

Opinion

Struggle for phosphorus and the Devonian overturn

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Organisms with external phosphatic shells diversified and became abundant at the beginning of the Early Paleozoic but gradually declined and were rare by its end. The decreasing availability of phosphorus in oceans is thought to be responsible for this evolutionary trend. Responses of organisms to changes in the phosphorus cycle can be traced to the late Neoproterozoic, and likely had a significant role in the Cambrian explosion, the Great Ordovician Biodiversification Event (GOBE), and the Devonian nekton revolution. Effective use of phosphorus by vertebrates during the Devonian nekton revolution caused the phosphorus pool to shift from benthic external shells to the skeletons of pelagic vertebrates, and moved the marine faunas toward the dominance patterns and ecological structure of the Modern Evolutionary Fauna.

Key role of phosphorus

Organisms began producing inorganic shells during the **Ediacaran** Period [~635–540 million years ago (mya); see [Glossary](#)] [1]. However, three main types of shell mineralization (calcium carbonate, calcium phosphate, and silicon dioxide) occurred extensively during the Cambrian Period (~540–485 mya) and became abundant in the order listed. Although, fossils with phosphatic shells are less prevalent than those with shells made of carbonate, the proportion, distribution, and utilization of phosphatic shells evolved during the **Early Paleozoic** (~540–360 mya). This history has received little attention but is significant for changes in the phosphorus cycle and their influence on living organisms, and conversely, for the influence of organisms on the phosphorus cycle.

Phosphorus is a biogenic element. Thus, it has a key role in the composition of organisms and their life processes [2]. Its abundance in the Earth crust is slightly more than 1.12×10^3 ppm ($\approx 0.1\%$ [3]), making it the 11th most abundant element. However, in modern sea water, there are only 6×10^{-2} ppm (i.e., five orders of magnitude less [3]). This latter concentration differs depending on the depth and phosphorus forms in seas and oceans [2,4,5], and has changed significantly during the history of the Earth. The phosphorus cycle has been widely studied, especially as it relates to human activities. However, some models focus on the prehuman era [6], modified for the Precambrian [7] or focus on marine conditions [2]. Following these models when dealing with the complex marine environment, the availability of phosphorus can be seen to depend on phosphorus influx to the seas and oceans and its recycling [8]. These factors are controlled by weathering and denudation rates, climate, sea currents, rates of sedimentation, biodiversity, and other related factors (cf. [8]). Consequently, they can be responsible, for example, for the spreading of anoxia [9] or the accumulation of phosphate deposits [10,11] in combination with other factors, as discussed in [12]. Above all, however, phosphorus concentration and accessibility strongly influence not only primary [13], but also overall bioproductivity [4,5,9], because it is a limiting element with many consequences [6,8]. The critical role of phosphorus is evidenced by its use in the construction of the sugar-phosphate backbone of

Highlights

Phosphorus had a key role in the Early Paleozoic radiation events.

The decline of organisms with external phosphatic shells was caused by an increasing inaccessibility of phosphorus during the Early Paleozoic.

The dominant phosphorus pool shifted from benthic groups to pelagic vertebrates during the Devonian.

Recycling of phosphorus in the marine environment substantially moved phosphorus into the water column.

The Devonian phosphorus pool pattern is one of the key factors controlling marine diversity and ecological patterns up to the present time.

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DNA and RNA, the phospholipid components of cell membranes, and intracellular energy transfer through ATP in aerobic oxidation of the citric acid cycle. It is also a significant biomineralization element that organisms use for their skeletons in the form of various phosphates [14]. Its accessibility in sea water [8,15] versus the requirements of aquatic organisms [16], in comparison with equal proportions of other biogenic elements, illustrates its limiting function for biotic expansion. However, the role of phosphorus in evolution and biodiversity has been received rather limited study given that it could be one of the controlling or even critical life mechanisms. As an example, empirical knowledge combined with published data indicates a progressive decline of different, evolutionarily independent animal groups with phosphatic shells during Devonian times. Discussion of aspects of this complex process with a focus on the role of phosphorus has resulted in one possible explanation of complementary to others, such as the evolution of shallow burrowing [17].

