Title

Phosphorus mineral evolution and prebiotic chemistry: from minerals to microbes

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Abstract

Minerals are known to control the availability of non-volatile and bio-essential elements at Earth’s surface, e.g., phosphorus (P). Therefore, the role of minerals in prebiotic chemistry is a focal point of research into the origins of life. However, the mineralogical diversity of earliest Earth is not definitively known. This uncertainty is owed both to progressive change in the Earth system and an imperfect rock record of Earth history with increasing age. Hence, much is unknown about the planetary conditions under which terrestrial life first developed. Here, we review the plausible diversity of P-bearing phases at Earth’s surface during the emergence of life. We consider phases that were delivered by meteorites (exogenous phases), as well as those that developed solely as a result of Earth system processes (endogenous phases). We take into account the known formation conditions of individual phases, as well as the observed temporal distributions of P-bearing minerals found at Earth’s surface today. Our approach allows us to leverage what is known about changes in the Earth system in order to rule out the prebiotic relevance of many P-bearing phases. Meanwhile, we highlight a small number of phases that are of possible prebiotic relevance; specifically schreibersite, merrillite, apatite, olivine, and glass. Prebiotic mineral-chemical scenarios can be formulated for each phase, with distinct requirements for the environmental and tectonic state of early Earth. We can therefore directly relate the probability of mineral-chemical scenarios to the nature of early Earth, bridging the fields of geoscience and prebiotic chemistry.

Introduction

Minerals are known to control the availability of non-volatile and bio-essential elements at Earth’s surface. Therefore, the role of minerals in prebiotic chemistry is a focal point of research into the origins of life. However, the mineralogical diversity of earliest Earth is not definitively known. This uncertainty is owed both to progressive change in the Earth system and an imperfect rock record of Earth history with increasing age. Hence, much is unknown about the planetary conditions under which terrestrial life first developed. Here, we review the plausible diversity of P-bearing phases at Earth's surface during the emergence of life.

All organisms require the element phosphorus (P – atomic number 15) at a fundamental level in order to metabolise (adenosine triphosphate is the 'energy currency of life'), compartmentalise (phospholipids build cell walls), and replicate (phosphate-diester linkages are the backbone of DNA; (Bowler et al., 2010; Fernández-García et al., 2017; Kamerlin et al., 2013; Westheimer, 1987). However, just as P is key for extant forms of life, the importance of this element for the chemistry of life's origins is also clear. High P concentrations (typically as the oxidised species PO_4^{3-}) are a vital constituent of many recent prebiotic reaction schemes (e.g., Pasek et al., 2017; Patel et al., 2015), allowing for efficient pH buffering to ensure clean reaction steps. Phosphorus is required in abundance to drive efficient pre-enzymatic phosphorylation of organic compounds, without which it is challenging to access universal components of known biology e.g., nucleic acid.

Phosphorus can exist in the following principal redox states: P^{3-}, P^{0}, P^{1+}, P^{3+}, and P^{5+} (Pasek et al., 2017). The geochemical behavior of each species is distinctly different, yet almost all P at the Earth's surface is present in an oxidized state (P^{5+}). Crustal P^{5+} is hosted by the mineral apatite ($Ca(PO_4)_3[OH,Cl,F]$) in most crustal rocks. The poor solubility of this phase at ambient surface conditions is widely considered to be a crucial challenge facing prebiotic reaction pathways that require high dissolved P concentrations to function (Schwartz, 2006). This issue has spurred efforts to find either environmental conditions under which apatite is highly soluble (Burcar et al., 2016), or alternative mineral sources of P that would have been abundant on early Earth (Pasek et al., 2017). The probability that any given P-bearing phase may have interacted with a specific prebiotic environment is dependent upon the nature of the early Earth and the abundance of a given prebiotic mineral at the time. However, Earth history is especially poorly constrained for the time period in which life is thought to have emerged. As such, even strong experimental evidence that a P-bearing mineral may be useful in prebiotic chemistry has little explanatory power without a firmer grasp on what was and was not geologically possible on early Earth.

Here, we review what is known about P mineral diversity in modern and ancient terrestrial settings, as well as in meteorites that bring deliver P to Earth's surface. We focus on evaluating the formation conditions of each phase, in order to construct a time-series evolutionary history of P mineralogy on Earth. We examine which phases are likely to have been available during the Prebiotic Era. By considering the environmental, tectonic, and geochemical pre-conditions that go along with each phase, we are able to exclude some phases from consideration entirely, as well as provide an assessment of prebiotic plausibility and utility in other cases.

In this context, it is important to define what is meant by 'early', and to provide context for the initial conditions of the Earth system, and their rate and direction of evolution towards the present. We generalize our thinking to conservatively describe the 'early Earth' as encompassing the first billion years of Earth history (4.5-3.5 Ga). The Hadean Eon refers to the point in Earth history (4 Ga) beyond which there is essentially no preserved and exposed rock-record available to study. The earliest putative evidence of life in the rock record is rapidly approaching this boundary (> 3.85 Ga; e.g., Dodd et al., 2017); it is therefore becoming increasingly likely that the origin of life occurred at some time during the Hadean Eon. The 'Prebiotic Era', then, refers to whatever portion of the Hadean Eon was dominated by wholly prebiotic chemistry, as opposed to any form of extant biochemistry. In this review, we refer most generally to the early Earth, as well as more specifically to the prebiotic Earth, when discussing implications of our work for the origin of life.

Phosphorus pathways in planetary precursors

We begin by tracing P through those processes that formed Earth. Materials formed at each stage would have had the potential to interact with one another during the relevant timeframe for prebiotic chemistry (i.e., circa 4.53-4.0 Ga). For example, molecules native to asteroids might not form in situ in prebiotic terrestrial settings, but could have been transported to the early Earth's surface during impact events. The evolution of P cosmochemistry across Early Solar System history is illustrated in Figure 1, concluding with the formation of Earth.

Nebula-phase materials

Details of P cosmochemistry occurring in the Interstellar Medium (ISM) and in star-forming nebular gas clouds are currently scarce. Emission lines for the molecular species PO and PN have been observed in the ISM (Mininni et al., 2018). The ISM itself is depleted in P relative to diffuse molecular clouds and star-forming regions – most probably due to P freeze-out onto dust grains (Wakelam and Herbst 2008; Lebouteiller et al., 2005), although the chemical nature of this dust-bound P is not yet properly constrained. Regardless, this expected reservoir is often suggested to act as a P source during dust cloud collapse, star-formation, and the development of proto-planetary disks, with P being released to the gas phase during heating associated with these processes (Lebouteiller et al., 2005). The vast majority of nebular P is thus reprocessed during chemical partitioning into the disk, reducing the prebiotic relevance of pristine nebular P-bearing species.

Disk-phase materials

Gas phase chemistry in the disk is complex, varies significantly with temperature, and hence also varies with stellar distance and with time. The highest temperature at which P will condense to form a solid phase is ~ 1225 K (Fegley and Lewis, 1980). At this temperature, reaction of nebular gas species with already-formed native iron (Fe; e.g., in dust) results in the near wholesale removal of P from the gas-phase in around 10,000 years. This process triggered schreibersite (Fe_3P) formation when P reached a critical concentration of ~ 1 wt % in the metal (Pasek, 2019a; Pirim et al., 2014). Schreibersite is often observed to be non-stoichiometric, with P < 1 atom per formula unit (Pasek, 2019a; Zanda et al., 1994). These Fe[P] phases comprise the oldest P-bearing minerals to form in the Solar System and provide a starting point for tracking how P mineralogy may have evolved over the next 4.5 billion years. Secondary reprocessing of disk materials then set the redox state and concentration of P in asteroids and planetesimals, which were subsequently accreted by the Earth. These materials are sampled and delivered to Earth today by meteorites, providing us with a constraint on the minerals that may also have been delivered to Earth during its Prebiotic Era.

