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## ***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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Isotope fractionation between dissolved and suspended particulate Fe in the oxic and anoxic water column of the Baltic Sea. by M. Staubwasser, R. Schoenberg, F. von Blanckenburg, S. Krüger and C. Pohl.

This manuscript is one of the first reports on the iron isotopes distribution in seawater and the first dealing with an anoxic marine basin. It is therefore very topical and is a welcome addition to this growing field of the literature. This is especially important since the oceanic iron cycle is a key to anyone concerned by ocean bioproductivity or its capacity to absorb atmospheric carbon. The data produced show a consistent pat-

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tern and are interpreted by the authors within the framework of a previous model of the iron cycling in an anoxic basin established before the advent of the "iron isotope era". However, the whole picture seems complicated and the data are not easy to interpret. In doing so, the authors have to somewhat twist some of our previous (recent) knowledge on the iron isotope systematics in aquatic systems when it involves a change of Fe redox state and precipitation of oxyhydroxides. Specifically, because the iron isotope composition of the particulate matter is lighter than the coexisting dissolved iron in the most oxygenated waters, they have to explain that the reaction rate is opposite to what was found so far in experimental and freshwater studies because of different pH, alkalinity and iron concentrations. This is backed by previously published kinetic studies. However, the  $\text{A}^{\text{N}}$  iron shuttle model  $\text{A}^{\text{Z}}$  described in Millero (2006) that forms the basis of the author's interpretation arose from the Black Sea and a Norwegian Fjord that show a different Fe concentration pattern with depth. Although I am not saying that the authors are incorrect in their interpretation, I would have thought that they would use their new isotopic tool and our current knowledge about it to test previous models established before we had it at our disposal instead of trying to make the Fe isotope data to stick to previous conceptions. At least this is an exercise that should be reported in a new paragraph in the discussion. Also, while I recognize that there is much more iron at the bottom of the system, I found myself wondering why the authors did not consider much the flux of iron coming from the top (aerosols, rivers...) to interpret their depth profile... While I am used to see high quality data and well reported results from this group, this manuscript is at variance with previous ones. This is not the internal analytical uncertainty that matters when reporting Fe isotope data (as explained in section 3.2) but really the external reproducibility. Looking at Table 1 also makes the reader wondering how the average replicate uncertainties expressed as 2SE computed from only two analyses can be as good as that of the individual analyses... Figure 1 should therefore be redrawn with the right uncertainties representing correctly the long-term reproducibility of the measurements. The blanks are also quite high, as they may reach up to 10% of the sample's iron. More detailed info on the chemical treatment used to

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process the seawater is required. Another limitation of this manuscript is that important information for the isotopic interpretation is missing. For instance, the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio should be reported, be it ideally measured, or at least calculated. We have also no information on the amount and nature of organic matter that is discussed in the data interpretation, nor about the phytoplankton that should also play a role on the Fe cycling in seawater. Very little is said about the local oceanic currents occurring at the sampling site or about the possible other sources of Fe besides the bottom up diffusion from the euxinic deep waters. Some of the water may come from aerosols and rivers as well. A map showing the sampling site is missing. To summarize, these are important data reporting for the first time Fe isotope signatures from an anoxic marine basin. However, key information pertaining to the samples and data presentation is missing and the interpretation needs to be completed and in some places clarified as suggested in this review.

Specific comments: – Page 4798, l. 12: "CTD" should be defined the first time it is used. – p. 4800, l. 22: Consider replacing "transition" by "increase" and adding "among" after "... shows". – p. 4801, l. 8-9: It is question here of maximum of turbidity and suspended Fe there, but Fig. 1 shows that they are unrelated. – Top of p. 4802: Simple observations at the filters by SEM would allow to check the nature of particulate matter. – p. 4805, l. 10: Consider replacing "my" by "might". What do the author mean by "to align" in l. 11? Also, where are the  $\text{Fe}^{2+}$  concentration data presented? – p. 4805, l. 18: Consider replacing "... overall reaction, ..." by "... complete reaction path, ...". – p. 4806, bottom: Such HCl leach of sediment may generate stable metal isotope fractionation, so they should be rather avoided. – p. 4807, l. 10-13: This interpretation is at variance with what was explained above. Is it on purpose? – Part 4.3: This discussion is confusing: use depths to explain which samples are discussed. Also, what are the surface currents there? This is a potentially important information to interpret the data. – End of p. 4809: This reference to a 0‰ value for the continental crust from Beard et al. (2003) is misleading since they reference all their Fe isotope data relative to the continental crust, which is not the case of the present study that

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uses IRMM-14. I would rather use a paper defining the continental crust value with respect to IRMM-14. (My favourite one in this respect is Poitrasson, 2006, *Chem. Geol.* 235 : 195-200...). – p. 4810, l. 5: What do the author mean by "A large inventory..." ? – p. 4811, l. 32: This is vol. 277, not 227. – Table 1: "dissolved" is repeated twice in three columns. The correct uncertainty reproducing the long term reproducibility should be put instead of the internal precisions. – Fig. 1: An indication of the Fe redox state should be reported. [psu] should be replaced by g/l; It should be explained how the turbidity was obtained. Comma should be replaced by points in panel d and the panels should have their letters.

Given that this manuscript was available on the web through Biogeosciences Discussion, it was the topic of a reading-group discussion of the "Non-traditional stable isotope research group" from Observatoire Midi-Pyrénées that involved Cyril Abadie, Alisson Akerman, Jérôme Chmeleff, Svetlana Irina, François Lacan and Marie Labatut, from which this review was partly inspired.

Toulouse, 8th June 2012, Franck Poitrasson.

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