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Research paper

Schreibersite on the early Earth: Scenarios for prebiotic phosphorylation

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A R T I C L E I N F O

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A B S T R A C T

The mineral schreibersite, $(Fe,Ni)_3P$, provides a reactive source of phosphorus capable of forming phosphorylated molecules. These molecules may have been an important component of prebiotic chemistry, allowing their build-up and eventual commencement of autopoiesis. Discussed here are potential geochemical routes to providing schreibersite, as a potentially important prebiotic mineral, to the Hadean Earth. Two routes are identified: delivery of phosphides by meteoritic material and the reduction of phosphates to phosphides by high-temperature, low-redox conditions. About 1–10% of all crustal phosphorus is estimated to have been in schreibersite during the Hadean, making the long-term reaction of this mineral with organic-laden water plausible for many years. Ultimately, such conditions would have been conducive to the formation of life as we know it today.

1. Introduction

The formation of phosphorylated biomolecules such as nucleotides remains one of the larger challenges in origins of life research. Ultimately such molecules are necessary for the production of nucleic acids, and thus key to generating self-replicating molecules. These molecules are also necessary for metabolic processes as they form key molecules such as ATP and Coenzyme A. Given the commonplace nature of phosphorus in biology, it would seem that prebiotic chemistry also included phosphorylated molecules. However, the process of phosphorylation under plausible geochemical conditions has been claimed to be stymied by insoluble phosphate minerals that are poorly reactive towards alcohols (Keefe and Miller, 1995; Lazcano and Miller, 1996).

The formation of phosphorylated organic compounds proceeds via a generalized reaction:

$$R' - OH + R'' - OPO_3{}^{2-} \rightarrow R'' - OH + R' - OPO_3{}^{2-}$$

where R′ and R″ can be H-, a phosphate or polyphosphate, or an organic group. Ultimately, proposed prebiotic chemical reactions that produce phosphorylated organic molecules fall into three main types: dehydration processes, addition of energetic phosphates, or addition of energetic organics. Dehydration experiments include “dry down” experiments that remove water by heating (e.g., Ponnamperuma and Chang, 1971), or reactions that replace water with non-aqueous solvents, thus lowering total water activity. Such solvents may include formamide (Schoffstal, 1976; Costanzo et al., 2007) or eutectic melts of urea and other organic compounds (e.g., Lohrmann and Orgel, 1971; Österberg et al., 1973; Gull et al., 2014). These solvents, characterized by a dipolar nature and low vapor pressure, drive condensation reactions.

Energetic organic compounds that act to form organophosphates fall within the broader group of compounds called “condensing agents”. These include cyanate (e.g., Yamagata et al., 1979), and carbonyl sulfide (Leman et al., 2006), among many others (e.g., Keefe and Miller, 1995; Pasek and Kee, 2011). In general, these reactions promote the loss of water by joining two molecules, and are not necessarily selective in how or what molecules are joined.

A preferred way to form organophosphates is to use activated phosphates, such as triphosphate and trimetaphosphate. These compounds bear an energetic P-O-P bond that cleaves when reacting with an organic reagent. One of the strongest lines of evidence that this pathway is prebiotically plausible comes from studies of polyphosphate formation in volcanic vents (Yamagata

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et al., 1991). Despite a plausible geochemical provenance for polyphosphate formation, Keefe and Miller (1995) and Lazcano and Miller (1996) outlined key problems with assuming the early Earth had an abundance of polyphosphates, namely that exceedingly few of these minerals exist in nature today and that environments where they might form are encountered infrequently, suggesting little global role for polyphosphates.

1.1. Mineral phosphorylation

Ultimately, the phosphorus for phosphorylation must come from a mineral source. Unlike H, C, N, O, and even S, phosphorus as a rule does not have a significant volatile phase. As an exception to this, phosphine (PH_3) is a trace gas within the modern environment, and the reducing conditions necessary to form this gas are unlikely to have been widespread on the early Earth (Glindemann et al., 1999).

Hence P must come from a mineral. Phosphorus minerals are ultimately of two forms: phosphates and phosphides. The distinguishing characteristics of these minerals are due to the alternating geochemical behavior of P under differing conditions. At low temperature and under oxidizing conditions, phosphorus will form phosphate groups that make up phosphate minerals, a behavior best characterized as lithophilic phosphorus chemistry (rock-loving). At high temperature and under reducing conditions, phosphide minerals become dominant, resulting in siderophilic phosphorus chemistry (metal-loving). These two behaviors are well demonstrated by the chemistry of phosphorus in extraterrestrial materials, where chondritic meteorites bear both phosphides and phosphates. Thermodynamic equilibrium calculations for solar system conditions also bear this out: phosphides are the preferential P phase at high temperature, but oxidize to phosphates as temperatures decrease (e.g., Pirim et al., 2014).

