

# Biogeochemical Controls on the Redox Evolution of Earth's Oceans and Atmosphere

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**The redox state of Earth's atmosphere has undergone a dramatic shift over geologic time from reducing to strongly oxidizing, and this shift has been coupled with changes in ocean redox structure and the size and activity of Earth's biosphere. Delineating this evolutionary trajectory remains a major problem in Earth system science. Significant insights have emerged through the application of redox-sensitive geochemical systems. Existing and emerging biogeochemical modeling tools are pushing the limits of the quantitative constraints on ocean-atmosphere redox that can be extracted from geochemical tracers. This work is honing our understanding of the central role of Earth's biosphere in shaping the long-term redox evolution of the ocean-atmosphere system.**

KEYWORDS: biogeochemistry, oxygenation, biosphere, redox, evolution

## REDOX ON A PLANETARY SCALE

### Earth's Modern Oxygen Cycle

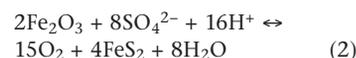
On the modern Earth, molecular oxygen (O<sub>2</sub>) is produced through photosynthesis in sunlit surface environments in which cyanobacteria, algae, and plants use energy from the Sun to transfer electrons from water to biomass. Much of the biomass produced by the photosynthetic biosphere is consumed rapidly through aerobic respiration, which gains energy by transferring electrons from biomass back to O<sub>2</sub>. These coupled processes can be denoted as:



Any photosynthetic biomass removed from the surface system via burial in marine or terrestrial sediments leads to a net accumulation of O<sub>2</sub> in the ocean-atmosphere system (moving from left to right in Equation 1). On geologic timescales, this organic matter can be consumed through exhumation and oxidation in terrestrial weathering environments and through thermal breakdown of organic carbon during metamorphism. Both of these processes lead, ultimately, to a net consumption of O<sub>2</sub> from the ocean-atmosphere system (moving from right to left in Equation 1). Thus, Equation (1) can be thought of conceptually as showing a “fast” O<sub>2</sub> cycle (photosynthesis/respiration), responding on timescales of less than ~10<sup>3</sup> years, and a

“slow” O<sub>2</sub> cycle (organic carbon burial and weathering/thermal breakdown), responding on timescales of ~10<sup>6</sup> years.

There is an additional long-term cycle that links O<sub>2</sub> to the cycling of sulfur (S) and iron (Fe) at Earth's surface:



Moving from left to right in Equation (2) denotes the sum of three processes: (1) photosynthesis; (2) consumption of biomass through microbial sulfate (SO<sub>4</sub><sup>2-</sup>) reduction, producing reduced

sulfur (S<sup>2-</sup>); (3) formation of pyrite (FeS<sub>2</sub>) via reaction between reduced sulfur and reactive iron in the environment (shown here as hematite, Fe<sub>2</sub>O<sub>3</sub>). In essence, the overall effect of this process is to transfer reducing power from water to pyrite via organic biomass, causing a net release of O<sub>2</sub>. The subsequent uplift/weathering and/or volatilization of reduced sulfur species in the crust balances this release of O<sub>2</sub> on geologic timescales (moving from right to left in Equation 2).

Oxygen can also be consumed via reaction with reduced volcanic volatiles that originate from Earth's crust and mantle and during the oxidation of reduced minerals in seafloor basalt as oxygen-rich seawater percolates through the oceanic lithosphere. In addition, the escape of hydrogen to space allows oxygen atoms produced by photochemistry to recombine as O<sub>2</sub>, irreversibly oxidizing Earth surface environments. Similarly, oxidized or reduced species can be subducted into Earth's mantle, leading to secular net oxidation/reduction of Earth's surface environments that is not necessarily irreversible but that can persist on timescales of mantle overturn (that is, on the order of ~10<sup>9</sup> years). For example, organic carbon deposited in deep-sea sediments can potentially be preserved as graphite during subduction, leading to a net export of reducing power from Earth's surface (FIG. 1).

