



# Vivianite is a key sink for phosphorus in sediments of the Landsort Deep, an intermittently anoxic deep basin in the Baltic Sea



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## ABSTRACT

Phosphorus (P) is an essential nutrient for marine organisms. Its burial in hypoxic and anoxic marine basins is still incompletely understood. Recent studies suggest that P can be sequestered in sediments of such basins as reduced iron (Fe)-P but the exact phase and the underlying mechanisms that lead to its formation are unknown. In this study, we investigated sediments from the deepest basin in the Baltic Sea, the Landsort Deep (site M0063), that were retrieved during the Integrated Ocean Drilling Project (IODP) Baltic Sea Paleoenvironment Expedition 347. The record comprises the whole brackish/marine Littorina Sea stage including past intervals of extensive hypoxia in the Baltic Sea that occurred during the Holocene Thermal Maximum (HTM<sub>HI</sub>) and the Medieval Climate Anomaly (MCA1<sub>HI</sub> and MCA2<sub>HI</sub>). Various redox proxies (e.g. the presence of laminations and high Mo contents) suggest almost permanent bottom water hypoxia during the Littorina Sea stage in the Landsort Deep. The bottom waters were likely even seasonally anoxic or sulfidic during the MCA1<sub>HI</sub> and MCA2<sub>HI</sub>, and permanently sulfidic during the HTM<sub>HI</sub>. With the use of micro-analysis of sieved minerals (SEM-EDS, XRD and synchrotron-based XAS), we show that Mn- and Mg-rich vivianite crystals are present at various depths in the Littorina Sea sediments. We also have indications for vivianite in the MCA1<sub>HI</sub>, MCA2<sub>HI</sub> and HTM<sub>HI</sub> deposits. The formation of vivianite thus likely explains the high Fe-bound P fraction throughout the whole Littorina Sea stage. Shuttling of Fe and Mn from the shelves into the basin and high inputs of P in settling organic matter are likely key drivers for vivianite formation. Our study shows that vivianite can likely form in near-surface sediments under a broad range of bottom water redox conditions, varying from hypoxic and anoxic to sulfidic.

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## 1. Introduction

Bottom water hypoxia (i.e. oxygen concentrations below 2 mg/l) is a growing problem in marine waters worldwide, and a well-known cause of the death of benthic organisms (Diaz and Rosenberg, 2008). The development of these so-called “dead zones” is in most cases the result of enhanced external inputs of nutrients into coastal waters. The nutrients may be responsible for increased primary production in the water column and the associated elevated flux of organic matter to the sea-floor may then result in an oxygen demand in bottom waters that outpaces supply (Diaz and Rosenberg, 2008).

Phosphorus (P) is a key nutrient for life on earth (Tyrrell, 1999). Enhanced P availability in the water column can therefore increase marine primary productivity and play an important role in the development of bottom water hypoxia in marine systems. Burial in sediments is the only removal pathway for P from the marine environment (Froelich et al., 1982; Ruttenberg, 2003). This P burial pool mainly consists of a mixture

of organic P, authigenic Ca-P (e.g. carbonate-fluorapatite), iron (Fe)-bound P, exchangeable P and detrital P (e.g. Ruttenberg, 2003). The contribution of these P pools to total P burial is, in part, controlled by the redox conditions in the deeper water column and surface sediments upon deposition (Ingall et al., 1993; Slomp and Van Cappellen, 2007).

Organic P is often a major P burial pool in sediments that are overlain by hypoxic, anoxic or sulfidic bottom waters, as is also observed in surface sediments from the Baltic Sea (e.g. Jilbert et al., 2011; Mort et al., 2010). This is thought to be the combined result of an increased input of organic matter from the productive water column in such settings and enhanced preservation of organic matter (including some P) in sediments under anoxic conditions, e.g. due to the slower kinetics of anaerobic degradation of organic matter and the lack in capability of anaerobic bacteria to oxidize certain organic compounds (Canfield, 1994; De Lange et al., 2008; Hartnett et al., 1998; Moodley et al., 2005; Raiswell and Canfield, 2012; Tsandev et al., 2012). The burial of organic P in hypoxic and anoxic systems is counteracted, however, by preferential release of organic P (P<sub>org</sub>) relative to organic carbon (C<sub>org</sub>) (Ingall and Jahnke, 1994; Ingall et al., 1993). This has been attributed to the production of phosphatases by carbon-limited microbes, which leads to the removal of phosphate groups from organic molecules, thereby