Many prebiotic phosphorylation reactions have relied upon phosphate minerals that bear ammonia ($NH_4H_2PO_4$), sodium (NaH_2PO_4), or potassium (KH_2PO_4). These minerals are unlikely to have been widespread on the surface of the early Earth due to their high solubility. More likely are minerals with divalent cations to balance the phosphate anion. These include Ca^{2+}, Mg^{2+}, Fe^{2+}, and the rare Earth elements. Such minerals are much poorer as phosphorylating agents (Beck and Orgel, 1965).

Primordial phosphorus minerals are fairly limited in number. Hazen (2013) outlined 17 phosphate minerals and three phosphide minerals likely present in the Hadean. The phosphate minerals consist of PO_4 tetrahedra and include such minerals as apatite, monazite, and whitlockite. Of the minerals on Hazen's list, few other phosphate minerals are likely to be widespread on the early Earth. Phosphide minerals include schreibersite, which is probably the most common of these, as the other phosphides do not make up significant fractions of the mineralogy of meteorites.

Phosphorylation using these minerals may occur as the mineral dissolves in water (or other solvent), providing phosphate that can in turn react with an organic substrate, or may occur on the mineral surface. If organic compounds bind to the surface of minerals, then phosphorylation reactions hypothetically become easier as the degrees of freedom for reactions decreases (e.g., Georgelin et al., 2013). Condensation reactions may be preferred on such materials.

1.2. Schreibersite phosphorylation on the early Earth

Pasek and Lauretta (2005) proposed that the meteoritic mineral schreibersite, $(Fe,Ni)_3P$ could have been a viable source of phosphorus on the early Earth. This argument was based on the ubiquity of phosphide minerals in meteorites, especially massive iron meteorites, and the generation of soluble and reactive phosphorus phases from the reaction of water with this mineral. These soluble phosphorus compounds include phosphate, pyrophosphate, phosphite, and hypophosphate typically (Fig. 1), and these compounds are formed by free radical reactions (Pasek et al., 2007, 2008). Additionally, when heated mildly (60–80 °C, pH 8–10) with nucleosides, schreibersite can phosphorylate nucleosides to produce nucleotides (Gull et al., 2015). Yields, while not high (<6%) are yet some of the highest for reactions occurring in water below 100 °C without a condensing agent. Given its simplicity, such a reaction might be viewed as being highly relevant to prebiotic chemistry, provided there was a source of nucleosides.

The relevance of schreibersite to prebiotic chemistry depends on its presence on the early Earth. There is little doubt that schreibersite was present during the time of prebiotic chemistry; meteorites bearing schreibersite are among the oldest objects in the solar system. Indeed, in contrast to other phosphate minerals such as

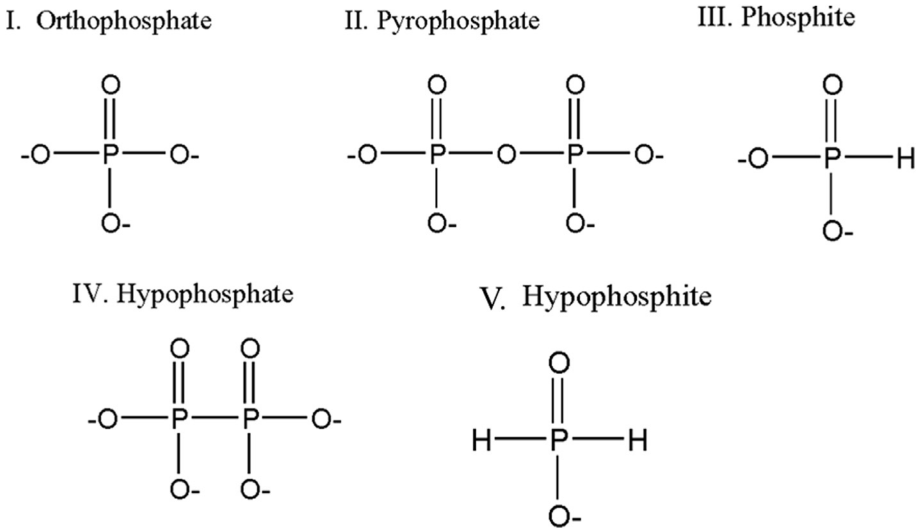

Figure 1. Structures of phosphorus salts produced during schreibersite corrosion. The oxidation of P within these salts is +5 for orthophosphate and pyrophosphate, +3 for phosphite, +4 for hypophosphate, and +1 for hypophosphite.

struvite ($MgNH_4PO_4 \times 6H_2O$), there is little doubt that schreibersite would have been present from meteorite in-fall (Hazen, 2013). A more applicable question is, “Was there enough schreibersite to promote chemistry outside of microenvironments?”

