

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 #2

Received and published: 21 July 2014

Lenz and colleagues present sediment and pore water geochemical data for a number of (intermittently) anoxic basins (so-called Deeps) in the Baltic Sea. The purpose of their study is to characterize modes of Mn carbonate and sulfide formation with special emphasis on recent changes related to expanding hypoxia in the Baltic Sea since 1980. Several working groups investigated the formation of authigenic Mn carbonates in the Baltic Deeps in the 1990s and early 2000s. As a result of these precursor studies (Suess 1979, GCA; Sternbeck & Sohlenius, 1996; Huckriede and Meischner, 1996, GCA; Boettcher & Huckriede, 1997, Marine Geology; Neumann et al., 1997, Continental Shelf Research; Neumann et al., 2002, GCA; Heiser et al., 2001, Marine Geology; all cited in the manuscript), the general mechanism of Mn oxide formation during in-

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flow of well-oxygenated water from the North Sea and subsequent transformation to Mn carbonate after the recurrence of anoxia is reasonably well established. One of the afore-mentioned articles (Heiser et al., 2001, Marine Geology, cited in the manuscript) noted a low Mn burial efficiency after a short-lived oxygenation event during the otherwise predominantly anoxic 1990s. This observation is the major connecting factor for the present study.

Lenz et al. use state of the art methods and present a nice data set which is unprecedented in spatial coverage and temporal resolution. It therefore provides an excellent basis for studying how sedimentary Mn cycling has evolved since the early 2000s. Most of the findings presented are consistent with previous conclusions. The authors also claim to revise certain aspects of the previously published model for the formation of authigenic Mn minerals in the Baltic Sea. Some of the arguments for this revision do not seem well developed, however, and therefore require additional discussion. Below is a list of comments that I ask the authors to address.

Page 9902, after Line 8: The authors claim that the high deep-sourced Mn flux (~ 130 $\mu\text{M}/\text{m}^2/\text{yr}$) in the Landsort Deep allows for a more continuous formation of Mn carbonates compared to the other Deeps. However, as noted earlier in the manuscript, pore water geochemical fluxes are quite variable. For instance, Brueggemann et al. (1998, Applied Geochemistry 13, 359-368) observed a diffusive benthic Mn flux of ~ 180 $\mu\text{M}/\text{m}^2/\text{yr}$ in the Gotland Deep in 1994 whereas Heiser et al. (2001) reported a flux of ~ 70 $\mu\text{M}/\text{m}^2/\text{yr}$ for 1997. Lenz et al. seem to assume that the high(er) Mn flux is a permanent feature in the Landsort Deep but do not provide any mechanistic explanation for this assumption. Note also that the Mn profile of the Landsort Deep site does not have a bottom water value, which makes me wonder how the ‘very high’ Mn flux was calculated.

Further below, the authors note the presence of MnS in sediments of the Landsort Deep and attribute its occurrence to higher rates of sulfate reduction, possibly enabled by a higher organic carbon flux. The coincidence of organic matter (or Br) and Mo

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enrichments is a common feature in marine systems (see e.g., Algeo & Lyons, 2006, *Paleoceanography* 21, PA1016). But is the organic matter flux in the Landsort Deep generally higher compared to the other Deeps? What is the ultimate reason for the higher Mn and organic carbon flux? Is there independent evidence for seasonal variability in the organic matter flux and, if yes, what is the reason for this variability? Hydrodynamic (frequency or intensity of inflow events), bathymetric (water depth, aerial extent) and other factors should be evaluated here in order to better characterize the environment in which abundant MnS may form.

Page 9904, below Line 3: For mechanistic reasons I feel the change in Mn burial efficiency should be discussed in the context of the decreasing duration and frequency of inflow events rather than the expansion or intensification of anoxia (see Scholz et al., 2013, *Chemical Geology*). Prior to 1980 the inflow events were typically more extended or took place as groups of events and the corresponding Mn carbonate layers are more pronounced compared to the more recent ones. Partial burial of Mn (oxyhydr)oxides during long-lasting events likely increased the residence time/concentration of Mn in the pore water and thus the extent of reaction with upward diffusing carbonate. By contrast, if anoxia returns rapidly after a single event, most of the Mn oxide still resides at the sediment surface or in the fluffy mud layer, which is why much or most of it may re-dissolve and become recycled into the bottom water through either re-suspension (Heiser et al., 2001, *Marine Geology*) or diffusion (present study). It is important to note in this context that because of the complex interaction between climate-controlled freshwater runoff and seawater inflow (i.e., haline stratification) as well as nutrient dynamics, the duration/frequency of inflow events is not the exact reverse of the intensity of anoxia.