Precambrian (before 540 mya)

The **Neoproterozoic** Era shift in phosphorus is considered to have been caused by massive denudation of continents due to **snowball Earth glaciations** (~715 and 635 mya [18,19]; cf. [10]). This shift has also been related to the rise in atmospheric oxygen [20] and its influence on the contemporary rise of metazoans [20–22]. However, phosphorus should also be recognized as one of the most significant direct factors leading to the origin of metazoans (cf. [23]). Along with oxygen, there must have been sufficient availability of phosphorous, as a limiting element, for animals to build single bodies comprising millions to billions of cells, each requiring phosphorus for membranes, DNA back-bones, and an energetic engine represented by the ATP–ADP citrate cycle. Thus, the existence of individuals comprising myriad cells and their reproduction (regardless of strategy) resulting in multiply cell numbers depends on the sufficient accessibility of all components, including the scarce ones. Hence, the increase in organic production through the rise of populations, increased species diversity, and the appearance and diversification of metazoans in particular, must have been linked to more intensive recycling of biogenic elements. This was accelerated by the increased anoxic burial of organic matter relatively depleted in phosphorus, but which nevertheless remained easily available [21]. Thus, the surplus of accessible phosphorus apparently continued in sea water across the Precambrian–Cambrian boundary (~540 mya), triggering phosphogenic events [24,25]. In addition, phosphatization became a significant mode of preservation [26], and organisms had enough of this critical element to support the Cambrian explosive radiation and, finally, for shell secretion on the threshold of the **Phanerozoic** (~540 mya–present). The distinct change-over related to the large biotic crisis during the Ediacaran–Cambrian transition manifested as the stepwise replacement of Ediacaran fauna by Cambrian fauna [27].

Early Paleozoic (540–360 mya)

The early Cambrian Period (~540–520 mya) was the golden age of phosphatic shells [28] and of the groups that produced them, such as linguliform brachiopods, tomotids, and the various groups producing tube-like shells classified as hydrozoans. In fact, this Period can be seen as an exceptional time of almost unconstrained accessibility and use of phosphorus in the global ecosystem. It was also a period of evolutionary experiments and tests of the vitality of morphologies and strategies accelerated by early biomineralization trends, which were influenced by sea water chemistry [29–31] and, in turn, influenced the ecological complexity of communities [31]. The most diversified animal groups as a whole are generally labeled the ‘Cambrian Evolutionary Fauna’ [32] (Box 1). The winners of these competitive experiments evolved successful life strategies and, conditioned by a rapid increase in primary production [33,34], could start to radiate and produce large numbers of species and specimens [35]. These novelties are classified as lower ranked taxonomical categories than those produced by the **Cambrian explosion** and subsequent evolutionary experiments. The result was a rapid increase in the diversity/disparity ratio. High

Glossary

Byronids: extinct group with affinities to cnidarians, producing tubular, narrow conical organophosphatic shells.

Cambrian explosion: early Cambrian (~540–520 mya) appearance of many groups related to the mass ability to produce shells.

Conulariids: extinct group with affinities to cnidarians producing pyramidal tetradial, organophosphatic shell.

Devonian nekton revolution: accelerated occupation of the water column by active swimmers during the Devonian (~420–360 mya).

Early Paleozoic (~540–360 mya): informal stratigraphic unit including Cambrian, Ordovician, Silurian, and Devonian.

Ediacaran (~635–540 mya): formal stratigraphic unit; the latest period of Neoproterozoic (for the updated stratigraphic chart, including ages of units, see <https://stratigraphy.org/chart>).

Great Ordovician Biodiversification Event (GOBE): rapid, polyphased, unparalleled increase in diversity in the marine realm that occurred during the Ordovician (~490–445 mya), some approaches reduce it to the first prominent pulse in the Middle Ordovician (~465–460 mya).

Neoproterozoic (~1000–540 mya): formal stratigraphic unit; latest Proterozoic era (i.e., the youngest portion of the informal unit of the Precambrian).

Orogeny: formation of mountain belts due to the convergent movements of lithospheric plates.

