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The rise of oxygen in Earth's early ocean and atmosphere

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The rapid increase of carbon dioxide concentration in Earth's modern atmosphere is a matter of major concern. But for the atmosphere of roughly two-and-half billion years ago, interest centres on a different gas: free oxygen (O_2) spawned by early biological production. The initial increase of O_2 in the atmosphere, its delayed build-up in the ocean, its increase to near-modern levels in the sea and air two billion years later, and its cause-and-effect relationship with life are among the most compelling stories in Earth's history.

Most of us take our richly oxygenated world for granted and expect to find O_2 everywhere—after all, it makes up 21% of the modern atmosphere. But free oxygen, at levels mostly less than 0.001% of those present in the atmosphere today, was anything but plentiful during the first half of Earth's 4.5-billion-year history. Evidence for a permanent rise to appreciable concentrations of O_2 in the atmosphere some time between 2.4 and 2.1 billion years (Gyr) ago (Fig. 1) began to accumulate as early as the 1960s[1]. This step increase, now popularly known as the 'Great Oxidation Event' or GOE[2,3], left clear fingerprints in the rock record. For example, the first appearance of rusty red soils on land and the disappearance of easily oxidized minerals such as pyrite (FeS_2) from ancient stream beds[3,4] both point to the presence of oxygen in the atmosphere. The notion of a GOE is now deeply entrenched in our understanding of the early Earth, with only a few researchers suggesting otherwise[5].

Far more controversial is the timing of the first emergence of O_2-producing photosynthesis, the source of essentially all oxygen in the atmosphere. Among the key questions is whether this innovation came before, or was coincident with, the GOE. Tantalizing organic geochemical data pinpointed pre-GOE O_2 production[6], but subsequent claims of contamination cast doubt[7,8]. Recently, new inorganic approaches have restored some of that lost confidence[9], and assertions of pre-GOE oxygenesis have bolstered research[10,11] that explores buffers or sinks, whereby biological O_2 production was simultaneously offset by consumption during reactions with reduced compounds emanating from Earth's interior (such as reduced forms of hydrogen, carbon, sulphur and iron). Delivery of these oxygen-loving gases and ions to the ocean and atmosphere, tied perhaps to early patterns of volcanism and their relationships to initial formation and stabilization of the continents[10,11], must have decreased through time to the point of becoming subordinate to O_2 production, which may have been increasing at the same time. This critical shift triggered the GOE. In other words, buffering reactions that consumed O_2 balanced its production initially, thus delaying the persistent accumulation of that gas in the atmosphere. Ultimately, however, this source–sink balance shifted in favour of O_2 accumulation—probably against a backdrop of progressive loss of hydrogen (H_2) to space, which contributed to the oxidation of Earth's surface[12–14]. Other researchers have issued a minority report challenging the need for buffers, arguing instead that the first O_2-yielding photosynthesis was coincident with the GOE[15].

As debate raged over the mechanistic underpinnings of the GOE, there emerged a far less contentious proof (a 'smoking gun') of its timing—namely, the disappearance of distinctive non-mass-dependent (NMD) sulphur isotope fractionations in sedimentary rocks deposited after about 2.4–2.3 Gyr ago[16] (Fig. 2). Almost all fractionations among isotopes of a given element scale to differences in their masses; NMD fractionations deviate from this typical behaviour. The remarkable NMD signals are tied to photochemical reactions at short wavelengths involving gaseous sulphur compounds released from volcanoes into the atmosphere. For the signals to be generated and then preserved in the rock record requires extremely low atmospheric oxygen levels, probably less than 0.001% of the present atmospheric level (PAL)[17], although other properties of the early biosphere, such as atmospheric methane abundance[18,19] and biological sulphur cycling[20], certainly modulated the NMD signal.

Aware of the possibility that the 'Great' in GOE may exaggerate the ultimate size of the O_2 increase and its impact on the ocean, Canfield[21] defined a generation of research by championing the idea that ultimate oxygenation in the deep ocean lagged behind the atmosphere by almost two billion years. Finding palaeo-barometers for the amount (or partial pressure) of O_2 in the ancient atmosphere is a famously difficult challenge, but the implication is that oxygen in the atmosphere also remained well below modern levels (Fig. 1) until it rose to something like modern values about 600 million years (Myr) ago. In this view, this second O_2 influx oxygenated much of the deep ocean while enriching the surface waters, thus welcoming the first animals and, soon after, their large sizes and complex ecologies above and within the sea floor.

From this foundation, a fundamentally new and increasingly unified model for the rise of oxygen through time is coming into focus (Fig. 1). Our story begins with the timing of the earliest photosynthetic production of oxygen and its relationship to the sulphur isotope record. After the GOE, we assert that oxygen rose again and then fell in the atmosphere and remained, with relatively minor exceptions, at extremely low levels for more than a billion years. This prolonged stasis was probably due to a combination of fascinating biogeochemical feedbacks, and those conditions spawned an oxygen-lean deep ocean. This anoxic ocean probably harboured sufficiently large pockets of hydrogen sulphide to draw down the concentrations of bioessential elements and thus, along with the overall low oxygen availability, challenge the emergence and diversification of eukaryotic organisms and animals until the final big step in the history of oxygenation and the expansion of life. All of this evidence comes from very old rocks, which present unique challenges—not the least of which is that constant recycling at and below Earth's surface erases most of the record we seek. But with challenge comes opportunity.

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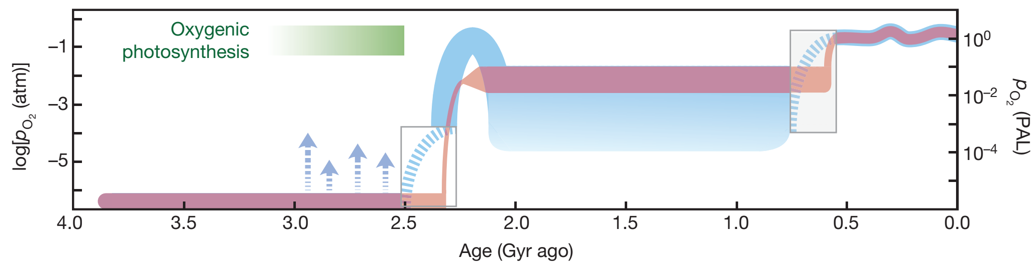

Figure 1 | Evolution of Earth's atmospheric oxygen content through time. The faded red curve shows a 'classical, two-step' view of atmospheric evolution[95], while the blue curve shows the emerging model (p_{O_2}, atmospheric partial pressure of O_2). Right axis, p_{O_2} relative to the present atmospheric level (PAL); left axis, log p_{O_2}. Arrows denote possible 'whiffs' of O_2 late in the Archaean; their duration and magnitude are poorly understood. An additional frontier lies in reconstructing the detailed fabric of 'state changes' in atmospheric p_{O_2}, such as occurred at the transitions from the late part of the Archaean to the early Proterozoic and from the late Proterozoic to the early Phanerozoic (blue boxes). Values for the Phanerozoic are taken from refs 96 and 97.

