



Phosphorus burial in sediments of the sulfidic deep Black Sea: Key roles for adsorption by calcium carbonate and apatite authigenesis

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Abstract

Sedimentary burial of the essential nutrient phosphorus (P) under anoxic and sulfidic conditions is incompletely understood. Here, we use chemical and micro-scale spectroscopic methods to characterize sedimentary P burial along a water column redox transect (six stations, 78–2107 m water depth) in the Black Sea from the shelf with its oxygenated waters to the anoxic and sulfidic deep basin. Organic P is an important P pool under all redox regimes, accounting for up to 60% of P burial. We find a general down-core increase in the relative importance of organic P, especially on the shelf where P bound to iron (Fe) and manganese (Mn) (oxyhydr)oxides is abundant in the uppermost sediment but rapidly declines in concentration with sediment depth. Our chemical and spectroscopic data indicate that the carbonate-rich sediments (Unit I, ~3000 years, ~0–30 cm depth) of the sulfidic deep Black Sea contain three major P pools: calcium phosphate (apatite), organic P and P that is strongly associated with CaCO₃ and possibly clay surfaces. Apatite concentrations increase from 5% to 25% of total P in the uppermost centimeters of the deep basin sediments, highlighting the importance of apatite formation for long-term P burial. Iron(II)-associated P (ludlamite) was detected with X-ray absorption spectroscopy but was shown to be a minor P pool (~5%), indicating that lateral Fe–P transport from the shelf (“shuttling”) likely occurs but does not impact the P burial budget of the deep Black Sea. The CaCO₃–P pool was relatively constant throughout the Unit I sediment interval and accounted for up to 55% of total P. Our results highlight that carbonate-bound P can be an important sink for P in CaCO₃-rich sediments of anoxic, sulfidic basins and should also be considered as a potential P sink (and P source in case of CaCO₃ dissolution) when reconstructing past ocean P dynamics from geological records.

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1. INTRODUCTION

Phosphorus (P), an essential macronutrient that helps control marine primary productivity, is removed from marine systems by burial in the sediment. The mechanisms by which P is sequestered in sediments are strongly dependent on bottom water redox conditions. Understanding the

impact of changes in bottom water oxygenation on benthic P cycling is of great importance in light of the globally increasing areal extent of oxygen-depleted coastal marine systems and the importance of P availability in eutrophication (Diaz and Rosenberg, 2008; Middelburg and Levin, 2009). In addition, an accurate interpretation of variations in P burial in paleorecords and the relation with depositional conditions benefits from an accurate understanding of redox-dependent P burial in modern sediments (Algeo and Ingall, 2007; Kraal et al., 2010).

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Under oxic bottom waters, dissolved phosphate (denoted as HPO_4^{2-} , the dominant phosphate ion at seawater pH) released during organic matter (OM) breakdown is initially scavenged by ferric iron (oxyhydr)oxides (Fe_{OX}) in surface sediments (Einsele, 1936; Mortimer, 1941; Slomp et al., 1996b). This Fe-bound P is released back to the pore-water during sediment burial as Fe_{OX} undergo reductive dissolution. Eventually, the released HPO_4^{2-} precipitates as authigenic P minerals at depth in the sediment or diffuses back to the sediment surface where it typically is either adsorbed to Fe_{OX} or escapes to the overlying water. Under marine conditions with millimolar levels of calcium, the accumulation of dissolved HPO_4^{2-} often leads to calcium phosphate precipitation, predominantly in the form of carbonate fluorapatite (CFA) (Van Cappellen and Berner, 1988; Ruttenberg and Berner, 1993). Calcium phosphates are the stable end product of P diagenesis and constitute the principal long-term P burial phase (Anderson et al., 2001).

In addition, Fe phosphate authigenesis may play an important role in sedimentary P sequestration. In the absence of free dissolved sulfide (referred to here as HS^- , the dominant form at seawater pH), reductive dissolution of Fe_{OX} can lead to the accumulation of both dissolved Fe^{2+} and HPO_4^{2-} and subsequent precipitation of Fe(II)–P phases such as vivianite, $\text{Fe}(\text{II})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. Evidence from modern and ancient marine systems suggests that iron(II) phosphate authigenesis is favored under anoxic sulfide-depleted conditions in the water column and sediment (März et al., 2008a,b; Slomp et al., 2013; Hsu et al., 2014; Egger et al., 2015); in the presence of dissolved HS^- , dissolved Fe^{2+} is precipitated in Fe sulfides that have little affinity for HPO_4^{2-} (Krom and Berner, 1980). As such, the balance between Fe^{2+} and HS^- release into pore-waters controls the fate of dissolved HPO_4^{2-} in sedimentary systems.