A hint of an answer is provided by investigating modern day sources of this mineral. By a large margin, schreibersite is found as a meteoritic mineral. It can be considered to be diagnostic of a meteoritic origin for rocks, given its ubiquity in meteorites. It was recognized as uniquely meteoritic early in the history of meteoritics (Berzelius, 1832). Since then, the few terrestrial occurrences of this mineral have included a co-occurrence with native iron from Greenland (Pedersen, 1981), and a few phosphide minerals occurring within tektites (Chao et al., 1964) and within fulgurites, which are glasses formed by cloud-to-ground lightning (Essene and Fisher, 1986; Pasek et al., 2012). Recently, Britvin et al. (2015) discovered a wide variety of phosphide minerals, including schreibersite, from the Hatrurim formation, in Israel. These minerals were likely produced when reducing gas (CH_4 or H_2) flowed through the nickeliferous rock during high-temperature contact metamorphism.

One line of evidence for the presence of this mineral on the early Earth is small concentrations of phosphite ($HPO_3{}^{2-}$) in 3.52 billion year old carbonate rocks (Pasek et al., 2013). This anion, one of the principal corrosion products of schreibersite, can bind with Ca^{2+} to form $CaHPO_3 \times nH_2O$. While the actual origin of this anion within this carbonate rock is not clear, a possible source is from schreibersite corroding in water on the early Earth.

Given the rather facile route to forming nucleotides from schreibersite under mild conditions (Gull et al., 2015), as well as other organic compounds (Pasek et al., 2013) identifying plausible sources of schreibersite or other phosphide minerals on the early Earth might help address the origin of nucleic acids. Three plausible routes to schreibersite on the early Earth will be discussed within this manuscript. These include meteoritic sources delivering massive amounts of material during a heavy bombardment period, reactions between water and rock producing reducing environments (e.g., serpentinization) at low temperature, and high-temperature alteration of low oxygen-fugacity rocks.

Results of this work are directly relevant to prebiotic model systems that allow for the development of life, such as the Nuclear such as the geothermal field model (Mulkidjanian et al., 2012), which relies on reduced phosphorus compounds as a source of phosphorus. If schreibersite were present on the early Earth through means such as meteorite delivery, then phosphorylation could have occurred readily, including in the geyser model. Phosphorylated biomolecules would hence have been an emergent phenomenon of aqueous alteration of schreibersite-bearing planets.

1.3. *Mechanistics of schreibersite phosphorylation*

If schreibersite can be considered a “Miracle” mineral with respect to its relatively uncommon ability to phosphorylate organics at low temperatures in contrast to other phosphate minerals, then the outstanding question is “How are organics phosphorylated by schreibersite?” Three possible solutions present themselves. Two of these pathways are broadly extensible to other terrestrial phosphorus minerals: (1) Schreibersite generates phosphate at a concentration sufficient to promote phosphorylation through thermodynamic equilibrium (following, in part, the pathway of Powner et al., 2009), or (2) polyphosphates generated by schreibersite corrosion are present in sufficient concentration to promote phosphorylation. Pyrophosphate is known to form from schreibersite corrosion at yields of 10–20% of the total P oxyanions (Pasek et al., 2007). Phosphorylation by polyphosphates is well known in prebiotic chemistry, though disputed in importance (Keefe and Miller, 1995; Lazcano and Miller, 1996). These two pathways do not depend significantly on the specific mineralogy of the mineral source of phosphorus (outside of corresponding cations), and hypothetically environments where soluble phosphate or polyphosphates could be formed from phosphate minerals would be sufficient for phosphorylation.

However, it is possible that schreibersite does not phosphorylate organic compounds through these pathways, but relies on another pathway intrinsic to its oxidation. Thus we are presented with a third option. (3) Phosphorylation occurs by reaction with a reduced or otherwise inaccessible-to-phosphate-chemistry P compound. Unlike phosphate minerals, schreibersite must oxidize to produce its novel chemistry, and in doing so, a reactive intermediate capable of phosphorylating organics may arise spontaneously. Such an intermediate may not be found with phosphate minerals. An example of such an intermediate would be the phosphite radical ($PO_3{}^{2-}$), which forms spontaneously as schreibersite corrodes. If such an intermediate is necessary for phosphorylation by schreibersite corrosion, then schreibersite, or more generally reduced P compounds, would be required for phosphorylation on the early Earth.

2. Methods

This paper will rely on data from the literature to propose and evaluate models, and will couple these models to thermodynamic and kinetic constraints when available. More specifically, thermodynamic calculations will be performed using the thermodynamic equilibrium program HSC Chemistry (Outokompu Research Oy) to address complex questions, which has been used previously to address chemistry of sulfur in the Solar System (Pasek et al., 2005), and the chemistry on Jupiter’s moon Europa (Pasek and Greenberg, 2012).

