Co-evolution of eukaryotes and ocean oxygenation in the Neoproterozoic era

Timothy M. Lenton^{1*}, Richard A. Boyle¹, Simon W. Poulton², Graham A. Shields-Zhou³ and Nicholas J. Butterfield⁴

The Neoproterozoic era (about 1,000 to 542 million years ago) was a time of turbulent environmental change. Large fluctuations in the carbon cycle were associated with at least two severe — possible Snowball Earth — glaciations. There were also massive changes in the redox state of the oceans, culminating in the oxygenation of much of the deep oceans. Amid this environmental change, increasingly complex life forms evolved. The traditional view is that a rise in atmospheric oxygen concentrations led to the oxygenation of the ocean, thus triggering the evolution of animals. We argue instead that the evolution of increasingly complex eukaryotes, including the first animals, could have oxygenated the ocean without requiring an increase in atmospheric oxygen. We propose that large eukaryotic particles sank quickly through the water column and reduced the consumption of oxygen in the surface waters. Combined with the advent of benthic filter feeding, this shifted oxygen demand away from the surface to greater depths and into sediments, allowing oxygen to reach deeper waters. The decline in bottom-water anoxia would hinder the release of phosphorus from sediments, potentially triggering a potent positive feedback: phosphorus removal from the ocean reduced global productivity and ocean-wide oxygen demand, resulting in oxygenation of the deep ocean. That, in turn, would have further reinforced eukaryote evolution, phosphorus removal and ocean oxygenation.

ife and the planet have 'co-evolved' through most of Earth's history¹, with the evolution of life affecting the environment and changes in the environment affecting evolution. This twoway feedback coupling became particularly strong during the Neoproterozoic era^{1,2}, which saw profound changes in eukaryotic life and the Earth system (Fig. 1). Climate cooled into a series of glaciations, including the extreme Sturtian and Marinoan events and the less severe Gaskiers. There were unprecedented fluctuations in the carbon cycle (Fig. 1c), and changes in ocean redox state culminated in the eventual oxygenation of parts of the deep ocean (Fig. 1b).

Previous studies³⁻⁵ have tended to focus on environmental change — especially oxygenation of the atmosphere and oceans — as a pre-requisite for the evolution of complex multicellular life. A minimum threshold of oxygen is necessary for the existence of animals, and over half a century ago it was argued that a rise in atmospheric oxygen initiated a rapid evolution of metazoans6. The argument has reappeared repeatedly7,8 and is currently back in vogue3,9, but several aspects of it can be questioned. First, many simple animals do not need a lot of oxygen¹⁰. Some sponges¹¹, for example, require roughly 0.1 ml l⁻¹ of dissolved O₂, and some bilaterian worms¹¹ need only around 0.02 ml l⁻¹ O₂ — equivalent to water equilibrated with roughly 0.0035 of the present atmospheric level (PAL) of O₂. Second, there has been sufficient oxygen in the atmosphere to ventilate the surface ocean above these O₂ concentrations¹² since the Great Oxidation approximately 2,400 Myr ago (Ma). Before that, once oxygenic photosynthesis had evolved by, at the latest, ~2,700 Ma (ref. 1), localized oxygen oases^{13,14} with O₂ >0.01 PAL would have existed in the surface ocean. Afterwards, deep convection of oxygenated high-latitude surface waters could potentially have ventilated parts of the Proterozoic deep ocean¹⁵. Finally, although there is compelling evidence for oxygenation of parts of the deep ocean late in the Neoproterozoic^{4,5,16}, there is as yet only indirect evidence^{17,18} for a rise in atmospheric oxygen at this time.

We thus think it is worth considering if there are mechanisms¹⁹ by which the deep ocean could have been oxygenated in the Neoproterozoic without requiring an increase in atmospheric oxygen. To approach the problem, we use a mechanistic framework that links the biogeochemical cycles of phosphorus, carbon and oxygen (and also considers nitrogen, sulphur and iron), focusing on the balance of oxygen supply and demand in ocean waters (Box 1), the processes of weathering on the continents (Box 2) and the redoxsensitive recycling of phosphorus from marine sediments (Fig. 2). We draw upon recent summaries of fossil and molecular clock information for the timing of the radiation of eukaryotes²⁰ and animals²¹, focusing on the evolution of key biological traits, including size, hard parts, motility and predation. Inspired by earlier work¹⁹, we consider how eukaryote evolution increased the efficiency of 'biological pumping' of carbon in the ocean, and thus shifted oxygen demand to greater depths in the water column. We argue that this increased phosphorus removal from the ocean into sediments, thus reducing deep ocean phosphate concentration, surface productivity and oxygen demand at depth, in a positive feedback process that could have propelled oxygenation of the deep ocean.

Early Neoproterozoic conditions

The early Neoproterozoic was part of the 'boring billion' (circa 1,850–850 Ma), so-called for the apparent slow pace of biological evolution and a widely assumed stasis in atmosphere–ocean oxygenation state. The continental crust was assembled in the supercontinent Rodinia in the earliest Neoproterozoic around 1,000 Ma. The climate was at least as warm as it is today, presumably because of increased greenhouse gas concentrations, with no evidence for glaciations between ~2,200 and ~715 Ma. Eukaryotes had already evolved, with recent estimates²⁰ placing their last common ancestor around 1,900–1,700 Ma and the divergence of major extant

¹College of Life and Environmental Sciences, University of Exeter, Exeter EX4 4QE, UK, ²School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK, ³Department of Earth Sciences, University College London, London WC1E 6BT, UK, ⁴Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, UK. *e-mail: t.m.lenton@exeter.ac.uk

REVIEW ARTICLE



Figure 1 | Timeline of biological and environmental changes spanning the Cryogenian, Ediacaran and Cambrian periods. a, Compilation of biological evidence (updated from refs 42,61): key animal traits (red dots); estimated contributions to marine export production inferred from biomarker and microfossil data (the yellow diamond marks the first substantial occurrence of eukaryotic biomarkers⁴⁴); first appearance of key eukaryotic phenomena, traits and clades (dashed lines indicate more debatable evidence).
b, Summary of ocean redox conditions at different depths, updated from ref. 16 (question mark indicates possible interval of intermediate-water euxinia).
c, Secular variation in the carbon isotope composition of marine carbonates.
d, Strontium isotope composition of sea water. Figure adapted from ref. 57.

clades before 1,200–1,000 Ma. Some early eukaryotes were multicellular, with fossils of red algae showing limited cell differentiation by ~1,200 Ma (ref. 22). Most of these early fossils occur in shallow marine sediments, but some were living in terrestrial lakes at roughly 1,200–1,000 Ma (ref. 23). Biomarker evidence suggests that the open ocean remained dominated by prokaryotes, although there may be a preservation bias caused by widespread microbial mats²⁴.

The atmosphere is widely thought to have had around 0.01-0.1 PAL O₂ through much of the Proterozoic eon²⁵. However,

NATURE GEOSCIENCE DOI: 10.1038/NGEO2108

we only really have a reliable lower limit on atmospheric oxygen of 0.01 PAL O₂ from palaeosols at around 1.85 and 1.1 Gyr ago (Ga)²⁶. There are relatively good constraints on oceanic redox state during the Proterozoic, albeit at sparse intervals²⁷ (for example, at 1.8, 1.7, 1.64, 1.45 and 1.2 Ga), indicating widespread ocean anoxia (40-100% of seafloor area). The deep ocean was predominantly ferruginous (iron-rich)12,27 but with euxinia (anoxic and sulphidic conditions) present at intermediate depths, presumably where highest oxygen demand was concentrated (for example, in upwelling zones) (Fig. 2a). Euxinic waters were sufficiently widespread to remove most molybdenum from the oceans²⁸, but not so extensive as to prevent enrichment of molybdenum in organic sediments, suggesting euxinic waters covered 1-10% of seafloor area^{29,30}. Conceivably there could have been fluctuations between ferruginous and more widespread euxinic conditions^{27,31}. Furthermore, some bottom waters¹⁵ may have had low concentrations of oxygen supplied by the overturning of high-latitude surface waters (Box 1).