### Nutrients as a Driver of Earth's Redox Balance

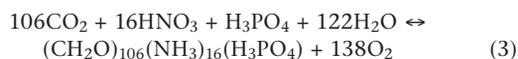
The global oxygen cycle is fundamentally a story of the redox cycling of carbon, sulfur, and iron through the Earth system. However, O<sub>2</sub> cycling is also fundamentally controlled by the availability of bio-essential elements (“nutrients”) in oceanic and terrestrial ecosystems. All organisms require a range of major and trace nutrients to produce biomass, which can be seen by elaborating on Equation (1) to include the major nutrients involved in oxygenic photosynthesis:

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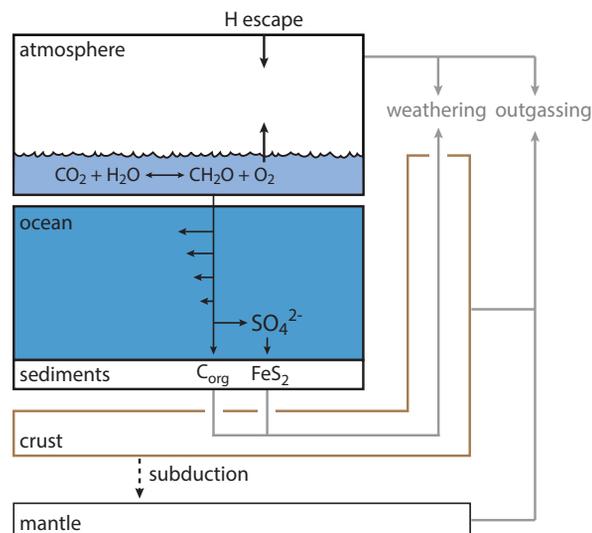
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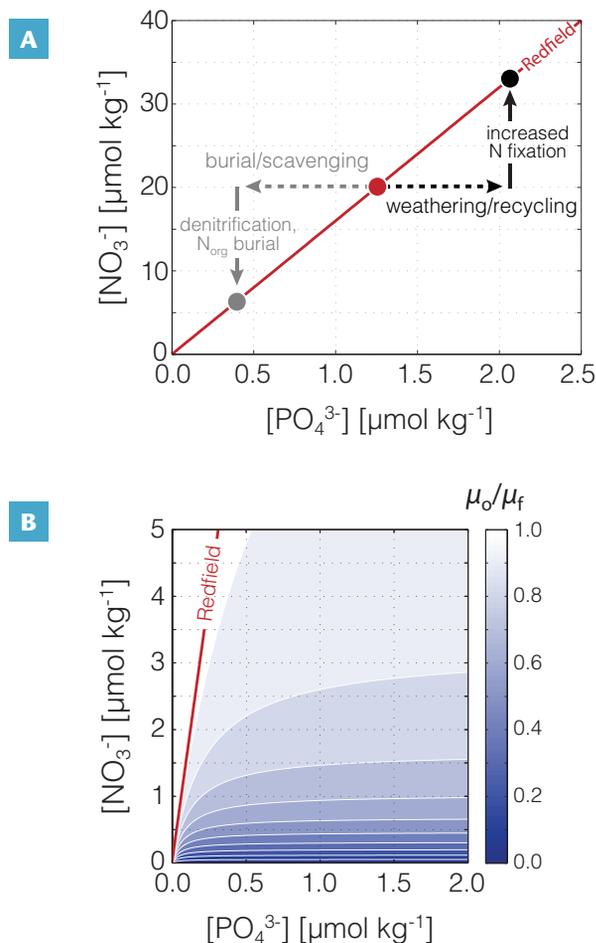


The stoichiometric coefficients in Equation (3) denote the bulk stoichiometry of photosynthetic biomass (the classical “Redfield ratio”, initially observed by US oceanographer Alfred Redfield in 1934), which can vary significantly as a function of taxonomic identity and organism growth status. A variety of trace elements—for example, Fe and Zn—are also incorporated into biomass, but for simplicity are neglected here. An important result is that every 138 moles of  $\text{O}_2$  produced by the photosynthetic biosphere requires a mole of bioavailable phosphorus (P, shown here as phosphate) and 16 moles of bioavailable nitrogen (N, shown here as nitrate). These nutrient elements can then either be recycled by respiration back to inorganic, bioavailable forms (“remineralized”) or buried in sediments. In the ocean, nutrients are generally taken up in sunlit surface waters and exported to depth with organic matter, leading to a vertical “biological pump” of organic carbon and nutrients into the ocean interior, with a corresponding demand for  $\text{O}_2$ .

There are strong stabilizing feedbacks that link the oceanic inventories of bioavailable nitrogen and phosphorus (Tyrrell 1999) and that draw together the long-term cycling of nutrients and  $\text{O}_2$  (Fig. 2). For instance, a transient increase in the size of the marine phosphorus reservoir is expected to catalyze increased rates of biological nitrogen fixation, increasing oceanic nitrogen content and bringing the mean ocean N and P budgets back to a “set point” specified by the growth requirements of phytoplankton (the “Redfield ratio”). Conversely, a transient decrease in the size of the marine phosphorus reservoir should inhibit growth of less competitive biological nitrogen fixers, such that



