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Key Points:

- P/Ca is higher in Neoproterozoic shallow marine carbonates than Phanerozoic and modern shallow marine carbonates
- Higher phosphate concentrations in Neoproterozoic than modern seawater indicates that early marine life was not phosphate-limited

Supporting Information:

Supporting Information may be found in the online version of this article.

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Carbonate-Associated Phosphate (CAP) Indicates Elevated Phosphate Availability in Neoproterozoic Shallow Marine Environments

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Abstract Phosphorus is essential for cell biology, yet scarce in modern marine environments wherein free phosphate is consumed by life or titrated by calcium to form apatite minerals. The environmental conditions under which the early biosphere emerged and phosphorus was integrated throughout biochemistry is yet unknown. We measured the phosphate concentrations of 2.8–2.5 Ga shallow marine carbonate facies across six Neoproterozoic shelf-ramp environments. We found that the P/Ca ratios of Neoproterozoic stromatolites, micrites, and crystal fans were >4-fold to 12-fold more enriched in carbonate-associated phosphate than modern marine coral skeletons and abiotic Phanerozoic carbonates. Our results support the view that Archean productivity was limited by the availability of electrons rather than phosphate or other nutrients, and help explain why phosphorus is so central to the molecules, metabolisms, and bioenergetics observed in cells.

Plain Language Summary Phosphorus is an essential element for life processes. Today, phosphorus is negligible in the surface oceans and exists in very low concentrations in the deep oceans, and thus is the primary limitation on net primary productivity. This circumstance sets up the paradox of why phosphorus plays a key role in the structures and processes of cell biology. Were phosphorus concentrations higher in the Archean oceans early in the evolutionary history of cell biology? In this work, we compared phosphate concentrations in shallow marine carbonates from the Neoproterozoic (2.8–2.5 billion years ago) and the Phanerozoic (<550 million years ago). We found that primary carbonate structures and fabrics from the Neoproterozoic yielded significantly higher phosphate concentrations than in the Phanerozoic, and interpreted this to mean that Archean seawater was more enriched in phosphorus than modern oceans.

1. Introduction

Present day seawater phosphorus (P) is limited to ~2.3 μM in the deep oceans and near zero in the photic zone due to biological uptake and adsorption onto mineral surfaces in the water column and sediments. Given how central PO₄³⁻ is for a myriad of tasks in cell biology, an apparent paradox is established if P was also a limiting element for the early biosphere. Thermodynamic models have determined major primary and secondary phosphorus-bearing minerals, such as apatite and vivianite, would have been less soluble in ferruginous Archean seawater due to circumneutral pH, thereby providing an enhanced mineral sink for dissolved phosphorus (Hao et al., 2020). A contradictory view based on estimates of geological fluxes of limiting elements on net primary productivity (NPP) demonstrated that early anaerobic metabolisms may have been limited by electron donors rather than phosphate (Ward et al., 2019). Prior to the evolution of oxygenic photosynthesis, limited availability of electron donors (e.g., ferrous iron and molecular hydrogen) necessary for anoxygenic photosynthesis may have suppressed rates of biological productivity to approximately 1000-fold less than today (Ward et al., 2019). With a much smaller biosphere to consume P within the photic zone, elevated phosphate levels could be incorporated into shallow marine carbonate minerals as carbonate-associated phosphate (CAP).

A growing body of evidence has raised the hypothesis that Archean seawater phosphate concentrations may have been higher than present day levels in open marine environments (Planavsky et al., 2010; Rasmussen, Muhling, & Fischer, 2021; Rasmussen, Muhling, Suvorova, & Fischer, 2021). Recent discovery of apatite nanoparticles associated with the Fe(II)-silicate greenalite within early diagenetic chert in 3.46 to 2.46 Ga BIFs from the Pilbara and Yilgarn cratons (Australia) and Kaapvaal craton (South Africa) supported this hypothesis (Rasmussen, Muhling, Suvorova, & Fischer, 2021). In modern marine basins, apatite is undersaturated and its growth is

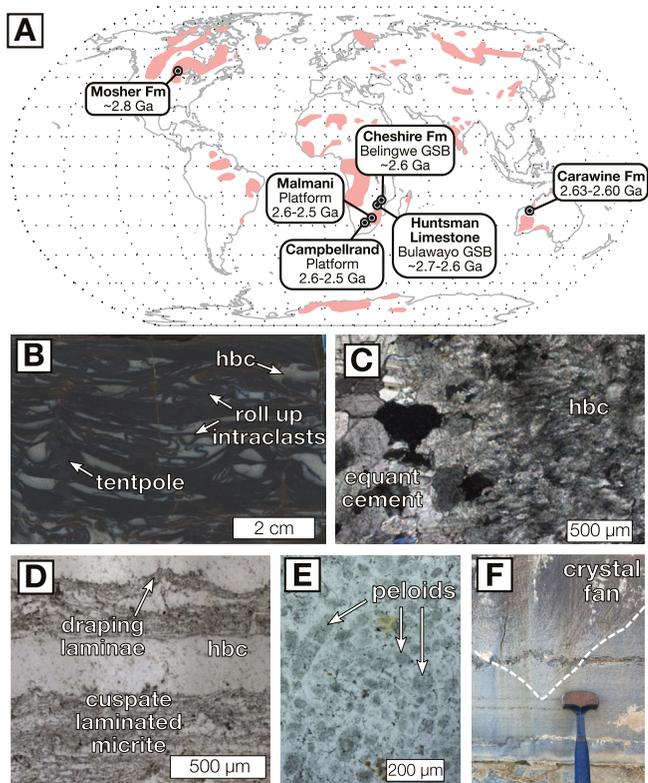


Figure 1. (a) Modern locations of the six Archean carbonate platforms with shallow marine environments. (b) Polished slab of tentpole microbialite and roll-up intraclasts with primary pores filled by syndepositional herringbone and diagenetic equant calcite cements. (c) Transmitted cross-polarized light photomicrograph of herringbone and equant calcite cement. (d) Diffuse transmitted light photomicrograph of cusped, laminated micrite with herringbone calcite cement. (e) Diffuse transmitted light photomicrograph of dolomitic peloid grainstone showing preservation of peloidal fabric with dark inclusions despite replacement by nonplanar dolomite. (f) Field photo of seafloor crystal fan with hammer for scale.

