



Marine arsenate evolution during Proterozoic oxygenation events and implications for biological phosphate metabolism



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Earth's atmosphere and oceans experienced two major episodes of ocean-atmosphere oxygenation that transformed the planet and shaped the evolution of the oxygen-rich biosphere between 2.45 and 0.541 billion years ago (Ga). These changes increased the abundance of oxidized chemicals in seawater, but their distribution and effects on the availability and utilization of essential nutrients remain poorly understood. Here we show that these oxygenation events were accompanied by stepwise increases in marine arsenate content—a toxic compound that closely resembles phosphate and interferes with its biological use. Arsenate concentrations rose during the first global oxygenation event and again after the end of the Sturtian global glaciation. Our results suggest that seawater contained much higher arsenate relative to phosphate than today for much of early Earth's history, likely restricting biological access to phosphate. After the Sturtian glaciation, increasing phosphate availability lowered the arsenate-to-phosphate ratio, reducing arsenate toxicity and enabling more efficient phosphate use in shallow coastal seas, thereby supporting the expansion of oxygen-dependent life.

The Paleoproterozoic Great Oxidation Event (GOE)—2.45–2.20 billion years ago (Ga) and the later 0.85–0.54 Ga Neoproterozoic Oxygenation Event (NOE), pinpoint two fundamental shifts in Precambrian redox history^{1,2}. These events transformed Earth's biosphere from one dominated by anoxic metabolisms to surface ecosystems reliant on free molecular oxygen (O₂) respiration³. To survive in this emerging O₂-rich world, life developed new metabolic pathways to cope with O₂ toxicity and the flood of oxidized chemical species in the environment. For example, a rise in seawater arsenate (AsO₄³⁻) levels during the GOE⁴ has been linked to biospheric development of arsenate resistance strategies⁵, which regulates the availability of phosphate to primary producers^{6–10}. However, we do not know how seawater arsenate concentrations evolved throughout the rest of the Proterozoic Eon, for instance, with the expansion of eukaryotic marine phytoplankton in post-Sturtian Snowball¹¹ shallow marine waters¹². Moreover, how these changes relate to the development of the biosphere and

the second major rise in atmospheric oxygen content during the NOE is unknown, considering the notorious toxic consequences of arsenic on all life forms, even when present in trace amounts¹³.

Trivalent arsenite (AsO₃³⁻), a form of arsenic (As) commonly found in low-O₂ environments, disrupts protein synthesis and activity¹³, with biological resistance to arsenite thought to have evolved long before atmospheric O₂ rose⁵. In modern oxidized settings, arsenate species dominate^{13–20}, where they compete with phosphate (PO₄³⁻) due to their similar chemical structures and reactivities^{6–10}. Because arsenate and phosphate have comparable acid strength, the same number of negatively charged oxygen atoms, and differ in size by just ~4%, they substitute for each other in biochemical reactions⁶. These shared properties severely inhibit efficient phosphorus (P) uptake and use by cells, resulting in rising dissolved arsenate to phosphate ratios proportionately curtailing primary production^{6–10,13–20}. In today's oxygenated biosphere, microbes, including

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phytoplankton, passively transport arsenate into cells through phosphate transporters^{13–20} and then detoxified by intracellular reduction to arsenite and either pumped out, methylated or sequestered within cellular compartments^{13–20}. In modern environments with high arsenate-to-phosphate ratios, microbial ecosystems must use effective arsenate detoxification and energy-intensive (high-affinity phosphate uptake) mechanisms to distinguish arsenate from phosphate for survival^{6–10}.

Here, we integrate Paleoproterozoic and Neoproterozoic marine arsenic and phosphorus records with mechanistic insights into modern arsenic–phosphorus co-cycling at the seawater–sediment interface to establish a conceptual framework linking arsenic speciation, phosphate metabolism, and Earth’s major Proterozoic oxygenation transitions. This framework suggests that secular changes in the seawater arsenate-to-phosphate ratio were not merely a consequence of rising oxygen levels but may have acted as a fundamental ecological and evolutionary driver of biological adaptation to increasingly oxygenated oceans. By coupling long-term geochemical change with cellular phosphate metabolism, our study proposes arsenic–phosphorus interactions as a previously underappreciated control on primary productivity, biosphere expansion, and Earth’s oxygenation trajectory.

Geological setting

The sampled section of sedimentary rocks from the Isles of Islay and the Garvellachs in the Dalradian Supergroup, Scotland, has been previously studied for their lithostratigraphy (Fig. S1), bulk mineralogy, clay mineral distribution, weathering dynamics, geochemistry and bottom water redox depositional conditions related to seawater phosphorus cycling^{21,22}. The samples, which span the pre-glacial, deglacial and post-glacial phases of the Neoproterozoic Sturtian Snowball Earth glaciation¹¹ (Fig. S1), were collected

from marine sedimentary outcrops^{21,22}. These sections cover the Grampian, Appin and Argyll groups. The pre-glacial sequence includes the Tonian Lossit Limestone Formation (LLF)—a 4 km-thick section deposited in warm, shallow, tropical marine waters^{21,22}. This formation consists of organic-rich mudstones, sandstones and various carbonate lithologies, some containing stromatolites. The LLF transitions conformably into the overlying Port Askaig Tillite Formation (PATF), which marks the deglacial phase^{21,22}. The PATF comprises a 1.1 km-thick sequence of poorly sorted, coarse-grained tillites interbedded with sandstones, mudstones, conglomerates and megaclasts. Above this lies, conformably, the Bonahaven Dolomite Formation (BDF), a ~300 m thick post-glacial fine-grained clastic sequence containing dolostones and evaporite minerals^{21,22}. The data presented in this study come from a subset of rock samples described and thoroughly characterized^{21,22}. The samples ($n = 14$ —five pre-Snowball, two tillites, three immediate-post Snowball and four late post-Snowball) were selected to represent lithologies associated with anoxic seawater conditions during the pre-Snowball Earth and tillite deposition period, brief seawater oxygenation immediately after the Sturtian Snowball Earth glaciation event (lower BDF) and late post-Snowball return to bottom water deoxygenation (upper BDF)^{21,22}.

Results and discussion

Multiple X-ray Absorption Near Edge Structure (XANES) and X-ray Fluorescence (XRF) analyses (Figs. 1 and S2) on thirteen samples revealed three distinct stages of arsenic speciation (Fig. 2a and Table S1). These stages align with changes in seawater redox conditions (Fig. 2b), from anoxic bottom waters in pre-Snowball and tillite deposits to temporary full-column oxygenation in the early post-Snowball interval and back to anoxia in the later stages and are consistent with bulk sedimentary phosphorus dynamics

