CHAPTER

4.7.3

Phosphorus bioavailability

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Introduction

Our discussion of the biogeochemical phosphorus (P) cycle begins with the stoichiometry of biological reactions. At its metabolic core, primary production is the reduction of inorganic carbon (CO_2) to organic carbon (approximated by CH_2O) and oxidation of a byproduct (electron donor). Prior to the advent of oxygenic photosynthesis, the most common electron donors for microbial metabolisms were H_2, H_2S, Fe^{2+}, or organic matter itself. It is typically surmised that the flux of these reductants to surface environments limited the productivity of the biosphere during this time (Kharecha et al., 2005; Canfield et al., 2006; Ward et al., 2019).

At some point in the early evolution of life—although exactly when is debated (Buick, 2008; Fischer et al., 2016)—the invention of oxygenic photosynthesis radically changed biological productivity. By using H_2O as an electron donor—an extremely abundant molecule at Earth's surface—productivity was no longer hampered by reductant fluxes. Instead, this likely ushered in the era of nutrient-limited productivity. Here, "nutrient" means a constituent of biomass (i.e., assimilatory rather than dissimilatory reactions became limiting). Beyond C, H and O, the next most abundant elements in biomass are N and P, respectively. As noted in the previous chapter, N can be microbially "fixed" from atmospheric N_2 into bioavailable form. Thus, as the most abundant bioessential element that lacks a gaseous or aqueous reservoir at Earth's surface, P is accordingly viewed as the ultimate rate-limiting reactant for biological productivity (Holland, 1984; Tyrrell, 1999). In other words, slow P supply via rock weathering struggles to match the atmospheric/oceanic availability of C, H, O, and N.

In the modern ocean, P limitation is manifest in the concentrations of C, N and P. In the open ocean, these elements are present in a ratio of approximately 106:16:1 (Redfield, 1963). While local factors can modulate this ratio, the stable global average reflects the steady-state impact of P limitation, with microbial N fixation keeping pace (Tyrrell, 1999). This ratio reflects a balance between the geological process of P supply to seawater, the biological processes of P incorporation into biomolecules and P recycling within the ocean, and the geological process of P removal from the ocean via burial in sediments. In the Archean, nearly all of these processes are likely to have operated differently, due to planetary evolution impacting climate conditions, tectonic mode, and the origin and evolution of life. It is thus widely appreciated that the Archean P cycle probably looked quite different from what it does today. Here, we summarize the learnings about the Archean P cycle through decades of experiment-, field-, and modeling-based studies. As the biosphere is thought to have been dominantly marine in the Archean (Planavsky et al., 2021), we focus our attention on the delivery of P to seawater, cycling within the ocean, and removal to sediments.

Sources of phosphorus to the Archean ocean

As mentioned above, most P at Earth's surface is present in mineral form. A P "source" to an aqueous environment is thus any process that solubilizes P. Here we discuss potential Archean P sources, considering their relative magnitude and how they may have changed through time.

Crustal weathering

The dominant source of P to modern seawater is weathering of P-bearing minerals in the crust (Ruttenberg, 2003). The rate of bioavailable P delivery to the ocean from crustal weathering depends on many

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factors, including: (1) climate, (2) P host phases in exposed crust, (3) exposure of material for weathering and erosion, (4) biological and chemical conditions in fluvial environments, and (5) the sign and magnitude of the P flux during oceanic crust alteration. Each of these conditions likely changed from the Archean to the present, and we individually consider the impact of these changes on P weathering below.

Climatic impacts on chemical weathering of the continents

The rate of chemical (i.e., silicate) weathering of the continental crust has long been viewed as a function of temperature and $p\mathrm{CO}_2$ (Walker et al., 1981; Berner et al., 1983). Models of the Archean atmosphere and climate suggest high $p\mathrm{CO}_2$ and warm temperatures (Krissansen-Totton et al., 2018; Catling and Zahnle, 2020), implicating high rates of silicate weathering (Satkoski et al., 2016; Hao et al., 2017a). Some modeling studies have inferred ~10× higher rates of P weathering per unit area in the Archean than at present (Hao et al., 2017b, 2020a), with rates strongly dependent on $p\mathrm{CO}_2$, which affects the acidity of weathering environments and rivers. However, empirical constraints from major element geochemistry of paleosols (Dzombak and Sheldon, 2022) and shales (Lipp et al., 2021) point to fairly constant weathering intensity through geologic time. Thus, while higher Archean P weathering intensity is plausible, future work should aim to reconcile predicted P fluxes with the Archean rock record.

