Phosphorus availability on the early Earth and the impacts of life

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Phosphorus (P) is critical to modern biochemical functions and can control ecosystem growth. It was presumably important as a reagent in prebiotic chemistry. However, on the early Earth, P sources may have consisted primarily of poorly soluble calcium phosphates, which may have rendered phosphate as a minimally available nutrient or reagent if these minerals were the sole source. Here, we review aqueous P availability on the early Earth (>2.5 Gyr ago), considering both mineral sources and geochemical sinks relevant to its solvation, and activation by abiotic and biological pathways. Phosphorus on Earth's early surface would have been present as a mixture of phosphate minerals, as a minor element in silicate minerals, and in reactive, reduced phases from accreted dust, meteorites and asteroids. These P sources would have weathered and plausibly furnished the prebiotic Earth with abundant and potentially reactive P. After the origin of a biosphere, life evolved to draw on not just reactive available P sources, but also insoluble and unreactive sources. The rise of an ecosystem dependent on this element at some point forged a P-limited biosphere, with evolutionary stress forcing the efficient extraction and recycling of P from both abiotic and biotic sources and sinks.

Phosphorus (P) is a critical element for biological systems. Phosphorylated organic molecules act as metabolic energy carriers; a sugar-phosphate backbone stabilizes nucleic acids; and phospholipid head groups enhance the hydrophilicity of cellular membranes[1]. P has chemical properties that give it this unique place in biochemistry. The small inorganic oxyanion orthophosphate (PO_4^{3-}; P_i) is capable of forming an ester bridge between two organic OH groups, which in nucleic acids maintains a negative charge that limits hydrolysis (more so for DNA than RNA). The phosphodiester bond hence allows for the persistence of nucleic acids for longer than would be expected under ambient and abiotic conditions (in the case of DNA, for millennia)[2].

In addition to a major role in nucleic acids, PO_4^{3-} moieties polymerize by condensation to form pyrophosphate ($P_2O_7^{4-}$) and polyphosphate, which are uniquely suited to serve as a metabolic energy store in modern biology as part of nucleotide triphosphates. The P–O–P bonds that connect the three $-PO_4^-$ moieties in adenosine triphosphate (ATP) and other nucleotide triphosphates may also be present as inorganic polyphosphate[3], and together nucleotide triphosphates and polyphosphate are widespread as universal energy-storage molecules across all life on Earth. The hydrolysis of P–O–P bonds releases about 20–40 kJ mol^{-1}, which closely corresponds to the energy required to synthesize new molecules and represents a discrete quantum for

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intracellular energy conversion[4]. Nucleotide triphosphates are the predominant energy carriers in cells, and they are simultaneously the precursors for the biosynthesis of the aforementioned nucleic acid information carriers.

The many critical roles P plays in biochemistry suggest that the molecules of life most probably incorporated this element during the early stages of prebiotic chemistry[5]. From a geochemical perspective, phosphate is the most abundant and stable molecular constituent that supports these biochemical processes[6]. Indeed, P may be the only element capable of performing all these tasks in modern biochemistry, hence its presence may have been critical for the development of life on Earth[6]. Arguments for life without P focus on a deep metabolic core[7] or on alternative nucleic acids[8], yet many prebiotic chemistry experiments rely on P_i due to its great utility as a catalyst and as a pH buffer. However, such reliance on P_i has long represented a challenge to the prebiotic plausibility of proposed reaction schemes in origin-of-life scenarios.

Inorganic P_i generally is poorly reactive towards organic molecules in the absence of enzymes[9]. This challenge is compounded by poor solubility of P_i in naturally occurring surface waters. Common divalent cations (for example, Fe, Mg, Ca) limit P_i solubility at near-neutral pH, driving the precipitation of phosphate minerals that cap maximum P concentrations in solution[10]. Meanwhile, alternatives to P_i—such as the ion phosphite ($HP^{3+}O_3^{2-}$)—are thermodynamically unstable under modern Earth's surface conditions and require highly reducing conditions (Supplementary Fig. 1), but still may have been formed on the early Earth[11–13]. Additionally, unlike the other major elements involved in biogenesis—carbon, hydrogen, oxygen, nitrogen and sulfur—which all bear a substantial volatile phase, the gaseous phase of P is not stable under ambient conditions (Supplementary Fig. 1). As such, P in life ultimately had to derive from mineral phases[14].

Here, we review and evaluate how the geochemical conditions of the early Earth (defined as prior to the rise of abundant atmospheric oxygen 2.5 Gyr ago (Ga); covering the Hadean eon from 4.55 to 4.0 Ga and Archaean eon from 4.0 to 2.5 Ga) may have been conducive to making P more available (acting as either a reagent in prebiotic chemistry or a nutrient for life), and how the evolution of nascent biosphere may have affected early P cycling.

The inventory of P on the early Earth

Today, terrestrial P is distributed between surface and deep reservoirs (Fig. 1). Several large geological events dramatically shaped this present-day distribution, as well as P availability on the early Earth. Considering P's moderate volatile behaviour during the condensation[15], the total global P reservoir built up rapidly (over ~10 Myr[16]) to nearly modern levels following the accretionary formation of the Earth (Fig. 1b). After the moon-forming impact, core–mantle differentiation at >4.4 Ga resulted in large-scale redistribution of terrestrial P from the bulk silicate Earth to the core along with the segregation of iron and nickel (Fig. 1b), due to the siderophile behaviour of P at high temperature and pressure[17,18]. Given the overall higher P content in meteorites (~1,000 ppm[14], even in chondrites) than early (ultra)mafic crust (~30 ppm[19]), a late veneer of material then could have added a substantial amount of P to the Earth's surface, probably as a mix of phosphates and phosphides such as schreibersite[20].

Compositionally and rheologically distinct crustal rock probably began forming in the early Hadean (<4.4 Ga)[21]. The composition, tectonic mode and volume of this crust is debated[22]. However, evidence for extensive mantle depletion by the early Archaean implies that a voluminous and enriched crustal component—comparable in bulk composition to the modern crust—developed relatively early in Earth's history[23]. If continental crust grew to near-modern levels rapidly then the P concentration of average upper crust may have increased 1.5- to 2-fold by the start of the Archaean eon[19] (Fig. 1b).

The continental crustal P reservoir is commonly assumed to be dominated by the phosphate mineral apatite ($Ca_5(PO_4)_3(OH,Cl,F)$)[24].