**FIGURE 1** Schematic of Earth’s global oxygen cycle. Black arrows = oxygen sources; grey arrows = oxygen sinks. Oxygenic photosynthesis produces  $\text{O}_2$  in the surface ocean, and some of this is released to the atmosphere. A corresponding amount of organic matter ( $\text{CH}_2\text{O}$ ) is exported from the sunlit surface ocean, creating a respiratory demand for  $\text{O}_2$  in the ocean’s interior (the ‘biological carbon pump’). A fraction of the reducing power contained in this organic matter is deposited in marine sediments, either directly as organic carbon or through burial of reduced sulfur. This burial represents a net release of  $\text{O}_2$ . On geologic timescales, this reducing power is reintroduced to the surface system via uplift, and consumed via weathering or through metamorphic production of reducing gases. Additional long-term fluxes include the escape of hydrogen to space, subduction of oxidized or reduced species into the deep Earth, and the degassing of primitive reducing volatiles from Earth’s mantle.



**FIGURE 2** Processes that regulate the mean ocean nutrient budgets. **(A)** The Redfield line (in red) is the ratio of N to P in marine phytoplankton and in the deep oceans. A point on the line (red circle) is taken as an example of what happens under two scenarios: enhanced weathering/recycling of P and elevated burial/scavenging of P. Dashed and solid arrows denote adjustments following the perturbations to the ocean phosphate ( $\text{PO}_4^{3-}$ ) budget from an initial state. **(B)** Long-term regulation of the mean ocean N and P budgets is driven by competition between N fixing ( $\mu_f$ ) and nonfixing phytoplankton ( $\mu_o$ ) (Tyrrell 1999). When P is in excess relative to N, the N fixers outcompete other phytoplankton (low  $\mu_o/\mu_f$ ) and push the ocean N/P ratio back toward that required for the growth of nonfixing plankton (the Redfield ratio).

continued loss of nitrogen from the ocean interior through microbial denitrification and the sedimentary burial of organic nitrogen will draw the nitrogen reservoir down until the N/P set point is reached (Fig. 2). This simple thermostatic behavior can be modulated by the taxonomically diverse nutrient requirements of plankton and ocean circulation, but requires only that nitrogen fixation incur an energetic cost due to the difficulty of enzymatically breaking down  $\text{N}_2$  (Tyrrell 1999). In this framework, the long-term fertility of the biosphere (and, thus, the capacity of Earth’s biosphere to produce  $\text{O}_2$ ) is controlled most directly by the availability of P in Earth’s oceans. Earth’s surface  $\text{O}_2$  cycle must, therefore, be considered in the context of the processes that regulate oceanic P cycling.

### The Importance of Ocean Redox Structure for Oxygen and Nutrient Cycling

The impacts of atmospheric chemistry and planetary nutrient cycling on Earth’s surface  $\text{O}_2$  are tightly linked through ocean redox structure. First, it is the abundance of  $\text{O}_2$  in the atmosphere and the cycling of nutrients through the biological pump that structure the ocean

redox landscape. At the same time, this redox landscape feeds back on marine nutrient cycling through a range of mechanisms that can, ultimately, act as either positive or negative feedbacks on long-term biospheric O<sub>2</sub> production.

Deep ocean O<sub>2</sub> is governed by the balance between O<sub>2</sub> supply through gas exchange at the ocean surface and through downward mixing of O<sub>2</sub>-rich waters, and by O<sub>2</sub> demand through aerobic respiration once a water mass is no longer in communication with the atmosphere. Thus, under a constant ocean circulation regime, O<sub>2</sub> supply is controlled principally by atmospheric O<sub>2</sub> abundance, whereas O<sub>2</sub> demand is controlled principally by the intensity of the biological carbon pump (and, hence, nutrient abundance). This relationship can be understood heuristically by considering a simple three-box ocean model of oxygen and nutrient biogeochemistry (Fig. 3). In this model, we can derive a simple expression for the global average O<sub>2</sub> concentration in the ocean interior at steady state ([O<sub>2</sub>]<sub>int</sub>):

$$[O_2]_{int} = [O_2]_{vent} - \lambda([PO_4^{3-}]_{int} - [PO_4^{3-}]_{vent}) \quad (4)$$

