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Perspective

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Biogeochemistry of Earth before exoenzymes

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Microorganisms that transform and oxidize organic material (that is, heterotrophs) play a fundamental role in the geochemical cycling of key elements in the ocean. Through their growth and activity, heterotrophic microorganisms degrade much of the organic matter produced by phytoplankton in the surface ocean, leading to the regeneration and redistribution of nutrients and carbon back into the water column. However, most organic matter is physically too large to be taken up directly by heterotrophic microorganisms. Consequently, many heterotrophs secrete exoenzymes that break down large molecules outside the cell into smaller substrates that can then be directly taken up by the cell. The complex nature of the biochemical systems that microorganisms use to secrete these enzymes suggests that they were unlikely to have been present in the earliest heterotrophs. In a pre-exoenzyme ocean, heterotrophic microorganisms would only be able to access a small fraction of organic matter such that most dead phytoplankton biomass would have passed directly through the water column and settled onto the seafloor. Here we synthesize existing geobiological evidence to examine the fate of organic matter in the absence of exoenzymes in early oceans. We propose that on an Earth before exoenzymes, organic matter preservation, metal availability and phosphorus recycling would have operated differently than they do on the contemporary Earth.

The ocean is home to complex and diverse microorganisms that have played an intimate role in the evolution and habitability of our planet. The rise and diversification of autotrophic metabolisms such as oxygenic photosynthesis on the early Earth are well studied, but little is known about the other side of the redox ledger: the early evolution of microbial heterotrophy. All biomass consists primarily of large molecules (that is, macromolecules), such as polysaccharides, proteins and lipids[1]. Heterotrophic microorganisms cannot take up these macromolecules directly because membrane pores large enough for those molecules to pass through would allow an unacceptable amount of internal cellular biomass to leak out[2]. Heterotrophs must therefore break down large molecules to less than ~600–1000 Da before uptake into the cytoplasm or forgo metabolizing large molecules altogether. To break down large molecules outside the cell, many heterotrophs secrete degradative enzymes (referred to as exoenzymes).

Because of this fundamental mismatch—most organic matter (OM) is biosynthesized as macromolecules, but heterotrophs take up small molecules—exoenzymes act as gatekeepers for the marine carbon cycle[3]. Exoenzyme activity has been detected in all habitable marine environments, from the water column[3] to the seafloor[4] and deep subsurface[5]. Moreover, laboratory experiments using both natural

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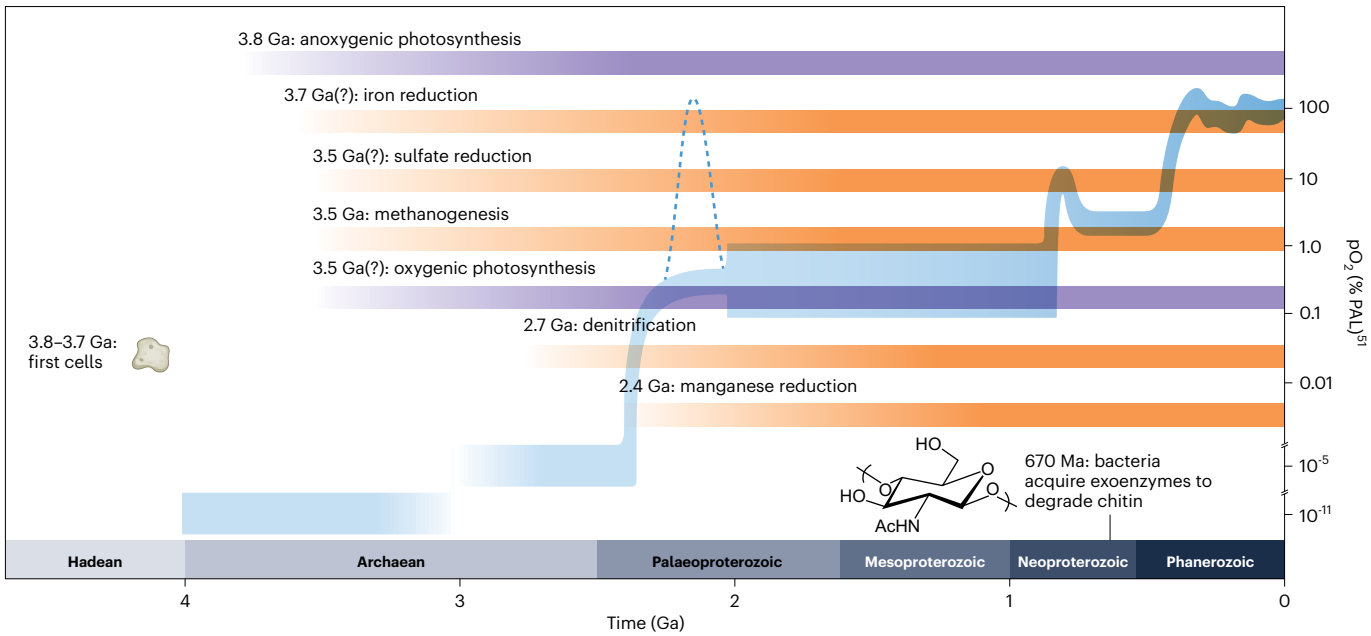