However, stark differences in P mineralogy are found between Earth's mafic and felsic rocks[25]. Much of Earth's P in the oceanic crust and mantle is hosted by mafic silicates (for example, olivine, $(Mg,Fe)_2SiO_4$, volcanic glass, ~30–100 ppm but in a much more widespread material), rather than in the form of apatite[25–27]. The evolution of the global crust towards more felsic compositions over time[28–30] hence implicates a corresponding secular evolution of crustal P mineralogy[27] (Fig. 1c).

A much smaller but pivotal P inventory for life's origin and evolution was the hydrosphere. Zircon records and modelling efforts suggest oceans formed in the early Hadean[31,32]. The dissolution of P liberated from crustal rocks and extraterrestrial impactors would have shaped the global availability of P for prebiotic chemistry, and then for life, across the Hadean eon. The final and most notable repartitioning of terrestrial P occurred during the origin and rise of life, probably in the late Hadean or early Archaean[33], which would have resulted in hydrospheric P entering the biosphere. Biospheric P would have been primarily bound in organic molecules. This organic P reservoir was probably much smaller than modern P in the biosphere in absolute quantity, given that total primary productivity has been estimated at 1–10% of the modern level[10,34].

In summary, the total P inventory of the Earth quickly grew to a modern level after Earth's formation, being redistributed into different reservoirs during major geological events on the Earth. P availability for prebiotic chemistry during the rise of minor—yet prebiotically crucial—surficial P reservoirs, such as the hydrosphere, remains poorly constrained.

P in prebiotic chemistry

P in a prebiotic context would be available if it was reactive and/or soluble, and ultimately capable of becoming incorporated into prebiotic molecules (Fig. 2). High P_i concentrations may promote the formation of organophosphates with phosphate as a substrate[35]. This style of phosphorylation chemistry employs concentration-dependent processes to drive formation of organophosphates. In the above cases, driving phosphorylation via concentrating P_i requires substantial (~100 mM) phosphate concentrations to produce small quantities of organophosphate[9]. Prebiotic P availability may also have been enhanced by conversion into inherently chemically reactive forms, capable of generating prebiotic phosphorylated organic compounds (Fig. 2a–d). For example, the reactions of P_i with nitriles leads to acylated organophosphates[36], and the reaction of P_i with imidazole and cyanate leads to an activated phosphoamidate that can phosphorylate simple organics[37] (Fig. 2d). In both systems, the reactivity of an organic compound towards P_i in water affords a secondary, more reactive P compound that then phosphorylates an organic substrate.

Reactive, reduced-oxidation-state P was delivered by impacts. The late veneer of extraterrestrial material accreted by Earth after core formation delivered some quantity of this material to surface environments[38], which would have been supplemented by terrestrial P-reduction pathways[11,12]. This reduced P material would have also included some amount of organic phosphonates[39] with a C–P bond, identified in the carbonaceous meteorite Murchison[40]. If the late veneer was dominated by carbonaceous material[41], then phosphonates would have been a substantial constituent of Earth's early P inventory.

For example, the reaction of schreibersite with ammonium hydroxide in water generates amidophosphates such as diamidophosphate and monoamidophosphate[42], both of which have been demonstrated to phosphorylate organic compounds, leading to polymers[43]. These reactions generate reactive P compounds through coupling their production with the oxidation and hydrolysis of schreibersite. If active on a large scale, these reduced P minerals could have provided a reactive source of P for prebiotic chemistry.