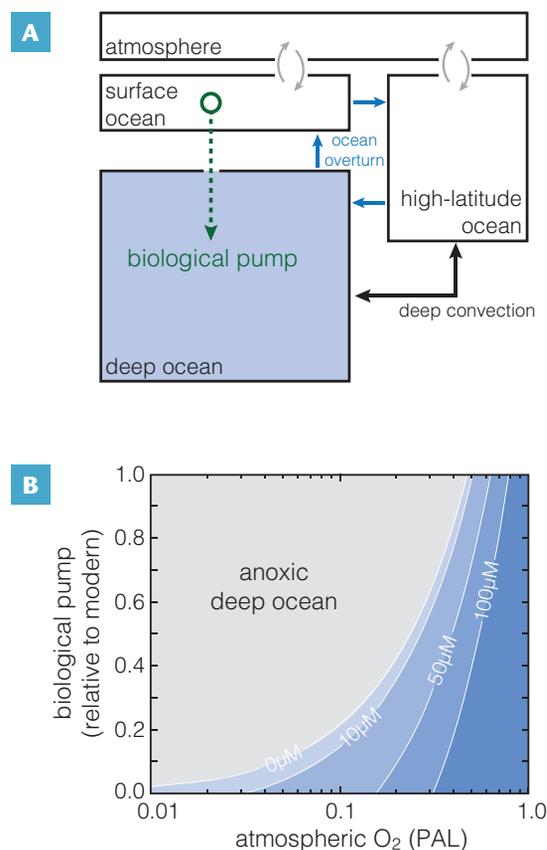
where [O<sub>2</sub>]<sub>vent</sub> and [PO<sub>4</sub><sup>3-</sup>]<sub>vent</sub> denote the oxygen and phosphate concentrations of cold, high-latitude waters ventilating the ocean interior, [PO<sub>4</sub><sup>3-</sup>]<sub>int</sub> denotes the phosphate abundance of the ocean interior, and λ denotes the stoichiometric relationship between the amount of phosphate released during consumption of O<sub>2</sub> during aerobic respiration (see Equation 3). The term in parentheses describes the fraction of nutrients mixed into the high-latitude surface ocean that is consumed during photosynthesis (currently with a value of ~1 μmol kg<sup>-1</sup>) and can be thought of as depicting the efficiency of the biological pump.

Using this approach, one can estimate the steady state concentration of O<sub>2</sub> in the deep ocean as a function of both atmospheric O<sub>2</sub> abundance and biological pump efficiency (Fig. 3). This analysis shows that the ocean interior can be driven to the point of pervasive anoxia by either dropping atmospheric O<sub>2</sub> abundance or by increasing the strength/efficiency of the biological pump. For example, with a modern biological pump this model predicts that the ocean interior would become pervasively anoxic at an atmospheric O<sub>2</sub> abundance ~40% that of the modern Earth. Alternatively, with an atmospheric O<sub>2</sub> abundance of 10% of the modern Earth even a relatively weak biological pump operating at ~20% of modern intensity would provide sufficient O<sub>2</sub> demand in the ocean interior to drive the ocean toward extensive anoxia. Despite being incapable of capturing the impact of differences in ocean circulation, remineralization length scale of organic carbon in the water column, or spatial variability in deep O<sub>2</sub>, this model illustrates an important principle—it is the combination of atmospheric O<sub>2</sub> abundance and the activity level of the ocean biosphere (as governed by ocean nutrient inventory) that fundamentally dictates the marine redox landscape.

There is, however, an important caveat to this analysis. It implicitly assumes that the abundance of O<sub>2</sub> in the ocean–atmosphere system and the marine inventory of bioavailable phosphorus can be varied independently of one another. In reality, the throughput of bioavailable phosphorus fundamentally controls the ocean–atmosphere O<sub>2</sub> abundance at steady state (Lenton and Watson 2000), while ocean redox state controls the recycling and bioavailability of phosphorus in marine systems (Van Cappellen and Ingall 1994; Reinhard et al. 2017). To gain intuition for this, one can consider the dynamics regulating the most significant O<sub>2</sub> production and removal fluxes on the modern Earth—the burial and oxidation of organic carbon (Fig. 1). The efficiency of organic carbon burial in

marine sediments, and, thus, the amount of O<sub>2</sub> released by the biosphere at a given nutrient abundance, increases as O<sub>2</sub> decreases. At the same time, all of the processes that consume O<sub>2</sub>, including oxidation of organic carbon in the crust, slow down as O<sub>2</sub> drops. This combination provides strong negative feedback against decreasing atmospheric O<sub>2</sub>—as atmospheric O<sub>2</sub> drops, the sources of O<sub>2</sub> tend to increase while the sinks tend to decrease, pushing atmospheric O<sub>2</sub> back up. Lowering atmospheric O<sub>2</sub> beyond a certain level requires either a decrease in the inputs of bioavailable P to the marine system or an increase in the inorganic sinks of P from the oceans (e.g., less efficient use of bioavailable P by the marine biosphere).

