Phosphate mineral authigenesis in anoxic coastal sediments

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Introduction

Many modern coastal environments suffer from eutrophication and low-oxygen conditions, as a consequence of anthropogenic nutrient loading over the past century. High productivity in these environments is often exacerbated by enhanced regeneration of phosphorus (P) from the underlying sediments, which occurs naturally under low-oxygen conditions (eg., Jilbert et al., 2011). Burial of authigenic P-bearing minerals constitutes a permanent sink for P in the sediments of anoxic coastal environments. Changes in the rate and distribution of P mineral authigenesis influence the efficiency of P regeneration, and thus may impact upon the recovery of coastal systems from their modern eutrophied state. However, a proper understanding of P mineral authigenesis in anoxic coastal systems is currently lacking.

Aim

In this study, we investigate phosphate mineral authigenesis in the Baltic Sea (Fig. 1), home to one of the largest euxinic zones in the modern coastal ocean. We use a combination of sediment and porewater geochemical analyses to assess the role of authigenesis in the P cycle of the Baltic, both today and throughout the current brackish phase of Baltic history (~8000 yr BP to present).

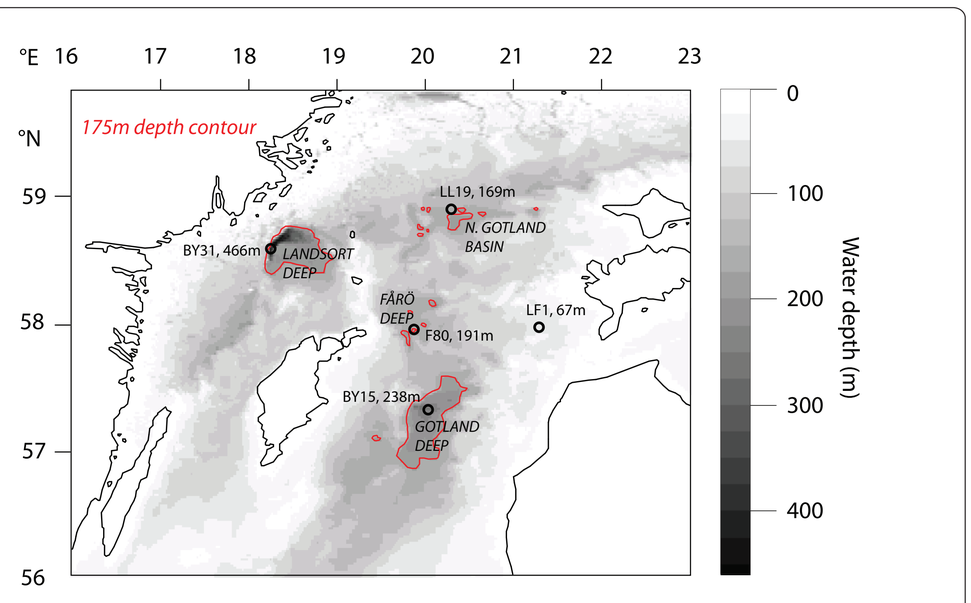


Fig. 1 Bathymetric map of the Baltic

Nature of sedimentary authigenic P minerals

Fig. 2 Extraction results

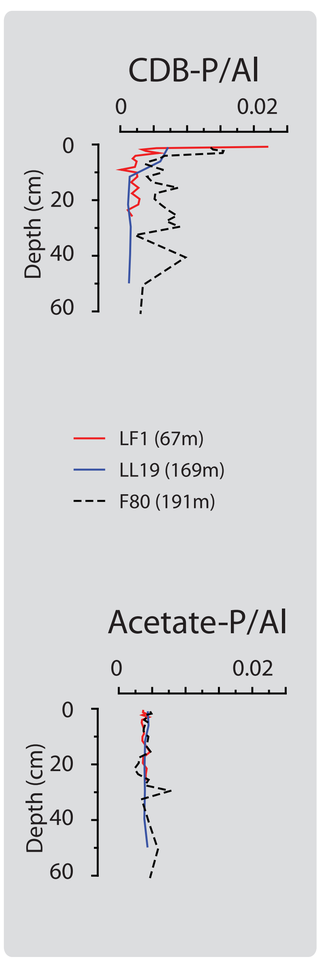


Fig. 3 Microanalysis of Fe-phosphates

