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Rethinking early Earth phosphorus Geochemistry

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Phosphorus is a key biologic element, and a prebiotic pathway leading to its incorporation into biomolecules has been difficult to ascertain. Most potentially prebiotic phosphorylation reactions have relied on orthophosphate as the source of phosphorus. It is suggested here that the geochemistry of phosphorus on the early Earth was instead controlled by reduced oxidation state phosphorus compounds such as phosphite (HPO_3^{2-}), which are more soluble and reactive than orthophosphates. This reduced oxidation state phosphorus originated from extraterrestrial material that fell during the heavy bombardment period or was produced during impacts, and persisted in the mildly reducing atmosphere. This alternate view of early Earth phosphorus geochemistry provides an unexplored route to the formation of pertinent prebiotic phosphorus compounds, suggests a facile reaction pathway to condensed phosphates, and is consistent with the biochemical usage of reduced oxidation state phosphorus compounds in life today. Possible studies are suggested that may detect reduced oxidation state phosphorus compounds in ancient Archean rocks.

meteorites | origins of life | phosphonates | prebiotic | redox chemistry

Fig. 1. Structures of biological P molecules at pH 8. (*Left*) Inorganic P molecules are shown. (*Right*) Representative organic P molecules are shown.

Phosphorus (P) is a key biologic element and is the limiting reagent in many ecosystems. Phosphorus is ubiquitous in biochemistry because phosphorylated biomolecules play major roles in replication and information (as RNA and DNA), metabolism (as ATP, NADPH, and other coenzymes), and structure (as phospholipids). Several key properties of P as phosphate make it advantageous to biologic systems, including thermodynamic instability coupled with kinetic stability, charge and coordination state, and a constant oxidation state under typical redox conditions (1). These features are especially critical to the formation of large informational polymers, and hence highly relevant to the origin and development of early life.

Phosphorus Geochemistry and Cosmochemistry

The major forms of P in life are summarized in Fig. 1. Inorganic P compounds used by life include orthophosphate, pyrophosphate and other condensed phosphates, phosphite, hypophosphite, and phosphine. These inorganic forms are either used by organisms as sources of P for the synthesis of organic-P biomolecules or are possible metabolic by-products of P metabolism (PH_3). Additionally, orthophosphate acts as a buffer in many cells, keeping pH constant at ≈ 7. Organic forms of P include compounds with C–O–P linkages and compounds with C–P linkages, and both are formed from inorganic P by using enzymes.

Phosphorus is a lithophile element at the redox conditions on the surface of the Earth, and hence orthophosphate is the dominant form of inorganic P on the surface of the Earth today. The concentration of orthophosphate is water-buffered by the solubility of orthophosphate minerals like apatite, $Ca_5(PO_4)_3(OH,F,Cl)$, on the present-day Earth, and of whitlockite, $Ca_9MgH(PO_4)_7$, and brushite, $CaHPO_4 \cdot 2H_2O$, before the rise of life-mediated apatite deposition (2). Because phosphate minerals are sparingly soluble ($[PO_4^{3-}] \approx 1\ \mu M$ at pH 7, 25°C), and because the geochemical cycling of phosphate is slow, the concentration of orthophosphate is typically the major limiting nutrient for the development of life over long timescales (3).
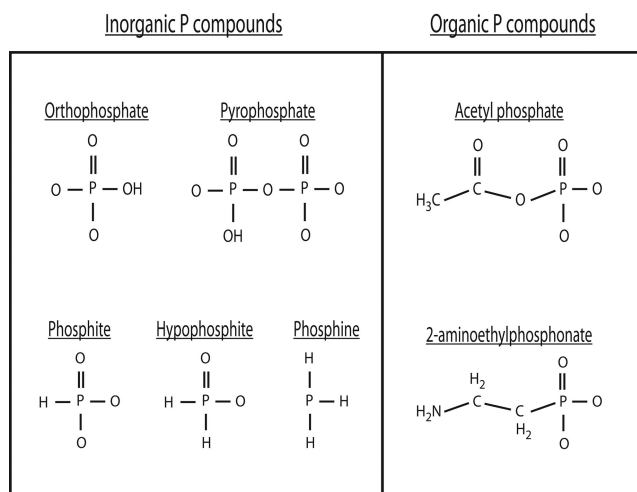
The dominance of orthophosphate is predicted from the thermodynamics of P phases at the redox conditions on the surface of the Earth (Fig. 2*A*). Orthophosphate minerals are the major carriers of P on the surface of the Earth, because no reduced oxidation state P (hereafter, reduced P) compounds are stable under terrestrial redox conditions. Other P phases may form in low concentrations by geologic processes, but these phases are not in thermodynamic equilibrium and slowly hydrolyze or oxidize to form orthophosphate. The condensed P compounds pyrophosphate and triphosphate are produced in micromolar concentrations in the vicinity of hydrothermal vents (4), and phosphine may be produced through volcanic processes, albeit at low total pressures (5). Despite these minor production pathways for potentially reactive P, the majority of P on the surface of the Earth today is in orthophosphate minerals.

