

Interactive comment on “Isotope fractionation between dissolved and suspended particulate Fe in the oxic and anoxic water column of the Baltic Sea” by M. Staubwasser et al.

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Staubwasser and colleagues present Fe isotope data for particulate and dissolved Fe species in a water column (Gotland Deep, Baltic) that changes from oxic at the surface to sulfidic (euxinic) in the deep water. The systematic changes in Fe isotope compositions in both pools are interpreted to reflect the dramatic changes in redox conditions with depth. A peak in particulate Fe at intermediate depth (in the suboxic zone of the profile) is interpreted to result from the upward diffusion of dissolved Fe from the euxinic deep water and re-oxidation as Fe-oxides above the O₂/H₂S boundary. The observed changes in isotope composition, however, seem to be in the opposite direc-

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tion of isotope fractionation expected for the conversion of dissolved Fe²⁺ to Fe-oxide. The authors argue for a kinetic effect that may reflect a much higher oxidation rate at elevated pH, which cause non-equilibrium isotope fractionation that is contrary to previous observations.

I must admit I am struggling coming to grips with the biogeochemical processes occurring in this water column, which is why I am having trouble buying into the interpretation of the isotope data. I agree with the other reviewer (Poitrasson) that more background information on the general oceanographic conditions, including biological processes, would be useful. If hydrogen sulfide appears below 150m water depth, as suggested by the authors based the negative oxygen values and previous observations from this location, then I would expect the dissolved Fe max to appear above that depth, not below where Fe would be removed as sulfide. This inferred overlap between the two dissolved species suggests to me that the dissolved Fe is primarily complexed with sulfide, as shown by Dryssen and Kremling (1990). Further, the authors suggest dissimilarity iron reduction in the water column as the mechanism for Fe solubilization, but in the presence of sulfide, a more likely mechanism is sulfidization. The shape of the profile suggests a dominantly sedimentary or near-bottom source.

Another somewhat puzzling observation is the location of the particle max within the low oxygen zone. This particle max is the result of upward diffusion of dissolved Fe from the euxinic bottom water, and the authors suggest that the particles forming at intermediate depth are primarily Fe-oxides. It strikes me though that there is a substantial gap between the particle max (130m) and the depth where oxygen concentration reach close to zero (100m). The authors make much of the pH effect on Fe oxidation rates, but seem to be ignoring the effect of the very low oxygen concentrations, which would slow down the oxidation rate substantially. The pH doesn't strike me as unusually high, so I am not sure how important an effect this would be, and I would expect oxygen to be the primary determinant for oxidation rates. It would be helpful to provide some specifics on the oxygen concentration measurements, and to make clear whether the

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oxygen concentrations within this layer are below meaningful detection, which is an important piece of information with regards to the Fe chemistry. Related to this, the layer 100-150m is variably referred to as suboxic or anoxic in the text. "Suboxic" is a rather ambiguous term, I suggest avoiding it or defining it in terms of dominant redox-process (see related rant by Thamdrup and Canfield 2009, *Geobiology* 7: 385-392). Either way, it would be helpful to provide additional data such as nitrate or Mn that can be used to better constrain the water column redox.

Given these caveats, I am not convinced that the particles that form at the intermediate-depth particle maximum are really Fe-oxides, or that oxidation rates would be accelerated, which is the premise for the interpretation of the Fe isotope data at this depth. The argument that the light Fe isotope composition of particles formed in the water column of the Gotland Basin is comparable to observations of light particles in the hydrothermal plume from the Mid Atlantic Ridge (page 4805) is misleading. The reason for the light isotope values in the plume investigated by Bennett et al (2009) is the formation of sulfide particles, which is consistent with the inferred kinetic isotope fractionation during sulfide precipitation (e.g., Butler et al 2005). In the present study, in contrast, the authors argue for Fe-oxide precipitation, which is generally predicted to cause isotope fractionation in the opposite direction – at least according to previous experimental studies and field observations, including the Rainbow hydrothermal plume where sulfide formation is negligible (Severmann et al 2004, *EPSL* 225: 63-76).

An alternative explanation for the low particle isotope composition at 100m might be the lateral advection of isotopically light reactive Fe from the shelf, consistent with the Fe-shuttle deducted from sedimentary isotope variations in the Gotland Basin (Fehr et al. 2008, *GCA* 72: 807-826). The authors argue that there is no evidence for re-suspended silicates from the shelf, but their method did not accomplish total dissolution of the particles (method for digestion procedure is incomplete, what was the concentration and duration of the extraction?), so if silicates were present, they might not have been digested. Also, lateral transfer may include Fe that started off as dissolved benthic

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efflux and subsequently precipitated during lateral transport. This would imply though that the dissolved and particulate pool at this depth have a different source, which I agree is not very convincing either.

The isotope composition in the deepest layer of the profile is consistent with experimentally determined equilibrium isotope fractionation between aqueous FeS and mackinawite (Guilbaud et al. 2011, *GCA* 75, 2721-2734; Wu et al. 2012, *GCA* 89:46-61), so no need to invoke dissimilary Fe reduction, which would likely cause much larger isotope fractionations in the dissolved pool.

The bottom line is, these are challenging isotope data, and an incomplete understanding of the biogeochemical processes taking place in the water column makes it even more difficult to interpret the isotope variations. So while I don't disagree that there may be circumstances where the experimentally determined isotope fractionation for Fe-oxide precipitation might not apply, but I don't think the authors have sufficient information to make that argument convincingly. That should take away from the fact that these are very interesting data, the first of this kind reported for an anoxic water column.

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