

## Pb isotopes and glacial/interglacial weathering intensity

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To gauge the impact of weathering on Quaternary CO<sub>2</sub> cycles, we need better constraints on the flux of cations from the continents. For the substantial portion of the continents that have been glaciated in the Quaternary, early stage weathering of U+Th rich accessory phases freshly exposed during glacial periods should preferentially release radiogenic Pb. Thus the seawater Pb isotopic composition might act as a regional proxy for the riverine alkalinity flux to the oceans. Here we discuss the development of this proxy at high resolution and its application to sediments from Feni Drift (ODP Site 980) spanning the last 45 ka.

Pb isotope data from ferromanganese crusts (*I*) have been used to postulate greater weathering intensity during interglacial than glacial periods, but low temporal resolution precluded investigation of the detailed structure of the record at glacial inception and termination. To obtain higher resolution, we applied a tested method of Pb extraction from authigenic Fe oxide phases in marine sediments (2). The results contrast with existing crust data in that the Pb isotope variation is much larger (<sup>206</sup>Pb/<sup>204</sup>Pb ranges from 18.90 to 21.09 cf with 18.96 to 19.22 in crusts) with the most radiogenic Pb occurring at the Last Glacial Maximum. The Pb signal shows strong correlation to other proxy records from the same and nearby sites. A pronounced ~1.2 to 2 ka periodicity, particularly during MIS 3, most likely reflects transport of a terrestrial weathering signal from North Atlantic land masses. This preliminary investigation raises several issues pertaining to the direct interpretation of leached Fe oxides as archives of seawater Pb isotopic composition. Although the radiogenic signal is consistent with early stage weathering, the extreme variation in Pb isotope ratios may reflect a predominance of Fe oxide formation in terrestrial rather than marine environments, thus highlighting the importance of understanding continent-ocean Pb transport pathways and their implications for environments of Fe oxide formation prior to marine deposition.

### References

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## Mechanisms of Fe isotope fractionation during dissimilatory Fe(III) reduction by *S. putrefaciens* and *G. sulfurreducens*

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Microbial dissimilatory iron reduction (DIR) is widespread in anaerobic sediments and is a key producer of aqueous Fe(II) in suboxic sediments that contain reactive ferric oxides. Here we compare Fe isotope fractionations produced by similar cultures of *G. sulfurreducens* and *S. putrefaciens* during reduction of hematite and goethite. Both species produce aqueous Fe(II) that is depleted in the heavy Fe isotopes, as expressed by a decrease in <sup>56</sup>Fe/<sup>54</sup>Fe ratios or δ<sup>56</sup>Fe values. The low δ<sup>56</sup>Fe values for aqueous Fe(II) produced by DIR reflect isotopic exchange among three Fe inventories: aqueous Fe(II) (Fe(II)<sub>aq</sub>), sorbed Fe(II) (Fe(II)<sub>sorb</sub>), and a reactive Fe(III) component on the ferric oxide surface (Fe(III)<sub>reac</sub>). The fractionation in <sup>56</sup>Fe/<sup>54</sup>Fe ratios between Fe(II)<sub>aq</sub> and Fe(III)<sub>reac</sub> was 2.95 ‰, and this remained constant over the timescales of the experiments (280 d). The Fe(II)<sub>aq</sub>-Fe(III)<sub>reac</sub> fractionation was independent of the ferric Fe substrate (hematite or goethite) and bacterial species, indicating a common mechanism for Fe isotope fractionation during DIR. Moreover, the Fe(II)<sub>aq</sub>-Fe(III)<sub>reac</sub> fractionation in <sup>56</sup>Fe/<sup>54</sup>Fe ratios during DIR is identical within error of the equilibrium Fe(II)<sub>aq</sub>-ferric oxide fractionation in abiologic systems at room temperatures. This suggests that the role of bacteria in producing Fe isotope fractionations during DIR lies in catalyzing coupled atom and electron exchange between Fe(II)<sub>aq</sub> and Fe(III)<sub>reac</sub> so that equilibrium Fe isotope partitioning occurs.

Although Fe isotope fractionation between Fe(II)<sub>aq</sub> and Fe(III)<sub>reac</sub> remained constant, the absolute δ<sup>56</sup>Fe values for Fe(II)<sub>aq</sub> varied as a function of the relative proportions of Fe(II)<sub>aq</sub>, Fe(II)<sub>sorb</sub>, and Fe(III)<sub>reac</sub> during reduction. In the case of hematite reduction, the effect of Fe(II)<sub>sorb</sub> on the δ<sup>56</sup>Fe values of Fe(II)<sub>aq</sub> was insignificant, <0.05 ‰. Sorption of Fe(II) produced small, but significant effects during reduction of goethite, reflecting the higher proportion of Fe(II)<sub>sorb</sub> and larger measured Fe(II)<sub>aq</sub>-Fe(II)<sub>sorb</sub> fractionation. The isotopic effects of sorption on the δ<sup>56</sup>Fe values for Fe(II)<sub>aq</sub> were largest during the initial stages of reduction when Fe(II)<sub>sorb</sub> was the major ferrous Fe species during goethite reduction, on the order of 0.3 to 0.4 ‰, but decreased to <0.2 ‰ with continued reduction; our results show that the effect of sorption is much less than has been proposed in other studies. These experiments provide a breakthrough in our understanding of the mechanisms that produce Fe isotope fractionation during DIR, and form the basis for interpretation of Fe isotope variations in modern and ancient natural systems where DIR may have driven Fe cycling.