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Archean phosphorus liberation induced by iron redox geochemistry

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The element phosphorus (P) is central to ecosystem growth and is proposed to be a limiting nutrient for life. The Archean ocean may have been strongly phosphorus-limited due to the selective binding of phosphate to iron oxyhydroxide. Here we report a new route to solubilizing phosphorus in the ancient oceans: reduction of phosphate to phosphite by iron(II) at low (<200 °C) diagenetic temperatures. Reduction of phosphate to phosphite was likely widespread in the Archean, as the reaction occurs rapidly and is demonstrated from thermochemical modeling, experimental analogs, and detection of phosphite in early Archean rocks. We further demonstrate that the higher solubility of phosphite compared to phosphate results in the liberation of phosphorus from ferruginous sediments. This phosphite is relatively stable after its formation, allowing its accumulation in the early oceans. As such, phosphorus, not as phosphate but as phosphite, could have been a major nutrient in early pre-oxygenated oceans.

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P

osphorus limitation in the Archean eon has been proposed to have limited the fecundity of the early Earth\textsuperscript{14}. Although the extent of removal by iron oxyhydroxide (IOH) has been a matter of question due to competition by silica\textsuperscript{6} and arsenic\textsuperscript{7}, a phosphorus-depleted Archean ocean would have affected the development and diversification of life on the Earth. The effect of diagenesis on Archean phosphorus (P) remobilization is largely unknown, due to numerous factors such as oxygen levels, sedimentary rates, and temperature\textsuperscript{9} that may affect the phosphate speciation and mineralization. The main pathway for remobilization of sedimentary phosphate today is through the decay of organic matter, although the early Archean microbial reduction of ferric to ferrous iron may have remobilized IOH-bound P, as ferrous phosphates are significantly more soluble in water\textsuperscript{10}. Remobilization would have allowed the release of P into the interstitial waters, though some would have been rebound by IOH in overlying sedimentary layers. The operating hypothesis for phosphate diagenesis is that phosphate does not change oxidation state; in most geochemical studies, phosphates are considered synonymous with total phosphorus. An alternative to phosphate is the ion phosphite (HPO\textsubscript{3}\textsuperscript{2−}), an ion that is more soluble in the presence of divalent cation salts than phosphate. Geochemical occurrences of phosphate are sparse: it has been found in trace amounts in hydrothermal water systems of Hot Creek Gorge, Mammoth Lakes, CA\textsuperscript{11}, and within some rocks struck by lightning\textsuperscript{12}. Mulikdjanian et al.\textsuperscript{13} proposed that the geothermal reduction of phosphate to phosphite occurs principally by high-temperature heating in the presence of carbon and iron, within volcanic hydrothermal systems thought to be common on the early Earth. After the discovery of phosphite in geothermal waters by Pech et al.\textsuperscript{11}, reduced P was also found in modern, natural water samples\textsuperscript{14, 15}, though biological redox cycling is the likely source of phosphate in these systems. These results were geochemically surprising, as the prevalent oxidizing conditions on Earth should confine P to the pentavalent oxidation state, and P occurs principally as the mineral apatite in surface rocks\textsuperscript{16}. In contrast, the ability to use reduced P compounds as a sole P source is widespread in microbiological systems\textsuperscript{17, 18}. These organisms, such as the bacteria, Desulfotignum phosphitoxidans, can use phosphite as part of their metabolic cycle\textsuperscript{19}. If these organisms are ubiquitous, their widespread occurrence is consistent with the presence of unrecognized sources of reduced P species.

We propose here that phosphorus may not have been ecosystem-limiting on the early Earth, because of the existence of a hitherto unrecognized phosphate reduction process extensively active on the early Earth. We demonstrate that phosphate was reduced to phosphite by ferrous iron, even at the low temperatures (<200 °C) of sedimentary diagenesis. Such conditions would have been widespread on the Archean Earth, before the oxidation of the atmosphere, known as Great Ox cynisation Event (GOE) at c. 2.4 Ga\textsuperscript{20–22}. In the nominal reaction, phosphate (HPO\textsubscript{4}\textsuperscript{2−}) is reduced to phosphite (HPO\textsubscript{3}\textsuperscript{2−}) by the concurrent oxidation of iron (II). Phosphate formed through reaction with iron(II) would have been extensively mobilized because of its high solubility in water, compared with phosphate, and the total P concentrations may have approached 100–1000 times those predicted from IOH binding experiments. The presence of reduced phosphorus compounds would hence not be limited to the requirements of meteoritic impact and weathering for release\textsuperscript{23, 24}, and could potentially account for the elevated levels of phosphate present in early Archean carbonates\textsuperscript{25}.

