

Response to review by Silke Severmann

We thank Dr Severmann for her time invested in reviewing this manuscript. Dr Severmann's comments are centered around four aspects of our manuscript: 1) the general information on the Baltic Sea redox state and the overall redox profile; 2) processes related to the formation of Fe-sulfides and the Fe source in the basin's euxinic bottom layer; 3) the controls of Fe(II)-oxidation rates in the zone of the Fe_{SPM} maximum; and 4) the origin of low $\delta^{56}Fe$ of suspended Fe at 100 m. Dr Severmann suggests an alternative interpretation with diffusive Fe efflux from shallow (shelf) oxic sediments surrounding the basin, subsequent oxidation, and suspended transport to the basin to form an Fe-rich particle maximum, based on her previous publication (Severmann et al. 2008). Additional comments relate to details of a reference on Fe isotope fractionation in hydrothermal plumes cited by us.

We believe that a number of the above issues were already discussed in detail in our manuscript. Wherever we feel that our original discussion contributes significantly to our response of the raised issues, we quote appropriately. References to the literature that do not appear in the original manuscript are given in full.

1) Concerning the comment on the introduction of the topic:

Initial remarks by Dr Severmann (2nd paragraph) state:

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.

Additional information will be added as laid out in our response to Dr Poitrasson.

2) Concerning Dr. Severmann's comments on sulfide related processes within the euxinic layer:

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.

Towards the end of the review (6th paragraph), Dr Severmann suggests:

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.

We would like to begin our response by noting that increasing concentrations of dissolved Fe_{dis} within the euxinic water are compatible with increasing ambient H_2S concentration according to the law of mass action as long as the ion activity product does not exceed the solubility constant of the dominating FeS phase. An initially parallel concentration increase is generally observed in marine euxinic basins, as we explained in the introduction chapter within our general description of the marine Fe redox cycle (with references to Framvaaren Fjord, Baltic Sea, Black Sea):

Modern anoxic basins, such as in the central Baltic Sea, show intense redox cycling of Fe across the redox boundary in the water column by reductive dissolution of Fe_{10H} , upward diffusion, oxidative precipitation on contact with dissolved oxygen and resettling of particulate Fe_{10H} (Millero 2006). Removal from this cycle occurs ultimately by settling of Fe_{10H} out of the water column and burial. In the euxinic layer below the redox boundary layer, dissolved Fe and dissolved H_2S concentration increases initially with depth to a level where the solubility equilibrium of pyrrhotite (FeS) and greigite (Fe_3S_4) is reached (Landing and Westerlund 1988; Dyrssen and Kremling 1990; Lewis and Landing 1991). Below this depth Fe is ultimately

removed from the water column by sulfide precipitation. The high Fe inventory of anoxic basins is thought to be maintained by diagenetic dissolved Fe (Wijsman et al. 2001) or lithogenic reactive Fe (Anderson & Raiswell, 2004) transported from adjacent sediments along the oxic basin's margin.

Concerning removal of Fe by sulfide precipitation in our Eastern Gotland Basin (EGB) 2005 profile, we state in our chapter 2 “Baltic Sea hydrography and state of iron redox cycling”:

A comparison of the fall 2005 profile data of Fe_{dis} and H_2S to the penultimate anoxic period studied in detail during 1981 and 1985 by Dyrssen and Kremling (1990) shows that both Fe_{dis} and H_2S at 180m are at the low end of concentrations measured in the euxinic waters. The 2005 data are well below the equilibrium concentrations of FeS indicative of sulfide precipitation and determined for the euxinic profiles in 1981 and 1985. FeS precipitation below the sampled depth in 2005, however, may have occurred.

In line with this argument, we opened the discussion of the euxinic layer (chapter 4.2 “Fe isotopes in the euxinic zone”) with the following remark:

Discussion of the euxinic water column is limited to its upper, only mildly euxinic part (150 – 180 m depth). Here, the Fe_{dis} concentration profile in the light of previously defined conditions of FeS precipitation in the EGB (Dyrssen and Kremling 1990) indicates that conditions of sulfide precipitation had not yet been reached at that depth in the most recent stagnant period of the EGB at the time of sampling.

Our argument for absent Fe-sulfide formation in our 2005 profile is confirmed by a very recent study we unfortunately were unaware of at the time of writing by Dellwig et al. (2010, “a new particulate Mn-Fe-P shuttle at the redoxcline of anoxic basins”, *Geochim Cosmochim Acta* 74, 7100-7115). Extensive SEM-EDX scanning of suspended particles from the EGB did not reveal the presence of sulfidic particles within the euxinic layer in 2006 and 2007 – at essentially identical euxinic conditions compared to the 2005 water column. In the light of the thermodynamics summarized in our manuscript and independent field evidence from the Dellwig et al. (2010) study there is no reason to consider Fe-sulfide precipitation, sulfidization of Fe particles, or isotope fractionation associated with the formation of Fe sulfides in our EGB water column data of 2005.