Fig. 1 | Emergence of known heterotrophic and autotrophic metabolic processes in the early oceans that may have given rise to exoenzymes. Heterotrophic metabolic processes are shown in orange and autotrophic metabolic processes in purple. The graded colours reflect the uncertainty in the emergence of these processes. The blue curve depicts the evolution of Earth's atmospheric oxygen levels relative to the present atmospheric level (PAL)[51]. The only exoenzyme whose origin has been dated is chitinase, which appeared in bacteria approximately 670 Ma (ref. 11). The exact timing of the emergence of exoenzymes is therefore unconstrained, although we speculate that the most likely time was during or slightly after the Neoarchaean (2.8–2.5 Ga) as that was a fertile time for the emergence of more complex heterotrophic metabolisms.

bacterioplankton communities[6] and marine isolates[7] have shown that exoenzymes play a key role in the microbial oxidation of OM. As OM constitutes a major reservoir of macronutrients and metals, and because most OM at the Earth's surface is recycled (<0.5% becomes buried and incorporated into sedimentary rocks[8]), exoenzyme activity also substantially influences the fluxes and reservoirs of elements in the ocean.

The dominance of macromolecules in biomass is a fact of life. However, the cellular export systems needed to secrete these enzymes have been shown to be biochemically complex[9]. We propose that it is unlikely that such complexity would have evolved at the same time as the earliest metabolisms, meaning that the earliest heterotrophs were unlikely to be able to metabolize organic macromolecules efficiently. Indeed, the earliest functional proteins, which appeared near the origin of life at approximately 3.7 Gyr ago (Ga) (based on putative evidence from the rock record)[10], would have catalysed more fundamental metabolic processes than extracellular hydrolysis of organic compounds. Yet these proteins themselves would have been macromolecules, meaning that their biosynthesis must have preceded their efficient recycling via exoenzymes. Recent work on the diversification of exoenzymes required to degrade chitin (a complex polymer found in the cell walls of fungi and arthropods) revealed that bacteria acquired these genes roughly 670 Ma (ref. 11) (Fig. 1). This leaves a gap in time of approximately 3 Gyr in which exoenzyme production as we know it now might have arisen. We speculate that exoenzymes may have emerged during, or slightly after, the Neoarchaean (2.8–2.5 Ga) when the rock record shows that heterotrophic life began to diversify and evolve more intricate and complex metabolic processes, for example the reduction of nitrate[12], iron[13] and manganese[14]. It is therefore likely that there was a period in the early history of life during which autotrophs produced macromolecules, but heterotrophs could not efficiently metabolize them. In this Perspective we examine the evidence and likely consequences of that metabolic gap on the biogeochemical evolution of the early oceans.

Enzyme secretion is inherently complex

The past two decades have seen remarkable progress in our understanding of the molecular biology underlying exoenzyme secretion. At present, 11 distinct protein secretion systems have been named, of which 6 were discovered since 2004[9,15]. These systems are diverse, but each is quite complex. For example, the simplest known secretion system is the type Va secretion system, in which proteins act as 'autotransporters' with one part functioning as an enzyme (the 'passenger domain') and another part creating a pore in the cell membrane through which the passenger domain exits the cell[9]. This apparently straightforward mechanism is deceptively complicated. For instance, the timing with which domains of these proteins fold is essential to their function: the pore domain must fold into a torus and be inserted into the membrane to function as a membrane pore, but the passenger domain must remain unfolded until it has passed through the pore, or it will not fit. A host of accessory proteins working in concert are required to ensure that these steps happen in the appropriate order[16]. Other secretion systems are considerably more complex. For instance, the type 2 secretion system, which is frequently used to secrete exoenzymes, involves the coordinated action of more than 12 separate proteins[17].