Phosphorus mineral diversity in meteorites

Phosphide, both as a minor-components in Fe-metal and as individual mineral phases, dominates in enstatite chondrites, as well as carbonaceous and ordinary chondrites that did not experience significant aqueous or thermal metamorphism. However, given the sheer rarity of unaltered chondrites, we do not consider this reservoir separately in our compendium of meteorite P data (Table 1). Thermally metamorphosed and aqueously altered chondrite classes contain oxidised phosphate minerals – in particular merrillite and members of the ternary end-member OH/F/Cl-apatite series (Table 1). Oxidation was likely mediated by metasomatism following the mobilization of early condensed ices into fluids and vapours, which was either driven by early metamorphism and/or impact-heating events (McSween and Labotka, 1993; Zhang et al., 2016).

Phosphides also dominate in iron-rich reducing achondrites (Table 1), whereas phosphate minerals dominate in more oxidizing silicate-rich achondrites (Table 1). Primary phosphates may co-exist with phosphide phases in pallasite (‘stony-iron’) meteorites (Buseck, 1977)). It has also been suggested that a phosphide-fluid reaction sequence explains the presence of phosphorylated carbon compounds in comets (e.g., Wild 2 – Brownlee et al., 2012) and in the organic-rich carbonaceous chondrites (CCs, e.g., Murchison; Graaf et al., 1995). All of the materials indicated in Table 2 and Figure 1 have the potential to have interacted with Earth surface and therefore set in-motion different pre-biogeochemical processes. However, in reality, this potential is sensitive to the relative and absolute abundance of these phases, as well as the constraints imposed by inherently stochastic delivery during impact bombardment.

Modern exogenous fluxes

The flux of meteoritic minerals to Earth must have been greater in the past than it is today, with planetary bombardment being at its height during the Hadean Eon (4.5 to 4.0 Ga) and, most likely, during the overlapping Prebiotic Era. Acknowledging this, we will now review and assess evidence pertaining to the composition of objects involved in Earth’s early impact history.

One means of evaluating the significance of exogenous P delivery (relative to endogenous weathering sources) is to quantify and extrapolate modern meteoritic fluxes to Earth. The data necessary to perform this analysis are given in Table 1, which lists the major meteorite classes, the reported diversity and relative abundance of P-bearing minerals found in each, and the relative abundances of these different meteorite classes in our collections. It should be noted that some of these classes have been argued to be under-represented compared to the fraction of material by mass that actually falls to Earth, because of preservation bias (e.g., a bias against preserving easily weathered irons or pallasite meteorites; (Binzel et al., 1993). Otherwise, however, we assume that the relative abundances of material present in collections is a reasonable proxy for the material flux to Earth now.

We systematically assembled available data regarding the number and mass abundance of meteorites of all major classes present in global collections (Table 1). We combined these data with estimates for the average P content of each class, using data taken from a variety of sources in the literature. Errors is propagated for both fall statistics and geochemical compositions.

Literature reports were also used to assume the speciation of P mineralogy within each meteorite class. However, owing to a general lack of quantitative data for this parameter, we are forced to use a simplified relative abundance classification scheme, namely: common (0.1), minor (0.01), rare (0.001), and very rare (0.0001). These are estimates, not measurements, and thus cannot be associated with error terms. However, we note that these approximations are likely to be broadly accurate: the most likely deviation is that minor to very rare phases are relatively much rarer than we have assumed.

Figure 2 illustrates a ranked P mineral flux to Earth based on mean P content as determined using data taken from Metbase (https://metbase.org), meteorite class, mass statistics, and available information on phase abundance within and the mean P content of each class. We exclude minerals produced exclusively during terrestrial weathering. Phosphorus delivered as schreibersite comprises the largest fraction of all exogenously delivered P minerals (45.1 %), followed by the relatively insoluble phases merrillite (19.2 %) and apatite (15.4 %). The high mass fraction of schreibersite is due mainly to its presence in iron meteorites, which make up ~ 50.4 % by mass of known falls.

The remaining 20 % of exogenously delivered P is dominated by the more abundant phosphate minerals found in achondrites: sarcopside, johnsomervilleite, graftonite, and stanfieldite. The estimated flux of all other P phases is relatively minor by comparison (3.8 %), but is again dominated by phases found in irons – this time a more even split between oxidized and reduced P minerals, followed by a wealth of rare phases present in abundances much less than 1 %.

Overall, the meteoritic P flux is evenly split phosphide and phosphate (45.9 vs 54.1 % - Figure 2). Phosphate delivery is somewhat diverse (5 major phases), whereas phosphide delivery is overwhelmingly dominated by schreibersite. One important caveat for these data is the changing nature of accreting impactor populations over time. For example, several recent models suggest that enstatite a/chondrite material contributed more substantially to early exogenous fluxes (Piani et al., 2020; Sikdar and Rai., 2020). However, enstatite-like material is highly reducing and hence has schreibersite dominated P mineralogy (Table 1). Such a shift is therefore unlikely to change the basic outcome of Figure 2.

We lack error constraints on the modal abundance of P phases within each meteorite class; constraints on these terms are unlikely to change the results by orders of magnitude. Nonetheless, the present values should not be taken as final estimates, especially for rarer species. Overall, given that merrillite, apatite, and schreibersite dominate within each meteorite class that has so far been observed, these phases must also have dominated specific P mineral flues to the Earth's surface over time.

Phosphorus pathways during planetary evolution

Planet formation

Phosphorus availability at a planetary surface is dependent both on its concentration and redox speciation. An important initial question to resolve is therefore: what was the relative abundance of P in its different redox states at the Earth's surface in the aftermath of its formation?

The phosphorus content of the Earth cannot be assumed from cosmic abundances. Phosphorus is a moderately volatile element (with a condensation temperature between 1100-1300 K; see (Wood et al., 2019) and therefore may not have fully condensed at Earth's heliocentric distance. Instead, the P content of the BSE is estimated from its correlation with a non-volatile (refractory) element (e.g., Nd) in mantle-derived basalts (see Mallmann and O'Neill, 2009; Palme and O'Neill, 2014). The P content of the Bulk Silicate Earth (BSE) is depleted beyond the extent that volatility alone can explain (Fegley and Lewis, 1980; Palme and O'Neill, 2014; Schönbächler et al., 2010). This additional depletion occurs because P can exhibit siderophile behaviour, causing it to partition into a planet's iron-rich core (e.g., Righter et al., 2010; Righter et al., 2018).

At equilibrium, P partitioned into the metal phase becomes reduced (P^0, as well as P^{-1}; Pirim et al., 2014), whilst P left in the silicate fraction is oxidised (P^{5+}). Experimental constraints on conditions relevant to an early terrestrial magma ocean highlight that even the most reducing conditions consistent with the observed end-stage chemistry of the BSE would still stabilise oxidised P^{5+} in silicate melts (Righter et al., 2018). Hence, residual mantle P would have been left entirely in the oxidized redox state following core formation. Although P's chemistry means it is partially lost to Earth's core, it conversely behaves as an incompatible element during mantle melting and is therefore concentrated into mantle melts and, consequently, newly formed crust is thus P-enriched relative to the mantle. Early crustal P is estimated at 100-1000 ppm in early Hadean crust vs. 87 ppm in Bulk Silicate Earth (Cox et al., 2018; Jenner et al., 2013; Keller and Schoene, 2012; O'Neill and Jenner, 2012; Palme and O'Neill, 2014). Overall, crustal P abundances would not have differed all that greatly from primitive planetary building blocks, such as chondritic meteorites (Palme and O'Neill, 2014).

The key point for the early P cycle is that the thermodynamics of core and crustal formation do not produce scarcity in bulk P. Instead, scarcity is created in terms of reactive (reduced) P. This leads to planetary crusts that broadly lack reduced P species and instead contain only relatively 'insoluble' phosphate (P^{5+}; Fig. 1). No phase is entirely insoluble, and even phosphate-containing minerals will contribute P to lakes, rivers, and the oceans. The speciation of P-bearing minerals at the surface of early Earth is therefore also of relevance to the origin of life.

Crustal evolution

Phosphorus mineralogy on the early Earth will have been controlled predominantly by which rock compositions characterized the early crust as it evolved. Crustal compositional evolution can broadly be described by two end-member compositional scenarios:

(A) A voluminous and broadly ultramafic-mafic (low Si) proto-crust (Fig. 3), in which apatite is mostly absent.