Pyrophosphate, triphosphate and cyclic phosphates are known to occur as minerals[44,45], and are produced via some geochemical
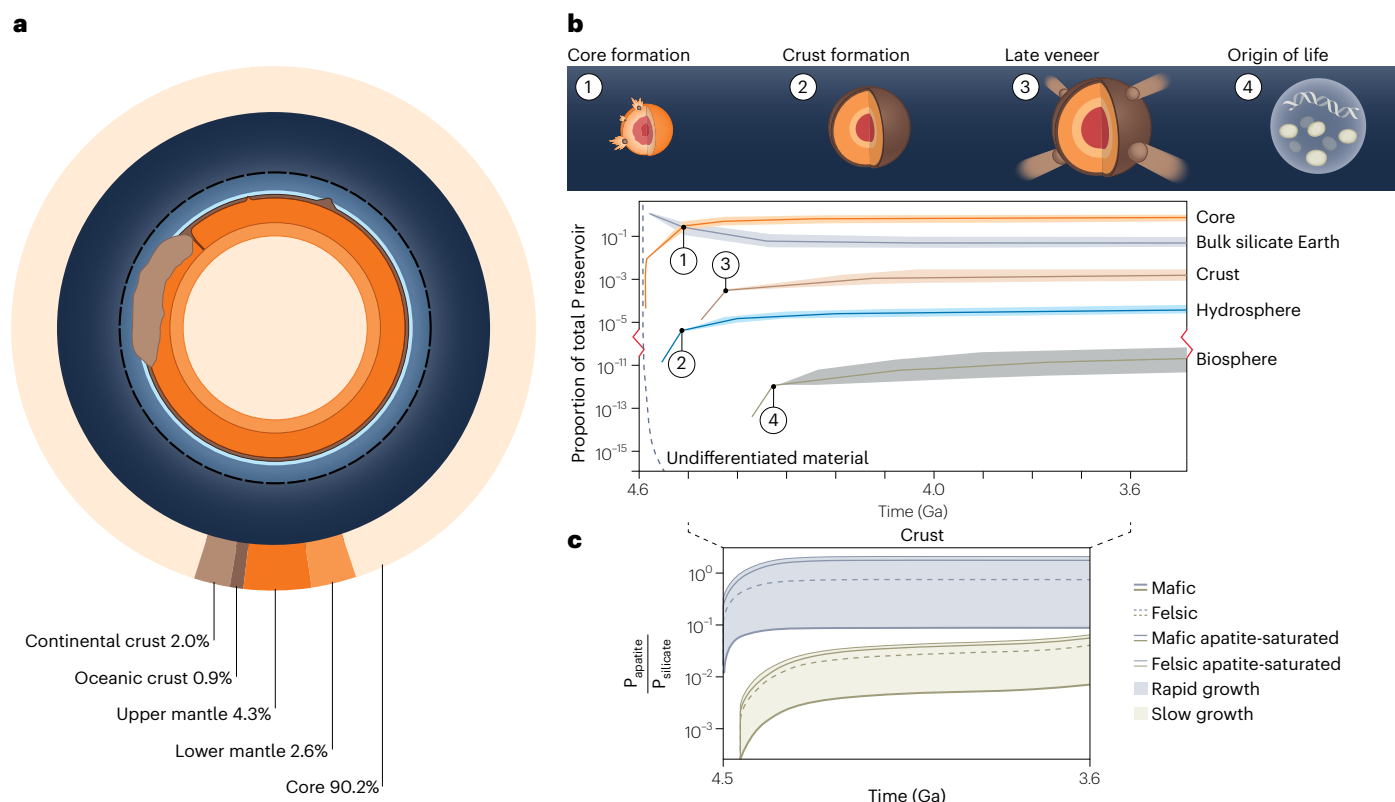
Fig. 1 | Modern and ancient P inventories of the Earth. a, Distribution of P in the Earth today. Inside the black dashed line, a schematic cross-section of Earth (not to scale) is shown (colour-coded). Outside the black dashed line, the percentage contribution to Earth's total P reservoir by each layer is shown to scale (width). **b**, Semi-quantitative reservoir partitioning of P on Earth over time, with key events illustrated[27,100]. **c**, End-member scenarios for fraction of total crustal P as apatite over time (remainder as silicate). The displayed evolution histories reflect a relative sequence of major geological events as there are still large uncertainties for their absolute ages.
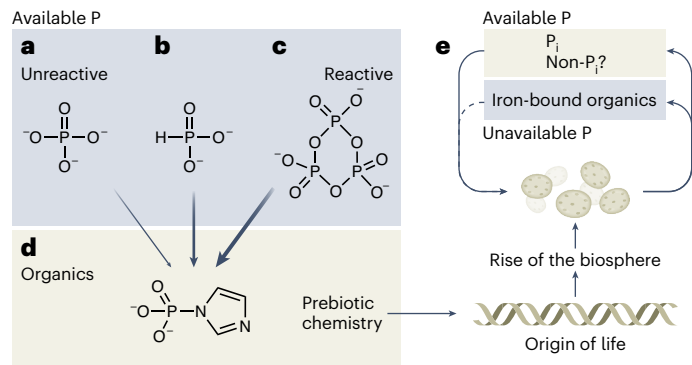
Fig. 2 | Prebiotic versus biotic P availability. Prebiotically available P is that which can be incorporated into and actively partook in prebiotic chemistry, that is, solubilized and reactive. **a**–**d**, P_i (**a**), moderately reactive phosphite (**b**), including organic phosphonates (where H– is replaced by R–); and highly reactive cyclic trimetaphosphate (**c**) can all convert to organics containing P (**d**), for example, phosphoamidate. **e**, Transition to nutrient-type regime of P availability, where enzymatic organophosphate degradation makes inorganic P_i available, enzyme-mediated phosphate uptake makes P_i a limiting nutrient and recycling pathways[101] alongside alternative P utilization mechanisms[53] operate to sustain the biosphere. Dashed path from the box labelled with iron-bound and organics denotes limited recycling from this P reservoir.

reactions[46]. These materials, especially the cyclic form of triphosphate, have been demonstrated to act as phosphorylation reagents and lead to the production of higher-order organics[47,48], such as RNA[49]. Although a widespread source of polyphosphates is not yet clear, the oxidation of reduced P compounds may produce these molecules[50].

The above phases highlight many routes to make P available for the origin of life. Broadly, these can be generalized into the following: (1) enhancing the solubility and steady-state concentration of P_i to push reactions towards phosphorylated biomolecules; (2) forming reactive organophosphates that then react with organics to form lower-energy organic biomolecules; and (3) supplying reduced P compounds that then react with oxidants and organics to form biomolecules (Fig. 2). The steady-state supply of this range of otherwise ephemeral[51] abiotic alternative P sources (for example, amidophosphates, polyphosphates, activated organophosphates) may have persisted for some amount of time (1 Gyr) due to the continued arrival of reactive P from impacts and other geologic events[46,52], even after the origin of life.

