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Active redox cycling of phosphorus on the early Earth

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Phosphorus is a critical bio-limiting nutrient in Earth's ecosystems. A new study published in Nature Communications reports high availability of phosphite for possibly biological uptake in the late Archean ocean, suggesting an active redox cycling of phosphorus on the early Earth.

Phosphorus (P) is one of the six essential elements (CHONPS) for life. In biological systems, it is most commonly found as a phosphate group that forms the backbone of nucleotides, energizes cellular processes via ATP, and helps build cell membranes as phospholipids. Because the phosphate group has unique chemical properties[1] and plays a crucial role in biology, many researchers believe that organophosphate has been important since the emergence of cellular life on the early Earth[2]. However, the Earth's environment has changed dramatically over geological time, which might have altered the way phosphorus is cycled and its availability to living systems[3].

Today, the phosphorus cycle is largely driven by the weathering of continental rocks and the recycling of organic phosphorus within the oceans. In these environments, phosphorus is predominantly present in the form of orthophosphate ($H_xPO_4^{x-3}$, $x = 0–3$), which is the most oxidized and stable state (Fig. 1). However, dissolved orthophosphate can readily bind with common metal cations, such as calcium, magnesium, aluminum, and iron, forming poorly soluble minerals[4]. Abundant minerals, like ferrihydrite and carbonates, can also adsorb dissolved orthophosphate during their sedimentation, limiting the bioavailability of phosphorus in surface waters[5]. Consequently, phosphorus is often considered as a limiting nutrient, controlling the overall biological productivity in modern ecosystems.

Unlike many other bio-essential nutrients, phosphorus is relatively inert in redox reactions within modern biogeochemical cycles. The reduction of orthophosphate is thermodynamically unfavorable, even under anoxic conditions. Nevertheless, certain microorganisms in oxygen-depleted waters can produce trace amounts of reduced phosphorus species, such as phosphite ($H_xPO_3^{x-3}$, $x = 1–3$) or phosphine (PH_3) gas (Fig. 1). These reduced forms are typically short-lived in modern oxygen-rich atmosphere and rely on continuous microbial activities for replenishment. This ephemeral nature has even led to suggestions that detecting reduced phosphorus on oxidizing planets like Venus might serve as a signature of extraterrestrial life[6].

For much of Earth's history, the oceans remained largely anoxic[7], so it has long been suspected that reduced forms of phosphorus were more prevalent on the early Earth[8]. A recent study by Baidya et al., published in Nature Communications[9], reported moderate levels of phosphite in late Archean banded iron formations (BIFs). This work adds valuable data to the limited record of reduced phosphorus in ancient sedimentary rocks. Previously, trace to moderate levels of phosphite had been detected only in early to middle Archean rocks, including carbonates and metamorphized sedimentary rocks[10,11]. Together, these geological records now span a wide range of geological time (Fig. 2), suggesting that phosphite might have been a common compound in early Earth environments. To better relate the BIF records to ocean chemistry, Baidya et al.[9] further examined phosphite adsorption onto hydrous ferric oxides (HFO), proposed to be a key precursor of BIFs, and estimated dissolved phosphite concentrations comparable to those of orthophosphate in the Archean ocean. This work represents an important step toward quantifying the role of reduced phosphorus in early marine ecosystems.

Multiple sources likely contributed to the availability of reduced phosphorus on the early Earth (Fig. 2). Some extraterrestrial materials contain substantial levels of reduced phosphorus compounds[12], including metal phosphides found in iron meteorites, alkyl phosphonic acids in carbonaceous chondrites, and phosphine in comets. Impact rates were likely far more frequent in the Earth's early history. Several high-energy terrestrial processes have also been shown to partially convert orthophosphate into reduced phosphorus species, including lightning strikes[13,14], volcanic eruptions[15]; serpentinization reactions[16], and diagenetic or metamorphic activities[11,17,18]. Such processes, which were likely more common on a geologically vigorous early Earth, could have considerably increased the availability of reduced phosphorus.