The first oxygen from photosynthesis

Because oxygenic photosynthesis is the only significant source of free oxygen on Earth's surface, any evaluation of our planet's oxygenation history must begin by asking when this metabolism evolved. Yet despite decades of intensive investigation, there is no consensus. Current estimates span well over a billion years—from ~3.8 (ref. 22) to 2.35 (ref. 15) Gyr ago—almost one-third of Earth's history. Part of the problem lies with difficulties in differentiating between oxidation pathways that can be either biotic or abiotic and can occur with and without free oxygen. Banded iron formations, for example, are loaded with iron oxide minerals that often give these ancient deposits their spectacular red colours. The prevailing view for many years was that microbial oxygen production in the shallow ocean was responsible for oxidizing iron, which was locally abundant in the otherwise oxygen-free ocean. More recent studies, however, explain this iron oxidation without free O_2—specifically, through oxidation pathways requiring only sunlight (ultraviolet oxidation[23] and anoxygenic photosynthesis[24,25]). Microbial fossils of Archaean age (older than 2.5 Gyr; see Fig. 2 for time units) have very simple morphologies, and it is therefore difficult to link them to specific metabolisms, such as oxygen-producing photosynthesis. Similarly, the significance, and even the biogenicity, of Archaean stromatolites and microbially induced sedimentary structures have long been debated[26].

Other researchers vied to find more definitive indicators of microbial oxygen production. Among them, Brocks *et al.*[6] published organic biomarker data thought to record the presence of cyanobacteria and eukaryotes in 2.7-Gyr-old rocks. Biomarkers are molecular fossils derived from primary organic compounds that, in the best case, can be tied uniquely to specific biological producers present at the time the sediments were deposited. Cyanobacteria are important because they were the earliest important producers of O_2 by photosynthesis. Recognition of sterane biomarkers from eukaryotes strengthens the identification of oxygen production because O_2 is required, albeit at very low levels[27], for biological synthesis of their sterol precursors. If correct, these data would extend the first production and local accumulation of oxygen in the ocean to almost 300 Myr before the GOE as it is now popularly defined (that is, based on the disappearance of NMD fractionations of sulphur isotopes). Contrary studies, however, argue that O_2 is not required to explain these particular biomarkers[15]; others challenge the integrity of the primary signals, suggesting later contamination instead[8]. Very recent results from ultraclean sampling and analysis also raise serious concern about the robustness of the biomarker record during the Archaean[28]—and in particular point to contamination for the results of Brocks *et al.*[6] Ironically, some the best earliest organic evidence for oxygenic photosynthesis may lie more with the common occurrence of highly organic-rich shales of Archaean age than with sophisticated biomarker geochemistry (Box 1).

Over the past decade, a body of trace-metal and sulphur data has grown—independent of the biomarker controversy—that also points to oxygen production long before the disappearance of NMD sulphur isotope fractionations (Fig. 2). This evidence for early oxygenesis allows for at least transient accumulation of the gas in the atmosphere and even for hotspots of production in local, shallow, cyanobacteria-rich marine oases[29]. Despite some controversy surrounding these inorganic proxy approaches (reviewed in ref. 30), many researchers interpret strong trace-metal enrichments in marine sediments as convincing signatures of significant oxidative weathering of pyrite and other sulphide minerals on land long before the GOE—implying O_2 accumulation in the atmosphere. Sulphide minerals in the crust are often enriched in the metals of interest, such as molybdenum (Mo) and rhenium (Re), and when oxidized those metals are released to rivers and ultimately the ocean.

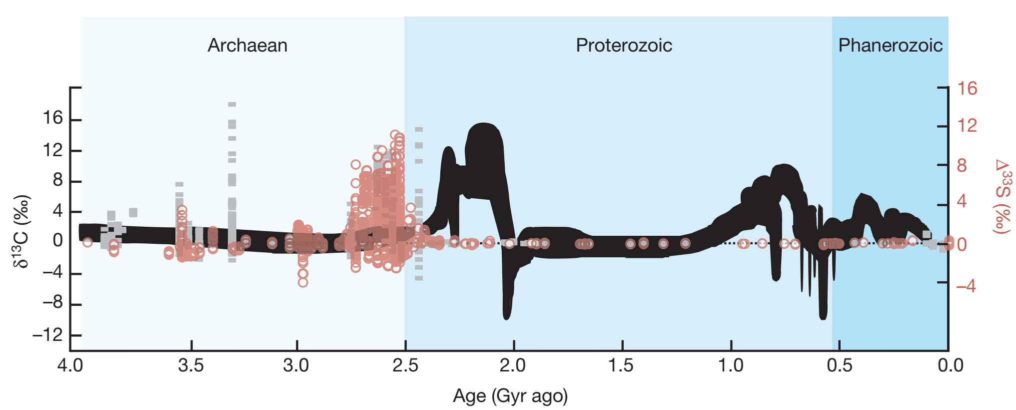

Figure 2 | Summary of carbon (black) and sulphur (red and grey) isotope data through Earth's history. Data are shown as δ^{13}C (left axis and Δ^{33}S ($= \delta^{33}S - 0.515\delta^{34}S$; right axis). Grey sulphur data were generated by secondary ion mass spectrometry (SIMS); red circles designate all other data—bulk and small sample (micro-drilled and laser) analyses. Notable features include the large range of Δ^{33}S values during Archaean time, the large δ^{13}C excursion during the early Proterozoic, relative stasis in δ^{13}C during the mid-Proterozoic, and the large negative δ^{13}C excursions during the late Proterozoic. Data are from references as compiled in refs 33 and 53.

