LETTER

The evolution of the marine phosphate reservoir

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Phosphorus is a biolimiting nutrient that has an important role in regulating the burial of organic matter and the redox state of the ocean–atmosphere system[1]. The ratio of phosphorus to iron in iron-oxide-rich sedimentary rocks can be used to track dissolved phosphate concentrations if the dissolved silica concentration of sea water is estimated[2–5]. Here we present iron and phosphorus concentration ratios from distal hydrothermal sediments and iron formations through time to study the evolution of the marine phosphate reservoir. The data suggest that phosphate concentrations have been relatively constant over the Phanerozoic eon, the past 542 million years (Myr) of Earth's history. In contrast, phosphate concentrations seem to have been elevated in Precambrian oceans. Specifically, there is a peak in phosphorus-to-iron ratios in Neoproterozoic iron formations dating from ~750 to ~635 Myr ago, indicating unusually high dissolved phosphate concentrations in the aftermath of widespread, low-latitude 'snowball Earth' glaciations. An enhanced postglacial phosphate flux would have caused high rates of primary productivity and organic carbon burial and a transition to more oxidizing conditions in the ocean and atmosphere. The snowball Earth glaciations and Neoproterozoic oxidation are both suggested as triggers for the evolution and radiation of metazoans[6,7]. We propose that these two factors are intimately linked; a glacially induced nutrient surplus could have led to an increase in atmospheric oxygen, paving the way for the rise of metazoan life.

In almost all modern aquatic systems, primary production of organic matter is typically thought to be limited by either phosphorus or bioavailable nitrogen[8]. Temporally extended deficiencies in fixed nitrogen availability are buffered by biological fixation of a virtually limitless supply of atmospheric N_2. By contrast, phosphorus is sourced primarily by weathering of continental materials; accordingly, it is generally thought that phosphorus ultimately limits net primary productivity on geological timescales[8,9]. An estimate of marine phosphate reservoir size through time is therefore essential to unravel basic aspects of biological and geochemical evolution[10].

Ratios of phosphorus to iron in ferric oxides scale with ambient concentrations of dissolved phosphate ($[P_D]$), as predicted by distribution coefficient (K_D) relationships: $[P_D] = (1/K_D)P/Fe$ (ref. 4). P/Fe ratios in ferric oxyhydroxides within hydrothermal plumes emanating from mid-ocean ridges remain constant during transport[3]. Similarly, P/Fe ratios in modern iron-oxide-rich sediments seem to remain essentially constant or show only slight decreases during burial, despite mineralogical transformations[5]. Consequently, P/Fe ratios in ferruginous sediments can be used to track dissolved phosphate concentrations in ancient sea water[2]. Because the K_D value for phosphate-iron oxyhydroxide sorption varies inversely with dissolved silica concentrations owing to competitive adsorption of aqueous silica species[11], it is also important to consider the evolution of the silica cycle when using P/Fe ratios as a palaeoproxy. Marine silica concentrations have varied drastically through Earth's history, significantly influencing phosphate sorption by iron oxyhydroxides.

The data for this study (~700 individual samples of iron-oxide-rich rocks) include new results and those obtained from a comprehensive literature survey. Consistent with previous studies in which iron formations were used to decipher ancient seawater chemistry[2,12], we passed our samples through a series of strict filters to select for authigenic iron-rich rocks that most probably retain bulk seawater signatures. All samples have a negligible detrital component and contain only minor amounts of pyrite, siderite, and manganese phases (Supplementary Information).

We identify four well-defined stages in P/Fe ratios in iron-oxide-rich rocks through time (Fig. 1). These stages reflect both shifts in the size of the marine phosphate reservoir and the evolution of the global silica cycle. Stages one and two, defined by distal hydrothermal sediments from fourteen different localities of Phanerozoic age (<542 Myr), span the Quaternary period to the Cretaceous and the Jurassic period to the Cambrian, respectively. The molar P/Fe ratios multiplied by one hundred ($P/Fe_{(100)}$) in stage one yield an average of 2.55 with a range of <1 to 8.6 and a standard deviation of 1.2. In stage two, there is an average $P/Fe_{(100)}$ ratio of 0.38 with a range from <1 to 1.8 and a standard deviation of 0.26 (Fig. 1).