For the cases considered here, once the abundances of the elements are supplied, the HSC program then calculates the distribution of elements amongst the various chemical species (listed below) by solving the minimum thermodynamic energy state using the White algorithm (White et al., 1958) coupled to mass balance calculations. Species considered include iron and nickel oxides: Fe_2O_3, Fe_3O_4, NiO, Ni, FeO (an analog to wüstite), Fe_2SiO_4, $FeTiO_3$, Fe_2TiO_4, Fe, and FeOOH; the phosphorus-bearing minerals Fe_3P, Ni_3P, $Ca_5(PO_4)_3OH$, $Ca_3(PO_4)_2$ (analog to whitlockite), and $FePO_4 \times 2H_2O$ (strengite); as well as other minerals to balance elements such as SiO_2 and $CaSiO_3$. Gases considered include N_2, H, H_2, H_2O, O, O_2, O_3, C, CO, CO_2, CH_4, P, PH, PH_2, PH_3, P_2, P_3, P_4, PO, PO_2, P_2O_3, P_2O_4, P_2O_5, and P_4O_{10}. Solutes considered include H_2O liquid with H^+, OH^-, H_3PO_4, $H_2PO_4{}^-$, $HPO_4{}^{2-}$, $PO_4{}^{3-}$, H_3PO_3, $H_2PO_3{}^-$, $HPO_3{}^{2-}$, H_3PO_2, $H_2PO_2{}^-$, $H_4P_2O_7$, $H_3P_2O_7{}^-$, $H_2P_2O_7{}^{2-}$, $HP_2O_7{}^{3-}$, $P_2O_7{}^{4-}$, FeO^+, $FeOH^{2+}$, $FeOH^+$, Ni^{2+}, $NiO_2{}^{2-}$, and $NiOH^+$. Thermodynamic data for the above species are all included as part of the HSC database.

The data for several species not included in the HSC database come from literature sources. More specifically, awaruite (Ni_3Fe) comes from Foustoukos et al. (2015), adenosine, and the adenosine monophosphates H_2AMP, $HAMP^-$, and AMP^{2-} from Alberty (2003).

A first set of calculations solved for aqueous phosphorus chemistry by investigating condensation reactions in aqueous solution. These reactions, which are pH dependent, solve for the thermodynamic equilibrium constant K by $K = e^{\frac{-\Delta G^0_{rxn}}{RT}}$. These reactions calculated K as a function of pH, and reactant concentration. The second set of calculations sought to identify gas-solid chemistry as a function of mineral redox buffers, specifically focusing on P gas chemistry and P mineral decomposition temperatures. In these calculations, a small quantity (10) of $Ca_3(PO_4)_2$ was added to a system containing an excess of SiO_2 (1000), and the mineral redox buffer (1000× each stoichiometric coefficient) being investigated. The temperature was changed from 500 to 2000 °C, at 1 atm. The decomposition point and P gas chemistry was recorded for each redox mineral buffer. The final set of calculations was done using an Eh-pH calculation tool in the HSC program. This tool, which solves for mineral stability as a function of temperature, element concentration, redox and acid-base chemistry, provides the major element aqueous speciation under specific conditions. For these calculations, the abundance of Ni, P, and Fe was all set to 10^{-8} M, and solved for at temperatures of 25 and 300 °C.

3. Results

3.1. Phosphorylation processes

Phosphorylation of organic compounds takes place when the addition of physiochemical energy or an increase in the activity of phosphate drives phosphorylation reactions towards products. Results of calculations demonstrate the thermodynamics of polyphosphate (pyrophosphate) generation from orthophosphate, amount of AMP predicted to form as a result of phosphorylation of adenosine from high concentrations of orthophosphate, and yield of AMP as a function of polyphosphate (pyrophosphate) to phosphate ratio (Fig. 2). These calculations were performed at 298 K (25 °C) at 1 atm of pressure. The production of polyphosphate and AMP from orthophosphate requires acidic conditions and high concentrations of inorganic phosphate. Results are roughly comparable to those of Holm (2014) who made similar claims for production of polyphosphates in glasses. In contrast, the formation of AMP from polyphosphates proceeds better at higher pH, though a pyrophosphate to phosphate ratio of 0.01 and higher is still necessary.