Results

Archean rock analysis. Pasek et al.\textsuperscript{25} first reported the presence of phosphate in early Archean sedimentary carbonates from the Pilbara Craton, Australia, and attributed this phospohite to reactive, meteoritic sources of phosphorus on the early Earth. Here, we expand on the suite of early Archean rocks and report data on the samples collected from the supracrustal succession of the Isua belt and the Akilia enclave, western Greenland. The age on the Isua Supracrustal Belt is 3.7–3.8 Ga\textsuperscript{26}, whereas the age of the Akilia enclave is controversial, either c. 3.85 Ga\textsuperscript{27}, 28 or c. 3.65 Ga\textsuperscript{29, 30}. Both Isua and Akilia rocks have experienced deformation, metasomatism, and metamorphism, that in Isua has reached amphibolite facies, and in Akilia, granite facies\textsuperscript{27, 31–35}. Isua samples were collected from the “low strain” domain\textsuperscript{36} in the northwestern part of the belt and represent chemical sediments, such as banded iron formations (BIF) and metacherts, and metacarbonates that have metasomatic origin. Apatite occurring in BIF and metacherts have trace element signatures consistent with Archean seawater\textsuperscript{37}. The studied Akilia sample is from the quartz-amphibole-pyroxene unit. The protolith of that unit, either chemical sediment or metasomatised ultramafic rock\textsuperscript{27, 34}, has been debated in the literature. The trace element characteristics of the whole-rock and apatite in the best preserved parts of the quartz-amphibole-pyroxene unit are consistent with a sedimentary origin\textsuperscript{38}.

The samples were analyzed, using High Performance Liquid Chromatography-Inductively Coupled Plasma-Mass Spectrometry (HPLC–ICP–MS), to identify P speciation within the rock extracts (Table 1, Fig. 1, Methods, Supplementary Fig. 1). The analyses show that phosphite was present in these rock samples at levels of 1–100 ppm by weight (as HPO\textsubscript{3}\textsuperscript{2−}), or about 0.01% to a few percent of the total P. These findings show that phosphite was indeed present in Archean rocks, and that phosphite may have been common in early oceans, especially since reduction occurs rapidly, and phosphite is readily extractable (see below). Although the source of phosphite was not established in the Pilbara carbonates, it was previously hedged to be meteoritic\textsuperscript{25, 26} because of the high flux of meteorites to the Earth in early Archean and Hadean\textsuperscript{23}. At present, we do not know the phase associated with this phosphite in these rocks, nor do we know if the phosphite was formed during diagenesis or metamorphism, or even if it was captured when the rocks were initially deposited.

Thermodynamic modeling. In addition to meteoritic sources, reduction of phosphate to phosphite by abiotic redox reactions may have provided phosphite to the Archean oceans. Though the source of phosphate in these Archean rocks cannot be specifically identified, the reduction of phosphate by Fe(II) is facile. We modeled the reduction of phosphate by common geochemical reducing agents, including hydrogen, ammonia, hydrogen sulfide,
and ferrous iron, among others (see Methods, Supplementary Figs. 2, 3), with the result showing that only a few inorganic reagents are capable of reducing phosphate. Reduction of phosphate by ferrous iron (as FeO) occurs up to a few percent of the total phosphorus at relatively low temperature (<200 °C), whereas other reductants either do not reduce phosphate to any significant extent, or do so at high temperature (>500 °C). However, given that ferrous iron was likely stable on the Earth's surface before GOE, it is quite likely that reduction of phosphate by low-temperature oxidation of iron is the source of phosphate within the Archean rocks.