Cellular cycling of P

In a biological context, available P can be thought of in terms of nutrient availability: the abundance of soluble P (including P_i and sometimes reduced species[53], and probably without any relevant substitution of other elements or molecules) that is accessible to living cells. Rather than its ability to react extracellularly (as is the case for prebiotic P availability), P availability in living systems is dependent on the acquisition of P and its intracellular utilization, coupled to the long-term environmental cycling and balancing of P sources and removal by minerals. This is constrained by the following: (1) P speciation; (2) solubility; (3) enzymatic activity and specificity; and/or (4) chelators that increase P release from minerals (Fig. 3).
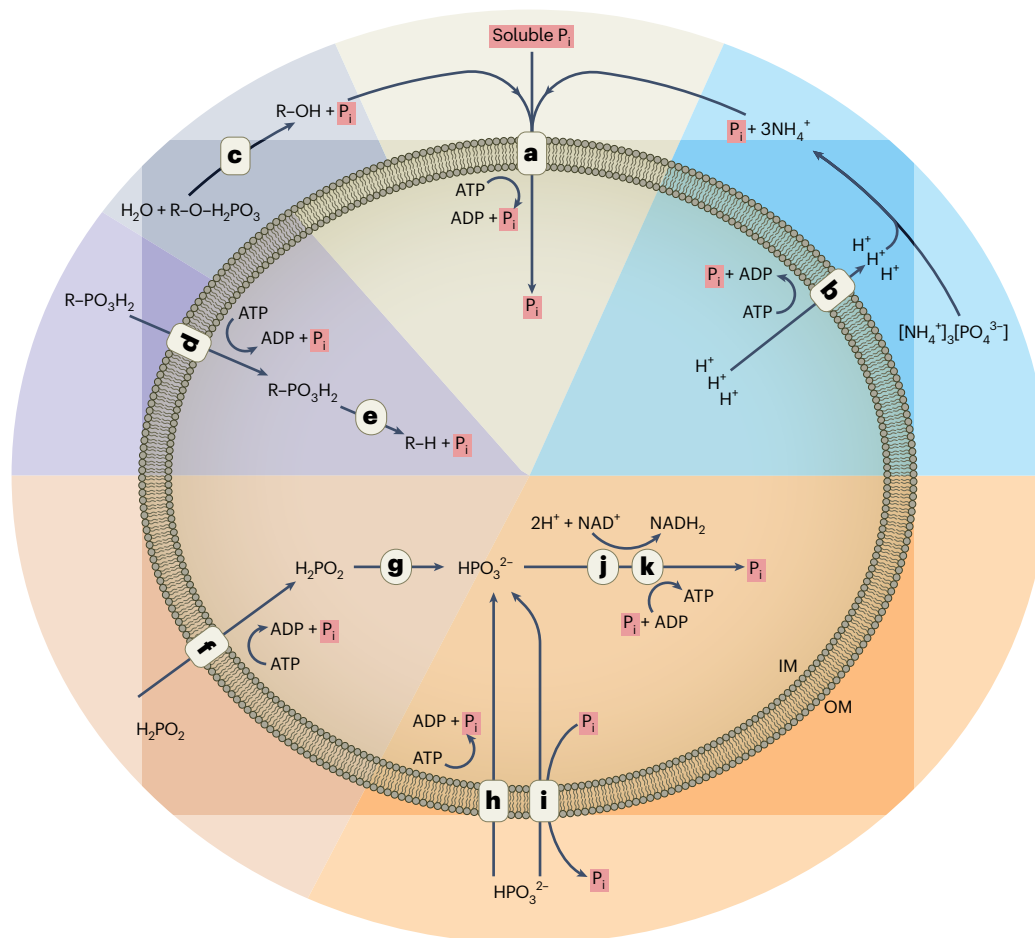
Fig. 3 | Cellular acquisition of various P species. Two concentric circles represent the inner membrane (IM) and outer membrane (OM), and demonstrate the modes by which cells acquire their intracellular P_i pool (red), where R– implies an organic radical such as a sugar or methyl group. **a**–**k**, Shaded regions highlight the mechanisms associated with different P species: yellow, soluble P_i (**a**); blue, mineral phosphates (for example, ammonium phosphate; **b**); grey, organophosphates where 'R' represents a carbon substrate bound to P_i via an ester linkage (**c**); purple, phosphonates where 'R' represents a carbon substrate covalently bound to the P atom of phosphite (**d**,**e**); light orange, hypophosphite (**f**,**g**); dark orange, phosphite (**h**–**k**). Panel labels represent the enzymes responsible for mediating P acquisition and transformations as follows: P_i transporters (for example, the inorganic phosphate transporter system or the phosphate specific transporter) acquire soluble P from the environment[102] that are environmentally dependent[103] (**a**); acidification of the environment solubilizes mineral-bound phosphates (for example ATPase-mediated proton translocation; **b**)[104]; organophosphate esters are hydrolysed to P_i and an alcohol (for example extracellular bacterial alkaline phosphatase; **c**)[60]; an ATP-dependent transporter internalizes phosphonates (**d**), which are transformed to P_i and a hydrocarbon (for example, C–P lyase; **e**)[53]; an ATP-dependent transporter (that is, HtxBCD) internalizes hypophosphite (**f**), which is oxidized to phosphite (that is, HtxA, which utilizes 2-oxoglutarate and oxygen as co-substrates in the presence of ferrous iron; not depicted; **g**)[53]; an ATP-dependent transporter (that is, PtxABC) internalizes phosphite (**h**), which is oxidized to P_i while generating NADH (that is, PtxDE; **j**)[53]; a phosphite-phosphate antiporter (that is, PtdC) internalizes phosphite (**i**), which is then oxidized to P_i while generating NADH and ATP (that is, Ptx-Ptd gene cluster; **k**)[62]. ADP, adenosine diphosphate.

Inorganic P (P_i) is also the most bioavailable form of P, as it is immediately available for enzymatic reactions without prerequisite chemical modification. In contrast, direct cellular uptake of organic P (Org-P) is rare: only sugar phosphates have been shown to be directly utilized without hydrolysis at high levels of Org-P[54]. In modern environments, concentrations of P_i frequently limit growth[55] due to high biological demand coupled with low environmental concentrations[56] that result from the low solubility of common phosphate minerals such as apatite, adsorption of P_i by iron and manganese hydroxoxides, and/or its co-precipitation with carbonates[57]. Consequently, life has evolved adaptations to acquire P from the environment (Fig. 3). Many organisms produce enzymes that allow for the utilization of alternative P species by hydrolytic release of P_i from organophosphorus compounds (for example, phosphoesters, phosphonates) and condensed phosphates (for example, polyphosphate, pyrophosphate). The best known and most widely studied of these 'phosphate-scavenging' enzymes, alkaline phosphatase, is a non-specific phosphohydrolase capable of liberating P_i from organophosphate monoesters as well as inorganic phosphoanhydride structures (for example, pyrophosphate) and even phosphite[58], and is widespread among bacteria[59,60].

