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Development of a modified SEDEX phosphorus speciation method for ancient rocks and modern iron-rich sediments

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Abstract

We report the development of a modified method for evaluating different reservoirs of sedimentary phosphorus (P) in ancient marine sedimentary rocks and in modern Fe-rich sediments. Utilising the existing SEDEX scheme for P partitioning in modern sediments, we initially demonstrate limitations in the application of the original scheme to sediments and rocks containing crystalline hematite and magnetite. We tested additional extractions for these crystalline Fe phases, using both synthetic minerals, and modern and ancient sediments. The addition of 6 h oxalate and 6 h citrate-dithionate-acetate extractions considerably enhanced the total recovery of synthetic magnetite and hematite to 88.7 ± 1.1% and 76.9 ± 3.8%, respectively. In addition, application of the 6 h oxalate extraction to synthetic P-containing magnetite recovered 93.9 ± 1.7% of the Fe present and 88.2 ± 12.8% of the co-precipitated P. Based upon these results we developed a modified SEDEX extraction scheme. The modified scheme was applied to modern Fe-rich sediments from Golfo Dulce, Costa Rica, which resulted in 16% higher Fe-bound P recovery. Application of the scheme to a variety of ancient marine rocks increased the recovery of Fe-bound P by up to 22%. We also highlight the potential for authigenic carbonate fluorapatite to convert to more crystalline apatite in ancient rocks during deep burial and metamorphism. We suggest that in such systems minimum and maximum estimates of the total reactive P pool may be calculated with and without the inclusion of crystalline P. It is noted that the application of the revised method may have important implications for understanding the cycling of P in ancient marine environments.

Keywords: Phosphorus; Sequential extractions; Magnetite; Hematite; SEDEX

Highlights

- We present a revised method for quantifying sedimentary P phases in modern Fe-rich sediments and ancient sedimentary rocks.
- This modified SEDEX scheme is particularly targeted at sediment and rock samples that contain crystalline Fe (oxyhydr)oxide minerals such as hematite and magnetite.
- This is the first scheme to determine magnetite-bound P.
- The revised scheme provides a highly specific determination of crystalline Fe oxide-bound P and suggests a way to estimate maximum and minimum reactive P.

1. Introduction

Phosphorus (P) is a key element for life on Earth. A structural component of all organisms, P forms the backbone of DNA and RNA, and is crucial in the transmission of chemical energy through ATP molecules. Phosphorus supply to the oceans exerts a critical control on primary productivity in many areas of the global ocean, which in turn affects organic carbon production and burial, and ultimately the production of oxygen through time (Berner et al., 2003; Berner and Canfield, 1989; Berner and Maasch, 1996; Garrels and Perry, 1974). On geological timescales, P is generally considered the ultimate limiting nutrient (Codispoti, 1989; Redfield, 1958; Tyrrell, 1999; Van Cappellen and Ingall, 1996). As a consequence, the delivery and subsequent behaviour of P in marine environments has been the focus of considerable attention, both in modern (e.g., Eijsink et al., 2000, Ingall and Jahnke, 1994, Ingall et al., 1993; Ruttenberg and Berner, 1993, Slomp et al., 1996a, 2004, Van Cappellen and Ingall, 1994) and ancient settings (e.g., Bjerrum and Canfield, 2002, Boyle et al., 2014, Creveling et al., 2014, Lenton et al., 2014, März et al., 2008, Planavsky et al., 2010, Reinhard et al., 2017). While bulk sediment digestions can give useful information on the fluxes and behaviour of P in marine environments (e.g., Reinhard et al., 2017), this insight is limited as it does not identify P phases that may be reactive or potentially bioavailable during diagenesis.