Contrast the chemistry of P in the Solar System to the geochemistry of P (Fig. 2*B*). The cosmochemical behavior of P includes both a lithophile phosphate phase and a high-temperature siderophile phosphide phase. Siderophile P as phosphide is rarely encountered on the surface of the Earth; however, both lithophilic and siderophilic P are encountered in meteorites. Phosphates like apatite and whitlockite are the major carriers of P in lunar meteorites, basaltic achondrites, and shergottite-nakhlite-chassigny class (SNC) meteorites, whereas phosphides like schreibersite, $(Fe,Ni)_3P$, are the major carriers in iron meteorites, pallasites, and enstatite chondrites. Inter-

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Fig. 2. Thermodynamic stability diagrams for P species. (*A*) Eh-pH diagram for P species at 298 K, 10^{-6} M, with dashed lines represe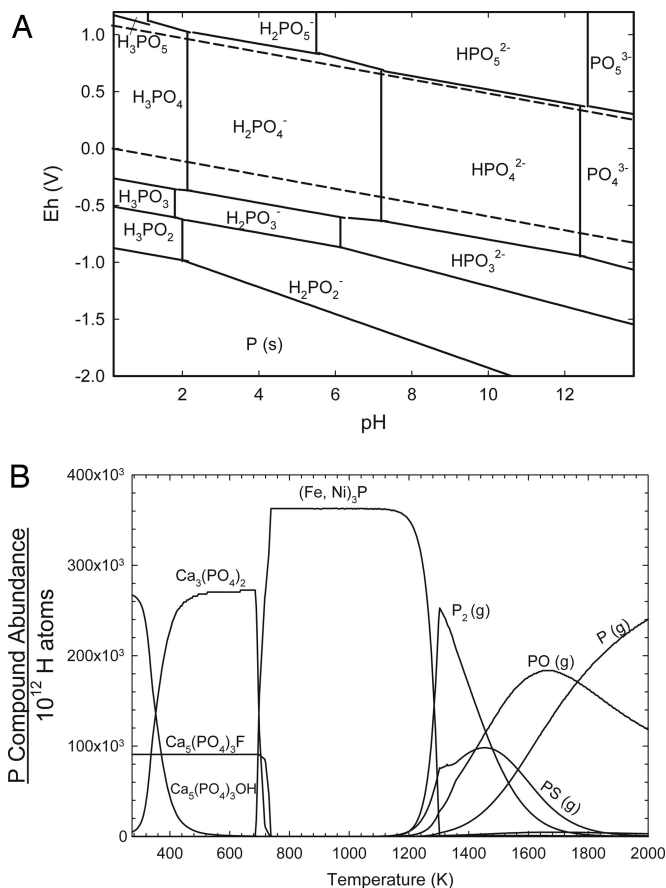nting the present-day atmosphere *(Upper)* and lower limit on water stability *(Lower)*. (*B*) Condensation sequence for P minerals assuming 10^{-4} bar and solar elemental abundances.

planetary dust particles and ordinary and carbonaceous chondrites have a mixture of both phosphates and phosphides (6).

Phosphorus in the Origin of Life

The incorporation of phosphate into organics through abiotic processes has been pursued extensively, with the critical step consisting of the removal of water during condensation. Techniques used for the phosphorylation of organics include adding condensing agents to mixtures of orthophosphate and organics (7), heating orthophosphate with organics (8, 9), adding condensed phosphates to organics (10), or a combination of these methods (7, 11, 12). Geochemical environments where these processes may take place include a dry pond with wet/dry cycles (12), hydrothermal vents (4), or mineral surfaces (2, 10). Many of these reactions depend on the loss of water in an aqueous setting, with the critical reactive intermediate being a high-energy condensed phosphate compound like pyrophosphate, triphosphate, or trimetaphosphate. However, the geochemical pathways that led to the abiotic production of condensed phosphates in high yield on the early Earth are not understood (13), although the dehydrative heating of whitlockite and brushite has been invoked for their formation (2).

Because of the difficulty of organic-phosphate condensation in solution, researchers have explored alternatives to phosphate in the origin of life. Thioesters may have preceded condensed phosphates in metabolism (14), a suggestion that is supported by experiments showing that thioesters condense phosphates to

pyrophosphate (15). Other studies have replaced the phosphate linkage in RNA with glyoxylate (16), or have replaced the sugar-phosphate backbone with peptides (17). Although these studies provide intriguing alternatives to phosphate in life, none address the necessary transition to P-based replication and metabolism.