The existence of widespread ocean anoxia has been used to infer that atmospheric oxygen was well below the present level for most of the Proterozoic. However, ocean redox state also depends on the limiting nutrient concentration in the ocean, which determines organic carbon production and hence oxygen demand at depth (Box 1). Creating widespread deep ocean anoxia (in simple box models) at current concentrations of the ocean macro-nutrients phosphorus and nitrogen only requires atmospheric oxygen to drop to 0.5-0.7 PAL O₂ (refs 32,33). This is well above the 0.01-0.1 PAL O₂ range often given for the Proterozoic²⁵. If limiting nutrient levels (and oxygen demand) were lower than present in the Proterozoic, atmospheric oxygen would have had to have been lower to produce widespread anoxia. However, if early Proterozoic phosphorus levels were above present levels³⁴, and phosphorus was the ultimate limiting nutrient then as it is now, the atmosphere could conceivably have had >0.5-0.7 PAL O₂ and the deep ocean would have remained anoxic (Box 1).

The limited extent of euxinic waters^{12,31} in the Proterozoic ocean is consistent with euxinia requiring greater oxygen demand than just anoxia, including the exhaustion of nitrate and iron. Furthermore, the development of euxinia tends to be self-limiting because it requires the localized exhaustion of nitrate³⁵, which, if the resulting water is upwelled, can no longer support productivity and oxygen demand. This makes sulphate reduction extremely rare in today's ocean, despite a large reservoir of sulphate. It means that where euxinia did occur in the Proterozoic ocean, oxygen demand must have been fuelled either by nitrogen fixation³⁵, localized buildup and upwelling of ammonium³⁶, or a supply of nitrate-rich surface waters from elsewhere. Lower sulphate levels³⁷ than present (probably 500-3,000 µM) can also help explain restricted euxinia in the Proterozoic ocean. Taken together, these considerations mean that limited euxinia cannot immediately rule out high phosphorus levels in the Proterozoic ocean. Therefore, widespread anoxia could have occurred under near-present oxygen levels.

Turning to what could have maintained the Proterozoic ocean in an anoxic and partially euxinic state, it was originally proposed¹⁹ that organic matter derived from single-celled phytoplankton sank slowly through the water column, concentrating oxygen demand near oxygen production. This mechanism can help explain euxinia at shallow depths. However, it would have reduced oxygen demand in deeper waters, making them less prone to anoxia, because their oxygen supply comes from the atmosphere through the overturning of high-latitude surface waters (Box 1). To help explain widespread Proterozoic deep ocean anoxia, we invoke an additional positive feedback mechanism (Fig. 2a): more phosphorus is recycled from organic matter in sediments overlain by anoxic water, particularly when fully euxinic³⁸, and the removal of phosphate by sorption on ferric oxyhydroxides is prevented because those minerals no longer form in the water column or persist during early diagenesis³⁹. Crucially, the majority of phosphorus burial and recycling in the

Box 1 | Controls on ocean oxygenation state

Oxygen concentration in a water parcel below the depth of winddriven mixing depends on the balance of oxygen supply and demand fluxes. Oxygen supply flux is determined by the concentration of oxygen in the surface waters that exchange with this location (in turn equilibrated with the atmosphere above), the rate of mixing or advection of oxygen to the parcel at depth, and any removal of oxygen on the way there (by remineralization). The oxygen demand flux in the water parcel is determined by: the supply flux of limiting nutrient to the surface photic zone above; the fraction of this that goes into export production; the stoichiometry of oxygen demand to nutrient in the resulting sinking organic material; and the rate of sinking of the organic matter through the water parcel (determining the amount of remineralization that occurs within it). If oxygen is exhausted in a water parcel, bacterial respiration will preferentially use the electron acceptor that gives the highest free energy yield per unit of organic carbon, following a well-established hierarchy: NO3, Fe³⁺, SO₄ and methanogenesis. Phosphorus is the ultimate limiting nutrient determining oxygen demand over long timescales, even though nitrogen is often proximately limiting (that is, it runs out first), as long as biological nitrogen fixation tends to counteract any deficit of nitrogen due to denitrification.

In a simple three-box ocean model⁹¹, the water parcel at depth becomes the entire deep ocean (d) and warm, low-latitude surface waters (l) where nutrients are fully utilized are distinguished from cold, high-latitude surface waters (h) where nutrients are incompletely utilized but oxygen enters to ventilate the deep ocean. All sinking material is assumed to be remineralized in the water column, leading to a relationship for oxygen concentration in the deep ocean^{33,91}:

ocean (around 80% today) occurs on shallow continental shelves that comprise only a minor fraction (around 10% today) of the seafloor area. Today these shelf sea floors are largely oxygenated, but if much slower sinking of organic material in the Proterozoic ocean created anoxia (and potentially euxinia) at shallow depths — including the bottom of the shelf seas — this would have been accompanied by a large flux of phosphorus recycling from the sediments. This in turn would have increased the concentration of phosphorus in the ocean, fuelling more new production and anoxia^{40,41} in a strong positive feedback, which box models indicate can tip the open ocean into a globally anoxic state^{32,41}.

Evolution of the biological pump

Shortly before the Neoproterozoic glaciations, there seems to have been a significant diversification of eukaryotes⁴², including a rise in ecological prominence of algae, and the appearance of various protozoans and possibly fungi (Fig. 1a). The Chuar Group (~770–742 Ma) hosts vase-shaped microfossils interpreted as the remains of testate amoebae⁴³, together with the first substantial expression of eukaryotic biomarkers⁴⁴. Scale microfossils appear in the broadly correlative Fifteenmile Group⁴⁵. This is the first clear evidence of a eukaryote-dominated biological pump.

A shift from a cyanobacteria-dominated biological pump to a eukaryote-dominated one is likely to have led to faster sinking fluxes of organic carbon (Fig. 2b) through an increase in average cell size, greater propensity of such algae to form particulate aggregates, and ballasting due to tests and scales^{46–48}. This need not have immediately altered total oxygen demand, which is set by the flux of limiting nutrients into surface waters and how completely they are utilized (Box 1). However, a faster biological pump would have spread the same oxygen demand out over a greater depth of the water column¹⁹, weakening peak oxygen demand, and shifting the zone of maximum

$O_2(d) = O_2(h) - r[P(d) - P(h)]$

Where $O_2(h)$ (~325 µM today) is the oxygen concentration in high-latitude surface waters where deepwater formation occurs; [P(d) – P(h)] (0.91 µM today) represents the amount of phosphorus in upwelling deep water that is used to generate export production in high-latitude surface waters; and r = 170 is the Redfield ratio of O_2 consumption to phosphate production during remineralization. Using these values, the deep ocean becomes anoxic ($O_2(d) = 0$) when $O_2(h)$ and therefore atmospheric $O_2 \approx 0.5$ PAL. However, even under today's atmospheric O_2 of 1 PAL, if all the upwelling P(d) = 2.15 µM was utilized (that is, P(h) = 0), the deep ocean would go anoxic.

The 3-box model⁹¹ shows no dependence of O₂(d) on either thermohaline circulation $(d \rightarrow l \rightarrow h \rightarrow d)$ or high-latitude overturning $(d \leftrightarrow h)$, nor can it explore the effect of changes in remineralization depth. However, a 4-box model⁹² that distinguishes intermediate-depth waters shows that intermediate and deepwater O2 levels are sensitive to all of these factors. Deep waters generally have higher O₂ (and are hence harder to turn anoxic) than intermediate waters because thermohaline and overturning circulations ventilate them first, and more remineralization happens per unit volume in the shallower intermediate waters. A multibox model³² captures these effects and also incorporates positive feedback between bottom-water anoxia and phosphorus recycling from sediments. This creates a threshold at $O_2 \approx 0.7$ PAL, when anoxic waters expand vertically on to the bottom of the continental shelves and phosphorus recycling from shelf sea sediments tips the deep ocean into a globally anoxic state³².

oxygen demand from shallow waters to deeper waters and shelf sea sediments (Fig. 2b). If this suppressed anoxia in shelf sea bottom waters (by transferring oxygen demand from the water column to the sediments), it would have led to significantly more efficient phosphorus removal, both in organic matter³⁸ and adsorbed to iron oxides³⁹. The phosphorus concentration of the deep ocean would then have dropped to a new steady state — where phosphorus sinks again balanced the source from weathering (over 10⁴-year timescales) causing a concomitant global drop in productivity. This would have lowered total oxygen demand globally, reducing the volume in which it could have supported sulphate reduction and euxinic conditions, and thus causing a shift towards more ferruginous conditions.