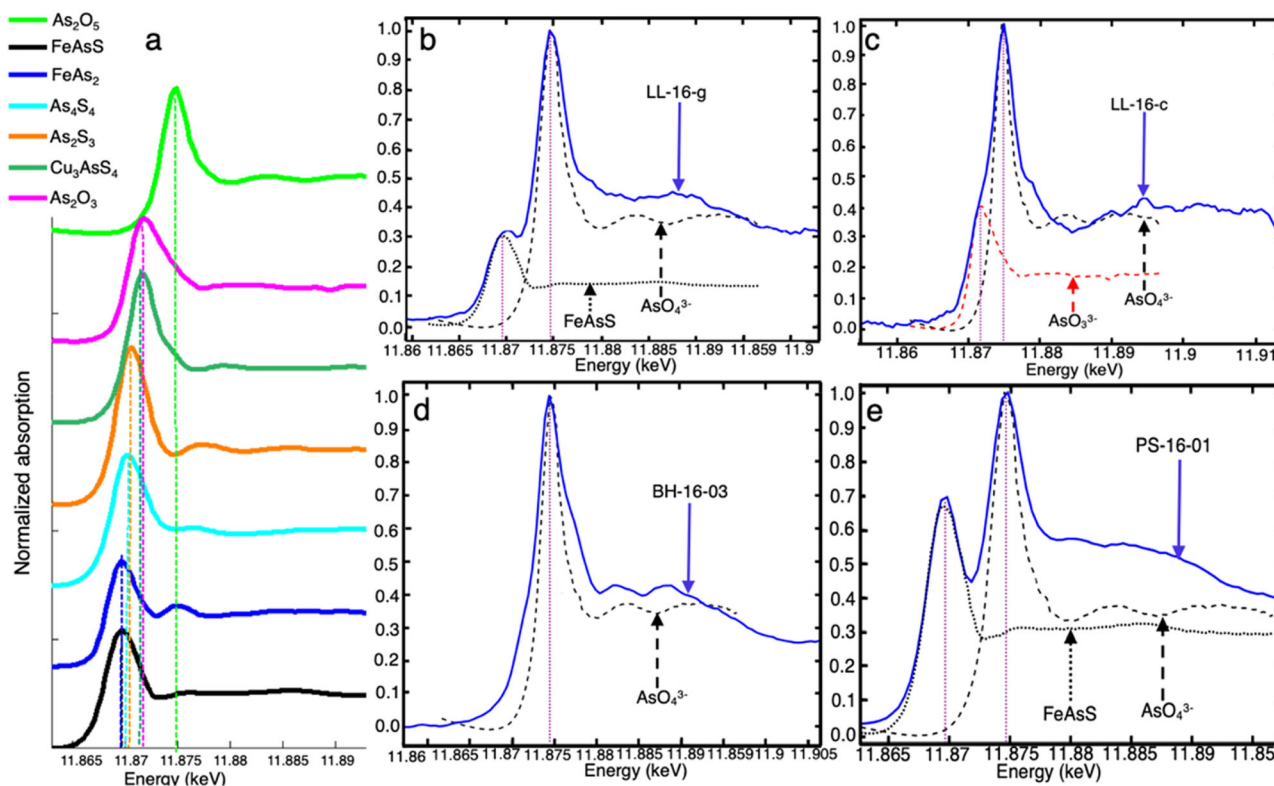


Fig. 1 | Examples of measured XANES spectra for inorganic arsenic (As) mineral standards, samples and LCF spectra fit. a XANES mineral standards for arsenic sulfides, arsenate and arsenite, representing minerals most prevalent in sedimentary environments. Arsenate= As_2O_5 or AsO_4^{3-} . Arsenite, As_2O_3 or AsO_3^{3-} . Arsenopyrite, FeAsS . Löllingite, FeAs_2 . Pararealgar, As_4S_4 . Orpiment, As_2S_3 . Enargite, Cu_3AsS_4 (a copper sulfate mineral). **b, c** Representative XANES spectra for the pre-Snowball Earth Lossit Limestone Formation samples LL-16-c and LL-16-g; **d** the immediate

post-Snowball Earth Bonahaven Dolomite Formation sample BH-16-03; and the late post-Snowball Earth Bonahaven Dolomite Formation sample PS-16-01. The LCF fits were performed with the Athena software. See ref. 4 for Archean–Early Paleoproterozoic XANES trends. See ref. 21 for a previous report on the seawater iron speciation data, redox reconstruction and a detailed analysis of bulk and dissolved phosphorus dynamics across the sampled succession.

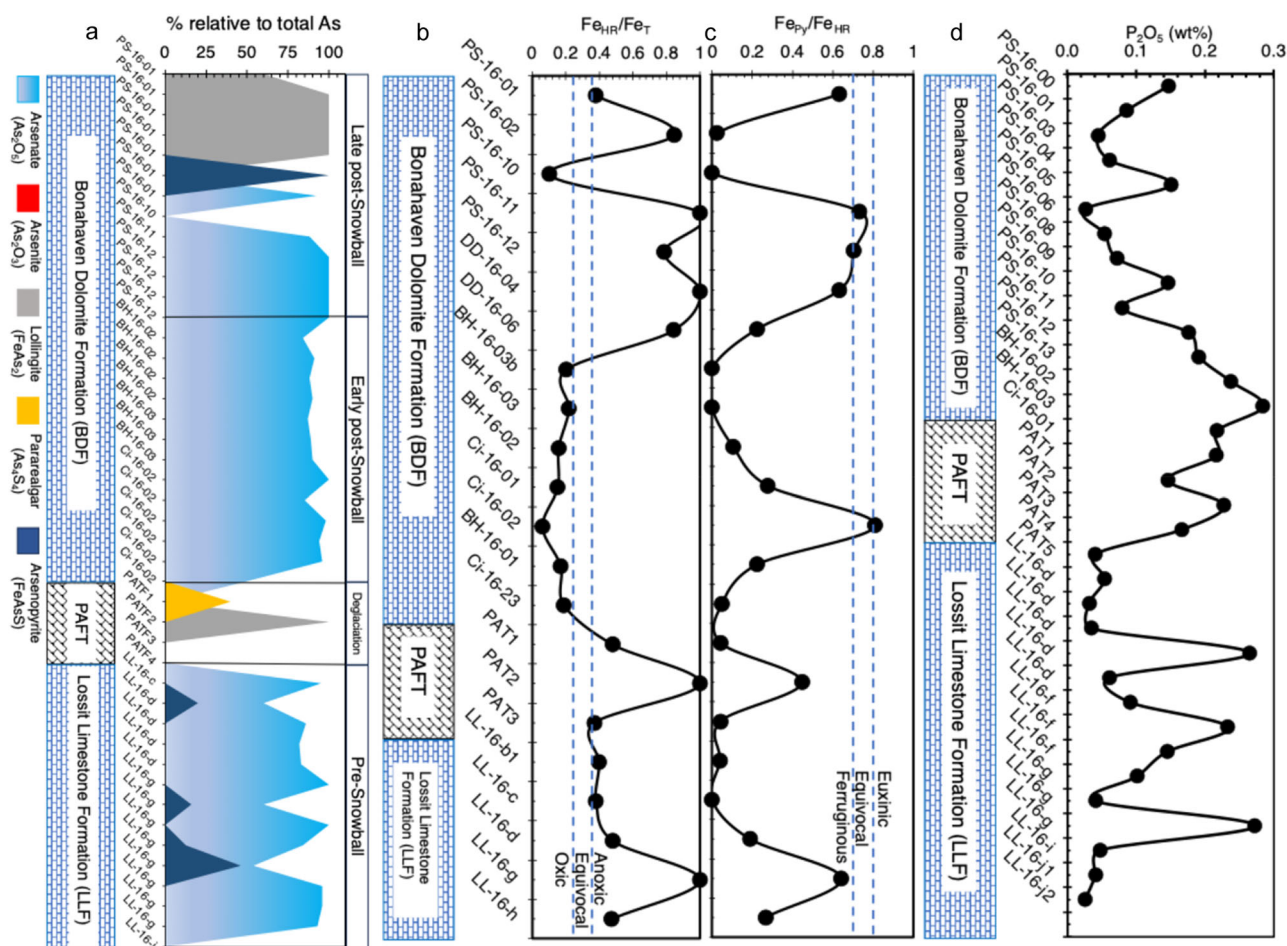


Fig. 2 | Arsenic (As) speciation, iron (Fe) speciation and phosphorus (P) distribution across the studied succession. **a** XANES data showing the distribution of arsenic (As) mineral species. **b** Highly reactive iron (Fe_{HR}) to total iron (Fe_{T}) and pyrite iron (Fe_{Py}) to highly reactive iron ratios for representative samples. The data in

b and **c** are adapted from ref. 21. **c** Bulk sedimentary phosphorus profile for representative samples across the sampled succession, described in and adapted from ref. 21. PATF Port Askaig Tillite Formation, PAT Port Askaig Tillites, GOE Great Oxidation Event.

(Figs. 2c and 3). A similar immediate post-Snowball oxygenation event recorded in shallow continental margin marine sedimentary rocks in Mongolia suggests this oxygenation event may have been widespread²³. In pre-Snowball samples, arsenic is present in varying amounts as arsenate and arsenopyrite (FeAsS). During deposition of the glacial tillites, reduced Fe-As sulfides such as pararealgite (As_4S_4) and lollingite (FeAs_2) were dominant. In the immediate post-Snowball period, only oxidized arsenate was detected. However, further up in the sequence (late post-Snowball), a mixture of lollingite (FeAs_2) and arsenate was observed (Fig. 2a). Notably, trivalent arsenite was not detected in any of the samples, similar to previous studies targeting the Archean-Paleoproterozoic boundary⁴ and an Ediacaran terrestrial arsenic-rich volcanic lake²⁴. This could be due to preservation biases, lower affinity for iron oxides compared to arsenate²⁵, low concentrations or complete transformation to Fe-As sulfides.

Total iron content associated with operationally defined iron oxide acid leachates mineral phases (Fig. S3 and Table S2) decreased towards the end of the pre-Snowball interval before increasing across the Snowball transition and remaining relatively elevated thereafter (Fig. 4a). Co-extracted sulfur concentrations are lowest and least variable in the immediate post-Snowball interval, before increasing to values comparable to those of the pre-Snowball succession in the late post-Snowball samples (Fig. 4b). Iron oxide-associated arsenic show greater variability in the pre-Snowball and syn-glacial rocks up to the earliest post-Snowball oxygenation stage (Fig. 4c). On the contrary, phosphorus concentrations are more variable near the onset of the post-Snowball oxygenation event and onwards (Fig. 4d).

