

most direct effect of human activity on the oceanic N cycle is the massive application of fertilizers full of bioavailable N, much of which makes its way to the ocean either via rivers or through long-range atmospheric transport<sup>15</sup>.

Currently, we can only speculate about how these perturbations, and their interactions, will alter the marine nitrogen cycle and affect its homeostasis. Given that most stabilizing feedbacks operate on timescales of decades and longer, it is likely that we will see widespread temporal imbalances in the marine nitrogen cycle. Indeed, the available time series from instrumental records and sedimentary records spanning the past 200 years suggest that changes in major biological fluxes can be large, although their relationship to forcing agents and their net effect on the overall N budget remain uncertain. It is also unclear to what degree changes in the N cycle will affect the working of the other biogeochemical cycles in the ocean, in particular the biological carbon pump. Perhaps the largest uncertainty stems from the question of whether and how fast organisms and ecosystems can adapt to the changed environmental conditions, and

whether they do so through phenotypic or genotypic changes. Clear latitudinal trends in the N:P ratio of phytoplankton communities have been found<sup>14,15</sup>. It remains to be seen whether the shifting boundaries of major ocean biomes can alter the large-scale patterns of plankton N:P ratios, and how that would modify the stabilizing feedbacks.

Redfield's pioneering view of the ocean as a system capable of homeostatic regulation helped pave the way for the broader and now commonplace recognition that life alters its environment at a global scale. Many of his insights have endured the ongoing confrontation with new data and refined explanatory models. Yet he was keenly aware of the limitations of his explanations: "Whatever its explanation, the correspondence between the quantities of biologically available nitrogen and phosphorus in the sea and the proportions in which they are utilized by the plankton is a phenomenon of great interest". In light of the pace of basic discoveries and the growing imprint of humankind on the ocean, our understanding of the oceanic N:P ratio is likely to continue to encounter new surprises. □

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# The elements of marine life

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Today, the ratio of carbon to nitrogen and phosphorus in marine organic matter is relatively constant. But this ratio probably varied during the Earth's history as a consequence of changes in the phytoplankton community and ocean oxygen levels.

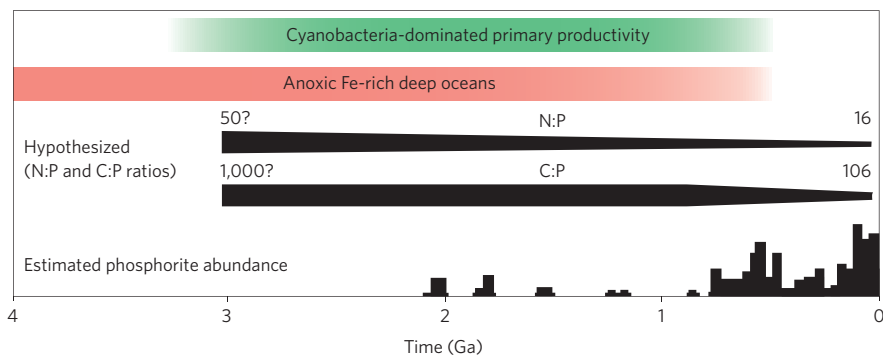
Few observations have had as profound an impact on biological and chemical oceanography as Alfred Redfield's recognition that the elemental stoichiometry of most marine life is nearly constant<sup>1</sup>. As originally noted by Redfield in the 1930s — and subsequently confirmed by thousands and thousands of measurements — there is a strong linear correlation (with a slope of 16:1) between dissolved nitrate and phosphate levels in the modern oceans. This correlation between nitrate and phosphate gave rise to the concept that marine life had a fixed carbon:nitrogen:phosphorus ratio (C:N:P = 106:16:1), which subsequently became known as the Redfield ratio. This ratio has become a cornerstone in our understanding of marine carbon and

nutrient cycling. But given that the oceans have been subject to major biological and geochemical evolutionary events throughout the geologic record, we should question whether C:N:P ratios have really remained invariant through the Earth's history<sup>2</sup>.

The Redfield ratio may arise from the physiology of phytoplankton<sup>3</sup>, but this notion is based largely on empirical observations<sup>4</sup>. The covariation of dissolved nitrate and phosphate in modern marine settings, from which the Redfield ratio has been inferred, may be based on biological feedbacks but is also strongly dependent on the mixing of water masses with disparate N:P ratios<sup>4</sup>. Furthermore, although the Redfield ratio seems to be a global phenomenon, different groups of phytoplankton have widely varying

C:N:P ratios. For instance, the N:P ratios of modern marine primary producers span an order of magnitude<sup>4–6</sup>.

