

## ***Interactive comment on “Are recent changes in sediment manganese sequestration in the euxinic basins of the Baltic Sea linked to the expansion of hypoxia?” by C. Lenz et al.***

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We thank the reviewer for the comments on our manuscript and provide detailed answers to each point raised below. Line numbers refer to the original manuscript.

1: The authors generally consider the formation of pure  $\text{MnCO}_3$ , rhodochrosite, in the text and their thermodynamic calculations, although it is known, that the authigenic phases formed actually consist of CaMn carbonate solid-solutions with a wide range of compositions and thermodynamic properties (Suess, 1979; Jakobsen & Postma, 1989; Böttcher & Dietzel, 2010).

We do not assume the formation of pure  $\text{MnCO}_3$ . We refer the reviewer to page 9891, C5600

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line 3-6 where we write: "In anoxic settings, Mn enrichments are typically assumed to consist of Mn carbonates, which are often associated with calcium and can contain other impurities (e.g. Jakobsen and Postma, 1989, Manheim, 1961, Sternbeck and Sohlenius, 1997, Suess, 1979)".

Given the lack of data on thermodynamic properties of the Mn carbonates minerals in these sediments, we followed the approach used in earlier studies (e.g. Carman and Rahm, 1997). But to improve our results, we now have replaced the calculation of the saturation index (SI) for rhodochrosite and calcite by that for the  $Mn_{0.74}Ca_{0.26}CO_3$  solid solution according to Katsikopoulos et al. 2009. Still given the broad variability of  $MnCO_3$  contents in the solid solution and our lack of knowledge of other constituents, the results only give an indication of the possibility to form certain Mn bearing carbonates. We have changed the corresponding sections in the paper. This means we changed Figure 3 (see below) and the methods section in (2.6 Saturation state, page 9897 line 13):

"Thermodynamic equilibrium calculations have been performed for the pore waters of LF3, LL19, BY15, F80 and LD1 using version 3.1.1 of the computer program PHREEQC (Parkhurst and Appelo, 1999) with the LLNL database. The data base does not contain the authigenic carbonate phase present in the Baltic Sea. Data from the literature (Jakobsen and Postma, 1989; Sternbeck and Sohlenius, 1997; Leland and Stevens, 1998; Huckriede and Meischner 1996; Kulik et al., 2000) suggests that carbonates mainly consist of Mn and Ca. Therefore, an approximation of the solubility product of (Mn, Ca)  $CO_3$  solid solutions was generated using the equations given in Katsikopoulos et al. 2009. The stoichiometric solubility product (Kst) was calculated using  $Mn_{0.74}Ca_{0.26}CO_3$  (Kulik et al 2000) as a common ratio measured for (Mn, Ca) $CO_3$  solid solutions in Baltic Sea sediments. An equilibrium constant pK of 0.377 (Emerson et al. 1983) was used for Mn sulphide. The solubility of iron sulfide from Rickard (2006) was added to the calculations as well as  $MnHS^+$  as a solute (Luther et al., 1996) because it is likely abundant in pore water in sulfidic sediments (Heiser et

al., 2001). Carbonate alkalinity was calculated from titration alkalinity as described by Carman and Rahm (1997).”

We have also modified the corresponding text in the discussion where we write (page 9901 line 14): “When bottom waters in the deep basins of the Baltic Sea are anoxic, pore waters in the surface sediments are typically undersaturated with respect to Mn-Ca solid solutions down to a depth of ~5 to 8 cm (Figure 3)(Carman and Rahm, 1997; Heiser et al., 2001).”

2. Most details facing analytical instruments, sensors, standards used, analytical precision etc. are missing in the Material & Methods part.

We have added additional information where relevant:

We now write: Section 2.2. (page 9894-12): “greiner tubes” Section 2.2. (page 9894-20): “ICP-OES (Perkin Elmer Optima 3000), Section 2.2. (page 9894-25): “the pH with a pH electrode and meter (Sentron). Section 2.2 now ends with: “All colorimetric analyses were performed with a Shimadzu spectrophotometer. Replicate analyses indicated that the relative error for the pore-water analyses was generally <10 %.” Section 2.3 (page 9895- 6): “Based on laboratory reference materials and replicates, the relative error for organic C was generally less than 5%.” Section 2.3 (page 9895-10): “The accuracy and precision of the measurements were established by measuring laboratory reference materials (ISE-921 and in-house standards) and sample replicates; relative errors were <5% for all reported elements.”