The marked change in P/Fe ratios between stages one and two is coincident with the initial radiation of diatoms, when marine silica concentrations are thought to have decreased substantially[13,14]. Dissolved marine silica concentrations are assumed to have been <0.1 mM since the Cretaceous and, taking a conservative estimate, ~0.67 mM between the Cambrian and the mid-Jurassic, which is near cristobalite saturation (see Supplementary Information for a discussion of constraints on dissolved silica concentrations). Recent
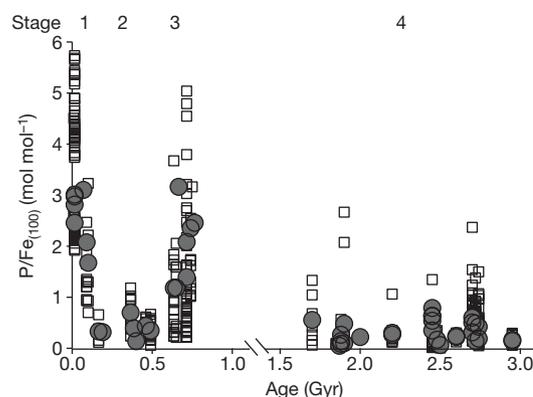

Figure 1 | P/Fe molar ratios through time in iron-oxide-rich distal hydrothermal sediments and iron formations with low amounts of siliciclastic input. Open squares are individual samples; filled circles are formation averages. The P/Fe ratio reflects the size of the marine phosphate reservoir; phosphate sorption onto ferric oxyhydroxides follows a distribution coefficient (K_D) relationship. The ratio is also influenced by the concentration of dissolved silica, because phosphate and silica hydroxides compete for sorption sites on ferric oxyhydroxides. Two outliers are not shown ($P/Fe_{(100)}$ = 8.6 90 Myr ago and $P/Fe_{(100)}$ = 6.8 750 Myr ago). See Supplementary Information for a box plot of the data.

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experimental results indicate that an approximately sevenfold increase in dissolved silica from modern concentrations (that is, from <0.1 to 0.67 mM) would cause an 85.6% decrease in the amount of phosphate sorbed to ferric oxides (Supplementary Fig 1). This decrease is virtually identical to the magnitude of the observed increase in P/Fe ratios occurring subsequent to the expansion of siliceous phytoplankton (85%), when dissolved silica concentrations would have decreased. Thus, when viewed in light of varying silica content, marine phosphate concentrations seem to have been roughly constant though the Phanerozoic, in accordance with independent estimates for marine phosphate concentrations[15].

Stage three occurred during the Cryogenian period ($\sim$750–620 Myr ago). Samples for this time interval are from seven iron formations associated with the low-latitude, snowball Earth glaciations[6] and contain an average P/Fe$_{(100)}$ ratio of 1.96 with a range from <1 to 6.8 and a standard deviation of 1.2. This average is markedly higher than those seen during the early and middle Phanerozoic. Dissolved marine silica concentrations in the Neoproterozoic era were probably high relative to the Phanerozoic; the radiation of radiolarians and siliceous sponges in the earliest Phanerozoic resulted in a shift to a biologically controlled silica cycle and probably caused a decrease in marine silica concentrations[13]. Therefore, Cryogenian iron formations point to very high marine phosphate concentrations. Using even the most conservative estimates for dissolved silica concentrations, assuming that concentrations were similar to those in the early Phanerozoic ($\sim$0.67 mM), P/Fe ratios in Cryogenian iron formations suggest that marine dissolved phosphate concentrations were more than five times greater than Phanerozoic levels. Neoproterozoic iron formations were deposited in a shelf or slope setting under shallower conditions than the majority of deep-water (substorm wave base to abyssal depths) deposits in our compilation. Because of the non-conservative, nutrient-type behaviour of dissolved phosphorus in the ocean, shallow waters would be expected to show signs of phosphate depletion, making the anomalous enrichments we see in the shallow Cryogenian iron formation samples even more remarkable. The occurrence of high P/Fe ratios in seven separate, geographically widespread successions (see Supplementary Information for formation details) supports our assertion that the observed high P/Fe ratios reflect global conditions during glacial periods in the Cryogenian rather than conditions unique to isolated basins.