Arsenic-to-sulfur ratios are inversely related to sulfur along sequence stratigraphy (Fig. 4b, e). This decoupling indicates that leached arsenic is unlikely to be primarily associated with pyrite and is supported by no correlations between arsenic and sulfur within the independent lithological units (Fig. S4). By contrast, As/Fe and P/Fe ratios display comparable stratigraphic trends (Figs. 4f, g and S5) and are linearly correlated on a cross plot ($R^2 = 0.8939$) (Fig. S6a)—suggesting that iron exerted a comparable first-order control on the behavior of both elements, consistent with observations in modern and ancient marine sediments^{26,27}. We pinned down the inverse stratigraphic correlation between total leached iron (Fig. 4a) and its corresponding As/Fe and P/Fe stratigraphic trends (Fig. 4f, g) to varying concentrations of arsenic and phosphorus hosted in the different Fe oxide mineral phases. For example, iron carbonate leachates were completely devoid of phosphorus, while containing small quantities of arsenic (Fig. S3). Equally, hematite enriched more arsenic than phosphorus, and magnetite more phosphorus than arsenic. In addition to the possible dilution effect of a large fluctuating dissolved iron pool, the identical total As/Fe and P/Fe stratigraphic profiles suggest that the composite iron oxide pool responded similarly to changing environmental conditions (e.g., redox, water chemistry, sedimentation rate, diagenesis, arsenic and phosphorus availability and organic matter cycling) through time, regardless of the intrinsic properties and abundance of each iron oxide mineral phase. The strong stratigraphic and linear correlation further suggests that the processes governing arsenic-phosphorus loading onto the total Fe mineral assemblage affected arsenic and phosphorus similarly, even though their absolute

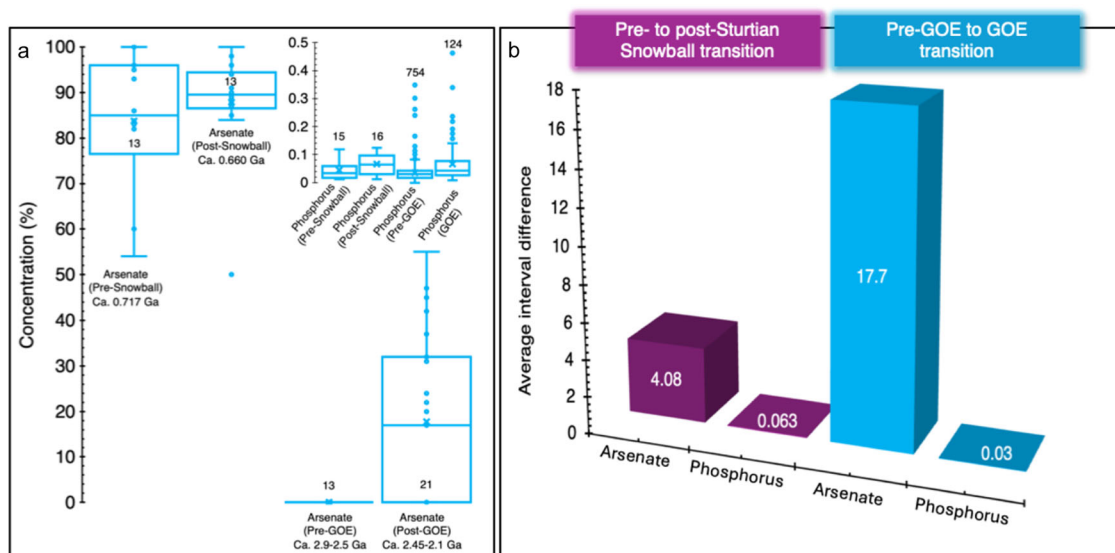


Fig. 3 | Arsenate (AsO_4^{3-}), bulk phosphorus (P) and arsenic (As) distribution in near-continental marine sedimentary rocks across Earth's history. a Box plot for arsenate and bulk phosphorus distribution in fine-grained near-continental margin sediments. Arsenate concentrations are expressed as weight per cent relative to the total arsenic content of the bulk rock. Phosphorus concentrations are relative to the bulk rock mass. Phosphorus pre-GOE, $n = 754$; Phosphorus GOE, $n = 124$. Phosphorus pre-Snowball, $n = 15$. Phosphorus post-Snowball, $n = 16$. Arsenate pre-GOE, $n = 13$. Arsenate post-GOE, $n = 21$. Arsenate pre-Snowball, $n = 13$. Arsenate post-Snowball, $n = 13$. **b** A bar graph showing the average proportional change in bulk

sedimentary phosphorus and arsenate content from pre-GOE (~3.46–2.5 Ga) to GOE (~2.45–2.1 Ga), calculated as (GOE) – (pre-GOE), and from pre-Snowball (PSB) to the immediate post-Snowball (IPSB), ~0.720–660 Ga intervals, calculated as (IPSB) – (PSB). For the box plot, individual points represent the underlying observations. The center line indicates the median. The × symbol represents the mean. The lower and upper edges of the box represent the first (25th percentile) and third (75th percentile) quartiles, respectively, with the box spanning the interquartile range (IQR). Whiskers extend to the smallest and largest values within $1.5 \times \text{IQR}$ of the lower and upper quartiles. Values beyond the whiskers are plotted as outliers.

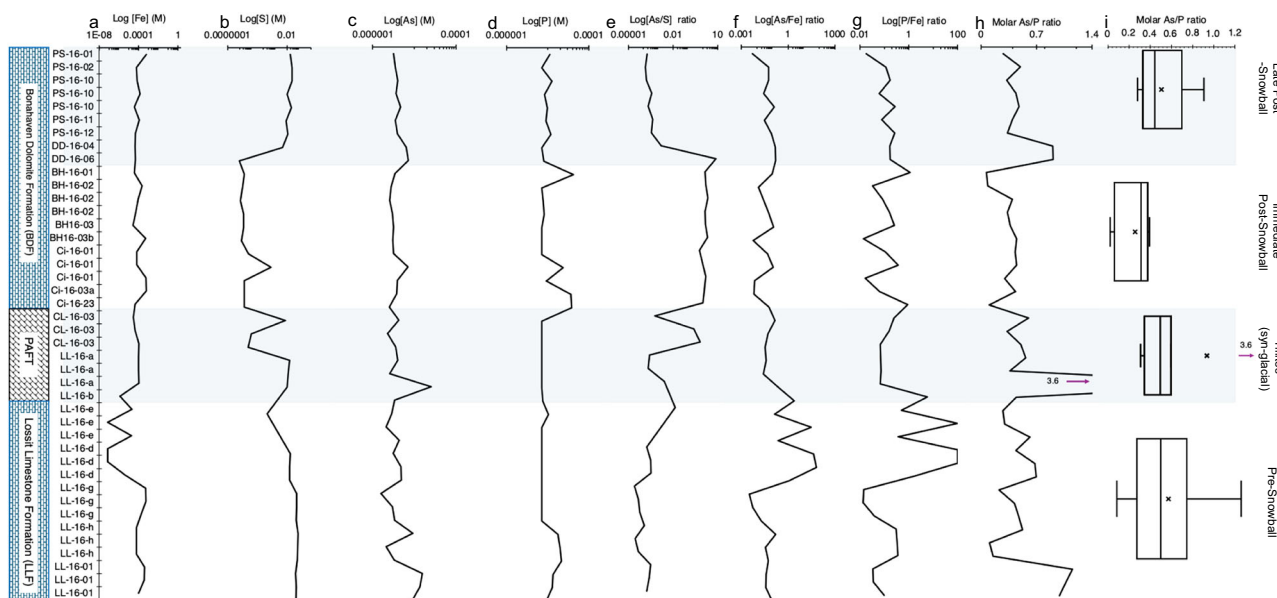


Fig. 4 | Relationship among molar iron (Fe), sulfur (S), arsenic (As) and phosphorus (P) across the studied section in iron oxide acid-leachates. a–d Molar As, P and Fe concentrations in total iron oxide leachates. **e–i** Molar As/S, As/Fe, P/Fe and As/P ratios in total Fe oxide leachates across the anoxic pre-Snowball ($n = 15$), anoxic syn-glacial tillites ($n = 7$), oxic immediate post-glacial ($n = 11$) and anoxic late post-Snowball ($n = 9$) deposits. For the box plot, individual points represent the

underlying observations. The center line indicates the median. The × symbol represents the mean. The lower and upper edges of the box represent the first (25th percentile) and third (75th percentile) quartiles, respectively, with the box spanning the interquartile range (IQR). Whiskers extend to the smallest and largest values within $1.5 \times \text{IQR}$ of the lower and upper quartiles. Values beyond the whiskers are plotted as outliers.

concentrations may have varied independently. Moreover, a lack of correlation between arsenic and phosphorus suggests their source supply to seawater was not directly coupled (Fig. S6b), similar to observations in present-day near-continental margin settings²⁸. In the modern ocean, arsenic is often derived from marine sources such as hydrothermal fluids

and regeneration²⁸, while, in addition, significant phosphorus supply to seawater originates from continental weathering²⁹.