Dominant P host phases in weatherable material on continents

While $p\mathrm{CO}_2$ and temperature affect the rate of P liberation from the crust, their impact is constrained by the dominant P host phases. In many papers (e.g., Guidry and Mackenzie, 2000; Filippelli, 2002; Ruttenberg, 2003), including the modeling studies referenced above (Hao et al., 2017b, 2020a), apatite minerals are treated as the sole host phase of crustal P. While apatite indeed dominates the crustal P reservoir (80%–95%; Jahnke, 1992; Walton et al., 2021), silicate-hosted P is nonnegligible (5%–20%; Walton et al., 2021), most importantly including olivine-hosted P in mafic rocks. As olivine is more readily weathered than apatite, the prevalence of mafic versus felsic crust could influence the global rate of P weathering (Horton, 2015; Greber et al., 2017; Cox et al., 2018).

Reconstructions of crustal composition through time are fraught with uncertain models of tectonic evolution. Qualitatively, the exposed crust likely evolved toward a more felsic composition through Earth history due to the progressive impact of partial melting and crustal differentiation. The net impact of this secular trend on P weathering fluxes would depend on the relative impacts of P content (which is highest in intermediate magmatic rocks; Lee and Bachmann, 2014) and weatherability (which is higher in mafic than felsic crust). On top of this secular trend are transient perturbations. For instance, volcanism can act as a source of highly weatherable P to seawater (although the effects can be locally variable and even include depletion; Foreman et al., 2021), and transient intervals of volcanism have been hypothesized to have played a role in stimulating early oxygenation events via P delivery (Meixnerová et al., 2021).

In addition to P hosted in igneous and metamorphic rocks, the growth of the sedimentary rock reservoir on the continental crust would have provided more P-rich material for weathering (up to several wt.% P compared to ~0.1% avg. in magmatic rocks; Rudnick and Gao, 2003). Sedimentary P host phases include organic matter, diagenetic and detrital apatite, and Fe-associated P (Ruttenberg, 2003). Progressive growth of the sedimentary reservoir may thus have increased P delivery to the ocean through the Archean (Walton et al., 2023b).

Subaerial exposure of weatherable material

Besides the weathering rate per unit area, the total amount of exposed land area (and topographic variability) may have changed dramatically through Earth history. These reconstructions are highly debated, as they similarly rely on uncertain models of early tectonic evolution. Overall, the large spread in modeled Archean land exposure—from nearly zero subaerial land (Flament et al., 2008) to modern day exposure (Armstrong, 1981), and everywhere in between (e.g., Veizer and Jansen, 1979; Campbell, 2003)—creates a massive source of uncertainty that is superimposed on estimates of the total P flux to the ocean from continental weathering as modeled in the studies discussed above.

Secondary biological and chemical reactions during riverine transport

This will be discussed further in **Section 3**, but briefly: precipitation of secondary P-bearing minerals and/or P adsorption to particles can trap P upstream and diminish the riverine P flux to seawater. For instance, Hao et al. (2017b) considered the formation of secondary apatite and vivianite, but found in their simulations that the low pH of Archean river water muted the formation of these phases. The low Eh of Archean fluvial environments would have precluded extensive Fe (hydr)oxide formation, meaning reduced Fe phases would be the most pertinent to consider as potential P traps. Of these, vivianite (hydrated Fe^{2+} phosphate) was revisited by Brady et al. (2022), who found it to be highly soluble under plausible Archean conditions (high $p\mathrm{CO}_2$, high Fe^{2+}, and low $p\mathrm{O}_2$). Thus, fluvial P trapping may have been less common in the Archean than at present.

Sign of oceanic crust alteration

Lastly, while the sections above focus on continental crust, seafloor weathering (i.e., oceanic crust alteration) may have also been a P source in the past. Today, hydrothermal alteration of oceanic crust is a minor P sink (Wheat et al., 1996), constituting 2%–3% of P removal from seawater per year (Ruttenberg, 2003). However, due to changes in crustal composition (higher proportion of ultramafic crust in Archean) and ocean chemistry (anoxic Archean deep ocean), these settings may have instead acted as a P source to Archean seawater (Syverson et al., 2021), in part due to greater rates of serpentinization that partially reduces phosphate to the more soluble form phosphite (Pasek et al., 2022), but ultimately limited in global magnitude by the extent of seafloor hydrothermal systems (Filippelli, 2022). Whatever the size of this flux, it is possible that seafloor basalt alteration provided additional P to the Archean ocean; it is worth noting that changes in the P source/sink from seafloor weathering have also recently been invoked as important for the Phanerozoic P budget (Sharoni and Halevy, 2023).