This last calculation is done at equilibrium conditions, that is, solving for the concentration of AMP as a function of adenosine, pH, and the pyrophosphate to phosphate ratio:

$$[\mathrm{AMP}] = \mathrm{K}\frac{[\mathrm{PPi}]}{[\mathrm{Pi}][\mathrm{A}]}$$

where the brackets imply activities (concentrations in moles/L in ideal aqueous solutions), PPi is pyrophosphate, Pi is phosphate, A is adenosine, and K is the equilibrium constant $\left(\mathrm{K} = e^{\frac{-\Delta G^0_{rxn}}{RT}}\right)$. Under these conditions, there are no limiting reagents. In reality, phosphorylation would occur to the extent permissible by the mass balance of the reactants. The quadratic formula can solve for an actual concentration of AMP formed from pyrophosphate, starting with varied initial concentration of solutes:

$$[\mathrm{AMP}] = \frac{\left(\mathrm{K}[\mathrm{PPi}]_\mathrm{i} + \mathrm{K}[\mathrm{A}]_\mathrm{i} + [\mathrm{Pi}]_\mathrm{i} - \sqrt{\left(\mathrm{K}[\mathrm{PPi}]_\mathrm{i} + \mathrm{K}[\mathrm{A}]_\mathrm{i} + [\mathrm{Pi}]_\mathrm{i}\right)^2 - 4(\mathrm{K}-1)\left(\mathrm{K}[\mathrm{PPi}]_\mathrm{i}[\mathrm{A}]_\mathrm{i}\right)}\right)}{2(\mathrm{K}-1)}$$

where the “i” subscript denotes the initial concentration of the reactants and products. Nonetheless, the results from this method provide similar results as Fig. 2C: a higher pyrophosphate to phosphate ratio and high pH promote phosphorylation of adenosine.

These pyrophosphate phosphorylation yields should be viewed as maxima. Competing reactions, such as the hydrolysis of pyrophosphate, will decrease the reactivity of pyrophosphate towards organic substrates. Additionally, these results may be checked against schreibersite corrosion products. Schreibersite reacts with water to form phosphorus oxanions, including pyrophosphate and phosphate. The pyrophosphate to phosphate ratio is between 0.1 and 0.5, typically (Pasek et al., 2007). The amount of phosphorylated product formed by nucleoside phosphorylation (Gull et al., 2015) in the schreibersite system is lower than the amount predicted by the equation above, although it appears as though the phosphorylated product is still generated at the expense of pyrophosphate (e.g., pyrophosphate decreases in concentration as AMP increases). Notably, these calculations eliminate the possibility of phosphorylation of adenosine by phosphate in the schreibersite corrosion experiments of Gull et al. (2015). The activity of phosphate is too low to promote phosphorylation, and hence some other reactive P compound must be promoting the reaction.

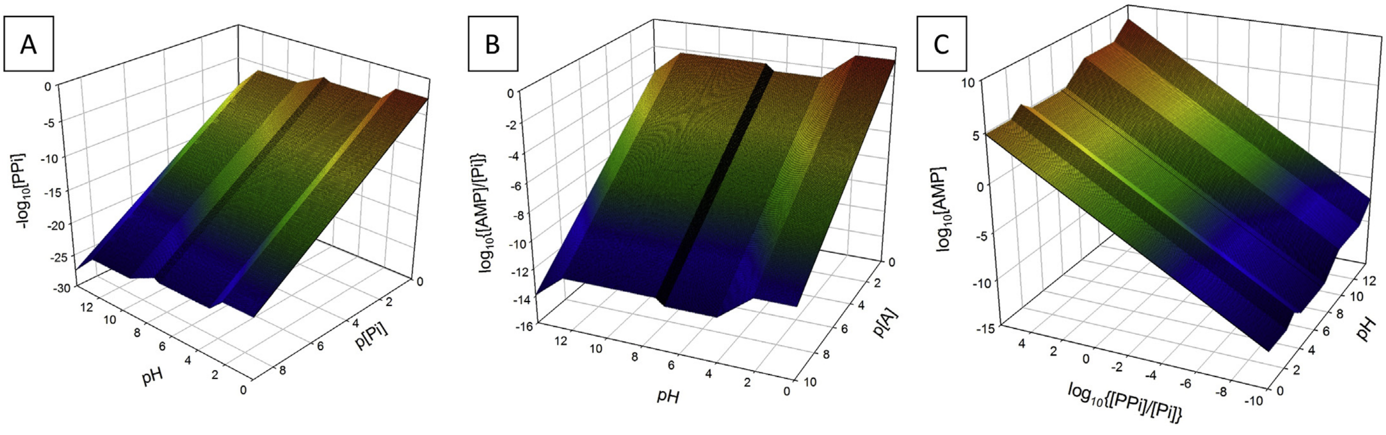

Figure 2. Equilibrium calculations for aqueous systems. The function “p” is the negative log base ten. Units are in activity, or moles/L if we assume ideal solutions. (A) Pyrophosphate (PPi) production as a function of pH and phosphate (Pi). (B) Adenosine monophosphate (AMP) to phosphate ratio as a function of pH and adenosine (A) concentration. (C) Adenosine monophosphate concentration (AMP) as a function of pH and the pyrophosphate to phosphate ratio.

