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$_2$) 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$_2$. These coupled processes can be denoted as:

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2 \quad (1)$$

Any photosynthetic biomass removed from the surface system via burial in marine or terrestrial sediments leads to a net accumulation of O$_2$ 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$_2$ 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$_2$ cycle (photosynthesis/respiration), responding on timescales of less than ~10$^3$ years, and a "slow" O$_2$ cycle (organic carbon burial and weathering/thermal breakdown), responding on timescales of ~10$^6$ years.

There is an additional long-term cycle that links O$_2$ to the cycling of sulfur (S) and iron (Fe) at Earth's surface:

$$2\text{Fe}_2\text{O}_3 + 8\text{SO}_4^{2−} + 16\text{H}^+ \rightarrow 15\text{O}_2 + 4\text{FeS}_2 + 8\text{H}_2\text{O} \quad (2)$$

Moving from left to right in Equation (2) denotes the sum of three processes: (1) photosynthesis; (2) consumption of biomass through microbial sulfate (SO$_4^{2−}$) reduction, producing reduced sulfur (S$^2−$); (3) formation of pyrite (FeS$_2$) via reaction between reduced sulfur and reactive iron in the environment (shown here as hematite, Fe$_2$O$_3$). 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$_2$. The subsequent uplift/weathering and/or volatilization of reduced sulfur species in the crust balances this release of O$_2$ 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$_2$, 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$^9$ 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$_2$ 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:

$$2\text{Fe}_2\text{O}_3 + 8\text{SO}_4^{2−} + 16\text{H}^+ \rightarrow 15\text{O}_2 + 4\text{FeS}_2 + 8\text{H}_2\text{O} \quad (2)$$
106CO2 + 16HNO3 + H3PO4 + 122H2O ⇔ (CH2O)106(NH4)16(H2PO4) + 138O2

(3)

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 O2 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 O2.

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 O2 (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 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 N2 (Tyrrell 1999). In this framework, the long-term fertility of the biosphere (and, thus, the capacity of Earth’s biosphere to produce O2) is controlled most directly by the availability of P in Earth’s oceans. Earth’s surface O2 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 O2 are tightly linked through ocean redox structure. First, it is the abundance of O2 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 O2 production.

Deep ocean O2 is governed by the balance between O2 supply through gas exchange at the ocean surface and through downward mixing of O2-rich waters, and by O2 demand through aerobic respiration once a water mass is no longer in communication with the atmosphere. Thus, under a constant ocean circulation regime, O2 supply is controlled principally by atmospheric O2 abundance, whereas O2 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 O2 concentration in the ocean interior at steady state ([O2]int):

\[
[O2]_{\text{int}} = [O2]_{\text{vent}} - \lambda ([PO4^{3-}]_{\text{int}} - [PO4^{3-}]_{\text{vent}})
\]

where [O2]vent and [PO4^{3-}]vent denote the oxygen and phosphate concentrations of cold, high-latitude waters ventilating the ocean interior, [PO4^{3-}]int denotes the phosphate abundance of the ocean interior, and \( \lambda \) denotes the stoichiometric relationship between the amount of phosphate released during consumption of O2 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 \(-1 \mu\text{mol kg}^{-1}\)) and can be thought of as depicting the efficiency of the biological pump.

Using this approach, one can estimate the steady state concentration of O2 in the deep ocean as a function of both atmospheric O2 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 O2 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 O2 abundance \(-40\%\) of the modern Earth. Alternatively, with an atmospheric O2 abundance of 10% of the modern Earth even a relatively weak biological pump operating at \(-20\%\) of modern intensity would provide sufficient O2 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 O2, this model illustrates an important principle—it is the combination of atmospheric O2 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 O2 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 O2 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 O2 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 O2 released by the biosphere at a given nutrient abundance, increases as O2 decreases. At the same time, all of the processes that consume O2, including oxidation of organic carbon in the crust, slow down as O2 drops. This combination provides strong negative feedback against decreasing atmospheric O2—as atmospheric O2 drops, the sources of O2 tend to increase while the sinks tend to decrease, pushing atmospheric O2 back up. Lowering atmospheric O2 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 O2 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
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% O₂ by volume, with reducing gases generally present at trace abundance. Indeed, this abundance of O₂ (and its photochemical by-product, ozone, O₃) 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 O₂ 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 O₂ has changed by many orders of magnitude throughout Earth’s history, in concert with dramatic shifts in biogeochemical cycling, tectonic events, perturbations 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 O₂ in Earth’s atmosphere would have been extremely low, with production largely through CO₂ photolysis, yielding ground-level O₂ abundances of ~10⁻¹² 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 H₂ and CH₄; O₂ would have been virtually absent from oceanic environments. Following the emergence of oxygenic photosynthesis, the potential for locally nontrivial dissolved O₂ 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 ~10⁻⁷ PAL (Zahnle et al. 2006). Such low atmospheric O₂ abundances are consistent with a wide range of independent geologic evidence (Holland 1984). Atmospheric O₂ would be regulated in this Earth system state via consumption by reduced volcanic gases and reaction with reduced Fe and S in the Earth’s crust, with localized regions of elevated O₂ in shallow seas (Fig. 4). An important wrinkle to this framework comes in the form of transient “whiffs” of atmospheric O₂ during the Neorarchean, as deduced from trace element, isotopic, and mineralogical records (see Lyons et al. 2014).

