

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.

Anonymous Referee #1

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The recent manuscript by Lenz et al. deals with a postulated impact of increasing hypoxia in a temperate marginal sea, the Baltic Sea, on the formation conditions of Mn(II)-bearing carbonates. The latter have been considered to represent the very early diagenetic products after so-called inflow events, when oxygenated North Sea water is mixing with anoxic deep waters, thereby leading to the precipitation of the formally dissolved divalent manganese in form of Mn(IV)oxide layers. In principle this is a very interesting topic that is still not fully understood and of interest for the global scientific community.

The present authors carried out a detailed geochemical analyses of solid phases and pore waters from ²¹⁰Pb-dated surface sediments from overall 7 Baltic Sea stations
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and another station that is positioned in the North Sea-Baltic Sea transitional area.

Although the topic is of high interest and the manuscript presents a large set of data, there are some major questions wrt. both the analyzed data as well as there interpretation:

-In general 1: The authors generally consider the formation of pure MnCO₃, 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). -In general 2: Most details facing analytical instruments, sensors, standards used, analytical precision etc. are missing in the Material & Methods part. -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 -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. -9891-14: The authors state that the formation of MnCO₃ 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 CO₂ produced compared to hydrogen sulfide. -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. -9897-14: The authors follow the approach already used by Carman & Rahn giving essentially the same results as published in 1997. The question remains, why pure MnCO₃ and CaCO₃ were used

for these calculations? Solid-solutions are the actual phases with solubility products deviating from ideal mixtures (see above). What is the actual mineralogy considered by Emerson et al. (1983) for MnS? The authigenic phases observed in the Baltic Sea are unusual and different MnS modifications will have their distinct thermodynamic stabilities. The authors refer to Heiser et al. (2001) to justify that the ion pair $MnHS^+$ 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? -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 CO_2 (and if present H_2S) 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. -9900-18: Are these really Fe(III)-phosphates or actually $FeOOH$ with adsorbed phosphate? -9901-5: Why 'now'? Isn't this the general case for the Baltic deep? -9901-16: The increase of supersaturation in $MnCO_3$ after inflow events was not shown by Meischner & Huckriede (1996), only assumed. -9901-25: reference? -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 $MnCO_3$ instead of MnS precipitation. -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 $MnCO_3$ precipitation? The reaction rate of H_2S von MnO_2 is very high and an increase in alkalinity will also lead to an enhanced $MnCO_3$ precipitation rate. -9904-23: Here it would be appropriate to refer to Neubert et al. (2008, Geology) and Nagler et al. (2011, Chem Geol). -9914-Fig.2: Why are the dissolved sulfide data

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called 'HS-'? Although this is the dominant species at the expected pH, there will be some $H_2S(aq)$, that was measured together with bisulfide in the pore water. 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? 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 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.

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