The discovery of trace quantities of alkyl phosphonic acids in the Murchison meteorite (18) identified an alternative to phosphorylation by orthophosphate and its derivatives. Alkyl phosphonic acids have C–P bonds, and are significantly more stable than alkyl phosphates. A series of projects followed the detection of these phosphonic acids that attempted to connect possible pathways for their formation to origins of phosphorylated biomolecules (19–21). Although the detection of organic phosphonates in meteorites is intriguing, phosphonates make up only a small fraction (0.1%) of the total P in Murchison, and the bulk of the meteoritic material that falls to the Earth today has no phosphonates (6). Nonetheless, the detection of reduced P phases in meteorites encouraged researchers to search for other sources of P available to the early Earth.

Reduced P Geochemistry and Prebiotic Chemistry

I suggest here that the geochemistry of P on the early Earth was significantly influenced by siderophile P from extraterrestrial material, namely schreibersite, $(Fe,Ni)_3P$, which reacts with water to form reduced P compounds. Many reduced P compounds are significantly more soluble and reactive than orthophosphate, and therefore were superior prebiotic reagents on the early Earth. Extraterrestrial P minerals likely provided the reactive prebiotic P necessary for the origin of phosphorylated biomolecules and would have shaped the chemistry of P in the oceans of the early Earth. The development of life as we know it was contingent on an available early source of P, and reduced P compounds were an excellent source of P. The metabolic pathways in life are also indicative of the geochemistry of P on the early Earth, an argument similar to that used by biogeochemists in describing the metallome (22).

Schreibersite is a ubiquitous meteoritic mineral and is especially abundant in iron meteorites, but is also present in interplanetary dust particles (IDPs) (6) and other meteorite types. With growing evidence for a late heavy bombardment period on the early Earth (23, 24) at 3.8–3.9 Ga, extraterrestrial P would have been a significant component of the total P on the Earth's surface. Impacts probably delivered between 10^{15} and 10^{18} kg of reduced P during this period.

Furthermore, for high-velocity impacts of objects >100 m in diameter, the projectile partially evaporates and is distributed over the adjacent region as fine-grained particles (25). For the largest impacts of the late heavy bombardment, the whole Earth would have been covered by small particles of mafic and metallic particles, the chemistry of which would have been reduced relative to the surface of the Earth (26).

In addition to the dispersal of siderophilic P from the impactor during impact, the vapor plume of material that results from a large impact is chemically reducing and could have reduced phosphates in the target material or in the impactor to phosphides.[†] As evidence for this claim, a majority of the P in Lunar impact melts is in schreibersite (27), indicating both that a substantial fraction of the P delivered during impacts was reduced and that the impact process could reduce phosphate to phosphides (28). Additionally, iron end-member schreibersite may have formed recently during an impact in Puglia, Italy.[‡]

[†]Sheffer A, Melosh HJ, Thirty-sixth Lunar Planetary Science Conference Proceedings, March 14–18, 2005, League, TX (abstr).

[‡]Triscari M, Sabatino G, Quartieri S, Pisano C, 82nd Congresso Societá Italiana di Mineralogia e Petrologia, September 18–20, 2002, Pende, Consenza, Italy.
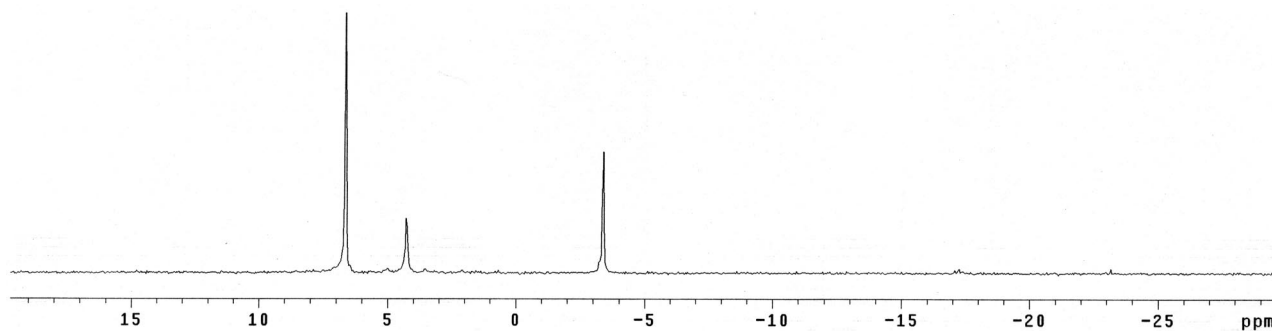
Fig. 3. NMR spectrum of Fe^{2+}, H_2O_2, and HPO_3^{2-} in solution after 1 day. From left to right, the peaks are orthophosphate (6.5 ppm), phosphite (4 ppm), pyrophosphate (-4 ppm), and triphosphate (small peak at -17.5 ppm).