The microbial ecology of enzyme secretion is similarly complex. Exoenzyme production is metabolically costly and individual cells do not always benefit directly from exoenzyme secretion because the products of extracellular hydrolysis are unlikely to diffuse back to the enzyme-secreting cell[18]. Many enzyme-producing microorganisms therefore adopt strategies to improve the 'economics' of enzyme production. These strategies include quorum-sensing behaviour in which exoenzymes are only produced when groups of enzyme-producing cells surpass a threshold concentration[19] and 'selfish uptake'[20], in which cells directly take up small-molecule products without diffusive loss. These mechanisms require further biochemical complexity to manufacture and sense compounds such as acylated homoserine lactones[21], which mediate coordinated exoenzyme production, or the complex assemblies that are involved in rapidly binding and

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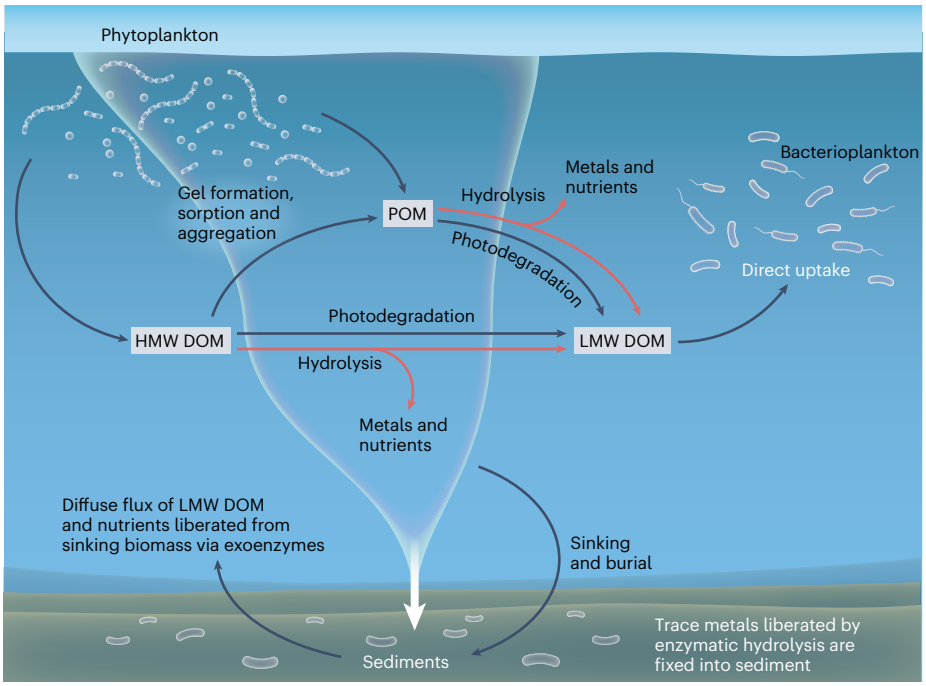

Fig. 2 | Important exoenzyme-mediated, abiotic and biotic processes in the early oceans. Phytoplankton consume and assimilate metals and nutrients into their biomass. Cell death and aggregation convert this biomass into POM. Phytoplankton also release HMW DOM as a by-product of their metabolism. Microorganisms can only access POM and HMW DOM via exoenzymes, releasing carbon, nutrients and metals associated with the biomass. Abiotic processes (such as photodegradation) also break down POM and HMW DOM. Microorganisms in sediments degrade organic material deposited on the seafloor, further liberating carbon, nutrients and trace metals. In a pre-exoenzyme ocean, most of the phytoplankton-derived OM would have passed through the water column and settled onto the seafloor.

transporting hydrolysis products into the cell[22]. Thus, the production of exoenzymes not only requires complex secretion systems, but also relies on biochemical signalling pathways and cooperation among cells.