This mechanism could help explain why there seems to have been a shift away from partially euxinic conditions to more purely ferruginous conditions before the Sturtian glaciation¹⁶, despite a general trend of sulphate accumulating over Proterozoic time³⁷. Notably, the Fifteenmile Group shows oxygenated surface waters and mostly ferruginous conditions below storm wave base¹¹, and the Chuar Group sees widespread ferruginous conditions^{16,49} in a basin in contact with the open ocean. The predicted decrease in ocean phosphorus level and change in redox state should in turn have reinforced eukaryote evolution on the (more oxygenated) shelves (Fig. 2b), because it would have stopped sub-surface H₂S production, which tends to inhibit (aerobic) eukaryotes.

The deepest parts of the Proterozoic ocean would probably have had a less negative balance of oxygen supply and demand than intermediate waters above them (Box 1), and those deep waters in closest contact with high-latitude surface waters through ocean overturning would be the easiest to oxygenate. Hence if a global reduction in oxygen demand occurred before the Sturtian glaciation, these high-latitude deep waters may have been the first to oxygenate (or if there were already some oxygenated deep ocean waters¹⁵, they

Box 2 | Weathering controls on carbon dioxide, phosphorus and oxygen

To illustrate the controls on carbon dioxide in the atmosphere and ocean (*C*), phosphorus in the ocean (*P*) and oxygen in the atmosphere (O_2), we consider a simplified system of these three coupled reservoirs. This extends previous work on the Neoproterozoic⁵³ to include a crucial constraint from balancing the CO₂ cycle. CO₂ is supplied to the atmosphere–ocean system by degassing (*D*) and removed by silicate weathering (where $F_C \approx 7 \times 10^{12}$ mol yr⁻¹ and $C \approx 3.2 \times 10^{12}$ mol, giving a residence time of $\tau_C \approx 5 \times 10^5$ years today). Silicate weathering depends on uplift (*U*), any changes in weatherability (*W*) — due to biotic amplification of weathering, location of the continents or outpouring of large igneous provinces — and is an increasing function of CO₂, *f*(*C*), directly and through the effect of CO₂ on temperature (which is implicit here):

$$\frac{dC}{dt} = F_C[D - UWf(C)]$$

At steady state, which is achieved on a timescale of $\tau_C \approx 5 \times 10^5$ years, the silicate weathering flux must balance the degassing flux, UWf(C) = D. Therefore any changes in uplift (U) or weatherability (W) are counteracted by changes in C on this timescale, and only changes in degassing (D) alter the absolute flux of silicate weathering. Crucially, bulk silicate weathering is also the key source of phosphorus to the ocean (where $F_p \approx 3.6 \times 10^{10}$ mol year⁻¹ and $P \approx 3.1 \times 10^{15}$ mol, giving a residence time of $\tau_p \approx 9 \times 10^4$ years today). We include the biological possibility of selective weathering of phosphorus relative to bulk silicate rock as a factor, S. Phosphorus is removed from the ocean by burial, which is an increasing function of phosphorus concentration, b(P):

$$\frac{dP}{dt} = F_P[SUWf(C) - b(P)]$$

would have expanded in volume) (Fig. 2b). Further along the path of the thermohaline circulation, deep waters would have been progressively harder to oxygenate. The most stubbornly anoxic waters would have been at intermediate depths beneath upwelling zones with high nutrient supplies to the surface (that is, those locations that become anoxic today).

A global decrease in nutrients and new production would have tended to reduce organic carbon burial, but at the same time more efficient transport of organic carbon to depth would have increased it - leaving the sign of the net effect (that is, whether it is negative or positive) uncertain. The carbon isotope record of carbonates ($\delta^{13}C_{carb}$) shows relatively stable positive values of around +5‰ through most of the early Neoproterozoic⁵⁰ (Fig. 1c). This suggests the proportion of carbon being buried in organic form then was higher than today, consistent with a more efficient biological pump. However, the strontium isotope (87Sr/86Sr) record (Fig. 1d) suggests much lower rates of continental erosion at the time, and therefore lower absolute burial fluxes. Hence the burial flux of organic carbon is inferred to have been less than that of today, with no significant changes until much later in the Neoproterozoic⁵¹. Thus, there seems to be no clear organic carbon burial driver for rising atmospheric oxygen in the early Neoproterozoic.

The shift to a more efficient biological pump before the Cryogenian glaciations has also been proposed as a mechanism to lower atmospheric CO₂ and cool the climate⁴⁸. The argument is that it promoted sulphate reduction, thus making the ocean less acidic and lowering atmospheric CO₂, as long as H₂S was removed by reaction with Fe to form pyrite (FeS₂). However, we argue that spreading oxygen demand over a greater depth of the water column does the opposite of promoting euxinia. The proposal⁴⁸ is also at odds with widespread ferruginous ocean conditions at the time^{11,16,49} (Fig. 1b).

Steady state for the phosphorus cycle is achieved faster than CO_2 on a timescale of $\tau_P \approx 9 \times 10^4$ years, with burial balancing inputs from weathering: b(P) = SUWf(C). Therefore transient changes in weathering inputs will lead to transient changes in P. However, on the $\tau_C \approx 5 \times 10^5$ year timescale of CO_2 steady state, silicate weathering flux is set by degassing, therefore b(P) = SD and only selective weathering of phosphorus by biology can decouple phosphorus burial from degassing. This in turn has implications for atmospheric oxygen, because oxygen is supplied to the atmosphere by organic carbon burial, which depends on phosphorus burial and on the carbon/phosphorus burial ratio, which is a declining function of oxygen concentration^{38,40}, $r(O_2)$. Oxygen is removed by oxidative weathering, which here depends only on the supply of new rock by uplift (because it only becomes sensitive to oxygen at very low concentrations):

$$\frac{dO_2}{dt} = F_0[b(P)r(O_2) - U]$$

Today, $F_o \approx 7.8 \times 10^{12}$ mol year⁻¹ and $O_2 \approx 3.7 \times 10^{19}$ mol, giving a residence time of $\tau_o \approx 5 \times 10^6$ years — much longer than that of CO₂. However, if $O_2 \approx 0.1$ PAL in the early Neoproterozoic, it could have had a comparable residence time to CO₂ and they may have reached steady state together. Either way, at steady state, $SDr(O_2) = U$ and only changes in uplift, degassing or selective weathering of phosphorus by biology could have driven changes in atmospheric oxygen. Therefore, increases in the overall weatherability of the land surface (W) due to biology, tropical location of the continents or the outpouring of large igneous provinces — should not have altered atmospheric oxygen.

Weathering into glaciations

The favoured mechanism for climate cooling in the Neoproterozoic is CO₂ drawdown caused by an increase in chemical weathering rate (or weatherability) of the land surface⁵²⁻⁵⁴. Chemical weathering also affects the oxygenation state of the planet through the liberation of reactive phosphorus from rocks, which ultimately determines the flux of organic carbon that can be buried in the ocean, and thus the long-term source of atmospheric oxygen. Hence it has been suggested that an increase in bulk silicate weathering rate (continental weatherability) could have caused both global cooling and a rise in atmospheric oxygen in the Neoproterozoic⁵³. However, there is no evidence as yet for a significant rise in atmospheric or oceanic¹⁶ oxygen levels before the Cryogenian glaciations. This can be explained by the fact that increases in the flux of silicate weathering cannot generally be sustained on geologic timescales without a corresponding increase in the supply flux of CO₂ from degassing processes (Box 2). Thus, if an increase in continental weatherability caused CO₂ drawdown and cooling into the Cryogenian glaciations⁵²⁻⁵⁴, this need not have caused a rise in atmospheric oxygen (Box 2).

