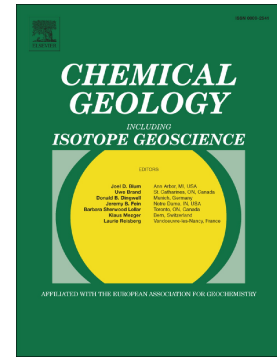


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Phosphorus cycling in marine sediments: Advances and Challenges

Delphine Defforey¹ and Adina Paytan^{1,2*}

¹*Department of Earth and Planetary Sciences, University of California, Santa Cruz, 1156 High St., Santa Cruz, CA, 95064, USA.*

²*Institute of Marine Sciences, University of California, Santa Cruz, 1156 High St., Santa Cruz, CA, 95064, USA.*

*Corresponding author: apaytan@ucsc.edu

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Abstract

Phosphorus (P) is a critical macronutrient for all living cells, as it provides the phosphate-ester backbone of nucleic acids, plays a crucial role in the transmission of chemical energy by the ATP molecule and is also a structural constituent in many cell components. While P cycling in the marine water column has been the subject of many studies and reviews, many aspects of the sedimentary P cycling remain poorly understood. This is mainly due to low P concentrations in sediments and analytical difficulties associated with isolating distinct P forms from sediment samples. The aim of this review is to highlight the advances made in our understanding of P cycling in marine sediments as a result of improved instrumentation and novel approaches. Some of these techniques range from sediment sequential extractions (SEDEX) to spectroscopic techniques (^{31}P NMR) and innovative isotope tracer experiments (stable oxygen ratios in phosphate, radioactive P isotopes). While our understanding of P cycling has considerably improved, numerous aspects of sedimentary P cycling including the fate of organic P in sediments as a function of redox conditions, organic matter content and burial depth, as well as turnover rates of different sedimentary P compounds remain poorly constrained. The techniques presented in this review, along with yet to be utilized innovative approaches used in soil and lacustrine sediment P research, will play an important role in addressing these important questions and further our understanding of this critical component of the P global biogeochemical cycle.

Introduction

Phosphorus (P) is an essential nutrient for life that plays a key role in regulating primary productivity in some marine systems and, over geological timescales, in the world's oceans (Elser et al., 2007; Krom et al., 1991; Mather et al., 2008; Wu et al., 2000).

Despite its importance to marine P cycling, there is still a limited understanding of the chemical structure of sedimentary organic and inorganic P and P cycling dynamics within marine sediments. This gap in our understanding of a key component of the global P cycle is largely due to the low natural abundance of P in marine sediments, and analytical difficulties associated with isolating P forms from sediments (Ruttenberg, 2014).

Economic and scientific interests in phosphorites (marine sedimentary deposits containing greater than 5–40 wt% P_2O_5) have led to many studies focused on sedimentary P geochemical forms, sinks, and rates of burial using sediment sequential extractions (Delaney, 1998; Ruttenberg, 2014). Advances in instrumentation have since enabled the use of innovative methods such as ^{31}P nuclear magnetic resonance spectroscopy, X-ray spectroscopy and isotope geochemistry that go beyond operationally defined P reservoirs and allow direct observations of the chemical structure of sedimentary P and processes altering P in this environment.

The focus of this review is on these recent advances, and how they have improved our understanding of the nature and cycling dynamics of P in marine sediments. This review includes four main parts. The first focuses on P fluxes to the seabed, and how techniques including sequential extractions and ^{31}P nuclear magnetic resonance spectroscopy have substantially improved our understanding of the P forms in sinking particulate matter,

and the biogeochemical processes altering them as they are exported to the seafloor. The second part of this review focuses on the techniques that have contributed to our knowledge of sedimentary P forms and the controls of P preservation in sediments. The third part is dedicated to the approaches (sequential extractions, x-ray spectroscopy, enzymatic assays, isotopes) that have yielded insights into the biotic and abiotic processes altering P once it reaches the seawater-sediment interface. Lastly, the fourth section of this review focuses on the future directions the field of sedimentary P research could take to further our understanding of this complex aspect of the global P cycle.

1. Phosphorus fluxes to the seabed

Phosphorus is delivered to the seafloor in the form of sinking particulate matter which consists of various inorganic minerals and organic compounds (Benitez-Nelson et al., 2007; Li et al., 2017b; Paytan et al., 2003; Sekula-Wood et al., 2012; Sokoll et al., 2017). Sinking and suspended marine particulate matter samples are routinely analyzed for reactive P and in most cases also for total P, with the non-reactive fraction attributed to particulate organic P and calculated by difference (Benitez-Nelson, 2000; Martiny et al., 2014). The distribution of particulate P in seawater generally follows that of particulate organic carbon (C) and nitrogen (N) in the open ocean, indicative of internal biological sources (Figure 1). The ratio of C:P in particulate matter typically increases with depth as a result of preferential remineralization of P (Faul et al., 2005). In coastal waters, closer to shore, inorganic P associated with terrestrial particulates could be more dominant (Paytan et al., 2003). Particulate P in the ocean originates from external sources derived from weathering products and anthropogenic activities (e.g. mining, fertilizer use,

biomass burning) on land and delivered via rivers and atmospheric deposition as well as particles produced internally in the marine water column, primarily through biological processes in the surface ocean (Ruttenberg, 2014). Some dissolved P may also adsorb or be incorporated into sinking particles like Fe-Mn oxyhydroxides or clay minerals and delivered to the sediment in association with these phases (Ho et al., 2009; Lyons et al., 2011). In coastal settings, allochthonous particulate P is transported primarily by rivers (Howarth et al., 1995) while atmospheric deposition plays a greater role in the open-ocean (Mahowald et al., 2008). While it is common to assume that the majority of sinking P is associated with marine biologically produced organic matter, it has been shown that a significant fraction of the sinking total particulate P pool, particularly in coastal settings, is composed of a variety of inorganic phases as well (Benitez-Nelson et al., 2007; Dong et al., 2016; Faul et al., 2005; Lyons et al., 2011; Paytan et al., 2003). The relative abundance of organic and inorganic particulate forms and the specific association of P with these sinking particles vary considerably in space and time, and with depth in the ocean (Dong et al., 2016; Lyons et al., 2011). These various inorganic and organic P components are influenced in very different ways in response to changes in water column biogeochemistry and undergo transformations in the water column before reaching the sediment (Figure 2). Once at the sediment–water interface, recalcitrant particulate P forms, such as detrital phosphates, are passively buried while the more reactive particles undergo further transformations (Ruttenberg, 2014). While total P in sinking and suspended particulate matter in the oceanic water column has been measured (Benitez-Nelson, 2000; Paytan and McLaughlin, 2007; Ruttenberg, 2014) relatively little work has been conducted to shed light on specific phases carrying P through the water column and

changes in the composition of particulate P during sinking. Below we summarize some of the observations regarding P in oceanic particulate matter, based on methods used for the analyses, to enable comparison with P in marine sediments.