Dr Severmann's suggestion of a bottom sediment source of dissolved Fe to the euxinic water column in the EGB might be concluded from the shape of the Fe_{diss} profile just by itself, but we would like to point out that the profile does not extend to the bottom. We only report concentration data for the upper 50 m of the ~85 m euxinic layer. Therefore the profile's shape is arguably not conclusive. As euxinic basins usually accumulate euxinic sediments, it appears reasonable to us to assume the presence of euxinic sediments and pore water at the floor of the euxinic EGB, although we do not have sediment data from the time of the 2005 cruise to verify this. Significant Fe efflux is hard to reconcile with euxinic sediments. We argued that efflux from euxinic sediments is an unlikely scenario given the substantially higher concentrations of total sulfide generally observed in euxinic sediment pore water from the EGB in comparison to water column concentrations at Fe-sulfide saturation (see quoted section below). This is in agreement with consensus view on the EGB (Pohl & Hennings 2005; Dellwig et al. 2010) and not different from euxinic marine basin elsewhere.

Concerning the potential occurrence of dissimilatory iron reduction and sulfidization, we would like to point Dr Severmann towards the discussion of that issue in chapter 4.2 of our manuscript “Fe isotopes in the euxinic zone”:

Euxinic EGB $\delta^{56}Fe_{dis}$ values of ~ -0.4 ‰ could therefore in principle be the result of early diagenetic dissimilatory reduction of Fe_{IOH} in the sediments and subsequent efflux of low $\delta^{56}Fe_{dis}$ into the water column. However, the generally higher sulfide concentration in interstitial water than in the overlying water column and common amorphous FeS precipitation in the EGB sediments (Carman & Rahm, 1997, Fehr et al. 2010) limits such efflux from the euxinic sediments. An alternative explanation for the EGB euxinic $\delta^{56}Fe_{dis}$ values is dissimilatory Fe reduction in the water column, which is an established reaction in such environments (Anderson and Raiswell, 2004). The observed increase in EGB $\delta^{56}Fe_{SPM}$ from -0.4 to -0.1‰ between euxinic depths of 150 and 170 m is similar to typical early-diagenetic sedimentary reactive Fe profiles where iron reducing microbes mobilize Fe and leave the residual Fe_{IOH} enriched in heavy Fe isotopes (Staubwasser et al. 2006). A minimum in Fe_{SPM} concentrations and a $\delta^{56}Fe_{dis}$ in the mildly euxinic EGB water column sampled here are similar to $\delta^{56}Fe_{SPM}$ in the overlying suboxic layer. This suggests a simple near-quantitative mass

transfer of reactive Fe_{IOH} into dissolved Fe ($< 0.45 \mu\text{m}$). Microbial reductive dissolution of a fraction of sinking Fe_{IOH} particles in the water column is therefore a likely alternative explanation for increasing concentrations of Fe_{dis} . The direct transformation of Fe_{IOH} to Fe sulfides, as suggested by Dyrssen and Kremling (1990) and demonstrable by low fractions of soluble Fe^{2+} within total euxinic Fe_{dis} (Breitbarth et al. 2009), is compatible with the above interpretation. Such transformation between solid phases appears to take place without Fe isotope fractionation, at least in the sediment column (Staubwasser et al. 2006) and therefore would not affect Fe isotope ratios in Fe_{SPM} . As suggested for sedimentary early diagenesis, the decreasing concentration of Fe_{IOH} is probably due to competing dissimilatory Fe reduction (producing truly soluble Fe^{2+} and isotopically altered Fe_{SPM}) as well as Fe_{SPM} disintegration and transformation to FeS (producing dissolved $\text{Fe}(\text{II}) < 0.45 \mu\text{m}$ of the same isotopic composition as initial Fe_{SPM}). Thus, the EGB data lend support to the conclusion by Anderson & Raiswell (2004) that the high inventory of Fe_{dis} in marine anoxic basins is maintained by dissolution of reactive Fe_{IOH} particles.