The importance of exoenzymes to early Earth biogeochemistry

Organic matter

Organic matter is the dominant pool of reduced carbon in marine systems and serves as the primary energy and carbon source for heterotrophic microorganisms. Organic geochemists operationally divide marine OM into particulate (POM, >0.2 µm), high-molecular-weight dissolved (HMW DOM, >1,000 Da) and low-molecular-weight dissolved (LMW DOM, <1,000 Da) fractions. The 1,000 Da cutoff for LMW DOM was historically derived from the size limitations of commercially available ultrafiltration membranes, but this threshold coincides conveniently with the size limitations for molecules that microorganisms can take up directly. In the contemporary ocean, microorganisms can access POM and HMW DOM directly using exoenzymes[20]. In a pre-exoenzyme ocean, heterotrophs would only be able to access LMW DOM and would rely on other processes to access POM and HMW DOM (Fig. 2), such that much of the decaying phytoplankton biomass would have transited the water column and settled onto the seafloor.

We can envision two classes of processes by which early heterotrophs could utilize POM and HMW DOM in the absence of exoenzymes. First, abiotic photochemical processes can liberate LMW DOM from HMW DOM and POM. For instance, in the modern ocean, photochemical reactions (photodegradation) release highly bioavailable organic acids such as pyruvate and glyoxylate from HMW DOM and POM at rates of tens of nanomoles per litre of seawater per hour[23]. Second, it has been hypothesized that a fraction of exoenzymatic activity observed in the ocean reflects cytoplasmic (intracellular) enzymes released via cell lysis[24]. However, these cytoplasmic enzymes are not optimized for activity in seawater, in which substrate concentrations, ion concentrations and pH differ from cell cytoplasm, and there is no reason to believe that such 'accidental' exoenzymes were more effective in the Archaean ocean than they are today. The fact that OM cycling appears to be mediated primarily by secreted exoenzymes in the contemporary oceans implies that OM recycling efficiency was lower in their absence.

OM that is not metabolized rapidly is more likely to be preserved through aggregation. For example, HMW DOM can convert abiotically to POM through the formation of sticky polymer gels, enhancing burial by producing the nuclei around which microscopic particles aggregate into sinking marine snow[25]. This scenario is consistent with recent modelling showing that net primary productivity was much lower on the early Earth than at present but carbon burial efficiency was higher[26]. An increase in carbon preservation efficiency offsetting a decrease in net primary productivity could explain why the secular variation of carbon isotopes in marine carbonates, which reflects changes in the ratio of organic to inorganic carbon removed from the ocean during burial in sediments, has remained relatively constant through time[27]. One consequence of more efficient carbon burial is that the elemental inventory of the phytoplankton biomass is not solubilized and returned to seawater, thus potentially explaining lower overall net primary productivity at that time[28].

Trace metals

All organisms require trace metals to carry out essential cellular functions—namely to act as structural and reactive centres in enzymes[29]. Therefore, the emergence or expansion of certain metabolisms hinged on the availability and abundance of trace metals (for example, Fe, Mn, Zn and Cu) in the ancient oceans[29].

Trace metals are taken up by phytoplankton in the surface ocean and assimilated into biomass. In the modern ocean, most of these assimilated metals are recycled and returned to the water column via microbial degradation of sinking biomass. The vertical profiles of

bioessential trace metals thus characteristically exhibit low concentrations in surface waters but enhanced concentrations in deeper waters as particles of sinking biomass are broken down by heterotrophic microorganisms[30]. Trace metals associated with biomass are typically found within large proteins (that is, metalloenzymes), which require exoenzymes to be assimilated by heterotrophs.

On the early Earth, and in the absence of exoenzymes, metal-bearing compounds associated with dead biomass would be largely inaccessible to heterotrophic microorganisms and transported directly to the seafloor. The efficient burial of these compounds would have greatly reduced the recycling of these critical metals into the water column, thereby limiting their availability for further phytoplankton growth. Burial of these trace metals in marine sediments would have removed them from the Earth's habitable shell until igneous or tectonic processes eventually returned them to the surface. Given that the bioavailability of trace metals on the early Earth probably had a direct bearing on the formation of metalloenzymes (that is, the bioinorganic bridge proposed by Anbar and Knoll[31]), the trajectory of microbial evolution may have been influenced by the limited decomposition of OM. How might evolution have proceeded if trace metal availability in ancient seawater was different; that is, would the formation of different metalloenzymes have led to different microbial metabolisms? Although some metalloenzymes can use different metals for their cofactor, and thus one could argue that the metabolic evolution was insensitive to the availability of specific metals[32], other metalloenzymes have specific metal requirements, such as nickel for methyl-coenzyme M reductase, which plays an important role in the formation of methane by methanogenic archaea.