-9890-6 and 09893-7: ‘well dated sediment cores’. Looking on the raw data presented in the appendix for two investigated sites of this study there are some unusual trends (maxima) observed in the 210Pb profile, that question the term ‘well-dated’. Unfortunately these results are not discussed in detail in the manuscript.

The age model for one of the two sites mentioned above (BY 15) was published by Jilbert and Slomp in Geology (2013) and is discussed in detail in the supplement of

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that paper. We have therefore removed the description of the age model for BY15 from our paper and refer to the relevant published work. However, we have included a brief discussion of the age models for LD1 and F80 in an appendix to the current submission.

We note that deviations of  $^{210}\text{Pb}$  profiles from an exponential decline with depth are not unusual in Baltic Sea sediments and are likely the result of variations in sedimentation rate, due to non-constant lateral and vertical sediment fluxes. Usually, such deviations are small and do not change the overall trend of the  $^{210}\text{Pb}$  profile, as is the case for BY15 (Jilbert and Slomp, 2013). For LD1, the  $^{210}\text{Pb}$  deviations are larger, possibly due to the high and variable concentrations of authigenic minerals (see Micro XRF maps in Figure 5) which dilute the mass-normalized  $^{210}\text{Pb}$  activity. We accept that these factors make LD1 the least well-dated of all cores in this study.

Continued work on the sediment geochemistry for site F80 in our lab recently revealed that the previously published age model for F80 could be improved, using LA-ICP-MS profiles of Mo and Mn, and coupling these to known events in the oxygen history of the Fårö Deep. We now present this revised age model in the supplementary information file and use that revised age model in the paper.

-9890-20: -Why should hypoxia increase the reaction rate between hydrogen sulfide and Mn-oxide? This is always a very fast reaction that will take place in top sediments as soon as sulfate reduction starts.

Here, we wish to explain our observation that Mn-carbonates no longer form after inflow events. We postulate that this is due to the much quicker return of high sulfide concentrations in the bottom water and surface sediments after an inflow event. The Mn oxides are thus more quickly exposed to high sulfide concentrations and as a consequence, are lost before Mn carbonates can form.

We have now changed the text in the abstract to make this clearer: “We postulate that, because of the quicker return of high sulfide concentrations in the water column,

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the reduction of Mn oxides following an inflow has become so rapid that the Mn<sup>2+</sup> is released to the water column before Mn carbonates can form.”

-9891-14: The authors state that the formation of MnCO<sub>3</sub> and MnS is driven by 'exceptionally high alkalinity'. This is not completely correct. Pore water alkalinity consists mainly of dissolved carbonate (DIC) thereby promoting the formation of the Mn(II) bearing carbonate but preventing the formation of MnS. Since sulfate reduction is the main process responsible for alkalinity generation in the sediments of the Baltic Sea deeps, there is twice as much of CO<sub>2</sub> produced compared to hydrogen sulfide.

In the introduction, we are directly citing the paper of Lepland and Stevens (1998) who in their paper state that high alkalinity is important for the formation of both Mn carbonates and Mn sulfides. Note that in our data for station LD1 (especially the XRF maps, fig. 5), MnS and Mn carbonates are present in layers that overlap suggesting a similar environment of formation.

-9895-25: How did the authors prevent sediment disturbance upon the use of cores with such a small diameter? Why did they observe a loss of 50% during the replacement of water by the Spurr method? Normally, the water volume deficit should be compensated by the resin. –

The XRF-maps show intact laminations, which is an indication that no major disturbance occurred during sampling. The application of the Spurr's resin method to surface sediments, as done here, is not directly comparable to that of deeper sediments because of the much higher water content of the former. This explains the greater loss of length that occurs during the dehydration step when the water is replaced with acetone, which has a far lower surface tension. This step has to be repeated several times and takes up to 10 days in which the sediment sub-cores stand upright. This is explained in the methods section (9896 lines 1-5) and in the paper where this method was first applied to surface sediments (Jilbert and Slomp, 2013; Geology).

