Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.29126

Mackinawite partial oxidation to green rust produces a large,abiotic uranium isotope fractionation

ROMAIN GUILBAUD[1], MORTEN B. ANDERSEN[2], HELEN M. FREEMAN[3], JEFFREY PAULO H. PEREZ[4], DAVID UHLIG[5] AND LIANE G. BENNING[4]

[1]Géosciences Environnement Toulouse, CNRS
[2]Cardiff University
[3]Priestley Centre for Climate Futures, University of Leeds
[4]GFZ Helmholtz Centre for Geosciences
[5]Freie Universität Berlin

The isotopic variability of uranium (U) isotopes is being increasingly used on ancient sedimentary rocks to reconstruct palaeo-redox conditions in Proterozoic oceans, with particular focus on the extent of past marine anoxia. However, low-oxygen settings, i.e. the transition zones between strictly anoxic and fully oxic conditions, may have characterised large expanses of Precambrian continental margins, where oxygen-breathing, complex life emerged and diversified. Accurate reconstructions of oxygen levels in such conditions are therefore required, but current geochemical proxies fail in identifying transitional redox conditions.

It is well known that under euxinic (anoxic and sulphide-containing) conditions, U(VI) is reduced to immobile U(IV) in the sediments, incorporating the heavier isotopes into the solid, reduced phase. Here, we explore the mineralogical transformations occurring during the partial oxidation of mackinawite, a preponderant mineral in euxinic conditions. We show that green rust forms as a by-product of mackinawite oxidation, along with uraninite and polysulphide. The mechanism involves the reaction between U(VI) and aqueous FeS(aq), and records a large, abiotic uranium isotope fractionation favouring the incorporation of the heavier U isotopes into uraninite (UO_2). We suggest that sediments depositing under redox transitions between euxinic and oxic conditions may therefore record heavy U isotope signatures.