Hence, large impacts chemically reduced lithophile P and dispersed fine-grained siderophile P globally to oceans and lakes, providing abundant reduced P to the Earth.

Gulick (29) was the first to suggest that the reduced P compounds hypophosphite and phosphite may have been more relevant to the origin of life than orthophosphate, basing his argument on the difference in solubility between these compounds and orthophosphate. However, his argument was dismissed at the time by leaders in the field (30), because he provided no pathways for the reduction of orthophosphate to form these compounds. Later developments suggested that orthophosphate could be reduced through volcanism (31), or through electric discharge in phosphate dust (32), but these pathways only provide local enrichments of reduced P. Conversely, the late heavy bombardment provided an abundant, global source of reduced P compounds to surface of the early Earth.

Schreibersite oxidizes in water to completion on relatively short geologic timescales ($1-10^4$ years), especially if distributed as fine-grained particles, and forms several P species in aqueous solution (33, 34). These species are mixed oxidation states, and include phosphite (HPO_3^{2-}), with P^{3+}; orthophosphate (HPO_4^{2-}), with P^{5+}; hypophosphate ($HP_2O_6^{3-}$), with P^{4+}; and pyrophosphate ($HP_2O_7^{3-}$), with P^{5+}. Under UV, hypophosphite ($H_2PO_2^-$), with P^{1+}, forms, and under acidic conditions, phosphine (PH_3), with P^{3-}, is produced. Under oxidizing conditions with H_2O_2, the peroxyphosphates HPO_5^{2-}, with P^{7+}, and $HP_2O_8^{3-}$, with P^{6+}, form. Thus, at room temperature and with simple aqueous reagents, schreibersite can form P compounds with a multitude of oxidation states. The primary product of schreibersite oxidation by water is phosphite, HPO_3^{2-}, with $>50\%$ of the total aqueous P in this form (33, 34). A majority of these P compounds likely originate through free-radical combination reactions (35). These corrosion products would have been available shortly after impact and the steady-state oceanic concentration would have been between 10^{-5} and 10^{-2} moles of reduced P compounds per liter of ocean water.

In addition to inorganic P compounds from schreibersite, organic compounds react with some of the schreibersite oxidation products to form organic P compounds at concentrations proportionate to the concentration of organics in solution. Acetate reacts with schreibersite to form C–P compounds like acetylphosphonate and hydroxymethylphosphonate, and potentially some C–O–P compounds including phosphoglycolate. The most likely reaction pathway is through a phosphite radical ($^\bullet PO_3^{2-}$) reacting with an organic radical, as evidenced although electron paramagnetic resonance spectroscopy and other data (35).

Phosphite (HPO_3^{2-}) is more soluble than orthophosphate by a factor of $\approx 1,000$ times over similar pH and temperatures. Thus, in a hypothetical early Earth ocean in which P chemistry consisted of both orthophosphate and phosphite, the concentration of phosphite would determine the bulk of dissolved P in the ocean. Phosphite is also much more reactive than orthophosphate, capable of forming condensed phosphates, organic C–P compounds, and even C–O–P compounds (35). Despite its increased reactivity over orthophosphate, phosphite is stable in the absence of strong oxidizing agents and could have persisted on the early Earth in excess of a billion years.

Phosphite can participate in a large set of reactions because of its relative thermodynamic instability. The interactions of phosphite with organic compounds are much more varied than orthophosphate reactions, and these reactions are used extensively in organophosphorus chemistry. As an example, phosphite readily reacts with aldehydes by the phospho-aldol reaction to form phosphonates (36), and although these conditions should not be considered prebiotic, they point to the reactive possibilities of reduced P. After the discovery of phosphonic acids in Murchison, a series of solutions of phosphite and simple organics (formaldehyde, acetone, and primary alcohols) were exposed to UV light, forming simple phosphonic acids (19, 21, 37). One of these phosphonic acids, phosphonoacetaldehyde, rapidly forms dimers in a process analogous to complex sugar synthesis (38). Several model pathways postulate putative RNA-like structures based on C–P linkages (20), although the chemical stability and formation pathways of these molecules has been called to question (39). A potentially fruitful area for future prebiotic P studies is the prebiotic synthesis of phosphonates like 2-aminoethylphosphonate because of the ubiquity of C–P compounds in biology (see "Biotic Evidence" below), and may highlight a specific role for reduced P in catalysts, or cell membranes and walls.