The corresponding composite molar As/P ratios, which broadly track the As/Fe and P/Fe trends, decrease systematically from the pre-Snowball to the post-Snowball succession. They exceed unity in the anoxic pre-/syn-

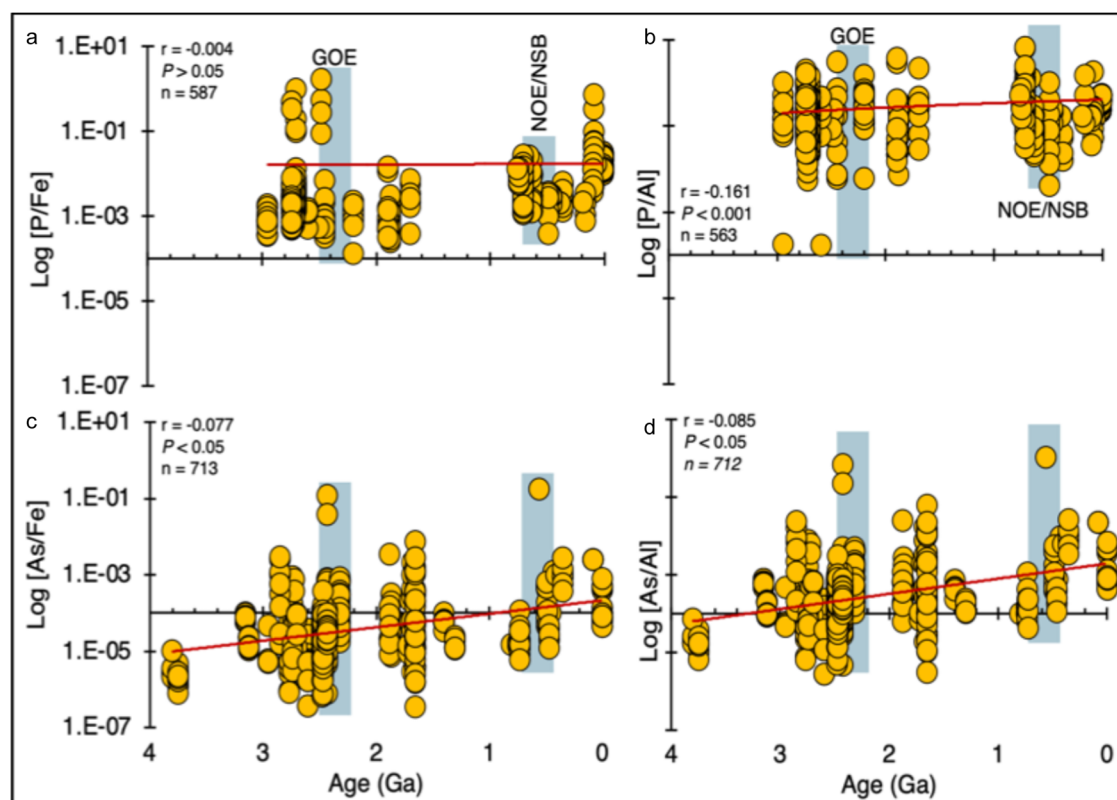


Fig. 5 | Distribution of P and As in iron formations (IFs) and near-continent-margin siliciclastic sedimentary (FNMS) rocks formed across Earth history in relation to Fe and Al content. a P/Fe ratios in FNMS deposits ($n = 587$, $p > 0.05$). **b** P/Al ratios in marine iron formations (IFs) formed throughout Earth's history ($n = 563$, $p < 0.001$). **c** As/Fe ratios in IFs ($n = 713$, $p < 0.05$). **d** As/Al ratios in IFs

($n = 712$, $p < 0.05$). Correlation was assessed using a two-sided t -test; no adjustment for multiple comparisons was applied. Across GOE, phosphorus and arsenic speciation XANES data are described in refs. 4,21, respectively. Bulk IF and fine-grained siliciclastic sedimentary rock arsenic and phosphorus data are adapted from refs. 4,27,42.

glacial deposits, with the highest ratios observed within the tillites (Fig. 4h, i). The lowest values coincide with the oxygenation event in the immediate post-Snowball sequence. Although they increase in the anoxic late post-Snowball interval (approaching unity), they do not return to the elevated ratios that characterized the pre-Snowball and tillite successions (Fig. 4h, i). Compared to iron oxides, sheet silicate ratios are persistently low and show no variability across all intervals (Fig. S5), consistent with a previously suggested strong detrital contribution to sedimentary phosphorus content across the basin²¹.

Compiled arsenic, phosphorus, iron and aluminum data from marine iron formations (IFs) and near-continent margin siliciclastic deposits spanning Earth's history reveal that secular variations in As/Fe and P/Fe ratios preserved in iron oxides are a characteristic feature of the marine sedimentary record (Fig. 5 and Table S3). Most notably, As/Fe and P/Fe ratios in marine IFs increase progressively through geological time, indicating a fundamental co-secular shift in the marine arsenic and phosphorus cycles and their interaction with iron deposition.

Implications for redox evolution of the biological arsenic cycle

Distinguishing between long-term secular oxygenation trends and shorter-lived oxygenation events is important. Our study investigates how major Proterozoic oxygenation intervals influenced marine arsenic speciation and, by extension, arsenate-to-phosphate ratios. The temporal framework spans the two principal Precambrian oxygenation transitions represented in our dataset—the GOE and the NOE^{1,2}. The GOE fundamentally transformed marine arsenic speciation through widespread oxidation of reduced arsenic species to arsenate⁴, permanently altering the biology of the global arsenic cycle⁵. During the succeeding Mesoproterozoic, oxygen concentrations remained substantially lower than today but sufficiently elevated to maintain persistent, although fluctuating, oxygenation in shallow marine

environments², where phytoplankton would have been exposed to continuous arsenate stress, similar to modern oxygenated oceanic surface water settings¹⁶. The NOE represents a second prolonged interval of increasing oxygenation beginning ~850 Ma and extending through the Cryogenian into the Ediacaran—characterized by substantial fluctuations in ocean redox rather than a single discrete oxygenation event².

The Sturtian Snowball Earth represents one interval within this broader Neoproterozoic oxygenation trajectory, characterized by oscillatory anoxic-oxic-anoxic cycles, coupled to global climate change. Our interpretation does not depend on oxygenation beginning during the Sturtian, nor does it require a single post-glacial oxygenation pulse to generate long-term changes in marine arsenic cycling. Rather, the Sturtian interval forms part of the evolving oxygenation state associated with the NOE, during which repeated changes in marine redox conditions would be expected to influence arsenic speciation. While these changes extend the temporal framework over which arsenic speciation may have evolved, it does not change the underlying mechanistic relationship between oxygenation, arsenate production and phosphate acquisition explored in this study.

Thus, while a transient post-glacial oxygenation event alone may not have produced a persistent biological response or permanently altered marine phosphorus cycling on its own, our data suggest that major changes in marine oxygenation were accompanied by major changes in marine arsenic speciation, similar to modern observations. Building upon the well-established physiology of arsenate-phosphate interaction across present-day redox gradients^{6–10}, we propose that Precambrian redox fluctuations would have similarly altered environmental arsenate-to-phosphate ratios and therefore influenced the energetic cost of biological phosphate acquisition and that this cost first increased during the GOE. We encounter a reversal within the NOE interval linked to the Cryogenian Sturtian Snowball supply of phosphate to seawater. This interval is unique because eukaryotic algae

are proposed to have proliferated at this time¹² and subsequently animals evolved. This physiological basis of our hypothesis is extensively documented in modern organisms and forms the mechanistic framework for our interpretation. Our study therefore establishes this previously unexplored connection rather than demonstrating direct biological causality over geological timescales. It constrains the redox evolution of the marine arsenic cycle, while the biological implications are interpreted through well-established physiological principles rather than inferred directly from the geological record.

The shift in arsenic speciation indicates that redox was crucial in controlling its speciation and distribution during this critical interval. For example, the coincidence of arsenate preservation in the immediate post-glacial rocks with an episode of full seawater column oxygenation and reduced arsenic species in the anoxic tillites is likely related to limited availability of arsenite oxidants like O_2 and nitrate during the syn-glacial phase. These observations align with a broader narrative on rising O_2 levels across the GOE and a change in sedimentary arsenic speciation⁴. Reduced arsenic species were likely dominant in the anoxic, sulfate-poor Neoproterozoic oceans⁴. However, during the GOE, a notable shift towards the predominance of oxidized arsenic species (arsenate) and reduced arsenic sulfides characterized marine sedimentary rocks⁴. A similar oxygenation shift is recorded following the transition from anoxic pre-Snowball and Snowball icehouse state to oxygenated greenhouse seawater conditions²². However, unlike the GOE transition that was marked by the deposition of both arsenate and arsenic sulfides⁴—indicative of a redox-stratified water column, the immediate post-Snowball interval contains mainly arsenate (Fig. 2a), suggesting full water column oxygenation and strong seawater oxidizing conditions and the absence of a redoxcline or seawater stratification. This widespread arsenate enrichment pulse, however, progressed into the initial stages of the late post-Snowball, when, according to the iron redox proxy, bottom waters again became anoxic (Fig. 2b).

Although total arsenic can accumulate in anoxic sediments, reducing conditions generally favor the transformation of arsenate to arsenite or arsenic sulfides, limiting long-term arsenate accumulation except where kinetic constraints, mineral associations or localized oxidizing micro-environments stabilize arsenate. This behavior can first be explained by the strong binding affinity of arsenate for iron oxides under oxic conditions²⁵. Then, when these conditions turn anoxic, the iron oxides can be reductively dissolved, releasing adsorbed arsenate into solution, where it can subsequently be reduced microbially to arsenite³⁰ and arsenic sulfides³¹, thereby limiting net arsenate preservation. However, dissolved arsenate concentrations exceeding $\sim 1 \mu M$ (~ 114 times the average concentration of arsenic in the modern ocean) have been shown to inhibit microbial reductive dissolution of iron oxides³⁰. In addition, ferruginous anoxic conditions, like those that prevailed at this time, suppress sulfide-mediated dissolution of iron oxides and widespread formation of arsenic sulfides.