limited by PO_4^{3-} rather than Ca^{2+} concentrations (Jahnke, 1984); and because Archean seawater Ca^{2+} concentrations are thought to have been similar to that of the modern—based on the emergence of archetypical carbonate depositional environments (Grotzinger, 1989), and comparable calcium-to-alkalinity ratios (Ca:ALK) as the modern oceans (Blättler et al., 2017; Halevy & Bachan, 2017)—phosphate concentrations would have been 5–50 times higher to support apatite growth and survival in Archean seawater (Krajewski et al., 1994; Oxmann & Schwendenmann, 2014; Rasmussen, Muhling, Suvorova, & Fischer, 2021).

In this work, we developed an approach to test the hypothesis that phosphate levels were significantly higher on Neoproterozoic carbonate platforms where we find much of the geological evidence for the earliest life. We examined partitioning of dissolved phosphate into lattice-bound carbonate phases (Ingalls et al., 2020), with a particular focus on syndepositional cements and biologically mediated fabrics. Under an oxygenated atmosphere, oxygenic phototrophy and phosphorus sorption to iron oxides (Bjerrum & Canfield, 2002) deplete phosphorus within the photic zone of carbonate ramps. We predicted that higher than modern phosphate levels in deep sea settings (>2 km water depth) might also support elevated phosphate concentrations in anoxic shallow marine environments due to low nutrient utilization prior to the Great Oxidation Event (GOE; ~2.35 Ga; Fischer et al., 2016). If so, carbonates formed from Archean seawater would have recorded higher phosphate concentrations than modern marine carbonates.

Ingalls et al. (2020) demonstrated that dissolved PO_4^{3-} concentrations are incorporated proportionally into the diverse carbonate phases and textures precipitated from closed-basin lakes. This work provided a means for empirical reconstruction of Ca:ALK and dissolved phosphate levels in ancient carbonate environments. However, in the absence of extreme Ca^{2+} limitation as in hyperalkaline and evaporitic environments, carbonate phosphorus-to-calcium (P/Ca) scales instead with seawater phosphate concentrations (Dodd et al., 2021). Precambrian Ca:ALK was likely similar to modern values (Blättler et al., 2017; Higgins et al., 2009), and thus, we focused our interpretations on paleo-phosphate levels.

2. Materials, Methods, and Results

2.1. Neoproterozoic Carbonates and Localities, and Phanerozoic Marine Samples

Due to lithospheric recycling, our sedimentary record of the Precambrian Earth is commensurately limited to several well-preserved Neoproterozoic carbonate platforms. These carbonate platforms contain fabrics and textures that also comprise much of the earliest morphological evidence for life (e.g., crinkly laminations, columnar and dendritic stromatolites; Allwood et al., 2009). We subsampled 112 microfabrics and representative facies from the carbonate record of six different Archean marine shelf environments (Figure 1a; Text S1 in the Supporting Information S1): The >2.5 Ga Campbellrand-Malmani platform (South Africa; Sumner & Grotzinger, 2004; Fischer et al., 2009), the ~2.6 Ga Cheshire Formation of the Belingwe Greenstone Belt (GSB; Zimbabwe; Hofmann et al., 2004), the ~2.7 to 2.6 Ga Huntsman Limestone of the Bulawayo GSB (Zimbabwe; Schopf et al., 1971), the 2.63 to ~2.60 Ga Carawine Fm (Australia; Murphy & Sumner, 2007; Rasmussen et al., 2005), and the ~2.8 Ga Moshier Carbonate Fm of Steep Rock Group (Canada; Fralick & Riding, 2015; Wilks & Nisbet, 1985, 1988).

Our goal was to compare Archean marine phosphate levels to those of phosphate-limited Phanerozoic and modern marine environments. However, the partitioning relationship between dissolved inorganic phosphorus and carbonate-associated phosphate is not fully resolved, so a more robust comparison is made between like materials. As such, we measured a suite of modern and Phanerozoic shallow marine carbonate sediments and limestones. We measured P/Ca of ooid grains from Little Ambergris Cay of the Turks and Caicos carbonate

platform as a modern analog environment for the Archean carbonate platforms and analog facies for Archean grainstones. We analyzed brachiopods and cements from Late Ordovician and early Silurian-age limestones and skeletal grainstones from Anticosti Island, Quebec, Canada, previously described and analyzed for carbonate-associated sulfate (Present et al., 2015). Finally, we analyzed Cambrian limestones to marbles of the Orr Formation that experienced a gradient of contact metamorphism due to Late Jurassic intrusion of the Notch Peak pluton and exhumation during Miocene block faulting (Lloyd et al., 2017). The Big Horse Limestone Member of the Orr Formation was a shallowing upward shelf platform sequence containing peloids, ooids, algal-rich beds, and fossiliferous beds (Hover-Granath et al., 1983). Although these Cambrian limestones experienced varying degrees of thermal and fluid-rock alteration, we included them in our data set because it is unlikely that Phanerozoic carbonate rocks have undergone a greater degree of alteration (and thus P/Ca depletion by our model of the impact of water-rock exchange on P/Ca) than the Archean rocks in our sample set.