a. Sequential extraction techniques

While SRP and total P in particulate matter are frequently measured, much less is known about the distribution of P within specific phases or compounds in these particles. Due to low abundance and the fine-grained nature of most marine particulate matter and sediments, it is difficult to identify, separate and quantify the different sedimentary P pools in sinking or suspended particulate matter (Ruttenberg, 1992). A successful and commonly used approach for studying P forms in marine solid-phases is the use of sequential extraction techniques, which are operationally defined based on the reactivity of a particular P phase in a given extractant solution (Ruttenberg, 1992). One of these techniques is the SEDEX method, (Figure 3) a widely used multistep sequential extraction technique that quantitatively separates solid-phase P into five reservoirs: (1) loosely sorbed P; (2) ferric iron-bound P; (3) authigenic carbonate fluorapatite (CFA) + biogenic apatite + CaCO₃-associated P; (4) detrital apatite and (5) organic P (Ruttenberg, 1992; Ruttenberg et al., 2009). Reactive P can then be determined from this sequential extraction, and is defined as bioavailable or having been associated with biotic processes in the water column prior to burial and includes fractions 1 through 3 and 5 above (Ruttenberg 2014; Paytan and McLaughlin, 2007). An important aspect of the SEDEX procedure is that it enables the separation of authigenic calcium fluorapatite (CFA) from the detrital igneous and metamorphic apatites, which are nonreactive P forms. This is

important since most CFA is formed in sediments and is considered to be a component of reactive P, while detrital apatite is not (Ruttenberg, 1992; Ruttenberg and Berner, 1993). However, it is also important to note that some studies have reported incomplete separation of these two phases (Eijsink et al., 2000; Kraal et al., 2012).

The SEDEX procedure has been used on sinking particulate matter collected in sediment traps. The first study using this procedure (Faul et al., 2005) analyzed samples from open ocean environments, polar environments, and coastal environments, representing a range of productivity levels, temporal distributions, and water depths. The analyses suggest that P in sinking particulate matter is typically composed of reactive P components including acid-insoluble organic P (~40%), authigenic P (~25%), and oxide associated and/or labile P (~21%), with lesser proportions of non-reactive detrital P (~13%). The concentrations and fluxes of all particulate P components, with the exception of detrital P, typically decrease with depth, indicating some regeneration of reactive P components.

Transformation from more labile forms of P to authigenic P is evident. Following this work similar analyses were done focusing on temporal changes in P distribution in the sinking particles at several coastal locations including the Cariaco Basin (Benitez-Nelson et al., 2007), Santa Barbara Basin (Sekula-Wood et al., 2012), Guaymas Basin in the Gulf of California (Lyons et al., 2011) and at the South China Sea (Dong et al., 2016).

Collectively, these studies report considerable temporal variability at each site and differences between sites, demonstrating the dynamic nature of particulate P in coastal systems. Dissimilarities in particulate inorganic P in coastal sites relate predominantly to differences in the magnitude of terrigenous fluxes from rivers (Meybeck, 1993). The

more labile (e.g. Fe and Mn associated) and organic P forms are controlled by processes that affect ocean productivity such as seasonal upwelling and transformation related to water column chemistry and particularly oxygen levels (Dellwig et al., 2010; Lomnitz et al., 2016).

b. ^{31}P nuclear magnetic resonance spectroscopy

While using SEDEX or other sequential extraction procedures (Anderson and Delaney, 2000; Lukkari et al., 2007a, 2007b) can provide information on P associated with different operationally defined categories of compounds, in such schemes organic P compounds are all grouped together. Organic P can constitute a substantial fraction of sinking particulate matter, and the particulate organic P pool is composed of many compounds of various degrees of reactivity and bioavailability (Lee et al., 2004; Wakeham and Lee, 1993). One way to gain insights into the makeup of organic P in marine particulate matter and in sediments is through the use of solution or solid-state ^{31}P nuclear magnetic resonance spectroscopy (^{31}P NMR). ^{31}P NMR is a spectroscopic technique that provides information about the bonds of P and therefore the P species present in the sample based on the magnetic properties of the atomic nucleus (Condon et al., 1997). Using this procedure, it is possible to detect multiple P forms at once and account for all the P in a sample since ^{31}P is the only naturally occurring P isotope. Both solid-state and solution ^{31}P NMR have been used to identify the classes of organic P compounds in sinking marine particles and sediments (Benitez-Nelson et al., 2004; Cade-Menun et al., 2005; Carman et al., 2000; Ingall et al., 1990; Paytan et al., 2003; Sannigrahi et al., 2006; Sundareshwar et al., 2001). Solid-state ^{31}P NMR allows samples

to be analyzed directly with little preparation while solution ^{31}P NMR gives a better spectral resolution allowing the identification of more P species (Cade-Menun et al., 2005).

Solution ^{31}P NMR results from a set of sediment trap samples spanning different ocean settings indicate that both inorganic P (orthophosphate, pyrophosphate, and polyphosphate) and organic P compounds (orthophosphate monoesters, orthophosphate diesters, and phosphonates) are present (Paytan et al., 2003). The inorganic P is primarily present as orthophosphate with small amounts of pyro- and polyphosphates. The organic P compounds consisted of P-monoesters and P-diester with a small contribution from phosphonates (<6%). The composition of organic P in these sinking particles was more similar to marine plankton than to dissolved organic P. Using solid-state ^{31}P -NMR Benitez-Nelson et al. (2004) found that P-esters comprise the largest fraction of particulate organic P but that phosphonates are also an important constituent of sinking particulate P in the Cariaco Basin (up to 18%). They also found that the depth distribution of phosphonates suggested that phosphonates may be utilized by bacteria in the anoxic waters of the basin. In contrast, using the same procedure on samples from various depths in the water column in the Equatorial Pacific, Sannigrahi et al. (2006) could only identify P-esters in the sinking particles. In another study that uses solid-state ^{31}P -NMR to screen for the presence of phosphonates in cultured strains of *Trichodesmium erythraeum*, Dyhrman et al. (2009) found that phosphonates comprise an average of 10% of the cellular particulate phosphorus pool in this species. Although not directly comparable, this is within the range of the phosphonates fraction of total organic P reported for

seawater (Karl and Björkman, 2015). As noted in Cade-Menun et al. (2005), it is hard to directly compare data obtained by solution ^{31}P NMR to that of solid-state ^{31}P -NMR due to the differences in sample processing and the limitations on peak resolution. Overall, consistent with the SEDEX, ^{31}P -NMR results show that spatial and temporal variability in the molecular composition of sinking particulate P exists in the ocean and more variability can be found at coastal sites and in anoxic basins.

c. Other methods for characterizing P in sinking particles

Other methods for determining the composition of particulate P exist and have been used in the soil sciences (see section 4) but have either not been used or have been used infrequently to study marine particulate matter. These methods include molecular identification techniques (HPLC, GC, and GC/MS) applied to plankton-net and sediment trap material (Wakeham et al., 1997). In this study and similar studies that followed, amino acids, carbohydrates and lipids, as well as uncharacterized organic matter were observed. While P compounds were not specifically mentioned, it is likely that the identified proteins contain organic P. Scanning transmission X-ray microscopy and carbon X-ray absorption near edge structure spectroscopy were also used in a study by Brandes et al. (2004). This study looked at the spatial heterogeneity of sinking particulate organic matter collected from sediment traps from the Arabian Sea and found that the particles are primarily composed of protein, an aliphatic rich phase, a carboxylic-acid-rich phase, and a phase with complex unsaturated and quinone character; waxy and intact cell walls were also observed. The study corroborated the results from molecular level work and similarly it is expected that the identified proteins and cell walls contain

organic P. Indeed, using these high resolution X-ray methods (in combination with ^{31}P NMR), Diaz et al. (2008) identified polyphosphates, which are derived from living organisms in both phytoplankton samples and sinking particulate matter. Cosmogenic radionuclides (^{32}P and ^{33}P) were used to study P turnover rates in the water column and although no specific P compounds were characterized, the study suggests that turnover rates within the particulate pools are rapid and vary over seasonal timescales (Benitez-Nelson and Buesseler, 1999). Another method that could be used to determine the composition of sinking particulate P, and has been applied to evaluate dissolved organic P in seawater, is based on measuring the activity of substrate specific enzymes. Several studies have measured alkaline phosphatase activity in sinking particulate matter (Suzumura et al., 2012; Yamada et al., 2012) and found variable activity with depth and sampling location indicating the presence of P-monoesters. Another example is the use of an enzyme-based method to quantify polyphosphate in particulate matter (Martin et al., 2014). The study demonstrated that polyphosphates are liberated preferentially over bulk P from sinking particles in the Sargasso Sea, an area with limited P availability, and suggested that high relative levels of polyphosphates and fast cycling may form a feedback loop that contributes bioavailable P for primary production.