-9897-14: The authors follow the approach already used by Carman & Rahn giving

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essentially the same results as published in 1997. The question remains, why pure  $\text{MnCO}_3$  and  $\text{CaCO}_3$  were used: Solid-solutions are the actual phases with solubility products deviating from ideal mixtures (see above).

Indeed, we find the same results as Carman and Rahm (1997), see answer to comment 1 (above).

What is the actual mineralogy considered by Emerson et al. (1983) for  $\text{MnS}$ ?

The  $\text{MnS}$  phase described in Emerson et al. (1983) is Alabandite. While  $\gamma$ - $\text{MnS}$  may be the actual phase forming in the Baltic Sea, no thermodynamic data for this phase have been published. The equilibrium constant from Emerson et al. (1983) gives reasonable results that are in accordance with our solid phase results that show formation of  $\text{MnS}$ .

The authigenic phases observed in the Baltic Sea are unusual and different  $\text{MnS}$  modifications will have their distinct thermodynamic stabilities. The authors refer to Heiser et al. (2001) to justify that the ion pair  $\text{MnHS}^+$  may have to be considered in the thermodynamic evaluation of the pore waters. But how can the reported field study from the Baltic prove this?

We do not wish to prove this. We are using this knowledge in our calculations given that its presence has been suggested.

-9898-10: The saturation states of the pore waters are in particular controlled by the pH of the solutions (not shown in the ms). In the present study these have been measured in filtered pore waters after extensive centrifugation (up to 30 min). This allows significant degassing of  $\text{CO}_2$  (and if present  $\text{H}_2\text{S}$ ) leading to a shift in pH towards higher values thereby enhancing the saturation degrees wrt. carbonate and sulfide minerals. Instead of discussing other effects like phosphate availability (9904-13) the authors should discuss the potential impact the sampling procedure had on their analytical results.

We have added all the pore water and sediment data including the pH values in the

supplement of the manuscript. We have no indication for major effects of the length of the centrifugation time on the pH or sulfide values. Note that most sediments were centrifuged much shorter than 30 minutes, which was only the maximum time used in cases with particularly stiff sediment (e.g. the deeper sediment at LF3). Note also that our sulfide concentrations are similar (or higher) and that pH values are within a similar range to those reported for Baltic Sea sediments in other studies (e.g. Carman and Rahm, 1997). However, we are aware that degassing always impacts ex-situ pH measurements, regardless of the method of pore water collection used. Note also that an upward shift of e.g. 0.5 pH unit would not affect the observed trends and contrasts with depth and between stations in the saturation state calculations. Also, the saturation state calculations are not critical to the main message of the paper; see above.

We have now added a statement about the effect of degassing on pH values in the methods section (9894 line 25): “Note that degassing may impact ex-situ pH measurements and may lead to a rise in pH (Cai and Reimers, 1993; L&O).”

-9900-18: Are these really Fe(III)-phosphates or actually FeOOH with adsorbed phosphate?

Dellwig et al. (2010) write: “Most of the analyzed particles are star-shaped, of about 5 micrometer in size, and occur as single particles or aggregates without any morphological differences between Mn-oxides, Fe-oxyhydroxo-phosphates, and mixed phases. Throughout the redoxcline, these minerals show a general succession with maximum abundance of Mn-oxides above the redoxcline followed by mixed phases and almost pure Fe-phosphates within and below the redoxcline, respectively”. Further in the manuscript, they write that the Mn-Fe-phosphates are formed through: “stepwise replacement of Mn(IV) by Fe(III) on sinking MnOx particles followed by immediate adsorption or even co-precipitation of phosphate”. Thus, Fe(III) phosphates refers to both precipitates of Fe-(III)-P and sorbed P on Fe-oxides.

To avoid confusion, we have changed the term in the manuscript to “mixed phases of Mn oxides and Fe-(III)-associated phosphates”. Note that this is not relevant to our discussion which concentrates on Mn, not Fe and phosphate.

-9901-5: Why 'now'? Isn't this the general case for the Baltic deeps?

