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Shelf-to-basin shuttling of iron and manganese as a driver of phosphorus burial in the Landsort Deep during past periods of hypoxia

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Bottom water hypoxia (i.e. low oxygen conditions) in coastal systems is an increasing world-wide problem. Enhanced external phosphorus inputs may contribute to the development of hypoxia by increasing primary production in the water column. The associated elevated flux of organic matter to the seafloor may then result in an oxygen demand in bottom waters that outpaces supply. The mechanisms leading to removal of phosphorus from the Baltic Sea system through burial in the sediment are still incompletely understood.
The Baltic Sea is currently hypoxic and has experienced two earlier periods of hypoxia during the Holocene. These are the Holocene Thermal Maximum (ca 8000–4000 yrs ago) and the Medieval Climate Anomaly (ca 700–1000 yrs ago) (Zillen et al., 2008). Based on sediment records for the Gotland Deep area, Jilbert and Slomp (2013) suggest that particle shuttles of iron and manganese oxides from the shelves act as drivers for authigenesis of phosphorus-bearing minerals in the deep euxinic basins. Here, we present geochemical results for a long sediment record (0 – 90 mbsf) from the deepest basin in the Baltic Sea (Landsort Deep, 451 m, Site M0063), which was retrieved during the International Ocean Discovery Programme (IODP) Baltic Sea Paleoenvironment Expedition 347 in 2013. Bulk sediment and pore water geochemical analyses, results of sequential extractions for phosphorus, iron and sulfur, and various micro-analyses are combined to assess whether shelf-to-basin shuttling of manganese and iron affects the long-term burial of phosphorus in the Landsort Deep.
We find that highly organic-rich sediments were deposited in the Landsort Deep following the transition from a lacustrine to a brackish/marine environment. This is reflected, for example, in the organic carbon content and pore water geochemistry. Elevated molybdenum and organic carbon/phosphorus ratios in the sediment allow the two major hypoxic periods during the early and mid-Holocene to be identified. All sediments, but particularly sediments which were deposited during these two hypoxic periods, contain high concentrations of phosphorus, manganese, iron/aluminum and calcium. Results of sequential phosphorus extractions using the SEDEX method suggest that iron-bound phosphates and authigenic calcium phosphates are major phosphorus burial phases in the Landsort Deep throughout the whole Holocene but especially during the hypoxic periods. Vivianite crystals (>63 μm, reduced iron phosphates) were observed at various depths within the sediment record and were characterized with XRD, SEM/EDX and XAS. We propose that the enhanced formation and burial of P-bearing minerals in the Landsort Deep during past periods of hypoxia are closely coupled to the shuttling of manganese and iron into this deep basin.