In addition to our new analyses, we compiled P/Ca ratios from Ocean Drilling Project (ODP) reports of carbonate-rich marine sediment cores (Table S2 in the Supporting Information S1) from the Cenozoic western equatorial Atlantic (Ceara Rise, ODP Sites 925, 926, and 929; Delaney & Anderson, 1997) and equatorial Pacific (ODP Legs 138 and 130; Filippelli & Delaney, 1996). Reported P/Ca ratios were analyzed by the same spectrophotometric colorimetry molybdenum blue method employed in our study. In both studies, sediment samples were extracted shipboard and assigned ages based on biostratigraphic control points and sedimentation rates (Delaney & Anderson, 1997). The authors applied the sequential extraction technique of Ruttenger (1990) to separate five P-bearing sedimentary components: adsorbed, oxide-bound, organic, detrital, and authigenic. Detrital and authigenic P phases are primarily apatite minerals, which are avoided by our digestion method. Oxide-bound phosphorus represents the fraction of P burial that derives from the water column as P binds with Fe oxides in the oxygenated water column, which we determined was not the primary mode of P burial in our sediments (see Section 2.6). We compiled the P/Ca ratios of the adsorbed P fraction, as inorganic P tends to adsorb to carbonate surfaces and is likely the component that partitions into carbonate minerals during early diagenesis. Further, we only used data from sediments older than Pleistocene to select for sediments that have undergone some degree of early diagenesis and post-burial compaction and dewatering, if not lithification. This better aligned the ODP data with our Archean and Phanerozoic datasets.

2.2. Carbonate Fabrics

We sub-sampled 112 powders from representative carbonate facies from six Archean shallow marine localities. We targeted a range of syndepositional carbonate fabrics in samples from the six Archean platforms for petrographic description prior to microsampling for geochemical analyses. We sampled primary calcitic marine cements (e.g., herringbone and radial-fibrous calcite; Sumner & Grotzinger, 1996; Sumner & Grotzinger, 2000) that filled primary pores in microbialite (Figure 1b), fenestral laminated mudstone (Figure 1c), and intraclast and roll-up structure grainstone facies (Figure 1b) prior to compaction. We also sampled equant and sparry calcite that occluded residual porosity and veins (Figure 1d). We sampled peloid, intraclast, and oncoid grainstone/rudstone facies that were subjected to neomorphic recrystallization and dolomitization but retained primary fabrics and sedimentary structures (Figure 1e).

2.3. Carbonate-Associated Phosphate (CAP) as a Proxy for Ancient Phosphate Levels

We followed the CAP analytical methods of Ingalls et al. (2020; details in Text S2 in the Supporting Information S1). Carbonates were digested in 0.33 M HPLC-grade acetic acid to avoid leaching of organic phosphorus phases and other phosphorus-bearing minerals like hydroxyapatite and carbonate fluorapatite, as well as dolomite, which may have closer association with iron oxide phases and thus could yield overestimates of dissolved phosphate levels due to adsorption of P onto water column iron oxides. Digestions by hydrochloric or nitric acids yields consistently higher P/Ca measurements by both assay and ICP-MS, which are attributed to leaching of phosphate minerals (rather than lattice-bound P) and organic P (Ingalls et al., 2020).

Previous work has demonstrated that the partition coefficient of phosphorus into carbonate is <1 (Algeo & Ingall, 2007; Dodd et al., 2021). Thus, the P preserved in carbonate rocks represents a minimum bound on the dissolved or early diagenetic P fraction. Just like the incorporation of other trace constituents into carbonate phases (e.g., Nielsen et al., 2013), the presence of other cations (Fe, Mn) and anions may assert additional

controls on phosphate incorporation into carbonate. The presence of iron, a known inhibitor of calcium carbonate formation, can impact the kinetics of precipitation which, in turn, may impact trace element partitioning into carbonates (DePaolo, 2011; Jiang & Tosca, 2019). The presumed slightly lower pH of Archean seawater also may have enhanced P incorporation in shallow marine carbonate minerals (Dodd et al., 2021). Comparatively little study has been done on the impact of these factors on phosphate incorporation into carbonate, and so CAP data should be considered within the context of these uncertainties (see Section 2.6).

2.4. Assessment of Preservation of Depositional CAP and the Impact of Burial Alteration

We tested deep-time CAP preservation in carbonate facies similar to those found in our Archean sample set in the substantially younger and well-preserved Eocene Green River Formation (GRF). Aragonite fans, oolites, early diagenetic dolospar, and crinkly laminations accumulated within the Laney Member of the GRF during a period of balance-fill hydrology and high carbonate saturation state in the Sand Wash Basin (Ingalls et al., 2022; Roehler, 1993). These facies yielded P/Ca values of 0.211 ± 0.027 – 0.533 ± 0.094 mmol/mol, comparable to P/Ca of lattice-bound P in Pleistocene tufas precipitated from very low Ca:ALK water where one would expect high levels of phosphate to accumulate (Ingalls et al., 2020). Thus, diverse carbonate facies formed in an alkaline phase of the Green River Formation appeared to accurately capture expected P/Ca values at least over timescales of tens of millions of years.

We assessed the impact of late-stage fluid-mediated alteration on CAP by measuring a suite of carbonate samples collected systematically across a ~ 5 km transect of a well-studied contact metamorphic aureole alteration gradient (Lloyd et al., 2017) (Notch Peak, UT). We found that P/Ca values decreased with increasing degree of alteration. P/Ca values exponentially decreased close to the pluton intrusion as metamorphic grade and maximum temperatures increased (0.085 – 0.049 mmol/mol; Figure S1a in the Supporting Information S1). P/Ca values also decreased nearly linearly with decreasing dolomite $\delta^{18}\text{O}$ values (Lloyd et al., 2017) (Figure S1b in the Supporting Information S1)—a valuable metric of alteration—which we interpreted as removal of CAP during water-rock exchange. The one sample that diverged from this trend had textural indicators of later-stage water-rock recrystallization and has been previously interpreted as a product of fluid-buffered alteration with waters of a different composition (Lloyd et al., 2017).