Page 9904, below Line 20: Strictly speaking this observation only implies that Mn oxides are not the main burial phase for Mo, which is not surprising given that most of the Mn oxides are dissolved and/or converted to (Mo-poor) carbonate prior to burial. Importantly, Scholz et al. (2013, *Chemical Geology*) did not claim that Mn oxides are

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the main carrier phase but that they are likely to contribute to Mo transport into the deep water (see Dellwig et al., 2010, *GCA*) and to the sediment surface. This contribution likely complicates the Mo isotopic mass balance of the sediments to some extent, which has implications for the use of Mo isotopes as a paleo-redox proxy. Other mechanisms supply Mo to the sediment as well (Naegler et al., 2011, *Chemical Geology*) and may have become more dominant in the recent past (Scholz et al., 2011, *Chemical Geology*). Given that Mo and Mn have a differing mobility/diagenetic behavior under anoxic-sulfidic conditions, the lack of correlation between Mn and Mo in the solid phase does not necessarily imply that Mo has not been shuttled by Mn. In fact, repeated Mn dissolution and re-precipitation coupled to negligible Mn accumulation in the sediment (which is what the authors observe) is actually an important characteristic of the Mn shuttle for Mo (Algeo and Tribouillard, 2009, *Chemical Geology* 268, 211-225). Moreover, Mo fixation (regardless if shuttled by Mn or Fe (oxyhydr)oxides, Fe sulfides, organic matter or other carrier phases) necessarily requires hydrogen sulfide (e.g., Helz et al., 1996, *GCA* 60, 3631-3642), which is why the shuttle mechanism itself does not negate the use of Mo accumulation rates as a qualitative redox-indicator. If the authors wish to entirely exclude Mo contributions from Mn and Fe (oxyhydr)oxides, I suggest adding a proper discussion of Mo geochemistry of sediments and pore waters. Otherwise, I suggest deleting this misleading statement.

Page 9905, below Line 4: I suggest replacing 'elevated Mo contents' with 'Fe-based redox-proxies' (e.g., Poulton et al., 2004, *Nature* 431, 173-177). Mo concentrations are a poor indicator of euxinic conditions, as permanent euxinia in restricted systems typically results in a Mo drawdown from the water column and eventually decreasing Mo concentrations in the sediment (Algeo and Lyons, 2006, *Paleoceanography* 21, PA1016). In fact, the highest Mo concentrations have been recorded in temporarily euxinic systems (such as Baltic Deeps) where regular inflow of oxic (and Mo-replete) water occurs (Algeo and Lyons, 2006, *Paleoceanography* 21, PA1016). Moreover, open-marine and non-euxinic systems may display very high Mo concentrations as well (e.g., Scholz et al., 2011, *GCA* 75, 7257-7276).

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Page 9905, below Line 11: The deep Mn flux in the Landsort Deep is related to Mn carbonate dissolution and thus a remnant of intermittently oxic/anoxic conditions. Therefore, the presence of Mn enrichments in the sediments does not indicate permanent anoxia but a transitional state, which does not negate the Calvert and Pedersen model. Instead of pointing out the need for multiple proxies (which is kind of common sense anyway), the authors could develop the sedimentary finger print of the Landsort Deep towards an indicator for the transitional state between intermittent and permanent anoxia.

Page 9905, line 26: I would argue that the decreased abundance/intensity of Mn enrichments in most of the Deeps is a pretty accurate reflection of the reduced frequency and duration of inflow events since the late 1970s.

Minor comments:

I think it would be generally more useful to use the full names of the basins instead of acronyms for the sampling stations in the discussion. Page 9894, Line 25: I doubt that pH measurements after 30 minutes of centrifuging yield meaningful results. Page 9900, Line 11: Could add 'Scholz et al., 2013, Chemical Geology'. Page 9901, Line 8: Replace 'conclude' with 'suggest'. Page 9905, Line 5: Delete 'sediment' before 'euxinia'. By definition, euxinia refers to the water column. Table 1 and 2: Add the names of the basins to the stations. Fig. 1: Add the names of all basins to the cross section.

Interactive comment on Biogeosciences Discuss., 11, 9889, 2014.

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