Exoenzymes exert a secondary influence on trace metal cycling through the generation of organic molecules (ligands) that interact and stabilize trace metals by complexation reactions. A significant fraction of trace metals in the modern ocean are bound to organic ligands[33]. Therefore, organic ligands are a key control on the biogeochemical cycling of trace metals in the ocean today[34] and probably have been since life evolved[35]. Seawater has a mixture of organic ligands that differ in their binding affinities. Strong binding ligands are secreted by microorganisms to scavenge essential metals such as iron (for example, siderophores), whereas weaker ligands include common biomolecules produced through the activity of exoenzymes or cell lysis that have surface functional groups (for example, carboxyl, phosphate, amine) that can form complexes with metals in seawater[36,37]. For example, oligopeptides and amino acids, both products of extracellular peptidases, can act as organic ligands for Mn, Mo, Se and Zn[38]. The emergence of exoenzymes would therefore have generated binding sites for trace metals, leading to their complexation with organic molecules.

Phosphorus

Phosphorus (P) is essential for all organisms and is thought to have limited primary productivity in various stages of Earth history[39]. Phosphorus availability in ancient oceans is traditionally considered through the lens of supply (continental weathering versus submarine hydrothermal discharge), major sinks (iron formations, shales, deep-sea sediments) and recycling efficiency[40], the latter of which implicates microorganisms that must break down P-bearing organic molecules. However, the unwritten assumption is that the microbial enzymes needed to recycle P-bearing molecules existed in the early oceans.

Although dissolved inorganic phosphate (DIP) is the preferred P source for microorganisms, it is quickly consumed by primary producers and becomes depleted in surface waters. As a result, dissolved organic P dominates the total dissolved P pool in many oceanic regions[41]. The degradation of dissolved organic P in the water column by heterotrophs ultimately regenerates the pool of bioavailable P. The majority of dissolved organic P originates from phytoplankton-derived macromolecules such as nucleic acids and membrane phospholipids[42] that require exoenzymes to initiate their degradation. In the modern ocean many marine microorganisms secrete enzymes, such as alkaline phosphatase, to acquire P. Metagenomic data from the Global Sampling Expedition show that a large fraction (at least 30%) of alkaline phosphatases produced by marine microorganisms in the ocean are extracellular[43]. Accordingly, the activity and abundance of extracellular phosphatases play a key role in the regeneration of bioavailable P in the ocean.

Phosphorus recycling is enhanced under anoxic conditions through the dissolution of iron oxide minerals, leading to the release of scavenged P, as well as the preferential release of organic-bound P from OM during anaerobic remineralization[44]. In the case of the latter, the cellular- or population-level mechanisms that underpin anaerobic P remineralization are not fully elucidated. It has been suggested that redox-dependent changes can lead to the release of intracellular stored P to pore waters as dissolved phosphate[45]. However, it is also well established that hydrolysis by extracellular phosphatases plays a prominent role in releasing phosphate from P-bearing organic molecules. Regardless, these processes can release substantial P back into pore waters and the water column, where it can be readily reutilized by biota. It is hypothesized that increased oxidative continental weathering and sulfate delivery to the oceans following the onset of the Great Oxidation Event approximately 2.4 Ga would have sustained higher levels of microbial sulfate reduction[46]. The increased abundance of sulfide in the water column and pore waters across the Great Oxidation Event would therefore be expected to trigger more efficient recycling of bioavailable P, in turn enhancing primary productivity[47]. However, for this enhanced P recycling to have occurred, exoenzyme activity in the ocean must have expanded or increased to sustain degradation of P-bearing organic compounds. Thus, despite lack of definitive evidence that they existed by the time of the Great Oxidation Event, these exoenzymes are implicated in the Earth's transition to a persistently oxygenated atmosphere and the geochemical evolution of the oceans.