Early modelling work⁵² showed that continental weatherability must have increased by a factor of 3 to 4 in the early Cryogenian period to produce the cooling necessary to account for glaciations. Evolution of the terrestrial biosphere was suggested as a cause⁵², but as yet there is no compelling evidence for such developments in the Neoproterozoic era. Instead, geological drivers of increased weatherability may have been sufficient to cause Cryogenian glaciations. Widespread rifting of the supercontinent Rodinia began around 825 Ma (or possibly earlier) and produced smaller land masses that ended up in equatorial latitudes. This alone would have tended to increase the weatherability of the land surface, by making it wetter and placing it in the warmest locations. The resulting drawdown

NATURE GEOSCIENCE DOI: 10.1038/NGEO2108

of atmospheric CO₂ and cooling is estimated to have been large, but insufficient to have triggered global glaciations⁵⁴. Hence an additional causative factor has been invoked⁵⁴: the emplacement of highly weatherable large basaltic provinces from 825 Ma onwards. This is based on the idea that a series of mantle super-plumes broke up Rodinia^{50,55}. If a large basaltic province erupted in a moist tropical location (or was moved into the tropics by continental drift), it may have been sufficient to trigger extreme glaciations⁵⁴. The Franklin Large Igneous Province is a good candidate, dated at 716.5 Ma, around the inception of the Sturtian glaciations⁵⁶ — and an outpouring of readily weatherable volcanic rocks is consistent with a decrease in seawater ⁸⁷Sr/⁸⁶Sr before the Sturtian^{50,57} (Fig. 1d).

Biological and geological mechanisms for enhancing continental weatherability are complementary, such that any life already on land would accelerate the weathering of basalt provinces. Emplacement of basalt provinces would be expected to lead to some temporary pulses of phosphorus to the ocean as they began to weather, in turn driving intermediate ocean waters toward euxinic conditions. Consistent with this, the upper part of the Chuar Group (>742 Ma) shows a possible short-lived shift from ferruginous to euxinic water conditions^{16,49} (Fig. 1b). Changes in molybdenum cycling suggest that there may have been enough sulphidic water (1–4% of the ocean) to remove molybdenum from the oceans⁵⁸, consistent with a short-lived, global pulse of phosphorus weathering⁵⁹.

Animal origins and the effects of filter feeding

Whatever drove the climate to cool culminated in a long and severe interval of glaciations, including the Sturtian and Marinoan postulated Snowball Earth events. It has long been thought that these glaciations posed a major barrier to the survival — let alone evolution — of eukaryotic life. Yet the pre-glacial fossil record⁴² (including red algae, green algae, lobose and euglyphid amoebae, and possible fungi) indicates that numerous eukaryote lineages continued through the glaciations (Fig. 1a). Perhaps the glaciations themselves, or the refugia for life within them, were not as harsh as has sometimes been assumed. After all, extreme cold environments today can harbour diverse prokaryote and eukaryote communities, including animals⁶⁰. Compilations of eukaryotic diversity over time do, however, show a significant drop in diversity during the interval of glaciations⁶¹ (which may be a sampling issue), and a major turnover in the taxonomic composition of pre- and post-glacial biotas.

More controversially, several recent studies argue for the presence of simple animal life in the form of sponges during and even before the interval of glaciations^{21,62,63}. The last common ancestor of all extant animals is estimated from molecular clocks²¹ to have lived around 800 Ma, before the Cryogenian glaciations, with stem group sponges splitting from the rest of the Metazoa roughly 780 Ma and crown group sponges arising roughly 700 Ma. There is argued to be body-fossil evidence of sponges before the Marinoan glaciation⁶² and steroid biomarkers for sponges⁶³ before the end of the Marinoan glaciation (at 635 Ma) — but these claims require further assessment⁶⁴. The apparent consistency with molecular clock estimates involves some circular reasoning⁶⁴ in that the calibration of the molecular clock assumes biomarker evidence⁶³ of sponges at 713 Ma.

If sponges were present during the Cryogenian period, this would undermine the argument that the appearance of the first metazoans was a response to increasing ocean oxygenation. Between the Cryogenian glaciations there is evidence for persistently ferruginous deep ocean conditions (Fig. 1b), with no clear shifts or trends in deep ocean redox state, and an ongoing mixture of oxygenated and anoxic outer shelf seas¹⁶. Marginally oxic shelf sea floors would not have prohibited the presence of sponges as some are well adapted¹¹ to low O₂ (~0.1 ml l⁻¹), and actively generate an internal water current through their aquiferous system — a unique mechanism adapted for both feeding and breathing (turbulent-flow gas exchange)⁶⁵.

REVIEW ARTICLE



Figure 2 | Key steps and feedbacks in the co-evolution of eukaryotes and ocean redox state. Schematic diagrams of a generic shelf sea and upwelling ocean margin, showing redox state (O₂, oxygenated; Fe²⁺, anoxic ferruginous; H₂S, anoxic euxinic), key interactions (solid arrows indicate direct relationships and dashed arrows indicate inverse relationships), and sinking rates. Four stages are depicted. **a**, Background Proterozoic ocean state. **b**, Onset of eukaryotic algae. **c**, Onset of benthic filter-feeding animals. **d**, Onset of swimming animals with guts. A key positive feedback is that anoxia supports phosphorus recycling from sediments, increasing productivity and oxygen demand, whereas oxygenation of bottom waters increases phosphorus removal into sediments, decreasing productivity and oxygen demand.

Box 3 | Mechanisms for the evolution of Eumetazoa

Given that oxygen availability was not a significant constraint on animal evolution^{11,47}, what else can explain the delayed and dramatic appearance of this singularly influential clade? A null hypothesis is that there was no external impetus for animal proliferation. It simply took a long time to evolve the uniquely complex gene regulatory networks necessary to build tissue- and organgrade animals⁴⁷. However, the developmental evolution required involves significant changes in cellular differentiation, and an alternative perspective is that exceptional selection pressures were necessary to explain the origin of Eumetazoa.

Animal development requires the evolution of altruistic somatic cells with irreversible differentiation, which forgo their own long-term reproduction to facilitate that of separate reproductive cells. This contrasts with plants and fungi where most somatic cells are capable of de-differentiation and independent replication. A key breakthrough was probably the evolution of a cellular differentiation hierarchy93,94 between a proto-germ line retaining infinite division potential, the reproduction of which is facilitated by differentiation in other somatic cell lineages. This required multi-level selection for conflict mediation⁹⁵, whereby the opportunity for independent cell division by non-reproductive cells is restricted (for example, by limiting the number of somatic cell divisions) when the evolutionary interests of the cell and the organism conflict. This in turn was facilitated by sophisticated gene regulatory circuitry94 with conflict modifier loci95, probably involving a juvenile larval stage⁹⁴ and utilization of ancestral cellular adhesion functions⁹⁶.

Whenever sponges arose, their filter-feeding activity could have contributed to the ventilation of shelf seas⁶⁶ (Fig. 2c). Sponges are capable of clearing the water column of organic material⁶⁷, especially the smallest picoplankton⁶⁸ and dissolved organic carbon⁶⁹ (DOC), thus transferring oxygen demand from the water column to the sediment interface. The clearing of turbid cyanobacteria-dominated conditions allows light to penetrate deeper in the water column, supporting a shift to high-light-demanding eukaryote algae⁴⁷. More importantly, the preferential removal of picoplankton by sponges presents a powerful selective pressure for larger-sized eukaryotic phytoplankton. This leads to more efficient export production, further reducing oxygen demand in shallow waters and transferring it to the sediments and deeper waters. Furthermore, filter feeding provided a new pathway of phosphorus removal to sediments (which would also be enhanced by faster sinking algae), thus lowering ocean phosphate concentration and global oxygen demand. The resulting oxygenation would have facilitated the spread and proliferation of higher-oxygen-demanding Eumetazoa.