The $1 \mu M$ dissolved arsenate experimental threshold may not be a demonstrated concentration for the Precambrian environments investigated here, and because our data do not directly constrain dissolved seawater or porewater arsenate concentrations, we do not assume this mechanism as definitive evidence for As preservation. However, this threshold presents an experimentally supported mechanism that may help explain the preservation of arsenate throughout the Precambrian oceans. We note that direct comparison of the experimental $1 \mu M$ dissolved arsenate threshold with modern seawater arsenic concentrations is also unlikely to be appropriate for Precambrian oceans. Multiple independent studies suggest that the early Earth experienced substantially higher hydrothermal heat fluxes and enhanced volcanic activity, as demonstrated by widespread ferruginous marine conditions relative to today³². Hydrothermal fluids commonly contain arsenic concentrations several orders of magnitude greater than modern seawater³³. This is in addition to hydrothermal arsenic fluxes likely being considerably larger under Precambrian tectonic conditions. Moreover, because arsenic exhibits a nutrient-type distribution—modulated by biological uptake, regeneration, redox cycling, coupled to adsorption onto iron oxides, hydrothermal inputs and sedimentary remobilization^{26,33,34}—

dissolved arsenate concentrations increase with depth in the fully oxygenated modern ocean³⁴. Collectively, these observations suggest that dissolved arsenic concentrations, and particularly arsenate availability in iron-rich depositional environments, could have differed substantially from those of the iron-poor modern ocean.

Although our XANES data do not allow reconstruction of absolute dissolved arsenate concentrations, they do demonstrate systematic changes in arsenic speciation that closely track major established redox transitions during both the GOE and the NOE intervals. We therefore consider the proposed inhibition of microbial Fe(III) reduction by elevated arsenate concentrations to be one plausible mechanism consistent with these ancient oceans. Further, the experimental threshold refers to dissolved arsenate concentrations in the immediate microbial environment (e.g., sediment porewaters or benthic redox interfaces), where diagenetic microbial iron reduction would have been most prevalent, rather than average open-ocean concentrations. Consequently, comparison with the average modern seawater arsenic concentration may not necessarily be the most appropriate benchmark.

This consideration is particularly relevant for the Precambrian, where hydrothermal fluxes, volcanic activity, ferruginous ocean chemistry, phosphorus availability and marine redox conditions differed fundamentally from those of the modern ocean. Although our data do not constrain absolute dissolved arsenate concentrations, they indicate systematic changes in arsenic speciation across the GOE and NOE interval, consistent with established controls on marine arsenic cycling in the contemporary ocean. Therefore, inhibition of microbial Fe(III) reduction by elevated arsenate concentrations is a plausible mechanistic explanation for the persistence of arsenate in sedimentary deposits in and near immediately oxygenated intervals. Moreover, the deposition and preservation of iron oxides, a well-recognized phenomenon of the Precambrian oceans³², suggest near-quantitative preservation of iron oxides despite widespread anoxia throughout the Precambrian. This would have enhanced arsenate preservation and therefore its detection in Paleoproterozoic and Neoproterozoic sedimentary rocks.

The persistence of arsenate in the late post-Snowball ferruginous anoxic setting may therefore also suggest sustained elevated arsenate concentrations in overlying oxic seawater well beyond the early post-glacial oxygenation event. This observation is consistent with the preservation of arsenate in both the redox-stratified, iron oxide-depositing Paleoproterozoic ocean⁴ and the Neoproterozoic pre-Sturtian ferruginous interval^{21,22} (Fig. 2b), collectively indicating that Proterozoic oceans likely contained substantially higher dissolved arsenic concentrations than modern seawater. Moreover, the recurrence of arsenate preservation across these distinct ferruginous anoxic settings points to a possible and persistently expanded marine arsenic reservoir in Proterozoic oceanic settings over long time scales. Importantly, our interpretation does not require that arsenate remained dissolved and unaltered throughout burial. Rather, the preservation of arsenate likely reflects its continued association with ferric iron-bearing phases and/or stabilization within mineral matrices formed during deposition and early diagenesis. The key observation is that measurable arsenate remains preserved despite conditions that would ordinarily favor reduction. Under these assumptions, the data thus suggest that the continuous enrichment of arsenate in the late-postglacial interval reflects arsenic cycling governed not only by iron redox transformations but also by arsenic concentration, sulfur availability and water-column redox structure.

We note that, except for anoxygenic phototrophic oxidation³⁵ of arsenite to arsenate, microbial processes involved in arsenite oxidation require either the direct or indirect presence of O_2 in the environment. For example, the accumulation of typical microbial electron acceptors used for arsenite oxidation, like nitrate, iron oxides, manganese oxides and sulfate in marine settings, depends largely on the presence of O_2 in the environment^{36–40}. While iron oxides were abundant in the anoxic Archean ocean^{26,40}, and although arsenite was likely more abundant at this time than in Proterozoic seawater⁴, the coupling of arsenite precipitation to the reduction of iron oxides appears to have been low⁴. Moreover, manganese

oxides, nitrate and sulfate only became abundant in seawater following the rise of O₂ in the atmosphere^{36–40}, which conveniently coincides with the widespread rise of arsenate and As sulfides in the ocean⁴.

In our samples, the presence of both oxidized arsenate and reduced Fe–As sulfides in the pre-Snowball Earth succession suggests the possibility of a redox-stratified water column, characterized by arsenate precipitation in oxic surface waters and Fe–As sulfide in anoxic bottom waters (Fig. 2a), similar to the Paleoproterozoic ocean⁴. Microbial oxidation of arsenite, reliant principally on O₂ and the supply of O₂-generated arsenite oxidants like nitrate, Fe oxides, Mn oxides and sulfate from the oxic ocean surface^{36–40}, likely contributed proportionately to the enrichment of arsenate in the deoxygenated bottom waters and sediments. Importantly, the studied samples show little association with hydrothermal activity²¹, suggesting that sulfide was mainly produced by microbial sulfate reduction throughout the sequence. In this situation, microbes can reduce arsenate anaerobically, coupled with sulfate reduction, to produce Fe–As sulfides²¹. Recent studies on arsenite-oxidizing genes suggest that biological oxidation of arsenite to arsenate was likely restricted in Archean seawater despite high arsenite levels and favorable thermodynamics⁴¹. This aligns with geochemical evidence of limited arsenite oxidation⁴. In anoxic Archean settings, electron acceptors, as suggested above, were likely rare or transiently available. Moreover, detoxifying arsenate by reduction to arsenite for expulsion¹³ was likely prioritized over metabolizing arsenite to arsenate for energy gains—akin to strategies seen in modern arsenic-rich hydrothermal environments¹⁸, supported by molecular clock dating of arsenic resistance genes⁵.

The presence of large amounts of arsenate in our Neoproterozoic samples deposited beneath anoxic waters before the Sturtian Snowball Earth glaciations (Fig. 2a) indicates that beginning with the GOE, anaerobic arsenite oxidation likely became more prevalent, consistent with increasing arsenite oxidant sources^{36–40}. In habitats expressing both *ain* (arsenite oxidase) and *arx* (anaerobic arsenite oxidase) genes, such as in redox-stratified Proterozoic seawater, the presence of both gene systems could hypothetically have generated a more dynamic arsenic cycle, where both aerobic and anaerobic arsenite oxidation pathways are available. However, it is not entirely clear which process would dominate or prove more efficient. Regardless, because the *ain* gene supports aerobic arsenite oxidation and the *arx* gene supports anaerobic oxidation, this would allow for substantial arsenite oxidation to arsenate in the redox-stratified, electron acceptor-richer Proterozoic oceanic settings compared to the Archean.

We propose that slower abiotic and more efficient biotic arsenic oxidation and reduction processes, which are overall controlled by O₂ availability, modulate the trends observed in our data. This conclusion is supported by Fe speciation data, considering that the Fe speciation proxy recorded mainly bottom water redox conditions²¹, with uranium isotope systematics in an immediate post-Sturtian Snowball sedimentary unit in Mongolia indicating a widespread oxygenation event²³. This leads us to the supposition that systematic changes in arsenic speciation are consistent with the global seawater redox state and the availability of arsenic oxidants for syngenetic and early diagenetic microbial arsenite oxidation.

The absence of arsenate in the tillites points to persistent and dominant anoxic conditions in the water column during the icehouse, and a dearth of more efficient microbial arsenite oxidants like O₂ and nitrate due to perhaps strong water column deoxygenation. This observation is supported by the hypothesis that the return of globally distributed BIF deposition during the Cryogenian was associated with extensive ocean deoxygenation beneath thick marine ice cover, which suppressed ocean–atmosphere gas exchange, enabled the accumulation of dissolved ferrous iron and BIF precipitation³². The deficiency of reduced arsenic species in the overlying immediate post-Snowball period aligns satisfactorily with complete water column oxygenation²¹ (Fig. 2b)—which, as expected, limits large-scale precipitation of reduced arsenicals from seawater^{17,20,34}. Moreover, the oxygenation and arsenic speciation trends align closely with variations in bulk sedimentary phosphorus profiles (Fig. 2c) and with inferred rising dissolved seawater phosphate concentrations²¹, which are believed to have modulated primary productivity and O₂ production across the studied succession²¹.