2. Phosphorus forms in marine sediments

P in marine sediments originates predominantly from sinking particulate matter in the water column or in coastal settings delivered from land by currents. However, this material is transformed at the sediment-water interface and within the sediment post-burial, and thus differs in composition from the sinking pool. Characterizing the nature

and chemical structure of sedimentary P forms is essential for understanding the controls of P preservation and burial in marine sediments, a key factor controlling the inventory of oceanic P over geological timescales (Ruttenberg and Berner, 1993). The low abundance of P and different reactivity of naturally occurring P compounds in marine sediments make it difficult to identify, separate and quantify different sedimentary P reservoirs and glean an overall perspective of the nature of P in marine sediments. Below, we summarize the different approaches that have been used to characterize sedimentary P both operationally (sequential extraction) and directly (compound-specific analyses, spectroscopic techniques).

a. Sequential extraction techniques

Similarly to sinking particulate matter, solid-phase P in marine sediments is present in both inorganic and organic forms, and it is difficult to identify, separate and quantify the different sedimentary P pools (Ruttenberg, 1992). The SEDEX method has been applied in numerous studies of marine sediments enabling estimates of P burial rates in the world's oceans and shed light on the influence of sedimentary redox conditions on the relative contribution of each sink to P burial and the burial of organic matter. Sediments overlain by an oxygenated water column often bear large amounts of P bound to iron and manganese oxides (Acharya et al., 2016; Berbel and Braga, 2014; Defforey and Paytan, 2015), while sediments overlain by anoxic bottom waters are more depleted in these phases and often harbor more P bound to calcium minerals (Filippelli and Delaney, 1996; Kraal et al., 2012; März et al., 2014). It is important to note though that in some cases, reduced iron-bound P (including vivianite) has been suggested to be an important sink in

anoxic sediments (Dijkstra et al., 2017, 2016b; Egger et al., 2015; Li et al., 2015). These applications of the SEDEX scheme have also demonstrated that the size of the bulk sedimentary organic P pool tends to decrease with depth, consistent with microbial utilization of organic P forms in the sediment or sink switching (the transfer of P from one pool to another, see section 3a), until it reaches an asymptotic value that remains low and at constant detectable values. While the use of sequential extraction techniques has substantially improved our understanding of the nature of sedimentary P pools and associations with other elements and its dynamics within marine sediments (see section 3a), the chemical structure of inorganic and organic P compounds within sedimentary phases, the mechanisms underlying their preservation and their reactivity cannot easily be gleaned from snap shot analyses of sedimentary fractions.

b. Compound-specific analyses

Another means of studying P speciation in marine sediments is through the use of compound-specific analyses. An example of such analyses is the extraction of phospholipids in sediments using chloroform, methanol and water (White et al., 1979) or dichloromethane and methanol (Zink et al., 2003), followed by chromatographic separation and quantification. Phospholipids play an important role in the formation of cell membranes and various organelles, and may be an important source of bioavailable P to deep subseafloor microorganisms (Suzumura, 2005). Less reactive forms of phospholipids have also been shown to withstand remineralization in surface waters and to be exported to the seafloor where they could act as a P sink (Suzumura and Ingall, 2004). However, thus far, the focus of most phospholipid studies in the marine

environment has been on using phospholipids as biomarkers rather than a component of the sedimentary organic P pool (Suzumura, 2005). Nucleic acids (DNA, RNA) are another example of organic P forms that are rarely studied as a component of the sedimentary organic P pool in the marine environment (Dell'Anno and Danovaro, 2005), and are instead used for deep-sea microbiology assessments. Natural, inorganic polyphosphates can also be studied using targeted analyses such as photometric techniques or NMR, but the heterogeneity and complexity of natural samples make these analyses challenging. Photometric techniques (e.g. using the fluorochrome 4',6-diamidino-2-phenylindole) are an effective means of directly quantifying polyphosphate concentrations reliably (Aschar-Sobbi et al., 2008; Diaz and Ingall, 2010). The role of polyphosphates in marine sediments is further discussed in section 2d.

c. ^{31}P nuclear magnetic resonance spectroscopy

The use of solid-state and solution ^{31}P nuclear magnetic resonance spectroscopy (^{31}P NMR) on marine sediment samples has provided valuable insights into the chemical composition of the bulk organic P sedimentary pool (Carman et al., 2000; Laarkamp, 2000; Paytan et al., 2003; Sannigrahi and Ingall, 2005). Applications of ^{31}P NMR on marine sediments with high organic to inorganic P ratios and high P concentrations indicate that orthophosphate constitutes 50 – 70% of total sedimentary P, pyrophosphate 0 – 4%, polyphosphate 0 – 8%, phosphonates 0 – 15%, P-monoesters ~30% and P-diesters up to 16% (Paytan et al., 2003; Sannigrahi and Ingall, 2005). However, ^{31}P NMR is difficult to apply to open ocean sediments due to their low organic P content. Sample pretreatments are an effective means of countering this issue by removing mineral phases

and concentrating organic P to enhance the use of solid-state and solution ^{31}P NMR on sediments with low organic matter content (Carman et al., 2000; Defforey et al., 2017; Sannigrahi and Ingall, 2005). The 2-step pretreatment proposed in Defforey et al. (2017) helps to prepare samples for solution ^{31}P NMR by quantitatively removing the majority of mineral P from marine sediment samples. It also removes polyvalent bridging cations that can interfere with NaOH- Na_2EDTA extraction and speciation of organic P in marine sediments (Turner et al., 2005), thus enabling the detection of P compounds that would otherwise be below the detection limit of NMR spectrometers. When this pretreatment was applied to natural sediment samples in Defforey et al. (2017), orthophosphate monoesters and pyrophosphate were detected, in addition to orthophosphate. The formation of insoluble complexes between certain monoesters (e.g. phytate) and polyvalent cations on clays or iron/aluminum (oxyhydr)oxides could protect those organic P compounds from microbial degradation and result in their accumulation in marine sediments (Celi and Barberis, 2005; Defforey et al., 2017). The presence of pyrophosphate (a product of the biosynthesis of many macromolecules) in marine sediments from different localities raises the question of the role this compound may play in sedimentary P cycling (Cade-Menun et al., 2005; Defforey et al., 2017; Paytan et al., 2003; Sundareshwar et al., 2001). Future studies should apply ^{31}P NMR to coastal and open ocean sediments and attempt to identify specific compounds rather than broad classes (e.g. orthophosphate monoesters, diesters) in order to better study the sorption mechanisms involved in organic P preservation and how these are affected as a function of burial depth and redox conditions.