Deep ocean oxygenation and its causes

The first suggested evidence for more widespread oxygenation of oceanic waters comes a few million years after the Marinoan glaciation⁵. A plausible mechanism is that glaciation left an easily weathered, finely ground rock surface, which, in the warm, wet aftermath of glaciation, produced a pulse of phosphorus weathering to the ocean³⁴, consistent with massive phosphorite deposits at the time⁷⁰. Initially, increased phosphorus input to the ocean would have led to an increase in new production, oxygen demand and anoxia (10⁴-year timescale). Then it would have tended to increase organic carbon burial and atmospheric oxygen (10⁶-year timescale), consistent with elevated marine sulphate concentrations⁷¹. However, the signal of ocean oxygenation⁵ (increased molybdenum, vanadium and uranium) is short-lived. Hence anoxic and ferruginous conditions may have returned to their previous extent, consistent with other analyses^{16,71,72} (Fig. 1b). This Kin selection⁹⁷ is a mechanism by which somatic cells can evolve to not reproduce — if the soma and germ line share genetic material. This will happen if both the germ line and the soma are descended from an obligate single cell bottleneck and are thus closely genetically related. But for a single-cell bottleneck to consistently occur in an ordered manner, a tightly controlled gene regulation program is necessary in the first place — requiring altruistic somatic cells that obey developmental instructions to facilitate the bottleneck. This 'catch-22' situation is the essence of the problem involved in explaining animal origins.

To explain the altruistic origins of Eumetazoa, a direct causal link with extreme glaciations has been hypothesized98: in the kind of localized refugia⁶⁰ where eukaryotic cells were likely to have survived Neoproterozoic glaciations, fluctuations in temperature, water potential and resource availability led to extreme and repeated founder effects, raising genetic relatedness and promoting kin selection for intercellular cooperation. Founder effects and restricted dispersal have been linked to the evolution of altruism both theoretically99 and empirically100. High genetic relatedness (and low probability of successful independent reproduction) lifted a constraint on the evolution of an altruistic soma for the first time in Earth's history. This permitted the evolution, by kin selection, of an obligate separation between undifferentiated reproductive cells and a terminally differentiated soma. Once this type of development had become 'locked in', the increased degree of specialization permitted by terminal differentiation allowed the explosive exploration of form seen in Ediacaran (and Cambrian) fossils.

fits with mechanistic reasoning (Box 2) that once excess CO_2 was removed from the surface Earth system and the silicate weathering flux again balanced degassing, no net increase in phosphorus weathering flux could be have been sustained — thus causing a return to the original atmosphere and ocean oxygenation state.

An alternative interpretation⁵ of the redox proxies is that there was some persistent, widespread oxygenation after the Marinoan, and that local changes caused the drop in trace metal abundances. This could be supported if, in the high-CO₂ aftermath of a snowball Earth, silicate weathering was limited by the supply of new rock73. Then elevated phosphorus weathering fluxes - and with them an increase in atmospheric oxygen - could have been sustained for tens of millions of years⁷³. However, the balance of evidence is against persistent, widespread oxygenation after the Marinoan, as deep ocean basins record anoxic and ferruginous conditions¹⁶ leading up to the Gaskiers glaciations (635-580 Ma) (Fig. 1b). Shallow shelves and sometimes outer shelves were oxygenated at this time¹⁶, consistent with the appearance of macroscopic, differentiated eukaryotes on them⁷⁴ (Fig. 1a), but these environments had already long been oxygenated. The iconic fossils from the Doushantuo Formation (635-551 Ma), including putative animal embryos, come from relatively shallow oxygenated water near a ferruginous deep basin^{16,72} with euxinic conditions at intermediate depth⁷² (Fig. 1b).

The first compelling evidence for widespread deep ocean oxygenation is found after the Gaskiers glaciation^{4,16} (580 Ma), and persisted for tens of millions of years — although other parts of the deep ocean still remained anoxic and ferruginous well into the Palaeozoic era (Fig. 1b). Increased nutrient loading to the ocean in the glacial aftermath, fuelling organic carbon burial and a rise in atmospheric oxygen, has been invoked to explain persistent ocean oxygenation⁴. However, the Gaskiers is widely thought to have been a 'normal' glaciation, and so it would not be expected that especially high CO_2 and temperature would drive a large pulse of phosphorus weathering in its aftermath. Instead, it is instructive to consider

REVIEW ARTICLE

alternative explanations for persistent and widespread (if not global) deep ocean oxygenation.

One possible explanation is that there was (finally) a rise in atmospheric oxygen at this time, but that it wasn't due to glaciation. Generating a sustained increase in phosphorus weathering (and hence atmospheric oxygen) requires either a mechanism to sustain an increase in silicate weathering flux on geologic timescales, or a mechanism to preferentially increase phosphorus weathering relative to bulk silicate weathering (Box 2). Land colonization driving a shift from seafloor to continental weathering could have allowed a sustained increase in silicate weathering flux, and is consistent with increasing seawater 87Sr/86Sr both before and after the Gaskiers57 (Fig. 1d). Life on land would also be expected to preferentially increase phosphorus weathering relative to bulk silicate weathering in pursuit of essential nutrients⁵³, leading to increased phosphorus burial in the ocean (Box 2), consistent with major phosphorite deposits at the time⁷⁰. However, there is as yet no direct evidence for a phase of land colonization around the Gaskiers, and rising seawater ⁸⁷Sr/⁸⁶Sr can arguably be better explained by changes in the isotopic composition of material undergoing weathering.

An alternative explanation is that the appearance of Eumetazoa triggered co-evolutionary feedbacks within the ocean that oxygenated it, without any change in atmospheric oxygen⁴⁷. Cnidarians have an estimated²¹ crown group origin around 700 Ma, and probably had benthic ancestral forms. Both bottom-dwelling soft corals⁷⁵ and cnidarian medusa⁷⁶ are capable of pumping water for active ventilation and suspension feeding. Together with sponges, these could have augmented the removal of DOC and smaller phytoplankton from the water column, substantially enhancing its oxygenation (Fig. 2c).

In addition, the first zooplankton — possessing guts and the capacity to swim — would have introduced a powerful new clearing agent into the oceans, further oxygenating the water column and triggering a shift from cyanobacterial towards eukaryotic dominance of the surface ocean² (Fig. 2d). Whenever the first jelly forms appeared in the plankton (either ctenophore 'comb jellies' or cnidarian jelly-fish), they could have increased the efficiency of the biological pump, as jelly biomass can sink very rapidly⁴⁶. The seminal 'oxygen happens' hypothesis¹⁹ argued that the key event oxygenating the water column was the evolution of the first bilaterian zooplankton, which produced rapidly sinking faecal pellets⁴⁶. However, meso-zooplankton seem to post-date the Gaskiers aftermath by tens of millions of years.

Regardless of whether the precise mechanism involved benthic filter feeding or planktonic grazing, the evolution of Eumetazoa would have shifted oxygen demand to shelf sea sediments and deeper waters in the open ocean. This in turn would have reduced total phosphorus recycling from sediments, thus reinforcing through positive feedback the shift to a more oxygenated ocean state (Fig. 2d). The resulting changes could have fed back to facilitate the rise of more mobile and predatory animal forms⁷⁷. The the same time, the efficiency of organic carbon burial is likely to have increased, which would have counteracted an overall reduction in organic carbon production owing to reduced nutrients. An overall increase in organic carbon burial⁵¹ might be consistent with a positive excursion in the $\delta^{13}C_{carb}$ record (Fig. 1c) and increased continental erosion indicated in the ⁸⁷Sr/⁸⁶Sr record⁵⁷ (Fig. 1d) in the aftermath of the Gaskiers glaciations.