Phanerozoic (~540 mya to present): last eon in Earth history starting with the Cambrian, typified by life expansion and shell development.

Snowball Earth glaciations: the most extended glaciation events in Earth history, which occurred during the mid Neoproterozoic (~715 and 635 mya).

Sphenothallids: extinct group with affinities to cnidarians, producing tubular, bilateral organophosphatic shells.

Box 1. Concept of the evolutionary faunas

A large-scale pattern model of family diversification during the Phanerozoic was developed by J. Sepkoski during 1980s. It was based on an extensive database of fossil taxa and applied to the marine fauna. Three evolutionary faunas were recognized (Figure 1) [32,61]. The Cambrian Evolutionary Fauna is the oldest Phanerozoic evolutionary stage of marine faunas characterized by the highest family diversity of trilobites (Arthropoda, Trilobita), linguliformean brachiopods (Brachiopoda, Linguliformea, typified *inter alia* by organophosphatic shells), monoplacophorans (Mollusca, Monoplacophora), hyoliths (unclear affinity, Hyolitha), and eocrinoids (Echinodermata, Eocrinoidea). It dominated during Cambrian and the earliest Ordovician, when it was replaced by the Paleozoic Evolutionary Fauna. This follow-up evolutionary stage is typified by rhynchonelliformean brachiopods (Brachiopoda, Rhynchonelliformea, with calcareous shell), anthozoans (Cnidaria), cephalopods (Mollusca, Cephalopoda), ostracods (Arthropoda, Crustacea, Ostracoda), stenolaematans (Bryozoa, Stenolaemata), stelleroids (Echinodermata, Stellerioidea), crinoids (Echinodermata, Crinoidea), and graptolites (Hemichordata, Graptolithina). These dominated from the Ordovician to the end of Permian (i.e., to the most intensive mass extinction ever documented). The Modern Evolutionary Fauna is the youngest evolutionary stage of marine faunas, which dominated from the earliest Mesozoic (Triassic) onward. It is characterized by rhizopod protists (Cercozoa), demosponges (Porifera, Demospongiae), bivalves (Mollusca, Bivalvia), gastropods (Mollusca, Gastropoda), malacostracans (Arthropoda, Crustacea, Malacostraca), gymnoleamatans (Bryozoa, Gymnolaemata), sea urchins (Echinodermata, Echinoidea), and various vertebrates. Although the dominance of the evolutionary faunas and phosphorus cycle changes might appear independent given their seeming heterochrony, they are likely causally linked as documented in the present study.

