



Fe-isotope fractionation during early diagenetic Fe-reduction

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During early marine diagenesis solid ferric Fe-phases are reduced and ferrous Fe is released into the pore water. If the overlying water column is reducing much of the ferrous Fe may escape from the sediments. In most places of the modern ocean the water column is oxic. In this case the sediment surface layer accumulates ferric Fe-oxyhydroxide phases derived from the ferrous Fe released below that layer. Fe escaping from continental margin and shelf sediments is thought to be an important source of dissolved Fe to the ocean.

Previous laboratory experiments have demonstrated that Fe-isotopes are fractionated during microbial Fe-reduction. We have developed a leaching technique for Fe-oxyhydroxides based on a solution of KCl in N_2H_5OH that does not fractionate Fe-isotopes and from which Fe can be conveniently purified for mass spectrometric analysis. Fe-isotope data of natural ferric Fe leached from two marine surface cores from different redox environments in the Arabian Sea are presented. One core is laminated and from the sediments inside the nitrate-reducing oxygen minimum zone (OMZ), the other is from the oxic waters below the OMZ. Both cores show light ferric Fe $\delta^{56}Fe$ (IRMM-14) values compared to the bulk sediments resembling the crustal average. The laminated core shows a rapid decrease in the concentration of leachable Fe accompanied by an increase in $\delta^{56}Fe$ values -0.90 to -0.30. The oxic core shows little change in ferric Fe-concentration and $\delta^{56}Fe$ (-1.65 to -1.90) in the 4-5 cm thick brown oxic surface layer. In the green reducing sediments below that depth ferric Fe-concentrations drop off and the $\delta^{56}Fe$ increases to -0.60. In both cores the increase in ferric Fe $\delta^{56}Fe$ within the section of Fe-reduction is initially consistent with the fractionation expected during microbial dissimilatory Fe-reduction. At greater depths $\delta^{56}Fe$ values deviate from the expected trend, suggesting that other pathways become

important, possibly Fe-reduction by H₂S with a different fractionation factor.

The oceanographic implication of this result is that it may be possible to discriminate diagenetically derived Fe from continental sources such as fluvial and aeolian Fe. The Fe-isotopic composition of seawater may therefore provide a clue on the relative magnitude of these sources. The other interesting aspect comes from the observation that the $\delta^{56}\text{Fe}$ values in the core with the oxic surface layer are generally lighter than those of the entirely reducing core. This suggests that the early diagenetic redox-cycling of Fe results in the accumulation of isotopically light Fe. Consequently, some light $\delta^{56}\text{Fe}$ values found in Archaean shales may be the result of an early diagenesis starting under oxic conditions.