The ensuing 'Shuram' extreme negative $\delta^{13}C_{carb}$ anomaly⁷⁸, ending 551 Ma (Fig. 1c), with its decoupled $\delta^{13}C_{org}$ variations, is unlikely to have been triggered by the onset of filter feeding or planktonic grazing oxidizing a massive pool of dissolved organic carbon that had accumulated in the ocean⁷⁹, because this would have rapidly drained the atmosphere of oxygen⁸⁰. The $\delta^{13}C_{carb}$ anomaly has more recently been interpreted as due to burial diagenesis⁸¹, requiring a mechanism for globally synchronous alteration⁸², such as a flux of isotopically light terrestrial organic material from land colonization⁸³. However, a lack of co-variation between $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ rules out a diagenetic origin for the anomaly⁸⁴. Self-sustaining, massive release of methane from hydrates might offer a viable explanation without depleting atmospheric oxygen⁸⁵, but at this stage we leave the Shuram as an ongoing puzzle (reviewed in ref. 82).

Testing models for deep ocean oxygenation

The timing of key evolutionary events and geochemical changes in the Neoproterozoic remain uncertain. We have reviewed two main groups of hypotheses: those involving changes in weathering affecting phosphorus input to the ocean (and hence organic carbon burial and atmospheric oxygen), and those involving evolutionary innovation affecting phosphorus removal and recycling within the ocean (and hence oxygen demand and ocean oxygenation state). Both sets of hypotheses could be better quantified in more detailed models, and potentially falsified with new data.

Three-dimensional ocean models can be used to establish which combinations of atmospheric oxygen concentration, marine phosphorus concentration and remineralization profile with depth can reproduce available proxy data for ocean redox states at different times. By opening the phosphorus cycle in such models — that is, simulating inputs to the ocean, and interactive removal processes they could then be used to examine whether changes in the biological pump can indeed change ocean oxygenation state, and, if so, by how much. They could also be used to examine the effect of changing the input of phosphorus from weathering on ocean redox state, and identify which observations can distinguish between the different hypotheses.

Hypothesized changes in silicate weathering fluxes could be tested with new lithium and osmium isotope proxies, and a proxy for phosphorus weathering could also be sought. A sequential extraction method for phosphorus in marine sediments could be used to test for predicted changes in phosphorus removal and recycling with depth, and this could be complemented by assessment of changes in the depth (and/or form) of phosphorite deposition. Finally, predictions for changes in organic carbon burial could be tested against the δ^{13} C record, and fed into more traditional box models to estimate the effects on atmospheric oxygen over multi-million-year timescales. Such analyses would test our arguments that the evolution of complex eukaryotes could have caused ocean ventilation and that ocean oxygenation did not require a rise in atmospheric oxygen. They would also help to quantify the net effect of eukaryote evolution and ocean oxygenation on atmospheric oxygen.

We have argued that oxygen was not a key player in the origin of animals¹¹ (alternative explanations for which are explored in Box 3). Instead, early animals may have played a key role in the widespread (although not universal) Ediacaran oxygenation of the deep oceans, which in turn may have facilitated the advent of many subsequent animal traits such as mobility and carnivory⁷⁷.

The arrival of bilaterians and the evolution of a through-gut marked the beginning of an essentially modern marine biosphere, with structurally familiar food webs². This had several profound impacts on the Earth system. In particular, mobile animals began to mix and oxygenate the sediments (a process known as bioturbation). There is evidence for locomotion on the sea floor⁸⁶ at ~565 Ma and for feeding on the sediment surface⁸⁷ >555 Ma, with three-dimensional burrowing appearing before the base of the Cambrian⁸⁸. Oxygenation of the upper sediments by bioturbation would have added sulphate to the ocean⁸⁹, lessening the role of methanogenesis in organic decomposition, but crucially would also have removed phosphorus⁹⁰. The resulting reduction in phosphate concentration and organic carbon burial would ultimately have caused a decrease in atmospheric O_2 (R. A. B. *et al.* Manuscript in preparation). These predicted effects of bioturbation could help explain the return of widespread anoxic and sometimes euxinic conditions in the earlymid Palaeozoic ocean. Thus, animal evolution, far from being a response to rising atmospheric oxygen, might actually have sent oxygen in the opposite direction.

REVIEW ARTICLE

Received 26 July 2013; accepted 4 February 2014; published online 9 March 2014

References

- Lenton, T. M. & Watson, A. J. Revolutions that made the Earth. (Oxford Univ. Press, 2011).
- Butterfield, N. J. Animals and the invention of the Phanerozoic Earth system. *Trends Ecol. Evol.* 26, 81–87 (2011).
- Knoll, A. H., The multiple origins of complex multicellularity. *Annu. Rev. Earth Planet. Sci.* 39, 217–239 (2011).
- Canfield, D. E., Poulton, S. W. & Narbonne, G. M. Late-Neoproterozoic deepocean oxygenation and the rise of animal life. *Science* 315, 92–95 (2007).
- Sahoo, S. K. *et al.*, Ocean oxygenation in the wake of the Marinoan glaciation. *Nature* 489, 546–549 (2012).
- Nursall, J. R. Oxygen as a prerequisite to the origin of the Metazoa. *Nature* 183, 1170–1172 (1959).
- Raff, R. A. & Raff, E. C. Respiratory mechanisms and the metazoan fossil record. *Nature* 228, 1003–1005 (1970).
- Towe, K. M., Oxygen-collagen priority and the Early Metazoan fossil record. Proc. Natl Acad. Sci. USA 65, 781–788 (1970).
- Catling, D. C., Glein, C. G., Zahnle, K. J. & McKay, C. P. Why O₂ is required by complex life on habitable planets and the concept of planetary "oxygenation time". *Astrobiology* 5, 415–438 (2005).
- Budd, G. E. The earliest fossil record of the animals and its significance. *Phil. Trans. R. Soc. B: Biol. Sci.* 363, 1425–1434 (2008).
- Sperling, E. A., Halverson, G. P., Knoll, A. H., Macdonald, F. A. & Johnston, D. T. A basin redox transect at the dawn of animal life. *Earth Planet. Sci. Lett.* **371–372**, 143–155 (2013).
- Poulton, S. W. & Canfield, D. E. Ferruginous conditions: a dominant feature of the ocean through Earth's history. *Elements* 7, 107–112 (2011).
- Kasting, J. F. Box models for the evolution of atmospheric oxygen: an update. *Glob. Planet. Change* 97, 125–131 (1991).
- 14. Kendall, B. *et al.* Pervasive oxygenation along late Archaean ocean margins. *Nature Geosci* **3**, 647–652 (2010).
- Slack, J. F., Grenne, T., Bekker, A., Rouxel, O. J. & Lindberg, P. A. Suboxic deep seawater in the late Paleoproterozoic: evidence from hematitic chert and iron formation related to seafloor-hydrothermal sulfide deposits, central Arizona, USA. *Earth Planet. Sci. Lett.* 255, 243–256 (2007).
- Canfield, D. E. *et al.* Ferruginous conditions dominated later Neoproterozoic deep-water chemistry. *Science* **321**, 949–952 (2008).
- Frei, R., Gaucher, C., Poulton, S. W. & Canfield, D. E. Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes. *Nature* 461, 250–253 (2009).
- Partin, C. A. *et al.* Large-scale fluctuations in Precambrian atmospheric and oceanic oxygen levels from the record of U in shales. *Earth Planet. Sci. Lett.* 369–370, 284–293 (2013).
- Logan, G. B., Hayes, J. M., Hieshima, G. B. & Summons, R. E. Terminal Proterozoic reorganization of biogeochemical cycles. *Nature* 376, 53–56 (1995).
- Parfrey, L. W., Lahr, D. J. G., Knoll, A. H. & Katz, L. A. Estimating the timing of early eukaryotic diversification with multigene molecular clocks. *Proc. Natl Acad. Sci. USA* 108, 13624–13629 (2011).
- Erwin, D. H. *et al.* The Cambrian conundrum: early divergence and later ecological success in the early history of animals. *Science* 334, 1091–1097 (2011).
- Butterfield, N. J. Bangiomorpha pubescens n. gen., n. sp.: implications for the evolution of sex, multicellularity, and the Mesoproterozoic/Neoproterozoic radiation of eukaryotes. Paleobiology 26, 386–404 (2000).
- Strother, P. K., Battison, L., Brasier, M. D. & Wellman, C. H. Earth's earliest non-marine eukaryotes. *Nature* 473, 505–509 (2011).
- Pawlowska, M. M., Butterfield, N. J. & Brocks, J. J. Lipid taphonomy in the Proterozoic and the effect of microbial mats on biomarker preservation. *Geology* 41, 103–106 (2013).
- Canfield, D. E., The early history of atmospheric oxygen: homage to Robert M. Garrels. *Annu. Rev. Earth Planet. Sci.* 33, 1–36 (2005).
- 26. Rye, R. & Holland, H. D. Paleosols and the evolution of atmospheric oxygen: a critical review. *Am. J. Sci.* **298**, 621–672 (1998).
- Planavsky, N. J. et al. Widespread iron-rich conditions in the mid-Proterozoic ocean. Nature 477, 448–451 (2011).
- Scott, C. *et al.* Tracing the stepwise oxygenation of the Proterozoic ocean. *Nature* 452, 456–459 (2008).
- Reinhard, C. T. et al. Proterozoic ocean redox and biogeochemical stasis. Proc. Natl Acad. Sci. USA 110, 5357–5362 (2013).
- Kendall, B., Gordon, G. W., Poulton, S. W. & Anbar, A. D. Molybdenum isotope constraints on the extent of late Paleoproterozoic ocean euxinia. *Earth Planet. Sci. Lett.* **307**, 450–460 (2011).