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facilitating the uptake of the remaining organic carbon (Steenbergh et al., 2011, 2013). Given that the released phosphate (mainly  $\text{HPO}_4^{2-}$  in seawater; henceforth termed  $\text{PO}_4$ ) cannot be retained by anaerobic bacteria, sedimentary  $C_{\text{org}}/P_{\text{org}}$  ratios in sediments overlain by hypoxic or anoxic bottom waters are generally elevated relative to 106, the Redfield  $C_{\text{org}}/P_{\text{org}}$  ratio for marine organic matter (Gächter et al., 1988; Ingall and Jahnke, 1997; Ingall et al., 1993; Jilbert et al., 2011; Van Cappellen and Ingall, 1994).

In many marine settings, P released from organic matter is retained in the surface sediment through sorption to Fe-oxides (e.g. Slomp et al., 1996). This Fe-oxide bound P is, however, typically an insignificant P fraction in sediments that are overlain by anoxic or sulfidic bottom waters because dissimilatory Fe(III) reduction and dissolution of Fe-oxides by reaction with hydrogen sulfide ( $\text{HS}^-$ ) generally remove all reactive Fe-oxides (Canfield et al., 1992). The lack of Fe-P recycling in surface sediments below anoxic bottom waters may limit the accumulation of porewater  $\text{PO}_4$  in some systems and may hamper the subsequent formation and burial of authigenic apatite-P at depth (Reed et al., 2011b; Ruttenberg and Berner, 1993; Slomp et al., 1996). Authigenic apatite-P may still form in sediments in anoxic basins, where the highly productive surface waters in these marine zones provide a large input of degradable organic matter (including organic P) to the underlying sediments, thereby supporting a sink-switching of organic P to authigenic Ca-P (Ruttenberg, 2003). Recently, it has been demonstrated that authigenic Ca-P is a major P sink in organic-rich sediments in the anoxic and sulfidic deep basin of the Black Sea (Dijkstra et al., 2014). In anoxic sediments that are low in  $\text{PO}_4$ , however, apatite formation can be negligible (Reed et al., 2011a). Also other factors, such as porewater alkalinity, fluoride and calcium ( $\text{Ca}^{2+}$ ) concentrations, may play a role in the formation of authigenic apatite-P (Ruttenberg, 2003). Although P-bearing minerals can thus still form in sediments overlain by a hypoxic or anoxic water column, they are often characterized by ratios of organic carbon to total P ( $C_{\text{org}}/P_{\text{tot}}$ ) above the Redfield ratio of 106, illustrating that P released by organic matter degradation is generally not fully retained through authigenic mineral formation (Algeo and Ingall, 2007).

Recent studies for the Black Sea, Baltic Sea and Chesapeake Bay show that brackish/marine sediments which are (intermittently) overlain by anoxic or sulfidic bottom waters may be enriched in Fe-bound P (Dijkstra et al., 2014; Jilbert et al., 2011; Li et al., 2015). In all three systems, this P burial pool accounted for more than 20% of the total sedimentary P pool. The Fe-bound P fraction was quantified with the citrate-dithionite-bicarbonate (CDB)-step of the sequential P extraction (SEDEX; Ruttenberg, 1992). This extraction scheme does not differentiate between Fe-oxide bound P and Fe(II)-phosphates such as vivianite ( $(\text{Fe}_3\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) (e.g. Nembrini et al., 1983). Although some Fe-oxides may survive transport through a low oxygen water column, the burial of Fe-oxide bound P is generally assumed to be low in sediments overlain by anoxic or sulfidic bottom waters (Jilbert and Slomp, 2013a; Mortimer, 1941; Reed et al., 2015). The Fe-bound P fraction in such sediments may thus represent Fe(II)-phosphates. In the Baltic Sea, distinct Fe and P enrichments with a mean Fe/P ratio of 1.65 (as quantified with scanning electron microscope energy dispersive spectroscopy (SEM-EDS)) were observed in the Fårö Deep, an intermittently sulfidic deep basin in the Baltic Sea. Given the similarity to the Fe/P ratio of vivianite (1.5), the enrichments were suggested to consist of vivianite (Jilbert and Slomp, 2013a). Synchrotron-based X-ray absorption spectroscopy (XAS) of Chesapeake Bay surface sediments also point towards the presence of vivianite in sediments overlain by seasonally hypoxic or anoxic bottom waters (Li et al., 2015). At present, the exact phase and composition of the Fe(II)-phosphates are unknown, as are the underlying mechanisms that lead to their formation and their fate upon long-term burial in hypoxic, anoxic or sulfidic basins.