Meteorites (i.e., “extraterrestrial weathering”)

Besides weathering of Earth’s crust, the delivery of weatherable extraterrestrial material may have at times constituted a nonnegligible source of P to the Archean ocean. While apatite is the dominant P-bearing phase in chondrites, iron meteorites are dominated by schreibersite (iron nickel phosphide) (Pasek and Lauretta, 2008), which constitutes roughly half of all estimated extraterrestrial P influx (Walton et al., 2021). Since aqueous corrosion of schreibersite readily yields reactive dissolved P (Pasek and Lauretta, 2005)—which has been shown to facilitate prebiotic reactions (Pasek et al., 2007; Gull et al., 2015)—iron meteorites could have been an important source of P to the nascent Archean biosphere. However, as the Archean extraterrestrial P flux is estimated at $<10^6$ g/yr (Pasek and Lauretta, 2008), this is unlikely to have rivaled crustal weathering as a sustained source of P to the global biosphere (Fig. 4.7.3.1).

Lightning

Due to their high energy, lightning strikes can split molecular bonds and alter chemical speciation in ways that are difficult to achieve metabolically. This is true for N fixation, as lightning splits the triple bond in N_2 gas and creates bioavailable N ions. Similarly, in modern fulgurites (shock-heated glassy conglomerates created by lightning strikes), lightning generates the reduced P phases phosphide (P^{3-}) and phosphite (P^{3+}) from original phosphate (P^{5+}) (Pasek and Block, 2009). The production of reduced P phases is potentially important in terms of P supply to the nascent or early biosphere, as such phases are more reactive and soluble than phosphate minerals (Pasek, 2008).

On the modern Earth, it has been estimated that lightning strikes supply ~10^6 g/yr of reduced P to surface environments (Pasek and Block, 2009). Even allowing for changes in lightning frequency and subaerial landmass between the Archean and present (Hess et al., 2021), this represents a ~10^5 times smaller flux than modern

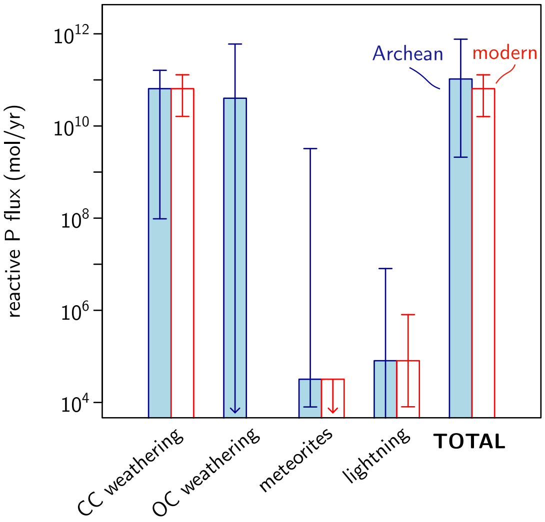

FIGURE 4.7.3.1 **Summary of published P source fluxes to Archean and modern seawater**. Dominant P sources are continental crust (CC) weathering (Meybeck, 1982; Ruttenberg, 2003; Hao et al., 2020a), oceanic crust (OC) weathering (Krissansen-Totton et al., 2021; Syverson et al., 2021), meteorites (Pasek and Lauretta, 2008), and lightning (Pasek and Block, 2009). Unless the emergent land area was very low, continental weathering has likely dominated global P supply to the ocean throughout Earth’s history. OC weathering is a P sink on the modern Earth (Ruttenberg, 2003).

continental weathering (Fig. 4.7.3.1). Thus, while potentially a locally important source of P to the early biosphere, or to prebiotic reactions, lightning is unlikely to have supplied appreciable P to the Archean ocean.

Summary: sources of P to the Archean ocean

We close by compiling the above estimates of Archean P source fluxes. Superimposing the estimated ranges and associated uncertainty leaves open both the possibility of greater- and less-than-modern P delivery fluxes to seawater (Fig. 4.7.3.1). The sources of uncertainty that would best be minimized with future studies include: (1) aerially-exposed continental land mass area and topography, and (2) impact of secondary reactions during P transport. In comparison, P source fluxes from meteorites (i.e., extraterrestrial weathering) and lightning are much smaller, and while perhaps important locally, did not contribute substantially to global P supply unless crustal weathering was very limited.

Cycling of phosphorus within the Archean ocean

Upon reaching seawater, P undergoes numerous abiotic and biotic chemical reactions. In this section, we consider P behavior in Archean seawater, focusing on its bioavailability.

Aqueous P speciation

The first question about P in Archean seawater concerns the dominant aqueous species. At surface conditions, even across the plausible range of seawater pH and Eh, P is most stable as phosphate (P^{V}) and dissociates into the anions $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}, as well as forms complexes with Mg^{2+}, Na^+, Fe^{2+} and Ca^{2+} (Ruttenberg, 2003). It is thus typically assumed that phosphate has been the dominant marine P species throughout Earth history.