Phosphorus delivery to modern marine sediments mainly occurs in association with organic matter, Fe (oxyhydr)oxide minerals, and as recalcitrant detrital P of geological origin (Faul et al., 2005; Froelich et al., 1982; Schenau and De Lange, 2000; Slomp et al., 1996b; Stockdale et al., 2016). Under both oxic and anoxic conditions, a major proportion of the labile organically-bound P (P_{org}) can be released by microbial respiration as dissolved inorganic P (DIP) (Anderson et al., 2001; Froelich et al., 1988; Ingall and Jahnke, 1994; 1997; Jahnke, 1996; Krom and Berner, 1981; Ruttenberg, 2003; Ruttenberg and Berner, 1993; Van Cappellen and Ingall, 1994). In addition, reductive dissolution of Fe (oxyhydr)oxide minerals, which most commonly occurs either via dissimilatory Fe reduction (Thamdrup, 2000) or direct reaction with dissolved sulfide (Canfield, 1989; Poulton et al., 2004b), releases P associated with these phases. Some DIP released from organic matter or Fe (oxyhydr)oxides during early diagenesis, may be taken up by Fe (oxyhydr)oxides formed at the sediment-water interface, if the overlying water column is oxic (Slomp and Van Raaphorst, 1993; Slomp et al., 1996b). By contrast, under anoxic water column conditions, P may be extensively recycled back to the water column (Ingall and Jahnke, 1994; 1997; Jensen et al., 1995; Van Cappellen and Ingall, 1994). Generally deeper in the sediment, DIP may be partially removed from solution by precipitation as either carbonate fluorapatite (CFA; Ruttenberg and Berner, 1993) or vivianite (e.g., Egger et al., 2015; Hsu et al., 2014; Slomp et al., 2013; Xiong et al., in review), in a process known as 'sink switching'. In order to evaluate these diagenetic processes and to constrain the fate of P in sedimentary environments, it is important to be able to quantify the phase partitioning of P within the sediment.

Extraction techniques have been widely employed to provide more detailed insight into the speciation and behaviour of P in the marine realm. The method of Aspila et al. (1976) allows determination of inorganic P and total P (P_T) in sediments, with the difference being attributed to organic P. However, this technique does not allow quantification of a variety of important phases, including the detrital fraction that is essentially unreactive in marine environments. A major step forward was achieved with the development of a sequential extraction procedure for P by Ruttenberg (1992). This technique (termed SEDEX) quantifies five operationally-defined sedimentary P reservoirs (Table 1): exchangeable P (P_{sorb}), Fe (oxyhydr)oxide-bound P (P_{Fe}), authigenic P (P_{auth}; comprising authigenic CFA, $CaCO_3$-bound P and biogenic apatite), detrital P (P_{det}), and organic P (P_{org}). The general technique, including some minor modifictions (e.g. Schenau and De Lange, 2000), has proven to be a robust and highly useful method for examining the phase partitioning of P in modern marine settings (e.g., Egger et al., 2015, Eijsink et al., 2000, Kraal et al., 2015, Matijević et al., 2008, McParland et al., 2015, Poulton and Canfield, 2006, Ruttenberg and Berner, 1993, Schenau and De Lange, 2001, Slomp et al., 1996a, 2004).

Due to the enhanced information on P cycling afforded by the SEDEX method, several studies have attempted to apply the method (or variations of it) to many other environmental particles, including ancient marine rocks (e.g., Creveling et al., 2014, Huang et al., 2007, Kraal et al., 2010, März et al., 2008, Mort et al., 2007, 2008, Westermann et al., 2013). However, the original method was not developed – and is therefore not necessarily appropriate – for application to such ancient sediments. Ancient sedimentary rocks often contain minerals of increased crystallinity compared with modern sediments, as well as important P-bearing phases that may not be adequately accounted for by the original SEDEX method. For example, throughout the majority of early Earth history, large areas of the global ocean were characterised by anoxic and Fe-containing (‘ferruginous’) water column conditions (Poulton and Canfield, 2011), which led to the deposition of sediments that are often enriched in crystalline hematite and magnetite (e.g., Canfield et al., 2008, Poulton et al., 2004a). Magnetite is not specifically targeted by the original SEDEX extraction scheme, while tests on highly crystalline hematite (Raiswell et al., 1994), suggest that the pH 7.6 citrate-dithionite-bicarbonate (CDB) extraction utilised in the existing SEDEX protocol (Figure 1) is unlikely to fully dissolve this phase in ancient rocks. Crystalline Fe (oxyhydr)oxide minerals may also be present in some modern marine sediments, resulting in the potential for incomplete recovery of P from these phases. Thus, to successfully apply P speciation both to ancient sedimentary rocks and modern sediments containing appreciable amounts of crystalline Fe (oxyhydr)oxide minerals, a modified method is required.