At the same time, ocean redox plays an important role in controlling the recycling and bioavailability of phosphorus, which, in turn, impacts long-term biospheric O<sub>2</sub> production. When the ocean interior is pervasively oxygenated, as on the modern Earth, bioavailable phosphorus is removed primarily through burial in marine sediments either as an authigenic mineral phase, or as a sorbed species on sedimentary Fe-oxides, or as a constituent of organic matter, with the remainder removed largely in association with Fe-oxide minerals in deep-sea hydrothermal systems (Ruttenberg 2014). In contrast, anoxic conditions can lead to a range of recycling processes that can dramatically impact phosphorus bioavailability. Anoxic and sulfidic



**FIGURE 3** (A) Schematic depiction of a three-box model for oxygen and phosphorus distributions within the ocean. Oxygen is introduced through gas exchange at the ocean surface and then mixed throughout the ocean via overturning circulation and deep convection. Organic matter produced by photosynthesis sinks into the ocean interior (the ocean “biological pump”), and creates respiratory O<sub>2</sub> demand. (B) Steady state dissolved O<sub>2</sub> concentrations in the deep ocean as a function of both atmospheric O<sub>2</sub> level and the strength of the biological pump relative to that of the modern ocean. Contours are labeled according to dissolved O<sub>2</sub> concentration; the grey shaded region denotes conditions under which the deep ocean is expected to become anoxic. PAL = present atmospheric level.

conditions, either in the water column (“euxinia”) or in surface marine sediments, result in remobilization of Fe-oxide-bound phosphorus and can change the style of organic phosphorus recycling, both of which can potentially lead to more effective recycling of bioavailable phosphorus under sulfidic anoxia (Van Cappellen and Ingall 1994). In contrast, anoxic but iron-rich (“ferruginous”) conditions can lead to effective scavenging and removal of bioavailable phosphorus through two principal mechanisms: the formation of Fe-phosphate mineral phases and coprecipitation of P with other Fe-bearing minerals (see Reinhard et al. 2017 and references therein).

## THE EVOLUTION OF OCEAN-ATMOSPHERE REDOX ON EARTH

Earth’s modern atmosphere is strongly oxidizing, being composed of ~21% O<sub>2</sub> by volume, with reducing gases generally present at trace abundance. Indeed, this abundance of O<sub>2</sub> (and its photochemical by-product, ozone, O<sub>3</sub>) gives rise to a series of compelling “biosignatures” in the atmosphere that are, in principle, detectable from remote distances through atmospheric spectroscopy (Meadows et al. 2018). An important consequence of this high O<sub>2</sub> level in the atmosphere is that the oceans are generally very well-oxygenated, despite a large and robust biosphere and attendant respiratory demand in the ocean’s interior. However, atmospheric O<sub>2</sub> has changed by many orders of magnitude throughout Earth’s history, in concert with dramatic shifts in biogeochemical cycling, tectonic events, perturbations to global climate, and biological innovations, all of which have impacted ocean redox structure.

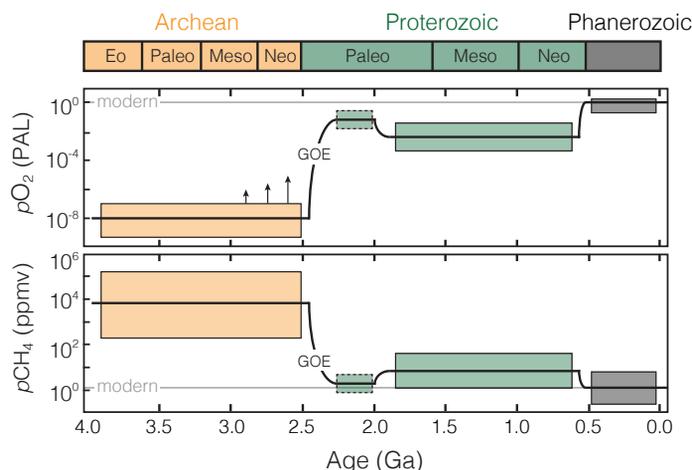
Prior to the evolution of oxygenic photosynthesis, the abundance of O<sub>2</sub> in Earth’s atmosphere would have been extremely low, with production largely through CO<sub>2</sub> photolysis, yielding ground-level O<sub>2</sub> abundances of ~10<sup>-12</sup> times the present atmospheric level (PAL) (Kasting et al. 1979). This means that the redox state of the atmosphere would once have been dominated by some combination of H<sub>2</sub> and CH<sub>4</sub>; O<sub>2</sub> would have been virtually absent from oceanic environments. Following the emergence of oxygenic photosynthesis, the potential for locally nontrivial dissolved O<sub>2</sub> abundances in the shallowest marine systems would have emerged (so-called “oxygen oases”). This conceptual framework finds support from both theoretical models (Olson et al. 2013) and geochemical observations (e.g., Planavsky et al. 2014). Nevertheless, the preservation of significant sulfur mass-independent fractionation (S-MIF) isotope signals in marine sediments deposited prior to ~2.3 Ga indicates a pervasively anoxic atmosphere (Farquhar et al. 2000), likely on the order of ~10<sup>-7</sup> PAL (Zahnle et al. 2006). Such low atmospheric O<sub>2</sub> abundances are consistent with a wide range of independent geologic evidence (Holland 1984). Atmospheric O<sub>2</sub> would be regulated in this Earth system state via consumption by reduced volcanic gasses and reaction with reduced Fe and S in the Earth’s crust, with localized regions of elevated O<sub>2</sub> in shallow seas (Fig. 4). An important wrinkle to this framework comes in the form of transient “whiffs” of atmospheric O<sub>2</sub> during the Neoproterozoic, as deduced from trace element, isotopic, and mineralogical records (see Lyons et al. 2014).