Rather than scavenging for P_i, some organisms, such as the prevalent marine N-fixing bacterium *Trichodesmium*, can utilize highly recalcitrant organophosphonates, even in the presence of more bioavailable phosphoesters[61]. Organisms may also use the inorganic phosphonate, phosphite (HPO_3^{2-}, +3 valence), as a sole source of P for growth[53]. The utilization of phosphite as a nutrient source is termed assimilatory phosphite oxidation (APO), where HPO_3^{2-} is oxidized to PO_4^{3-}, and subsequently incorporated into cell mass[53,62]. APO has been observed for decades[63] in bacteria isolated from natural soils, waters and industrial samples (for example, wastewater)[53,62]. Based on genomic analysis[53], ~1.5% of bacteria are capable of performing APO, and the utilization of HPO_3^{2-} as a P source may provide organisms with a selective advantage in P_i-limiting environments, as HPO_3^{2-} is a thousand times more
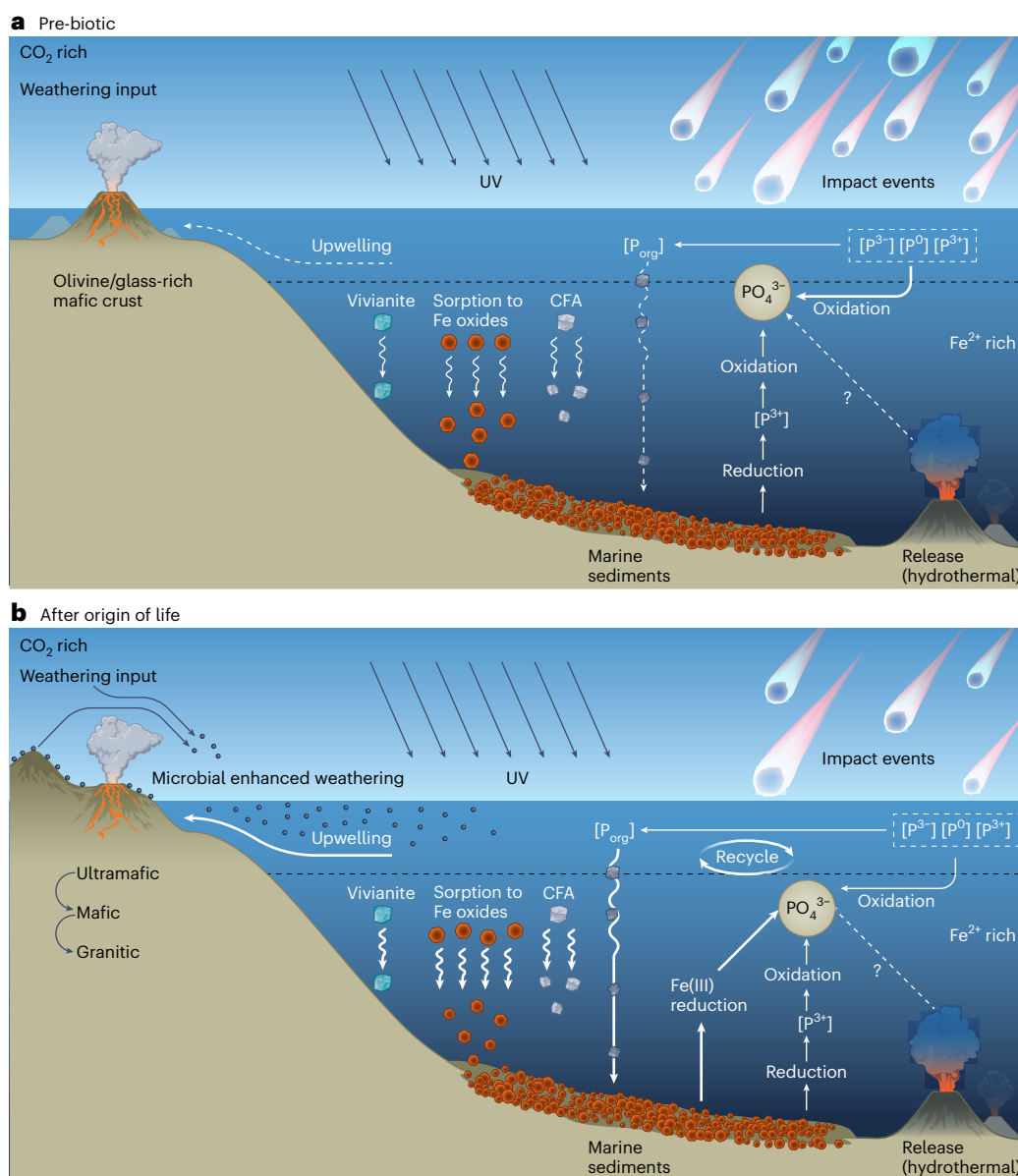
Fig. 4 | P sources, sinks and recycling pathways. a, Before life, P was made available by subaerial and submarine crustal weathering, abiotic iron-redox recycling[11] and impactor delivery. Secondary mineral sinks played a crucial role in determining final P availability. **b**, After the origin of life, biological sinks and recycling pathways eventually came to dominate the global P cycle. This transition may have happened early, if P availability was low, but may have taken 1–3 Gyr if P availability was initially high, although 3.2-Gyr-old Barberton greenstone belt rocks suggest a biologically active ocean[105]. This upwelling might have become stronger with the large-scale emergence of land at the middle to late Archaean.

soluble than P_i, and its enzymatic oxidation yields energy that can be harnessed by the cell[62].

In 2000, *Desulfotignum phosphitoxidans* FiPS-3 was isolated from anoxic marine mud and represented the first bacterium capable of dissimilatory phosphite oxidation (DPO)[64]. Organisms performing DPO can utilize HPO_3^{2-} as the sole electron donor and energy source, coupling its oxidation to cellular growth and replication. A second DPO species, *Candidatus (Ca.) Phosphitivorax anaerolimi* Phox-21 was later identified in wastewater through 16S rRNA gene sequencing and genome-resolved metagenomics[65]. More recent comprehensive metagenomic enrichment studies have identified 21 additional DPO strains from diverse anaerobic environments that are widespread across the tree of life, spanning gram-positive (monoderm) and gram-negative (diderm) bacteria[66]. The newly identified, broad

phylogenetic diversity of DPO organisms was recently validated via the cultivation of the monoderm *Phosphitispora fastidiosa*, which represents the second existing DPO isolate[67]. The emerging recognition of the prevalence of DPO microorganisms suggests life impacts P redox cycling, as demonstrated by the fact that the concentration of HPO_3^{2-} used for growth of FiPS-3 is a hundred times higher than that required for utilization of HPO_3^{2-} as a P source, suggesting that environmental DPO might also release comparatively large amounts of PO_4^{3-} to the environment in locations where phosphite concentrations are elevated.