In addition, we tested whether or not this pattern of CAP being flushed from primary carbonate fabrics during burial alteration held true for the Archean samples by measuring late-stage sparry calcite veins and secondary porosity fill. The spars that were above the method detection limit ($n = 6$) had the lowest mean and median values of all facies: 0.033 ± 0.019 and 0.036 mmol/mol, respectively. One of the analyzed spars was below method detection limit. Altogether, our suite of alteration tests indicated that water-rock alteration lowers carbonate P/Ca, and thus, in deep-time records with extensive burial alteration histories, P/Ca values should be considered minimum bounds on depositional P/Ca.

2.5. CAP of Archean Carbonate Platform Facies

Neoproterozoic P/Ca of shallow marine carbonates ranged over an order of magnitude (Data Set S1), likely in part due to the tendency for diagenesis with inherently P-deplete burial fluids to remove CAP. Herein, we focus on unbiased empirical descriptors of the data, but these values could underestimate depositional values. Carbonates from the Campbellrand platform comprised our largest data set ($n = 72$) with a median (M) P/Ca value of 0.120 mmol/mol and a mean ($\mu \pm 1\sigma$) of 0.112 ± 0.090 mmol/mol. The Cheshire Formation ($M = 0.160$, $\mu = 0.168 \pm 0.118$ mmol/mol) and Huntsman Limestone ($M = 0.142$, $\mu = 0.142 \pm 0.123$ mmol/mol) yielded the highest median and mean values and internal variability between fabrics. Overall, the median and mean Archean values, including all fabrics, were 0.113 and 0.130 mmol/mol, respectively.

Significant differences in median P/Ca values were found between Archean fabrics (Table 1; Figure 2d). Stromatolitic fabrics were the most phosphate-enriched ($M = 0.164$ mmol/mol). The least phosphate-enriched fabric, secondary spar ($M = 0.036$ mmol/mol), was statistically different from all Archean fabrics except marine cements according to a pairwise Wilcoxon test ($p = 0.344$, where $p < 0.005$ is statistically different) and most similar to Phanerozoic marine carbonate ($p = 0.847$; Figure 2d). Although Archean marine cements also yielded a low median P/Ca (0.056 mmol/mol), they were statistically different from Phanerozoic marine ($M = 0.044$ mmol/mol; $p = 2.6 \times 10^{-4}$).

Table 1
Archean Carbonate Platform and Phanerozoic Marine Carbonate P/Ca Data

Age and facies	Mean P/Ca (mmol/mol ± 1σ)	Median P/Ca (mmol/mol)	n
Archean shallow marine carbonates (all facies)	0.130 ± 0.099	0.113	112
micrite	0.158 ± 0.111	0.126	27
stromatolite	0.170 ± 0.107	0.15	29
crystal fans	0.138 ± 0.064	0.138	7
grainstone or packstone	0.110 ± 0.050	0.136	13
marine cements (e.g., herringbone calcite)	0.074 ± 0.059	0.056	28
spar	0.033 ± 0.019	0.036	6
Phanerozoic to modern (all)	0.038 ± 0.036	0.025	405
shallow marine cements and grains	0.052 ± 0.036	0.044	252
shallow water and deep sea corals	0.014 ± 0.007	0.01	153

To test the hypothesis that CAP was more enriched in Neoproterozoic carbonates than those that precipitated in Phanerozoic or modern oceans, we compared the P/Ca values to new analyses of the described suite of modern and Phanerozoic shallow marine carbonates and a compilation of published P/Ca values of modern deep sea and shallow corals (Chen et al., 2019) and Cenozoic ODP cores (Delaney & Anderson, 1997; Filippelli & Delaney, 1996) (Data Set S2). All published data were analyzed using a similar spectrophotometric assay as was conducted in our analyses to enable data set comparisons. Phanerozoic and modern marine carbonates fell into two distinct data populations: corals and all other biogenic and abiotic cements and grains. Deep sea and shallow