d. X-ray spectroscopy

Over the past decade, several studies have sought to characterize P speciation on a micrometer and sub-micrometer scale using an array of microscopic and spectroscopic techniques. Brandes et al. (2007) applied P near-edge X-ray fluorescence spectroscopy (P-NEXFS) to map different organic and inorganic P reference compounds and minerals, as well as P in sediments from Effingham Inlet (Canada) to investigate P forms at a sub-micron scale resolution. They observed that most P was located in small, 0.6–8 μm scale P-rich domains and consisted of Ca-phosphates or polyphosphates, whose presence support observations that polyphosphates can play an important role in marine P cycling. This was further evidenced by Diaz et al. (2008), who used synchrotron-based soft X-ray spectromicroscopy on marine sediments from the same location and reported spectral features consistent with polyphosphate, apatite and a transitional phase between the two, indicative of the diagenetic transformation of polyphosphate to apatite. This proposed mechanism could have important implications for our understanding of the underlying mechanisms of CFA formation in marine sediments, a process that is not always easily accounted for in sediments (Ruttenberg, 2014; Ruttenberg and Berner, 1993). Recently, Cosmidis et al. (2015) presented synchrotron-based scanning transmission x-ray microscopy (STXM) analyses of Ca-phosphate reference compounds and polyphosphates at a ~ 25 nm scale. They also calibrated methods to measure Ca/P ratios and carbonate content using x-ray absorption near edge spectroscopy (XANES) at the C, K-, Ca $L_{2,3}$ - and P $L_{2,3}$ - edges. It would be interesting for future studies to apply these Ca-phosphate fingerprinting methods to marine sediment samples to further our understanding of the formation mechanisms of Ca-phosphates in this matrix on a nanometer scale.

Additional studies have used a combination of SEDEX, P near-edge XANES and other spectroscopic techniques in an effort to directly identify P forms extracted in operationally defined sequential extraction schemes, and identify understudied P sinks. Egger et al. (2015) used a combination of SEDEX with microscopic and spectroscopic techniques including micro X-ray fluorescence (μ XRF), P near-edge XANES, scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) and X-ray diffraction (XRD) to investigate the role of less studied authigenic P phases like vivianite in sediments from the Bothnian Sea. Results from this study suggest that vivianite could be an important burial P sink in brackish coastal environments worldwide. Similarly, Kraal et al. (2015) applied SEDEX and P K-edge XANES to sediment samples from an oxygen minimum zone in the Arabian Sea and found that a good agreement between the two approaches for Fe-bound P and Ca-phosphates. However, they observed that, when using sequential extraction techniques alone, polyphosphate could be included in the detrital apatite fraction (e.g. it is not removed by the preceding extraction steps), and could be an important unaccounted for P pool in sediments underlying productive surface waters. Kraal et al. (2017) also used a similar approach to study P cycling in sediments from the Black Sea, and observed that carbonate-bound P can be an important sink for P in carbonate-rich sediments of anoxic and sulfidic basins. These studies highlight the complexities and heterogeneities of P cycling in sediments as a function of sedimentary redox conditions and organic matter content, and underscore the need to use a combination of complementary techniques rather than sequential extractions or porewater profiles alone. An example of such an approach is that of Li et al. (2015), who used a

combination of SEDEX and spectroscopic techniques including solid-state and solution ^{31}P NMR and P K-Edge XANES on sediments from Chesapeake Bay in order to directly characterize important P phases and better elucidate P and Fe dynamics in anoxic sediments. As noted in Li et al. (2015), solid-state ^{31}P NMR and P K-edge XANES are a helpful addition to SEDEX in order to better identify apatite in sediment samples, while solution ^{31}P NMR is helpful in providing insights into the composition of the organic P pool. In another study combining x-ray diffraction (XRD) analysis, pore-water chemistry, diffusive transport modeling and laboratory culture experiments with bacteria, Schulz and Schulz (2005) were able to demonstrate the role of bacteria in polyphosphate-accumulating and phosphorite formation. Following this study, Goldhammer et al. (2010) were able to show that bacterial apatite formation is a significant P sink under anoxic bottom-water conditions using SEDEX and incubations with radioactive ^{33}P . These and similar studies demonstrate the utility of using multiple and complimentary tools and analyses to studying P cycling in natural systems.

3. Phosphorus dynamics in marine sediments

Despite the extensive knowledge of the global P cycle, our understanding of P cycling dynamics remains limited. Economic and scientific interests in phosphorites have resulted in many studies focused on sedimentary P geochemical forms, sinks and rates of burial (Delaney, 1998; Filippelli, 1997; Ruttenger and Berner, 1993; Schenau et al., 2000; Schuffert et al., 1998). Despite this, little is known about P cycling in deep-subseafloor sediments, with most biotic and abiotic processes are inferred from sediment

sequential extractions or molar ratios. Understanding P cycling dynamics in marine sediments is crucial, since the preservation of buried P depends on a number of factors such as the chemical structure of P compounds, sedimentation rate, redox conditions, biotic and abiotic transformations and diagenetic processes (Ingall and Van Cappellen, 1990; Jaisi and Blake, 2010; Ruttenberg and Berner, 1993). Below we summarize some of the observations regarding P cycling in marine sediments based on sequential extractions, and recent applications of stable and radioisotope tracers, which enable insights into P sources, P cycling efficiency, abiotic transformation and specific enzymatic processes altering P compounds in marine sediments.

a. Processes inferred from sequential extractions and X-ray spectroscopy

The development of sequential extraction techniques has shed light on important P transformations occurring in marine sediments (Anderson and Delaney, 2000; Filippelli, 1997; Ruttenberg, 1992; Ruttenberg and Berner, 1993). The numerous applications of the SEDEX scheme (Ruttenberg, 1992) have revealed solid-phase P depth profiles showing a decrease with depth of certain forms (iron-bound P, organic P) and a parallel, almost mirror image, increase in other forms (CFA) (Filippelli and Delaney, 1996; Ruttenberg and Berner, 1993). These covarying depth profiles illustrate the exchange of P between reactive particulate phases due to biological and diagenetic alterations (Figure 4), which can cause P to be released back to the water column or be converted to less labile forms and retained permanently in the sediment (Ruttenberg, 2014). These transformations change the form in which P is ultimately buried via “sink switching” (Ruttenberg and

Berner, 1993). Such processes include microbial breakdown of organic P compounds and production of dissolved inorganic and organic P, release of dissolved P from sediments to bottom waters, uptake of porewater phosphate via sorption onto mineral phases (e.g. Fe, Mn oxides) and the precipitation of phosphate during authigenic mineral formation (carbonate fluorapatite) as a result of organic matter respiration and changes in redox conditions (Paytan and McLaughlin, 2007; Ruttenger, 2014). Redistribution of sedimentary P in secondary phases such as CFA significantly enhances P burial efficiency. The use of X-ray spectroscopy combined with SEDEX has shed light on the role of previously largely ignored authigenic P phases, such as vivianite, in P burial (Egger et al., 2015). This study found that in the Bothnian Sea, authigenic manganese-rich vivianite was responsible for ~40-50% of total P burial below the sulfate-methane transition zone and suggested that this P sink could be widespread in coastal surface sediments, in addition to deep marine sediments with non-steady state diagenetic conditions. Egger et al. (2015) further proposed a sink switch from iron oxide-bound P to vivianite driven by anaerobic oxidation of methane. Combining X-ray spectroscopy with sequential extraction methods has also shed light on the previously underestimated role of P strongly associated with calcium carbonate as an important sink for P in the Black Sea (Kraal et al., 2017). It is becoming apparent that sequential extractions alone provide an incomplete picture of P burial dynamics in sediments. Indeed, while they have provided a valuable picture of sedimentary P processes and helped constrain the magnitude of different P fluxes in sediments, there is a growing need for tools that enable further insights into the chemical structure of the components of operationally-defined P reservoirs and sinks, as well as quantitative insights into sedimentary P transformations.