A shift in the ecology of primary producers could therefore result in a non-Redfield ocean. In the modern ocean, different marine biomes have disparate C:N:P ratios. Therefore, as the balance of biomes changes, so too could the mean elemental stoichiometry of marine life. There have been several well-documented transitions in the phytoplankton composition of the ocean throughout the Earth's history<sup>7,8</sup>. The most recent was, perhaps, the evolution of diatoms around 200 million years ago. Diatoms are ubiquitous in modern ecosystems, but only reached their present abundance in the past 20 million years. Regions in which



**Figure 1** | Trends in C:N:P ratios through time. Ratios of C:P and N:P may have been higher in the Precambrian (more than 540 million years ago), when the oceans were anoxic and cyanobacteria were the dominant primary producers. Higher C:P ratios may have led to inhibited apatite burial in marine sediments and may thus provide an explanation for the limited number of Precambrian phosphorites. Phosphorite abundances based on deposit occurrences and updated from ref. 14.

productivity is dominated by diatoms can be characterized by low N:P ratios. For example, there is an N:P ratio of 11:1 in some diatom-rich portions of the Southern Ocean. This opens up the possibility that for the 90% of the Earth's history for which diatoms did not exist, N:P ratios may have been quite different from today. Moreover, eukaryotic algae — phytoplankton similar to diatoms — only became the predominant phytoplankton between 800 and 600 million years ago.

Prior to that, the phytoplankton community was dominated by cyanobacteria<sup>8</sup>, which evolved at least three billion years ago<sup>9</sup>. Relative to other groups of phytoplankton, cyanobacteria are extremely plastic in their elemental composition: their C:P and N:P ratios can span more than one order of magnitude<sup>5,6</sup>. Much of this variability arises as a response to nutrient stress, suggesting that a shift in nutrient regimes is essential in driving a large-scale deviation from the Redfield ratio in marine ecosystems.

Massive shifts in marine nutrient cycles occurred during the protracted oxygenation of the Earth's surface. For most of the Earth's history, the global ocean was largely anoxic and iron-rich (ferruginous)<sup>9,10</sup>. These ferruginous conditions were initially thought to have vanished about 1.8 billion years ago, following the last gasp of banded iron formation deposition. However, beneath an oxygenated surface layer, deeper water iron-rich conditions may have persisted until at least 580 million years ago<sup>9,10</sup>.

Under widespread anoxia, the cycling of N and P would be very different from what occurs today (Fig. 1). Marine N speciation is directly controlled by ambient oxygen concentration. Most importantly, at the interface between anoxic and oxic

conditions large amounts of bioavailable N can be removed from the marine system through denitrification and anaerobic ammonium oxidation (anammox). Both processes transform bioavailable N to N<sub>2</sub>. In a global ocean characterized by oxygenated surface waters and anoxic deep waters, extensive loss of bioavailable N probably led to substantial N stress<sup>11</sup>, spurring extensive biological N fixation, and, potentially, mean C:N ratios that deviated substantially from the Redfield ratio.

The marine phosphorus cycle was probably similarly shaped by changing oxygen levels and marine iron concentrations. In particular, ferric iron oxyhydroxides, which would have been plentiful in ferruginous waters, scavenge large amounts of phosphate<sup>12</sup>. Phosphate may therefore have been trapped in the deeper portions of the ocean during this time, potentially introducing pronounced phosphorus stress to surface ecosystems. This deep-sea phosphorus trap probably reduced overall marine productivity<sup>12</sup> and may have further driven the oceans away from Redfield C:N:P ratios. Cyanobacteria were the predominant phytoplankton in the oceans while ferruginous conditions prevailed<sup>8</sup>, so their stoichiometric plasticity could potentially have accommodated far higher C:P ratios than possible in the modern ocean.

It stands to reason that oxygenation and the radiation of different phytoplankton groups could have shifted the elemental stoichiometry of marine life. Conversely, some deviations from the Redfield ratio in biomass may be too subtle to have driven large-scale changes in biogeochemical cycling. For instance, although diatoms can have distinctive C:N:P ratio, it is not clear whether diatom diversification led to any significant shift in the average N:P ratio of

marine biomass. However, C:N:P ratios were most probably strikingly different from the Redfield ratio in a cyanobacteria-dominated ferruginous ocean — the marine conditions through most of the Earth's history. In particular, C:P ratios might be expected to have been substantially higher in early cyanobacteria-dominated oceans.

Persistently high C:P ratios in the Earth's early ocean would have had significant consequences for marine biogeochemical cycling. For instance, the formation of the diagenetic mineral apatite is the most important pathway of marine P burial in the modern oceans. When organic matter with a higher C:P ratio is remineralized in marine sediments, less P will be released to the pore waters for each unit of organic carbon decomposed, leading to lower apatite saturation and hence limited apatite formation. We can assume that less organic P was buried as apatite when biomass C:P ratios were high, leading to a P cycle that was very different from that in modern oceans. Further, high mean C:P ratios in a cyanobacteria-rich ferruginous ocean could be a key factor responsible for the paucity of Precambrian phosphorus-rich deposits<sup>13</sup>. In this light, deviation from the Redfield ratio can provide a simple explanation for a prominent but enigmatic feature of the sedimentary record — the general lack of old phosphorites.

Large variations may well have characterized the elemental stoichiometry of marine life through time. In this light, Redfield's greatest contribution might not have been the discovery of a fixed or static biological law, but rather his drawing attention to how the elemental stoichiometry of marine life regulates biogeochemical cycling. □

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