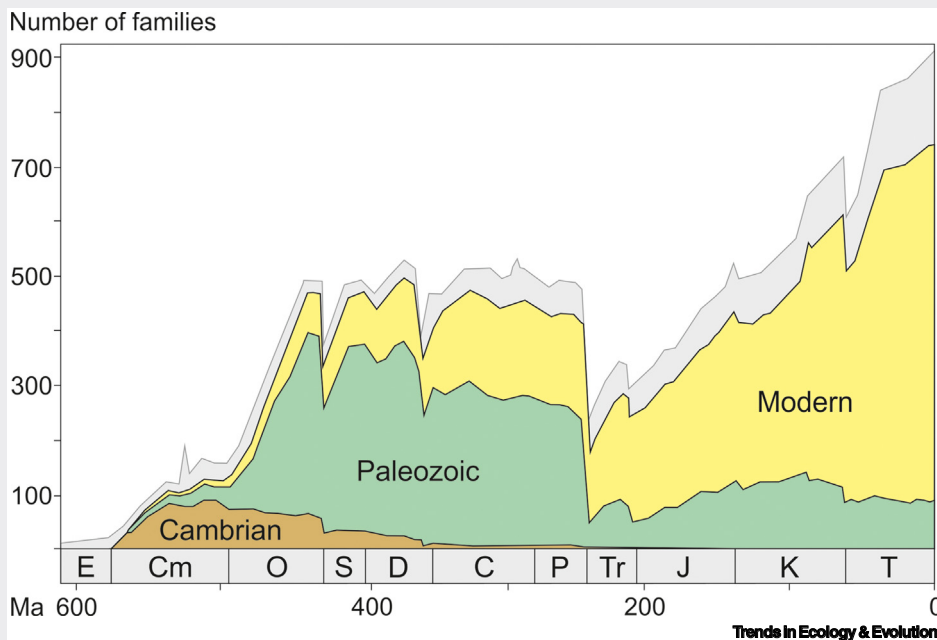


Figure 1. Diversity of marine animals and evolutionary faunas. The trends are illustrated by the number of families in periods of the latest Proterozoic and Phanerozoic (time calibration in millions of years); modified after [32]. The gray shading indicates poorly preserved families. Abbreviations; C, Carboniferous; Cm, Cambrian; D, Devonian; E, Ediacaran; J, Jurassic; K, Cretaceous; O, Ordovician; P, Permian; S, Silurian; T, Tertiary (Paleogene, Neogene); Tr, Triassic.

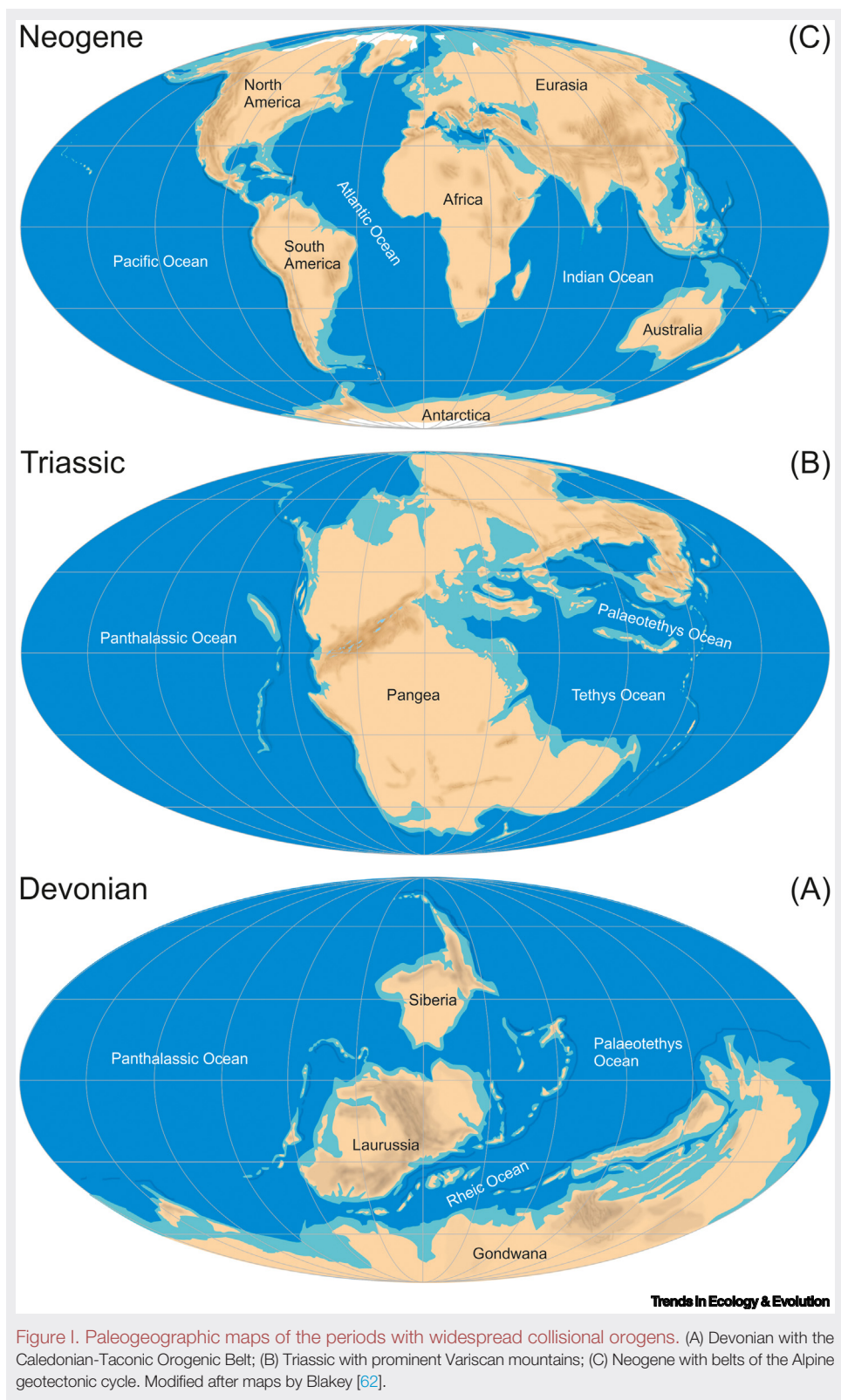
numbers of successful organisms often producing high numbers of offspring, naturally needed more phosphorus. The element was still available, as shown by relative abundance of phosphatic shells in the fossil record, but its usage in this way had become a luxury. This scenario is thought to have contributed significantly to the **GOBE** [36,37]. It also shows that the Cambrian disparity radiation was replaced by the Ordovician (~485–445 mya) diversity radiation and the flux of phosphorus began to change. The groups producing compact phosphatic shells, which require enormous amounts of phosphorus in proportion to their body size, started to decline. The consumption of phosphorus as a component of cells rapidly increased during the GOBE and is coincident with