b. Enzymatic assays

A relatively small number of studies have measured enzymatic activities in marine sediments compared to water, soils and lacustrine sediments (especially for enzymes related to P uptake). Indeed, many protocols used for enzymatic assays were developed on soil samples (Bell et al., 2013; Dick and Tabatai, 1978; Marx et al., 2001; Tabatai and Bremner, 1969) or water samples (Hoppe, 1993) and have had to be modified and optimized for use on marine sediment samples (Coolen and Overmann, 2000; Köster et al., 1997; Schmidt, 2016). Studies that have investigated the activity of phosphoenzymes in marine sediments have focused on phosphatases, especially alkaline phosphatase, an enzyme produced by a majority of marine microorganisms with the potential to hydrolyze a broad range of dissolved organic P compounds containing monophosphate ester bonds (Hoppe, 2003). These studies have shown that phosphatase activity is detectable in marine sediments, and tends to decrease with sediment depth as organic matter content decreases (Hewson et al., 2007; Kobori and Taga, 1979; Köster et al., 1997; Schmidt, 2016). It is important to bear in mind when interpreting enzymatic assay data that the detection of phosphatase activity does not necessarily imply that these are produced *in-situ* (Steenbergh et al., 2011). Previous studies have also highlighted the role of phosphatases can play in relieving carbon limitation by removing phosphate groups from organic substrates and making them more accessible to heterotrophic microorganisms (Biche et al., 2017; Köster et al., 1997; Steenbergh et al., 2011). However, little attention has been paid to the activity of other phosphoenzymes, including phosphonases, pyrophosphatase or nucleases. This is an important knowledge gap that, once addressed,

will help better constrain the rates of P turnover in marine sediments, and the impact of deep seafloor microorganisms on P cycling

c. Oxygen isotopes in phosphate ($\delta^{18}\text{O}_p$)

Unlike other major nutrients such as nitrogen or carbon, P only has one stable isotope, which prevents the use of stable P isotope ratios as a tool for studying P cycling dynamics. However, since most P in nature is found strongly bound to oxygen, the isotopic composition of oxygen in phosphate ($\delta^{18}\text{O}_p$) can be used instead. The P–O bond in phosphate is resistant to oxygen isotope exchange with water during inorganic reactions under the temperature and pH of most natural systems, therefore phosphate is considered to be relatively stable under diagenetic conditions (Blake et al., 1997; Lécuyer et al., 1996). Accordingly, any variability in $\delta^{18}\text{O}_p$ is the result of mixing of isotopically distinct phosphate sources (Young et al., 2009), the exchange of oxygen due to enzymatic activity as phosphate molecules cycle through living cells (Blake et al., 2005) or when enzymes are excreted outside the cell (Liang and Blake, 2009, 2006). Phosphate is taken up by living cells and processed by extracellular and intracellular phosphoenzymes, many of which are dominated by hydrolytic cleavage reactions that result in the exchange of oxygen in phosphate with oxygen in cellular water (Blake et al., 1997). Previous work has demonstrated that intracellular inorganic P cycling by pyrophosphatase leads to temperature-dependent isotopic fractionation that imparts the equilibrium $\delta^{18}\text{O}_p$ on phosphate cycled within cells (Blake et al., 2005; Chang and Blake, 2015). The temperature dependence of the whole organism oxygen isotope fractionation between bioapatite and water has been measured empirically and in laboratory experiments

(Kolodny et al., 1983; Longinelli and Nuti, 1973; Puc at et al., 2010). The temperature dependence of the oxygen isotope fractionation between dissolved phosphate and water has also been recently measured (Chang and Blake, 2015). The most commonly used equation historically is that of Longinelli and Nuti (1973), which depicts the temperature-dependent isotopic equilibrium between water and bioapatite:

$$\delta^{18}\text{O}_{\text{p-eq}} = [(111.4 - T)/4.3] + \delta^{18}\text{O}_{\text{w}} \quad (1)$$

where $\delta^{18}\text{O}_{\text{p-eq}}$ corresponds to oxygen isotopic composition of bioapatite at equilibrium, T is temperature ($^{\circ}\text{C}$) and $\delta^{18}\text{O}_{\text{w}}$ is the oxygen isotopic composition of the surrounding water. Other relationships have been derived based on apatite from fish grown in temperature-controlled experiments (Puc at et al., 2010) and on fractionations between dissolved phosphate and water, catalyzed by pyrophosphatase (Chang and Blake, 2015). Puc at et al. (2010) reported a +2‰ offset compared to the Longinelli and Nuti (1973) equation, a result confirmed by Chang and Blake (2015), Blake et al. (2016) and Li et al. (2016). This offset has important implications in terms of paleotemperature calculations, as this study shows that most previously published marine paleotemperatures have been underestimated by up to 8 $^{\circ}\text{C}$. The findings from these studies highlight the need to use thermometry equations obtained using the same analytical methods as those used on samples. In addition, Chang and Blake (2015) further underscores the importance of separating bioapatite–water and dissolved phosphate–water oxygen isotope fractionation equations, the latter being particularly pertinent to marine P cycling studies as dissolved phosphate is the relevant phase for several sedimentary P forms (e.g. loosely-sorbed P,

iron-bound P, porewater phosphate). The activity of extracellular enzymes such as alkaline phosphatase lead to disequilibrium isotope effects in the inorganic phosphate produced in the reaction via kinetic effects and the replacement of one oxygen from phosphate with oxygen from water (Kirby and Nome, 2015) in hydrolyzed phosphoesters (Blake et al., 2005). Different enzymatic pathways cause different degrees of fractionation, several of which have been constrained (Blake et al., 2005; Liang and Blake, 2009, 2006; von Sperber et al., 2014). In addition, laboratory studies have also carefully determined the fractionations associated with abiotic sorption and desorption processes, as well as those associated with the precipitation of dissolved phosphate as apatite, and determined that these fall within the range of +1‰ (Jaisi et al., 2010; Liang and Blake, 2007). The degree of deviation from calculated equilibrium can give information regarding different P sources or P cycling efficiency, and provides the basis for interpreting $\delta^{18}\text{O}_p$ data. Oxygen isotope ratios of phosphate have become more widely used to study phosphorus cycling dynamics in water bodies (Colman et al., 2005; Li et al., 2017a; McLaughlin et al., 2006, 2004, 2013a; Young et al., 2009), but only a few applications focusing on marine sedimentary P cycling exist. Jaisi and Blake (2010) used a combination of sequential sediment extraction analyses (SEDEX) and $\delta^{18}\text{O}_p$ from authigenic and detrital apatite in sediments from the Peru Margin. They reported $\delta^{18}\text{O}_p$ values for authigenic apatite between 20.2–24.8‰ at all sites, and $\delta^{18}\text{O}_p$ values for detrital apatite between 7.7–15.4‰; these ratios did not change with depth. This study showed that detrital phosphates retain their source signature due to their low bioavailability, and can be reliable tracers of P sources at least in well-constrained systems where other processes like mixing of sources or precipitation/uptake/adsorption could be ruled out.