Implications for seawater phosphate bioavailability

The end of the Sturtian Snowball Earth glaciation triggered a surge in photosynthetic eukaryotic algae activity on the Neoproterozoic ocean margin¹², believed to have been fueled by elevated seawater phosphate levels that drove a spike in primary productivity and oxygenation^{12,21,23,42}. Previous reports indicate that deglaciation of the Sturtian Icehouse was the source of this excess dissolved phosphate supply to seawater, masterminded by clay minerals^{21,22}, with average post-Snowball near-continental marine sedimentary archives surpassing those observed during the GOE interval^{21,42} by at least fourfold (Fig. 3a). This post-glacial phosphate boost is coupled with the proliferation of marine photosynthetic algae in other post-glacial Sturtian formations¹² and seawater oxygenation²¹. Thus, the cyanobacteria and photosynthetic algae that oxygenated the Paleoproterozoic and Post-Sturtian Snowball ocean likely experienced severe arsenate stress (Fig. 3a).

For such photosynthetic communities to have driven global or local seawater–atmosphere oxygenation, they would have required robust mechanisms to mitigate against arsenate toxicity^{6–10,13}. Modern evidence suggests three plausible adaptive response strategies marine primary producers may have employed to cope with the corresponding upsurge in arsenate stress that began with the GOE: (1) Strong arsenate detoxification using biological pumps to avoid accumulation in biomass¹³. Thus, the emergence of arsenate detoxification genes close to the GOE has been explained by a sudden increase in seawater arsenate content⁴⁵. (2) Low arsenate/phosphate ratios in seawater to reduce competition between arsenate and phosphate^{6–10,14,17} might have influenced phosphate bioavailability, driving the emergence and spread of high-affinity phosphate uptake⁴³. (3) High-affinity phosphate uptake to discriminate against arsenate uptake^{6,13–19}. The Paleoproterozoic origin of low phosphate affinity genes is thought to indicate elevated phosphate concentrations exceeding modern levels of >3 μM⁴³. On the other hand, the evolution of phosphate stress uptake genes in the Paleo-Mesoarchean associated with <1 μM seawater phosphate concentrations, subsequent expansion together with alternate phosphorus cycle genes during the Paleoproterozoic, may have been linked to a shrinking phosphorus reservoir, perhaps due to the expansion of the biosphere after the GOE⁴³.

After considering post-depositional processes such as reductive co-recycling of phosphate and arsenate at the sediment–water interface²⁶, a striking average significant increase in bulk arsenate and phosphorus content of up to ~4.08 and only by ~0.063 folds, respectively, is recorded in the immediate post-Snowball Earth samples relative to pre-Snowball (Fig. 3a, b). Similarly, a muted average phosphorus increase of just ~0.03-fold in fine-grained near-continental margin marine siliciclastic rocks deposited across the pre-GOE–GOE transition coincides with a ~17.7-fold rise in sedimentary arsenate content (Fig. 3b). To evaluate potential seawater dissolved arsenic and phosphorus levels, acid-leachable phosphorus and arsenic bound to Fe oxide sinks²¹, excluding pyrite, which also strongly binds arsenic, point to a broad stepwise decline in dissolved arsenic-to-phosphorus ratios from the pre-Snowball to post-Snowball interval (Fig. 4i). However, competitive adsorption among silica, phosphate and arsenate on Fe-oxide surfaces may influence their partitioning during deposition, as silica can compete with phosphate for sorption sites^{44,45}. However, experimental constraints suggest that such effects in the presence of arsenate might enhance the relative adsorption of phosphate on Fe-oxide in the presence of silica^{46,47}, suggesting the potential for higher dissolved seawater As/P trends. Nevertheless, under these conditions, arsenic and phosphorus levels bound to Fe-oxides remain correlated with dissolved arsenic and phosphorus content^{46,47}, allowing these minerals to capture and preserve ancient seawater trends in the sedimentary rock record^{18,27,48}. Our analysis simulates the widely recognized environmental observation that the dissolution of iron oxides in the sedimentary pile returns As and P to the aqueous phase, fueling biological productivity and, in the case of arsenic, toxicity. By comparing our As/P ratios with those observed in modern seawater, for which the dissolved concentrations of As and P are known, we do not find our As/P ratios to be too dissimilar from those expected in contemporary marine seawater. The molar As/P ratio range, however,

exceeds unity in the pre-Snowball and syn-glacial tillite samples, a threshold known to inhibit biological phosphate uptake, particularly in oligotrophic ocean gyres, where elevated arsenic relative to phosphorus constrains primary production^{7,8,10,14,17,20}. In contrast, such ratios are uncommon in modern near-continental margin waters but are characteristic of shallow submarine hydrothermal systems, where arsenic-rich fluids may promote phosphate limitation¹⁸.

The occurrence of As/P ratios above unity in the pre-Sturtian Snowball and syn-glacial near-margin deposits, but not in the post-Sturtian Snowball interval, suggests that arsenic-rich, phosphorus-poor waters may have been more widespread along continental margins before and during Snowball Earth, compared to the present, and potentially extending back to the Paleoproterozoic⁴. This inference is supported by the elevated As/P ratios in anoxic intervals within the Sturtian succession, where seawater redox stratification would have promoted the mobilization of reduced arsenic species from sediments and hydrothermal sources, followed by oxidation to arsenate across redox interfaces. If analogous processes operated more broadly throughout the Proterozoic, offshore waters may thus have sustained As/P ratios substantially higher than those of the modern ocean gyres. Such a scenario is consistent with independent geochemical evidence for widespread phosphorus-limiting pre-Cryogenian oceans^{21,27,42}. These patterns are consistent with our arsenate and bulk phosphorus data, bulk As/Ti ratios for IFs⁴, and new evidence from As/Al distribution for the same sample set. Together with their corresponding bulk As/Fe, P/Fe and P/Al ratios, and considering that Al is a poorly mobile element (Fig. 5), these trends suggest varying shifts in dissolved seawater arsenic and phosphorus content as a function of Earth's redox history.

The bulk concentration of phosphorus in Pre-GOE versus GOE fine-grained near-continental margin deposits and Pre-GOE versus our Neoproterozoic samples show no significant differences (Fig. 3a). However, the phosphorus levels in the GOE and Neoproterozoic samples are significantly different ($p < 0.05$). Despite the persistently high bulk phosphorus content in the tillites and post-Snowball intervals²¹ (Fig. 2d), no statistically significant difference was found for the average rock content of phosphorus deposited between the three Neoproterozoic climatic intervals investigated (pre-Snowball, syn-glacial and post-Snowball). This revelation suggests that it is the continuous and long-term delivery of elevated phosphorus to seawater, rather than the comparable but short-term spikes recorded in the anoxic pre-Snowball rocks (Fig. 2c), that drove post-Sturtian Snowball seawater oxygenation²¹ (Fig. 2b).

The significant change in the P/Al, As/Fe and As/Al ratios preserved in IFs deposited across Earth history, but less so for P/Fe (Fig. 5), is consistent with a variable and gradual increase in the delivery of phosphorus and arsenic to seawater by oxidative weathering through time^{4,21,42}. This is in addition to hydrothermal emissions contributing considerable amounts of arsenic to seawater^{4,18,33}, while at the same time acting as a phosphorus sink⁴⁸. The notable lack of a comparable trend between P/Fe and P/Al ratios likely reflects the fact that a substantial amount of Fe and P in IFs may be associated with Fe silicates, such as greenalite⁸, with no evidence available for arsenic species, which exists in different stable oxidation states under various redox conditions, unlike phosphorus. Combined with biological, organic matter and Fe cycling²⁹, these factors likely underpinned long-term seawater arsenic and phosphorus dynamics with changing ocean redox. Although absolute seawater arsenic and phosphorus concentrations cannot be recovered directly from iron oxides due to potential diagenetic modification, their relative As/P proportions are expected to retain first-order information about temporal changes in dissolved seawater As/P ratios. This is because the scavenging behavior of P, like that of As, by iron oxides reflects changing ambient seawater reservoir proportions and preserves the relative variations through time, despite some diagenetic loss^{26,27,48}.

Empirical support for this assumption is provided by modern marine hydrothermal iron oxyhydroxides, where burial diagenesis may remove up to ~50% of initially adsorbed P⁴⁸. Yet, the relative stratigraphic variations remain coupled to dissolved seawater trends, forming the basis on which iron oxides are used to reconstruct temporal marine P content through

Earth's history^{27,44,45,49}. Importantly, the entire studied succession experienced comparable post-depositional histories, with metamorphism limited to greenschist facies. As such, post-depositional processes cannot readily explain the pronounced and systematic post-Snowball decline in As/P ratios. If post-depositional alteration were the dominant control, one would expect a homogenization of As/P ratios through time, rather than the distinct stratigraphic trend observed. Moreover, it was proposed that the iron oxides contained in the studied samples formed predominantly in the water column²¹. By mass balancing the quantity of bulk iron oxide deposited across the distinct Pre-Snowball, syn-glacial and post-Snowball sequences—and considering stratigraphic redox changes—it was further suggested that diagenesis and metamorphism exerted a negligible control on quantitative sedimentary iron oxide content and phosphorus cycling²¹.

