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Biogeochemistry

Early phosphorus redigested

Atmospheric oxygen was maintained at low levels throughout huge swathes of early Earth history. Estimates of phosphorus availability through time suggest that scavenging from anoxic iron-rich oceans stabilised this low-oxygen world.

Simon W. Poulton

Unravelling the timing, driving forces and consequences of Earth's atmospheric oxygen history is a complex endeavour. It is well-established that oxygen levels were vanishingly low before ~2.3 billion years ago (Fig. 1), but the debate over subsequent levels, including the timing of the transition to near-modern levels, rages on¹⁻³. Firmer constraints on atmospheric oxygen concentrations during Earth's 'middle ages' are critical for a host of reasons, not least because the most recent estimates are highly divergent: some² fall below the probable minimum oxygen requirements of the earliest forms of animal life, whereas others³ sit above these requirements. This uncertainty clearly undermines efforts to constrain the role of oxygen in early animal evolution¹⁻³. Writing in *Nature*, Reinhard and colleagues⁴ provide a new take on Earth's oxygenation history, by reconstructing the availability of phosphorus in the ocean over the last 3.5 billion years. Their reconstruction provides support for a prolonged low-oxygen world.

Phosphorus (P) is generally considered the ultimate limiting nutrient for primary productivity on geological timescales⁵. The bioavailability of P through time can thus be considered a key control on organic carbon (C) production and ultimately oxygenation. Reconstructing P concentrations in the ancient oceans is, however, notoriously difficult. Previously the approach has been to measure the P content of iron-rich chemical sediments such as banded iron formations^{6,7}, which are thought to reflect dissolved concentrations in the ocean at their time of formation. This has led to wildly variable results⁶⁻⁸, dependent on the precise way in which dissolved phosphate concentrations are back-calculated from total P contents in the rocks (Fig. 1). Furthermore, the temporal record of iron-rich, marine chemical sediments is discontinuous, preventing reconstruction of dissolved phosphate concentrations across key intervals of Earth history.

Recognising these limitations, Reinhard and colleagues⁴ take a different approach by compiling a spectacular dataset of P concentrations in 7,970 shale samples from marginal marine environments. Shales have the advantage over banded iron formations in that they are ubiquitous throughout Earth history. Reinhard and colleagues⁴ identify a clear increase (about 4-fold on average) in the P content of shales deposited after about 800 million years ago, relative to more ancient settings. The authors evaluate these data within a quantitative biogeochemical framework which also considers the potential role of nitrogen (N) limitation. The results are of major potential significance for understanding Earth's protracted oxygenation history.

Reinhard and colleagues⁴ argue that low P concentrations in shallow marine shales deposited throughout the majority of early Earth history reflect enhanced scavenging from anoxic, iron-rich oceans, leading to severe P biolimitation. This P scarcity before approximately 800 million years ago led to increased molar C/P ratios in the biomass of primary producers, with C/P ratios of 300:1 or more, compared to the modern Redfield ratio of 106:1. The model outputs also

suggest that P is the major limiting nutrient in both pervasively anoxic and well-oxygenated oceans. Between these regimes, however, there exists a range of intermediate oxygenation states under which productivity and global oxygen production may be N-limited. Reinhard and colleagues⁴ interpret this as a bi-stability in atmospheric oxygen levels controlled by P-limitation, which resulted in a stable low-oxygen world prior to 800 million years ago. Unfortunately, however, model uncertainties make it difficult to constrain precisely how low atmospheric oxygen was in this low-oxygen world⁴.

The authors' arguments are compelling, but interpretation of the dataset that forms the basis for this study does hinge on several important assumptions, not least that the P contents of marginal marine shales track first order trends in dissolved phosphate. Three main factors control dissolved P concentrations in the ocean – weathering influxes, removal to the sediment, and the potential for redox-promoted recycling of P back to the water column. Reinhard and colleagues' interpretation requires the removal process to be the main control, and although changes in weathering influxes of P have likely been large through Earth history, the authors suggest that this would be unlikely to lead to large-scale shifts in organic C burial (and thus atmospheric oxygen), unless the changes were extreme. Further consideration of the potential role of weathering-induced changes in P bioavailability will likely require more detailed study of specific periods in Earth history.

The issue of redox-promoted P recycling is particularly difficult to resolve. Phosphorus recycling is enhanced under anoxic conditions, particularly through the production of dissolved sulphide, which results in the dissolution of iron oxide minerals and release of scavenged P, and the preferential mining of P from organic matter during bacterial sulphate reduction⁹. These processes can result in significant fluxes of P back to the water column, substantially increasing C/P ratios in the deposited sediment⁹. Reinhard and colleagues⁴ implicitly include a recycling component in their model, but the extent to which the degree of recycling has evolved through time is currently poorly understood. Sulphidic marginal marine environments became more prevalent through early Earth history^{1,10} as a consequence of rising sulphate concentrations in the ocean, initially in association with possible 'whiffs' of oxygen prior to Earth's first persistent rise in atmospheric oxygen, and subsequently during Earth's 'middle ages' (Fig. 1). Enhanced P recycling to the water column would be a natural consequence of this oceanic redox evolution, such that the relatively constant P content of shales deposited across Earth's first rise in atmospheric oxygen and beyond may actually correspond to a progressive increase in P bioavailability in the water column.

Notwithstanding these potential complications, Reinhard and colleagues⁴ provide a remarkable record of the shallow marine phosphorus inventory through time. While the debate on oxygen concentrations across Earth's 'middle ages' will doubtless continue, the authors have identified a shift in the P content of shallow marine shales after about 800 million years ago that broadly coincides with the probable development of more oxygenated conditions in the ocean, major perturbations to Earth's climate, and the emergence of animal life. Providing a more accurate constraint on the timing, cause and consequences of this shift should be a future focus.

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Figure Caption

Figure 1. Reconstructions of oxygen, phosphorus and ocean redox conditions through time. a, Excluding possible whiffs of oxygen (blue arrows), there were two main rises in atmospheric O₂ concentrations, around 2.3 billion and 800 million years ago (ref 1). However, O₂ concentrations between these periods are less clear^{2,3}. b, Estimates of phosphorus concentrations in the ocean are similarly variable^{6,7,8}. Reinhard and colleagues⁴ compile P concentrations from shales, and identify a 4-fold increase in P concentrations around 800 million years ago. This leads them to argue that P-limitation supported low levels of O₂ for most of Earth's history. Estimates from the shale record are based on the suggestion⁴ that P concentrations prior to 800 million years ago were similar to those defined by ref 8. Upwards black arrows indicate minimum estimates; downwards black arrows represent maximum estimates. c. Sulphide became more prevalent in anoxic oceans after about 2.7 billion years ago, potentially increasing phosphorus recycling back to the water column.