In order to quantify a more complete spectrum of the Fe (oxyhydr)oxide minerals commonly present in sediments and rocks, Poulton and Canfield (2005) developed a sequential extraction procedure for Fe, which targets both magnetite and highly crystalline hematite (Figure 1). This provides a template to modify the SEDEX procedure to include P associated with these additional mineral phases. Here, we initially test the efficiency of the original SEDEX method to extract hematite and magnetite. We then report the development of a revised extraction scheme for P, which we test using both synthetic Fe minerals and modern and ancient marine sediments.

2. Samples and methods

The details and main characteristics of all minerals and natural samples used in this study are outlined in Table 2.

2.1. Synthetic minerals

Synthetic ferrihydrite, lepidocrocite and goethite were prepared according to the standard methods of Cornell and Schwertmann (1996), and we utilised minerals that were previously synthesized and characterised by X-ray diffraction (XRD) (Poulton et al., 2004b). Hematite was provided by BDH Laboratory supplies, and its purity was confirmed by XRD (SI Figure 1). We also analysed a magnetite-hematite composite sample. This sample was prepared via the standard method for magnetite preparation described in Cornell and Schwertmann (1996) and had previously been used in the development of a sequential Fe extraction by Poulton and Canfield (2005). Partial oxidation of magnetite to hematite during subsequent storage was confirmed by XRD (SI Figure 2). HNO_3-HF-$HClO_4$ digests (see below) of this sample gave a total Fe composition of 71.8 ± 2.3 wt%, while a separate ammonium oxalate extraction aimed at dissolving magnetite (Figure 1; Poulton and Canfield, 2005) suggests that 79.2 ± 1.2% (56.9 wt% Fe) of the total Fe is present as magnetite.

An additional synthetic magnetite sample with co-precipitated P was prepared following the protocols of Cornell and Schwertmann (1996). 560 ml of a mixed $NaH_2PO_4{\cdot}2H_2O/FeSO_4$ solution

(0.39 mM:0.3 M) was heated at a constant 90°C, and 240 ml of a KOH/KNO_3 solution (3.33:0.27 M ratio) was added dropwise in an anaerobic chamber, with constant stirring. The reaction was allowed to continue for 1 h. Once cool, the mineral/solution slurry was centrifuged, and washed with 18.2 MΩ resistance water before drying at 90°C. After drying, the solid was ground to a powder and stored frozen to prevent oxidation. XRD analysis confirmed that magnetite was the only mineral phase present (SI Figure 3). Complete chemical characterisation by XRF and ICP-OES (following dissolution with 12 N HCl) confirmed a co-precipitated P content of 9.7 ± 0.7 mmol/kg.

2.2. Natural mineral samples

A natural sample of crystalline apatite from Madagascar was analysed. XRD analyses suggest that the dominant minerals were hydroxyapatite or fluorapatite (SI Figure 4). A natural sample of magnetite drilled from a sample of banded iron formation (BIF) from the Isua Greenstone Belt was used to represent crystalline magnetite found in ancient sedimentary rocks. XRD analysis showed the sample was predominantly formed of magnetite and quartz (SI Figure 5). HNO_3-HF-$HClO_4$ digests of this Isua BIF sample gave a total Fe composition of 61.9 ± 1.5 wt%, and an ammonium oxalate extraction (Figure 1) suggested that magnetite Fe (Fe_{mag}) contributed 70.1% of total Fe (43.8 wt% Fe).

2.3. Modern marine sediments and ancient marine sedimentary rocks

Extractions were performed on modern sediments from Golfo Dulce, Costa Rica, from a short core comprising Fe (oxyhydr)oxide-rich marine mud. Golfo Dulce is a 200 m deep tropical fjord where the water column is anoxic and nitrate-rich (‘nitrogenous’) beneath a depth of ~100 m (Thamdrup et al., 1996). Despite the reducing water column and sediment conditions, reactive Fe (oxyhydr)oxide mineral phases persist in the deposited sediment (Thamdrup et al., 1996). In terms of ancient sedimentary rocks we focussed on several units from different time periods. Drill core samples were analysed from low metamorphic grade black shales of the ~1.88-1.83 billion year old Animikie group, Superior Province, North America, that were deposited under a range of water column conditions, including anoxic and sulfidic (euxinic), ferruginous, and oxic (see Poulton et al., 2004a, 2010). We additionally analysed outcrop samples of low metamorphic grade marine shales from the ~1.65 billion year old Chuanlinggou Formation, North China Craton (Li et al., 2015; Meng et al., 2011), that were deposited under ferruginous and oxic conditions (Doyle, 2018). Drill core samples were analysed from the 715-542 million year old southern Timan Region of North Russia, that were mostly deposited under oxic conditions, but with two samples where the water column redox conditions were unclear (termed ‘equivocal’; see Johnston et al., 2012). Finally, we analysed a sample from the Jurassic bituminous shales section of the Jet Rock Series at Saltwick Nab, Yorkshire, which were deposited under anoxic conditions (Howarth, 1962).