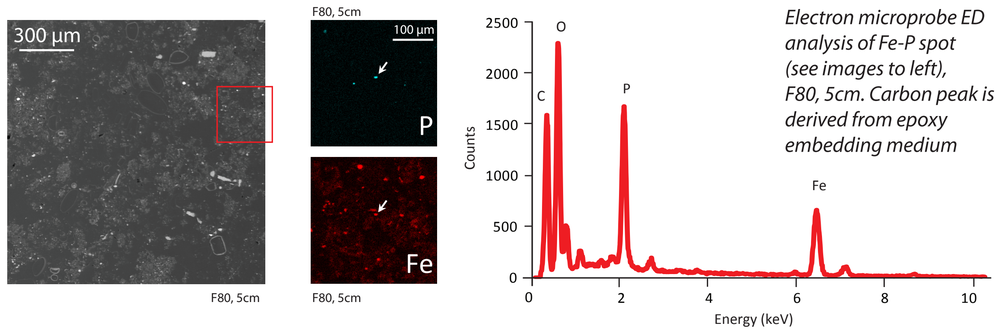
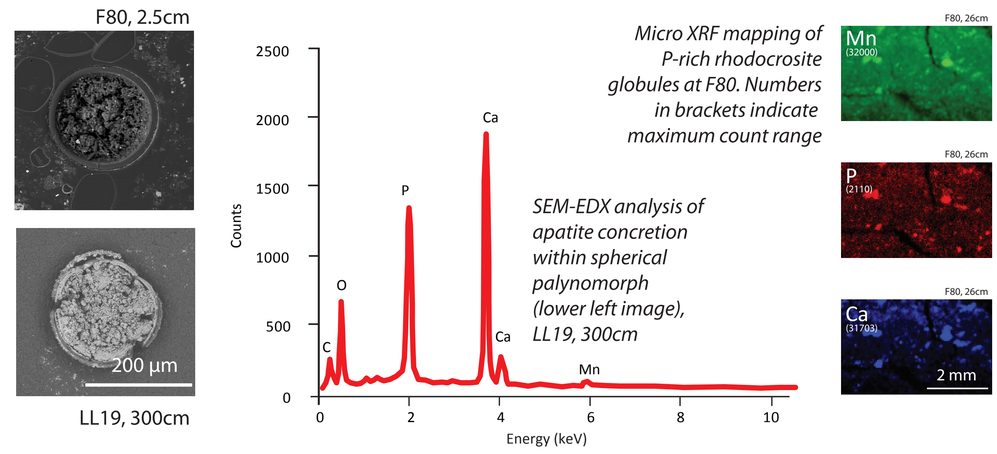


Fig. 4 Microanalysis of Mn and Ca-phosphates



Sequential sediment extractions (Ruttenberg, 1992) yield two authigenic P phases:

CDB-P: mainly iron (Fe)-associated P, eg., P bound to Fe oxyhydroxides, reduced Fe phosphate minerals such as vivianite, $Fe_3(PO_4)_2 \cdot 8(H_2O)$.

Acetate-P: mainly calcium (Ca)-associated P, eg., carbonate fluorapatite, biogenic apatite, P associated with rhodocrosite (mixed Mn-Ca carbonate)

In the surface sediments of the deep euxinic basins of the Baltic (eg., site F80), CDB-P is enriched relative to shallower sites (Fig. 2). In euxinic conditions, high CDB-P contents must reflect authigenesis of reduced Fe phosphates such as vivianite. Acetate-P contents are similar at all sites, except for occasional peaks at deep basin sites. This distribution suggests a background flux of apatite from the water column at all sites, and occasional P incorporation into rhodocrosite during ventilation of the deep basins.

Microanalysis of epoxy-embedded sediments reveals the distribution of the authigenic P phases in the sediments. Discrete 10µm-scale Fe-phosphate particles are present in deep basin sediments (Fig. 3), confirming vivianite authigenesis at these locations. Apatite is present within 200µm-scale spherical palynomorphs at all sites and all sediment depths (Fig. 4, left and centre). Layers rich in 200-1000µm-scale globules of P associated with rhodocrosites are found intermittently at deep basin sites (Fig. 4, right).