Future research directions

Resolving the earliest phases of microbial evolution is challenging from both geochemical and biological standpoints. The geological record is nearly devoid of direct evidence for microbial evolution, making it difficult to resolve the evolutionary history of life. In the absence of a physical record, scientists rely on the molecular record of extant bacterial genomes. In the past decade, ancestral sequence reconstruction, known as palaeogenetics, has been used to reconstruct and analyse the history of enzyme families across geological timescales[48]. These reconstructions often rely on leveraging information contained in horizontal gene transfer events that can reflect adaptation to changing environmental conditions by acquiring new biological functions. However, the extent to which horizontal gene transfer played a role in the evolution of exoenzymes is unclear[49]. In these cases, it may be more informative to consider the origin of genes involved in regulatory and secretion systems alongside exoenzymes. Evidence of the efficiency of OM recycling and the production of soluble organic ligands through time would also help. Although it has been suggested that a large DOM reservoir has existed over the course of the Earth's history[50], as far we are aware, it has not been interpreted specifically in the context of exoenzymes.

Microorganisms employ diverse pathways and metabolic strategies to meet their energetic and nutritional requirements. Given that most OM in the oceans consists of complex macromolecules, there would be a strong selective pressure for heterotrophs to be able to access these types of compounds. Therefore, the emergence of exoenzymes represents a key step in the early evolution of heterotrophy, which allowed microorganisms to handle complex marine OM and, in doing so, impact the geochemical cycling of key elements. Developing a more complete understanding of the processes that modulate geochemical cycling on the early Earth requires us to consider not only the presence of heterotrophic metabolisms, but also the strategies they

use to recycle OM. Newly developed approaches and the increasing abundance of genomic data may provide important temporal clues for deciphering the emergence and diversification of exoenzymes.