Although it seems clear that O<sub>2</sub> was present at trace abundance for most, if not all, of Hadean and Archean time (at levels of ~10<sup>-12</sup> – 10<sup>-7</sup> PAL), the abundances of the most important reducing gases, H<sub>2</sub> and CH<sub>4</sub>, are not well-constrained. Photochemical models predict that a nontrivial abundance of reducing atmospheric gas (either H<sub>2</sub> or CH<sub>4</sub>) must be present in order to preserve distinct exit channels for photolytic sulfur from the atmosphere and,

thus, support the preservation of S-MIF signals. But the precise quantitative requirements are unclear. More recently, it has been suggested that the apparent mass fractionation of xenon isotopes in the Archean atmosphere requires a total hydrogen mixing ratio in the atmosphere above ~1% (corresponding to an atmospheric CH<sub>4</sub> abundance of ~0.5%) in order to support the requisite atmospheric escape rates (Zahnle et al. 2019). This is broadly consistent with photochemical and coupled biosphere-atmosphere models for the Archean Earth system (Kharecha et al. 2005; Ozaki et al. 2018).

A variety of geochemical and geologic observations, including the disappearance of S-MIF signals from the rock record, indicate that the initial accumulation of O<sub>2</sub> in Earth’s atmosphere occurred at ~2.4–2.3 Ga. This is often referred to as the Great Oxidation Event (GOE). How “great” this event was, however, remains an open question. The disappearance of S-MIF signals from the sedimentary record only requires a relatively small change in the overall size of the atmospheric O<sub>2</sub> reservoir. For example, a shift in atmospheric *p*O<sub>2</sub> from 10<sup>-7</sup> to 10<sup>-4</sup> PAL, more than sufficient to shut down S-MIF signals, would require the net accumulation of only ~0.01% of the modern atmospheric O<sub>2</sub> inventory. Nevertheless, it is manifestly evident in a range of sedimentological and geochemical records that this geologically brief interval marks an important shift in the background redox state of Earth’s atmosphere (Holland 1984).

More recently, it has been suggested that there was a protracted—but ultimately transient—period of elevated atmospheric O<sub>2</sub> abundance between ~2.2 Ga and 2.0 Ga (Fig. 4). This period coincides with a striking perturbation to Earth’s carbon cycle, evident in an extended period of <sup>13</sup>C-enriched carbonates deposited worldwide—the so-called “Lomagundi Event” (Schidlowski et al. 1976). Early estimates suggested that this carbon cycle perturbation represented a long-term pulse of organic matter



**FIGURE 4** Evolving redox state of Earth’s atmosphere in terms of the two major redox-active species in Earth’s atmosphere: 1) partial pressures of oxygen (*p*O<sub>2</sub>) relative to the present atmospheric level (PAL); 2) partial pressures of methane (*p*CH<sub>4</sub>) in parts per million by volume (ppmv). Shaded boxes (Archean in orange; Proterozoic in green; Phanerozoic in grey) show ranges derived from the geologic record and theoretical models, while the black line on each of the two graphs shows one plausible trajectory through these models. Upward arrows denote possible Meso- to Neoproterozoic “whiffs” of atmospheric O<sub>2</sub>, though their timing, duration, and magnitude are not fully known. A putative transient high-O<sub>2</sub> interval is also shown with the dashed shaded box (in the Paleoproterozoic), though the atmospheric composition during this period is not well-constrained. Values for the modern atmosphere are shown as grey lines. GOE = Great Oxidation Event.