In addition, our conclusion is again in agreement with Dellwig et al (2010), who found that suspended matter within the euxinic layer of the EGB was dominated by a FeOOH-PO_4 phase showing extensive signs of dissolution, whereas no FeS phase was present. In the absence of iron oxide sulfidization, our argument for dissimilatory Fe reduction on the basis of the down-the-profile evolution of Fe isotope in suspended particulate Fe coincident with a Fe_{SPM} minimum remains the most plausible conclusion.

3) Concerning the controls of Fe(II) oxydation and the general redox situation:

Dr Severmann states:

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 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 intermediatedepth 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.

We will adjust the “redox” terminology in line with Thamdrup and Canfield (2009) as suggested. Dissolved oxygen is routinely measured on IOW cruises as outlined in Grasshoff (1983) with an uncertainty of 0.02 ml/l (Feistel et al. 2008 “BALTC: Monthly time series 1900 - 2005” In: State and evolution of the Baltic Sea, 1952-2005, edited by Nausch et al.). The low oxygen section roughly between 100 and 130 m is a recurrent feature of the EGB (Neretin et al, 2003 “Manganese cycling in the Gotland Deep, Baltic Sea” *Marine Chemistry*, 82, 125-143; Turnewitsch and Pohl 2010 “An estimate of the efficiency of the iron- and manganese-driven dissolved inorganic phosphorus trap at an oxic/euxinic water column redoxcline” *Global Biogeochemical Cycles*, 24, art. no. GB4024; Dellwig et al. 2010). It is the result of baroclinic intrusions of oxygenated water in summer, which unlike the major Baltic inflows are of insufficient density to sink to the bottom (Matthäus et al. 2008 “The inflow of highly saline water into the Baltic Sea” In: State and evolution of the Baltic Sea, 1952-2005, edited by Nausch et al.). This oxygen minimum zone is associated with intense Mn(II) oxidation, the presence of MnO_x

phases and high turbidity (Neretin et al. 2003; Turnewitsch and Pohl 2010). The concentration of suspended Mn is about an order of magnitude higher than Fe in the Fe_{SPM} maximum. The Mn_{SPM} layer reaches from ~ 60 m to ~ 125 m, overlapping with the top of the Fe_{SPM} maximum situated on average between 110 and 160 m. Dissolved Mn on average increases steadily downwards beginning at about 100 m depth. A nitrate maximum between ~ 40 and 125 m overlaps broadly with the Mn_{SPM} maximum. The composition of suspended matter in the Mn_{SPM} layer is dominated by MnO_x (Neretin et al. 2003; Dellwig et al. 2010), and in the Fe_{SPM} layer by a MnO_x - $FeOOH$ - PO_4 phase with decreasing Mn content with depth (Dellwig et al. 2010).

The pH control on Fe(II) oxidation rate in the aquatic environment is consensus knowledge (Stumm and Morgan 1996 "Aquatic Chemistry", Wiley, pp 683). A recent study (Pham and Waite 2008) on Fe(II) oxidation rates in seawater at nM Fe concentration confirms once more the pH control (see their fig. 3), but highlights the complexity of the reaction. Fe-species, rates of intrinsic oxidation reactions and the Fe-oxyhydroxide precipitation rate (all pH dependent) and Fe concentration affect the removal rate $dFe(II)/dt$. We would like to point Dr Severmann to our discussion in chapter 4.1.2 "Kinetic control of isotope fractionation during Fe oxidation and precipitation in the suboxic Eastern Gotland Basin". Fe(II) oxidation and ferric Fe-oxyhydroxide precipitation rates increase with pH, while the back-reduction becomes less effective (Pham & Waite 2008). According to Anbar (2004) this leads to an increasingly kinetic isotope exchange reaction between Fe(II) and Fe(III).

4) Concerning the comment on on the isotopic value of the 100 m sample and the suggestion of lateral advection of reactive Fe from the shelf:

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 Feshuttle 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 of as dissolved benthic 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 profile section around 100 m is inside the MnO_x particle maximum (see discussion above). The properties of that section and the possibility of advected suspended material from the shelf in that water body has been discussed in detail by Neretin et al. (2003) and discarded on the ground that authigenic Mn concentration is too low in the shelf sediments surrounding the EGB. The concentration of suspended Mn is an order of magnitude higher than Fe in that profile section and dominated by authigenic particles (Neretin et al. 2003; Dellwig et al. 2010). The average settling rate of particles from that zone is almost 1m per day and there is no indication of any density boundary to sustain a confined resuspension layer. Dr Severmann's impression concerning the digestion method for suspended matter of previous studies is not correct. We used the concentration measurements from total digestions in high-pressure HNO_3 -HF assays (Pohl et al. 2004; Pohl and Hennings 2005) to make our argument. Silicate material is present throughout the water column, but not focused into distinct suspension layers in the water column. Detrital Fe is the largest Fe component above and inside the pycnocline. As such, all available data and all previous studies point towards the conclusion that the turbidity maximum at 100 m in our 2005 profile is the result of MnO_x precipitation and that Fe-isotope values there probably reflect interaction of Fe_{diss} and Fe_{SPM} with the MnO_x phases. All MnO_x dissolve when sinking into suboxic (ferruginous) and euxinic water (Dellwig et al. 2010). We would like to stress that we do believe that settling lithogenic reactive Fe compensates for (authigenic) particulate Fe flux out of the anoxic water