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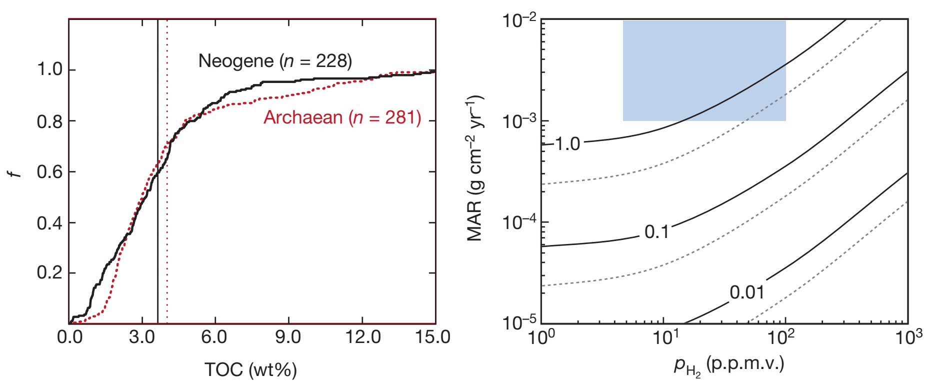
BOX 1

Evidence for oxygen-producing photosynthesis before the GOE

In the face of recent challenges to the Archaean biomarker record, the abundant organic matter from this interval takes on a more general importance. Specifically, how was this copious organic matter produced, and was O_2 a by-product? Photosynthetic life requires both light and a source of reducing power—an electron donor. Because the ubiquitous H_2O molecule is the electron donor for oxygenic photosynthesis, it is reasonable to expect that the initiation of oxygenic photosynthesis would 'supercharge' carbon fluxes through the biosphere. Nevertheless, organic-rich shales are a common component of the Archaean rock record, and the amount of total organic carbon (TOC) of pre-GOE (Archaean) shales is indistinguishable from TOC recorded in similar modern and near-modern environments (Box 1 Figure, left).

Three alternative electron donors could power delivery of significant quantities of organic carbon to marine sediments during the Archaean without releasing O_2: hydrogen sulphide (H_2S), ferrous iron (Fe^{2+}) and molecular hydrogen (H_2). Photosynthesis based on H_2S is difficult to maintain at steady state without an external carbon source[99], and many organic-rich Archaean shales were deposited from Fe^{2+}-containing waters[32], arguing against an H_2S-based pathway. Photosynthesis based on Fe^{2+} is another possibility, but this metabolism generates two physically associated particulate species (organic carbon and solid Fe-oxide minerals) at a relatively constant ratio, and these will mutually annihilate through microbial iron reduction at roughly the same ratio.

H_2-based photosynthesis is more difficult to assess. We can, however, obtain some estimates of the TOC values as a function of H_2 fluxes to the photic zone (Box 1 Figure, right). Even given the very conservative assumptions used here, it is difficult to explain typical Archaean TOC values by H_2-based photosynthesis, let alone the most elevated values from the record. We are thus left with oxygenic photosynthesis as the most likely explanation for organic-rich shales in the pre-GOE ocean.



Box 1 Figure | The significance of organic carbon content in sedimentary rocks of Archaean age (>2.5 Gyr old). Left, cumulative frequency (f) distributions for the total organic carbon content (TOC) of Neogene/recent (black trace) and Archaean (dotted red trace) organic-rich sedimentary rocks from references as compiled in ref. 60. Also shown are the overall average TOC contents for the two data sets (vertical lines). Note that the data for the two time periods are virtually identical. Right, the combinations of atmospheric H_2 content (partial pressure of H_2, p_{H_2}) and sediment mass accumulation rate (MAR) required to attain a given TOC value (TOC = $flux_{H2}$/MAR). Black solid contours correspond to a TOC value of 5 wt%, while grey dashed contours correspond to a value of 10 wt%. The shaded blue box denotes a plausible range for these two parameters, assuming a shelf-to-outer slope depositional setting[100] and results from Archaean ecosystem modelling[101]. Contours are labelled according to the preservation efficiency of organic carbon (that is, a value of 1.0 refers to 100% preservation). For comparison, the preservation efficiency of carbon produced in surface waters in modern anoxic basins (that is, where preservation efficiency is highest in the modern ocean) are of the order of ~1–2% (ref. 102). We assume a vertical advection rate of 1.0 m d^{-1}, typical of regions of vigorous upwelling in the modern coastal ocean[103], and an elevated deep-ocean H_2 concentration of 100 nM, both of which are extremely conservative for our purposes.

The most publicized examples of such diagnostic metal enrichments—the so-called whiffs of oxygen—come from 2.5-Gyr-old organic-rich shales drilled in Western Australia. All Archaean rocks have experienced complex histories at and beneath Earth's surface, and it is important to consider the potential overprints on primary geochemical records during and after burial[9]. However, no coherent secondary alteration model has yet emerged to explain the 'whiff' metal enrichment patterns, particularly given their strikingly sympathetic behaviour with other, independent indicators of depositional chemistry and the rhenium–osmium systematics that yield both robust depositional ages for the rocks and persuasive evidence against appreciable alteration[9,31]. Parsimony currently lies with O_2-related processes.

It may at first seem counterintuitive to suggest that O_2 was oxidizing pyrite and other sulphide minerals, which freed up trace metals for delivery to the ocean by rivers, beneath an atmosphere presumed to have had very low O_2 levels—perhaps much less than 0.001% of PAL. However, such oxidation is possible with only subtle increases in atmospheric O_2 content[9,32]. Also, recent results allow for another intriguing possibility: once NMD signals that formed in an oxygen-poor atmosphere were captured in pyrite and other minerals in sedimentary rocks, they would have been recycled when those rocks were later uplifted as mountain ranges and the pyrite was oxidized[33]. In other words, rivers may have delivered recycled sulphur with a strong NMD signal to the ocean, which can be captured in coeval sediments, long after O_2 rose, either transiently or permanently, to a point that precluded additional signal generation and preservation in the atmosphere. This 'crustal memory effect' allows for the possibility of large and persistent increases of atmospheric oxygen for tens of millions of years or more without complete loss of the NMD fingerprint; it would have taken repeated cycles of weathering, dilution, burial and uplift beneath an oxygenated atmosphere to erase the NMD signal completely. The message is that sulphur isotope records of NMD fractionation, when viewed through the filter of sedimentary recycling, may complicate efforts to date the GOE precisely, and atmospheric oxygen levels for periods of the Archaean may have been much higher than previously imagined. That said, the broad cause-and-effect relationships remain intact: more conventional mass-dependent

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sulphur isotope records, which roughly track the availability of sulphate in the ocean and thus oxygen in the ocean–atmosphere system and related microbial activity without recycling artefacts, show at least general agreement with the NMD signal and dramatic and probably coupled climate change[21,34]. Further work on the early sulphur cycle will more firmly establish the isotope distributions among the various surface reservoirs and thus refine the potential importance of early recycling as an overprint on the atmospheric NMD record.

