

Ni isotope fractionation during marine phytoplankton uptake: Implications for a limited and fractionated bioavailable Ni pool in the modern ocean

**TZU-HAO WANG¹, QIONG ZHANG^{1,2}, YU-TE HSIEH^{1,3},
ROSALIND E. M. RICKABY¹ AND GIDEON M
HENDERSON¹**

¹University of Oxford

²The Hong Kong University of Science and Technology

³National Taiwan University

Presenting Author: tzu-hao.wang@earth.ox.ac.uk

Nickel, as a bio-essential element, its isotopes have been used to disentangle the important roles of Ni in biogeochemical cycling. However, two puzzles from previous studies reporting that Ni is never fully depleted in the surface ocean and the inconsistency of Ni isotopic fractionations in the global surface ocean still remain challenging to interpret. Ni isotope profiles in different ocean basins are reported to be either homogeneous or isotopically heavy at the surface. Marine phytoplankton uptake is then assumed to remove isotopically light Ni but never directly measured. This study aims to (1) provide the first Ni isotope data in cultured marine phytoplankton and (2) understand the links connecting seawater, phytoplankton and ligands in the ocean.

An enrichment of isotopically heavy Ni compared to the starting medium is observed in harvested cells for all species selected in this study under a range of Ni concentrations but with different magnitudes and trends. This observation suggests that marine phytoplankton preferentially take up heavy Ni isotopes. The isotope fractionation factors for selected species are estimated by fitting to Rayleigh distillation law. The elemental ratios, Proteomics analysis and subcellular measurements are also applied to explain observed physiological and isotopic responses.

The positive Ni isotope fractionations observed here is at odds with the previous assumption that marine phytoplankton are enriched in isotopically light Ni as a mechanism to explain the isotopically heavy surface ocean in some parts of the surface ocean. It implies that the bio-available Ni pool may have been fractionated by ligands before being biologically utilized. The stronger binding of some ligands compared to biological uptake mechanism can preferentially enrich isotopically heavy Ni due to the second highest stability of Ni complexes among first-row transition metals [1]. This complexation may appear irreversible on timescales relative to the rate of biological uptake and indicate that not all dissolved Ni is bio-available in the modern ocean. This study provides strong insights into explaining global Ni seawater profiles and reminds the lack of understanding in Ni-related ligands in the modern ocean.

[1] Irving and Williams (2007), J. Chem. Soc. 0, 3192-3210.