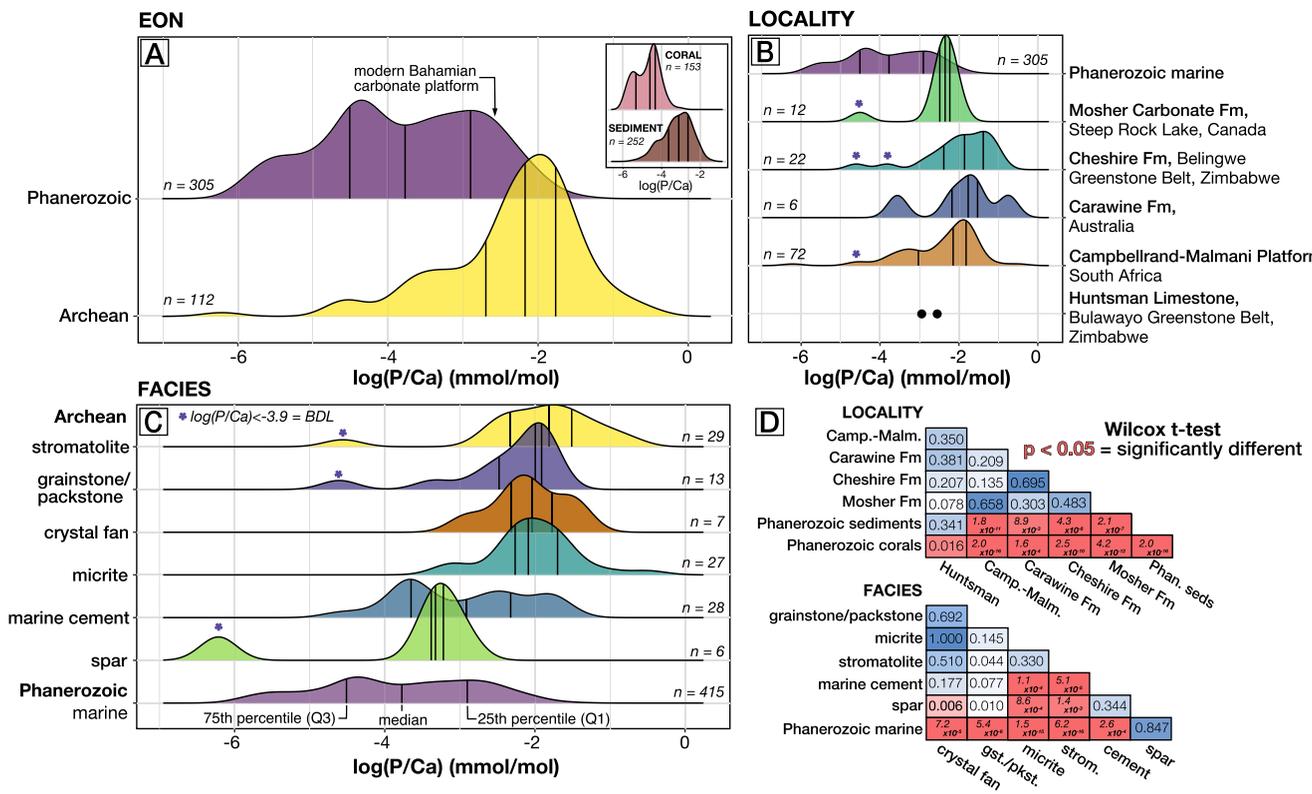


Figure 2. Carbonate-associated phosphate molar ratios for Phanerozoic to modern corals and marine sediments, and facies from Archean carbonate platform records. P/Ca is plotted on a log scale to illustrate order of magnitude differences between (a) eons, (b) localities, and (c) facies. (d) Results from Wilcox *t*-tests demonstrate that carbonates from Archean shallow marine settings are on average higher and statistically distinct from Phanerozoic marine sediments, with the exception of two samples from the Huntsman Limestone.

water corals record 1–three orders of magnitude lower P/Ca (0.003–0.050 mmol/mol) than modern platform sediments (0.074–0.083 mmol/mol), sediments from Cenozoic ODP cores (0.004–0.219 mmol/mol) and Phanerozoic marine cements (0.049–0.118 mmol/mol), likely due to vital effects associated with biomineralization. Wilcoxon *t*-tests demonstrated that the difference between the population means of all Archean shallow marine localities were significantly higher than Phanerozoic corals and marine sediments (except for the Huntsman Limestone, $n = 2$; Figure 2d). Due to the post-depositional processes discussed previously, our measurements likely provide a lower bound on Archean phosphate contents because of CAP loss during carbonate diagenesis and metamorphism.

2.6. CAP Enrichment Independent of Iron Content

It has been hypothesized that the Precambrian Fe cycle was intimately linked to the P cycle due to the propensity of iron oxides to sorb phosphorus from seawater (e.g., Berner, 1973; Bjerrum & Canfield, 2002; Jones et al., 2015; Planavsky et al., 2010). In particular, Bjerrum and Canfield (2002) argued that Archean to early Proterozoic marine orthophosphate would have been an order of magnitude lower than modern due to P scavenging by iron oxides in the water column.

To test whether or not the CAP enrichments observed in the Neoproterozoic platform carbonates resulted from adsorption of phosphate onto iron oxides within the water column, which could misrepresent water column phosphate concentrations, we measured Fe/Ca in 27 of the same subsampled microfabrics as analyzed for P/Ca (Text S3 in the Supporting Information S1), spanning all facies. We found no statistically significant correlations between Fe/Ca and P/Ca (p -value < 0.05 on Pearson's correlation coefficient; Text S3 in the Supporting Information S1). Importantly, no Fe/P correlation was determined within individual data populations of key facies, that is, marine cements and stromatolites, with p -values of 0.23 and 0.48, respectively (Figure S2 in the Supporting Information S1). These data demonstrated that iron enrichment does not ensure phosphate enrichment in carbonates, and vice versa. Finally, spar, a definitively secondary fabric with uniformly low P/Ca values, yielded Fe/Ca up to 13.9 mmol/mol. Overall, the data indicated that phosphate enrichments were independent of local dissolved Fe content.

3. Discussion and Conclusions

3.1. Implications for Phosphate Concentrations in Neoproterozoic Shallow Marine Environments

Carbonate P/Ca values varied within individual platforms by approximately an order of magnitude (Figure 2b). This degree of P/Ca variability could reflect diagenetic and metamorphic processes to which carbonate rocks are particularly susceptible. Based on our assessment that P/Ca varies locally as a function of known alteration, we found that CAP contents are systematically lowered during burial alteration, and thus analyses of primary fabrics likely provide a lower limit on the depositional value. Internal variability could also record changes in the local sources and sinks of P, and/or differing rates and mechanisms of carbonate precipitation on the seafloor (Dodd et al., 2021; Sumner & Grotzinger, 2000, 2004). For example, in modern shallow marine environments, any increase in P input is consumed by biological processes resulting in an increase in net primary productivity rather than phosphate mineralization, although remineralized organic matter can lead to increased authigenic apatite in shallow marine sediments (Krajewski et al., 1994; Rutenberg & Berner, 1993). The Archean biosphere likely contained a higher abundance of microbial mats compared to the modern due to the absence of burrowing fauna, and thus, organic matter remineralization within sediments could have occurred at higher rates and led to an enhanced P sink within sediments rather than the water column. However, marine cements lack C isotope evidence of enhanced organic matter remineralization (Fischer et al., 2009), and grainstones/packstones, crystal fans, and micritic fabrics were no less abundant in CAP than the microbial carbonate facies (Figures 2c and 2d), as would be expected if elevated P levels were due solely to remineralization of abundant microbial mat material.

