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Stable iron isotope signals indicate a "pseudo-abiotic" process driving deep iron release in methanic sediments

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Microbial iron reduction in shallow subsurface sediments leads to the liberation of isotopically light iron, whereas several abiotic iron reactions rather lead to an enrichment of heavy iron isotopes in the pore water. Hence, iron isotope analyses are used to discriminate dominant iron reactions in shallow sediments. In this study we investigate whether iron isotopes are also useful to discriminate between biotic and abiotic reactions in deep methanic sediments. Samples derived from fine-grained deposits of the Helgoland mud area, North Sea, where iron release from methanic intervals was previously suggested to be coupled to methanogenic fermentation of organic matter and anaerobic methane oxidation [1]. A combination of iron isotope geochemistry with reactive transport modelling hints towards a combination of processes affecting the stable isotope composition of dissolved iron in these deposits. The dominant process releasing iron at depth does not seem to lead to notable iron isotope fraction. The pore water at the deep Fe source has a δ^{56}Fe signature of -0.08 ± 0.10‰, which is similar (within uncertainty) to the isotopic composition of sequentially leached ferric substrates (hydroxylamine-HCl-leach: -0.07‰, dithionite-leach: 0.18‰, oxalate-leach: -0.05‰). Under the assumption that iron reducing microbes generally prefer isotopically light iron, the deep Fe reduction in this setting thus appears to be "pseudo-abiotic": If fermentation is the main reason for Fe release at depth, the fermenting bacteria transfer electrons directly or indirectly to Fe(III), but without notable related isotopic fractionation. Our findings contribute to the debate on the pathway for deep iron release by showing that the main underlying process is mechanistically different to the microbial Fe reduction dominating in shallow sediments and encourages future studies to focus on the fermentative degradation of organic matter as a source of iron in methanic sediments [2].

[1] Aromokeye et al. (2021), *ISME J* 15, 965–980, doi: 10.1038/s41396-020-00824-7.

[2] Henkel et al. (2024), *EGUsphere* [preprint], doi: 10.5194/egusphere-2024-1942.