(B) Large volumes of relatively felsic (high Si) and apatite-dominated continental crust along with a more mafic (broadly apatite undersaturated) oceanic crust (Fig. 3). There may be limited or extensive amounts of this continental crust, depending on its growth rate, and this crust may be only partially felsic, or widely felsic (Fig. 3; Lipp et al., 2020).

These are all strikingly different views of the Early Earth – and yet, all are currently permissible within the bounds of available constraints from rheological and thermal models as well as composition-age plots of crustal rocks. For example, fine-grained sediments, which formed during the weathering of crustal material across large surface areas, have been used as a proxy for crustal average composition (Rudnick and Gao, 2014). Depending on the chemical proxies one chooses to focus on, however, as well as the way that various possible biases are accounted for (e.g., chemical mobility changes as a consequence of atmospheric and surface oxidation), the same data can be interpreted as reflecting a more mafic or similarly felsic upper continental crust in deep time (Greber et al., 2017; Greber and Dauphas, 2019; Tang et al., 2016). Hence, the same concept of non-uniformitarianism that has gained traction in thinking about exogenous P fluxes to the early Earth may also be relevant for endogenous sources.

We can assess the interplay of tectonic, compositional, and crustal regimes in the context of early P mineral diversity by leveraging recent advances in the study of accessory mineralogy – specifically, the Mineral Evolution Database.

The Mineral Evolution Database

Although apatite and silicate phases are the dominant P reservoirs in the modern crust, phosphorus mineralogy is actually highly diverse. Over 600 sperate species in which P is a stoichiometric component are currently listed in the Mineral Evolution Database (MED; rruff.info/ima/). This fine-scale heterogeneity of crustal P mineralogy is potentially important to consider in the case of prebiotic chemistry, as even globally rare phases may be locally abundant and therefore relevant to small-scale environmental processes leading up to the origin of life. We investigate the temporal distribution and paragenetic associations of these rare P minerals using the MED.

Accessory P minerals are often difficult to model thermodynamically and also lack specific experimental and field investigation. Recently, however, large-scale datasets that specifically describe the accessory mineralogy of exposed crustal rocks have become available (e.g., the Mineral Evolution Database – MED). The Mineral Evolution Database (http://rruff.info/ima/), in association with mindat (https://www.mindat.org), combines spatial (locality) with temporal (age) data for individual mineral occurrences on Earth (Grosch and Hazen, 2015; Hazen, 2013; Hazen et al., 2008; Hystad et al., 2019; Morrison et al., 2018). For this study, we processed MED data for all of the P minerals so far used in prebiotic experiments, as well as additional instances of phosphates that might come under future scrutiny in this context.

Phosphorus Mineral Evolution Database (PMED) age data is sourced from the literature on specific mineral-locality occurrences listed on mindat.com and http://rruff.info/ima/. These ages can be of any kind – from isotopic to stratigraphic. Age data has been carefully filtered on the basis of paragenesis for this work i.e., high temperature primary vs low temperature secondary species. This provides greater certainty that meaningful age data is being interpreted in each case.

The temporal resolution of PMED declines in step with the rock record, terminating at 4 Ga. It is therefore challenging to obtain a representative dataset of occurrence over Earth history for each mineral. Compounding this problem, many of the phases of interest are short-lived under ‘ambient’ conditions; not surviving diagenesis, lithification, or metamorphism. It is especially challenging to compile accurate age distributions for these phases. Therefore, for those species that derive from more stable primary phases, the age relationships of parental minerals and suitable environmental conditions for their alteration have also been ascertained. This approach helps to extend the temporal range of known mineral localities where specific P-phases of interest could have formed.

Phosphorus mineral evolution

In this work, we have evaluated the paragenetic relationships and prebiotic plausibility of all phosphorus-bearing mineral species in PMED. Should the reader wish to check the details of a candidate mineral that is not discussed here, all of the information equivalent to that reported in this article is available online at med.com, mineralweb.com, handbookofmineralogy.com. 65 separate mineral species were targeted for detailed investigation, all of which are of some relevance to the question of early Earth phosphorus availability. This set contains either phases that have been previously used in 'prebiotic' chemistry projects, or that have formation conditions of some potential relevance to early Earth.

Table 2 presents compiled data on P mineral host lithology, oldest occurrence, number of occurrences, and conditions of formation for P-bearing phases of prebiotic interest. These data can be used to assess which mineral species plausibly existed in the Prebiotic Era and then, of those, which (if any) have any notable potential for driving prebiotic chemistry.

We classify P minerals according to the possible paragenetic relationships laid out in Figure 4. We divide possible tectonic regimes into the following categories: a primitive regime with stagnant lid tectonics (Fig. 4A), an evolved regime with vertical sagduction tectonics (Fig. 4B-1), and an alternative evolved regime, equivalent to the one operable on Earth today, of subduction-driven plate tectonics (Fig. 4B-2). In Model B-1, early continental crust was generated via cyclic vertical sinking and melting of hydrated mafic crust (Johnson et al., 2017). In Model B2, continental crust is produced by the vertical passage of mafic rocks beneath an overriding plate of material i.e., slab subduction. Slab dehydration then results in high-pressure hydrous melting of overlying crust and arc mantle (Fig. 4B-2). This nuance becomes important when considering that accessory phosphate mineralogy is diverse and will vary hugely between the different felsic rock types that characterize models B-1 and B-2. Specifically, invoking material formed only in an e.g., subduction regime in a prebiotic model then requires the early Earth to have hosted such settings.

Those species whose environmental conditions of formation involve processes that are definitively known to have developed at some point after the Hadean Eon are filtered out (highlighted in red). For example, pseudomalachite forms only via oxidative weathering and hence can only have occurred since the Great Oxygenation Event, at ~ 2.45 Ga (Table 2). Despite this inherent limitation, pseudomalachite has been used as a mineral-phosphorylating agent in some prebiotic experiments (Costanzo et al., 2007). Whilst results from these projects still have relevance for highlighting potential chemical avenues of interest, they cannot provide outright solutions to the problem of concentrating P on early Earth given their use of materials that did not plausibly occur in the Hadean Eon.

We can rule out a number of other similar mineral species as prebiotically relevant based on their paragenetic associations (Table 2). Whilst ages of oldest occurrence are challenging to ascertain for secondary species, we can confidently identify these ages for primary igneous species. For example, minerals containing oxidized Fe^{3+} as a stoichiometric component occur only after 2.45

Ga. This outcome adds confidence to any inferences about secondary species made solely on the basis of paragenetic mode.

The potential of each phase in Table 2 for driving prebiotic chemistry is dependent on its abundance, reactivity, and complementarity to a prebiotic chemical model i.e., reaction schemes that are proposed to have operated in hot springs, submarine vents, etc. Several species in Table 2 can be identified as extremely rare – with only a few occurrences present in the entirety of the database (highlighted in purple). There are then those species which were both plausibly present in the Hadean and likely to have been abundant at the time, but which have thus far proven essentially completely unreactive for prebiotic chemistry, e.g., xenotime and monazite (Pasek et al., 2017). These highly insoluble and unreactive P minerals are highlighted in blue. Until new experiments prove otherwise, these species can be considered essentially irrelevant for origin of life studies. 'Likely' Prebiotic phases are highlighted in green and 'uncertain' phases in orange.

Many of the primary species highlighted here as of 'uncertain' prebiotic occurrence form in sag/subduction regimes (Fig. 4B-1/2). Triplite, hydroxylherderite, vivianite, whitlockite, and herderite are known to occur (as igneous phases) in granitic pegmatites, which result from extreme fractional crystallization and differentiation (Table 2). There is currently little evidence that granite pegmatites occur in the rock record beyond ~ 3 Ga (Sweetapple and Collins, 2002). Preservation bias of these relatively rare lithologies might be invoked to explain their absence in the early Archean rock record, yet it is also contentious whether or not the geodynamic conditions required to produce them could have prevailed much before this time. Pegmatites are found in I-A-type (igneous-derived) and S-type (sediment-derived) felsic magmatic suites.

