Stable iron isotope signals as indicators for iron reduction pathways in deep methanic sediments

Susann Henkel1,2, Bo Liu1, Michael Staubwasser3, Simone Kasemann2, Anette Meixner2, and Sabine Kasten1,2,4
1Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Bremerhaven, Germany, susann.henkel@awi.de
2MARUM - Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany
3University of Cologne, Zülpicher Str. 49a, 50674 Köln, Germany
4University of Bremen, Faculty of Geosciences, Klagenfurter Str., 29359 Bremen, Germany

A number of studies have shown that iron reduction in marine sediments is not confined to sulfate- or sulfide-containing depths but may also affect deep methanic intervals. In particular dynamic depositional settings often show the release of dissolved iron below the sulphate-methane transition (SMT). The specific process behind this deep iron release is not well understood. It has been suggested that anaerobic oxidation of methane (AOM) mediated by Fe oxide reduction plays an important role. So there might be a close, so far unaccounted link between the Fe and C cycles in deep marine sediments.

Here we present a compilation of inorganic geochemical data including δ56Fe values of pore water and reactive Fe fractions for sediments of the Helgoland mud area (North Sea) for which a coupling between deep iron reduction and AOM has been proposed [1]. The sediments show a shallow SMT and increasing dissolved Fe concentrations of up to 400 µM further below. High sedimentation rates led to a fast burial and preservation of reactive Fe (oxyhydr)oxides, enabling deep iron reduction as we observe it today.

Isotopic fractionation of Fe has been demonstrated for DIR in culture experiments and in shallow marine sediments. Such studies build upon the principle that microbes preferentially utilize light Fe isotopes (54Fe) causing a fractionation between solid ferric and dissolved ferrous iron. For alternative biotic Fe reduction pathways in methanic environments, there are practically no data. We hypothesized that any microbially mediated iron reduction process would result in a similar preferential release of 54Fe and, thus, shift pore water δ56Fe towards negative values. Furthermore we hypothesized that the microbial utilization of a specific Fe (oxyhydr)oxide pool would result in a relative enrichment of 56Fe in the residual ferric substrate.

Close to the sediment-water interface pore water δ56Fe in the mud area is generally negative and shows a downward trend towards positive values as it can be expected for in-situ dissimilatory iron reduction (DIR) [2]. The Fe isotope signal close to the sulfidic interval is ~1‰ heavier than above and below as Fe sulfide precipitation preferentially removes 54Fe from pore water. A
pronounced downward shift of pore-water $\delta^{56}$Fe to more negative values within the methanic zone is a clear indication for microbial Fe reduction coupled to organic matter degradation. However, this shift does not coincide with the main interval of Fe release for which potential for Fe-AOM had been demonstrated [1]. In this deeper interval, the released Fe has an isotopic composition that matches that of the ferric substrates. We conclude that either 1) Fe-AOM plays a subordinate role for Fe release at depth or 2) does not go along with significant Fe isotope fractionation, which might be explained by different ways of electron transfer between microbe and the iron oxide compared to DIR.