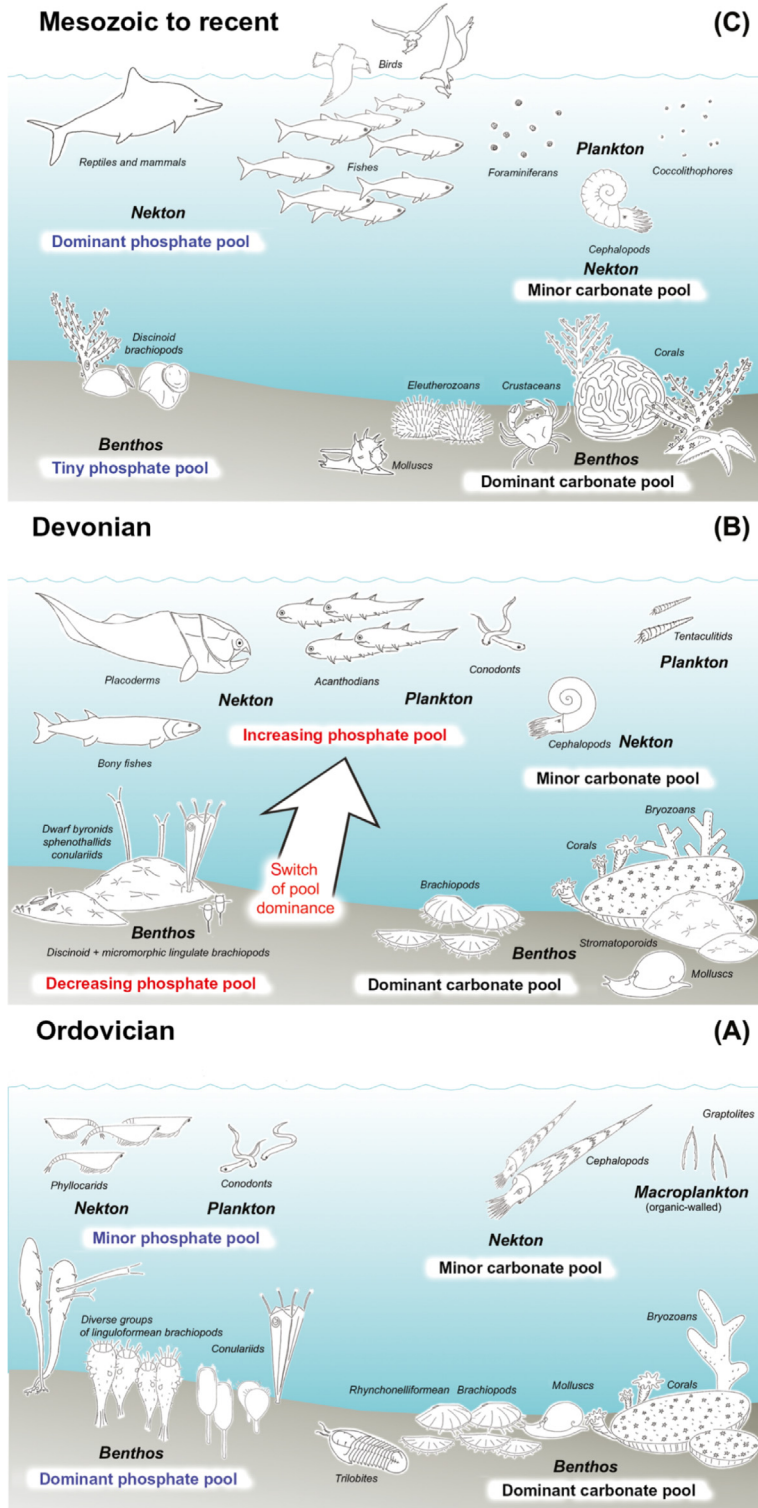
the general decline of linguliform brachiopods (Linguliformea) [38–40]. The organisms producing phosphatic shells with a much lower phosphorus requirement relative to their body declined more slowly [**conulariids, sphenothallids, byronids**, and also some trilobites (Trilobita)] [41]. The deteriorating availability of phosphorus also resulted in the decline and subsequent disappearance of very abundant cosmopolitan phyllocarid crustaceans (Phyllocarida) of the genus *Caryocaris*, preserved in the fossil record due to their presumably taphonomically phosphatized carapaces [36,42]. By contrast, organisms with efficient phosphorus management flourished. Typical of these were the conodonts (Conodonta, chordates) [43], which prospered and used phosphorus only for reinforcing important elements of their digestive tract used to efficiently gain and process food.