Stage four spans the Palaeoproterozoic era and the Archaean eon (1.7–3.0 billion years ago) and is represented by iron formations and distal hydrothermal sediments from 24 localities. The P/Fe$_{(100)}$ ratio in stage four is 0.37 with a range from <1 to 2.9 and a standard deviation of 0.42. This average P/Fe$_{(100)}$ ratio is approximately equal to that found in early- and mid-Phanerozoic rocks but is significantly less than ratios found in iron formations deposited during the snowball Earth glacial period. Dissolved silica concentrations in the Archaean and Palaeoproterozoic oceans may have been as low as cristobalite saturation ($\sim$0.67 mM) but it is more likely that they were near amorphous silica saturation[14,16] ($\sim$2.2 mM). Correspondingly, phosphate concentrations in Earth's early oceans are estimated to have been, at minimum, equivalent to Phanerozoic levels but are more likely to have been several times higher ($\sim$4 times assuming 2.2 mM dissolved silica). However, because most of the Archaean and early Proterozoic samples in our compilation contain mixed-valence iron oxides, some caution should be exercised when making comparisons to exclusively ferric-iron-dominated rocks (Supplementary Information).

Changes in the global biogeochemical cycle of phosphorus can be related to the evolution of Earth's surface conditions (Fig. 2). It is likely that the major removal fluxes for phosphate from modern oceans were attenuated during the Precambrian. Ferric oxyhydroxides represent a substantial sink in modern oceans[17], but the importance of this sink would have been lower in the Precambrian because of less phosphate sorption onto ferric oxides at high concentrations of dissolved silica. In addition, substantial portions of the deep ocean were probably anoxic
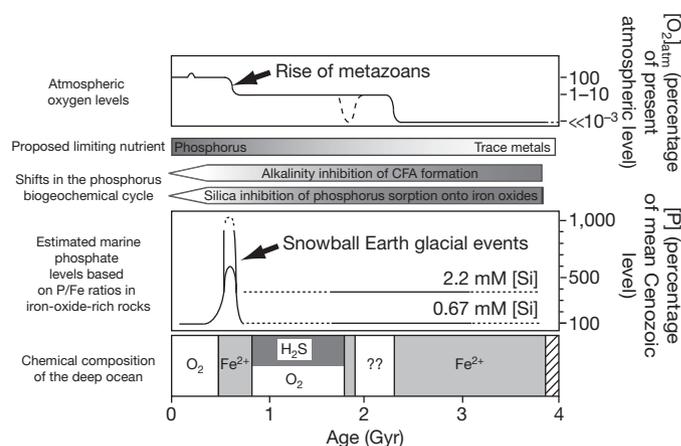

Figure 2 | Model for the coevolution of atmospheric and oceanic redox state and limiting nutrients for marine primary productivity. The redox model is from refs 10, 30. Phosphate concentrations are extrapolated from average P/Fe ratios for individual formations. Our compilation of P/Fe data suggests that there were elevated seawater phosphate concentrations in the Precambrian and a peak in phosphate levels associated with the Neoproterozoic snowball Earth glaciations. This late Precambrian increase in dissolved phosphorus concentration may have stimulated high rates of organic carbon burial and a corresponding increase in atmospheric oxygen levels—paving the way for the rise of metazoans. CFA, carbonate fluorapatite. Square brackets denote concentration.