The GOE

In light of these new perspectives, the GOE might be best thought of as a protracted process rather than a discrete event marking the loss of NMD sulphur fractionations from the sedimentary record. The GOE defined this way becomes a transitional interval of yo-yo-ing biospheric oxygenation[5] during which the ups and downs of O_2 concentrations in the atmosphere reflected a dynamic balance between time-varying early oxygen production and its concurrent sinks—a scenario more consistent with Holland's initial definition of an extended GOE[2]. It is likely that the sources overcame the sinks, at first intermittently and then permanently. And any volatility in atmospheric oxygen content, reflecting perhaps trace-gas behaviour with a relatively short residence time, could be blurred in the NMD sulphur record by sedimentary recycling. Based on available evidence, this critical transitional period took place between roughly 2.5 and 2.3 Gyr ago[34–36], but suggestions of oxygenic photosynthesis much older than 2.5 Gyr ago, although not beyond dispute, are emerging[37] and challenging our conventional views of the GOE.

As stressed above, Earth's O_2 ultimately comes from photosynthesis. In the ocean today, as in the past, the lion's share of that O_2 is just as quickly consumed through decay—or more specifically, through aerobic microbial respiration. For the atmosphere to receive a boost in its oxygen content, some of that primary production in the surface ocean must escape this short-term recycling and become buried long-term beneath the sea floor. This organic-carbon burial changes the stable isotopic composition of dissolved inorganic carbon (ΣCO_2) in the ocean because the organic matter has a lower ratio of $^{13}C/^{12}C$ compared to the remaining inorganic carbon in the host sea water. This fractionation occurs during photosynthetic carbon fixation. The standard view is that the varying carbon isotope composition of sea water, recorded often with fidelity in limestone and dolostone (a magnesium-rich carbonate rock), should track temporal patterns of organic-carbon burial. For example, a dramatic increase in organic burial should manifest in a positive carbon isotope excursion. This approach has been used widely to estimate carbon burial and the O_2 content of the atmosphere through time[38]. Although the carbon isotope details of this transition are a work in progress, and emerging data are pointing to early isotope shifts[34], there is at present no evidence for a large, globally synchronous positive $\delta^{13}C$ shift in carbonate rocks across the GOE transition (Fig. 2) as defined by the permanent loss of NMD sulphur signals—suggesting that it is not a simple matter of a big increase in organic burial as the trigger.

As a corollary to the idea of O_2 production well before the GOE, a balance between carbon burial and compensatory buffering must have initially permitted appreciable oxygen production via photosynthesis without permanent accumulation in the atmosphere[10,11,13,18,39] (Fig. 1). Recent buffer models generally assume that the redox state of the mantle and magmas derived from it did not change significantly leading up to the GOE[40–42]—an idea that no doubt will be revisited in future work. From this position, these models instead emphasize decreases in delivery of reduced gases (H_2 and S species, in particular) and thus waning O_2 buffer capacity as a function of fundamental shifts in the nature of volcanoes. More to the point, a shift from dominantly submarine to increasingly subaerial volcanism as continents grew and stabilized could have led to release of more oxidized gases[10,11]. If correct, the broad temporal overlap of the GOE and first-order tectonic reorganization classically assumed to mark the Archaean–Proterozoic boundary is anything but a coincidence, and the magnitude of the NMD sulphur isotope anomaly through this transition probably varied in part with tectonic controls on volcanic release of sulphur-bearing gases[20]. Various nutrient-based buffering scenarios have also been proposed, and these too may link to long-term trends in volcanism[43]. Regardless of the specific buffer(s), and absent evidence for dramatic increases in organic burial, the balance between sources and sinks ultimately tipped in favour of photosynthetic production perhaps tens of millions of years before the permanent loss of the NMD sulphur isotope signal in rocks dating from 2.4 to 2.3 Gyr ago—and transiently perhaps hundreds of millions of years earlier.

That the first of the great 'Snowball Earth' glaciations is roughly coincident with the GOE[1,44] is probably no coincidence either. Most models for the pre-GOE atmosphere assert that comparatively large amounts of methane (CH_4), along with higher hydrocarbon gases such as ethane (C_2H_6) resulting from methane photochemistry, were produced and persisted under the generally low sulphate (SO_4^{2-}) conditions of the Archaean ocean and low O_2 in the ocean and atmosphere[45–48]. Methane is readily oxidized in the presence of free oxygen, as well as in the absence of oxygen (anaerobically) when coupled to microbial reduction of a number of different oxidants, most notably sulphate[49]. Also, in the absence or near absence of oxygen and sulphate, a greater amount of labile organic matter is available for microbial methane production (methanogenesis). Imagine a pre-GOE world, then, with mostly vanishingly small amounts of O_2 in the ocean and atmosphere; the ocean was dominated instead by high dissolved iron concentrations and the atmosphere by high methane and ethane with residence times perhaps orders of magnitude longer than today's. An important side issue here is that sulphate, which abounds in the ocean today, derives mostly from oxidation of pyrite on the continents in the presence of O_2, like the trace metals discussed earlier.

Methane and its photochemical products deserve our special attention because their roles as greenhouse gases may very well have helped to keep the early Earth habitable (by maintaining a liquid ocean) in the face of a Sun that was only about 70% to 80% as luminous as it is today[50]. This, of course, is the faint young Sun paradox discussed by Sagan[51] and many others. It follows from our understanding of the GOE that the rising O_2 content of the atmosphere might have displaced methane and other hydrocarbons, as well as H_2, as the dominant redox gas, leading to crashing temperatures and plunging the Earth into its first great 'Snowball Earth' ice age. And the timescales of atmospheric oxygenation, particularly when we consider the possibility of temporal blurring of the GOE in light of NMD sulphur recycling, may indeed mesh with the geologic record of early glaciation.