The ability of life to use P sources beyond P_i (for example, phosphite, organophosphorus compounds; Fig. 3) is either a product of a more recent evolutionary step to scavenge this vital element from various existing trace sources, or it could be a relic of an early environment where such alternative sources were more prevalent.
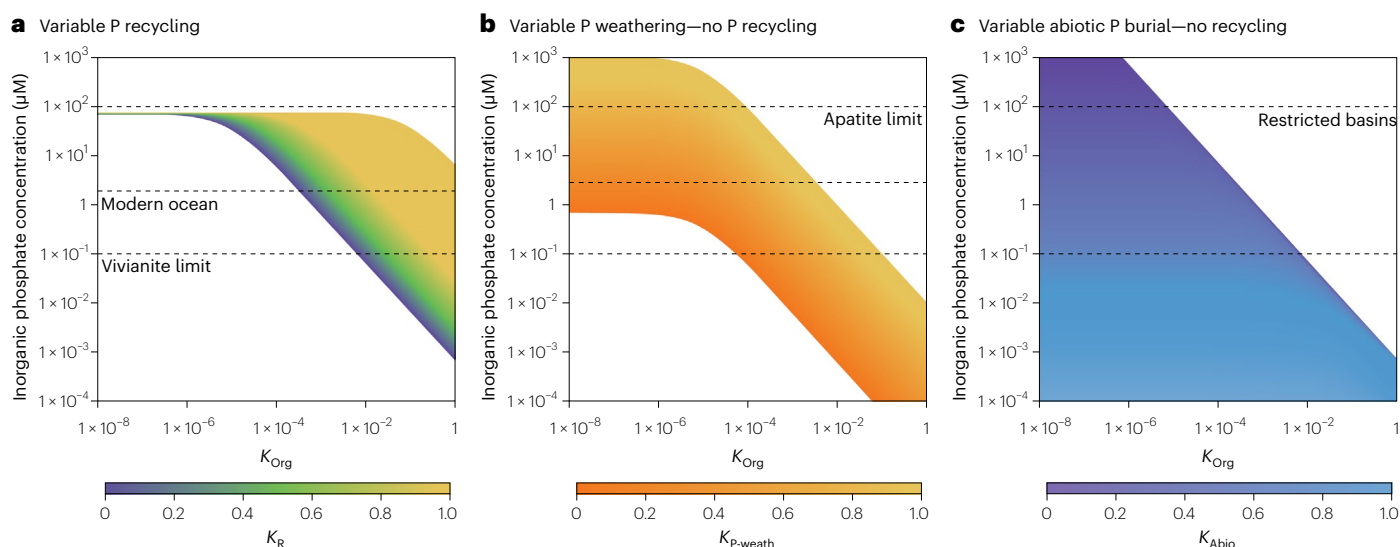
Fig. 5 | Simplified model of marine P_i availability. All results plotted as a function of biosphere size versus modern (K_{Org}). **a**, Fixed abiotic P burial efficiency ($K_{Abio} = 10^{-5}$) with variable extent of biomass P recycling (K_R; when K_R is equal to 1, all biologically buried P is recycled by life back into the water column). P weathering flux is fixed at modern level. **b**, No biomass P recycling. Variable P weathering flux is relative to modern. **c**, No biomass P recycling. P weathering flux ($K_{P\text{-weath}}$) is fixed at modern level. Variable efficiency of abiotic P sinks (K_{Abio}). These results are broadly consistent with ref. 106 wherein life has caused P to be scarce in surface environments. Dashed lines roughly demarcate inorganic phosphate concentration regimes, as set by P mineral precipitation ceilings[10,92,107], and are not fully clear as these are dependent on pH, hence these are noted with a '?'.

By mapping the phylogenetic diversity of DPO to geological timescales, it was suggested that DPO organisms evolved prior to the rise of atmospheric O_2 (>2.5 Ga), supporting hypotheses that reduced P species were available on early Earth and could have supported the emergence of life[66]. Furthermore, given that some of these compounds are believed to be feedstock molecules for prebiotic chemistry (for example, the polyphosphates, phosphite, organophosphorus compounds), the current usage represents a carry-over from a time when P species beyond P_i were more prevalent seems a reasonable proposal.

Geological constraints on early P_i availability

The low solubility of common phosphate minerals during weathering has been suggested to present an inherently limiting factor for prebiotic chemistry[68]. We may gain insight into the extent that P mineral solubility during weathering and/or other factors were truly problematic for prebiotic chemistry by evaluating geological evidence for P_i availability in seawater over time. Water column P_i availability is in principle recorded by P mineral speciation and abundance in sedimentary rocks, representing the balance over time of P recycling pathways, sources and sinks (abiotic and biological; Fig. 4).

While still controversial, the oldest rocks preserved at Earth's surface do not appear to pre-date the origin of life. Therefore, we probably cannot gain a direct insight into the P cycle of prebiotic Earth from geological observations of ancient rocks. However, the nature of the early biogeochemical P cycle may offer indirect insights. For example, widespread P_i scarcity versus abundance in early oceans would have very different implications for our expectations for P_i availability on prebiotic Earth. The difficulty of making such an inference is that the P cycle is interlinked with many aspects of the Earth system, and that many of those crucial parameters remain uncertain for early Earth (Fig. 4a)[69]. To unpick these relationships, we ground the remainder of this Review with a simple model for steady-state closed-system P_i concentrations in aqueous environments (Fig. 5; details in Supplementary Information). Initial values for each parameter in the model—weathering input[70], burial rate by biologic processes, burial rate by abiotic processes and recycling from biomass[71]—are based on estimates of the modern P cycle.

Recycling pathways

Life is capable of recycling P back into the water column during organic matter remineralization, extending the oceanic residence time of P before its eventual long-term deposition within sediments (Fig. 4b)[72]. Indeed, freshly weathered P represents a small fraction of all P that is consumed by life each year in support of primary production[73]. This behaviour is explored in Fig. 5a, where recycling >99% of all P buried by biology results in an average ocean P_i concentration comparable to that observed today[73]. The capacity of life to recycle P from sinking biomass is thought to have increased as a function of oxidant availability in marine environments (Fig. 6). On the anoxic early Earth, all else being equal, steady-state P_i concentrations may therefore have been correspondingly lower than today (Fig. 5a). However, a competing effect arises from biosphere activity which, if also lower, would have yielded correspondingly elevated steady-state P_i concentrations. This is especially true for prebiotic Earth, where recycling and organic P burial should in effect have been inoperable ($K_R = 0$ and $K_{Org} = \sim 0$, where K is the fraction between 0 and 1 of the material cycling into a specific reservoir, for instance the amount of P that is recycled from biomass in Fig. 5a), leading to (initial) P_i availability being determined solely by abiotic P sources and sinks.

Sources

Today, essentially all freshly weathered crustal P derives from emergent land. There is still debate about the history of continental emergence, but there was substantial land above sea level by the middle to late Archaean[74,75]. Under a high partial pressure of CO_2 (pCO_2) atmosphere[76], large amounts of P from continental weathering would have afforded P_i concentrations close to today[10,77] (Fig. 5b). In addition, early continents may have been more mafic and therefore contained a higher fraction of P as a minor element in silicates (Fig. 1c). Apart from continental weathering, there is growing evidence for seafloor weathering (for example, of basalt) serving as a P source in the early seawater as opposed to representing a major sink, as is true for contemporary oceans[78,79]. Moreover, highly reactive iron phosphide phases delivered by impactors would have dissolved rapidly[80], although work remains to be done quantifying these fluxes at early Earth conditions. Hence,

depending on whether secondary mineral sinks inhibited seafloor P weathering, the scale of emergent land and the nature of the early C cycle, steady-state P_i availability may have differed strongly compared with modern (Figs. 5b and 6c).

