina, display distinctive isotope systematics suggesting a mechanism to explain the heavy Ni isotopic compositions of riverine waters recently reported by Cameron and Vance (2014, *GCA* 128, 195). Fe-oxide rich weathering residues from the top of the laterite profile, from which substantial amounts of Ni have been leached, are slightly depleted in heavy isotopes of Ni relative to unweathered, ultramafic bedrock. Meanwhile, veins of late-stage, Ni- and Mg-rich silicates that cut through lower layers of the laterite and precipitated from downwardly mobilized, dissolved Ni from the upper weathering residues are up to 1 ‰ heavier in $\delta^{60/58}\text{Ni}$ than the oxidized laterite. Our hypothesis is that isotopically light Ni is retained in the Fe- and Mn-oxide rich layer through adsorption and co-precipitation with these phases. The isotopically heavy complement is mobilized downward and outward, eventually contributing to riverine dissolved load.

To test this hypothesis, we have experimentally determined how Ni isotopes fractionate during (1) sorption to 2-line ferrihydrite, (2) co-precipitation with ferrihydrite, (3) adsorption occurring after and during time-induced partial conversion of ferrihydrite to goethite, and (4) sorption to birnessite (Mn-oxyhydroxide). In all experiments with ferrihydrite, regardless of fraction sorbed or duration of ferrihydrite aging, Ni associated with ferrihydrite was 0.3 ‰ lighter than coexisting dissolved Ni. The largest fractionation occurs during sorption to birnessite: sorbed Ni is isotopically lighter than dissolved Ni by 1.4‰, in terms of $\delta^{60/58}\text{Ni}$. The magnitude of fractionation is independent of the proportion of Ni sorbed, suggesting an equilibrium isotope effect, likely driven by a difference in Ni's coordination chemistry between solution and surface. Thus our experiments support the hypothesis that adsorption and co-precipitation of Ni with oxyhydroxide phases in weathering profiles leads to mobilization of dissolved Ni enriched in heavier isotopes.