Despite the thermodynamic stability of phosphate, some have inferred a nonnegligible role of phosphite (P^{III}) as an aqueous P species (HPO_3^{2-}) in Archean seawater (e.g., Pasek, 2008). As discussed above, certain P delivery routes, namely serpentinization, weathering of meteorites and lightning strikes, can provide P to seawater as reduced P. Reduced P has been invoked as a solution to the "phosphate problem" in the origin of life (Pasek et al., 2017), and is supported by the detection of phosphite in Archean carbonates (Pasek et al., 2013). Thus, while phosphate is likely to have always been the dominant stable phase for P dissolved in seawater, reactive phosphite may have locally and transiently played important roles in Archean biogeochemistry.

Abiotic chemical scavenging and precipitation

We now consider the controls on P concentrations in seawater, beginning with abiotic reactions. Phosphate adsorbs onto Fe (hydroxy)oxide minerals near modern hydrothermal systems (Berner, 1973), with the P/Fe ratio in settling particles set by ambient $[PO_4^{3-}]$ (Feely et al., 1998). Lower-than-modern P/Fe in Archean iron formations (IF's) was thus originally viewed as evidence of low-P seawater (Bjerrum and Canfield, 2002). This has been interpreted as reflecting intense scavenging of P from seawater by Fe (hydroxy)oxides during IF deposition (Bjerrum and Canfield, 2002; Alcott et al., 2022). While P scavenging onto Fe (hydroxy)oxides would be less effective in a high-silica ocean (Konhauser et al., 2007), Jones et al. (2015) demonstrated that scavenging would still occur under realistic Archean seawater compositions (i.e., considering Fe, P, Si, Mg, and Ca concentrations).

While it is thus demonstrated that Fe (hydroxy)oxides can scavenge P from seawater, recent work has highlighted the likely importance of Fe^{2+}-bearing phases in Archean IF genesis (Rasmussen et al., 2013, 2015; Halevy et al., 2017; Konhauser et al., 2017). Modern environmental studies have found that these phases can also scavenge P, with vivianite forming in ferruginous lake sediments (Vuillemin et al., 2020) and green rust also scavenging phosphate from solution (Hansen and Poulsen, 1999; Zegeye et al., 2012). Thus, the "Fe-scavenging" hypothesis has been recapitulated to include reduced Fe minerals removing aqueous P from Archean seawater (Derry, 2015; Reinhard et al., 2017; Hao et al., 2020b). It should be noted, however, that recent work has demonstrated greater vivianite solubility under Archean ocean conditions than previously expected (Brady et al., 2022), meaning P may not have been so widely scavenged by Fe minerals.

If P levels were not low due to Fe scavenging, it is plausible that apatite precipitation acted as an upper limit on dissolved P. Apatite is present in some of the oldest metasediments on Earth (Mojzsis et al., 1996; Lepland et al., 2002), and some authors have proposed that apatite precipitation from seawater occurred spontaneously in a high-P (10–100 μM) Archean ocean (Rasmussen et al., 2021, 2023). While such high P levels seem inconsistent with the lack of Archean phosphorites (Papineau, 2010), high concentrations of carbonate-associated phosphate (CAP) in Archean carbonates have been interpreted as supporting high dissolved phosphate concentrations in seawater (Ingalls et al., 2022). It should be noted that changes in temperature, pH, and [Ca]:ALK all potentially confound $[PO_4^{3-}]$ reconstructions using CAP in ancient carbonates (Crockford and Halevy, 2022), as does variable sampling of microtextures (e.g., herringbone calcite cements and microspar are less prone to “nugget” effects from microapatites than micrite; Richardson et al., 2022). For these reasons, existing Archean CAP data do not definitively rule out low ambient phosphate. In summary, to resolve the ambiguity about the role of apatite precipitation in controlling Archean dissolved phosphate levels, further study of P distribution in Archean marine sediments is required.

Biological P uptake and recycling

While abiotic reactions set a backdrop for P behavior in seawater, P cycling in the modern ocean is strongly modulated by the biosphere. The same may have been true in the Archean following the origin of life (Jusino-Maldonado et al., 2022; Walton et al., 2023a). Here, we separate our discussion of biological P reactions into two regimes, the transition between which may have occurred in the early Archean (or Hadean): the prebiotic and biological P cycle.

Prior to the origin of life, P abundance in seawater would have been controlled by the abiotic reactions described above. A long-recognized problem in origin-of-life research is termed the “phosphate problem”: how did P come to feature so prominently in biomolecules such as ATP, DNA, and phospholipids if phosphate is readily removed from solution by abiotic reactions at fairly low concentrations? Indeed, solutions to the “phosphate problem” typically invoke scenarios that circumvent the abiotic reaction pathways described above. For instance, alkaline lakes may have been viable habitats (Toner and Catling, 2020), since low [Ca]/ALK ratios allow high phosphate concentrations by inhibiting apatite precipitation. Other work has suggested that the “phosphate problem” was in fact not as severe as often imagined, either because highly reactive P sources could locally satisfy prebiotic P demand (Pasek et al., 2017), or P sinks (e.g., vivianite; Brady et al., 2022) were not as effective as previously thought (Fig. 4.7.3.2a). In any case, life eventually emerged and harnessed P in biomolecules, ushering in an entirely different regime (Fig. 2b-***d***) where seawater P availability would have become strongly impacted by biological uptake rather than solely by abiotic scavenging (Jusino-Maldonado et al., 2022).