3.2. Potential Sources of Elevated Marine Phosphate in the Neoproterozoic

Inorganic marine phosphate is derived from silicate weathering of the continents and seafloor basalts. Weathering of continental-derived apatite by acid rain and rivers may have been more efficient under Archean $p\text{CO}_2$ conditions (Sleep & Zahnle, 2001). Seafloor alteration of basalts, which have an order of magnitude higher P

concentrations than continental crust, may have also been enhanced due to higher rates of crustal recycling in the Archean (Horton, 2015) and hydrothermal activity on and off axis in the deep sea. In oxic oceans, metal-rich hydrothermal plumes constitute a phosphate sink by adsorption to Fe oxides; in Archean anoxic seas, plumes appear to have been a source of phosphate, as demonstrated by apatite nanoparticles associated with the Fe(II)-silicate greenalite within cherts from 3.46 to 2.46 Ga BIFs of the Pilbara, Yilgarn, and Kaapvaal cratons (Rasmussen, Muhling, Suvorova, & Fischer, 2021).

3.3. Implications for the Centrality of Phosphate in Intracellular Processes and the Biochemical Building Blocks of Life

Phosphate is central to the building blocks of life (e.g., phospholipids and nucleic acids) and intracellular metabolism and energy conservation (e.g., sugar phosphates and ATP synthesis and hydrolysis). Phosphate has also been the key limitation to NPP for much of Earth history (Planavsky et al., 2010)—at least since the dawn of oxygenic photosynthesis.

However, before life evolved the ability to use water as an electron donor, the availability of molecular hydrogen, sulfur, and perhaps iron established limits on the rates of biogeochemical cycling in Earth's biosphere rather than orthophosphate availability (Ward et al., 2019). Under the aforementioned assumption that Ca:ALK and carbonate saturation states were similar in Neoproterozoic shallow marine environments as the Phanerozoic (Blättler et al., 2017), a linear extrapolation of the P contents we measured indicates that dissolved phosphate concentrations were at minimum 4–12-times greater on the Neoproterozoic Earth. Our estimates suggest that the difference between Archean and modern shallow marine environments could be less dramatic than that of the deep sea (~5–50-times greater; Rasmussen, Muhling, Suvorova, & Fischer, 2021), but this difference could be due to the underestimation inherent to deep-time application of CAP. The CAP values presented here represent minimum estimates for Neoproterozoic dissolved P given the likely thermal alteration of these carbonates to ~200–350°C. Improved constraints on the pH and temperature of Neoproterozoic shallow marine seawater would further our understanding of the relationship between dissolved P levels in the Neoproterozoic and partitioning into carbonate minerals, and our ability to quantitatively compare to modern P levels. In general, our ~2.8–2.5 Ga record of phosphate enrichment in shallow environments dovetails the deep-sea BIF record from ~3.5–2.5 Ga (Rasmussen, Muhling, Suvorova, & Fischer, 2021), and supports the view that phosphate levels were much higher in Archean seawater than they have been in Phanerozoic marine basins.

Evidence that P levels were higher and not limiting for the biosphere over much of Neoproterozoic time suggested that P concentrations may have been similarly high or higher in yet older, prebiotic oceans. Such high P prebiotic conditions would have ramifications for the origin and early evolution of cells, that is, the phosphorylation of early biomolecules would have been more environmentally feasible—softening some of the challenges associated with the “phosphate problem” for the origin of life (Gulick, 1955). Just as importantly, the emerging datasets suggest that phosphate was not limiting for at least 1 billion years of evolution in the early biosphere. The chemical and energetic utility of phosphate for critical intracellular machinery and as a means of energy transduction are major factors in phosphate's importance to cells. We suggest that phosphate's centrality in cell biology and biochemistry hinged on this prolonged period of phosphate abundance, when productivity was constrained by life's inability to split water rather than geological phosphate fluxes.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Summary tables of all Archean and Phanerozoic marine carbonate P/Ca and Fe/Ca data can be found in Data Sets S1 and S2, respectively. Additionally, these data are included in our Open Science Framework depository (<https://doi.org/10.17605/OSF.IO/RDEVH>). Raw absorbance data for each analytical period and 96-well plate, including standard calibration curves, are published in the OSF data repository for this project. Photos of drill spots for all Archean samples are included in the OSF.