In addition to organic-phosphite compounds, phosphite forms pyrophosphate and triphosphate in solution with H_2O_2 and Fe^{2+}/Fe^{3+} in significant yields (5–30% and $\approx 0.5\%$, respectively; see Fig. 3) at room temperature. The reaction pathway leading to pyrophosphate from phosphite probably involves a series of radical reactions:

$$HPO_3^{2-} + {}^\bullet OH \rightarrow {}^\bullet PO_3^{2-} + H_2O \qquad [1]$$

$$^\bullet PO_3^{2-} + {}^\bullet OH \rightarrow HOPO_3^{2-} \qquad [2]$$

$$HOPO_3^{2-} + {}^\bullet OH \rightarrow {}^\bullet OPO_3^{2-} + H_2O \qquad [3]$$

$$^\bullet OPO_3^{2-} + {}^\bullet PO_3^{2-} \rightarrow P_2O_7^{4-} \qquad [4]$$
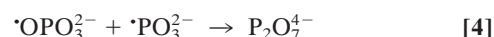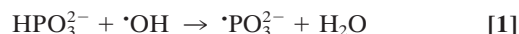
Reactions **1-3** are all well characterized, and the source of the $^\bullet OH$ radicals is the reaction of H_2O_2 with Fe^{2+} and Fe^{3+} and is known as the Fenton reactor (40). Triphosphate is likely formed by a radical reaction between $^\bullet P_2O_7^{3-}$ and $^\bullet PO_3^{2-}$. This reaction series is one of the most facile ways of producing pyrophosphate
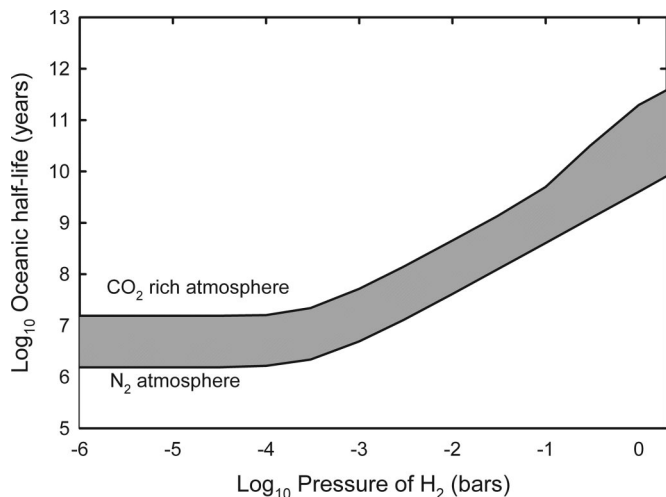
Fig. 4. Oxidative half-life for 1 mM solution of phosphite (HPO_3^{2-}) vs. atmospheric H_2 content. The top profile is based on the estimate of UV flux under a CO_2-rich atmosphere, whereas the bottom profile assumes no CO_2 (70).

Fig. 5. Eh-pH diagram for radical aqueous P species, 10^{-6} M, with dashed lines representing the present-day atmosphere (*Upper*) and lower limit on water stability (*Lower*).

and triphosphate from simple starting components yet described and does not rely on elevated temperatures or energetic condensing agents. Additionally, it does not invoke a dehydration step and occurs rapidly in aqueous solution. The production of condensed phosphates from phosphite would most likely occur in a region with a high production of oxidants, either in a shallow pond or near a tidal zone rich in radioactive material (i.e., a heavy mineral deposit; see ref. 41). In this respect, the oxidation of reduced P could have formed abundant condensed phosphates available for reaction and concentration all across the Earth's surface.

Phosphite is thermodynamically unstable but kinetically stable on the surface of the Earth. Solutions of phosphite show essentially no change over the course of years even when stored under air (42). The rate-limiting step in the oxidation of phosphite is the breaking of the P–H bond, which has a large activation energy ($\approx$370 kJ). The P–H bond is easily broken through a radical exchange reaction such as the reaction of phosphite with an $^{\bullet}OH$ radical to form H_2O and $^{\bullet}PO_3^{2-}$. Thus, the longevity of phosphite in solution is directly proportional to the amount of oxidizing radicals in solution. Phosphite is stabilized by mildly reducing conditions that remove oxidants from solution. For instance, under a reducing atmosphere ($P_{H2} = 0.1$ bar), the expected half-life of phosphite in the ocean by UV photolysis is between 10^8 and 10^{10} years (Fig. 4).

Biotic Evidence

The set of biochemical reactions that occurs in life today varies significantly from simple orthophosphate and organophosphate esters. Several organisms incorporate reduced P into their metabolic reactions, either as phosphonates or as inorganic reduced P compounds. These biochemical pathways strongly suggest the presence of an ancient P redox cycle in life.

Phosphonates are compounds with a C–P bond formed through a highly energetic process (43). Phosphonates are a ubiquitous but curious biochemical oddity and are found in many organisms, from bacteria to sea anemones to snail eggs to bovine brain tissue (ref. 44 and references therein). Lipid material and cell membranes are the major reservoir of phosphonates, but they also occur in proteins (45) and polysaccharides (46), but little is known about why they are produced (47, 48).