NATURE GEOSCIENCE DOI: 10.1038/NGEO2108

- Poulton, S. W., Fralick, P. W. & Canfield, D. E. Spatial variability in oceanic redox structure 1.8 billion years ago. *Nature Geosci.* 3, 486–490 (2010).
- Ozaki, K. & Tajika, E. Biogeochemical effects of atmospheric oxygen concentration, phosphorus weathering, and sea-level stand on oceanic redox chemistry: implications for greenhouse climates. *Earth Planet. Sci. Lett.* 373, 129–139 (2013).
- Canfield, D. E. A new model for Proterozoic ocean chemistry. *Nature* 396, 450–453 (1998).
- Planavsky, N. J. *et al.* The evolution of the marine phosphate reservoir. *Nature* 467, 1088–1090 (2010).
- 35. Boyle, R. A. *et al.* Nitrogen cycle feedbacks as a control on euxinia in the mid-Proterozoic ocean. *Nature Commun.* **4**, 1533 (2013).
- Godfrey, L. V., Poulton, S. W., Bebout, G. E. & Fralick, P. W. Stability of the nitrogen cycle during development of sulfidic water in the redox-stratified late Paleoproterozoic Ocean. *Geology* 41, 655–658 (2013).
- Kah, L. C., Lyons, T. W. & Frank, T. D. Low marine sulphate and protracted oxygenation of the Proterozoic biosphere. *Nature* 431, 834–838 (2004).
- Ingall, E. & Jahnke, R. Evidence for enhanced phosphorus regeneration from marine sediments overlain by oxygen depleted waters. *Geochim. Cosmochim. Acta* 58, 2571–2575 (1994).
- Colman, A. S. & Holland, H. D. in *Marine Authigenesis: from Global to* Microbial Vol. 65 (eds Glenn, C. R., Lucas, J. & Prévôt-Lucas, L.) 53–75 (SEPM, 2000).
- 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).
- Handoh, I. C. & Lenton, T. M. Periodic mid-Cretaceous Oceanic Anoxic Events linked by oscillations of the phosphorus and oxygen biogeochemical cycles. *Glob. Biogeochem. Cycles* 17, 1092 (2003).
- Javaux, E. in Origins and Evolution of Life: An Astrobiological Perspective (eds Gargaud, M., Lopez-Garcia, P. & Martin, H.) 414–449 (Cambridge Univ. Press, 2011).
- Porter, S. M. & Knoll, A. H. Testate amoebae in the Neoproterozoic Era: evidence from vase-shaped microfossils in the Chuar Group, Grand Canyon. *Paleobiology* 26, 360–385 (2000).
- Summons, R. E. *et al.* Distinctive hydrocarbon biomarkers from fossiliferous sediment of the Late Proterozoic Walcott Member, Chuar Group, Grand Canyon, Arizona. *Geochimica et Cosmochimica Acta* 52, 2625–2637 (1988).
- Cohen, P. A., Schopf, J. W., Butterfield, N. J., Kudryavtsev, A. B. & Macdonald, F. A., Phosphate biomineralization in mid-Neoproterozoic protists. *Geology* 39, 539–542 (2011).
- Lebrato, M. et al., Jelly biomass sinking speed reveals a fast carbon export mechanism. *Limnology and Oceanography* 58, 1113–1122 (2013).
- Butterfield, N. J. Oxygen, animals and oceanic ventilation: an alternative view. Geobiology 7, 1–7 (2009).
- Tziperman, E., Halevy, I., Johnston, D. T., Knoll, A. H. & Schrag, D. P. Biologically induced initiation of Neoproterozoic snowball-Earth events. *Proc. Natl Acad. Sci. USA* 108, 15091–15096 (2011).
- Johnston, D. T. *et al.* An emerging picture of Neoproterozoic ocean chemistry: Insights from the Chuar Group, Grand Canyon, USA. *Earth Planet. Sci. Letters* 290, 64–73 (2010).
- Och, L. M. & Shields-Zhou, G. A. The Neoproterozoic oxygenation event: Environmental perturbations and biogeochemical cycling. *Earth-Sci. Rev.* 110, 26–57 (2012).
- Derry, L. A., Kaufman, A. J. & Jacobsen, S. B., Sedimentary cycling and environmental change in the Late Proterozoic: Evidence from stable and radiogenic isotopes. *Geochim. Cosmochim. Acta* 56, 1317–1329 (1992).
- Carver, J. H. & Vardavas, I. M., Precambrian glaciations and the evolution of the atmosphere. *Ann. Geophys.* 12, 674–682 (1994).
- Lenton, T. M. & Watson, A. J. Biotic enhancement of weathering, atmospheric oxygen and carbon dioxide in the Neoproterozoic. *Geophys. Res. Lett.* 31, L05202 (2004).
- Donnadieu, Y., Godderis, Y., Ramstein, G., Nedelec, A. & Meert, J. A 'snowball Earth' climate triggered by continental break-up through changes in runoff. *Nature* 428, 303–306 (2004).
- Li, Z. X. *et al.* Geochronology of Neoproterozoic syn-rift magmatism in the Yangtze Craton, South China and correlations with other continents: evidence for a mantle superplume that broke up Rodinia. *Precambr. Res.* 122, 85–109 (2003).
- Macdonald, F. A. *et al.* Calibrating the Cryogenian. *Science* 327, 1241–1243 (2010).
- Shields-Zhou, G. A. & Och, L. M. The case for a Neoproterozoic Oxygenation Event: Geochemical evidence and biological consequences. *GSA Today* 21, 4–11 (2011).
- Dahl, T. W. et al. Molybdenum evidence for expansive sulfidic water masses in ~750 Ma oceans. Earth Planet. Sci. Lett. 311, 264–274 (2011).