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References

- Algeo, T. J., & Ingall, E. (2007). Sedimentary Corg:P ratios, paleocean ventilation, and Phanerozoic atmospheric pO₂. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 256(3–4), 130–155. <https://doi.org/10.1016/j.palaeo.2007.02.029>
- Allwood, A. C., Grotzinger, J. P., Knoll, A. H., Burch, I. W., Anderson, M. S., Coleman, M. L., & Kanik, I. (2009). Controls on development and diversity of Early Archean stromatolites. *Proceedings of the National Academy of Sciences*, 106(24), 9548–9555. <https://doi.org/10.1073/pnas.0903323106>
- Berner, R. A. (1973). Phosphate removal from sea water by adsorption on volcanogenic ferric oxides. *Earth and Planetary Science Letters*, 18(1), 77–86. [https://doi.org/10.1016/0012-821X\(73\)90037-X](https://doi.org/10.1016/0012-821X(73)90037-X)
- Bjerrum, C. J., & Canfield, D. E. (2002). Ocean productivity before about 1.9 Gyr ago limited by phosphorus adsorption onto iron oxides. *Nature*, 417(6885), 159–162. <https://doi.org/10.1038/417159a>
- Blättler, C. L., Kump, L. R., Fischer, W. W., Paris, G., Kasbohm, J. J., & Higgins, J. A. (2017). Constraints on ocean carbonate chemistry and pCO₂ in the Archean and Palaeoproterozoic. *Nature Geoscience*, 10(1), 41–45. <https://doi.org/10.1038/ngeo2844>
- Chen, M., Martin, P., Goodkin, N. F., Tanzil, J., Murty, S., & Wiguna, A. A. (2019). An assessment of P speciation and P:Ca proxy calibration in coral cores from Singapore and Bali. *Geochimica et Cosmochimica Acta*, 267, 113–123. <https://doi.org/10.1016/j.gca.2019.09.024>
- Delaney, M. L., & Anderson, L. D. (1997). Phosphorus geochemistry in Ceara Rise sediments. *Proceedings of the Ocean Drilling Program*, 154, 475–482. <https://doi.org/10.2973/odp.proc.sr.154.124.1997>
- DePaolo, D. J. (2011). Surface kinetic model for isotopic and trace element fractionation during precipitation of calcite from aqueous solutions. *Geochimica et Cosmochimica Acta*, 75(4), 1039–1056. <https://doi.org/10.1016/j.gca.2010.11.020>
- Dodd, M. S., Zhang, Z., Li, C., Algeo, T. J., Lyons, T. W., Hardisty, D. S., et al. (2021). Development of carbonate-associated phosphate (CAP) as a proxy for reconstructing ancient ocean phosphate levels. *Geochimica et Cosmochimica Acta*, 301, 48–69. <https://doi.org/10.1016/j.gca.2021.02.038>
- Filippelli, G. M., & Delaney, M. L. (1996). Phosphorus geochemistry of equatorial Pacific sediments. *Geochimica et Cosmochimica Acta*, 60(9), 1479–1495. [https://doi.org/10.1016/0016-7037\(96\)00042-7](https://doi.org/10.1016/0016-7037(96)00042-7)
- Fischer, W. W., Hemp, J., & Johnson, J. E. (2016). Evolution of oxygenic photosynthesis. *Annual Review of Earth and Planetary Sciences*, 44(1), 647–683. <https://doi.org/10.1146/annurev-earth-060313-054810>
- Fischer, W. W., Schroeder, S., Lacassie, J. P., Beukes, N. J., Goldberg, T., Strauss, H., et al. (2009). Isotopic constraints on the late archean carbon cycle from the transvaal supergroup along the western margin of the Kaapvaal Craton, South Africa. *Precambrian Research*, 169(1–4), 15–27. <https://doi.org/10.1016/j.precamres.2008.10.010>
- Fralick, P., & Riding, R. (2015). Steep rock lake: Sedimentology and geochemistry of an archean carbonate platform. *Earth-Science Reviews*, 151, 132–175. <https://doi.org/10.1016/j.earscirev.2015.10.006>
- Grotzinger, J. P. (1989). Facies and evolution of precambrian carbonate depositional systems: Emergence of the modern platform archetype. *Controls on Carbonate Platform and Basin Development*, (pp. 79–106). <https://doi.org/10.2110/pec.89.44.0079>
- Gulick, A. (1955). Phosphorus as a factor in the origin of life. *American Scientist*, 43(4), 479–489.
- Halevy, I., & Bachan, A. (2017). The geologic history of seawater pH. *Science*, 355(6329), 1069–1071. <https://doi.org/10.1126/science.aal4151>
- Hao, J., Knoll, A. H., Huang, F., Schieber, J., Hazen, R. M., & Daniel, I. (2020). Cycling phosphorus on the archean earth: Part II. Phosphorus limitation on primary production in archean ecosystems. *Geochimica et Cosmochimica Acta*, 280, 360–377. <https://doi.org/10.1016/j.gca.2020.04.005>
- Higgins, J. A., Fischer, W. W., & Schrag, D. P. (2009). Oxygenation of the ocean and sediments: Consequences for the seafloor carbonate factory. *Earth and Planetary Science Letters*, 284(1–2), 25–33. <https://doi.org/10.1016/j.epsl.2009.03.039>
- Hofmann, A., Dirks, P. H. G. M., & Jelsma, H. A. (2004). Shallowing-upward carbonate cycles in the Belingwe Greenstone Belt, Zimbabwe: A record of Archean sea-level oscillations. *Journal of Sedimentary Research*, 74(1), 64–81. <https://doi.org/10.1306/052903740064>
- Horton, F. (2015). Did phosphorus derived from the weathering of large igneous provinces fertilize the neoproterozoic ocean?: NEOPROTEROZOIC FLOOD BASALT WEATHERING. *Geochimica et Cosmochimica Acta*, 166, 1723–1738. <https://doi.org/10.1002/2015GC005792>
- Hover-Granath, V. C., Papike, J. J., & Labotka, T. C. (1983). The Notch Peak contact metamorphic aureole, Utah: Petrology of the big Horse limestone member of the Orr Formation. *GSA Bulletin*, 94, 889–906. [https://doi.org/10.1130/0016-7606\(1983\)94<889:tpcma>2.0.co;2](https://doi.org/10.1130/0016-7606(1983)94<889:tpcma>2.0.co;2)
- Ingalls, M., Blättler, C. L., Higgins, J. A., Magyar, J. S., Eiler, J. M., & Fischer, W. W. (2020). P/Ca in carbonates as a proxy for alkalinity and phosphate levels. *Geophysical Research Letters*, 47(21). <https://doi.org/10.1029/2020GL088804>
- Ingalls, M., Fetrow, A. C., Snell, K. E., Frantz, C. M., & Trower, E. J. (2022). Lake level controls the recurrence of giant stromatolite facies. *Sedimentology*. <https://doi.org/10.1111/sed.12967>
- Jahnke, R. (1984). The synthesis and solubility of carbonate fluorapatite. *American Journal of Science*, 284, 58–78. <https://doi.org/10.2475/ajs.284.1.58>
- Jiang, C. Z., & Tosca, N. J. (2019). Fe(II)-carbonate precipitation kinetics and the chemistry of anoxic ferruginous seawater. *Earth and Planetary Science Letters*, 506, 231–242. <https://doi.org/10.1016/j.epsl.2018.11.010>
- Jones, C., Nomosatryo, S., Crowe, S. A., Bjerrum, C. J., & Canfield, D. E. (2015). Iron oxides, divalent cations, silica, and the early earth phosphorus crisis. *Geology*, 43(2), 135–138. <https://doi.org/10.1130/G36044.1>
- Krajewski, K. P., Van Capellen, P., Trichet, J., Kuhn, O., Lucas, J., Martin-Algarra, A., et al. (1994). Biological processes and apatite formation in sedimentary environments. *Ecologiae Geologiae Helvetiae*, 87(3), 701–745.
- Lloyd, M. K., Eiler, J. M., & Nabelek, P. I. (2017). Clumped isotope thermometry of calcite and dolomite in a contact metamorphic environment. *Geochimica et Cosmochimica Acta*, 197, 323–344. <https://doi.org/10.1016/j.gca.2016.10.037>
- Murphy, M. A., & Sumner, D. Y. (2007). Tube structures of probable microbial origin in the near-archean carawine dolomite, hamersley basin, western Australia. *Geobiology*, 070627140740001. <https://doi.org/10.1111/j.1472-4669.2007.00114.x>
- Nielsen, L. C., De Yoreo, J. J., & DePaolo, D. J. (2013). General model for calcite growth kinetics in the presence of impurity ions. *Geochimica et Cosmochimica Acta*, 115, 100–114. <https://doi.org/10.1016/j.gca.2013.04.001>
- Oxmann, J. F., & Schwendenmann, L. (2014). Quantification of octacalcium phosphate, authigenic apatite and detrital apatite in coastal sediments using differential dissolution and standard addition. *Ocean Science*, 10(3), 571–585. <https://doi.org/10.5194/os-10-571-2014>
- Planavsky, N. J., Rouxel, O. J., Bekker, A., Lalonde, S. V., Konhauser, K. O., Reinhard, C. T., & Lyons, T. W. (2010). The evolution of the marine phosphate reservoir. *Nature*, 467(7319), 1088–1090. <https://doi.org/10.1038/nature09485>
- Present, T. M., Paris, G., Burke, A., Fischer, W. W., & Adkins, J. F. (2015). Large Carbonate Associated Sulfate isotopic variability between brachiopods, micrite, and other sedimentary components in Late Ordovician strata. *Earth and Planetary Science Letters*, 432, 187–198. <https://doi.org/10.1016/j.epsl.2015.10.005>