Subsequently, abrasion of Gondwana during the Late Ordovician to early Silurian glaciation (~445–441 mya [44]) and likely the weathering of rocks uplifted during the Caledonian and associated Taconic **orogeny** (~490–400 mya; **Box 2**) were the sources of phosphorus washed into the oceans from the plantless continents. Therefore, GOBE was followed by eutrophication (cf. [10,45]), resulting in the next shifts in bioproduction and increasing diversity [46], typically during rejuvenation during the Silurian Period (~444–420 mya) [47,48]. These processes were related to the global expansion of anoxia, which influenced the phosphorus flux. This trend continued to the Devonian Period (~420–360 mya). However, the gradual rise of vertebrates (Vertebrata) [48,49], noticeably accelerated by the expansion of gnathostomes (Gnathostomata) during the Devonian Period [49], was a key factor influencing the phosphorus cycle. The vertebrates significantly increased demand for, and consumption of, phosphorus, and intensified competition for phosphorus during the **Devonian nekton revolution** [50]. The saturation and availability of phosphorus, which supported a continued increase in diversity [46], were probably sustained only through the more intensive weathering caused by the incoming bioerosion of an extending vegetation cover on land¹ [51]. Vertebrates appear to have been successful, in part, because they use phosphorus selectively and carefully for reinforcement of some parts of the body. Anyway, they became a prosperous group from the Devonian onwards and were able to support their growing consumption of phosphorus accompanied by the low burial rate of phosphorus in sediments [52]. This had an obvious influence on the decline of groups with external phosphatic shells, such as conulariids [53], sphenothallids, byronids, and partly trilobites [54]. These groups