Furthermore, this study demonstrated that multiple generations of authigenic phosphates with distinct isotopic compositions could co-occur at similar depths, and that those formed from incorporation of dissolved inorganic P derived from remineralized organic matter could have $\delta^{18}\text{O}_p$ below calculated equilibrium. This latter observation was also reported in Joshi et al. (2015), which reported authigenic apatite $\delta^{18}\text{O}_p$ ranging from 12 to 18‰ in sediments from Chesapeake Bay. In this same study, the authors report $\delta^{18}\text{O}_p$ for iron-bound P between 17.8-22.4‰ and identify this pool as being largely composed of iron phyllosilicates, which are resistant to dissolution in an anoxic sediment column. The findings from these studies help shed light on the complexities of sedimentary P cycling, and provide insights that cannot be gleaned from sediment sequential extractions alone. While applications of $\delta^{18}\text{O}_p$ on solid-phase marine sediments are scarce, there have been some applications of this technique on sediment porewater dissolved inorganic P. A micro-extraction technique developed by Liang (2005) and modified by Goldhammer et al. (2011b) enhanced the use of $\delta^{18}\text{O}_p$ in marine sediment pore-waters with low P concentrations. Liang (2005) applied the procedure in the Peru Margin on cores collected from ODP Site 1230 and Goldhammer et al. (2011a) applied this method to sediments from the Benguela upwelling system, a modern site of phosphorite formation. They report pore-water $\delta^{18}\text{O}_p$ values both in equilibrium under high remineralization and high pore-water P concentrations, and in disequilibrium under low remineralization and low P. The authors of these studies suggest that preferential P regeneration in marine sediments does not always correspond to disequilibrium $\delta^{18}\text{O}_p$ values, contrary to results from water column studies (McLaughlin et al., 2006). Goldhammer et al. (2011a) propose that microbial P uptake strategies, which are controlled by ambient dissolved inorganic P

concentrations, play a key role in the variability of $\delta^{18}\text{O}_p$ signatures in pore-water. This work highlights the need for more sophisticated mass balance models that take into account diffusion, advection and microbial processes when interpreting sedimentary $\delta^{18}\text{O}_p$ data. Moreover, internationally certified standards and best practices guidelines for the application of $\delta^{18}\text{O}_p$ are greatly needed, especially regarding the appropriate use of equilibrium thermometry equations given the P phases studied and analytical methods used.

d. Radiotracer experiments

Radioactive P isotopes (^{32}P , ^{33}P) have been used to study P transformation in the marine environment, mainly in the water column (Benitez-Nelson and Karl, 2002; McLaughlin et al., 2013a; Van Mooy et al., 2015; Sokoll et al., 2017). Unlike stable isotopes though, in most applications this approach can perturb the system studied due to the addition of labeled phosphate, and integrates processes over short timescales (McLaughlin et al., 2013b). Nevertheless, this tool can provide quantitative information on the turnover rates of dissolved organic P and phosphate (Benitez-Nelson and Karl, 2002; McLaughlin et al., 2013a; Sokoll et al., 2017) and cycling rates of P between the +5 and +3 oxidation states (Van Mooy et al., 2015). However, applications of this tool to investigate P cycling in marine sediments are sparse.

Goldhammer et al. (2010) used ^{33}P -radiotracer incubations to investigate the pathways and partitioning of phosphate under anoxic and oxic conditions in sediments from the Benguela upwelling system. They found direct evidence of bacterial concentration of

dissolved inorganic phosphate as polyphosphate, as evidenced by significant incorporation of ^{33}P in all living assays as polyphosphate, and reported rates of inorganic P sequestration into authigenic apatite exceeding modeled steady-state net phosphate production modeled from pore-water phosphate concentrations. They showed that, under anoxic bottom-water conditions, bacterial apatite formation is a significant P sink in organic-rich sediments with low reactive iron content. The findings from this study have important implications for our understanding of P dynamics and the requisite roles of microorganisms in the mineral precipitation process in sediments of highly productive upwelling regions, and possibly sediments in systems with expanding water-column anoxia (Goldhammer et al., 2010). In contrast, recent ^{33}P -radiotracer incubations carried out on oxic and anoxic surface sediments in the Black Sea yield a different picture of sedimentary P dynamics (Dijkstra et al., 2016a). Indeed, Dijkstra and colleagues report a rapid uptake of ^{33}P via sorption to Fe (oxyhydr)oxides and find that microorganisms are not directly involved in sedimentary P immobilization in this system. Findings from this work highlight the impact of sediment geochemistry, microbiology, organic matter content, and redox conditions on the mechanisms of P sequestration, and thus the need for additional applications of this tool to gain quantitative information on the cycling of P in marine sediments.

4. Future directions

While our understanding of phosphorus forms in marine sediments and their relative reactivity has improved through the use of sequential extractions, spectroscopic techniques and isotope tracers, many aspects of sedimentary P cycling still need to be

better constrained. Future research could draw inspiration from approaches used in soil P research which, in addition to the techniques highlighted in this review, relies on techniques that include 2D NMR, diffusive gradients in thin films (DGT) and NanoSIMS (Kruse et al., 2015). A small number of studies have applied these methods to marine sediments, but these applications remain scarce. For example, Sulu-Gambari et al. (2016) used a combination of NanoSIMS, benthic flux measurements and microscopic identification of bacterial measurements to show that internal shifts in population dynamics of cable bacteria can induce strong seasonality in sedimentary iron-P dynamics in a marine lake. Sun et al. (2016) investigated vertical dissolved reactive P fluxes in polluted coastal sediments in North China using DGT and proposed that sulfide accumulation could enhance P release in anoxic sediments. DGT techniques are broadly applied in lake studies (Ding et al., 2016, 2015, 2011) and are a promising approach for future marine sedimentary P studies. While no studies have applied 2D NMR to marine sediments yet, Li et al. (2017b) used both 1D and 2D NMR, along with electron microprobes analyses, to better constrain seasonal variations in organic and inorganic P species in the Chesapeake Bay. An important next step would be to develop a 2D NMR procedure for marine sediments, in an approach similar to that of Vestergren et al. (2012) with soil samples. Future work should also continue to improve diagenetic models (Dale et al., 2016, 2013; Reed et al., 2011; Tsandev et al., 2012) and isotope models (Jaisi et al., 2017) to simulate P transformations in sediments with differing organic matter content, redox conditions, burial depths and sediment types. An emerging and promising field in sedimentary P research is the use of genomics tools to better understand the microbial controls of P uptake (Jones et al., 2016; Steenbergh et al., 2015) which, coupled with

spectroscopic analyses and/or isotope tracers has the potential to yield a comprehensive picture of the processes controlling P reactivity and burial in marine sediments. Such interdisciplinary work is key to improving our estimates of P fluxes between sedimentary reservoirs and thus our understanding of the complex dynamics of P biogeochemical cycling in the sedimentary environment.