2.4. Testing the efficiency of Fe extracted during each SEDEX step

We initially tested the extent to which the synthetic Fe minerals were dissolved by each step of the SEDEX technique (performed as individual extractions, rather than sequentially). We then ran the synthetic hematite and magnetite/hematite composite samples, in addition to the Golfo Dulce and Animikie Basin samples, through the original SEDEX extraction scheme sequentially, and measured the Fe released in each step. Since our focus here is on developing the SEDEX method for extraction of crystalline Fe oxides, and since adsorbed P is unlikely to be a significant component of ancient rocks and sediments, we did not include the first step (P_{sorb}) of the original SEDEX method (Figure 1). We do stress, however, that this step may still be applied in studies of modern Fe-rich sediments.

For the synthetic Fe minerals, 25-30 mg of sample was reacted at room temperature with each extractant solution of the SEDEX method (using 10 ml of extractant, except in the case of sodium dithionite extractions with hematite, where 40 ml of extractant was used to avoid saturation of the solution with respect to Fe). All extractions were carried out at least in duplicate. For the Golfo Dulce and Animikie Basin samples, 150-180 mg of sediment was extracted in 10 ml of solution for each SEDEX step. To check whether any Fe (oxyhydr)oxide minerals persisted after completing the SEDEX method, additional extractions were performed on the residual sediment, utilising a 6 h citrate-dithionite-acetate (CDA) extraction for hematite (note that a 6 h CDA extraction was performed rather than the more typical 2 h extraction (see also Canfield et al., 2007) since our aim is to target highly crystalline hematite remaining after initial extraction by CDB), followed by a 6 h ammonium oxalate extraction for magnetite (Poulton and Canfield, 2005).

2.5. Developing a revised method for the partitioning of P in ancient sediments

A major difference between the Fe (oxyhydr)oxide-targeting steps in the SEDEX and Fe speciation methods is the pH of the dithionite extraction solution (pH 7.6 for CDB in SEDEX; pH 4.8 for CDA in Fe speciation; Figure 1). As outlined above, however, dithionite extractions at pH 7.6 may not effectively extract crystalline hematite, either from ancient rocks or modern sediments (Raiswell et al., 1994). In addition, neither the CDB or CDA extractions target magnetite, which is instead extracted via ammonium oxalate (Poulton and Canfield, 2005; Figure 1). Therefore, we also performed a range of extractions on our synthetic Fe minerals to determine the optimum position for the insertion of these steps into our revised P speciation scheme. Alongside these extractions, we also tested whether ammonium oxalate and CDA extracted significant P from our natural apatite sample.

The original SEDEX scheme places wash steps with either 1 M $MgCl_2$ or 18.2 MΩ resistance water after most of the principle extraction steps, in order to reverse any secondary re-adsorption of extracted phosphate onto other remaining sedimentary phases. We also carried out this step for the measurement of any re-adsorbed P during the CDA and ammonium oxalate extractions. After all principal extraction steps, a maximum of three washes (5 ml of solution for 2 h) were performed: (i) $MgCl_2$, ii) $MgCl_2$, iii) 18.2 MΩ resistance water. It has been suggested that secondary adsorption of P onto residual sediment is not an important process during the CDB and HCl steps of the SEDEX procedure (Figure 1), and only a single $MgCl_2$ extraction is required following the Na acetate extraction (Ruttenberg, 1992; Slomp et al., 1996a). However, we suggest that the number of washes should be based on the amount of P detected in the previous wash, and we performed additional washes until the concentration of P in solution was <0.2 mg/kg, up to a maximum of 3 washes. As a result of the above tests, an optimal extraction scheme was developed and tested, firstly in relation to the dissolution of Fe from our synthetic hematite and magnetite/hematite composite samples, and subsequently in terms of the phase partitioning of both Fe and P in the Golfo Dulce and ancient Animikie Basin samples. Finally, our revised phosphorus speciation scheme was applied to the North China Craton, Timan Region and Saltwick Nab sedimentary rocks.