Box 2. Palaeogeography and orogenies

The significance of orogenies for recycling of phosphorus is mentioned several times in the current article. Two main types of orogen exist: accretionary and collisional. The former, exemplified by Andes, is important but the latter is considered to influence more intensively the processes of phosphorus influx on the surface of the Earth. Their formation rate and intensity are concentrated in a relatively short interval of geological time. As indicated by the terminology, these orogens are uplifted due to the collision of continental parts of the lithospheric plates, simply by continents. Thus, they are the result of continental drift driven by the movement of the Earth's mantle, which also cause the growth of the ocean crust in rifts situated in the central ocean ridges. During Earth history, continents as parts of plates were fragmented by rifting and amalgamated through collisions many times. However, there were few substantial orogenies influencing the Phanerozoic (~540 mya to present) global ecosystem. The Caledonian and associated Taconic orogeny (~490–400 mya) was caused by a collision of the paleocontinents Laurentia, Baltica, and Avalonia culminating at end of the Silurian, and forming the new paleocontinent Laurussia (**Figure 1A**). This was crossed by a collisional mountain range of the Caledonian-Taconic Orogenic Belt growing along the suture of the closed (subducted) Iapetus Ocean. Subsequent principal collisions were related to the Alleghenian-Variscan and Uralian orogenies (~400–300 mya) forming the supercontinent Pangea (**Figure 1B**). Several orogenic belts were formed during the Early Paleozoic due to the collisions of Laurussia, Gondwana and Siberia. The breakup of Pangea was the initial stage of the Alpine geotectonic cycle. Its processes gradually formed the distribution of modern continents and oceans, including several orogens such as orogenic belts between the African and Eurasian and between the Indian and Eurasian plates (~80 mya to present; **Figure 1C**). New orogens are expected to be formed and result in the amalgamation of a new supercontinent in the distant future. Fluctuations of the phosphorus influx derived from orogens also depend on the phosphorus content in the uplifted rocks and the denudation rate of the orogens.





Trends in Ecology & Evolution

Figure 1. Key changes in the phosphorus cycle. Visualization of the changes in the background of the significant groups of organisms involved. (A) Ordovician; (B) Devonian; (C) Mesozoic to Recent.

survived but became a very minor component of marine communities, with many dwarfing taxa. Therefore, the rise of vertebrates can be considered to herald the close of wasteful phosphorus usage and the onset of an advanced phosphorus marine cycle.

Some nonphosphatic benthic groups, such as dendroid graptolites (Dendroidea, hemichordates) and hyoliths (Hyalolitha, uncertain taxonomic position) [49] show contemporaneous trends in the rise and fall of their diversity and abundance, proving that phosphorus availability was a key piece of the complex causal puzzle impacting benthic communities.

From Late Paleozoic (360 mya) onward

The Variscan orogeny (~400–300 mya; Box 2), glaciation during the late Carboniferous to early Permian periods (including exposure and erosion of continental shelves; ~365–250 mya), and the Alpine orogeny (~80 mya to present; Box 2), are examples of geological processes supplying seas and oceans with phosphorus [55]. They also markedly increased the abundance of phosphate in phosphate deposits [10]. In contrast to earlier periods, phosphorus influx from land to seas and oceans was strongly controlled by vegetation cover and climate [56]. By contrast, the conspicuous phosphorus supply from orogeny might significantly contribute to rejuvenation of the ancient strategy of using phosphorus. The Alpine orogeny can be considered to have cotriggered an increase in the diversity of the then minor group of linguliform brachiopods during the Cenozoic Era [40,57]. These brachiopods are an unusual example of an invertebrate surviving with an external organophosphatic shell. Although it is a morphologically very conservative group, the genome sequencing of the extant lingulid *Lingula anatina* showed that it has evolved significantly during the history of linguliform brachiopods and displays clearly different, parallel-evolved coding of the phosphate mineralization of brachiopods and vertebrates [58]. This indicates that, along with phosphorus availability, the mechanism of its utilization also influenced the fitness of all groups with hard phosphatic elements and shells. Knowledge of molecular biology illustrates the high complexity of the biomineralization process, in which phosphorus availability is significant among the many limiting factors because, as hypothesized, the ability of organisms to biomineralize appears to be driven by ancestral genes of a ‘biomineralization toolkit’ [59]. Such a toolkit is considered to be common in metazoans and controlled independently in different lineages by regulatory gene networks; it can also explain the repeated switching on/off of biomineralization and the different mineralization strategies across lineages despite their phylogenetic proximity [59]. Thus, it is also questionable whether groups such as byronids really declined with the decrease in phosphorus availability or switched to forms without mineralized tubes. The parallel existence of mineralized and organic shells is not unusual (e.g., tubes of annelids). Thus, the discovery of byronids with non-mineralized organic shells [60] is to be expected.