Figure captions and tables

Figure 1 | Distribution of total particulate P in the North Atlantic Ocean. Total particulate P data were collected during the US GEOTRACES North Atlantic Zonal Transect (Lam et al., 2015) shown in panel (a). Panel (b) shows the distribution of total particulate P with depth along that transect. Panels (c), (d) and (e) show the total particulate P content along the transect at 40 meters below sea level (mbsl), 500 mbsl and 3,300 mbsl respectively.

Figure 2 | P transformations in the water column and in sediments, modified from Paytan and McLaughlin (2007). Reactive particulate P and dissolved P forms undergo biotic and abiotic transformations throughout the water column and in sediments, while detrital P is exported to the seafloor without such processes, where it is passively buried. The abbreviations used in this figure correspond to: PIP, particulate inorganic P; DIP, dissolved inorganic P; DOP, dissolved organic P. More details regarding the P transformations in marine sediments are provided in figure 4.

Figure 3| Conceptual diagram of the SEDEX procedure, modified from Ruttenberg (1992). Each step of this scheme targets a specific, operationally defined sedimentary P pool based on its reactivity in a given extractant solution.

Figure 4| Summary diagram of the main P processes occurring in marine sediments, modified from Goldhammer (2009). P_i refers to dissolved inorganic P, and the arrows indicate the movement of P between different sedimentary P reservoirs via biotic (mineralization, uptake, release, assimilation) and abiotic processes (adsorption, desorption, dissolution, precipitation). The grey arrows indicate P exchanges with the overlying water column via regeneration and the redox pump.

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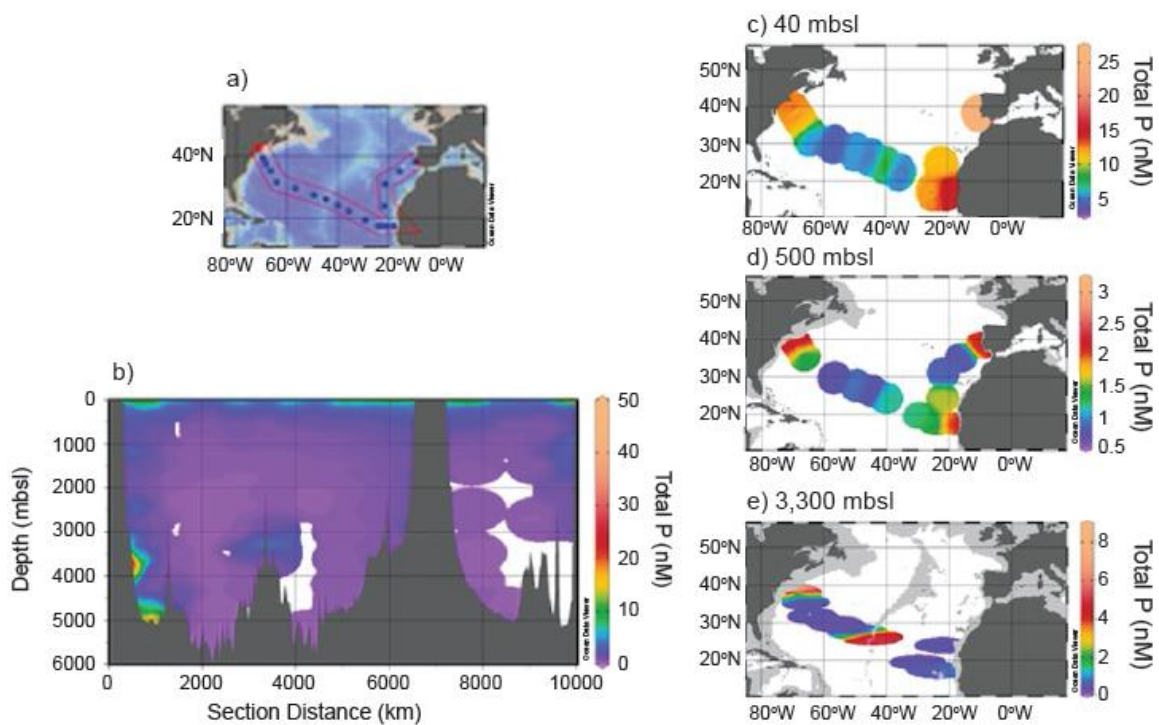