2.6. Chemical analyses

At the end of each extraction or wash step, samples were centrifuged and then aliquots of the supernatant were taken for the analysis of P, with the remaining supernatant decanted from the centrifuge tube. All Na acetate and HCl solutions, as well as $MgCl_2$ and 18.2 MΩ resistance water washes, were then analysed for P on a spectrophotometer via the phosphomolybdate blue method (Koroleff, 1976; Strickland and Parsons, 1972), with the solutions adjusted to a pH of 1-2 where necessary. This pH adjustment was performed by determining the volume of acid or base required to achieve the required pH using matrix matched standards. All other P measurements (CDB, ammonium oxalate and CDA) were analysed on a Thermo Fisher iCAP 7400 Radial ICP-OES, due to interference between the solution matrix and the phosphomolybdate complex (see Supplementary

Information for the ICP-OES method parameters). All Fe analyses were performed by flame atomic absorption spectroscopy (AAS). The reproducibility of Fe and P extractions were determined by replicate analyses, and are reported in terms of the relative standard deviation (RSD) at appropriate points in the text below.

Digests were also performed for the determination of total P and Fe via a HNO_3–HF–$HClO_4$ extraction on ashed samples. After evaporating to dryness, samples were redissolved in hot 50% (v/v) HCl, and P was analysed via the molybdate blue method outlined above, while Fe was analysed by AAS. The precision and accuracy of the method were determined by replicate analyses of the SBC-1 USGS international sediment standard, with RSD's of 5.5% and 4.0% for Fe and P, respectively, and with near-complete recovery for both elements (96% and 97%, respectively).

3. Results and Discussion

3.1. Testing the original SEDEX method for the extraction of Fe (oxyhydr)oxides

The extraction of synthetic ferrihydrite, goethite and lepidocrocite via a single 8 h CDB solution, as performed in the first step of the original SEDEX procedure, led to a recovery of 90-100% for all three minerals (Figure 2), in agreement with Ruttenberg (1992). However, when applied to our synthetic hematite and magnetite/hematite composite samples, the CDB extraction dissolved only 18.4 ± 0.7% of the total Fe in hematite, and only 5.6 ± 0.1% of the Fe in the magnetite/hematite sample. In the latter case, the majority of the dissolved Fe was likely from the dissolution of hematite. Recovery of Fe from the magnetite with co-precipitated P was higher, at 17.9 ± 2.2%, most likely due to the freshly precipitated nature of the mineral. However, despite this higher Fe recovery, only ~0.1% of the P contained in the co-precipitate was extracted by the CDB. No previous data for the efficiency of magnetite dissolution by CDB has been published for comparison. The extraction efficiency for crystalline hematite was substantially lower than that found by Ruttenberg (1992), and the poor recovery for both minerals confirmed that the original SEDEX method does not efficiently extract the more crystalline Fe oxides that are often key components of ancient sedimentary rocks and Fe-rich sediments. By contrast, a 2 h CDA extraction dissolved 59.7 ± 3.5% of our synthetic hematite mineral, which increased to 86.0 ± 0.7% with a 6 h CDA extraction (Figure 2), consistent with data highlighting the resistant nature of crystalline hematite (Canfield et al., 2007; Raiswell et al., 1994). Thus, the 6 h CDA extraction was considered the most appropriate extraction for this phase. This 6 h CDA extraction did, however, dissolve 16.1 ± 0.5% of the magnetite present in our composite magnetite/hematite sample, suggesting that the CDA extraction should be performed after the 6 h oxalate extraction, which dissolved 100.0 ± 1.6% of the magnetite Fe (Figure 2).

