Ferric Fe-isotopes in the early marine diagenetic cycle

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Early marine diagenesis under an oxic water column comprises a recurrent cycle of Fe-reduction / mobilization at depth and Fe-oxidation / precipitation in the surface layer. In reducing waters much of the ferrous Fe may escape from the sediments. Previous laboratory experiments have demonstrated that a fractionation of Fe isotopes occurs in many of the microbial and inorganic reduction and oxidation processes involved.

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. We present Fe-isotopes of natural ferric Fe leached from two marine surface cores from different redox environments in the Arabian Sea. One core is laminated and from the sediments inside the suboxic oxygen minimum zone (OMZ), the other is from the oxic waters below the OMZ. Both cores show light ferric Fe δ^{56}Fe (IRMM-14) values thoughout. The laminated core shows a rapid decrease in the concentration of leachable Fe accompanied by δ^{56}Fe values increasing from –0.90 to -0.30. The oxic core has a 4 - 5 cm brown oxic layer on top which shows little change in ferric Fe-concentration and δ^{56}Fe (-1.65 to -1.90). In the green sediments below the oxic layer ferric Fe-concentrations drop off and the δ^{56}Fe increases to -0.60.

In both cores the increase in ferric Fe δ^{56}Fe within the section of Fe-reduction is only initially consistent with the fractionation expected during microbial dissimilatory Fe-reduction, suggesting that other factors, possibly Fe-reduction by H_2S, become important at greater depth. The bulk of the sediments in both cores is continental detritus (δ^{56}Fe ~ 0) but the Fe-oxyhydroxides at the sediment surface before diagenetic modification are considerably lighter. This suggests that the reactive Fe has already been isotopically fractionated before deposition, for example during transport through the estuary, across the shelf, or down the continental margin. The overall lighter surface δ^{56}Fe values in the oxic core can best be explained by the early marine diagenetic Fe-cycle itself, which pumps isotopically light Fe from the zone of Fe-reduction into the oxic surface layer.

Molybdenum and molybdenum isotope diagenesis in continental margin settings: Geochemical balance and paleoproxy implications

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We measured Mo concentrations in marine pore fluids and sedimentary solid-phases, and solid-phase isotope values to ascertain Mo behavior during early diagenesis in reducing continental margin environments. We observe a non-linear relationship between oxygen penetration depth and Mo accumulation rate at sites where dissolved oxygen bathes the sediments. Coupled with this observation we observe linear relationships between (1) the accumulation rate of Mo and the organic carbon rain rate and (2) the isotope composition of Mo and the organic carbon rain rate. These combined relationships indicate that as oxygen penetration depth shallows to some critical depth, the reactions that govern authigenic Mo accumulation become sensitive to the rate of organic carbon delivery to the seabed and are independent of bottom water oxygen content. Our work suggests that continental margins are a net sink for Mo. Although the magnitude of this sink ($\sim 0.8 \pm 0.4 \times 10^8$ mol y^{-1}) remains speculative, it may represent more than half of the removal term. Furthermore, a sink of this magnitude could alter current views regarding the processes controlling the distribution and availability of Mo through time.