before and even during the Neoproterozoic[18], which would have removed the large phosphate sink associated with ferric oxyhydroxide formation during off-axis hydrothermal alteration of basalts[17]. Perhaps more importantly, the formation of carbonate fluorapatite during early diagenesis, the largest marine phosphate sink today[19], was probably much less effective during the early Precambrian. Carbonate fluorapatite solubility scales with carbonate alkalinity[20], which was almost certainly high before the onset of enzymatic carbonate formation in the late Neoproterozoic[21]. Lastly, high marine phosphate concentrations during the extensive Cryogenian glaciations are expected, given that weathering rates in modern glaciated settings are higher than those in comparable unglaciated catchments[22]. Enhanced post- and syn-glacial phosphorus delivery to marine systems results in part from an elevated detrital flux to, and high dissolution rates within, proglacial environments[22]. Importantly, in the Neoproterozoic, before soil stabilization by vascular plants, the temporal extent of enhanced phosphorus delivery from glaciated catchments was probably much greater than in the Pleistocene.

Because phosphorus is believed to be the nutrient ultimately controlling marine primary productivity on geological timescales[9], elevated marine phosphate concentrations should lead to higher levels of organic matter production and increased carbon burial. However, because of high biological metal demands, especially in diazotrophic (N_2-fixing) organisms, trace elements may also limit primary productivity. Non-ferrous trace-element stress is likely to have been severe in Earth's early oceans. Under an essentially anoxic atmosphere during the Archaean, there would have been limited continental weathering and delivery of dissolved redox-sensitive metals to the oceans[23] (for example cobalt, cadmium, molybdenum and vanadium, which are common cofactors and are crucial in many major metabolic processes, including nitrogen assimilation and fixation). Our study points to high phosphate concentrations in the Archaean and Palaeoproterozoic oceans, thereby strengthening earlier arguments asserting that non-ferrous trace metals, rather than phosphorus, were the most important factors limiting carbon fixation in Earth's early biosphere. Under a later oxidizing atmosphere and widespread euxinic (anoxic and sulphidic) or oxic conditions in the ocean, trace-element stress is also possible[24]. For instance, trace metals (for example, iron) seem to limit nitrogen fixation in regions of the modern ocean[24,25].

We suggest that a combination of upwelling iron-rich waters[18] and significantly elevated marine phosphorus concentrations following the snowball Earth glaciations would have caused a nutrient surplus—stimulating high rates of primary productivity and increased organic carbon burial. Unprecedented continental phosphorus fluxes would be expected following these glaciations (during post-glacial and inter-glacial time periods), given the extraordinary extent and duration of Cryogenian ice cover and the high levels of phosphorus delivery expected from glaciated catchments. Persistently high carbonate carbon isotope values for significant time periods of the Cryogenian[26] confirm this increase in organic carbon burial. Additionally, perturbations to the carbon cycle connected to the snowball Earth events, for instance extensive methane clathrate release, may have muted the carbonate carbon isotope signature for high post-glacial organic carbon burial[6,27]. A long-lived, glacially induced nutrient surplus and a corresponding organic carbon burial event would have resulted in a shift to more oxidizing ocean–atmosphere conditions in the late Neoproterozoic, because net burial of organic carbon results in a corresponding rise in atmospheric O_2 (ref. 10). The evolution and ecological expansion of metazoans is largely dependent on the oxidation state of marine systems[7]. Therefore, this redox shift could have paved the way for the rise of metazoans—providing a mechanistic explanation for the intimate link[6,28,29] between the snowball Earth events and early animal evolution.

METHODS SUMMARY

Data in the compilation reflect our analytical efforts and a literature survey and include distal hydrothermal sediments and samples from iron formations (Supplementary Table 1). The criteria used to filter the data are outlined in Supplementary Information. The new trace and major element concentrations were determined using a ThermoFinnigan Element II inductively coupled plasma mass spectrometer operated at Woods Hole Oceanographic Institution following a three-acid digest. Analytical precision and accuracy for our measurements were checked by multiple analyses of the geostandards IF-G and BHVO-1, and reproducibility was better than 5%. Reproducibility of literature data is estimated to be better than 10%. See Supplementary Information for additional method details.

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