In the wake of the GOE

Until recently, the widely accepted timeline regarding O_2 was that its concentration rose in the atmosphere only modestly at the GOE and waited patiently for almost two billion years before it climbed higher (Fig. 1). Several new studies, however, are suggesting a far more dynamic screenplay, with the possibility of a much larger increase early on and then a deep plunge to lower levels that extended over a few hundred million years after the onset of the GOE (Fig. 1). These scenes play out in the most prominent positive carbon isotope event in Earth's history—the Lomagundi excursion observed around the world in rocks dating from roughly 2.3 to 2.1 Gyr ago with $\delta^{13}C$ values extending well beyond +10‰ (ref. 52; Fig. 2).

Despite earlier occurrences of markedly positive carbonate $\delta^{13}C$ values[34], the onset of the Lomagundi excursion proper appears after widespread glaciation and the loss of NMD sulphur fractionations (Fig. 2). The anomalous carbon isotope behaviour of the Lomagundi excursion is most parsimoniously tied to intense burial of organic matter[53] rather than reflecting diagenetic carbonate precipitation, as previously proposed[54]. Assuming the Lomagundi excursion is tied to organic burial, the carbonate $\delta^{13}C$ record predicts release of roughly 10 to 20 times the present atmospheric oxygen inventory[52]. Recent findings suggest that oxygen was indeed very high during the Lomagundi excursion, including estimates of high sulphate and trace-metal levels in the ocean[53,55,56]. Equally tantalizing are suggestions of a precipitous drop in oxygen after the Lomagundi excursion[56,57]. The reasons for this rise and fall remain unresolved, although some models

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blame extreme weathering of crust that developed under the generally O_2-lean Archaean atmosphere. This crust was rich in pyrite, which, when oxidized, would produce acidity and enhance delivery of key nutrients—phosphorus in particular[57]. Independent of the mechanism, this inferred nonlinear, reversible increase in atmospheric oxygen after the GOE stands in stark contrast to the classic models invoking unidirectional oxygen rise (Fig. 1). Few data are currently available, but no strong biotic response to these large-scale redox fluctuations has been recognized.

Oxygen and life during Earth's middle age

In the late 1990s, few grasped the full rise and fall of O_2 that may be captured in the Lomagundi excursion, but in a seminal paper published in 1998, Canfield[21] set the tone for the ensuing consequences by modelling a persistence of low marine oxygen conditions throughout the mid-Proterozoic from roughly 1.8 to 0.8 Gyr ago—long after the GOE. He went a step further and suggested pervasive euxinia in the deep ocean. (Euxinia refers to waters free of oxygen and rich in hydrogen sulphide, H_2S, like those that characterize the Black Sea today.) Whether he intended it or not, that view soon became one of a globally euxinic 'Canfield' ocean that dominated Earth's middle age. Some years later, many researchers, including Canfield, struggled to define a combination of factors, particularly the controls on primary production that would have sustained euxinia across such large expanses of the open ocean[58–60].

Nevertheless, building on the idea of ocean-scale euxinia, Anbar and Knoll[61] presented an intriguing thought experiment: because important micronutrients such as Mo are readily scavenged from sea water in the presence of hydrogen sulphide, might the mid-Proterozoic ocean have been broadly limited in these key metals, which are required enzymatically for the fixation and utilization of nitrogen? In today's oxic world, iron limits primary production in vast parts of the ocean, while Mo abounds. The situation may have been reversed under the low-oxygen conditions of the mid-Proterozoic. This nutrient state would have throttled the early diversity, distribution and abundances of eukaryotes—an idea explored later through phylogenomic analysis of protein structures and the implied histories of metal utilization in prokaryotic and eukaryotic organisms[62]. Scott *et al.*[59] found evidence for the hypothesized Mo deficiency in the mid-Proterozoic ocean (Box 2). Importantly, though, the observed Mo drawdown and complementary Mo isotope data[63] are inconsistent with anything close to ocean-wide euxinia.

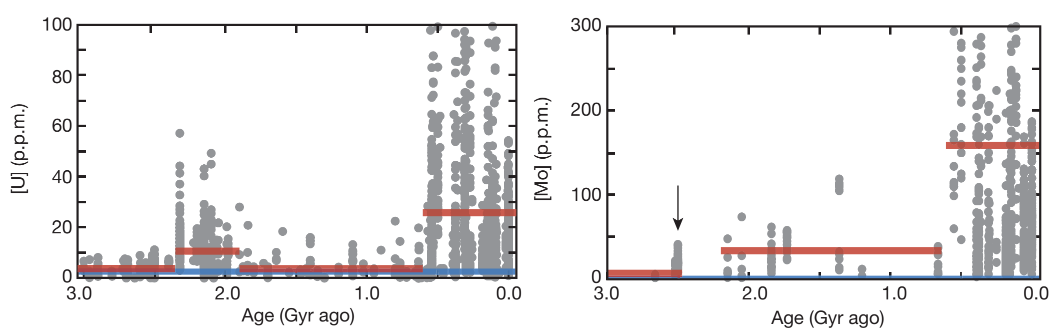
In the years following the initial excitement about mid-Proterozoic ocean-scale euxinia, a more nuanced and realistic model for ocean–atmosphere redox emerged. Oxygen was probably persistently or transiently very low in the atmosphere, perhaps even less than 0.1% of that present today (Fig. 1). For example, the apparent loss of manganese (Mn) from some mid-Proterozoic soils (palaeosols) opens up the possibility of markedly low atmospheric oxygen concentrations in the mid-Proterozoic well after the GOE[64]. Sedimentary chromium (Cr) isotope relationships[65] may, similarly, suggest limited terrestrial Mn oxidation for periods of the mid-Proterozoic hundreds of millions of years after the GOE. In modern environments, by analogy, Mn oxidation can proceed

BOX 2

Trace-element records of ocean redox evolution

Because the burial of redox-sensitive elements (RSEs) in marine sediments is greatly enhanced in anoxic settings, pervasive marine anoxia will result in RSE depletion in sea water. Further, the magnitude of enrichment of a given RSE in a local anoxic setting should scale with its marine reservoir size[104]. Large sedimentary RSE enrichments in local anoxic environments will only develop in a world with broadly oxic oceans (as on the modern Earth), whereas pervasively anoxic conditions will lead to decreased RSE reservoir sizes and thus muted sedimentary enrichments. If the redox state of the overlying water column can be independently constrained, then the magnitude of sedimentary RSE enrichments can be used to shed light on RSE reservoir size and thus global redox structure. Building from modern marine element mass balances and combining elements that respond to the presence of sulphidic conditions (Mo) with those that respond to anoxia with or without sulphide (U, Cr) it is possible to estimate the global redox landscape (percentage of various seafloor redox states, for example, anoxic, oxic, euxinic) using RSE data from locally anoxic environments (see, for instance, ref. 60).