References

1. Neidhardt, F. C. & Umbarger, E. H. *Chemical Composition of Escherichia Coli* 2nd edn (American Society of Microbiology, 1996).
2. Benz, R. & Bauer, K. Permeation of hydrophilic molecules through the outer membrane of gram-negativ bacteria: review of bacterial porins. *Eur. J. Biochem.* **176**, 1–19 (1988).
3. Arnosti, C. Microbial extracellular enzymes and the marine carbon cycle. *Annu. Rev. Mar. Sci.* **3**, 401–425 (2011).
4. Mahmoudi, N., Hagen, S. M., Hazen, T. C. & Steen, A. D. Patterns in extracellular enzyme activity and microbial diversity in deep-sea Mediterranean sediments. *Deep Sea Res. Pt I* **158**, 103231 (2020).
5. Schmidt, J. M., Royalty, T. M., Lloyd, K. G. & Steen, A. D. Potential activities and long lifetimes of organic carbon-degrading extracellular enzymes in deep subsurface sediments of the Baltic Sea. *Front. Microbiol.* **12**, 702015 (2021).
6. Datta, M. S., Sliwerska, E., Gore, J., Polz, M. F. & Cordero, O. X. Microbial interactions lead to rapid micro-scale successions on model marine particles. *Nat. Commun.* **7**, 119651 (2016).
7. Mahmoudi, N., Enke, T. N., Beaupré, S. R., Teske, A. P., Cordero, O. X. & Pearson, A. Illuminating microbial species-specific effects on organic matter remineralization in marine sediments. *Environ. Microbiol.* **22**, 1734–1747 (2020).
8. Burdige, D. J. Preservation of organic matter in marine sediments: controls, mechanisms, and an imbalance in sediment organic carbon budgets? *Chem. Rev.* **107**, 467–485 (2007).
9. Green, E. R. & Mecsas, J. Bacterial secretion systems: an overview. *Microbiol. Spectr.* **4**, 4.1 (2016). 13.
10. Dodd, M. S. et al. Evidence for early life in Earth's oldest hydrothermal vent precipitates. *Nature* **543**, 60–64 (2017).
11. Gruen, D. S., Wolfe, J. M. & Fournier, G. P. Paleozoic diversification of terrestrial chitin-degrading bacterial lineages. *BMC Evol. Biol.* **19**, 34 (2019).
12. Godfrey, L. V. & Falkowski, P. G. The cycling and redox state of nitrogen in the Archaean ocean. *Nat. Geosci.* **2**, 725–729 (2009).
13. Czaja, A. D., Johnson, C. M., Beard, B. L., Roden, E. E., Li, W. & Moorbath, S. Biological Fe oxidation controlled deposition of banded iron formation in the ca. 3770 Ma Isua Supracrustal Belt (West Greenland). *Earth Planet. Sci. Lett.* **363**, 192–203 (2013).
14. Warke, M. R., Strauss, H. & Schröder, S. Positive cerium anomalies imply pre-GOE redox stratification and manganese oxidation in Paleoproterozoic shallow marine environments. *Precambr. Res.* **344**, 105767 (2020).
15. Grossman, A. S., Mauer, T. J., Forest, K. T. & Goodrich-Blair, H. A widespread bacterial secretion system with diverse substrates. *mBio* **12**, e01956–01921 (2021).
16. Meuskens, I., Saragliadis, A., Leo, J. C. & Linke, D. Type v secretion systems: an overview of passenger domain functions. *Front. Microbiol.* **10**, 1163 (2019).
17. Korotkov, K. V., Sandkvist, M. & Hol, W. G. J. The type II secretion system: biogenesis, molecular architecture and mechanism. *Nat. Rev. Microbiol.* **10**, 336–351 (2012).
18. Vetter, Y., Deming, J., Jumars, P. A. & Krieger-Brockett, B. A predictive model of bacterial foraging by means of freely released extracellular enzymes. *Microb. Ecol.* **36**, 75–92 (1998).
19. Ebrahimi, A., Schwartzman, J. & Cordero, O. X. Cooperation and spatial self-organization determine rate and efficiency of particulate organic matter degradation in marine bacteria. *Proc. Natl Acad. Sci. USA* **116**, 23309–23316 (2019).
20. Reintjes, G., Arnosti, C., Fuchs, B. & Amann, R. Selfish, sharing and scavenging bacteria in the Atlantic Ocean: a biogeographical study of bacterial substrate utilisation. *ISME J.* **13**, 1119–1132 (2019).
21. Krupke, A., Hmelo, L. R., Ossolinski, J. E., Mincer, T. J. & Van Mooy, B. A. Quorum sensing plays a complex role in regulating the enzyme hydrolysis activity of microbes associated with sinking particles in the ocean. *Front. Mar. Sci.* **3**, 55 (2016).
22. Cuskin, F., Lowe, E. C., Temple, M. J., Zhu, Y., Cameron, E. A. & Pudlo, N. A. et al. Human gut Bacteroidetes can utilize yeast mannan through a selfish mechanism. *Nature* **517**, 165–169 (2015).
23. Moran, M. A. & Zepp, R. G. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnol. Oceanogr.* **42**, 1307–1316 (2003).
24. Baltar, F., Arístegui, J., Gasol, J. M., Sintes, E., van Aken, H. M. & Herndl, G. J. High dissolved extracellular enzymatic activity in the deep central Atlantic Ocean. *Aquat. Microb. Ecol.* **58**, 287–302 (2010).
25. Quigg, A. et al. From nano-gels to marine snow: a synthesis of gel formation processes and modeling efforts involved with particle flux in the ocean. *Gels* **7**, 114 (2021).
26. Kipp, M. A., Krissansen-Totton J. & Catling D. C. High organic burial efficiency is required to explain mass balance in Earth's early carbon cycle. *Glob. Biogeochem. Cycles* **35**, e2020GB006707 (2021).
27. Buick, R., Des Marais, D. J. & Knoll, A. H. Stable isotopic compositions of carbonates from the Mesoproterozoic Bangemall Group, northwestern Australia. *Chem. Geol.* **123**, 153–171 (1995).
28. Kipp, M. A. & Stüeken, E. E. Biomass recycling and Earth's early phosphorus cycle. *Sci. Adv.* **3**, eaao4795 (2017).
29. Moore, E. K., Jelen, B. I., Giovannelli, D., Raanan, H. & Falkowski, P. G. Metal availability and the expanding network of microbial metabolisms in the Archaean eon. *Nat. Geosci.* **10**, 629–636 (2017).
30. Bruland, K. W. & Franks, R. P. in *Trace Metals in Sea Water* (eds. Goldberg, E.D. et al.) 395–414 (Springer, 1983).
31. Anbar, A. D. & Knoll, A. H. Proterozoic ocean chemistry and evolution: a bioinorganic bridge? *Science* **297**, 1137–1142 (2002).
32. Morel, F. M. & Price, N. M. The biogeochemical cycles of trace metals in the oceans. *Science* **300**, 944–947 (2003).
33. Noble, A. E., Ohnemus, D. C., Hawco, N. J., Lam, P. J. & Saito, M. A. Coastal sources, sinks and strong organic complexation of dissolved cobalt within the US North Atlantic GEOTRACES transect GA03. *Biogeosciences* **14**, 2715–2739 (2017).
34. Toner, B. M. et al. Preservation of iron(II) by carbon-rich matrices in a hydrothermal plume. *Nat. Geosci.* **2**, 197–201 (2009).
35. Robbins, L. et al. Authigenic iron oxide proxies for marine zinc over geological time and implications for eukaryotic metallome evolution. *Geobiology* **11**, 295–306 (2013).
36. Benner, R. Loose ligands and available iron in the ocean. *Proc. Natl Acad. Sci. USA* **108**, 893–894 (2011).
37. Swaren, L., Alessi, D. S., Owttrim, G. W. & Konhauser, K. O. Acid-base properties of *Synechococcus*-derived organic matter. *Geochim. Cosmochim. Acta* **315**, 89–100 (2021).
38. Zhang, J., Kattner, G. & Koch, B. P. Interactions of trace elements and organic ligands in seawater and implications for quantifying biogeochemical dynamics: a review. *Earth Sci. Rev.* **192**, 631–649 (2019).
39. Reinhard, C. T. et al. Evolution of the global phosphorus cycle. *Nature* **541**, 386–389 (2017).
40. Kipp, M. A. A double-edged sword: the role of sulfate in anoxic marine phosphorus cycling through Earth history. *Geophys. Res. Lett.* **49**, e2022GL099817 (2022).
41. Lomas, M. W. et al. Sargasso Sea phosphorus biogeochemistry: an important role for dissolved organic phosphorus (DOP). *Biogeosciences* **7**, 695–710 (2010).
42. Hori T., Horiguchi M. & Hayashi A. *Biochemistry of Natural CP compounds* (Maruzen Ltd, 1984).
43. Luo, H., Benner, R., Long, R. A. & Hu, J. Subcellular localization of marine bacterial alkaline phosphatases. *Proc. Natl Acad. Sci. USA* **106**, 21219–21223 (2009).

