Manganese and trace metal cycling in the deeps of the Baltic Sea

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The sediments of the Landsort Deep and Gotland Basin (Baltic Proper) are well known for remarkable enrichments in Ca-rich Mn carbonate ($MnCO_3$). However, the environmental prerequisites favouring enhanced formation of $MnCO_3$ are still under debate. Previous models include North Sea inflow-related oxygenation of euxinic bottom waters enriched in dissolved Mn but also on-going $MnCO_3$ precipitation under euxinic conditions [1,2]. Here we compare water column time series of O_2 and H_2S covering the last 60 years with dated sediments from both basins suggesting long-lasting hypoxic but non-euxinic bottom waters as an important prerequisite for exceptional $MnCO_3$ formation. Because the hypoxic but still O_2-containing bottom waters prevent the escape of reduced Mn into the open water column, enhanced deposition of Mn-oxides (MnO_x) at the sediment-water interface likely fosters the transformation of MnO_x into $MnCO_3$. Intense Mn cycling close to the sediment surface also impacts sedimentary trace metals (TM) inventories via scavenging by MnO_x [3]. In accordance with TM enrichments seen in redoxcline-derived MnO_x particles, TM signatures in $MnCO_3$ layers differ from those observed in sapropelic sediments deposited during euxinic stagnation periods. While Mo is strongly enriched in both Fe sulphide- and Mn-rich layers, Se and U sequestration is favoured during euxinic water column conditions. In contrast, Co, Sb, and especially W strongly relate to Mn cycling. These TM patterns are also seen in pre-industrial Mn layers formed during the Medieval Climate Anomaly and Holocene Thermal Maximun and differ substantially from typical sapropels, e.g., Black Sea Unit II.

[1] Huckriede and Meischner (1996) *Geochim. Cosmochim. Acta* **60**, 1399-1413; [2] Lenz et al. (2015) *Biogeosciences* **12**, 4875-4894; [3] Dellwig et al. (2010) *Geochim. Cosmochim. Acta* **74**, 7100-7115.