For I-A-type pegmatites (igneous source materials), it would appear that the concentration of heat-producing and volatile elements due the recycling of continental crust is important for their formation, requiring an evolved geodynamic regime (Fig. 4B-1/2). A key pre-requisite for S-type granite formation is melting of metasedimentary material, along with subsequent fractionation (enhanced by the presence of volatiles). This melting often occurs in subduction-related orogens (London, 2018). S-type granites are therefore most plausible given some form of tectonic cycling of volatiles from the surface to depth (Fig. 4B-1/2). Hence, we can tie the presence or absence of pegmatitic mineral species on Early Earth to prevailing tectonic regimes. Pegmatitic species are unlikely to have occurred on an early Earth with stagnant lid tectonics (Fig. 4A) – regardless of whether some low-volume felsic magmatism was ongoing.

Although several of the rare accessory phases of plausible prebiotic occurrence in Table 1 have been shown to have some unique/useful role in experimental work, there is no strong geological case for their importance. The opposite case can be made for many of the secondary phases listed as of uncertain or likely prebiotic relevance in Table 1: these phases might have occurred, but it is unclear if any provide particular advantages in terms of solubility or reactivity relative to more obvious candidates (e.g., apatite). A better question to ask is thus: which of the phases in Table 1 do have significant prebiotic potential?

Phosphorus mineralogy and prebiotic P availability

Schreibersite

Schreibersite is a promising candidate for a prebiotic source of P owing to its high reactivity and solubility in natural waters of varied composition at ambient conditions (Bryant et al., 2013; Kee et al., 2013; Pasek, 2019b; Pasek et al., 2015, 2013, 2007; Pasek and Lauretta, 2008), yet is very rare in the terrestrial rock record (Table 1). For schreibersite to be a primary igneous mineral on early Earth requires that magmas were forming under exceptionally reducing conditions (Brett and Sato, 1984) – far more reducing than any conditions found on the modern Earth. Santosh et al. (2017) have suggested that igneous schreibersite was widespread in the Hadean Eon. However, Earth's mantle likely oxidised to near its modern state very rapidly (Trail et al., 2011; Williams et al., 2012; Yang et al., 2014).

It is conceivable that localised reducing environments could have occurred as ‘hold-overs’ from highly reducing conditions that prevailed during Earth’s formation. H_2-rich magmas may have migrated towards the surface and hence provided a flux of reducing material to the surface for up to several hundred million years (Bali et al., 2013; Rimmer and Shorttle, 2019). These putative reducing magmas may well have become saturated in reduced P minerals, or Fe-P alloys. Similarly, such ultra-reducing localized settings may provide a plausible host environment for alternative phosphide phases (e.g., Table 2; Britvin et al., 2015) and reduced P compounds (e.g., cyclophosphates; Britvin et al., 2020), which would otherwise appear to require the involvement of biology (Table 2). The plausibility of hydrothermal reduced-P-bearing systems is deserving of future study (Fig. 5).

Even more plausible is exogenous schreibersite delivery. Our review of meteoritic mineralogy strongly supports that this phase would have been among the most abundant P-bearing phases delivered to early Earth. However, unlike the other phases with strong prebiotic potential discussed in this review, schreibersite availability would have been stochastic. Direct delivery would only have been possible where impactor velocity and size permitted passage through the atmosphere and also avoided vaporization upon arrival at the surface. Indirect alternatives for exogenous reduced P delivery include settling of post-ablation vapor condensates (Douglas et al., 2020; Mehta et al., 2018) and production of reduced P in-situ, in impact craters (Pasek, 2017). The plausibility of prebiotic chemistry utilising these various exogenous sources of P has yet to receive detailed attention (Fig. 5).

Apatite

The apatite ternary end-members stand out as the most abundant phosphate phases listed in PMED. The presence of these phases in preserved early felsic igneous rocks (Table 2) confirms the likelihood that apatite would have comprised at least some non-trivial fraction of the crustal P reservoir. Apatite has a very low solubility in the majority of solutions found at the Earth's surface today (Brantley and Olsen, 2014). However, there are in fact several of ways to drastically increase apatite solubility. These mechanisms include site-specific chemical attack by cations, increased temperature, and physical weathering (Chaïrat et al., 2007; Harouiya et al., 2007)). The most dramatic and universally relevant control on apatite solubility is pH (Pearce, 1988). Apatite dissolution rate and solubility product increase by orders of magnitude across both the temperature and pH scales, implying that warm/hot and acidic aqueous environments will readily dissolve out apatite during water-rock interactions (Chaïrat et al., 2007; Strachan, 2017).

Experiments have also revealed high sensitivity of fluorapatite stability to the dissolved inorganic carbon (DIC – in seawater, an equilibria between carbonic acid, bicarbonate ion and carbonate ion) content of aqueous fluid in equilibrium with a source of CO_2 (Jahnke, 1984). In experiments reported by (Pan and Darvell, 2010, 2009), the solubility effect of pCO_2 on apatite was detectable even at very low pH i.e., zero carbonate DIC speciation. The authors attributed this continued effect on apatite solubility to complexation of Ca by bicarbonate (HCO_3^-) and carbonic acid in solution, whilst noting that the DIC effect is largest at high pH. Overall, the results of (Pan and Darvell, 2010, 2009) imply that pCO_2 is a relevant factor in controlling apatite solubility regardless of pH. We therefore expect inorganic carbon to have played an important role in solubilising apatite across a wide range of geochemical environments (e.g., Kakegawa et al., 2002).

Apatite is also among the most common exogenously delivered P-bearing phases (Fig. 2). Exogenous apatite does not obviously have a clear advantage over endogenous apatite for fueling high P availability during prebiotic chemistry (Table 3). A circumstance in which this situation would be reversed is given a putative mafic early crust (Fig. 4A; Fig. 5; Table 3), where endogenous silicate- and exogenous apatite-hosted P were both more available than the crustal apatite P reservoir. Especially in earliest Earth history, then, and potentially during the origin of life, it is possible that apatite may have only rarely occurred in the Earth's crust. In its stead, silicate phases would have dominated the mass balance of available P in surface-exposed environments.

Silicate phases

Silicate phases, whilst previously considered as exotic and reactive potential candidates for supplying P to prebiotic chemistry (e.g., Holm, 2014), have received little attention in the context of experimental prebiotic chemistry. However, silicate-hosted P may have dominated the crustal P reservoir on an early with little continental crust (Fig. 3). Crystalline mafic silicate phases (e.g., olivine, pyroxene) are generally slower to weather than apatite, but mafic silicate glasses are comparatively rapidly broken down across a range of physiochemical conditions (Prigiobbe et al., 2009; Strachan, 2017). Recent work has demonstrated the potential for net P fluxes out of apatite-absent ultramafic-mafic rocks during hydrothermal alteration by anoxic fluids rich in dissolved CO_2 (Syverson et al., 2020). This perspective is important for the plausibility of origin scenarios that rely on high P concentrations in submarine or subaerial hydrothermal environments, where higher temperatures would serve to accelerate the dissolution of crystalline and glassy mafic silicate phases.

A challenge in this regard, though, is that such models typically rely upon iron-oxide formation as a critical part of the prebiotic chemical network (e.g., Barge et al., 2015). Such phases would act to scrub phosphate from solution and thereby potentially impose local limits on P availability. On the other hand, recent experimental work has shown that iron-redox chemistry may circumnavigate these issues. Sorbed phosphate may be reduced and released as phosphite during hydrothermal alteration (Herschy et al., 2018) and/or prebiotic reactions involving P may take place on iron-oxide mineral surfaces directly (Wang et al., 2019; Fig. 5; Table 3).

Conclusions and outlook

Limited diversity of P minerals on early Earth

Despite the enormous diversity of P mineralogy observed today, mineral evolution indicates that very few are relevant to early Earth, with even fewer being potentially important for prebiotic chemistry. Alongside silicate phases, in which P comprises a minor component, only apatite is of clear relevance to prebiotic chemistry (Fig. 5; Table 3). Exogenous phases of importance are limited to merrillite, apatite, and schreibersite (Fig. 5; Table 3).

