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Experimental determination of uranium isotope fractionations during early diagenesis of ferruginous sediments: focus on Green Rust.

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Uranium (U) isotope compositions of ancient carbonates and shales are increasingly used as a redox proxy to reconstruct the extent of past ocean oxygenation. Indeed, the reduction of labile U(VI) into solid U(IV) as uraninite (UO_2) in euxinic (anoxic and sulphide-rich) settings is accompanied by a significant U isotope fractionation, with the heavy isotopes being preferentially incorporated into the reduced sediment. However, still little is known about the behaviour of U and its isotopes in ferruginous (anoxic and iron-rich) environments, which were prevalent for most of the Earth's history, thus limiting our ability to interpret U isotope signatures in ancient sediments that deposited under those conditions.

Here, we explored experimentally the fate of uranium during the diagenetic transformations of green rust, a predominant mineral in ferruginous environments. Sulphate and carbonate green rust ($GR(SO_4)$ and $GR(CO_3)$, respectively), the most abundant green rust species in marine environments, were reacted with dissolved U(VI) at pH 8.4, and the effects of diagenesis were explored over a range of times and temperatures, from 1 hour to 10 days at 25°C and 90°C.

Our results indicate that both green rust species have different reduction rates, and that uranium is immobilised in the sedimentary phase in the form of UO_2 during early diagenesis. We also report the first time the U isotope fractionation occurring during the abiotic reduction by $GR(CO_3)$. Reduced U is enriched in the heavy isotopes, contrasting with previous experimental work with chloride green rust GR(Cl) reporting the accumulation of heavy isotopes in the dissolved phase. We suggest that this discrepancy raises from opposite U isotope behaviours during adsorption and reduction, the latter being the mechanism targeted here. We infer that under green rust-rich, ferruginous environments, where U is reduced to uraninite, sediments may archive an isotopically heavy U isotope signature.