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## Iron isotope signals: Use and limitations in natural marine sediments

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Iron (Fe) reduction in marine sediments plays an important role during the degradation of organic matter and for benthic nutrient release into the water column. Dissimilatory iron reduction (DIR) in shallow sediments has been extensively studied and has been shown to go along with isotope fractionation: Iron reducers favour the light iron isotope <sup>54</sup>Fe, which is therefore preferentially released into pore water while the ferric substrate becomes isotopically heavier. Fe isotopes are thus considered to be a powerful tool for assessing the role of DIR in marine sediments and for tracing benthic fluxes into the water column that are characterized by respectively low  $\delta^{56}\text{Fe}$  values.

Here we decipher under which conditions Fe isotope signatures in pore water and the solid phase are also useful to unravel Fe reduction processes in deeper, methanic sediments. We investigated two different sites: (1) unlithified sediments (<5 m sediment depth) from the Helgoland Mud area, North Sea, where iron reduction is coupled to the methanogenic fermentation of complex organic matter [1] and (2) consolidated mud rock from the Nankai Trough off Japan (<1,180 m sediment depth), drilled during the International Ocean Discovery Program Expedition 370. For the Nankai Trough, microbial reduction of structural Fe(III) in smectite was suggested to promote the smectite-to-illite transition [2]. Iron isotope data of the Helgoland Mud area hint towards a deep Fe reduction process that does not preferentially release isotopically light Fe. We conclude that deep Fe reduction in this setting happens “coincidentally” when crystalline, conductive Fe oxides are used by microbes for electron transfer. In contrast, uniquely low  $\delta^{56}\text{Fe}$  values in pore water of Site C0023 in the Nankai Trough result predominantly from Rayleigh fractionation, where adsorption of aqueous Fe(II) preferentially removes the heavy isotopes from the pore water.

The two examples demonstrate that different processes control the isotope fractionation in unlithified and consolidated sediments.

References:

- [1] Aromokeye et al. (2020), *The ISME Journal: Multidisciplinary Journal of Microbial Ecology* 15, 965–980.
- [2] Kim et al. (2019), *Geology* 47(6), 535–539.