deposition corresponding to the release of ~10–20 times the current atmospheric O<sub>2</sub> inventory (Karhu and Holland 1996). This is consistent with a number of geochemical records that suggest a transient elevation in atmospheric *p*O<sub>2</sub> during this interval (Blättler et al. 2018). However, the quantitative scaling between <sup>13</sup>C enrichment and O<sub>2</sub> release during this period is somewhat obscure, and it is not yet clear how this O<sub>2</sub> release would have partitioned itself within the ocean–atmosphere–crust system. For example, isotope-enabled biogeochemical models are capable of producing “Lomagundi-type” carbon isotope excursions under conditions of relatively modest atmospheric *p*O<sub>2</sub> (Miyazaki et al. 2018), but this requires a net transfer of oxidizing power to the crustal sulfate reservoir. In any case, it seems reasonable that between ~2.2 Ga and 2.0 Ga the ocean redox landscape would have featured a pervasively well-oxygenated mixed layer with dissolved O<sub>2</sub> concentrations controlled largely by gas exchange with the atmosphere, and possibly widespread oxygenation of the ocean interior. Fully elucidating these features of the Earth system during this period awaits more precise quantitative constraints on atmospheric O<sub>2</sub> abundance (Fig. 4).

Though it is apparent that atmospheric O<sub>2</sub> increased after ~2.5 Ga, atmospheric abundances of O<sub>2</sub> over the ensuing ~2 Gy are uncertain. A lack of significant stable chromium (Cr) isotope fractionation in some ironstones, marine shales, and ancient soil horizons (paleosols) has been interpreted to reflect very low atmospheric *p*O<sub>2</sub>, perhaps as low as ~10<sup>-3</sup> PAL, for much of the period between ~1.8 Ga and 0.8 Ga. This is consistent with the observed mobilization behavior of iron (Fe) and manganese (Mn) in paleosols, records of rare earth element (REE) behavior in marine carbonates, and the stable oxygen isotope composition of Proterozoic evaporite minerals (summarized in Planavsky et al. 2018). Some workers have suggested much higher levels of atmospheric *p*O<sub>2</sub> during this period (Zhang et al. 2016), raising the possibility of significant time-dependent variability in atmospheric redox during the Mesoproterozoic (cf. Planavsky et al. 2016). In any case, the paradigmatic view is that atmospheric *p*O<sub>2</sub> was significantly lower than that of the modern Earth prior to ~600–800 Ma, somewhere between ~0.1% PAL and 10% PAL (Fig. 4). Regulation of atmospheric O<sub>2</sub> in this state is still unclear, but it is likely to have been controlled by incomplete oxidation of reduced C, Fe, and S in Earth’s crust together with muted biospheric O<sub>2</sub> production as a result of P scavenging from pervasively anoxic oceans.

Atmospheric CH<sub>4</sub> during Earth’s middle history is less well-constrained, because there are currently no available geologic proxies for the quantitative abundance of CH<sub>4</sub> in Earth’s atmosphere at intermediate redox states. Indeed, even under a mildly reducing atmosphere, proxy constraints are indirect and plagued by significant uncertainty. Photochemical models predict that once atmospheric O<sub>2</sub> is high enough to support significant ozone, CH<sub>4</sub> can be shielded from photochemical destruction and tends to “rebound” to relatively high values following an initial drop during the Great Oxidation Event (Claire et al. 2006), perhaps to as high as ~100 ppm. However, models of ocean biogeochemistry that take into account the potential for effective microbial sinks for CH<sub>4</sub> in marine environments tend to predict steady-state atmospheric CH<sub>4</sub> abundances that are much lower than ~100 ppm under Proterozoic conditions, more on the order of ~1–10 ppm (Olson et al. 2016), unless CH<sub>4</sub> abundances had been supplemented by significant fluxes from nascent terrestrial ecosystems (Zhao et al. 2018).

In any case, evidence from the rock record indicates a dramatic reorganization of Earth surface biogeochemistry and ocean–atmosphere redox state at some point in the late Proterozoic, perhaps as early as ~800 Ma (Lyons et al. 2014). This period may have marked a pervasive—though perhaps episodic—oxygenation of Earth’s deepest oceans, broadly in step with major shifts in biospheric complexity and perturbations to global climate. Earth’s ocean–atmosphere system has been largely oxidizing subsequent to this tumultuous interval. There have been very occasional excursions to more pervasively reducing environments in the ocean interior, but against a backdrop of strongly oxidizing atmospheric chemistry (Fig. 4). Regulation of atmospheric O<sub>2</sub> in this state has been principally through the incomplete oxidation of organic carbon in Earth’s crust and the increased efficiency of organic carbon burial when oxygenation of the ocean interior decreases (Daines et al. 2017).