Experimental phosphate reduction. Motivated by the feasibility of reduction from thermodynamic modeling, phosphate reduction by ferrous iron is demonstrated by laboratory simulation. Phosphate, when heated with iron (II) to 160–200 °C under a dinitrogen atmosphere, is reduced to phosphate at up to 4% of the total P speciation (Fig. 2, see Methods). These experiments confirm that moderate heating of phosphate in simulated sedimentary diagenetic or low temperature hydrothermal conditions in the presence of ferrous iron, can lead to production of phosphate, after only a few days of heating. Under higher temperatures (>200 °C), the models described above predict that more phosphate will be reduced, but experimentally we find that formation of the phosphate dimer (pyrophosphate, \( P_2O_7^{4-} \)) competes with reduction. Since this reaction releases \( H_2O \), it is possible that under higher pressures reduction is favored, instead of \( H_2O(g) \) loss. Thus, the phosphate present within the Archean samples is most consistent with the heating of phosphate along with the oxidation of iron (II), and required only relatively low temperatures to proceed, though higher temperatures may have also led to reduction.

Solutions experiments and modeling. Furthermore, ferrous and ferric phosphate salts are also more soluble than the equivalent iron phosphate salts, by a factor of \( 10^2-10^5 \times \) (see Supplementary Table 1). This increased solubility could have affected the ocean chemistry substantially, as shown by a simple thermodynamic mass-balance model that incorporates the above thermodynamic calculations with iron phosphate/phosphate solubility predictions. In this model, water flowing through ferruginous sediments, containing both iron phosphate and iron phosphate formed by reduction (Methods), preferentially extracts phosphate, flushing it out to the ocean at a concentration of \( 10^{-4}-M \) (Fig. 3a), and requiring relatively low amounts of water to completely extract phosphate. If hydrothermal fluid fluxes \(^{39}\) were active at present day rates or higher on the early Earth, the ocean could have reached iron-phosphate saturation with \( 10^{-4} \) M phosphate, globally, in less than one million years, assuming minimal phosphate oxidation (Fig. 3b).

Discussion
In such a scenario, the early Earth oceans were enriched with phosphorus as phosphate. The total phosphorus content of the early oceans could have been up to 1000× greater than if controlled by IOH-binding, as previously predicted. Given that most microbial systems primarily use phosphorus as phosphate, microbes would either have had to have waited for the (slow) oxidation of phosphate to phosphite, or would have had the genes necessary for phosphite oxidation, a similar scenario as modern microbes. Given that there is a widespread distribution of phosphite-utilizing genes in the modern microbiome \(^{17}\), and that microbial strains bearing these genes diverged billions of years ago (Methods), it is possible that the ability to use phosphite as a sole P nutrient is an artifact of ancient ocean chemistry, though horizontal gene transfer may be a more likely explanation. In either case, phosphorus may not have been as critical a limiting nutrient, relative to other key elements.

This model is predicated on two hypotheses. The first is that iron and phosphorus co-occurred within the sediments in the Archean. The thermodynamic calculations here modeled this behavior, assuming P was initially in vivianite (with parallels to modern lakes) \(^{40}\), however, calcium phosphate minerals may also be susceptible to reduction to produce phosphite \(^{12}\). Iron and phosphate, even if the latter occurs in calcium phosphates, were likely closely associated in many Archean sediments, and have already been co-located in hydrothermal plumes off the southern East Pacific Rise \(^{41}\), with later diagenesis perhaps altering these minerals to release phosphite.

Secondly, the oxidation of phosphite is presumed to be slow enough to allow high concentrations to accumulate. Oxidation of phosphite has both an abiotic and a biologic component. As evidence for the presumed stability of phosphite, abiotic oxidation experiments demonstrate low susceptibility for the calcium phosphate salt toward oxidation \(^{25}\). In addition, the oxidation of
ferrous phosphate is demonstrated to occur at temperatures higher than 300 °C in air, suggesting that at lower partial pressures of oxygen (~10⁻⁵ × present atmospheric level), little oxidation will occur under typical geologic conditions (phosphate oxidation half-life ~6 × 10⁵ years, see Supplementary Fig. 4). The abiotic oxidation of dissolved phosphate proceeds most effectively by a radical reaction, and oxidation of the phosphate solutions under air occurs slowly (half-life in air ~1000 years, see Methods, Supplementary Tables 2, 3), arguing that oxidation in early low O₂ environments should have occurred very slowly.