3.2. Meteoritic source scenario

The first scenario invoked for schreibersite being an active phosphorylating mineral on the early Earth is through its delivery by meteoritic material (Pasek and Lauretta, 2005). In this scenario, metal-laden meteorites reached the surface of the Earth in great abundance during the heavy bombardment period ~4 Ga (Pasek and Lauretta, 2008). There has been doubt recently cast on the timing and extent of the heavy bombardment period (Zellner and Delano, 2015), and it is possible that the bombardment rate was lower but persisted over longer timescales than estimates of the late heavy bombardment originally assumed. Given that schreibersite certainly came in part from meteoritic source, the question here becomes "How much?"

Platinum group element (PGE) abundances within the crust and bulk Earth can serve as a baseline for assessing the amounts of highly siderophilic elements that were delivered by extraterrestrial material. During the early differentiation of the Earth, PGEs may be confidently assumed to have preferentially fractionated into the Earth's core, leaving the mantle and crust extremely depleted in these elements. In the time since the differentiation of the Earth, the slow accumulation of PGEs by meteoritic material delivery could then account for the slight excess of PGEs present within the crust.

The average PGE and P abundances within different meteorite classes (Lodders and Fegley, 1998 and references therein) can be compared to the average PGE abundance within the Earth's crust (Wedepohl, 1995) to determine meteoritic contribution of P. On average, about 10^{17}–10^{19} kg of meteoritic material could have delivered all of the present day crustal PGEs. Iron meteorites (based on Willis, 1980) have a lower total flux as the PGE concentration within these meteorites is significantly higher. From these numbers we can estimate the mass of schreibersite delivered. This mass depends on meteorite type: carbonaceous chondrites tend to bear fewer phosphide minerals, and only about 1% of the P within these meteorites is in schreibersite. Ordinary chondrites have more phosphides, but are still phosphate-dominated, with about 10% of the P in schreibersite. Iron meteorites and enstatite chondrites bear about 100% of their P in phosphides (Pasek and Lauretta, 2008). To this end about $10^{13.5}$–$10^{15.5}$ kg of the Earth's current continental crustal phosphorus was at one time schreibersite. This is equivalent to between 3 parts per million to 0.04%. The P content of the Earth's crust is presently about 10^{19} kg.

These numbers are minima. Since the Earth's crust has an average age of about 2 billion years (Nelson and DePaolo, 1985), these numbers reflect the accumulated material for the last 44% of the Earth's history. Using lunar and terrestrial data, as well as a new bombardment model, Marchi et al. (2014) argued for about 10^{22} kg of total material delivered to the Earth by a heavy but steadily decreasing, late-accretionary bombardment. As a result, about 10^{17}–10^{19} kg of P as phosphides may have been delivered to the early Earth, more than enough to have completely altered crustal phosphorus chemistry (See Table 1).

3.3. Rock serpentinization as a source of phosphides

A second scenario for the presence of schreibersite on the early Earth is the formation of schreibersite by the low-temperature (<300 °C) reduction of phosphate minerals. In many ways, such a scenario is preferred of scientists proposing that life developed in the environment of hydrothermal systems (Mulkidjanian et al., 2012). Production of schreibersite in such an environment would couple phosphorylation to environments where organic synthesis may occur readily, following suggestions by Russell et al. (2014) and Sojo et al. (2016).

Table 1
Amount of phosphides delivered by different meteorites, assuming each meteorite type is the sole source of P. Fluxes are calculated by taking the geometric mean of the meteorite flux calculated from the PGEs.

Meteorite type	Present crust	Late accretionary estimate
	Total phosphide delivered (kg)	Total phosphide delivered (kg)
CI	5×10^{13}	1×10^{17}
CM	5×10^{13}	1×10^{17}
CV	4×10^{13}	1×10^{17}
H	4×10^{14}	1×10^{18}
L	5×10^{14}	1×10^{18}
LL	7×10^{14}	1×10^{18}
EH	8×10^{15}	2×10^{19}
EL	5×10^{15}	1×10^{19}
Irons[a]		
IAB[b]	9×10^{14}	4×10^{18}
IIAB	1×10^{15}	5×10^{18}
IIIAB	2×10^{15}	8×10^{18}
IVA	6×10^{14}	2×10^{18}

[a] Iron meteorite flux amount is based on Ir constraints alone, as opposed to Ru, Rh, Pd, Os, Ir, and Pt.

[b] The four groups here are chosen as they are the top four most common iron meteorite groups discovered as finds.

As of yet, there is no evidence for hydrothermally-formed schreibersite. Schreibersite can only form under the most reducing conditions, and the presence of water tends to prevent thermodynamic equilibrium from favoring schreibersite formation. The conditions necessary for schreibersite formation include highly reducing conditions dominated by H_2 or CH_4, coupled to a source of nickel within the host rocks. The presence of nickel within the host rocks allows for the preferential trapping of P within iron-nickel phosphide, lowering the thermodynamic barrier to phosphorylation. Nickel phosphide, as Ni_3P, is accessible under slightly less reducing conditions than Fe_3P. In this case, a hydrothermal route to phosphide production requires a nickel-rich, reducing environment. One environment may be the high-temperature alteration of olivine-rich rocks to lead to serpentinites, especially those bearing the mineral awaruite (Ni_3Fe). Even these in these environments, schreibersite formation requires extremely high H_2 and low oxygen content (Fig. 3).