Sinks

The third variable in determining P_i availability is the efficiency of P sinks. This includes Org-P sinks, wherein the rise of a productive biosphere (K_{Org}; Fig. 5a–c)—or indeed efficient prebiotic chemistry—can be expected to reduce P_i availability by many orders of magnitude if not offset by P recycling (K_R). Abiotic sinks today represent a great deal of permanently buried P, yet also a low percentage of initially buried P[71,73]. Varying the efficiency of abiotic sinks therefore has greatest impact when biological activity is limited or absent. In a prebiotic context, without P recycling, only with extremely inefficient abiotic P sinks can high P_i availability (greater than millimolar scale) be achieved (Fig. 5c).

It is informative in this context to consider the geological evidence for and against the operation of different abiotic marine P sinks over Earth's history (Fig. 6e). A classic scenario is P sorption by iron oxyhydroxides in the water column[81], rendering less P available to life. Low contents of P-associated iron oxide phases in Fe-rich Archaean marine sediments (that is, banded iron formations[82] and shales[83]) have been considered strong support for this scenario[81,84]. However, recent evidence suggests these phases many not be authigenic but instead the products of diagenesis[85]—therefore possibly irrelevant to the oceanic P cycle[86]. If so, P extraction from the water column may only have happened where P concentrations were high enough to trigger precipitation of minerals in which P is a stoichiometric constituent (Fig. 6e). Of these, the most widely studied are carbonate fluorapatite (CFA; $Ca_5(PO_4,CO_3)_3F$) and vivianite ($Fe_3(PO_4)_2 8H_2O$), both of which are observed to precipitate as authigenic phases in some modern Earth settings.

Today, seafloor weathering produces abundant secondary minerals, and P is largely sorbed to iron oxide alteration products[57,73] during basaltic alteration in Earth's oceans. It is possible that early ferruginous conditions resulted in vivianite precipitation in the water column or during seafloor weathering[10,87]. If so, widespread vivianite precipitation would have throttled P supply to the oceans that would otherwise have been competitive with or larger than the coeval continental riverine P weathering flux, limiting P_i availability to around 0.1 µM (Fig. 6e).

A challenge to this scenario is that thermodynamic considerations suggest vivianite may be much more soluble in the Si-rich oceans of early Earth than in modern analogue ferruginous basins[86]. Solubility experiments also reported high solubilities of vivianite in the presence of high Fe(II), for example, 10^{-4} to 10^{-3} M dissolved P_i at 10^{-4} to 10^{-3} M Fe(II), respectively, due to the aqueous complexation of Fe(II)–P_i[88]. Observations of ancient sediment reveal apparently primary precipitates of CFA[86] and elevated P/Ca ratios in Archaean carbonates that were proposed to reflect relatively P-rich ocean water[89]. In sum, these recent observations hint that ocean P_i availability may instead have been CFA-limited, at around 100 µM (Fig. 6e)[89,90], though changing pH, [Ca^{2+}] and alkalinity could have given rise to increases in P/Ca without a change in phosphate[91]. Disparate scenarios for early P_i availability converge towards the present, where biological P recycling coupled to high P demand from primary productivity became unambiguously important in setting overall marine P_i availability (Fig. 6e).

Availability of P_i on prebiotic Earth

Geological evidence suggests that marine P_i availability would have been capped, even in the most optimistic prebiotic scenarios (high P weathering fluxes, minimally efficient P sinks), at around 100 µM (Fig. 5c). This is within the relevant range for at least some prebiotic P pathways[44], but orders of magnitude lower than that required by many others (100 mM)[35]. In order to achieve high P_i availability (100 mM), the chemical composition of the system must itself differ strongly from that of bulk modern and/or (estimated) early seawater. This is plausible for a variety of carbonate-rich closed basins, whereby evaporative concentration can result in progressive evolution towards divalent-cation-poor[92] or organic-rich[93] compositions and thereby favour high saturation ceilings, for example, for CFA. Provided that other abiotic P sinks (for example, iron oxides) are inefficient and supply of P is rapid (for example, ultraviolet (UV) radiation of phosphite forming P_i[38] or elevated apatite weathering at high pCO_2[77]; Fig. 6a–c) in these same closed-system basins, exceptionally high P_i availability may be achieved. Success may also been obtained at small scales by exploring environmental forcing processes that temporarily generate P over-enrichments on small spatial scales, such as fully drying environments in evaporating ponds[94,95], at mineral–water interfaces[96,97], at air–water interfaces[98] and at protocell–water interfaces[99].

The availability of P_i for the origin of life therefore depended strongly on global parameters, such as atmospheric composition, high-energy processes (UV radiation, lightning and volcanic activity), impactor bombardment rate and average crustal composition (Figs. 4 and 6). These global parameters principally influenced P sources. At the same time, local processes such as basin water column composition, evaporation rate and mineral-interface behaviour acted to determine the efficiency of P sinks. Before the rise of a biosphere, and especially in closed-system aqueous environments, it is possible to envisage multiple scenarios where the balance of P sources to sinks resulted in high P_i availability. However, the incorporation of P into biomolecules via prebiotic chemistry necessarily parallels burial of P in organic matter (Fig. 5). Efficient prebiotic chemical pathways utilizing P would therefore have needed to develop in settings with extremely high P availability, rapidly invented mechanisms of exploiting P at low concentrations and/or recycling existing prebiotically synthesized organophosphates.