The pool model

The pool model can be illustrated and summarized in a series of images visualizing the main periods of change in the phosphorus cycle (Figure 1). At the beginning of the Phanerozoic Eon, during the Cambrian and Ordovician periods (~540–445 mya), the main pool of phosphorus was in the shells of benthic animal groups, with only a minor portion used by pelagic organisms (Figure 1A). By contrast, carbonate shells were secreted by the benthos in particular. During the Silurian Period (~445–420 mya), a changeover started that peaked during the Devonian Period (~420–360 mya; Figure 1B), whereby phosphorus use by pelagic organisms increased and it was intensively recycled in the water column. Although it was used mainly by swimming vertebrates, conodonts also flourished. Benthic groups or clades with external phosphatic shells decreased and most headed toward extinction. Thus, this changeover can also be seen to be related to the different position of phosphatic body elements. While earlier types of organism

used phosphorus for their outer shells, phosphorus later became hidden inside the bodies of organisms in the internal skeletons and elements. The pelagic phosphate pool expanded and was stabilized by Modern Evolutionary Fauna [32] (Figure 1C and Box 1). By contrast, the carbonate pool remained unchanged until the Mesozoic Era (~250–65 mya) when a partial shift to the pelagic realm can be linked to a cephalopod (ammonite) boom and particularly to an expansion of calcareous nannoplankton. Such pool patterns have significantly influenced the equilibrium between pelagic and benthic communities.

The minimal influence of mass extinctions on the model is worth noting. The main changes in the phosphate and carbonate pools occurred in the periods between the largest extinction events, being gradual and mosaic replacements of prevailing usages. The post-extinction rejuvenations only confirmed and stabilized the pre-extinction development: 'it was the same performance only with different actors', reflecting changes in the diversity and taxonomic composition but with the same trends in shell types.

The above general model was produced based principally on paleobiological data. Given that it is a global model, different aspects, such as local diversity dynamics, facies framework (including geochemical and taphonomical features), and tests of contemporary course of principal changes, can help to characterize its details further and indicate its degree of robustness.

Concluding remarks

Invertebrates with external phosphatic shells occupied a range of ecological niches. As predominantly sessile and apparently microphagous organisms, they were not hindered in their potential dispersion and success by a lack of food or substrate, as illustrated by other groups with similar trophic and habitat demands. Thus, their decline had to be related to other factors. In our pool model, the material of the shells is considered the limiting factor affecting their path toward extinction or evolution to organic-walled or soft-bodied forms. They were victims of a combination of circumstances in the long-term trend of phosphorus availability. From at least the late Precambrian, organisms have, to some extent, followed trends and changes in the dynamics of the phosphorus cycle. Phosphorus was richly available during the late Neoproterozoic Era and Cambrian Period, but started to decrease markedly thereafter, especially with the 'cell boom' requirements of the GOBE. However, the critical decline is related to the rise of vertebrates and, especially, their explosion during the Devonian Period, because it was at this time that phosphorus switched from being abundant to becoming a limiting biogenic element. It ultimately affected not only pelagic, but also benthic communities. This historical constraint is one of various significant environmental factors influencing modern ecosystems, an understanding of which is helpful for predictions of future organismal and environmental changes and evolution (see Outstanding questions).

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Declaration of interests

No interests are declared.

Resources

<https://goldschmidtabstracts.info/2017/3688.pdf>

Outstanding questions

Can the pool model reverse in specific conditions: for example, if the dominant phosphatic pool is reduced or weakened in vertebrates, can the phosphorus surplus substantially increase the abundance of benthos? Although this occurred in deep history, it also has real consequences. Can anthropogenic influences on the phosphorous pool provoke a significant response of benthic communities?

Vegetation increases weathering due to its bioerosion activity. By contrast, it retains most of the terrestrial phosphorus, providing it to heterotrophs to recycle. Can a reduction in vegetation cover lead to an increased influx of phosphorus to the marine environment in an amount that could significantly change the balance of marine ecosystems?

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