Fig. 1

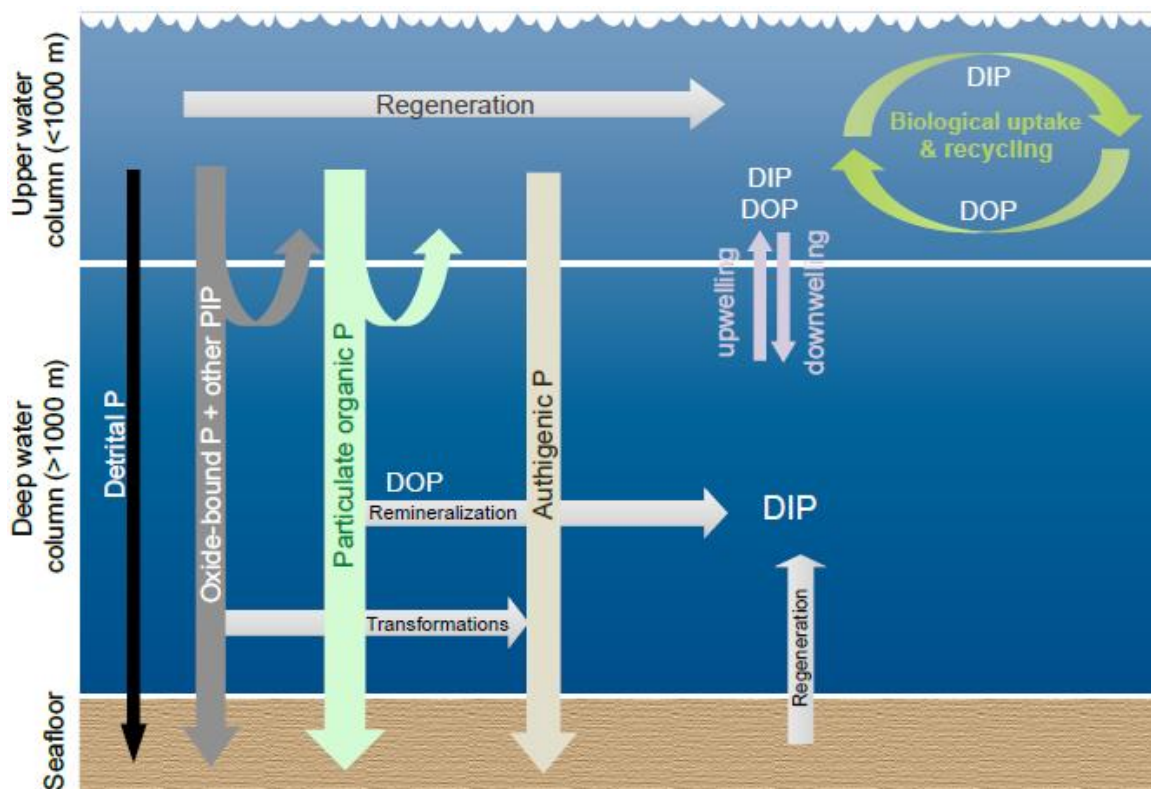


Fig. 2

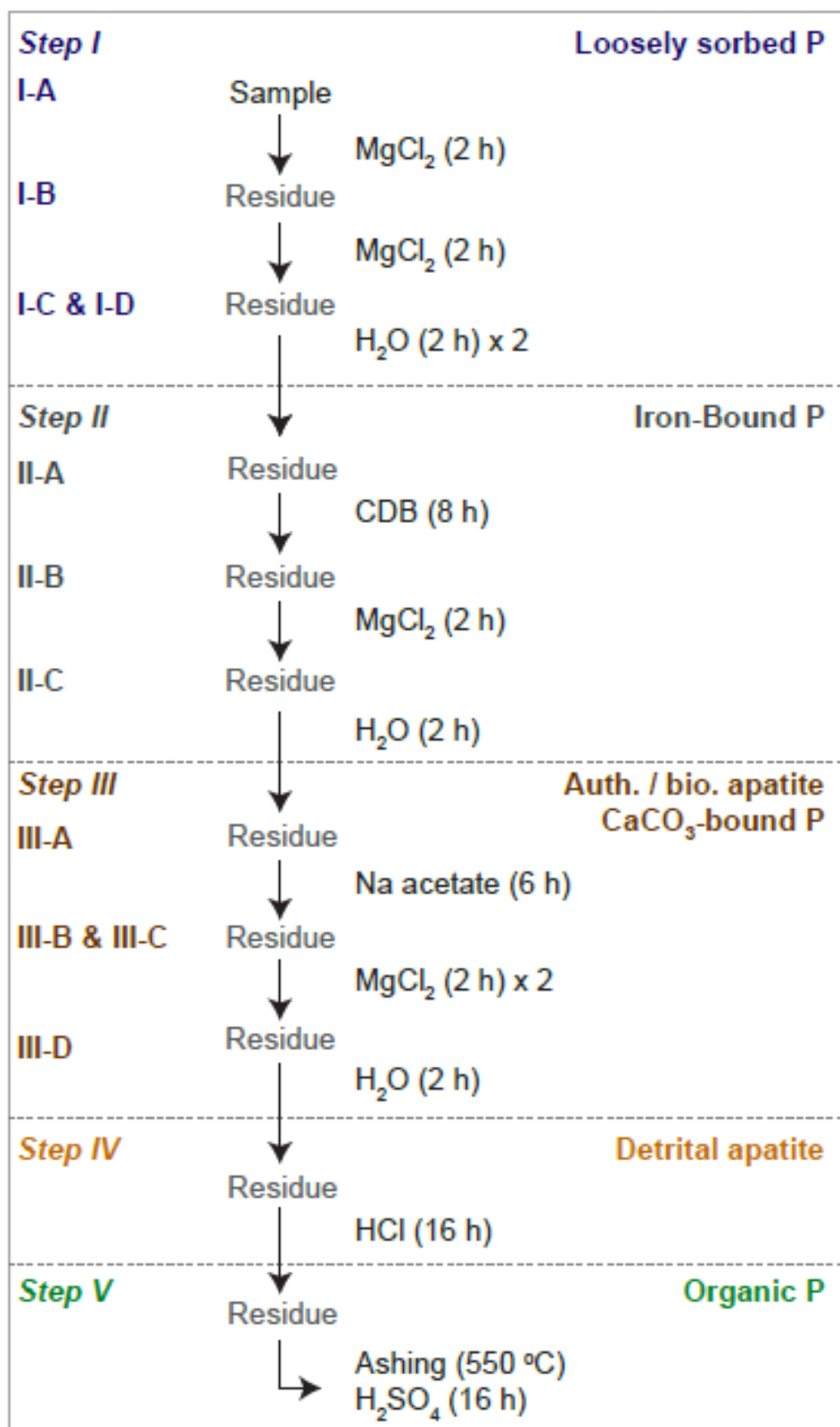


Fig. 3

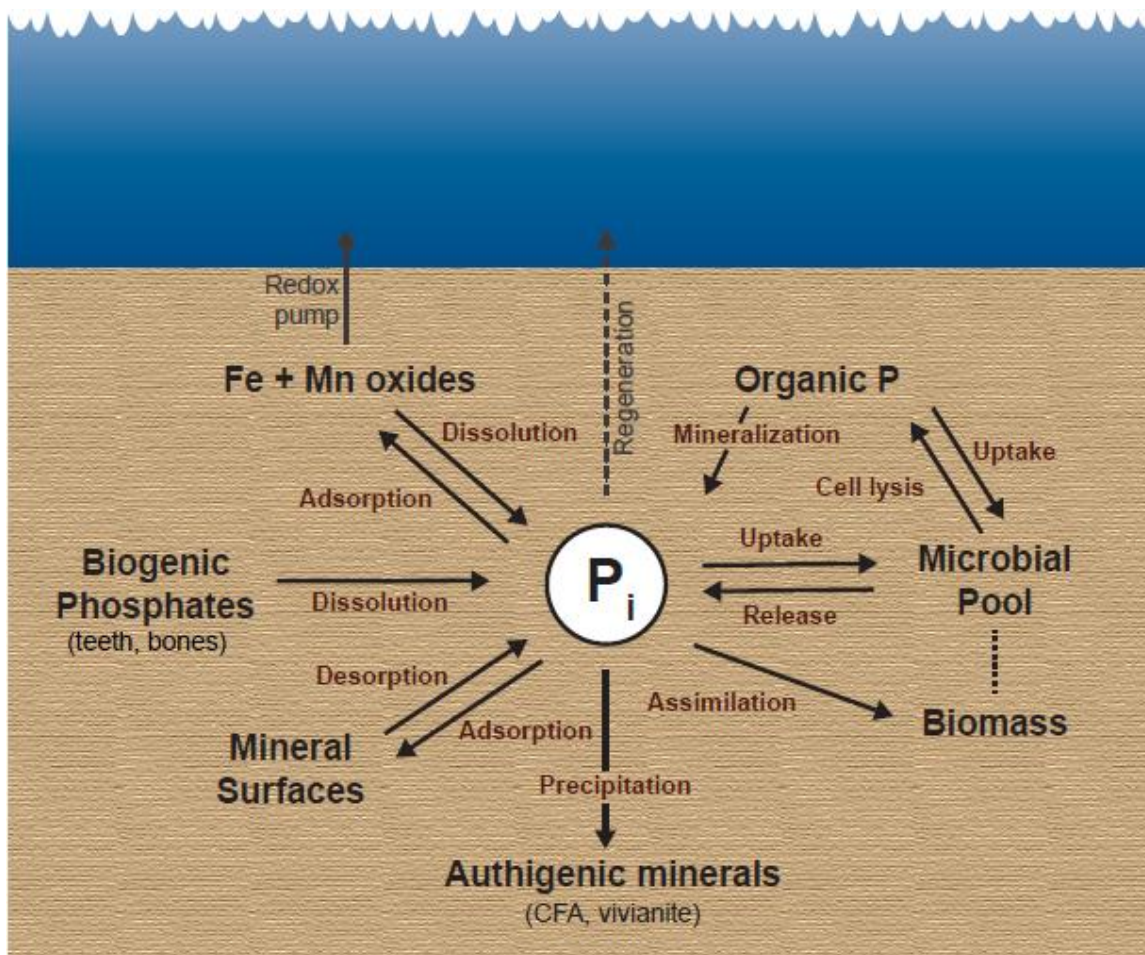


Fig. 4