NATURE GEOSCIENCE DOI: 10.1038/NGEO2108

REVIEW ARTICLE

- Nagy, R. M., Porter, S. M., Dehler, C. M. & Shen, Y. Biotic turnover driven by eutrophication before the Sturtian low-latitude glaciation. *Nature Geosci.* 2, 415–418 (2009).
- Vincent, W. F. *et al.* Ice shelf microbial ecosystems in the high Arctic and implications for life on Snowball Earth. *Naturwissenschaften* 87, 137–141 (2000).
- Knoll, A. H., Javaux, E. J., Hewitt, D. & Cohen, P. Eukaryotic organisms in Proterozoic oceans. *Phil. Trans. R. Soc. B: Biol. Sci.* 361, 1023–1038 (2006).
- Maloof, A. C. et al. Possible animal-body fossils in pre-Marinoan limestones from South Australia. Nature Geosci 3, 653–659 (2010).
- 63. Love, G. D. *et al.* Fossil steroids record the appearance of Demospongiae during the Cryogenian period. *Nature* **457**, 718–721 (2009).
- Antcliffe, J. B. Questioning the evidence of organic compounds called sponge biomarkers. *Palaeontology* 56, 917–925 (2013).
- Vogel, S. Current-induced flow through living sponges in nature. Proc. Natl Acad. Sci. USA 74, 2069–2071 (1977).
- Erwin, D. & Tweedt, S. Ecological drivers of the Ediacaran-Cambrian diversification of Metazoa. *Evol. Ecol.* 26, 417–433 (2012).
- 67. Reiswig, H. M. Water transport, respiration and energetics of three tropical marine sponges. J. Exp. Mar. Biol. Ecol. 14, 231–249 (1974).
- Perea-Blazquez, A., Davy, S. K. & Bell, J. J. Estimates of particulate organic carbon flowing from the pelagic environment to the benthos through sponge assemblages. *PLoS ONE* 7, e29569 (2012).
- De Goeij, J., van den Berg, H., van Oostveen, M., Epping, E. & van Duyl, F. Major bulk dissolved organic carbon (DOC) removal by encrusting coral reef cavity sponges. *Marine Ecol. Progress Series* 357, 139–151 (2008).
- Cook, P. J. & Shergold, J. H. eds. Phosphate deposits of the world: Volume 1, Proterozoic and Cambrian phosphorites. (Cambridge Univ. Press, 2005).
- Shen, Y., Zhang, T. & Hoffman, P. F. On the coevolution of Ediacaran oceans and animals. *Proc. Natl Acad. Sci. USA* 105, 7376–7381 (2008).
- 72. Li, C. *et al.*, A stratified redox model for the Ediacaran Ocean. *Science* **328**, 80–83 (2010).
- Mills, B., Watson, A. J., Goldblatt, C., Boyle, R. & Lenton, T. M. Timing of Neoproterozoic glaciations linked to transport-limited global weathering. *Nature Geosci.* 4, 861–864 (2011).
- Yuan, X., Chen, Z., Xiao, S., Zhou, C. & Hua, H. An early Ediacaran assemblage of macroscopic and morphologically differentiated eukaryotes. *Nature* 470, 390–393 (2011).
- Kremien, M., Shavit, U., Mass, T. & Genin, A. Benefit of pulsation in soft corals. *Proc. Natl Acad. Sci. USA* 110, 8978–8983 (2013).
- Jantzen, C., Wild, C., Rasheed, M., El-Zibdah, M. & Richter, C. Enhanced pore-water nutrient fluxes by the upside-down jellyfish Cassiopea sp. in a Red Sea coral reef. *Marine Ecol. Progress Series* 411, 117–125 (2010).
- Sperling, E. A. et al. Oxygen, ecology, and the Cambrian radiation of animals. Proc. Natl Acad. Sci. USA 110, 13446–13451 (2013).
- Condon, D. et al. U-Pb Ages from the Neoproterozoic Doushantuo Formation, China. Science 308, 95–98 (2005).
- Rothman, D. H., Hayes, J. M. & Summons, R. E. Dynamics of the Neoproterozoic carbon cycle. *Proc. Natl Acad. Sci. USA* 100, 8124–8129 (2003).
- Bristow, T. F. & Kennedy, M. J. Carbon isotope excursions and the oxidant budget of the Ediacaran atmosphere and ocean. *Geology* 36, 863–866 (2008).
- Derry, L. A. A burial diagenesis origin for the Ediacaran Shuram-Wonoka carbon isotope anomaly. *Earth Planet. Sci. Letters* 294, 152–162 (2010).
- Grotzinger, J. P., Fike, D. A. & Fischer, W. W. Enigmatic origin of the largest-known carbon isotope excursion in Earth's history. *Nature Geosci.* 4, 285–292 (2011).

- Knauth, L. P. & Kennedy, M. J. The late Precambrian greening of the Earth. Nature 460, 728–732 (2009).
- Lu, M. *et al.* The DOUNCE event at the top of the Ediacaran Doushantuo Formation, South China: Broad stratigraphic occurrence and non-diagenetic origin. *Precambr. Res.* 225, 86–109 (2013).
- Bjerrum, C. J. & Canfield, D. E. Towards a quantitative understanding of the late Neoproterozoic carbon cycle. *Proc. Natl Acad. Sci. USA* 108, 5542–5547 (2011).
- Liu, A. G., Mcllroy, D. & Brasier, M. D. First evidence for locomotion in the Ediacara biota from the 565 Ma Mistaken Point Formation, Newfoundland. *Geology* 38, 123–126 (2010).
- Martin, M. W. *et al.* Age of Neoproterozoic bilatarian body and trace fossils, White Sea, Russia: implications for Metazoan evolution. *Science* 288, 841–845 (2000).
- Jensen, S., Saylor, B. Z., Gehling, J. G. & Germs, G. J. B. Complex trace fossils from the terminal Proterozoic of Namibia. *Geology* 28, 143–146 (2000).
- Canfield, D. E. & Farquhar, J. Animal evolution, bioturbation, and the sulfate concentration of the oceans. *Proc. Natl Acad. Sci. USA* 106, 8123–8127 (2009).
- Zhang, L. *et al.* Impact of different benthic animals on phosphorus dynamics across the sediment-water interface. *J. Environ. Sci.* 22, 1674–1682 (2010).
- Sarmiento, J. L., Herbert, T. D. & Toggweiler, J. R. Causes of anoxia in the world ocean. *Glob. Biogeochem. Cycles* 2, 115–128 (1988).
- Knox, F. & McElroy, M. B. Changes in atmospheric CO₂: influence of the marine biota at high latitude. J. Geophys. Res. 89, 4629–4637 (1984).
- Blackstone, N. W. & Ellison, A. M. Maximal indirect development, set-aside cells, and levels of selection. J. Exp. Zool. 288, 99–104 (2000).
- Cameron, R. A., Peterson, K. J. & Davidson, E. H., Developmental gene regulation and the evolution of large animal body plans. *Am. Zool.* 38, 609–620 (1998).
- 95. Michod, R. E. Darwinian Dynamics. (Princeton, 1999).
- Nichols, S. A., Dirks, W., Pearse, J. S. & King, N., Early evolution of animal cell signaling and adhesion genes. *Proc. Natl Acad. Sci. USA* 103, 12451–12456 (2006).
- Hamilton, W. D. The evolution of altruistic behavior. *Am. Natural.* 97, 354–356 (1963).
- Boyle, R. A., Lenton, T. M. & Williams, H. T. P. Neoproterozoic 'snowball Earth' glaciations and the evolution of altruism. *Geobiology* 5, 337–349 (2007).
- Cohen, D. & Eshel, I. On the founder effect and the evolution of altruistic traits. *Theoret. Popul. Biol.* 10, 276–302 (1976).
- Brockhurst, M. A. Population bottlenecks promote cooperation in bacterial biofilms. *PLoS ONE* 2, e634 (2007).

Acknowledgements

This work was supported by the NERC project 'Re-inventing the planet: the Neoproterozoic revolution in oxygenation, biogeochemistry and biological complexity' (NE/I005978/1). We thank Susannah Porter for providing helpful comments.

Author contributions

T.M.L. wrote the paper with input from all co-authors.

Additional information

Correspondence and requests for materials should be addressed to T.M.L.

Competing financial interests

The authors declare no competing financial interests.