- Rasmussen, B., Blake, T. S., & Fletcher, I. R. (2005). U-Pb zircon age constraints on the Hamersley spherule beds: Evidence for a single 2.63 Ga Jeerinah-Carawine impact ejecta layer. *Geology*, *33*(9), 725–728. <https://doi.org/10.1130/G21616.1>
- Rasmussen, B., Muhling, J. R., & Fischer, W. W. (2021). Greenalite nanoparticles in alkaline vent plumes as templates for the origin of life. *Astrobiology*, *21*(2), 246–259. <https://doi.org/10.1089/ast.2020.2270>
- Rasmussen, B., Muhling, J. R., Suvorova, A., & Fischer, W. W. (2021). Apatite nanoparticles in 3.46–2.46 Ga iron formations: Evidence for phosphorus-rich hydrothermal plumes on early Earth. *Geology*. <https://doi.org/10.1130/G48374.1>
- Roehler, H. W. (1993). *Eocene climates, depositional environments, and geography, greater Green River basin, Wyoming, Utah, and Colorado* (U.S. Geological survey professional. U.S. Department of the Interior. Paper No. 1506- F).
- Ruttenberg, K. C. (1990). *Diagenesis and burial of phosphorus in marine sediments: Implications for the marine phosphorus budget (PhD Thesis)*. Yale University.
- Ruttenberg, K. C., & Berner, R. A. (1993). Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments. *Geochimica et Cosmochimica Acta*, *57*(5), 991–1007. [https://doi.org/10.1016/0016-7037\(93\)90035-U](https://doi.org/10.1016/0016-7037(93)90035-U)
- Schopf, J. W., Oehler, D. Z., Horodyski, R. J., & Kvenvolden, K. A. (1971). Biogenicity and significance of the oldest known stromatolites. *Journal of Paleontology*, *45*, 477–485.
- Sleep, N. H., & Zahnle, K. (2001). Carbon dioxide cycling and implications for climate on ancient Earth. *JGR: Planets*, *106*(E1), 1373–1399. <https://doi.org/10.1029/2000JE001247>
- Sumner, D. Y., & Grotzinger, J. P. (1996). Herringbone calcite: Petrography and environmental significance. *Journal of Sedimentary Research*, *66*(3), 419–429.
- Sumner, D. Y., & Grotzinger, J. P. (2000). Late Archean aragonite precipitation: Petrography, facies associations, and environmental significance. *Carbonate Sedimentation and Diagenesis in the Evolving Precambrian World*.
- Sumner, D. Y., & Grotzinger, J. P. (2004). Implications for Neoarchaeon ocean chemistry from primary carbonate mineralogy of the Campbellrand-Malmani Platform, South Africa. *Sedimentology*, *51*(6), 1273–1299. <https://doi.org/10.1111/j.1365-3091.2004.00670.x>
- Ward, L. M., Rasmussen, B., & Fischer, W. W. (2019). Primary productivity was limited by electron donors prior to the advent of oxygenic photosynthesis. *Journal of Geophysical Research: Biogeosciences*, *124*(2), 211–226. <https://doi.org/10.1029/2018JG004679>
- Wilks, M. E., & Nisbet, E. G. (1985). Archaeon stromatolites from the Steep rock Group, northwestern Ontario, Canada. *Canadian Journal of Earth Sciences*, *22*, 792–799. <https://doi.org/10.1139/e85-086>
- Wilks, M. E., & Nisbet, E. G. (1988). Stratigraphy of the Steep rock Group, northwest Ontario: A major archaeon unconformity and archaeon stromatolites. *Canadian Journal of Earth Sciences*, *25*(3), 370–391. <https://doi.org/10.1139/e88-040>