External input of metal (Fe, Mn) oxides has the potential to alter the relationship between bulk sediment geochemistry and P burial mechanisms. For instance, sulfidic deep basins within the Baltic Sea receive substantial amounts of Fe and Mn (oxyhydr)oxides. The deposition of Fe_{OX} from adjacent, oxygenated shelf sediments and their subsequent reductive dissolution can create Fe^{2+} -rich micro-environments where Fe(II)–P authigenesis occurs within bulk sulfidic sediment (Jilbert and Slomp, 2013; Reed et al., 2015; Dijkstra et al., 2016). Similarly, mixed Mn(II)–Ca–carbonate–phosphate phases may form as a result of anoxic diagenesis of sediment intervals rich in Mn oxides that were deposited in Baltic Sea deep basins following inflows of oxygenated waters (Suess, 1979; Jilbert and Slomp, 2013; Dijkstra et al., 2016). These conditions, in particular the highly dynamic oxygen regime, are rather specific and therefore these findings may not be representative for more open marine, anoxic settings in the past and present.

The Black Sea is well-suited to investigate the effects of long-term euxinia on sedimentary P dynamics including the role of Fe–P associations. It is the world's largest

strongly stratified marine basin and its deep (bottom) waters have been sulfidic for thousands of years (Wilkin et al., 1997). Surface sediments in the deep Black Sea consist of an upper layer of laminated coccolith ooze (Unit I, 2.7 ka–present), underlain by a less CaCO_3 -rich, dark-colored sapropel (Unit II, 7.6 ka–2.7 ka) (Degens and Ross, 1974; Hay et al., 1991; Arthur and Dean, 1998; Eckert et al., 2013). While the sediments of the Black Sea have been studied extensively for decades, there is surprisingly little information on sedimentary P burial. In the two only studies presenting detailed sediment P speciation so far, Dijkstra et al. (2014) and Ruttenberg (1990) reported significant amounts of P apparently present as Fe-associated P (up to 25% of total P) in sediments of the deep basin below more than 2000 m of sulfidic waters. Dijkstra et al. (2014) proposed that this P might be in the form of intra-cellular Fe(II)–P minerals formed within bacteria which were thus shielded from the sulfidic pore waters in which Fe(II)–P is thermodynamically unstable. In contrast to the sediment, Fe–P cycling in the water column of the Black Sea is relatively well-understood. Mixed Fe–Mn (oxyhydr)oxide phases that adsorb HPO_4^{2-} form above and within the redoxline around 100 m water depth (Shaffer, 1986; Dellwig et al., 2010). The potential for this shuttle to deliver Fe–Mn–P minerals to deep sediments is unclear, but is assumed to be negligible due to reductive dissolution of the oxide phases in the sulfidic waters below the redoxline (Dellwig et al., 2010). Overall, it is unclear what role Fe(II)–P minerals play in P burial under long-term sulfidic conditions.

In addition, the impact of anoxia on CFA formation is still incompletely understood (Tsandev et al., 2012; Lomnitz et al., 2015). While a limited organic matter flux can explain the lack of authigenic Ca–P formation in some anoxic deep sea settings, such as the Mediterranean Sea during sapropel formation (Kraal et al., 2010; Reed et al., 2011), other factors, such as a high alkalinity have been invoked to explain the lack of Ca–P formation in more productive regions (Schenau et al., 2000). Organic-rich sediments with very little CFA formation have been observed in for instance sulfidic deep basins in the Baltic Sea (Mort et al., 2010) and strongly reducing estuarine sediments (Kraal et al., 2015b). On the other hand, anoxic sediments from oxygen minimum zones host extensive apatite (and phosphorite) formation (Froelich et al., 1988; Schenau et al., 2000; Schulz and Schulz, 2005; Kraal et al., 2012).

Here, we investigate the cycling and burial of P in Black Sea sediments along a depth transect from the shelf with oxygenated bottom waters (78 m water depth, $150 \mu\text{mol O}_2 \text{ kg}^{-1}$) to the anoxic and sulfidic deep basin (2107 m water depth). Detailed chemical characterization of the pore-water and of solid-phase Fe, P and S pools was combined with micron-scale X-ray fluorescence element mapping (μXRF) and X-ray absorption spectroscopy (XAS) for Fe and P speciation. We show that besides authigenic apatite and organic P, P adsorbed onto CaCO_3 can represent a key P burial phase in sediments of anoxic and sulfidic basins.

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