Although this is a well-grounded approach, it is important to note that other factors (for example, organic fluxes, sulphide levels and bulk sediment accumulation rates) can affect the removal rate of a given RSE. These secondary effects translate into some degree of uncertainty in quantitative estimates; however, these should generally be minor relative to the robust first-order trends in RSE enrichment that we observe (Box 2 Figure) and the much greater errors associated with past practices of extrapolating redox conditions at single locations to the global ocean.



Box 2 Figure | Trace-metal records of evolving ocean redox conditions. Data have been filtered by independent methods to represent anoxic (left) and euxinic (anoxic and sulphidic; right) marine environments. Blue bars represent the range for upper continental crust. Red bars denote the average values for Archaean, early Proterozoic (left only), mid-Proterozoic and Neoproterozoic–Phanerozoic data. Data are from refs 56, 59, 60, 80. Large Phanerozoic U and Mo enrichments point to a dominantly oxic ocean (with low enrichments being linked predominantly to anoxic events or severe isolation). Large U enrichments in the early Proterozoic similarly suggest a well-oxygenated ocean, while persistently muted U enrichments in the mid-Proterozoic suggest the reversion back to a poorly ventilated ocean. Modest Mo enrichments in the mid-Proterozoic, however, suggest that only a moderate extent of this poorly oxygenated ocean was euxinic. The presence of significant Mo enrichments in the Archaean (arrow) suggests the presence of oxidative processes at least as far back as 2.5 Gyr ago[9].

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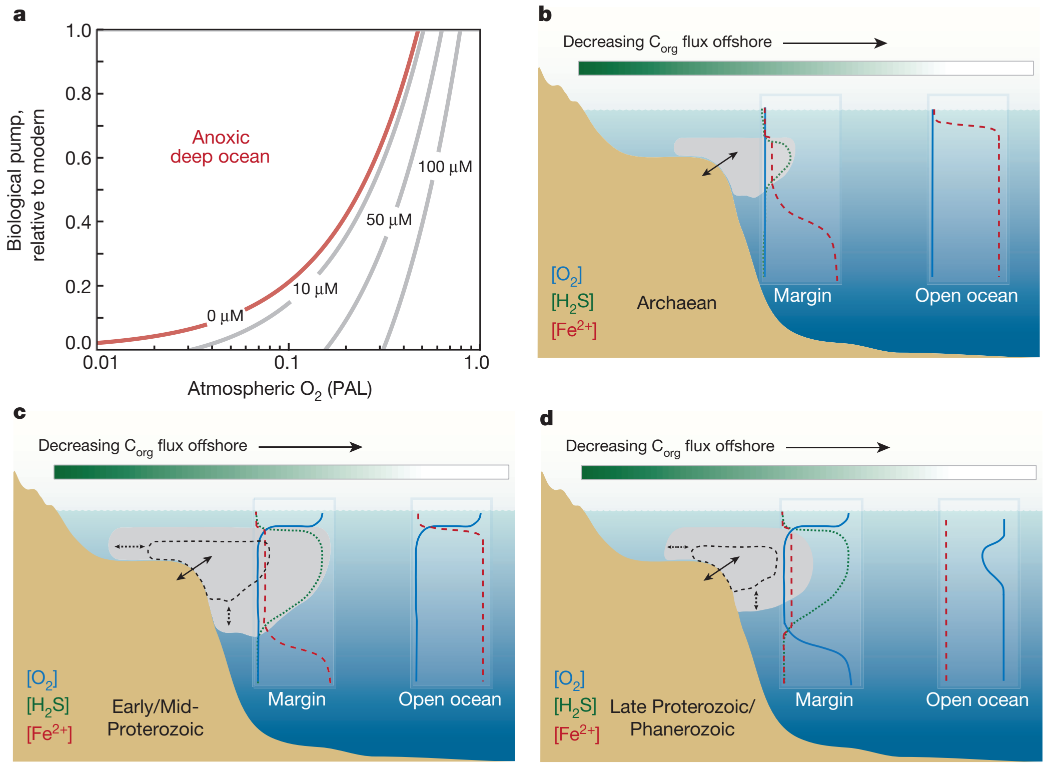

Figure 3 | Ocean ventilation and evolving ocean redox structure. **a**, Contours of globally averaged deep ocean O_2, which is largely set by a balance between O_2 introduced from the atmosphere and the respiration of settling organic matter in the ocean (the 'biological pump'). Calculations are performed as in Canfield[21] and Sarmiento *et al.*[98] but are recast in terms of atmospheric O_2 levels and carbon fluxes through the biological pump (both normalized to the modern Earth). Grey contours reflect globally averaged deep ocean O_2 concentration (in μM), with the red contour showing the boundary below which the modelled deep ocean becomes anoxic. **b**–**d**, Summary of an emerging model for the evolving first-order redox structure of the ocean (see text): **b**, Archaean; **c**, early/mid-Proterozoic; **d**, late Proterozoic/Phanerozoic. Left and right insets in each panel **b**–**d** show average profiles of O_2 (blue), H_2S (green) and Fe^{2+} (red); also shown (colour bar) is the general offshore decrease in local organic carbon (C_{org}) fluxes and its impact on the redox profile of the water column. Double-headed arrows denote expected expansion and contraction of sulphidic and/or ferruginous conditions (grey shading) along the productive and correspondingly reducing ocean margins. We emphasize that the Ediacaran, and much of the late Proterozoic more broadly, was most likely to have been marked by transient oscillation between states depicted in **c** and **d**. It is also important to note that small amounts of oxygen were probably present, locally and perhaps transiently, in the Archaean atmosphere and shallow ocean (**b**), perhaps as local oxygen oases for the latter[29].

rapidly at oxygen levels equivalent to $<10^{-3}$ PAL[66]—which would potentially place mid-Proterozoic atmospheric O_2 well below the commonly cited estimates based on traditional palaeosol work and assumptions of a persistently anoxic deep ocean (>1 to <40% PAL, respectively; Figs 1, 3a)[21,67]. Coupled ancient Cr-Mn cycling and our ability to extrapolate modern natural and experimental systems to quantify those ancient pathways precisely are active areas of research, as are the feedbacks necessary to modulate atmospheric O_2 at such low levels after its initial rise. Moreover, additional records of metal cycling on land through the Proterozoic will probably allow us to constrain better the timing and causes of increases in ocean and atmospheric oxygen contents that mark the shift to a very different late Proterozoic world.