Porewater context of vivianite authigenesis

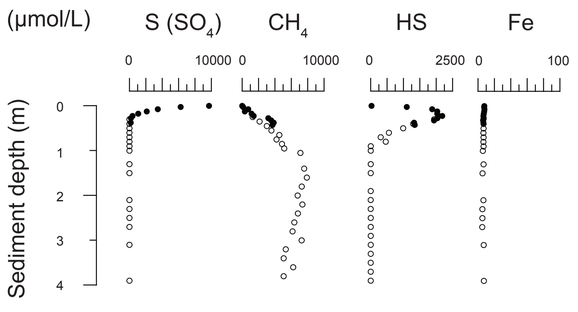


Fig. 5 Porewater profiles at F80

Vivianite authigenesis in marine sediments usually occurs below the sulfate-methane transition zone (eg., Burns 1997) where sulfide is absent and Fe can accumulate in porewaters. However, in the Baltic vivianite precipitates close to the sediment-water interface (Fig. 3) despite the high porewater sulfide and low porewater iron concentrations (Fig. 5). This suggests that vivianite precipitation occurs in protected microenvironments where Fe-oxyhydroxides are reduced in the absence of sulfide, allowing conversion of Fe-oxyhydroxide-bound P to vivianite.

Changes in space and time

Fig. 6 Sediment profiles

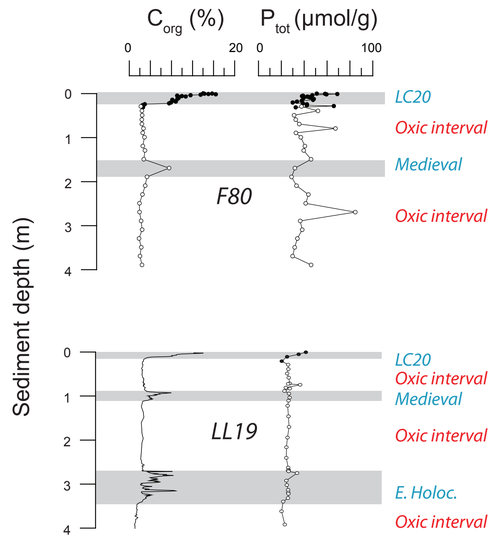
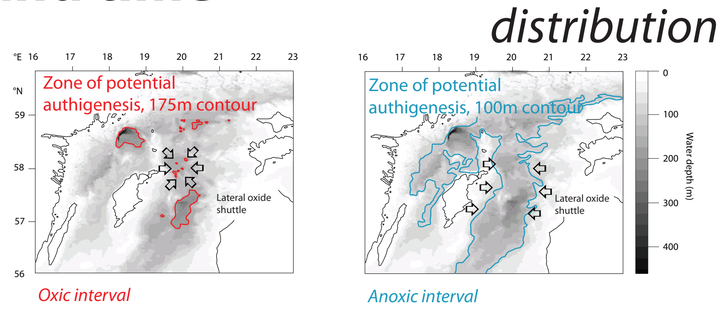


Fig. 7 Mineral distribution



Phosphate mineral authigenesis at F80 partly accounts for the higher total P concentrations relative to the shallower LL19 site throughout the Holocene (Fig. 6). However, during Baltic-wide *anoxic intervals* such as the Medieval and Early Holocene periods, authigenic minerals are also observed at LL19, albeit in lower concentrations. Authigenesis of Fe-phosphates and rhodocrosite-P are related to lateral and vertical transport of Fe and Mn oxides, which recharge deep anoxic waters with Fe and Mn. During generally oxic intervals, Fe and Mn oxides are focused into a few anoxic deep basins, whereas during Baltic-wide anoxia they feed a much larger anoxic zone (Fig. 7).

SUMMARY

Authigenic vivianite and rhodocrosite contribute to P burial in the sediments of anoxic coastal environments such as the Baltic Sea. During most of the Holocene history of the Baltic, their occurrence has been limited to the deep central basins, due to focusing of precursor Fe and Mn oxide phases into these locations. During intervals of widespread anoxia, authigenic P minerals are more extensively distributed, but less concentrated in the sediments. Vivianite forms within microenvironments in the shallow sediments, even when bulk porewater sulfide concentrations predict rapid removal of porewater iron. P-bearing rhodocrosites occur as intermittent layers in the sediments, associated with deep water ventilation events.

REFERENCES

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