Following the origin of life (Fig. 4.7.3.2b), the imprint of the biosphere on the marine P reservoir would have depended on a few variables. First is the stoichiometry of biomass, as the removal of P from seawater per mole of biomass (i.e., C) depends on the C:P ratio of primary producers. While modern marine phytoplankton have C:P of ~106:1 (Redfield, 1963), under low-P conditions, cyanobacteria can shift to C:P of >400:1 (White et al., 2006) by reducing membrane phospholipid content and minimizing cellular RNA storage. Models of Archean biological P cycling thus sometimes invoke elevated C:P of >106 (Planavsky, 2014; Reinhard et al., 2017).

The second relevant variable is the rate of P recycling within the ocean. Today, >99% of biomass (and its P) is recycled within the ocean (Hedges and Keil, 1995; Ruttenberg, 2003; Schlesinger and Bernhardt, 2013; Middelburg, 2019). This recycling is mediated by the heterotrophic oxidation of biomass, which occurs dominantly aerobically in modern seawater, although anaerobic remineralization pathways are significant in sediment porewaters (Canfield et al., 1993). Since oxygen exposure time is the dominant variable controlling the extent of organic matter remineralization (Hartnett et al., 1998), and dissolved oxygen was likely low in Archean seawater, it is typically inferred that anoxic Archean marine sediments had higher-than-modern organic burial efficiency (i.e., lower remineralization) (Katsev and Crowe, 2015; Laakso and Schrag, 2018; Kipp et al., 2021). Furthermore, not only was O_2 scarce, but so too was sulfate (Crowe et al., 2014), implying that anaerobic remineralization pathways would have also been restricted (Kipp and Stüeken, 2017). The net result is that P recycling within the Archean ocean was likely quite limited compared to today, meaning organic carbon would have been more efficiently buried following primary production.

The third and final variable is the rate of primary productivity (i.e., the total biological P demand). This depends on whether oxygenic photosynthesis had yet evolved. Prior to the advent of oxygenic photosynthesis (Fig. 4.7.3.2c), if primary productivity was limited by electron donors (Kharecha et al., 2005; Canfield et al., 2006; Ward et al., 2019), steady-state marine phosphate levels could have been high, or at least buffered by abiotic reactions, since the biological demand may have been limited if electron donors were in short supply. The P demand would thus scale with the ratio of electron donor supply to P supply; as an example, for photoferrotrophy, Fe^{2+} must have been upwelled in a >400 Fe:P ratio to avoid P limitation given its 4:1 Fe:C stoichiometry and a ~106:1 C:P ratio (Jones et al., 2015). Following the invention of oxygenic photosynthesis (Fig. 4.7.3.2d), P likely became the limiting nutrient, and due to the limited P regeneration noted above, seawater phosphate concentrations would likely have been kept low.

Burial of phosphorus in Archean marine sediments

We finally consider the burial of P in marine sediments. This is the archive with which we are left to study