## MAJOR REMAINING FRONTIERS

The history of ocean–atmosphere redox on Earth has been understood in broad strokes for many decades (Holland 1962), and this long-term evolutionary texture is very likely robust. However, placing quantitative constraints on ancient atmospheric composition and ocean chemistry is challenging, and many fascinating questions remain. In particular, the coming years will witness many exciting advances in efforts to place more precise constraints on background atmospheric O<sub>2</sub> during the Paleo- and Mesoproterozoic, to constrain the overall size and scope of Earth’s photosynthetic biosphere through time, better understand the mechanisms regulating the amount of atmospheric O<sub>2</sub> during different periods of Earth’s history and the transitions between them, and to develop a better mechanistic understanding of the processes that link major nutrient cycles to evolving ocean–atmosphere O<sub>2</sub>.

Many of the geochemical proxies for the abundance of O<sub>2</sub> in surface environments that have been the most useful in recent years are still being developed, and more direct coupling of proxy records with quantitative models will be central to the further refinement of quantitative estimates for atmospheric *p*O<sub>2</sub>. Issues of particular interest include constraining the duration, causes, and magnitude of Neoproterozoic “whiffs” of O<sub>2</sub>; estimating atmospheric *p*O<sub>2</sub> during the putative “oxygen overshoot” in the Paleoproterozoic; and more definitively constraining O<sub>2</sub> levels in surface environments during the Mesoproterozoic in the lead up to the rise of complex life. In some cases, proxy reconstructions for atmospheric O<sub>2</sub> will rely on independent constraints on other atmospheric properties, such that the development of better estimates for other atmospheric gases (such as CO<sub>2</sub>) will also be crucial for constraining O<sub>2</sub>.

Much the same can be said for attempts to constrain the productivity of Earth’s biosphere through time, a critical component of the O<sub>2</sub> cycle. A particularly exciting development in this regard is the exploration of the triple oxygen isotope composition of marine and lacustrine sediments during Earth’s history, which can potentially be used to constrain global photosynthetic productivity (Crockford et al. 2018) or be inverted to estimate atmospheric *p*O<sub>2</sub> (Planavsky et al. 2018). However, a number of challenges remain, including the potentially sporadic stratigraphic distribution of the sedimentary archives for the rare oxygen isotope signal, the need for more mechanistic models that couple surface isotope signals to atmospheric production and downstream recycling, and limits of precision that may ultimately be controlled by the need for independent constraints on atmospheric CO<sub>2</sub>.

Further development of empirical constraints from Earth's rock record will provide crucial tie points for theoretical models aimed at understanding the basic processes that regulate Earth's oxygen cycle, and the processes that link the surface redox landscape to nutrient recycling and the productivity of the biosphere. A striking example is the Earth system during mid-Proterozoic time, ~1.8–0.8 Ga. Models and existing geochemical data suggest that atmospheric O<sub>2</sub> was well below that of the modern Earth, but how such 'weakly oxygenated' conditions at Earth's surface would be regulated on long timescales is a major outstanding question. This is due in part to uncertainties in empirical reconstructions of atmospheric O<sub>2</sub>, but it is also related to the fact that Earth's O<sub>2</sub> cycle at intermediate redox states is likely to be strongly controlled by a range of processes not currently well represented in biogeochemical models. Foremost, parameterizations of nutrient scavenging under reducing conditions; the competitive dynamics between oxygenic and anoxygenic photosynthetic organisms; and the redox cycling of reduced C, S, and Fe in Earth's crust under low O<sub>2</sub> conditions all need to be improved. Some of these improvements will only be possible with new kinetic data.

Interesting questions remain even deeper into Earth's past. For example, it is still not definitively known whether the reducing capacity of Earth's mantle (as described in Stagno and Fei 2020 this issue) has changed over time, with potentially dramatic implications for processes controlling

atmospheric abundances of O<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, and a range of other redox-active species. As a result, our understanding of the background redox state of Earth's atmosphere during Hadean/Archean time would benefit significantly from better empirical constraints on mantle redox state during Earth's early history and better empirical and/or theoretical constraints on degassing fluxes throughout Earth's evolution. In addition, it remains unclear when oxygenic photosynthesis first emerged and began to influence the redox structure of Earth's surface oceans. Constraining the timing of this foundational biological novelty with confidence will ultimately require the leveraging of new geochemical redox proxies, the combination of new observations with existing and well-established approaches, and better quantitative models for evaluating "false positives" for the presence of O<sub>2</sub> in Earth's surface environments when Earth's atmosphere was reducing.

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