Here, we are referring to the contrast to the initial expansion (described in the previous sentence) when coming from an oxic, nearly Mn free water column. Dissolved Mn enriches in the newly anoxic water column. The water column now rather contains a more or less constant pool of Mn (as confirmed by the water column data of Pohl and Hennings 2005 and Turnewitsch et al. 2010) with no major additional inputs. Only changes in redox conditions “temporarily” change the Mn concentration.

We have now modified the sentence in line 5 to make this clearer: “Thus, in contrast to the period of initial expansion of hypoxia, the Mn pool in the water column now depends largely on ambient redox conditions”.

-9901-16: The increase of supersaturation in  $\text{MnCO}_3$  after inflow events was not shown by Meischner & Huckriede (1996), only assumed.

We agree with the reviewer. That is why we wrote: “strong oversaturation may be reached”.

To clarify this point further, we now write: “However, strong oversaturation is assumed to be reached following the inflow of oxygenated, saline North Sea water”.

-9901-25: reference?

Here the reviewer refers to the sentence: “We postulate the this water-depth effect between the deep basin sites is likely due to increased focusing of particulate Mn oxides precipitated during inflow events with water depth, combined with a high alkalinity linked to organic matter degradation by sulfate reduction”.

Given that this is a postulation, we had not added references. We have now added

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an additional sentence, to further support our statements: “Increased focusing of Mn oxides with water depth has been observed in other marine systems (e.g. Slomp et al., 1997) and high alkalinity in sulfate-bearing organic rich sediments overlain by an anoxic water column are typically linked to organic matter degradation through sulfate reduction (Berner et al., 1970).

-9902-25: How can more reducing conditions yield MnS formation? The pore waters of the LD are mostly sulfidic, in contrast to the euxinic water column. There will be no impact of external boundary conditions on the MnS formation. Textures and geochemistry of these minerals demonstrate that they often are formed under slow precipitation conditions in the sediment. And: More reducing conditions (means more sulfide?) should also rise the DIC level, thereby promoting MnCO<sub>3</sub> instead of MnS precipitation.

We observe increased formation of MnS and wish to provide a possible explanation for that observation. We did not investigate the texture and further geochemistry of the minerals formed in the surface sediment at our site. We simply speculate about the possible causes for the MnS formation and observe a correlation with Br and Mo that suggests a possible mechanistic link with the input of organic material and more reducing conditions. Of course, the decomposition of organic material would also raise the DIC level but again our data shows the formation of MnS in close proximity to the MnCO<sub>3</sub> and there is no indication of a change of environmental conditions between the formation of the two minerals in the sediments.

We have now modified the text on page 9903 to indicate better that these are speculations: Line 1: changed to “possibly suggesting rapid changes in Mn mineralogy in response to seasonal variability of the organic matter flux (Fig. 5). [...] Further work is required to determine conclusively what the mechanism of formation is of the MnS.”

-9904-17: As written correctly, this is a postulate, but what is the actual base for this? Why should Mn oxides be reduced faster without enhancing the rate of MnCO<sub>3</sub> precipitation? The reaction rate of H<sub>2</sub>S von MnO<sub>2</sub> is very high and an increase in alkalinity

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will also lead to an enhanced  $\text{MnCO}_3$  precipitation rate.

We refer to our answer to a similar comment above. Our postulation is based on the observation that there are less Mn carbonates in the sediment at all sites (except LD1) compared to several decades ago. This observation is in line with trends in burial of Mn during previous periods of hypoxia in the Baltic Sea as observed at site LL19. We wish to provide a possible mechanism for this change. Given the greater abundance of sulfide in the bottom waters of the Baltic Sea over the past decades (see Figure 6), it is likely that Mn oxides no longer survive long enough to allow for efficient retention of the  $\text{Mn}^{2+}$  as Mn-carbonate.

We have modified the text to make the link with the sulfide concentrations more clear: “We postulate that Mn oxides that are formed following modern inflow events are dissolved much faster than previously because of the more rapid return of sulfide in the surface sediments and the higher sulfide concentrations in the water column linked to the expansion of hypoxia. As a consequence. . .”

-9904-23: Here it would be appropriate to refer to Neubert et al. (2008, Geology) and Nögler et al. (2011, Chem Geol).