It is important to note, however, that reduced phosphorus compounds are thermodynamically unstable and prone to oxidation, even under the relatively reducing conditions relevant with the early Earth. Nonetheless, available data indicate that reduced phosphorus species like phosphite may have persisted in ancient seawater for much longer than in modern oxygenated environments[19], potentially facilitating microbial uptake. Similar to orthophosphate, these reduced phosphorus compounds could be removed from seawater by mineral adsorption[9] or co-precipitation. Furthermore, the intense ultraviolet radiation (prior to the development of the ozone layer) could have accelerated oxidation of reduced phosphorus in surface waters[20]. A comprehensive understanding of reduced phosphorus availability will require systematic evaluations of both their sources and sinks in early Earth environments.

Reduced phosphorus compounds may have conferred unique advantages during the origin and early evolution of life. Their high chemical reactivity, compared to orthophosphate, might have facilitated the abiotic synthesis of phosphorus-bearing biomolecules under milder conditions—without the need for extreme heating, potent catalysts, or intense radiation[21]. Moreover, certain reduced phosphorus species, such as phosphite, are substantially more soluble (~1000 times for phosphite) than orthophosphate in surface waters. Furthermore, Baidya et al. observed a much weaker adsorption of phosphite than orthophosphate onto HFO[9], which is proposed as a major sink for