Biologic oxidation may have been important in the Archean, although calculations of enzymatic oxidation rates suggest that the rate of biologic oxidation is close to the predicted abiotic oxidation rate (see Supplementary Fig. 5, Methods). In addition, biologic oxidation of the reduced P is driven by a few enzymes, several of which require O₂ for redox. This oxidation would have necessarily occurred over geologic timescales, possibly after the end of the Archean. If phosphate were a major P-bearing species in the Archean ocean, then its oxidation to phosphate near the time of the GOE 2.4 Ga could have been captured in the sedimentary record. The formation of the first global phosphorites occurred in the Proterozoic 1.7–2.2 Ga, but the timing of these events suggests the possibility, and the mass balance of P possibly present as phosphate in the ocean greatly exceeds the total reserves of phosphorites in Proterozoic rocks. The diageneis of ferrous iron and phosphate minerals to form phosphate in Archean rocks may account, at least in part, for the lower-than-expected P content associated with ferruginous sediment. The loss of crystalline or adsorbed water by ferruginous sediments at temperatures around 200 °C will result in the preferential extraction of the phosphite ion as water escapes the sediment, resulting in a lower total P in the rock than without reduction. The removal of 75% of phosphorus from a rock requires about 100 L of water to flow through 1 kg of rock, if buffered by the solubility of ferrous phosphate. If instead, the fluids have lower iron concentrations because of the precipitation of other minerals, then the extraction is instead dependent on the amount and rate of reduction of phosphate, requiring even less fluid (Fig. 3). Although the investigation here did not measure phosphate within late Archean banded-iron formation rocks (e.g., ref. 3), the processes active within the early Archean should not have varied significantly; reduction of phosphate requires only low-temperature diagenetic interaction with ferrous iron, which may have been favored during BIF deposition before the GOE.

Methods

Samples. Samples were collected from Southwest Greenland during field campaigns in the previous work in the Isua Supercrustal Belt and Akilia.

Phosphate to phosphate reduction experiments. Dibasic sodium phosphate (Na₂HPO₄, 1 mM) and ferrous chloride (FeCl₂·4H₂O, 3 mM) was dissolved in deionized water (10 mL) and stirred for 10 min, while adjusting to pH 4. This was reduced to dryness on a rotary evaporator, and the residues were heated under a constant nitrogen flow at 180 °C for 1 h. The heated residue was washed with deionized water (10 mL), filtered through 0.45 μm syringe filter before being again reduced to dryness and dissolved in deuterium oxide (1 mL) for ³¹P Nuclear Magnetic Resonance (NMR) analysis (Varian 400 MHz NMR at USF).

Analysis of the samples showed the presence of phosphate (singlet, 80%, 5.5 ppm), pyrophosphate (singlet, 15%, ~5.5 ppm), and phosphate (doublet, 5%, 3.2 ppm). Previous studies on phosphate heating have shown the effective production of pyrophosphate at temperatures exceeding 180 °C, but never the presence of phosphate from this process. To confirm that ferrous iron (Fe²⁺) is responsible for the reduction of phosphate, control experiments were conducted using metallic iron (Fe⁰) and ferric iron (Fe³⁺) in place of ferrous iron, also one experiment with no iron present. Both the iron experiments and the phosphate only experiment showed the presence of only P⁷⁺, confirming the role of ferrous iron in the reduction process. We decided to test this further and were also able to reduce phosphate (P⁷⁺) to hypophosphate (P⁵⁺) through the same process.

We note that the amount of phosphate obtained in our experiments was higher than expected from the in silico modeling below; this is thought because of the
model predictions using solution chemistry, while our experimental setup was non-solutional.

Phosphite salt solubility. Mg, Fe, Ca, and Al salts of phosphite were synthesized by the slow addition of a sodium phosphite solution (0.1 M) to a solution of metal chloride (in this case, MgCl2, FeCl2, CaCl2, and AlCl3). In each case, the resulting precipitate was collected, and dried under vacuum. The Fe2+ salt was stored in a glove box under N2. A 0.01 g sample of each powder was then placed in 10 mL of 0.5 M acetic acid/sodium acetate buffer. General methods were modified from those used for P speciation with ion chromatography (IC) and IC electro-spray mass spectrometry48–50, and optimized for HPLC–ICP–MS. A Dionex IonPa® AS17C chromatographic column, with an AG17 Guard Column fitted on the HPLC. All standards and samples and blanks were mixed or prepared using 18 MΩ water or doubly distilled 18 MD water, distilled acids, and ACS grade or better solid reagents. Calibration and single species standards were mixed just before analysis. Initial trials eluted 50 μL of sample with either 35 mM KOH or NaOH (recommended eluent for the AS17C column) as a mobile phase, but NaOH achieved poor separation under all conditions tried, and hence was abandoned. As liquids with high concentrations of total dissolved solids are known to deposit and coat the ICP–MS cones and lens, attempts to use 1 M KOH to lower the lowest concentration that could be used to adequately separate phosphorus species were taken. We applied multiple gradients from 0% KOH, 100% water to 100% 35 mM KOH in various combinations. Best results were found using linear gradients, using a starting concentration of KOH of 3.5 mM for the first 2 min and then ramping up to 35 mM KOH over the course of 10 min, and then ramping down to 10% KOH in a 1.0 mL/min flow rate. Peak pressures in the HPLC did not exceed 3000 PSI during the course of the run. Preferred analytical conditions on the HPLC are provided in the previous work1,4. The ICP–MS was run at 1300 W RF power to effectively ionize phosphorus, which has a high first ionization potential. Nebulizer flow and lens voltage was adjusted to optimize for maximal signal intensity on phosphorus.