Conclusions

The availability of P with respect to conditions in prebiotic environments and in early biological ecosystems was not necessarily synonymous. P availability probably changed as life evolved and altered the geochemistry of the Earth, and the environmental and chemical conditions that led to P incorporation into organic molecules in the absence of life are unlikely to reflect those that prevail in an active biological context. However, in settings where large sources and minimal sinks conspired to induce high P_i availability, similar thresholds from abiotic P-bearing mineral precipitation would have capped P_i concentrations. This reality allows us to inform our view of P_i availability in several

**Fig. 6 | Parameter space of global P cycling evolution**[11,27,52,72,77,78,89,108]. **a–f**, P delivery via impactors[38,46,52] (**a**), diversity of terrestrial primary minerals in which P is an intrinsic constituent[27] (**b**), weathering rate of apatite, based on two scenarios for pCO_2 evolution[109,110] (**c**), redox-dependent recycling capacity of P in oceanic environments[10,11,72,101] (**d**), end-member scenarios for oceanic P_i availability[10,73,81,86] (**e**), redox evolution of near-surface environments[76] where the actual amount of oxygen in the early atmosphere is unknown, but probably between 10^{-6} and 10^{-3}× present day, and a transition near the Cambrian to modern O_2 levels (**f**) and a geological timeline of Earth history (**g**). Had,

Hadean; Arch, Archaean, Pptz, Palaeoproterozoic; Mptz, Mesoproterozoic; Nptz, Neoproterozoic; Phan, Phanerozoic. Arrows pointing up (along y axis) indicate spatially or temporally variable processes that could positively perturb P availability. Arrows pointing down (along y axis) indicate hard ceilings on P availability, but which may be sensitive to local solution chemistry or basin dynamics. Red to yellow colour gradients in all cases are a visual guide from high to low for a given quantity. In **b**, this is used to convey a rough rate of transition from silicate-hosted to apatite-hosted crustal P.

plausible prebiotic environments with observations from geology and with models of P recycling.

We propose a step-change from higher to lower P_i availability after the origin of life (Figs. 4–6). This would have resulted from a combination of the following: (1) environments that better solubilized P; (2) the distribution of P as a minor element in easily weathered minerals at the Earth's surface; (3) the presence of energetic P molecules derived from reduced-oxidation-state P-bearing materials; and (4)
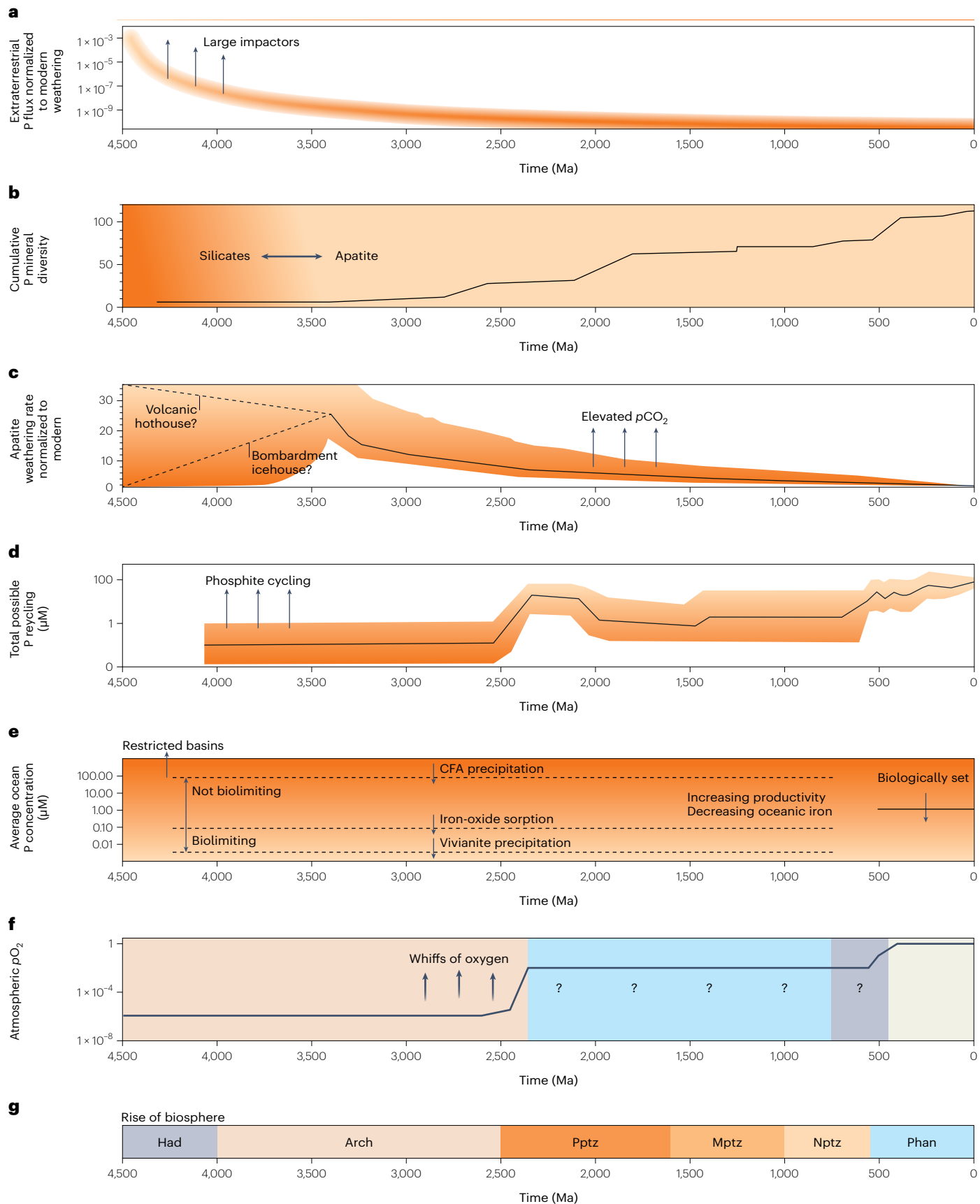
a lack of oxidative and biological P_i sinks. We suggest that subaerial closed-system basins, wherein high P mineral saturation ceilings could be achieved, and/or microscale environments capable of largely circumventing usual P saturation ceiling 'rules' could have achieved of the order of 100 mM P_i concentrations prior to the rise of Org-P sinks, sufficient to drive a range of prebiotic chemical pathways reliant on available P_i.

In contrast to previous suggestions of limited P availability across Earth's history, we conclude that P availability (both molecular and as a nutrient) may have been high—at least locally—in the era of prebiotic chemistry and early life. This point of origin may have resulted in a biosphere dependent on P, with the rise of life driving fierce competition for P in increasingly productive near-surface waters and prompting increased P recycling in response.

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C.R.W., J.H., S.E., J.D.C. and M.A.P. planned and wrote the paper. Data analysis was performed by all authors, who also edited the text.

Competing interests

The authors declare no competing interests.

Additional information

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