We rule out a number of phases as being prebiotically plausible that have previously been used in prebiotic analogue experiments. This restricts the mineralogical parameter space available for origin of life scenarios. This allows us to identify the specific challenges or advantages of a given mineral-chemical scenario for prebiotic chemistry. These issues are unique to each phase (Table 3). That the environmental conditions needed to liberate P from each phase can differ so much suggests that distinct mineral-chemical scenarios for prebiotic chemistry may be formulated (Table 3; Fig. 5). This outcome is useful for reducing the parameter space of possible scenarios for prebiotic chemistry. Moreover, a specific probability should be conferred to each scenario based on the assumed distribution of mineral phases on early Earth.

Mineralogy and the probability landscape of prebiotic chemistry

The probability landscape for elevated aqueous P concentrations on the prebiotic Earth heavily depends on the assumptions we make about early P mineralogy (Tables 1-3). If specific rare minerals are invoked in a chemical model, then the probability of that scenario is inherently limited by a coincidence of geological processes and environmental conditions (e.g., rare pegmatite formation followed by overlapping meteorite impact). Conversely, models that use species of global distribution may have their probability mainly controlled by other factors (e.g., occurrence of hydrothermal systems which promote P-mineral dissolution).

Looking again at globally distributed phases, a broadly mafic early crust will confer a probabilistic advantage to models invoking mafic silicate phases, whereas a felsic early crust will favor the involvement of (flour)apatite. We can therefore directly relate the probability of mineral-chemical scenarios to the tectonic and environmental state of early Earth, bridging the fields of geoscience and prebiotic chemistry.

This review has highlighted the importance of understanding long-term changes in Earth's accreted materials, crustal composition, and tectonic mode when reconstructing early available P mineralogy. Further constraints on early Earth P mineralogy will therefore help to discriminate between competing models of prebiotic chemistry.

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Competing interests: The authors declare no conflicts of interest.

Data and materials availability: : All data needed to evaluate the conclusions in the paper are present in the paper.

Figures and Tables

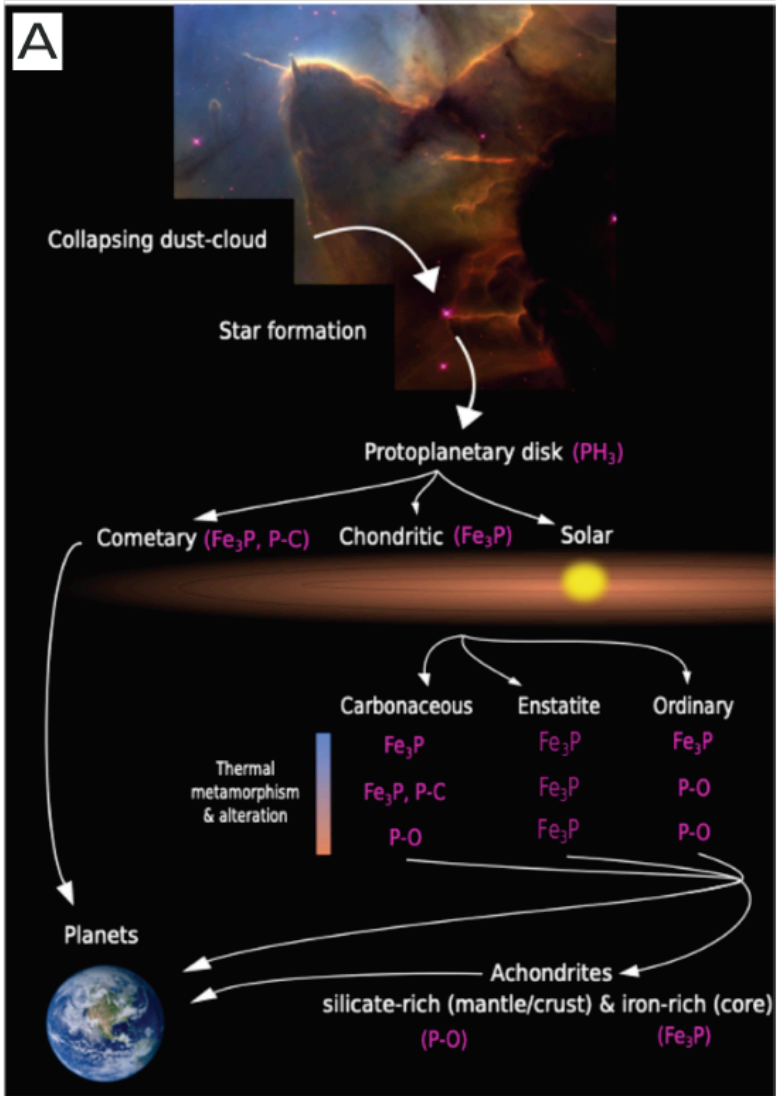

Figure 1: Pathways followed by P during early Solar System history. The early-Solar nebula would have condensed primarily reduced P as Fe_3P, both in comets and in chondrules (and hence chondrites). Thermal metamorphism and equilibration of chondrite parent bodies saw the oxidation of metal-bound P to form phosphate minerals. Following accretion of bodies large enough to experience melting, segregation of metal along with siderophile P to planetesimal cores created a dichotomy of reduced 'inner' P reservoirs and oxidized 'outer' reservoirs i.e. core vs. mantle material.