3.4. High temperature alteration of low oxygen-fugacity rocks

In contrast to low-temperature phosphide production, an alternative route to forming phosphides may be through high-temperature (500–1500 °C) reduction of phosphates. Examples of such a pathway may be found sporadically in the geologic literature. For instance, Britvin and others (2015) demonstrated that schreibersite occurs naturally in the Haturim Formation in the Middle East. These rocks, which include new minerals such as NiP_2 and Ni_5P_4, were formed at temperatures exceeding 1000 °C in nickel-rich rocks. In these reactions, a strong reductant such as carbonaceous material within the host rock served to power the extreme local reduction.

Similar to the phosphides in the Hatrurim formation, one group of rocks that bear phosphide minerals consistently are fulgurites, glasses formed by cloud-to-ground lightning (e.g., Essene and Fisher, 1986; Pasek and Block, 2009; Pasek et al., 2012). Fulgurites are formed by the high-temperature, rapid alteration of rocks, and present another route to schreibersite formation. In general, such a process would be difficult to invoke for widespread phosphide production, as reduction of phosphate to phosphides by lightning occurs only under certain conditions, and does not change phosphorus minerals completely (Pasek and Block, 2009). As a result, reduction of phosphate by lightning would only generate a few tons of reduced P each year.

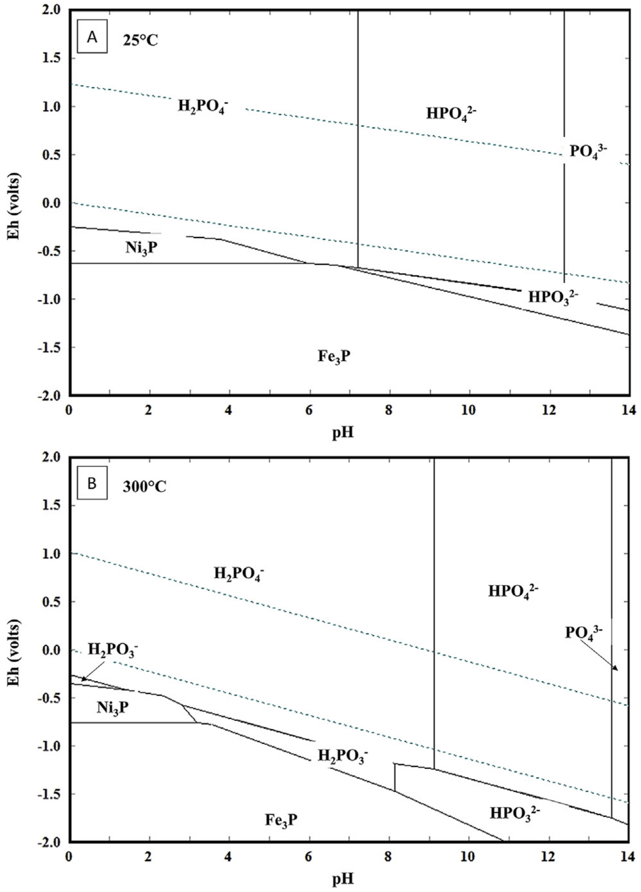

Figure 3. Eh-pH diagram of the Fe-Ni-P system at 25 °C and 300 °C. The concentrations of Fe, Ni, and P dissolved in solution are set to 1 μM. The two dashed lines correspond to 1 atm of O_2 (A) and 1 atm of H_2 (B).

A parallel to this process acting the surface of the early Earth comes from lunar geology. Lunar impact breccias are characterized by an abundance of schreibersite as a major phosphorus carrier. In some breccias, schreibersite may be more abundant that the corresponding phosphate minerals (Taylor and Hunter, 1982). Given that the Moon formed from Earth material, it is plausible that the early Earth may have had similar chemistry on its surface as the Moon.

A portion of lunar schreibersite was attributed by Pasek (2015) to have formed as a result of the high-temperature volatilization of phosphorus under low $f(O_2)$, phosphate minerals volatilize to form P, P_2, and P_4 gases. These gases can subsequently phosphidize iron metal to form schreibersite, despite the redox conditions being sufficiently high so as to promote formation of phosphates. In this respect, schreibersite is produced by kinetic reactions, instead of thermodynamic reactions.