The Perkin Elmer Elan DRC II series is equipped with a reaction cell situated in line to the detector used to eliminate the interferences, with the aid of a reaction gas to either combine the species of interest into a molecular species at a different mass or by reaction with the interfering species. Following the methods for analysis of arsenic (As with m/z = 75 is converted to AsO by m/z = 91 to avoid molecular interferences44), we charged the reaction cell with oxygen to convert Fe3+ to Fe2+ (m/z = 47). This was done to reduce/avoid the interference from 15N16O. Although the total abundance of 15N is low, the atmospheric pressure interface on the ICP already adsorbs a substantial amount of nitrogen, and it is always present. Therefore, conversion of 31Pt to 31Pt–P should work to lower the background and enhance the signal to noise ratio in a similar fashion, as arsenic conversion to AsO4. A series of standards was prepared from commercially available hypophosphorous acid, phosphoric acid, and phosphonic acid in analytical grade 18 MD DI-H2O to make 1 x 10−3 M solutions for each species, which in turn were serially diluted to make individual standards with concentrations ranging from 1 x 10−3 M to 1 x 10−6 M. Mixed species standards were also prepared over the same concentration range to check for adequate separation and detection, and to test the lower limits of instrument detection on the acquisition of P at m/z = 31 (standard mode) and P 0 at m/z = 47 (reaction mode). Standards were stored in brown glasses or opaque HDPE containers for not more than 4 days at 4 °C, and then discarded. No notable concentration difference was found for species stored in HDPE vs. glass. Analytical trials were conducted with these general conditions with detection on the ICP–MS as either P at m/z = 31 or as PO4 at m/z = 47 to confirm which detection method offered the best response (Supplementary Fig. 1).

Thermodynamics of reduction. Thermodynamic equilibrium modeling was done using HSC Chemistry (version 7.1, Outokumpu Research Oy at USF). Reactions were solved using this program’s reaction equilibrium calculator, including coupling phosphite (HPO32−) reduction to phosphate (HPO42−) with ammonium to nitrate, hydrogen sulfide to sulfate, methane to carbon dioxide, MnO to Mn2O3, Cr2O3 to CrO2−, H2 to H2O, and FeO to Fe2O. Reactions were redox balanced with H+ and H2O as needed, then solved for the reaction quotient K over from 0 °C to 500 °C. The pH was assumed to be 7, when calculating for the fraction of P reduced (Supplementary Fig. 2).

The redox-dependent chemistry of phosphorus on iron was investigated to greater extent using the equilibrium chemistry model, which uses the GIBBS energy solver41 to determine equilibrium quantities and solve the reaction mass balances. This program has been used previously to understand water-rock transitions52, model Europa ocean chemistry53, and determine lightening promoted rock vaporization thermodynamics54. Using this model, the phosphate to phosphite ratio was calculated for various iron/iron oxide redox buffers. Species considered include quartz (Q), iron metal (I), fayalite (F), wustite (W), magnetite (M), and hematite (H). Phosphate is produced at the highest yield in those models that have iron or wustite as starting reactants (Supplementary Fig. 3). A simple solution model was constructed to determine how much water was required to reasonably dissolve all the phosphate formed by reduction in the HSC Chemistry program. The equilibrium chemistry was calculated as a function of the added solids FeO, Fe2O3 (2:1 by mole, 1:1 by Fe content) vivianite, strengite, and the two phosphite salts FeHPO3 and Fe2(HPO3)3 with dissolution governing the two phosphite salts FeHPO3 and Fe2(HPO3)3, with dissolution governing the reactions:

\[ \text{FeO} + 1/2 \text{H}^+ + 1/2 \text{H}_2 \text{O} \rightarrow \text{FeHPO}_3 \]

\[ \text{Fe}_2 \text{(HPO}_3 \text{)}_3 + 3/2 \text{H}^+ + 3/2 \text{H}_2 \text{O} \rightarrow \text{Fe}_2(\text{OH})_2(\text{PO}_3 \text{)}_2 \]

\[ \text{Fe}_2 \text{O}_3 + 1 \text{H}^+ + 1/2 \text{H}_2 \text{O} \rightarrow \text{Fe}_2(\text{OH})_3(\text{PO}_3 \text{)}_2 \]

\[ \text{Fe}_3 \text{O}_4 + 1/2 \text{H}^+ + 1/2 \text{H}_2 \text{O} \rightarrow \text{Fe}_3(\text{OH})_4(\text{PO}_3 \text{)}_2 \]

From these reactions, the equilibrium constants K were calculated and the fraction of iron bound to phosphate were determined for a range of iron/iron oxide redox conditions and iron species.

Microbial divergence. Two bacterial species capable of utilizing phosphite are *Prochlorococcus* and *Synechococcus*. Both are capable of utilizing phosphite as a sole phosphorus source46. The divergence of these two species was estimated using the TimeTree knowledge-base47. These results are consistent with arguments made by previous workers47, 49.

Solutinal oxidation experiments. A set of experiments were designed to measure the oxidation of phosphate in aqueous solution under air. Two experiments were set up to promote oxidation, employing iron metal. Iron metal initiates oxidation of phosphate in the presence of oxygen48 by reacting with O2 to form OH radicals49, which oxidizes phosphate50. Two other experiments were set up in deionized water, and a final control experiment used no phosphate, only iron (to test P release from the iron). The conditions of the experiments are given in Supplementary Table 2. A total 30 mM of phosphate sodium phosphate hydrate (Na2HPO4·H2O; 98 %; Riedel-deHaën 04283, Seelze, Germany) was prepared in deionized water (volume: 20 mL). The pH of the solution was adjusted to 7.0 with sodium hydroxide (NaOH) and nitric acid (HNO3). To initiate the oxidation of phosphate, ca. 572 mg of high-purity iron powder (99.9 % < 200 mesh; Alfa Aesar 00737, Ward Hill, MA) was added into the solution (mg Fe/mole HPO42− = 0.95). The reaction vessels (Falcon 50 mL polypropylene tubes) were tightly sealed to prevent evaporation, which could cause a change in the concentrations of phosphate and the product phosphate. Reaction temperatures were 4 ± 2 °C and 22 ± 2 °C. In order to prevent
the oxidation of phosphate by ambient light, these experiments were performed in the dark.

The concentration of phosphate produced by the oxidation of phosphate was monitored during the course of experiments by extracting a small aliquot of the dark.

for the oxidation of phosphite by ambient light, these experiments were performed in

The reaction is effectively: 

The oxidation half-life ($t_{1/2}$) can thus be approximated as:

where $m_{c}$ is the mass of the enzyme present per unit volume in the seawater. We find $m_{ext}$ as:

where $C_{p}$ is the density of cells in seawater and is assumed to be $10^{6}$ cells/mL, though this is likely a significant overestimate over the depth of the ocean.$^{25}$ $m_{cell}$ is the mass of individual bacterial cells, estimated here at about 1 pg, or $10^{-15}$ kg.$^{26}$ $F_{phosh}$ is the fraction of cells capable of oxidizing the reduced phosphorus compounds, estimated at 1%.$^{27}$ Finally, $F_{ret}$ is the fraction of the cell mass of phosphate-oxidizing microorganisms, that is ptxD.

Using the above calculations, the biologic oxidation half-life vs. $F_{ret}$ is provided as Supplementary Fig. 5.

**Data availability.** All data generated or analyzed during this study are included within the paper and its Supplementary Information files, and on the corresponding author’s Research Gate (https://www.researchgate.net/publication/326017979_Archean_phosphorus_speciation_data).

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**Author contributions**


**Additional information**

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