The P–C bond of phosphonates is not susceptible to hydrolysis, thermal decomposition (49), or decomposition by UV light (50),
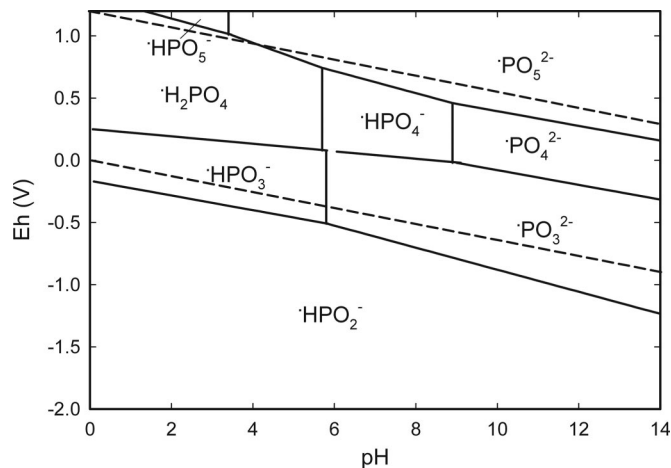
unlike the P–O–C bond of organophosphates; hence, phosphonates are more stable than organophosphates. An estimated 25% of all marine dissolved organic P compounds are phosphonates (51, 52), and 5% of organic soil P compounds are phosphonates (53). Many modern microorganisms use phosphonates as a P source when phosphate abundances are low, but most organisms will preferentially remove phosphates relative to phosphonates. As a result, phosphonates are concentrated in most environments (54).

The biosynthetic pathway for the production of phosphonates is a rearrangement of phosphoenolpyruvate to phosphonopyruvate, with subsequent chemical modification of phosphonopyruvate to form aminoethylphosphonate or phosphonoacetate or hydroxymethylphosphonic acid (44). The biodegradation of phosphonates in *Escherichia coli* proceeds through an inorganic phosphite intermediate and implies a genetic P redox cycle (55).

Approximately 1% of bacterial species (56) are capable of using reduced P compounds like phosphite and hypophosphite as sole P sources. Hypophosphite is oxidized by bacteria to phosphite, which is then incorporated into phosphonopyruvate by the pathways discussed above (57). One species of bacteria, *Desulfotignum phosphitoxidans*, uses phosphite/phosphate as its electron donor and receiver, respectively (58). Additionally, phosphine gas (PH_3) is detectable globally in the atmosphere and has been attributed to anaerobic metabolisms (59, 60).

These biochemical pathways are highly unusual given the dominance of orthophosphate in terrestrial geology and may be artifacts of ancient metabolic pathways (21). A plausible explanation for these biochemical pathways is that the geochemistry of P at the time these organisms evolved included reduced P compounds, and that the ability to incorporate reduced P through metabolic reactions was thus evolutionarily preferred. These organisms have retained the ability to use reduced P compounds because high-energy events can reduce orthophosphate to phosphite, as shown by the Eh-pH chemistry of free P radicals (Fig. 5). High-energy events like radioactive decay or photolysis could cause orthophosphate to spontaneously cleave to form a phosphite radical, followed by reduction to phosphite. Thus, the persistence of this genetic information may allow for the exploitation of a minor, but fruitful niche. Additionally, the ability to biosynthesize phosphonates and reduced P compounds would enable an organism to store P in forms unusable by many organisms, ensuring a constant source of P.

Potential Geologic Evidence

There are no known terrestrial reduced P minerals. However, reduced P minerals may be stable enough for detection in ancient rocks, based on the Murchison phosphonates. The organic C–P compounds in the Murchison meteorite were presumably synthesized early in the history of this meteorite, and remained subsequently unaltered for >4 Ga. Although the geologic history of the Murchison parent body was likely much less complex than the geologic history of the Earth, the stability of these compounds may point to the ability to detect reduced P compounds in ancient rocks on the Earth today, if conditions were amenable to preventing their oxidation.

Calcium phosphite ($CaHPO_3$) is stable under air even when heated at 95°C for 2 months. Assuming an activation energy for the oxidation of $CaHPO_3$ of $\approx$100 kJ per mole, calcium phosphite should remain essentially unchanged in excess of 10^5 years. It is unknown what would happen to $CaHPO_3$ under metamorphic conditions, but I provide two possible means of detecting reduced P compounds in ancient rocks.

The detection of small quantities of reduced P oxides (e.g., phosphite and hypophosphate) or reduced C–P compounds in ancient (>2.5 Ga) sedimentary or metasedimentary rocks would provide strong evidence for reduced P in early Earth geochemistry. Phosphates are well known in Archean rocks (61), and revisiting the mineralogy of these rocks coupled with a hunt for reduced P compounds may prove fruitful.