Implications for adaptive ecosystem evolution and phosphate metabolism

Seawater As/P ratio is mathematically determined by changes in both arsenate and phosphate concentrations, particularly in marine oxygenated environments where arsenate is the dominant dissolved arsenic species^{50,51}. However, while the seawater ratio reflects changes in both components, the physiological response is driven by arsenate because it competes directly with phosphate for cellular uptake⁶. This distinction forms the mechanistic basis of our study, particularly because evolving dissolved seawater arsenate distributions likely influenced phosphorus acquisition during a critical interval in Earth's history when life was adapting to increasingly oxygenated oceans. Phosphate is an essential nutrient, whereas arsenate is a structural analog of phosphate⁶. Because of their similar chemical structures, phosphate transport proteins cannot effectively distinguish between the two molecules. Consequently, at intervals when seawater arsenate-to-phosphate ratio likely increased, particularly during the GOE and NOE as demonstrated by our data, so too was the likelihood that cells increasingly imported more arsenate instead of phosphate⁶. Conversely, lower arsenate oceans would have reduced this competition, which directly links seawater As/P ratios to biological productivity^{6–10}.

Because the biological consequences of As/P ratios depend on arsenic speciation, under anoxic conditions, dissolved arsenic is dominated by arsenite, which is not efficiently transported by phosphate uptake systems. Consequently, in anoxic ecosystems, even relatively high total arsenic concentrations may exert only a limited influence on phosphate acquisition. In contrast, in oxygenated environments dominated by arsenate, the arsenic species that directly competes with phosphate for cellular uptake makes phosphorus acquisition increasingly difficult at the same environmental phosphate concentration as arsenate concentrations increase, because cells must discriminate between two chemically similar molecules⁶. The consequence is not necessarily lower phosphate availability in the environment, but a reduction in the efficiency with which organisms acquire and utilize phosphate.

Once transported into the cell, arsenate substitutes for phosphate in numerous biochemical reactions but forms unstable arsenate esters that rapidly hydrolyze⁶. This disrupts ATP generation and phosphorus metabolism, creating metabolic stress. To minimize arsenate uptake, microorganisms induce high-affinity phosphate acquisition systems^{6–10} (the Pho regulon/Pst transport system), which discriminate more effectively between phosphate and arsenate than constitutive low-affinity transporters^{6,43}. Although this adaptation reduces arsenate toxicity, it comes at an increased energetic cost because maintaining and operating these systems requires additional cellular resources. Consequently, increasing environmental arsenate content does not simply alter the As/P ratio; it fundamentally changes the energetic cost of phosphorus acquisition.

Phosphate stress in the nutrient-limiting modern ocean gyres is characterized by high dissolved arsenic-to-phosphorus ratios exceeding unity, corresponding to seawater arsenic and phosphorus contents of ~10–20 nmol L⁻¹ and ~0.2–10 nmol L⁻¹, respectively²⁰. Consequently, ocean gyre primary producers rely on high-affinity discrimination of arsenate to acquire sparse phosphate from seawater^{14,17}, resulting in much

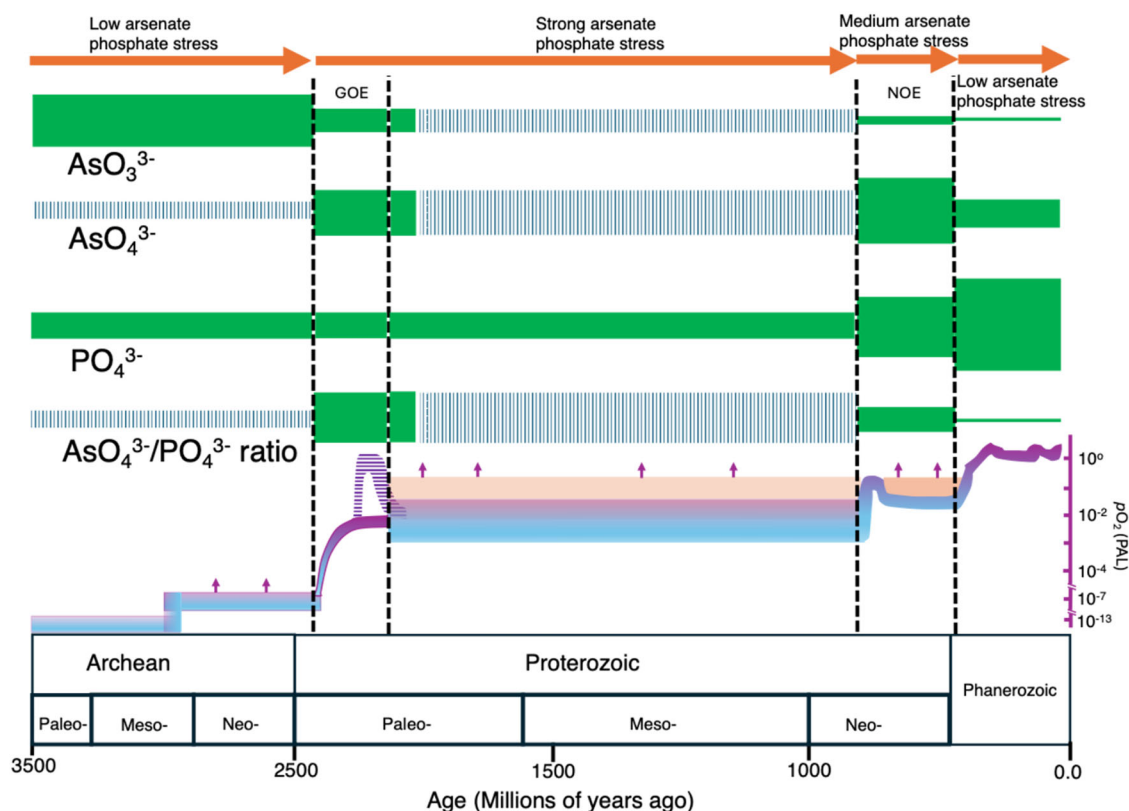


Fig. 6 | A proposed conceptual model showing the evolution of seawater arsenite, arsenate and phosphate through Earth's history, superimposed on a model of atmospheric oxygen evolution adapted from ref. 2. Bars indicate conceptualized

changes in the reservoir size of each variable. Dashed lines indicate intervals with considerable uncertainty in the proposed trends. PAL present-day atmospheric levels.

lower photosynthetic rates than those observed in continental margin settings^{17,20,28,34,52}. This is because continental margins receive substantial phosphorus from riverine inputs, sediment regeneration and benthic fluxes, lowering dissolved arsenic-to-phosphorus ratios despite similar dissolved arsenic concentrations^{28,52}. Intuitively, because such conditions would have been more widespread and even more intense in the phosphorus-deficient Proterozoic oceans, a considerable portion of life in the marine realm likely faced far greater arsenate stress than in the present-day ocean, especially further away from the continental margins, where arsenic concentrations exceed phosphorus²⁸.

At the same time, adaptive responses imply that over time marine organisms likely adapted to assimilate and metabolize phosphate more efficiently following the GOE rise in seawater arsenate content (Fig. 3a). This long-term conditioning would have minimized the initial shock when life first encountered the high seawater arsenate-to-phosphate levels in the GOE ocean, for example, through the systematic acquisition and spread of high-affinity discrimination of arsenate⁶ that evolved earlier in the Archean Ocean⁴³. The more favorable post-Sturtian Snowball lower As/P ratios, together with biological adaptation to arsenate stress, may therefore have contributed to the expansion of marine eukaryotic phytoplankton along seawater margins at this time¹² and the observed wave of seawater oxygenation²¹, further transforming ocean biogeochemistry. A drop in bulk phosphorus content (Fig. 2c) and dissolved seawater phosphate concentrations²¹ accompanies the return to anoxic bottom waters in the overlying later post-Snowball succession (Fig. 2b). The range of As/P ratios recorded in iron oxides increased slightly at this time, approaching unity, but remained below the higher levels that may have characterized parts of the pre-pleglacial and syn-glacial ocean margin. The persistence of such lower arsenic-to-phosphorus ratios at this time (Fig. 4i), coincident with a return to seawater anoxia, may have been due to dissolved seawater phosphate insufficiency, supported by the decline in bulk sedimentary phosphorus content (Fig. 2c).

As stated before, low seawater arsenate-to-phosphate ratios are crucial for primary producers dependent on continuous arsenate detoxification and high-affinity phosphate uptake to access low phosphate levels in today's O₂-rich biosphere^{6–10,13–20}. Modern aerobic microbes have adapted to this challenge by placing the *aio* gene for aerobic arsenite oxidation to arsenate on the same operon as high-affinity phosphate uptake genes¹⁵. This arrangement implies that biological arsenite oxidation is often paired with the upregulation of high-affinity discrimination of arsenate to circumvent phosphate starvation in oxygenated environments^{6,15}. On the other hand, the anaerobic arsenite *arx* gene operon is not associated with high-affinity arsenate-discriminating genes⁵³. Although it is still unclear how these genes co-evolved, in moderate phosphate-rich Archean oceans, arsenite oxidation to arsenate would have posed a substantial, even lethal, threat to early life—including on anoxygenic phototrophic arsenite oxidizers—due to the interference of arsenate with biological phosphate utilization^{6–10} in the absence of robust high-affinity phosphate uptake systems. However, the evidence shows that seawater arsenate content was low. Thus, since phosphate modulates primary production over geological timescales⁴², a rise in Proterozoic seawater arsenate content likely helped shape the pace of biological evolution. Studying this interplay between seawater arsenate and phosphate availability and co-evolution with arsenic and phosphorus cycling genes could help explain how life adapted to emergent, potent, oxidized chemical stressors and the over two-billion-year delay in fully oxygenating the ocean-atmosphere system after the GOE.