Newer data emphasizing detailed iron speciation within shales suggested that the deep ocean remained dominantly anoxic[68], as Canfield[21] predicted, in response to the still low oxygen values in the atmosphere. But unlike the classic 'Canfield' euxinic ocean, the limited data are best explained by mostly iron-rich anoxic conditions with euxinia largely limited to biologically productive ocean margins and restricted marginal basins[59,69–72]. Today, organic productivity is highest in zones of nutrient upwelling along continental margins, and we can imagine the same situation in the early ocean—much like oxygen-minimum zones in the modern world (Fig. 3b–d). Decay of that settling organic matter removes oxygen from the deeper waters, and the generally low O_2 conditions of the mid-Proterozoic would have exacerbated those deficiencies (Fig. 3a). Persistent and pervasive low-oxygen conditions in the ocean and atmosphere might also have been favoured by copious anoxygenic photosynthesis linked to microbial iron and/or H_2S oxidation in the shallow ocean[73].

Recognizing the likelihood of a more redox stratified mid-Proterozoic ocean was a major step forward but unfortunately the 'proof' resided mostly with very broad extrapolations of inferred conditions at only a few locations. The risk is not unlike surmising the global redox state of the modern ocean through measurements along the highly productive upwelling region off Peru–Chile or within the nearly isolated anoxic Black Sea. The call was out for new approaches.

In response to concerns about over-extrapolation, combined elemental measurements and mass balance modelling is now permitting first-order spatial estimates for conditions across the full extent of sea floor, including those portions long-since lost to subduction, while also providing a more direct measure of the elemental abundances in sea water[60]. For example, Cr and Mo, because of their differing sensitivities to H_2S-free conditions, constrain ocean anoxia to at least 30–40% of the sea floor, and very possibly much more, for large intervals of the mid-Proterozoic, with the likelihood of elevated levels of dissolved iron (Box 2). Those portions of the deep ocean that were not fully anoxic may well have contained only trace levels of oxygen, a condition often referred to as 'suboxic'[69,74]. Euxinic waters, defined by the presence of H_2S, were potentially common enough to pull the concentrations of some key bioessential metals below those favoured by prokaryotes and eukaryotes[60,75], even if limited to only ~1–10% of the sea floor[60] (relative to ≪1% today). Specifically, there may have been persistent molybdenum-nitrogen co-limitation linked to euxinia through much of the mid-Proterozoic, and those molybdenum deficiencies ultimately may have played a major role in limiting the extent of euxinia[58]. Although considered to be less efficient, enzymatic pathways other than Mo-based

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nitrogen fixation must also be considered in future studies. Furthermore, we cannot exclude the possibility of a very different phosphorus cycle at that time and lower-than-modern average phosphorus concentrations. Overall, a comprehensive network of nutrient-based feedbacks may have sustained oxygen at low levels with commensurate effects on marine life, including severe limits on eukaryote diversity and abundance. At the heart of these feedbacks were coupled rising and falling organic production, H_2S generation and metal availability within a relatively narrow range—as expressed in the famously 'boring' mid-Proterozoic $\delta^{13}C$ data, which are marked by exceptional consistency through time (Fig. 2).

Importantly, both modelled and measured evidence are lining up in favour of dominantly ferruginous, or iron-rich, conditions in the deep ocean through the Proterozoic[60,70,71], much like the earlier Archaean. An important implication is that the temporal distribution of economic-grade iron formations must reflect something other than just the redox state of the deep ocean—probably episodes of heightened plume activity within the mantle[76] and/or periods with higher iron concentrations in the hydrothermal fluids released on the sea floor[77]. Only near the end of the Proterozoic did oxygen take a big step up again, perhaps in response to first-order shifts in global-scale tectonics and glaciations in combination with biological innovations.

Another step towards the modern world

Despite a new wave of excellent work, much remains unknown about the redox structure of the ocean and atmosphere during the later part of the Proterozoic (formally known as the Neoproterozoic) between roughly 0.8 and 0.55 Gyr ago and its relationship with evolving life. This gap is a bit surprising given its relatively young age, the comparatively good quality and quantity of available rocks to study, and the abundant recent work on this interval. Yet, the common interpretations tread close to a worrisome circularity: the emergence of animals is typically attributed to a second big O_2 step long after the GOE (a so-called Neoproterozoic Oxidation Event[78]), but animals are just as often cited as evidence for the oxygenation. Other signs of Neoproterozoic oxygenation lie with evidence for deep marine O_2 (refs 79, 80) and problematic explanations for Earth's greatest negative carbon isotope excursion (Fig. 2)—the so-called Shuram-Wonaka anomaly[81,82], which is interpreted to be of either primary or secondary origin[83] (reviewed in ref. 82). Other data point instead, in seeming contradiction, to a persistence of expansive anoxic (iron-rich, that is, ferruginous, and euxinic) marine waters[84].

Amidst the apparent confusion, new research is steering us towards consistent threads that run through all these data by invoking anoxic conditions on productive late Neoproterozoic ocean margins and oxygenation, at least episodically, in the deeper waters (Fig. 3c, d). Indeed, some of the available trace-metal data point to very low extents of euxinic and ferruginous waters at times during the latest Neoproterozoic—also known as the Ediacaran (~635–542 Myr ago)—potentially in phase with major shifts in eukaryotic/animal innovation (reviewed in ref. 85; Box 2). However, we also expect large-scale temporal variability in marine redox conditions, and climate/glaciation may have been a driver of biogeochemical destabilization and a key factor behind the escape from the oxygen-lean stasis that characterized the mid-Proterozoic[86,87]. For instance, one can imagine that shifts in nutrient cycles at the end of the Marinoan 'Snowball Earth' glaciation, the second of two major ice ages in the Neoproterozoic, may have triggered the organic productivity/burial that then spawned the rise in oxygen in the early Ediacaran[80], and trace-metal enrichments suggest a widely oxygenated ocean at about 630 and 550 Myr ago[59,80]. The detailed timing and persistence of O_2 accumulation in the Neoproterozoic ocean and the transition into the younger Phanerozoic are not well known and allow for rising and falling oxygen concentrations during the Ediacaran, as well as the possibility of earlier, even pre-Snowball Earth, oxygenation that may have helped trigger the climate events that followed. It is also likely that shifts in global tectonics during the Neoproterozoic played a strong role in initiating late-Proterozoic global environmental change. Continuous diversification of algae (eukaryotic primary producers) throughout the Neoproterozoic may also have helped to initiate late-Proterozoic global environmental change by altering basic aspects of the marine carbon cycle.