Fig. 4 illustrates the mineral redox buffer conditions capable of generating P_4, P_2, and P gas as a function of temperature and at 10^{-4} bar of total pressure. The presence of iron appears to be critical to this process: iron-wüstite (IW), quartz-iron-fayalite (QIF), and iron-ilmenite-ulvospinel (IIU) are the only redox buffers that generate significant reduced P gases. Reduced P gases are formed at about 5% of the total P in the IW and QIF mineral redox buffer systems, and 100% of the gases for the IIU redox buffer system. In contrast, only PO and PO_2 gases are present at the higher $f(O_2)$ conditions, and these are unlikely to produce metal phosphides.

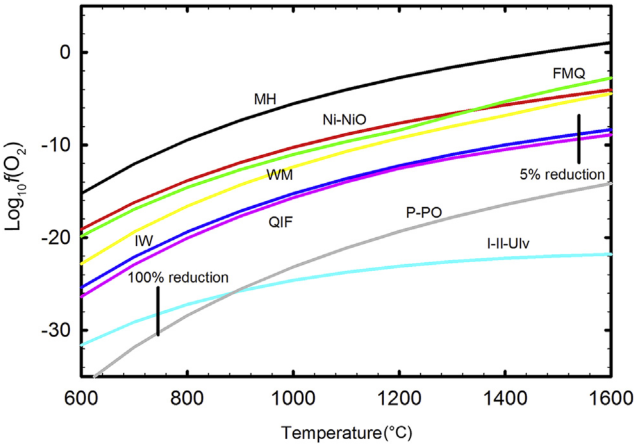

Figure 4. Reduction of phosphorus in the gaseous form as a function of oxygen fugacity and mineral redox buffers. Buffers are: magnetite-hematite (MH, black), Ni-NiO(red), fayalite-magnetite-quartz (FMQ, green), wüstite-magnetite (WM, yellow), iron-wüstite (IW, dark blue), quartz-iron-fayalite (QIF, magenta), P-PO gas-grey, and iron-ilmenite-ulvospinel (I-Il-Ulv, light blue). 5% reduction occurs at about 1550 °C at the IW and QIF redox, as well as at 750 °C at the I-Il-Ulv redox.

I hence estimate that, if early Earth rocks were subjected to a high-temperature heating event, and were of sufficiently reducing character, then about 5% of all phosphorus could have been trapped into phosphides on the early Earth in impact-processed rock. The present-day redox state of the mantle reaches about −1 to −4 log units below the fayalite-magnetite quartz buffer, not far from the conditions necessary to produce ∼5% reduced P gas as phosphate minerals are volatilized (Ballhaus et al., 1990; Frost et al., 2004; Frost and McCammon, 2008). If crustal rocks in the Hadean were close to mantle rocks in terms of composition, then metal-phosphides on the surface of the Earth would be feasible, and might bear up to 5% of the Earth's total P. This would be true for any sort of volatilization event, such as high-temperature volcanism, or impact.

4. Discussion and conclusions

Schreibersite may have served as a primordial phosphorylating agent, given its reactivity towards organic substrates under relatively mild conditions. Three potential sources of schreibersite have been outlined above. Of these, serpentinization producing schreibersite appears to be inefficient and unlikely to have operated on a large scale. Thus the most likely sources of schreibersite on the early Earth were a combination of meteoritic sources and production by high-temperature volatilization.

Assuming the late-accretionary model of Marchi et al. (2014) is correct, about 10^{18} kg of phosphide minerals fell to the Earth in the Earth's early history. Much of the mass of this material, which may have originated as schreibersite in the infalling material, was lost and vaporized in part as it traversed the atmosphere and as it impacted the Earth. Thus the final quantity of schreibersite to actually reach the surface of the Earth was closer to 10^{16}–10^{17} kg.

Correspondingly, as this material impacted the surface of the Earth, vaporization of surface rocks that likely included material at the iron-wüstite redox buffer would have generated reduced P gases that could then react with metal to form phosphides. During a single impact, possibly as much as 5% of the target rock's phosphorus could have become schreibersite. Consequently, the Hadean crust may have included a substantial phosphide fraction.

These two models combined suggest about 1–10% of the crustal phosphorus was at one point in a phosphide mineral. Most of this material would have been present in the Hadean. Ultimately, these phosphides would have oxidized to phosphate by action of water as the Earth cooled. The rate of oxidation depends on exposed surface area, composition of the fluids reacting with the schreibersite (e.g., salt content), and the oxidation potential of the fluid (Bryant et al., 2009). It may be reasonable to assume a long-term survival and slow corrosion of schreibersite on the Earth's surface, taking up to hundreds of millions of years to fully oxidize. As a result, a steady source of reactive P would have been present on the early Earth, enabling the phosphorylation of primordial molecules, and the building up appreciable concentrations of the components of self-replicating materials. Thus, the presence of schreibersite on the early Earth appears to be quite feasible and could have played a substantial role in prebiotic chemistry.

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