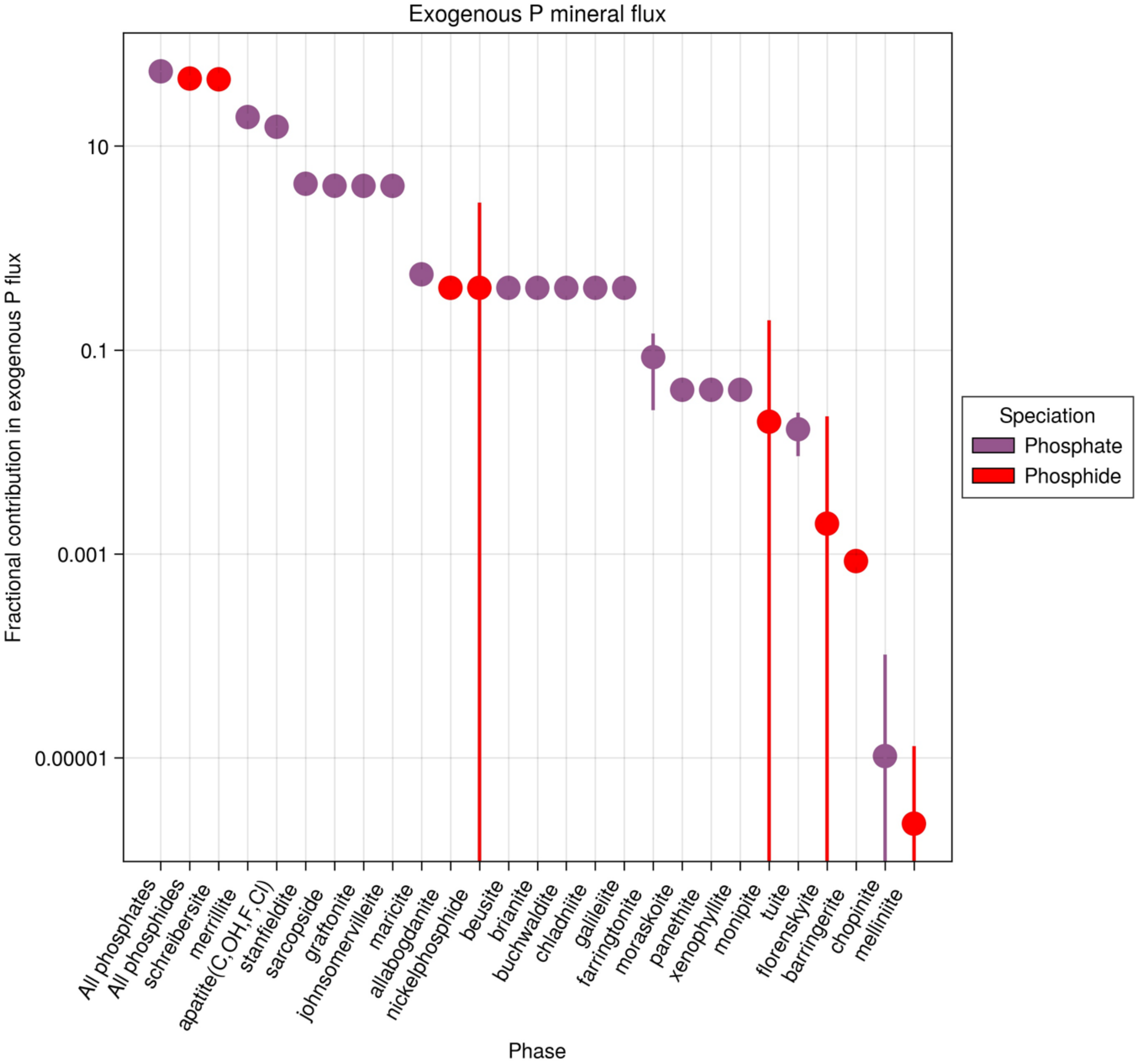

Figure 2: Percentage of total (modern) exogeneous P flux represented by various mineral species. Also indicated is whether or not the mineral species occurred in terrestrial settings on the Hadean Earth. Red colored symbols indicate phosphate phases. Blue colored symbols indicate a phosphide phase. Error bars are 2σ.

Table 1: Phosphorus mineralogy of meteorites

Meteorite Class	P minerals (listed in order of decreasing abundance)	Fall statistics (mass %)	P content (± 2σ)
Chondrites			
Ordinary	*OH/F/Cl-apatite, merrillite, maricite, tuite, phosphoran-olivine*	*37.8*	*1100 ± 58*
Carbonaceous	*Schreibersite, OH/F/Cl-apatite, merrillite, monipite*	*4.4*	*1280 ± 100*
Enstatite	*Schreibersite, perryite-nickelphosphide*	*0.5*	*1260 ± 224*
Stony-irons			
Irons	*Schreibersite, stanfieldite-graftonite-sarcopside, johnsomervilleite, allabogdanite, brianite, maricite-nickelphosphide-beusite-buchwaldite-chladniite-chopinite-moraskoite-panethite-xenophyllite*	*49.6*	*2340 ± 391*
Mesosiderite	*Merrillite, schreibersite, farringtonite*	*1.2*	*2805 ± 706*
Pallasite	*Schreibersite, stanfieldite-howardite-merrillite-farringtonite, barringerite, phosphoran-olivine*	*0.6*	*4140 ± 6070*
Asteroidal achondrites			
HEDs	*Apatite, merrillite,*	*2.7*	*507 ± 67*
Aubrite	*Schreibersite*	*2.4*	*291 ± 2720*
Angrite	*Apatite, merrillite*	*0.003*	*618 ± 146*
Primitive achondrites			
Ureilite	*Schreibersite, Cl-apatite, merrillite*	*0.01*	*693 ± 292*
Lodranite	*Merrillite, schreibersite*	*0.002*	*1370 ± 1770*
Acapulcoite	*Schreibersite, merrillite*	*0.004*	*1370 ± 1770*
Winonaite	*Schreibersite*	*0.0003*	*1900 ± 1340*

Note: Data compiled from MetBase (current as of December 2019).

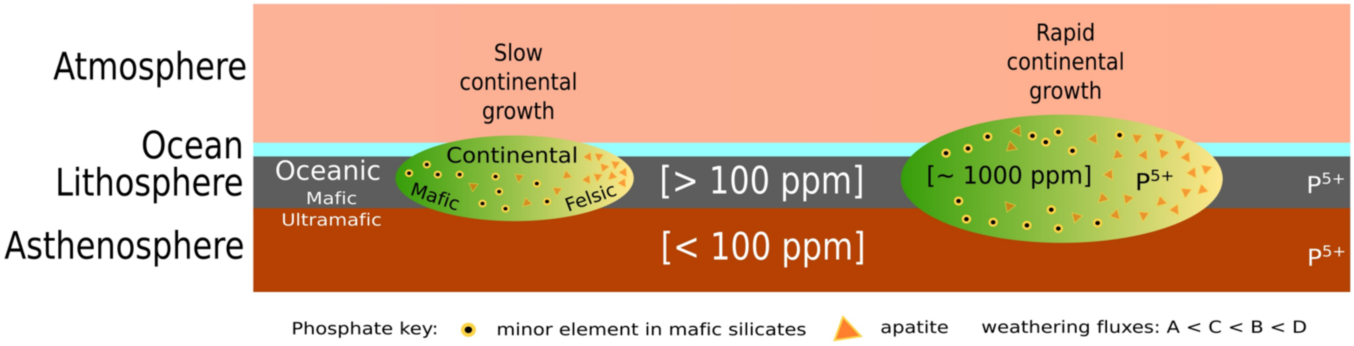

Figure 3: Uncertainties in crustal mode during the Prebiotic Era. Continental growth may be slow, or rapid. The composition of that continental material may be mafic (broadly apatite undersaturated) or felsic (apatite saturated). Not to scale.

Table 2: Phosphorus mineralogy of potential prebiotic relevance

Mineral name	Formulae	Paragenesis	Formation conditions and Lithologies	Geodynamic associations
Pyrophosphite	$K_2CaP_2O_7$	An	Fire	/
Pyrocoproite	$(Mg(K,Na))_2P_2O_7$	An	Fire	/
Arnhemite	$(K,Na)_2Mg_2(P_2O_7)\bullet 5(H_2O)$	An	Fire	/
Hylbrownite	$Na_3MgP_3O_{10}\cdot 12H_2O$	LTS (S)	Polymetallic sulphide-ox	/
Wooldridgeite	$Na_2CaCu^{2+}{}_2(P_2O_7)_2\cdot 10H_2O$	LTS (S)	Sediments + ore + ox	/
Gengenbachite	$KFe_3(H_2PO4)_2(HPO_4)4\cdot 6H_2O$	LTS (An)	Slag dumps	/
Haigerachite	$KFe^{3+}{}_3(H_2PO_4)_6(HPO_4)_2\cdot 4H2O$	LTS (S)	As-Pb-ox	/
Struvite-(K)	$KMg(PO_4)\cdot 6H_2O$	LTS (S/LH)	Dolostone, Pb-ox	/
Ludjibaite	$Cu_5(PO_4)_2(OH)_4$	LTS (S)	Cu-ox	/
Cornetite	$Cu_3(PO_4)(OH)_3$	LTS (S)	Cu-ox	/
Reichenbachite	$Cu_5(PO_4)_2(OH)_4$	LTS (S)	Cu-ox	/
Hureaulite	$Mn^{2+}{}_5(PO_3OH)_2(PO_4)_2\cdot 4H_2O$	HTS/LTS (S/LH)	Granite pegmatite + ox	/
Libethenite	$Cu_2(PO_4)(OH)$	LTS (S)	Cu-ox	/
Pseudomalachite	$Cu_5(PO_4)_2(OH)_4$	LTS	Cu-ox	/
Turquoise	$CuAl_6(PO_4)_4(OH)_8\cdot 4H_2O$	HTS/LTS (S)	Cu-ox	/
Kanonerovite	$Na_3MnP_3O_{10}\cdot 12H_2O$	LTS (S/LH)	Granite pegmatite + ox	B1 / B2
Pyromorphite	$Pb_5(PO_4)_3Cl$	LTS/Volcanic Sublimate	Pb-ox	/
Negevite	NiP_2	HTS	Ultra-reducing high-T metamorphism	/
Zuktamrurite	FeP_2	HTS	Ultra-reducing high-T metamorphism	/
Murashkoite	FeP	HTS	Ultra-reducing high-T metamorphism	/
Halamishite	Ni_5P_4	HTS	Ultra-reducing high-T metamorphism	/
Transjordanite	Ni_2P	HTS	Ultra-reducing high-T metamorphism	/
Cyclophosphate(s)	e.g., $(Ni,Fe)_2P_4O_{12}$	HTS	Ultra-reducing high-T metamorphism	/
Canaphite	$Na_2CaP_2O_7\cdot 4H_2O$	LTS (S/LH/A)	Lake sediments	/
Variscite	$Al(PO_4)\cdot 2H_2O$	LTS (S/LH/)	Sedimentary/volcanic rocks, UAFW chemistry (AS)	/
Brushite	$Ca(PO_3OH)\cdot 2H_2O$	LTS (A)	Clay-water interface, UAFW chemistry (AS)	/
Biphosphammite	$(NH_4,K)H_2(PO_4)$	LTS	Phosphate-rich rocks (AU)	/
Archerite	$H_2K(PO_4)$	LTS	Stalacites and wall rocks of caves	/
Phosphammite	$(NH_4)_2(PO_3OH)$	LTS	UAFW chemistry (AS)	/
Mundrabillaite	$(NH_4)_2Ca(PO_3OH)_2\cdot H_2O$	LTS	UAFW chemistry (AS)	/
Swaknoite	$(NH_4)_2Ca(PO_3OH)_2\cdot H_2O$	LTS	UAFW chemistry (AS)	/
Dittmarite	$(NH_4)Mg(PO_4)\cdot H_2O$	LTS	UAFW chemistry (AS)	/
Stercorite	$(NH_4)Na(PO_3OH)\cdot 4H_2O$	LTS	UAFW chemistry (AS)	/

