

The oceanic biogeochemistry of nickel and its isotopes

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Nickel (Ni) is an essential micronutrient for marine primary producers, but it is the least studied bioactive metal so far. Though surface Ni concentrations are never as depleted as some other bioactive trace metals, a large fraction of the residual photic zone Ni pool may not be bio-available, so that the importance of Ni as bio-limiting may have been underestimated. Here, we compile the growing Ni isotope database and add new data to show that a significant fractionation occurs in surface waters of subtropical areas. Both observational data and models link heavy Ni isotope signatures in the upper ocean (up to +1.69‰) to high nitrogen fixation rates (up to 391 $\mu\text{mol.m}^{-2}.\text{d}^{-1}$), suggesting a fractionation induced by diazotrophs or cyanobacteria more generally. The elevated Ni requirement of these organisms could result in the complete utilisation of the bio-available pool, leaving an isotopically heavy Ni pool in the upper ocean. Complementary analyses of the Ni isotope composition of cultured diatoms and cyanobacteria, as well as their media, will help us to constrain different phytoplankton uptake regimes.

We also present relationships between macronutrients and Ni/Ni isotope relationships in the global ocean. In addition to highlighting the bio-available Ni threshold at $\sim 2 \text{ nmol.L}^{-1}$, the very different systematics emphasise the biogeochemical divide between subtropical and subpolar regions. Steeper slopes are observed in the subtropics, confirming higher Ni requirements in these waters compared to subpolar regions. This global analysis also suggests a strong impact of denitrification on the removal of Ni in oxygen minimum zones.