Alternatively, if reduced P phases are oxidized over geologic timescales during metamorphism, it may still be possible to track the presence of reduced P by using stable O isotope techniques. The formation of P compounds from extraterrestrial material forms PO_3 groups from O from water. Subsequent oxidation of PO_3 groups to PO_4 could involve O from another isotopic source. The detection of two isotopically distinct phosphate phases in a single metasedimentary layer could indicate the presence of reduced P oxidized during metamorphism. However, the detection of any isotopic anomaly would be difficult because of isotope equilibration, and also because of contamination from biogenic sources (e.g., 62). Conversely, reduced P may present a caveat for Archean phosphate isotopic studies as indicators of biotic activity.

Conclusion

The geochemistry of P on the early Earth is proposed to have included reduced P compounds in addition to phosphates. These compounds originated from the oxidation of schreibersite in extraterrestrial material after the late heavy bombardment period $\approx$3.8 Ga. The oxidation of schreibersite in water forms several potentially prebiotic P species including phosphite, pyrophosphate and triphosphate, and phosphonates. Phosphite is specifically relevant to early Earth geochemistry because it is considerably more soluble than orthophosphate, it forms organic C–P compounds and pyrophosphate, and it is used as a P source by several bacteria. The ability of microorganisms to use inorganic reduced P and to metabolize C–P compounds could be a genetic artifact of an ancient reduced P geochemistry. Reduced P compounds may still be directly detected in Archean sedimentary or metasedimentary deposits, or indirectly detected as an isotopic signature of phosphates.

Materials and Methods

Experimental. One gram of NaH_2PO_3 was added to 25 ml of a solution of H_2O_2 (0.9 M, from a 30% H_2O_2 stock from VWR International), bicarbonate (0.5 M as $NaHCO_3$), and Fe^{2+} (1.4 M, as $FeCl_2$ powder) to determine the oxidation of phosphite in a Fenton-style reactor. After one week the solution was filtered, neutralized with NaOH, and analyzed by NMR after the addition of an aliquot of D_2O. Approximately 95% of the phosphite had been oxidized to orthophosphate and condensed P species.

Table 1. Kinetic and thermodynamic data for reactions considered.

No.	Reaction	K, k (s^{-1})
5	$H_2O \rightarrow H^{\bullet} + {}^{\bullet}OH$	7.5×10^{-11}–7.5×10^{-13}
6	$H^{\bullet} + H_2O \Leftrightarrow H_2\ (aq) + {}^{\bullet}OH$	$K = 2.8 \times 10^{-7}$
7	$H_2\ (g) \Leftrightarrow H_2\ (aq)$	$K = 8.4 \times 10^{-4}$
8	$H^{\bullet} + HPO_3^{2-} \rightarrow H_2 + {}^{\bullet}PO_3^{2-}$	2.0×10^9
9	${}^{\bullet}OH + HPO_3^{2-} \rightarrow H_2O + {}^{\bullet}PO_3^{2-}$	3.7×10^9
10	$H^{\bullet} + {}^{\bullet}PO_3^{2-} \rightarrow HPO_3^{2-}$	1.0×10^9
11	${}^{\bullet}OH + {}^{\bullet}PO_3^{2-} \rightarrow HPO_4^{2-}$	3.0×10^9
12	$2\ H^{\bullet} \rightarrow H_2$	1.55×10^{10}
13	$2\ {}^{\bullet}OH \rightarrow H_2O_2$	1.1×10^{10}
14	$H^{\bullet} + {}^{\bullet}OH \rightarrow H_2O$	7×10^9

Reaction 5 is from ref. 70, and reactions 7–14 are from ref. 75.

$Ca(H_2PO_3)_2$ and $CaHPO_3$ were synthesized from a reaction of $CaCO_3$ (99%, VWR International) with H_3PO_3 (97%, VWR International) in solution. The reaction was allowed to proceed to completion and dried down. A small portion of each gray-white powder was collected and dissolved in a 0.05 M solution of Na_4EDTA. An aliquot of the solution was mixed with an equal volume of D_2O and analyzed by ^{31}P NMR. The powders were then placed in round-bottom flasks, submerged in a hot-oil bath (95°C), and exposed to air. Samples of the powders were dissolved in the EDTA solution and analyzed every few days by NMR.

Each solution was analyzed by using ^{31}P NMR on a Varian 300 four-nucleus probe Fourier transform-NMR (FT-NMR spectrometer at 121.43 MHz and 24.5°C for 256–35,000 scans after prior work (33, 35). Spectra were acquired in both ^1H-decoupled and coupled modes.