44. Ingall, E. D., Bustin, R. & Van Cappellen, P. Influence of water column anoxia on the burial and preservation of carbon and phosphorus in marine shales. *Geochim. Cosmochim. Acta* **57**, 303–316 (1993).
45. Van Cappellen, P. & Ingall, E. D. Benthic phosphorus regeneration, net primary production, and ocean anoxia: a model of the coupled marine biogeochemical cycles of carbon and phosphorus. *Paleoceanography* **9**, 677–692 (1994).
46. Canfield, D. E. A new model for Proterozoic ocean chemistry. *Nature* **396**, 450–453 (1998).
47. Alcott, L. J., Mills, B. J., Bekker, A. & Poulton, S. W. Earth's Great Oxidation Event facilitated by the rise of sedimentary phosphorus recycling. *Nat. Geosci.* **15**, 210–215 (2022).
48. Garcia, A. K. & Kaçar, B. How to resurrect ancestral proteins as proxies for ancient biogeochemistry. *Free Radic. Biol. Med.* **140**, 260–269 (2019).
49. Zimmerman, A. E., Martiny, A. C. & Allison, S. D. Microdiversity of extracellular enzyme genes among sequenced prokaryotic genomes. *ISME J.* **7**, 1187–1199 (2013).
50. Fakhraee, M., Tarhan, L. G., Planavsky, N. J. & Reinhard, C. T. A largely invariant marine dissolved organic carbon reservoir across Earth's history. *Proc. Natl Acad. Sci. USA* **118**, e2103511118 (2021).
51. Lyons, T. W., Diamond, C. W., Planavsky, N. J., Reinhard, C. T. & Li, C. Oxygenation, life, and the planetary system during Earth's middle history: an overview. *Astrobiology* **21**, 906–923 (2021).

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Author contributions

N.M. and A.D.S conceptualized the Perspective. All authors extensively contributed ideas and provided critical feedback in the research, interpretation and writing.

Competing interests

The authors declare no competing interests.

Additional information

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