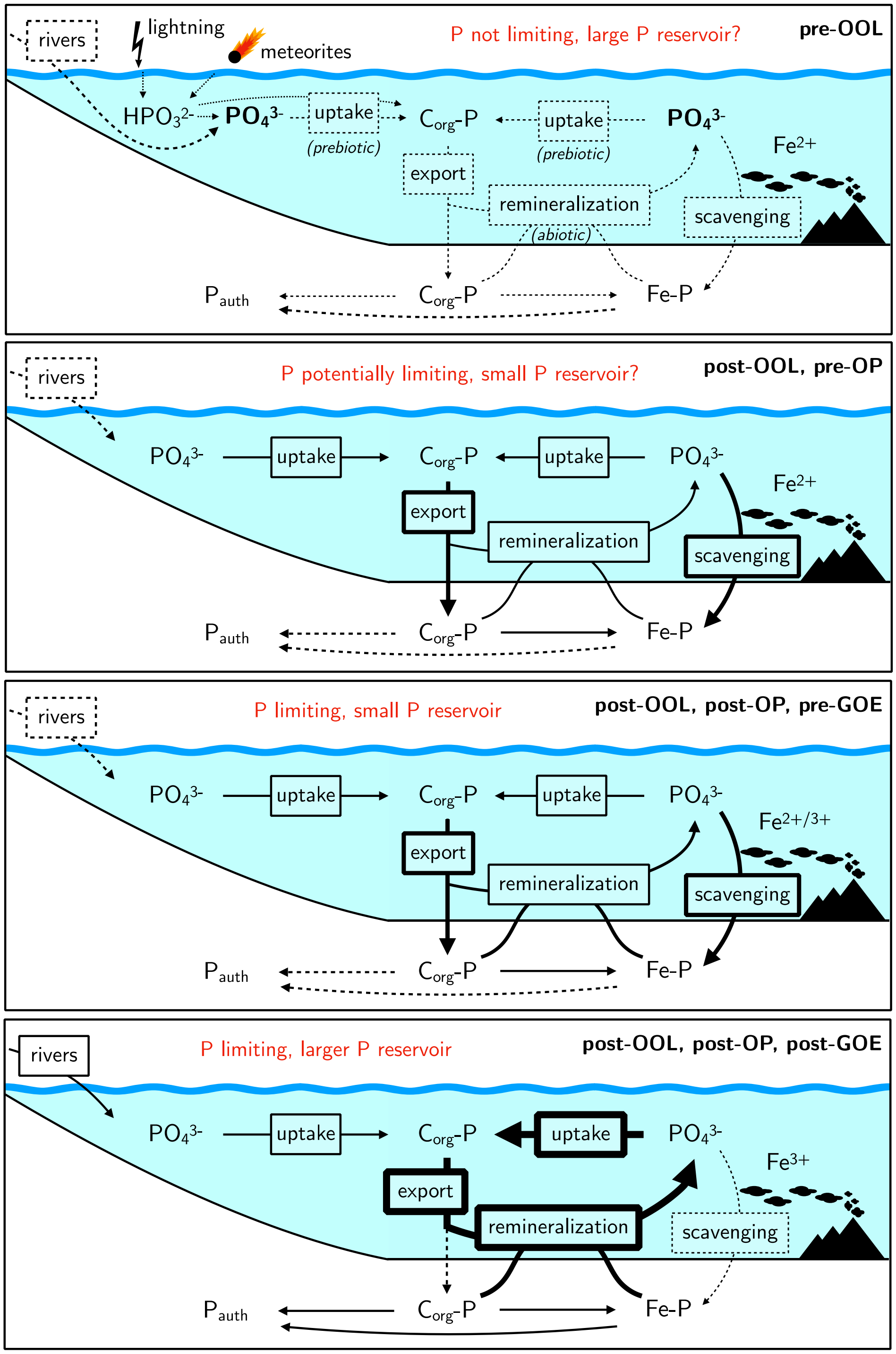

FIGURE 4.7.3.2 **Evolution of the Archean phosphorus cycle**. Flux arrows denote relatively larger fluxes moving from dashed to thin, solid to thick, solid lines. Dissolved phosphorus may have been readily available in seawater for prebiotic organic reactions prior to the origin of life, due to a lack of efficient sinks. In contrast, the emergence of biological P uptake/export and Fe^{3+} or mixed-valence Fe mineral sinks would have limited P bioavailability. A crucial transition was the emergence of oxygenic photosynthesis, since which point P has likely limited marine primary productivity. Growth of the marine oxygen and sulfate reservoirs after the GOE (in the early Paleoproterozoic) would have facilitated P recycling (Alcott et al., 2022), thus extending the P residence time and allowing greater primary productivity. *GOE*, great oxidation event; *OOL*, origin of life, *OP*, oxygenic photosynthesis.

the Archean P cycle. Thus, understanding the processes that governed P burial in these sediments is key to using these archives to reconstruct ancient P cycling. Unfortunately, diagenetic transformations within sediments render sedimentary P dynamics complicated. Here we unpack some of this complexity and discuss interpretations of Archean sedimentary P records.

What was the dominant source of P to Archean marine sediments?

We first consider the vectors which brought P to Archean marine sediments. Today, most P reaches marine sediments via the biological pump (Ruttenberg, 2003), with localized contributions from adsorption onto Fe (hydroxy)oxides. In contrast, some Archean depositional environments featured extreme Fe enrichment leading to deposition of IF's. In such settings, Fe phases may have dominated P supply to sediments (Bjerrum and Canfield, 2002; Alcott et al., 2022).

To initially discern the dominant routes of P supply to sediments, we turn to the stoichiometry of Fe-rich Archean sedimentary rocks. If Fe phases dominated P supply to sediments, a positive P versus Fe correlation might be observed, as in modern hydrothermal sediments (Fig. 4.7.3.3a). Indeed, some Archean IF's show strong P versus Fe correlations (Fig. 4.7.3.3a), but at lower P/Fe, implying lower dissolved P levels. Interestingly, higher P/Fe ratios are observed in late Archean to early Paleoproterozoic settings just before the GOE, potentially suggesting growth of the marine P reservoir.