Little is known about the specific relationship between early animals and oxygen. The earliest animals were sponges or sponge-grade[88–90], and their small sizes and high rates of internal ventilation suggest that they may have had relatively low oxygen demand. If one is inclined to link the rise of animals to a rise of oxygen, a logical corollary is that atmospheric oxygen during the preceding mid-Proterozoic must have been at least transiently very low to explain the apparent lack of animals—maybe (much) less than 1% of today's level (Fig. 1). Butterfield[91] suggested instead that the generally concurrent rise of animals and oxygen was mostly a coincidence or, alternatively, that animal evolution itself triggered the oxygenation event. By this argument, the long delay in animal emergence reflects instead the intrinsic timescales of evolution and the complexity of gene expression and cell signalling in animals, consistent with the apparent lack of animals during the much earlier O_2-rich Lomagundi excursion. Others researchers assert various scenarios that demand oxygen in appreciable amounts[88] to explain high animal diversity, large mobile bilaterians, the advent of biomineralization (skeletons), wide niche expansion including habitats below the sea floor, and complex predator–prey relationships[92]. At the same time, we know that animals will alter ecosystem structure and profoundly influence the carbon cycle[88,93], and thus local and broader oxygen levels, by burrowing into sediments, for example. In every case, environment and co-evolving life participate in myriad feedback loops, wherein changes to one generally affect the other. Thus, we warn against end-member arguments in this debate.

The way forward

Informed by increasing sophistication in elemental and isotopic proxy approaches, we can now say with much greater confidence when and why the redox structure of the ocean and atmosphere varied through time. Through this window, we can view an ocean and atmosphere that were mostly oxygen-starved for almost 90% of Earth's history.

So what are the next great opportunities in studies of early oxygen? Of particular value are proxies for seawater composition and linked numerical models that make it possible to extrapolate beyond local conditions and allow, perhaps for the first time, access to the chemical landscape of the ocean as a whole. We recall that the goal is to characterize conditions on a sea floor that is mostly lost through subduction, and the records that we do have from the ancient ocean margin are intrinsically vulnerable to local controls, such as basin restriction and elevated local levels of primary production. We also need additional quantitative tracers of oxygen levels in the atmosphere, given how hard it is to quantify its composition with confidence using mostly oxygen levels inferred for the ocean. And despite significant steps forward, too little is known about the precise timing of the emergence of oxygenic photosynthesis. In this search, organic and inorganic geochemical methods must be used with full awareness of all possibilities of overprinting and contamination. As always, novel approaches applied to more and better samples with the strongest possible age and sedimentological controls will continue to drive the research, with the latter providing independent constraints on depositional conditions that complement geochemical analysis.

The Proterozoic is book-ended by the two greatest geobiological events in Earth's history—the GOE and the dramatic changes among life and environment in the late Neoproterozoic—and these will continue to grab much of the attention. Armed with a better grasp of the history of oxygenic photosynthesis and the full range of evolving oxygen-consuming reactions as tied to processes both on and deep within the Earth, we will correctly tackle the first rise of atmospheric oxygen as the complicated, protracted, dynamic process that it must have been. Refined views of the history of continent formation will inform these discussions.

The billion or more years of history beyond the initial oxygenation of the atmosphere will remain a prime target, particularly given recent suggestions of a remarkable persistence of mostly very low oxygen levels, perhaps more akin to the Archaean than the modern world, and their strangle-hold on early complex life. Full resolution of the feedbacks involved will be a great

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leap forward. Finally, researchers will ask more and better questions about the unique confluence of global-scale climatic, evolutionary and tectonic events that once and for all broke the cycle of low oxygen on Earth, less than a billion years ago, and set the stage for everything that followed, including the emergence of animal life. Increasingly within that mix may be indications of dramatic Neoproterozoic oxygenation well before the Ediacaran[94], and even the 'Snowball Earth' glaciations, thus challenging us to unravel the complex cause-and-effect relationships. And we should not forget that just as environmental change can drive the evolution of life, the reverse is also true. A few billion years after the earliest life, the evolutionary clock may also have been timed just right for big change.

Finally, we summarize the changing understanding of the GOE. In 2002, Holland[2] coined the term 'Great Oxidation Event' to formalize the concept that had emerged long before—that the atmosphere shifted from being fundamentally reducing to oxidizing over an interval from roughly 2.4 to 2.1 Gyr ago. The presumed disappearance of NMD sulphur isotope signals narrowed that window to between 2.4 and 2.3 Gyr ago[35]. No doubt a fundamental shift did occur over this general interval as part of a much broader, long-term progression towards higher amounts of oxygen. But equally certain now is that biospheric oxygen did not follow the simple unidirectional, step-punctuated rise traditionally envisioned[95]. Instead, imagine something more like a roller coaster ride, with dynamic rising and falling oxygen levels in the ocean and atmosphere—starting perhaps as early as 3.0 Gyr ago—superimposed on a first-order trend from generally low to intermediate to high concentrations over a period of perhaps two and half billion years. In this light, the Great Oxidation Event was a transition (a Great Oxygen Transition or GOT, perhaps), more protracted and dynamic than event-like. And any assertions of greatness, particularly those tied specifically to the apparent loss of NMD sulphur isotope signals, may undersell the importance of oxygen variability that came well before and long after an isotopic milestone perhaps blurred by sedimentary recycling and complicated by processes not yet discovered. But 'great' works if we think longer-term, fundamental redox shift, and no matter how we define the GOE, the 'how, when and why' behind Earth's dynamic oxygen history will continue to motivate a generation of researchers.

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