Bobierrite	$Mg_3(PO_4)_2·8H_2O$	LTS	UAFW chemistry (AS)	/
Schertelite	$(NH_4)_2Mg(PO_3OH)_2·4H_2O$	LTS	UAFW chemistry (AS)	/
Hannayite	$(NH_4)_2Mg_3(PO_3OH)_4·8H_2O$	LTS	UAFW chemistry (AS)	/
Niahite	$(NH_4)Mn^{2+}(PO_4)·H_2O$	LTS	Phosphate-rich rocks	/
Lüneburgite	$Mg_3[B_2(OH)_6(PO_4)_2]·6H_2O$	LTS (A)	Evaporites + dolomitic marls (SD), UAFW chemistry (AS)	/
Childrenite	$Fe^{2+}Al(PO_4)(OH)^2·H_2O$	LTS	Granite pegmatites (GR)	B1 / B2
Wagnerite	$Mg_2(PO_4)F$	Primary/HTS	Granite pegmatites (GR), metamorphic	B1 / B2
Hydroxylapatite	$Ca_5(PO_4)_3OH$	HTS/LTS	Granite pegmatite (GR) , serpentinite (SP)	A / B1 / B2
Triplite	$(Mn_{2+},Fe_{2+})_2(PO_4)F$	Primary/HTS	Granite pegmatites (GR)	B1 / B2
Hydroxylherderite	$CaBe(PO_4)(OH)$	Primary/HTS	Be-Granite pegmatite (GR)	B1 / B2
Whitlockite	$Ca_9Mg(PO_3OH)(PO_4)_6$	HTS/LTS (S/LH)	Granite pegmatites (GR), P-rich rocks	B1 / B2
Monetite	$Ca(PO_3OH)$	LTS (S/LH)	Granite pegmatite + ox, UAFW chemistry	B1 / B2
Nahpoite	$Na_2(PO_3OH)$	LTS (S/LH/A)	Phosphatic Ironstone; alkaline magmatism (AK)	B1 / B2
Herderite	$CaBe(PO_4)F$	LTS (S/LH)	Be-Granite pegmatite (GR)	B1 / B2
Schreibersite	$(Fe,Ni)_3P$	Primary	Reduced igneous rocks, impact-craters/sediments (VP)	A / B1 / B2
Monazite-(La)	$La(PO4)$	Primary/HTS	Granite and gneiss (GR)	B1 / B2
Dorfmanite	$Na_2(PO_3OH)·2H_2O$	HTS/LTS	Alkaline magmatism (AK)	B1 / B2
Xenotime-(Y)	$Y(PO_4)$	Primary/HTS	AK, granites, gneiss, alpine veins (GR)	A / B1 / B2
Monazite-(Ce)	$Ce(PO_4)$	Primary/HTS/LTS (A)	Common igneous phase (GR)	A / B1 / B2
Vivianite	$Fe^{2+}_3(PO_4)_2·8H_2O$	Primary/HTS/LTS (S/LH/A)	Granite pegmatite (GR-P?), authigenic marine (AU)	A / B1 / B2
Chlorapatite	$Ca_5(PO_4)_3Cl$	Primary/HTS/LTS	Igneous, metamorphic (GR, MA)	A / B1 / B2
Wavellite	$Al_3(PO_4)_2(OH)_3·5H_2O$	LTS	Metamorphic, hydrothermal veins	A / B1 / B2
Newberyite	$Mg(PO_3OH)·3H_2O$	LTS	UAFW chemistry (AS)	/
Struvite	$(NH_4)Mg(PO_4)·6H_2O$	LTS	UAFW chemistry (AS)	/
Calcite	$CaCO_3$	HTS/LTS	Various	/
Iron (oxyhydr)oxides	$(CO^{2-}{}_3)$: $[Fe^{2+}{}_4Fe^{3+}{}_2(HO^-)_{12}]^{2+} · [CO^{2-}{}_3·2H_2O]^{2-}$	HTS/LTS	Various	/
Fluorapatite	$Ca_5(PO_4)_3F$	Primary/HTS/LTS (A)	Common igneous phase (GR, MA)	A / B1 / B2
Feldspar	$KAlSi_3O_8 – NaAlSi_3O_8 – CaAl_2Si_2O_8$	Primary/HTS	Common igneous phase (GR, MA)	A / B1 / B2
Garnet	$X_3Y_2(SiO_4)_3$ (Fe, Mg, Mn, Ca; Al, Cr, Fe)	Primary/HTS	Common igneous phase (GR, MA, UM)	A / B1 / B2
Olivine	$(Mg, Fe)_2SiO_4$	Primary	Common igneous phase (MA, UM)	A / B1 / B2
Pyroxene	$MgFe(SiAl)_2O_6$	Primary/HTS	Common igneous phase (MA, UM)	A / B1 / B2
Volcanic glass	/	Primary	Common igneous phase (GR, MA, UM)	A / B1 / B2

Color codes: Unlikely. Uncertain. Possible (rare). Possible (unreactive). Likely. **General paragenetic codes**: (A) – anthropogenic; HTS – high temperature secondary; LTS – low temperature secondary; LH – late hydrothermal; -ox – oxidative weathering; S – supergene. **Setting-specific paragenetic codes:** AS – alternative solvent. AK –