To assess the extraction efficiency of the original SEDEX method in terms of the dissolution of crystalline Fe (oxyhydr)oxide minerals, we compared the amount of Fe extracted by CDB (Ruttenberg, 1992) and CDA (Poulton and Canfield, 2005) for Golfo Dulce sediments and Animikie Basin sedimentary rocks (Figure 3). In both cases, the CDB extraction dissolved a lower concentration of crystalline Fe (oxyhydr)oxide phases relative to the CDA extraction (Figure 3). In addition, when the Fe_{mag} pool was added to Fe extracted by CDA (Figure 3), it is clear that the original SEDEX method failed to extract a large proportion of the crystalline Fe (oxyhydr)oxide minerals, and this was the case for both modern sediments and ancient sedimentary rocks.

3.2. A revised method for P speciation in ancient sedimentary rocks

Having demonstrated the limitations of the existing SEDEX technique for extracting more crystalline Fe (oxyhydr)oxide phases, the next step was to consider the optimal position for the additional extractions in the sequential P method. The CDA and ammonium oxalate extractions were performed at low pH (4.8 and ~2, respectively), and hence it was not appropriate to perform these extractions prior to the pH 4.0 Na acetate extraction (which targets P_{auth}) in the SEDEX scheme (Figure 1). It was essential to retain the CDB extraction for the first step of the revised scheme in order to dissolve the most reactive Fe (oxyhydr)oxide minerals (hereafter termed P_{Fe1}) prior to extraction by Na acetate (P_{auth}; Figure 4). This leaves the more crystalline Fe (oxyhydr)oxide minerals, since the Na acetate extraction only dissolved a minor amount of hematite and magnetite (Figure 5; see also Poulton and Canfield, 2005). Sequential extraction of our synthetic hematite and magnetite/hematite composite samples using the original SEDEX method revealed that these minerals were not appreciably dissolved by the 1 M HCl extraction used to target P_{det} (Figure 5).

By contrast, we found that ammonium oxalate dissolved ~17% of P in the natural apatite sample from Madagascar. Thus, the ammonium oxalate and CDA extractions to determine magnetite-bound P (hereafter termed P_{mag}) and crystalline Fe (oxyhydr)oxide-bound P (hereafter termed P_{Fe2}) were placed after the 1 M HCl of the original SEDEX procedure. Furthermore, given that a 6 h CDA extraction dissolved appreciable magnetite (Figure 2), the 6 h CDA extraction was placed following the P_{mag} extraction.

This results in the revised extraction scheme detailed in Figure 4. To test our revised scheme we first compared recoveries for our synthetic hematite and magnetite/hematite composite samples relative to recoveries from the original SEDEX scheme (Figure 5). Replicate analyses (n = 3) for synthetic hematite via the revised scheme gave RSD’s of 3.4% (8 h CDB), 6.4% (Na acetate), 1.0% (1 M HCl), 1.4% (ammonium oxalate), and 10.4% (CDA). The addition of the oxalate and CDA extraction in the revised scheme considerably enhanced the total recovery of magnetite and hematite (88.7 ± 1.1% and 76.9 ± 3.8%, respectively), relative to the original scheme (Figure 5). The natural Isua BIF sample also showed a good recovery via the revised method (data not shown), with the P_{mag} step extracting 45.8 ± 3.0 wt% Fe, which was in good agreement with our separate determination (see earlier) of 43.8 wt% Fe_{mag} in this sample. We took this evaluation a step further by testing the ability of the ammonium oxalate extraction to recover P from magnetite, as this was one P phase that was not tested during development of the original SEDEX technique (Ruttenberg, 1992). Replicate extractions recovered 93.9 ± 1.7% of the Fe present as magnetite and 88.2 ± 12.8% of co-precipitated P, confirming the utility of this extraction for the determination of P_{mag}.

We note here that it has been suggested that the solubility of authigenic carbonate fluorapatite (i.e., P_{auth}) may decrease during burial diagenesis, due to recrystallization (Shemesh, 1990; Slomp, 2011). This would make the primary authigenic CFA phase less prone to dissolution by its target extractant (Na acetate; Figure 4). In this case, recrystallized P_{aut} that was not extracted by Na acetate would likely be extracted as part of the detrital apatite pool (i.e., P_{det}) (Creveling et al., 2014). This is a difficult problem to address with sequential extraction schemes, which are clearly operationally-defined, but as discussed below this issue should be considered, particularly when applying the revised scheme to ancient rocks. As such, in Figure 4 we reflect this possibility by redefining the original P_{det} pool as P_{cryst}.