The paper by Neubert only deals with Mo fractionation in the water column and thus is not so relevant here. The paper by Nögler et al. 2011 does mention the process of Mo scavenging by Fe and Mn oxides but does not draw a conclusion about the importance of this process for the burial of Mo in the sediment.

-9914-Fig.2: Why are the dissolved sulfide data called 'HS-'? Although this is the dominant species at the expected pH, there will be some  $\text{H}_2\text{S}(\text{aq})$ , that was measured together with bisulfide in the pore water.

We agree with the reviewer that some  $\text{H}_2\text{S}$  will be present as well. We have now added a statement in the caption of the figure that “while dissolved sulfide is here expressed as  $\text{HS}^-$ , some  $\text{H}_2\text{S}$  is present as well.

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Looking on the pore water of station LD1, two things are unclear to me: First the sulfate profile looks rather unusual: A complete depletion of sulfate in the top cm of a short sediment core is normally not observed in the deeper parts of the Landsort deep. Could it be that some sediment loss took place during sampling?

To our knowledge, there is only one pore water profile of sulfate for surface sediments in Landsort Deep in the published literature (Mort et al., 2010; GCA – included in their supplementary information). While indeed the decline in sulfate at the sediment water interface is much sharper here, the sedimentation rate at this site and the concentrations of other pore water species (e.g.  $\text{NH}_4^+$ ) is also higher. This suggests a much higher rate of organic matter degradation at this location than the one in Mort et al., 2010. We have no indication for loss of surface sediment during sampling, and the porewater profiles for other constituents (e.g.  $\text{NH}_4^+$ , Alk) show the expected shape. The spatial variability in sediment characteristics in the deep basins of the Baltic Sea is known to be very high. Further work is needed to assess the range of sulfate gradients in the pore water in the Landsort Deep.

Second: It is stated in the methods part that the Mn fluxes were estimated from the gradient through the top 0.5 cm of the sediment. For station LT1, the first data point available is from about 2.5 cmbsf and no bottom water value seems to exist. So, the question remains which data were used to estimate the gradient to derive the flux? The same question comes up for station Fladen BS1: This is a site with oxic bottom water, but the calculated flux given in Table 2 is relatively high. A look on the details of the dissolved  $\text{Mn}^{2+}$  profile, however, shows that looking vertically upward Mn already goes down to zero below the sediment-water interface. So no flux out of the sediment would be expected.

Although a bottom water sample was taken at LD1, it was inadvertently not processed further and thus indeed no data for  $\text{Mn}^{2+}$  are available. As an approximation, we assumed a  $\text{Mn}^{2+}$  concentration similar to the one published for the Landsort Deep by Mort et al., 2010 of  $3.1 \mu\text{M}$ . This is now described in the text. At site BS1, the  $\text{Mn}^{2+}$  flux

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was based on the difference in concentration between the bottom water concentration of  $\text{Mn}^{2+}$  (2.5  $\mu\text{M}$ ) and the first measurement at 0.75 cm depth (22.9  $\mu\text{M}$ ). Indeed, the  $\text{Mn}^{2+}$  flux is relatively high for an oxic site. Because of the relatively coarse depth resolution of the profile, removal of  $\text{Mn}^{2+}$  between 0.75 cm and the sediment-water interface is expected. We have now removed the flux calculation for this site from the manuscript and concentrate on the remaining 7 sites.

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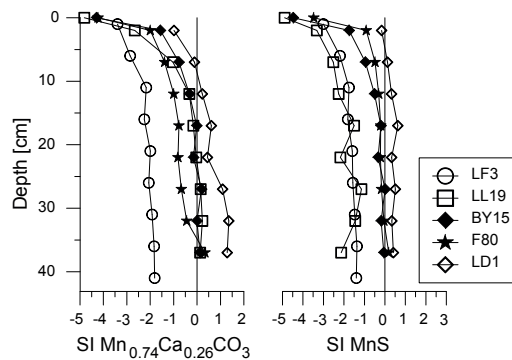
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**Fig. 1.** Figure 3 Saturation indices (SI) for  $\text{Mn}_{0.74}\text{Ca}_{0.25}\text{CO}_3$  and  $\text{MnS}$  as calculated from the pore water data with PHREEQC.