column, as we clearly state in the conclusions:

The water column data presented here suggest, that if the “benthic Fe shuttle” is active in the Eastern Gotland Basin (EGB), transport from the oxic shelf to the euxinic deep EGB is likely dominated by lithogenic reactive Fe from the oxic margins as 10 suggested by Anderson and Raiswell (2004).

Our study is focused on redox processes in the water column, not on sources and transport of sediment. However, near bottom nepheloid transport is an important process of sedimentation in the EGB (Leipe et al. 2008 *"Sedimentary records of environmental changes and anthropogenic impacts during the past decades"* In: *State and evolution of the Baltic Sea*, 395-439, edited by Nausch et al.). As such, one might speculate on remobilized diagenetic Fe from the shelf bypassing the water column through near bottom nepheloid flow. We are happy to adjust the relevant paragraph in the conclusion. Unfortunately, considerable swell during our fall 2005 cruise did not permit us to apply the pump-CTD near the sea floor, so we cannot verify this idea with water column data.

Concerning Dr Severmann's remarks on hydrothermal processes:

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).

We were referring to an observation by Bennet et al. (2009) made within the buoyant plume after the precipitation of sulfides. Bennet et al. (2009) were discussing a number of processes to explain an increasing $\delta^{56}\text{Fe}_{\text{SPM}}$ while precipitation progressed – similar to what we observe in the EGB – but explicitly ruled out effects related to Fe-sulfide formation (their Fig. 6). Bennet et al (2009, chapter 6.2.3, 4th paragraph) state:

All the processes identified above can modify the original isotopic composition of the vent fluid as the Fe precipitates in the buoyant hydrothermal plume. In this particular case, Fe-sulfide precipitation will have occurred in the first few seconds of venting *and*, by the time these samples were filtered on deck, complete oxidation of all Fe(II)aq will also have occurred. Additionally, the majority of Fe remaining in the dissolved Fe fraction is expected to be present as colloidal Fe-oxyhydroxides, and potentially as Fe-organic complexes although these will only make up a small fraction of the total Fe (Bennett et al. 2008). Therefore any fractionation caused by Fe-sulfide formation will have occurred prior to sampling

The high-oxygen environment of the deep Atlantic is arguably not the best comparison to the low-oxygen environment of the EGB, but the observation of Bennet et al. (2009) is clear in one aspect. Ongoing oxidative precipitation results in suspended particles gaining heavy isotopes. That requires Fe_{diss} to have a higher $\delta^{56}\text{Fe}$ than Fe_{SPM} , which is what we also observe in the EGB.

We disagree with the above statement by Severmann on general predictability of Fe-isotope fractionation in the aquatic environment during oxidative precipitation based on currently published experimental studies. These studies of equilibrium Fe-isotope exchange between Fe(II) and Fe(III) were done at pH ~2.5 and 5.5 (Johnson et al. 2002; Welch et al. 2003), and around 6.0 (Bullen et al. 2001). Our results demonstrate that equilibrium fractionation between Fe(II) and Fe(III) cannot simply be extrapolated to the marine environment, which has a pH > 7. It is obvious that reaction rates, reactive Fe species and iron oxyhydroxide precipitation rates differ (Pham and Waite 2008). We build our argument for a kinetically controlled isotope effect for the total oxidative precipitation reaction on the basis of general marine chemistry and accepted publications (Beard & Johnson 2004; Anbar 2004). The details underlying that kinetic control are not resolvable with the currently available limited set of experimental data. As such, the true reaction path remains unresolved. We do not wish to dispute Dr Severmann's conclusions on Fe isotope fractionation during hydrothermal venting at the Rainbow vent site reached in here 2004 study. However, extrapolation from field

observations that lack measurements of Fe isotopes in Fe_{diss} and relevant ancilliary parameters such as pH within the plume, like the Severmann et al. 2004 study, can obviously neither be used to support or reject our interpretation of Baltic Sea anoxic data.