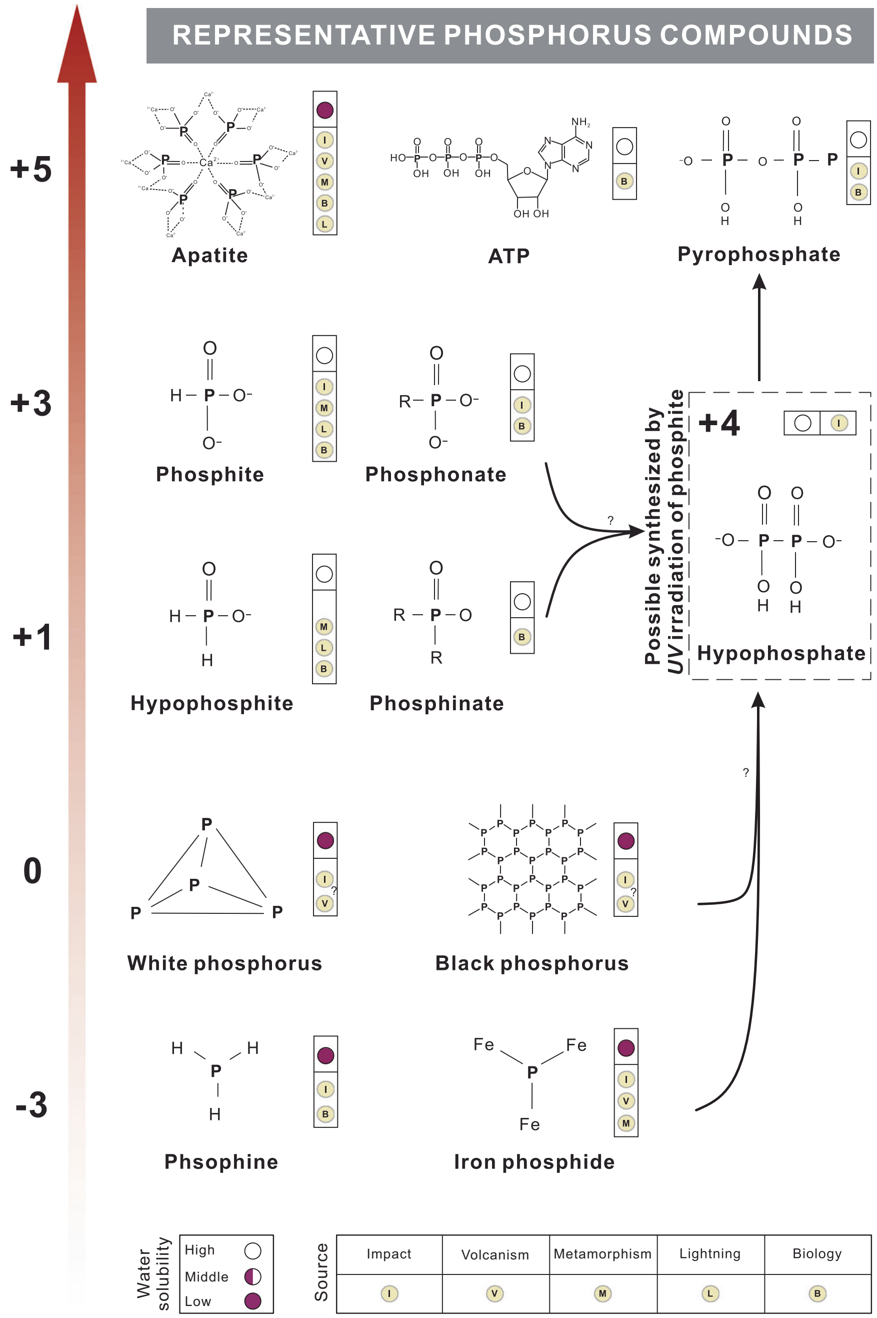

Fig. 1 | Redox states of phosphorus and their common compounds in the crust.

orthophosphate in the early ocean[5]. This increased solubility and availability may have been crucial for early microbial communities, especially since phylogenic evidence suggests that life was already capable of using phosphite by the late Archean[22]. In turn, enhanced availability of reduced P may have boosted early primary productivity, ultimately contributing to the oxygenation of the atmosphere by the end of the Archean[9].

In summary, the bio-limiting phosphorus might undergo active redox cycling on the early Earth, with reduced forms potentially playing a significant role in early ecosystems. Yet, many questions remain. Comparisons of sedimentary rocks of similar ages, from different settings and regions, is needed to reveal whether these reported signals of reduced phosphorus represent global phenomena or localized enrichments. Since many sources of reduced phosphorus stem from sporadic events, whether extraterrestrially or terrestrially sourced, the distribution of these reduced phosphorus compounds was likely highly spatially and temporally heterogeneous. Future research should also consider the possibility of diagenetic or metamorphic alteration of original signals in ancient sedimentary records, as such processes can induce the reductive transformation of

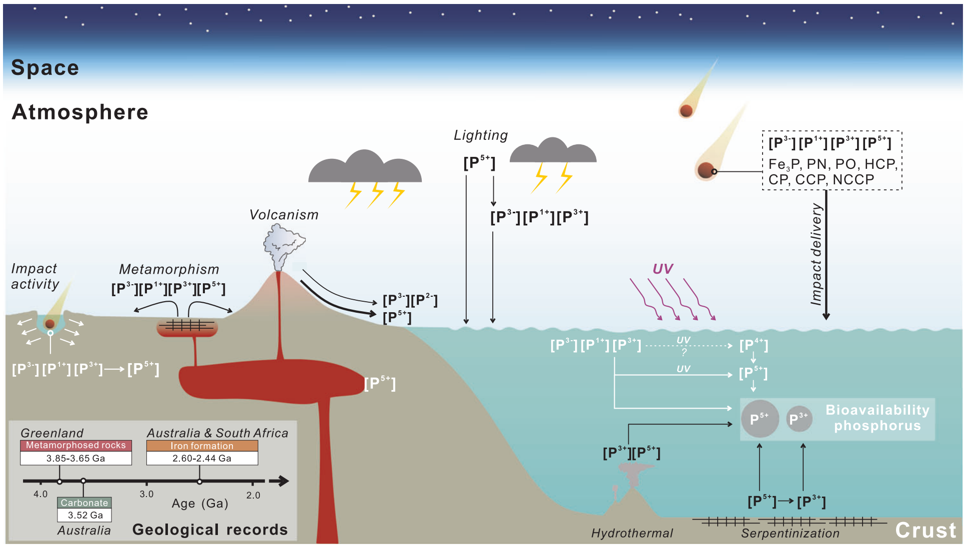

Fig. 2 | Major redox cycling pathways of phosphorus on the early Earth and available geological records of reduced phosphorus in ancient rocks.

orthophosphate per se. Moreover, a more comprehensive analysis and compilation of phosphorus speciation across diverse ancient rocks and spanning a wide range of geological ages is essential to fully understand the long-term evolution of reduced phosphorus availability and its roles in biological evolution. Finally, future efforts may also evaluate the redox cycling of phosphorus on other ocean worlds, such as early Mars and the icy moons, especially given the growing availability of samples and in-situ measurement data. Such insights will not only refine our assessment of the habitability of these planetary bodies but also enhance the reliability of using reduced phosphorus compounds as biosignatures in planetary exploration.

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Competing interests

The authors declare no competing interests.

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