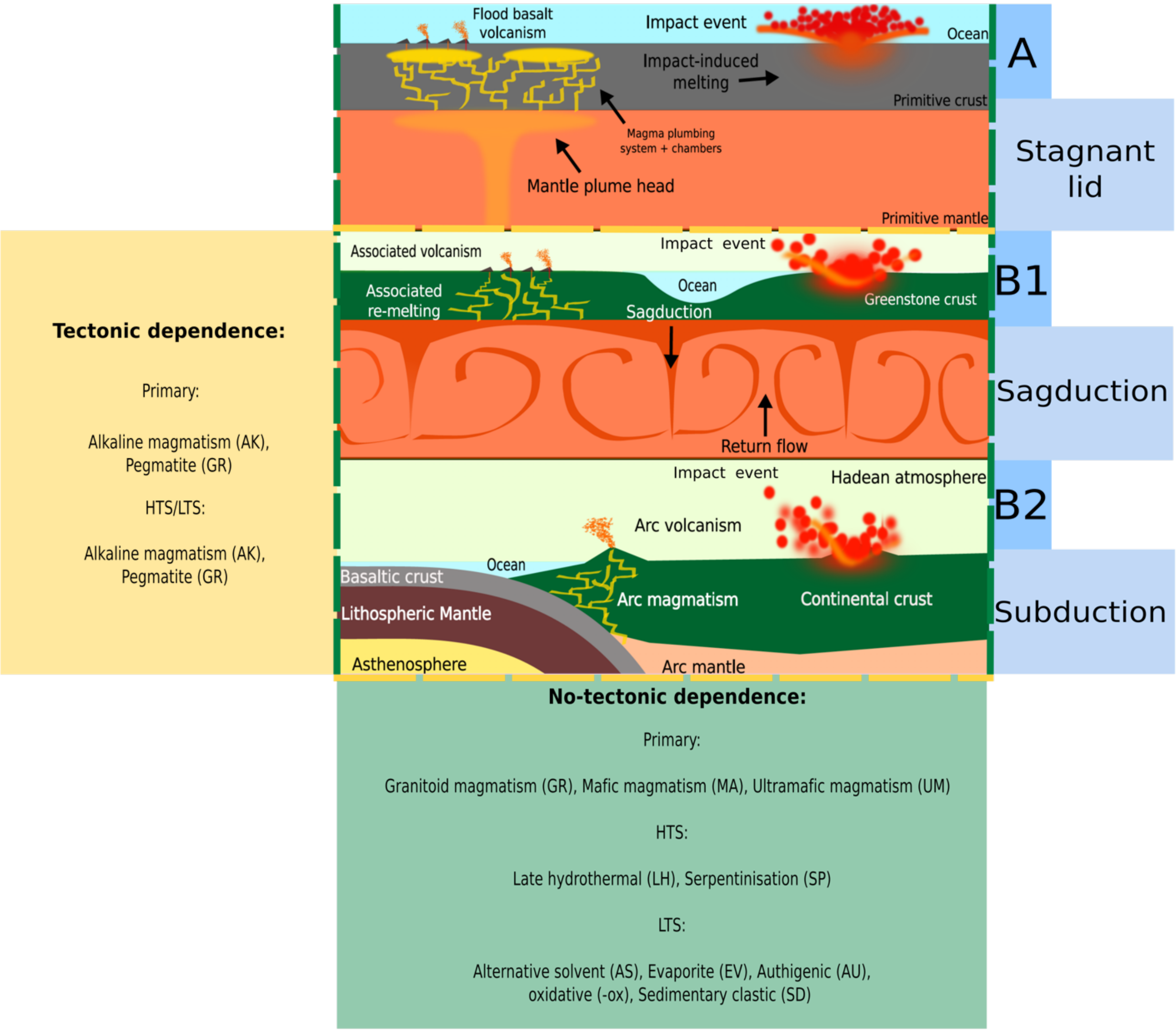

Figure 4: Possible geological processes and mineralization settings in the Hadean Eon. All scales are rough (but “sagduction” crust > Hadean crust > 3 Ga oceanic basaltic crust – adapted from Santosh et al., 2017; Johnson et al., 2013; Dasgupta & Hirschmann, 2010). The paragenetic modes associated with either all three or only regimes B1/B2 are indicated. HTS = high temperature secondary; LTS = low temperature secondary.

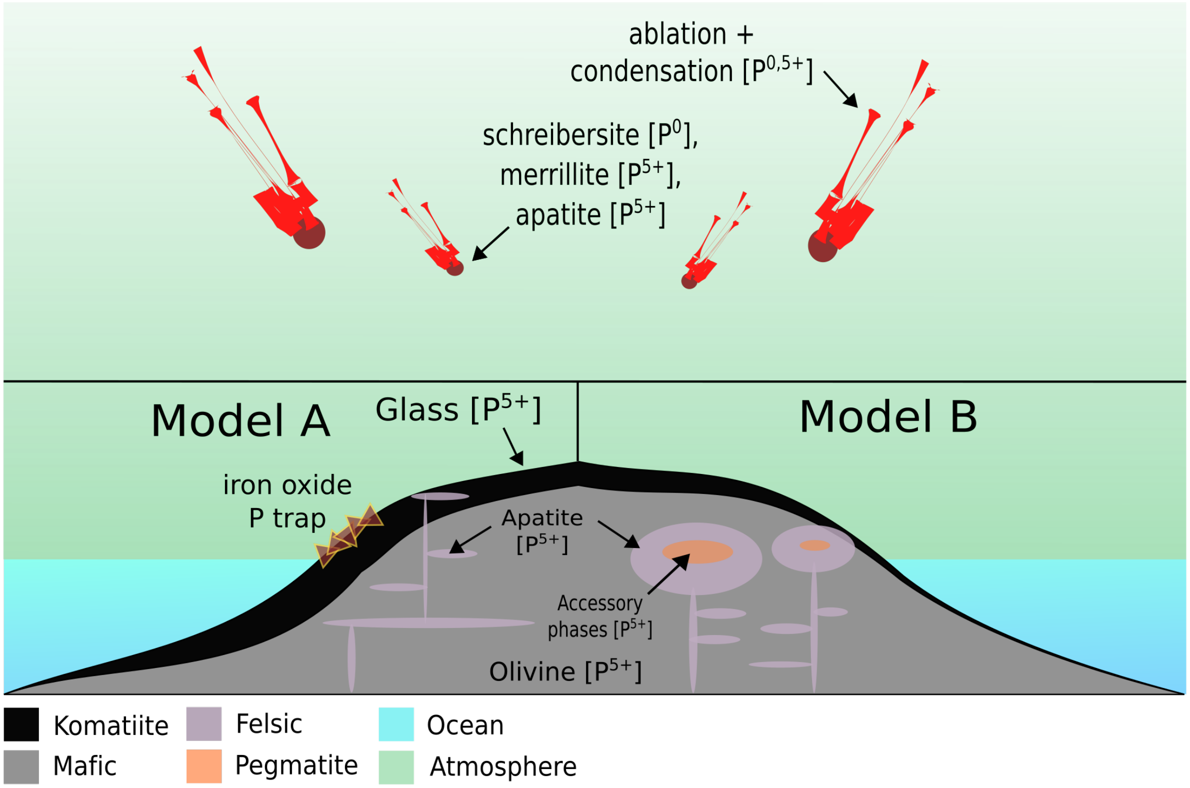

Figure 5: Prebiotically relevant phosphorus-bearing phases on early Earth. The relative abundance of prebiotically important endogenous phases is principally dependent on crustal composition. The abundance of meteoritic schreibersite is independent of these uncertainties.

Table 3: Challenges and advantages of specific phases as P sources in prebiotic chemistry

Phase	**Challenges / advantages**	**Ideal conditions**
Exogenous		
Schreibersite	Stochastic delivery; short window of post-deposition availability / highly soluble and reactive towards organics, common in meteorites	P-rich iron impactor directly depositing into low-volume target environment / ultra-reducing terrestrial environments
Alternative phosphides	Paragenesis appears to require biological intervention / highly soluble and reactive towards organics	P-rich impactor directly depositing into low-volume target environment / ultra-reducing terrestrial environments
Apatite/merrillite	Stochastic delivery; moderate post-deposition window of availability; poor solubility (depending on local conditions) / common in meteorites	P-rich impactor directly depositing into low-volume target environment
Vapor condensates	Stochastic delivery; very short post-deposition window of availability / high surface area; potentially highly soluble depending on redox state and chemical formula	Large P-rich impactor vaporising in vincinity of target enviornment
Endogenous		
Schreibersite	Very rare, if possible at all / linked to reducing conditions useful for other prebiotic chemistry	Massive P-rich iron impact generating H_2-rich magmas
Apatite	Poor solubility under many conditions; potentilly globally rare, depending on crustal regime / highly soluble under some specific circumstances; potentially globally abundant, depending on crustal regime	Raid early growth of felsic apatite-rich continental crust
Alternative phosphates	Very rare, if possible at all; generally very low solubility	Raid early growth of felsic apatite-rich continental crust; active tectonics
Mafic silicates	Low P-concentrations; P mobility governed by local iron-redox chemistry during weathering / potentially globally abundant, depending on crustal regime	Anoxic weathering regime; slow growth of felsic apatite-rich continental crust; no active tectonics

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