Alternatively, if organic matter dominated P export to Archean sediments, a positive P versus TOC correlation may be observed. This latter relationship is, however, difficult to assess, since diagenesis and thermal maturation variably alter the primary C/P ratio. Archean sedimentary P concentrations are typically lower than those of the average continental crust (Fig. 4.7.3.3c) and have $C/P > 106$. Collectively, this either suggests some recycling of organic-bound P from sediments back to the water column or initially lower marine P concentrations and different phytoplankton stoichiometry, which will be further discussed below.

In summary, some settings show evidence of P delivery to sediments via Fe scavenging. While similar evidence for P delivery via the biological pump is lacking, diagenesis has likely obscured such relationships by altering the preserved C/P ratio. Thus, quantifying the relative contribution of P export pathways to Archean sediments remains challenging. However, efforts have been made to attempt to overcome these issues that are discussed below (Thompson et al., 2019; Alcott et al., 2022).

What were the dominant ultimate host phases for P in Archean marine sediments?

It is well-documented that after reaching sediments, P can undergo multiple diagenetic transformations before being sequestered in a phase that persists on geological timescales (Ruttenberg and Berner, 1993). A substantial portion of this "sink-switching" is the remineralization of organic P into porewaters, where it can adsorb onto Fe minerals, precipitate as authigenic apatite (or in some settings, vivianite), or diffuse into overlying waters. Transformations among inorganic phases also occur; for instance, Fe (hydroxy)oxides can dissolve due to a change in redox conditions, liberating adsorbed P to porewaters. The net result of sink-switching in modern sediments is that organic matter, Fe minerals and authigenic apatite represent the most important ultimate host phases for P, in sub-equal quantities, with nonnegligible contributions from detrital apatite in nearshore settings (Ruttenberg, 2003).

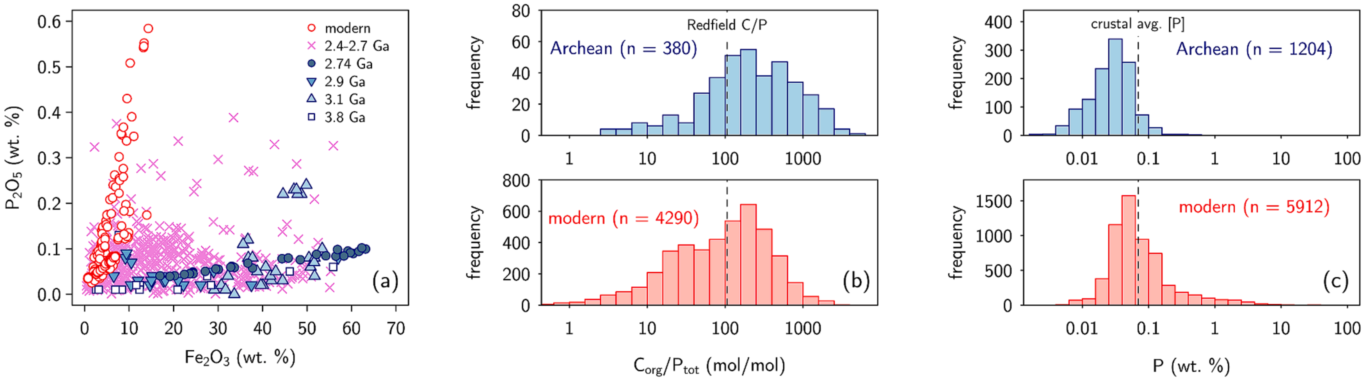

FIGURE 4.7.3.3 **P, Fe and TOC relationships in Archean and modern sediments**. (a) Comparison of modern (red circles; Lyle, 1986), late Archean-early Paleoproterozoic (purple crosses; Alcott et al., 2022), and earlier Archean (blue filled symbols; Rego et al., 2023 and refs. therein) P versus Fe data; (b) comparison of modern and Archean C/P data (Reinhard et al., 2017; Alcott et al., 2022); (c) comparison of modern versus Archean [P] data (Reinhard et al., 2017; Alcott et al., 2022), with crustal average from Rudnick and Gao (2003).

We pose two questions about P burial in Archean marine sediments. The first is: how much total P was buried compared to today? The answer depends on both the rate of P export (discussed above) and the rate of P release versus sequestration during diagenesis. It is known that modern anoxic sediments favor P release during diagenesis (Ingall and Jahnke, 1994), perhaps implying a similar recycling efficiency in the anoxic Archean ocean (Poulton, 2017). However, P release from anoxic sediments is also constrained by sulfate reduction [which drives organic remineralization and P release (Alcott et al., 2022), sequesters Fe in sulfides that don't efficiently adsorb P (Krom and Berner, 1980), and inhibits authigenic apatite precipitation (Papadomanolaki et al., 2022)]. Low sulfate in Archean seawater (Crowe et al., 2014) instead implies that more P would remain buried in sediments with restricted sink-switching (Kipp, 2022)—although high-temperature (>180°C) diagenesis in Fe-rich settings could reduce a minor fraction of phosphate to phosphite, modestly increasing the P flux back to seawater (Herschy et al., 2018). Despite high P burial efficiency, the total rate of P burial appears to have been muted, evidenced by lower-than-modern P concentrations in Archean siliciclastic sediments (Fig. 4.7.3.3c; Reinhard et al., 2017; Planavsky et al., 2023), Fe-rich sediments (Fig. 4.7.3.3a; Bjerrum and Canfield, 2002; Jones et al., 2015), and sediment-derived granites (Bucholz, 2022). This collectively suggests that the Archean P export flux to sediments was lower than at present.