A conceptual model for seawater arsenate phosphate dynamics through Earth history

Drawing on the history of the marine phosphate reservoir^{21,29,42,44,45,48,49,54–59}, linkages to atmospheric oxygenation^{1–3} and evolving seawater arsenic content^{4,60}, we propose a conceptual model describing how seawater arsenate-phosphate balance and speciation may have changed over time (Fig. 6). Despite the thermodynamic suggestion of high Archean seawater

arsenite concentration, the low oxidant power of seawater at this time likely kept dissolved marine arsenate content low⁴, while seawater phosphate content may have been relatively unlimited^{54,55} for the size of the biosphere at this time, coupled to Archean emergence of high-affinity phosphate uptake⁴³. Averagely higher arsenate levels in Proterozoic seawater dropped significantly into the Phanerozoic era (based on observations in the modern ocean) as increasing ocean-atmosphere oxygenation depleted Earth's surface arsenic reservoirs, for example, through intense O₂-driven weathering of sulfide arsenic-rich minerals on land^{4,61}, combined with declining marine hydrothermal activity. This proposition aligns with rising seawater sulfate levels beginning around the GOE and onwards due to increasing oxidative weathering of a vast continental sulfide reservoir by oxygen^{36,37}. Moreover, widespread ocean-atmosphere oxygenation would have limited the buildup of arsenite in seawater. This allowed arsenate levels to decrease relative to phosphate, which continued to enter the oceans mainly from the weathering of continental rocks^{21,41,62}.

Given that primary production (P) depends on dissolved phosphate availability^{29,42,44,45,47,49,54–59} (P_a), the effective rate of primary production ($\frac{dP_{(eff)}}{dt}$) can be conceptualized as a first-order conceptual framework describing the combined effects of dissolved phosphate availability (P_a) and phosphate uptake through cell membrane phosphate transporters (P_t) into biomass. This can be expressed as the sum of effective bioavailable phosphate ($P_{a,eff}$) and the effective phosphate uptake through membrane phosphate transporters into biomass ($P_{t,eff}$):

$$\frac{dP_{(eff)}}{dt} = P_{(a,eff)} + P_{(t,eff)} \quad (1)$$

If the rate of phosphate uptake into biomass is influenced by dissolved arsenate availability (A_a) and competition between arsenate and phosphate for uptake through phosphate transporters (A_t), then:

$$P_{(a,eff)} = P_a \cdot f(A_a)$$

$$P_{(t,eff)} = P_t \cdot g(A_t)$$

Where: $P_{(a,eff)}$ represents the effective phosphate bioavailability after accounting for competitive inhibition by dissolved arsenate.

$P_{(t,eff)}$ represents the effective phosphate transport into biomass after accounting for arsenate competition for phosphate transporters.

f and g are inhibitory functions (not specified) and are dimensionless modifiers.

All functions are conceptual and not parameterized.

Substituting these into Eq. (1) gives:

$$\frac{dP_{(eff)}}{dt} = (P_a \cdot f(A_a)) + (P_t \cdot g(A_t)) \quad (2)$$

Note: This formulation is intended as a conceptual framework rather than a parameterized kinetic model. All variables are defined with compatible dimensions. The expression is therefore dimensionally consistent.

Equation (2) implies that in low-phosphate, high-arsenate environments, more arsenate than phosphate passively enters the cell through low-affinity phosphate transporters⁶, affecting photosynthesis and oxygen production rates^{7–10,13–19}. But as indicated previously, when high-affinity phosphate transporters are active, cells can effectively discriminate against arsenate uptake by up to 4500-fold⁶. Thus, in the Paleoproterozoic and Mesoproterozoic surface oceans, where low-phosphate high-arsenate conditions likely prevailed, arsenate toxicity became a stumbling block to efficient primary productivity. Even with high-affinity phosphate uptake, competitive interference of arsenate with phosphate metabolism is energetically costly, reducing rates of photosynthesis. In contrast, after the Sturtian Snowball Earth glaciation, lower seawater arsenate-to-phosphate ratios meant cells faced less arsenate stress and could access phosphate more

readily and at a lower energy cost. This shift allowed primary producers to increase rates of photosynthesis and oxygen production, resulting in the acceleration of ocean-atmosphere oxygenation.

Conclusions

Our results suggest that the rise of atmospheric oxygen and the accompanying expansion of oxidized arsenic species in seawater introduced a previously underappreciated ecological constraint on marine primary producers. Elevated arsenate relative to phosphate may have impaired phosphate acquisition, thereby limiting biological phosphate cycling, marine productivity and, potentially, the pace of biospheric expansion following the GOE. This constraint may have diminished after the Sturtian Snowball Earth, when multiple lines of evidence indicate substantial expansion of the marine phosphate reservoir, reducing arsenate-to-phosphate ratios in continental-margin waters. We therefore propose that before the Neoproterozoic Snowball Earth glaciations, continental-margin environments, and potentially much of that which characterized the phosphate-depleted Paleoproterozoic and Mesoproterozoic ocean margin, were marked by substantially higher arsenate-to-phosphate ratios than those of the modern marine margins. Post-glacial phosphate enrichment would have reduced competition between arsenate and phosphate during biological uptake. Together with the earlier evolution of arsenate resistance mechanisms, this shift may have buffered marine ecosystems against the increasing arsenate burden associated with progressive ocean oxygenation. Increased phosphate bioavailability may, in turn, have enhanced nutrient acquisition by marine phytoplankton, facilitating their ecological expansion and diversification within increasingly oxygenated Neoproterozoic oceans. Declining arsenate–phosphate competition was probably one of several interacting environmental changes that collectively promoted the ecological success of eukaryotic phytoplankton following Snowball Earth.

Methods

X-ray Absorption Near Edge Structure (XANES) analysis was conducted at the Nanoscopy beamline, Synchrotron Soleil⁶³, France, on powdered samples, using a Si(111) double crystal monochromator and a 2 × 2 mm unfocused X-ray beam, as previously described^{4,24}. Samples were scanned around the As K-edge (11.862–11.897 keV) in 0.25 eV steps. Common sedimentary reference mineral standards with known oxidation states—specifically, FeAsS (arsenopyrite), FeAs₂ (lollingite), As₄S₄ (pararealgar), As₂S₃ (orpiment), As₂O₃ (arsenite), As₂O₅ (arsenate) and Cu₃AsS₄ (enargite)—were measured regularly to ensure energy stability. To enable the measurement of trace arsenic content, XANES data were acquired in X-ray fluorescence (XRF) mode, and the spectra were recorded using a KETEK Si drift diode detector (SDD) with a 50 mm² active surface. The XRF background peak was subtracted by processing in the PyMCA software⁶⁴. Multiple XANES scans ($n = 46$) for ~5 min each were conducted per sample, with the lack of spectral changes in the XANES features used to rule out photo-oxidation and reduction of arsenic during measurements. The sum of the XANES spectra for each sample measurement series produced high signal-to-low-noise ratio spectra for quantitative data fitting by the ATHENA software⁶⁵. The XANES spectra exhibited 11.8695–11.8705 keV peaks for arsenopyrite/lollingite or pararealgar/orpiment and ~11.875 keV for arsenate species, respectively. The absence of an 11.8719 keV peak indicated no detectable arsenite or enargite species, so these were excluded from the linear combination fitting (LCF) quantitative analysis. Similar signals for arsenopyrite/lollingite and pararealgar/orpiment led to a ~20% uncertainty in their relative proportions and a ± 10% accuracy for arsenate-to-total arsenic ratios. Less than 5% arsenic, if any, occurred as arsenite or enargite in the studied samples. Acid-leachable elemental concentrations associated with putative iron mineral phases were measured as described in ref. 21. This analysis ensured that As/P ratios were derived mainly from a ferric iron-targeted extraction rather than bulk-rock measurements, that comparative datasets are linked through a common ferric iron host phase, and that the principal conclusions are based on redox-controlled arsenic speciation dynamics rather than lithological differences among the sampled

units. The phosphorus data were published previously²¹, whereas the corresponding arsenic data are reported here for the first time. Bulk rock phosphorus and Paleoproterozoic arsenic XANES data were compiled from Refs. 4,21,27,42, while the iron speciation data come from ref. 21.

Data availability

Data supporting the findings of this study are available in the Supplementary Information and from Figshare at <https://doi.org/10.6084/m9.figshare.28357313>. The Figshare dataset contains elemental data for BIFs and near-continental-margin sediments, bulk P₂O₅ concentrations from the Neoproterozoic succession, and iron-speciation data. Arsenic-speciation data and key elemental concentrations of the iron-oxide leachates are provided in Supplementary Tables S1 and S2.

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Author contributions

E.C.F. designed research; E.C.F., A.E.B., A.S., and K.M. conducted research; E.C.F. collected samples; E.C.F., A.E.B., J.A., and C.R. analyzed data. E.C.F. wrote the paper with significant contributions from co-authors.

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Competing interests

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Additional information

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