3.3. Application to modern and ancient sediments

After confirming that our revised method resulted in an enhanced recovery of crystalline Fe (oxyhydr)oxide minerals, we then applied the technique to determine P partitioning in Golfo Dulce (Figure 6) sediments and in our suite of ancient sediments (Figure 7) (all data are reported in the Supplementary Information). The RSD's for P extracted by each stage of the revised method are presented in Table 3. In addition, the sum of the P extracted by the revised method had a RSD of 1.8%.

Figure 6A shows that for the modern Golfo Dulce sediments, a major proportion of total P was associated with the less crystalline Fe (oxyhydr)oxide pool (P_{Fe1}; average = 41.0 ± 2.6%), which was consistent with the high Fe (oxyhydr)oxide content (Fe_{ox} = 2.45 ± 0.24 wt%; Fe_{mag} = 0.72 ± 0.07 wt%) of these sediments (Figure 3). Importantly, however, the addition of the new Fe extraction steps increased the total recovery of Fe-bound P by up to 16%. P_{cryst} was low throughout these samples, and thus the overall speciation of P as a function of 'reactive' P (which is here calculated as the sum of P_{Fe1} + P_{auth} + P_{mag} + P_{Fe2} + P_{org}), is similar to that for total P (Figure 6).

The ancient sediments showed considerable variability in the partitioning of P (Figure 7A). P_{org} was particularly high in the North China Craton and Saltwick Nab samples, highlighting that P_{org} can be retained in ancient rocks that have experienced deep burial diagenesis and minor metamorphic alteration. The total proportion of Fe-bound P was relatively low in the Animikie Basin, Timan Region and Saltwick Nab sedimentary rocks, consistent with the generally low Fe (oxyhydr)oxide contents of these rocks (Animikie Basin: Fe_{ox} = 0.17 ± 0.07 wt%, Fe_{mag} = 0.24 ± 0.24 wt%; Timan Region: Fe_{ox} = 0.46 ± 0.28 wt%, Fe_{mag} = 0.48 ± 0.06 wt%; Saltwick Nab: Fe_{ox} = 0.06 wt%, Fe_{mag} = 0.10). However, the North China Craton samples showed that Fe-bound P can be a major constituent of the total P pool in ancient rocks, with up to 76% of total P occurring as Fe-bound P, of which an average of 22% would not have been extracted using the original SEDEX scheme. As with the other ancient samples, Fe (oxyhydr)oxide contents are relatively low for the North China Craton samples (Fe_{ox} = 0.37 ± 0.23 wt%, Fe_{mag} = 0.06 ± 0.02 wt%). However, these samples are distinct from the other ancient samples in that their Fe (oxyhydr)oxide contents, while low in absolute concentration, are high relative to the total pool of highly reactive Fe (Fe_{HR}). Highly reactive Fe includes Fe (oxyhydr)oxides (i.e., Fe_{ox} and Fe_{mag}), in addition to reduced Fe phases such as siderite (Fe_{carb}) and pyrite (Fe_{py}) which, at least partially, formed via the reductive dissolution of Fe (oxyhydr)oxides during diagenesis (Raiswell and Canfield, 1998; Poulton et al., 2004a). Thus, generally higher (Fe_{ox} + Fe_{mag})/Fe_{HR} ratios for the North China Craton (0.92 ± 0.03), compared to the Animikie Basin (0.23 ± 0.12), Timan Region (0.79 ± 0.09) and Saltwick Nab (0.06) samples, suggests significant preservation during diagenesis of the Fe (oxyhydr)oxide minerals that were originally delivered to the sediment. In consequence, it appears that a significant proportion of primary P_{Fe} was preserved in the North China Craton sediments, which is also supported by the low P_{auth} content of these samples relative to the other ancient samples (Figure 7). This further highlights the utility of the revised phosphorus extraction scheme for evaluating the diagenetic cycling of P in ancient marine sediments.