The second question is: Did the relative proportions of P host phases differ in the Archean? For instance, if the scarcity of oxidants meant that organic remineralization was muted (Kipp and Stüeken, 2017), perhaps more P remained bound to organic matter. Additionally, if the marine P reservoir was small, and export production fluxes were correspondingly low, then perhaps porewaters rarely became saturated with respect to apatite—which is supported by the lack of Archean phosphorites (Papineau, 2010).

Recent work (Thompson et al., 2019) has adapted P sequential extraction protocols (Ruttenberg, 1992) and applied them to Precambrian marine sedimentary rocks. This approach separates operationally defined phases: organic-bound P, authigenic apatite and "crystalline" apatite, and several Fe-bound P phases (Thompson et al., 2019; Alcott et al., 2022). While such sequential extraction has proven critical for tracking sink-switching and dominant reactive P species in modern sediments, a limitation of its application to Precambrian rocks is that authigenic apatite has been recrystallized, moving it into the "crystalline" pool, which in modern settings is strictly detrital (Thompson et al., 2019). Thus, a predominance of crystalline apatite at the expense of other pools in late Archean sediments (Alcott et al., 2022) likely reflects the metamorphic history of these rocks rather than a change in sink-switching. While this metamorphic overprinting limits our ability to quantify sink-switching in Archean marine sediments, increases in C/P ratios (as well as C_{org}/P_{org} and $C_{org}/P_{reactive}$ ratios) in late Archean sediments (Alcott et al., 2022) imply an onset of P regeneration, likely tied to growth of the sulfate reservoir (as a consequence of the onset of oxidative weathering), which perhaps helped to initiate the GOE via a positive productivity feedback (Alcott et al., 2022; Kipp, 2022). Going further, this additional nuance in the Archean phosphorus cycle seen through the lens of P speciation highlights the role of both continental P sources and internal P recycling in the Archean ocean in regulating primary productivity (Alcott et al., 2022).

In summary, while P host phases can be quantified in Precambrian marine sedimentary rocks, their diagenetic and metamorphic history requires careful assessment in order to recover primary signals. This means that while we cannot simply quantify the relative role of various P host phases in modern versus Archean sediments, we can gauge the extent of sedimentary P recycling and its role in Earth history.

Conclusion

In summary, the Archean was a critical interval in the evolution of Earth's biogeochemical phosphorus cycle. The prebiotic Earth, while traditionally thought to have been P-limited, may have in fact had ample P bioavailability due to reactive P sources (Pasek and Lauretta, 2008; Pasek and Block, 2009) and/or inefficient abiotic sinks (Brady et al., 2022). The origin of life was the first major transition in the P cycle, ushering in an era of biologically-mediated P cycling (Jusino-Maldonado et al., 2022; Walton et al., 2023a). After the origin of life, while P availability would have continued to be impacted by abiotic factors (e.g., Fe scavenging), it would have also been regulated by the dominant autotrophic metabolisms. In a world of strictly anoxygenic phototrophs, P limitation may have codepended on Fe availability (Jones et al., 2015). Since the origin of oxygenic photosynthesis, P has likely limited productivity and been buffered in seawater by primary production.

Conspicuously, Archean sediments are low in P, and phosphorites are lacking in the Archean. The onset of phosphorite deposition after the GOE (Papineau, 2010; Lepland et al., 2013) and rise of P sink-switching (Alcott et al., 2022) implies a relationship between redox evolution and P cycling, either related to growth of the sulfate reservoir and enhanced remineralization (Kipp and Stüeken, 2017; Kipp et al., 2020; Alcott et al., 2022), movement of the S oxidation/reduction threshold to sediments where S-bacteria can facilitate phosphogenesis (Lepland et al., 2014), or changes in weathering/P burial due to climatic/tectonic forcings (Papineau, 2010). The factors controlling P delivery to Archean sediments and its subsequent burial remain controversial. Further field, lab and modeling studies are needed to connect the late Archean sedimentary record to a mechanistic understanding of P cycling and its cause–effect relationships with Earth's oxygenation.

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