Modeling. The flux of reduced P on the early Earth was calculated from the total mass delivered to the Moon during this period [estimated at 5×10^{18} to 5×10^{20} kg (63)], multiplied by a factor of $\approx$10 to account for differences in between lunar fall rates and terrestrial fall rates. A majority of this material originated from the asteroid belt or was differentiated (23, 64). If this material was differentiated, then there were two early sources of P from extraterrestrial material: lithophile P and siderophile P. The abundance of P in the meteorites as lithophile P is $\approx$80 ppm, and as siderophile P was $\approx$3,000 ppm. Thus, the majority (95%) of P that fell to the Earth was siderophile P, as schreibersite and similar phosphides. Corrosion of iron meteorites occurs rapidly in seawater (34), and experiments suggest corrosion rates on the order of 0.1–10% of Fe_3P corroding per day for powdered schreibersite (33, 35). The concentration of these compounds in the early ocean is determined by dividing the total flux of extraterrestrial reduced P by the mass of the present-day ocean, and assumes complete, rapid corrosion of schreibersite with little oxidative loss, as discussed below.

The thermodynamically stable compounds in the Solar System were determined by using methods described in ref. 65, with Solar System abundances and a total pressure of 10^{-4} bar. The Eh-pH diagrams were constructed from data in HSC chemistry version 5.1 (Outokumpu Research Oy), with the following aqueous species added: H_3PO_5, $H_2PO_5^-$, HPO_5^{2-}, PO_5^{3-}, $H_4P_2O_6$, $H_3P_2O_6^-$, $H_2P_2O_6^{2-}$, $HP_2O_6^{3-}$, $P_2O_6^{4-}$ (ref. 42 and references therein) and for aqueous radical species ${}^{\bullet}HPO_3^-$, ${}^{\bullet}PO_3^{2-}$, ${}^{\bullet}HPO_2^-$ (66), ${}^{\bullet}H_2PO_4$, ${}^{\bullet}HPO_4^-$, ${}^{\bullet}PO_4^{2-}$ (67, 68), and ${}^{\bullet}H_2PO_5$, ${}^{\bullet}HPO_5^-$, and ${}^{\bullet}PO_5^{2-}$ (69).

The stability of phosphite under H_2 was determined by considering the set of reactions described on Table 1. The rate constants for reactions 10 and 11 were calculated by taking the ratio of the reaction equilibrium $\log_{10} K$ values for these two reactions and dividing by reaction equilibrium $\log_{10} K$ values for the reactions 12–14 and then multiplying by the rate constants for these three reactions and averaging to get the values on Table 1. Although these four reactions do not detail all of the possible reactions of HPO_3^{2-}, because reactions with other solutes could play a role in ocean water, the reactions with ${}^{\bullet}OH$ were likely the major oxidation pathway for HPO_3^{2-}. Reactions with other solutes should occur at a lower rate, as oxidation by ${}^{\bullet}OH$ radicals is a very efficient reaction.

The ratio of ${}^{\bullet}OH$ to $H^{\bullet}$ is influenced primarily by equilibrium reaction 6 with the concentration of H_2 (aq) determined from reaction 7. The photolysis of H_2O requires UV light ($<$240 nm), and it is estimated that the amount of water photolyzed reaches a steady-state concentration of $\approx 10^{-11}$–10^{-12} M for the top centimeters of water averaged globally over the day-night cycle (70). At these concentrations the rate of production of ${}^{\bullet}OH$ and $H^{\bullet}$ is balanced by the loss through combination reactions produc-

ing H_2O, H_2, and H_2O_2. The ratio of $^\bullet$OH to H$^\bullet$ is determined for specific concentrations of atmospheric H_2 (71), and these values are then used to estimate the longevity of HPO_3^{2-} in the water column. The set of reactions described on Table 1 is solved for specific time increments, and either the time it takes for 50% of the HPO_3^{2-} to oxidize to HPO_4^{2-} or the value $dHPO_4^{2-}/dt$ is determined at steady state, from which the half-life of HPO_3^{2-} is estimated in seconds. This value is then multiplied by the time it takes for water to diffuse over the average depth of the ocean (4 km), or

$$x^2/D = (400,000 \text{ cm})^2/2(\text{cm}^2 \text{ s}^{-1}) = 8 \times 10^{10}$$

where D is the eddy diffusion coefficient for water (72). This transforms the value for the oxidative half-life of HPO_3^{2-} for a 1-ml volume of water to the oxidative half-life for the whole ocean. Although crude, this method provides a first-order estimate of the time it would take to oxidize reduced P relative to atmospheric composition. This estimate is an underestimate of oxidative half-life compared with experimental results (73), and the actual half-lives are likely a factor of 10–100 times longer, when the inefficiency of UV light in the breakup of water and interactions with other solutes are considered.

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