In contrast to the North China Craton sediments, the P_{auth} fraction comprised a major proportion of the total P content of the Timan Region (54 ± 7%) and Saltwick Nab (56%) sediments (Figure 7), which is consistent with the 'sink switching' of reactive P observed in modern continental margin sediments (Ruttenberg and Berner, 1993). While the North China Craton samples have clearly not experienced significant transfer of reactive P to detrital P during burial diagenesis and metamorphism (Figure 7), we also note that the concentrations of P_{cryst} in the Timan Region (174 ± 28 mg/kg) and Saltwick Nab (149 mg/kg) sediments are consistent with concentrations of detrital P commonly found in modern continental margin sediments (e.g., 186 ± 21 mg/kg; Ruttenberg and Berner, 1993). Thus, while we cannot discount the possibility of some transfer of P_{auth} to P_{cryst} in these ancient settings, this appears to have been mininal. However, the Animikie Basin sediments are characterised by proportionately less, and highly variable, P_{auth} (23 ± 20%; range = 5-61%), combined with much higher proportions (73 ± 21%) and concentrations (433 ± 189 mg/kg) of P_{cryst} (this average excludes sample GF3-33 due to its anomalously high P_{cryst} concentration; see SI Table 3). Thus, while we cannot rule out the possibility that the delivery of detrital P may have been elevated during deposition of these particular sediments, these P speciation characteristics do suggest probable transformation of an important fraction of P_{auth} to P_{cryst}. This possibility will be of particular significance in studies where quantification of the initial P_{reac} pool is required, although we stress that the P_{org} and P_{Fe} fractions should remain largely unaffected after the 'sink switching' that occurs during early diagenesis is complete. We therefore suggest a general protocol whereby P_{reac} in ancient sediments is considered to fall within a minimum and maximum range. Here, a minimum value for P_{reac} may be calculated as the sum of P_{Fe1} + P_{auth} + P_{mag} + P_{Fe2} + P_{org}, whereas a maximum value is calculated by additionally including the P_{cryst} pool.

The ability to quantify magnetite-bound P is a novel strength of the revised speciation scheme. Over the last few years there has been increasing recognition of the major prevalence of anoxic ferruginous oceanic conditions across large periods of Earth history (e.g., Canfield et al., 2008; Guilbaud et al., 2015; Johnston et al., 2010; Planavsky et al., 2011; Poulton and Canfield, 2011; Poulton et al., 2010). Whilst nutrient reconstructions under such conditions have tended to focus on P uptake by Fe (oxyhydr)oxide minerals (e.g., Bjerrum and Canfield, 2002; Konhauser et al., 2007; Planavsky et al., 2010), magnetite often appears to be a prominent mineral in the deposited sediments (e.g., Poulton et al., 2010), and likely commonly occurs via transformation from green rust precursors (e.g. Halevy et al., 2017; Li et al., 2017). Green rust has a particularly large adsorptive capacity for nutrient uptake (e.g., Zegeye et al., 2012), and transformation to magnetite may result in significant retention of P, which raises the possibility of using magnetite-bound P in ancient shales as a tracer of past variability in oceanic P concentrations (c.f., Bjerrum and Canfield, 2002; Konhauser et al., 2007; Planavsky et al., 2010).

4. Conclusions

The SEDEX sequential P extraction scheme of Ruttenberg (1992) is the commonly used technique for quantifying different P pools in modern marine sediments, and has provided a wealth of information of P cycling in modern environments. However, the original SEDEX scheme was not designed for use with ancient sediments. Here, we provide a modification of this method to more specifically target important Fe phases, such as crystalline hematite and magnetite, which are common components of many ancient sediments and some Fe-rich modern sediments. We demonstrate that crystalline hematite was only partially extracted by the existing SEDEX scheme, while magnetite was not specifically targeted. Following robust calibration testing, we introduce two additional steps to the SEDEX scheme to specifically target these additional Fe-bound P phases. Testing of the revised method on modern and ancient sediments showed the reproducible nature of the extractions and the enhanced recovery of Fe-bound P. We provide details of a modified P SEDEX scheme specifically developed for application to ancient marine rocks, as well as modern Fe-rich sediments. We demonstrate that the P_{org}, P_{Fe1}, $P_{Fe2,}$ P_{mag} and P_{auth} fractions may provide insightful information in relation to P cycling in ancient marine settings and in Fe-rich modern sediments, but care needs to be taken with ancient rocks when considering possible transfer of authigenic P (P_{auth}) to more crystalline phases (P_{cryst}) during deep burial and metamorphism.

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