In this study, we present a sediment record (0–90 mbsf) from the Landsort Deep that was retrieved during the Integrated Ocean Drilling Program (IODP) Baltic Sea Paleoenvironment Expedition 347. This

record comprises the whole brackish Littorina Sea stage including three intervals of extensive hypoxia/anoxia that occurred during the Holocene Thermal Maximum (ca 8000–4000 yrs. ago) and the Medieval Climate Anomaly (ca 750–1000 yrs. ago; Zillén et al., 2008). We have combined porewater analyses, solid-phase geochemistry (total elemental composition, sequential extractions for Fe, sulfur (S) and P) and micro-analysis of sieved aggregates (SEM-EDS and synchrotron-based XAS) to demonstrate the presence of magnesium (Mg)- and manganese (Mn)-rich vivianite in sediments that were deposited during the Littorina Sea stage. Our study shows that Fe-bound P, in the form of vivianite, is a major P burial phase in the Landsort Deep.

## 2. Methods

### 2.1. Study area and site

The Baltic Sea has been subject to variations in salinity after the retreat of the last Weichselian ice sheet (Andrén et al., 2011; Björck, 1995). The deglaciation resulted in the formation of the Baltic Ice Lake around 16 kyr BP. Afterwards, the Baltic Ice Lake became connected to the ocean and the Yoldia Sea developed (around 11.7 kyr). The next stage, the Ancylus Lake, began after the isolation of the Yoldia Sea. The first brackish inflows into this freshwater lake were recorded at 9.8 kyr (Andrén et al., 2000; Berglund et al., 2005), marking the onset of a gradual transition towards more brackish/marine conditions. The current Littorina Sea was established around 7 kyr BP (Sohlenius et al., 2001). Sediment records of molybdenum (Mo), which is a proxy for the presence of  $\text{HS}^-$  near the sediment-water interface (Erickson and Helz, 2000), and  $C_{\text{org}}$  have been used to identify hypoxic intervals that occurred during the Holocene Thermal Maximum and the Medieval Climate Anomaly in the Gotland Basin and Fårö Deep (Jilbert and Slomp, 2013b; Lenz et al., 2014; Zillén et al., 2008). Jilbert and Slomp (2013b) further indicate that multiple hypoxic events can be distinguished during the Holocene Thermal Maximum ( $\text{HTM}_{\text{HI}}$ ) whereas the hypoxic interval during the Medieval Climate Anomaly appears to consist of two main events (i.e.  $\text{MCA1}_{\text{HI}}$  and  $\text{MCA2}_{\text{HI}}$ ).

At present, the water column of the Baltic Proper (Fig. 1) is permanently stratified with an upper layer of brackish water with salinities of 7–8 and more saline deep waters of 11–13 (Conley et al., 2009). The Baltic Proper today has experienced widespread hypoxia and severe cyanobacteria blooms since the 1950's, which are related to excess nutrient loading from agriculture and waste water (Carstensen et al., 2014; Funkey et al., 2014; Gustafsson et al., 2012).

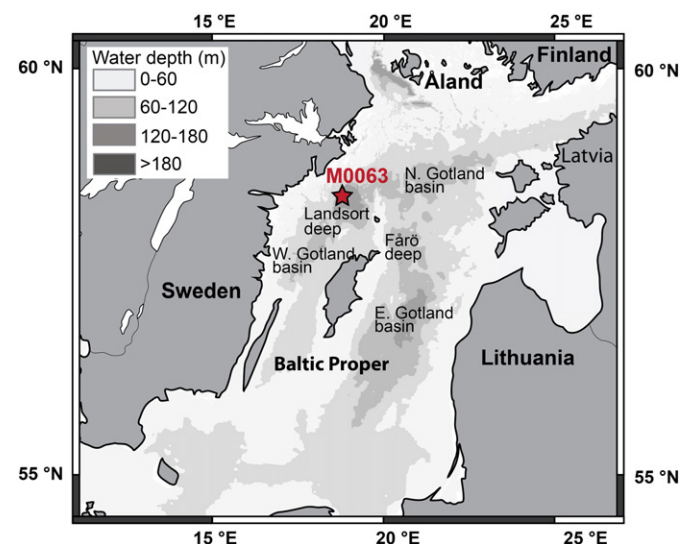


Fig. 1. Bathymetric map of the Baltic Proper with its key basins. Our study site (M0063) is located in the Landsort Deep, the deepest basin of the Baltic Sea.

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