Although it seems clear that O₂ was present at trace abundance for most, if not all, of Hadean and Archean time (at levels of ~10⁻¹² – 10⁻¹⁰ PAL), the abundances of the most important reducing gases, H₂ and CH₄, are not well-constrained. Photochemical models predict that a nontrivial abundance of reducing atmospheric gas (either H₂ or CH₄) 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 CH₄ abundance of ~0.5%) in order to support the requisite atmospheric escape rates (Fahnle 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 O₂ 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 O₂ reservoir. For example, a shift in atmospheric p O₂ from 10⁻⁷ to 10⁻⁴ PAL, more than sufficient to shut down S-MIF signals, would require the net accumulation of only ~0.01% of the modern atmospheric O₂ inventory. Nevertheless, it is manifestly evident in a range of sedimentological and geochronological 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 O₂ 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 ¹³C-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 O₂) relative to the atmosphere level (PAL); 2) partial pressures of methane (p CH₄) 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 Mesozoic–Neorarchean “whiffs” of atmospheric O₂, though their timing, duration, and magnitude are not fully known. A putative transient high-O₂ 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.
Atmospheric CH$_4$ during Earth’s middle history is less well-constrained, because there are currently no available geologic proxies for the quantitative abundance of CH$_4$ 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$_2$ is high enough to support significant ozone, CH$_4$ 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$_4$ in marine environments tend to predict steady-state atmospheric CH$_4$ 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$_4$ abundances had been supplemented by significant fluxes from nascent terrestrial ecosystems (Zhao et al. 2018).
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. Geochemical and existing geological evidence for atmospheric \(O_2\) 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 \(O_2\), but it is also related to the fact that Earth's \(O_2\) 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 \(O_2\) 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 \(O_2, CH_4, H_2,\) 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 geologic evolution. In data-sparse regions like the虏gebeny, 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 \(O_2\) in Earth's surface environments when Earth's atmosphere was reducing.

**ACKNOWLEDGMENTS**

We are grateful to the NASA Astrobiology Institute, the NASA Nexus for Exoplanet System Science (NExSS), the Alfred P. Sloan Foundation, and the NSF Earth-Life Transitions Program for financial support. We are also particularly indebted to Giada Arney, Devon Cole, Sean Crowe, Kurt Konhauser, Stefan Lalonde, Timothy Lyons, Stephanie Olson, Kazumi Ozaki, and Edward Schwieterman for the discussions and collaborations that underpin much of what is discussed here.

**REFERENCES**

Blättler CL and 16 coauthors (2018) Two-billion-year-old evaporites capture Earth's great oxygen cycle. Science 360: 320-323

Claire MW, Catling DC, Zahnele KJ (2006) Biogeochemical modelling of the rise in atmospheric oxygen. Geobiology 4: 239-269

Crockford PW and 9 coauthors (2018) Triple oxygen isotope evidence for limited mid-Proterozoic primary productivity. Nature 559: 613-616

Daines SJ, Mills BJW, Lenton TM (2017) Atmospheric oxygen regulation at low Proterozoic levels by incomplete oxidative weathering of sedimentary organic carbon. Nature Communications, doi:10.1038/ncomms14379

Farquhar J, Bao H, Thiemens M (2000) Atmospheric influence of Earth's earliest sulfur cycle. Science 289:756-758

Holland HD (1962) Model for the evolution of the Earth's atmosphere. In: Engel AFI, James HL, Leonard BF (eds) Petrologic Studies: A Volume in Honor of A. F. Buddington. Geological Society of America, New York, pp 447-477

Holland HD (1984) The Chemical Evolution of the Atmosphere and Oceans. Princeton University Press, Princeton, 598 pp

Karhu JA, Holland HD (1996) Carbon isotopes and the rise of atmospheric oxygen. Geology 24: 867-870

Kasting JF, Liu SC, Donahue TM (1979) Oxygen levels in the prebiological atmosphere. Journal of Geophysical Research: Oceans 84: 3097-3107

Kharecha P, Kasting J, Siefert J (2005) A coupled atmosphere-ecosystem model of the early Archean Earth. Geobiology 3: 53-76

Lenton TM, Watson AJ (2000) Redfield revisited 2. What regulates the oxygen content of the atmosphere? Global Biogeochemical Cycles 14: 249-268

Lyons TW, Reinhard CT, Planavsky NJ (2014) The rise of oxygen in Earth's early ocean and atmosphere. Nature 506: 307-315

Meadows VS and 16 coauthors (2018) Exoplanet biosignatures: understanding oxygen as a biosignature in the context of its environment. Astrobiology 18: 630-662

Miyazaki Y, Planavsky NJ, Bolton EW, Reinhard CT (2018) Making sense of massive carbon isotope excursions with an inverse carbon cycle model. Journal of Geophysical Research: Biogeosciences, 123: 2485-2496

Olson SL, Kump LR, Kasting JF (2013) Quantifying the areal extent and dissolved oxygen concentrations of Archean ocean oases. Chemical Geology 362: 35-43

Olson SL, Reinhard CT, Lyons TW (2016) Limited role for methane in oxygen for animal respiration 1,400 million years ago. Proceedings of the National Academy of Sciences of the United States of America 113: 11447-11452

Ozaki K, Tajika E, Hong PK, Nakagawa Y, Zahnle KJ, Gacesa M, Catling D (2019) Collapse of atmospheric methane. Nature Geoscience 12: 609-616

Planavsky NJ and 8 coauthors (2016) Sufficient oxygen for animal respiration 1,400 million years ago. Proceedings of the National Academy of Sciences of the United States of America 113: E2550-E2551

Reinhard CT and 9 coauthors (2017) Evolution of the global phosphorus cycle. Nature 541: 386-389

Ruttenberg KC (2014) The global phosphorus cycle. In: Karl DM, Schlesinger WH (eds) Treatise on Geochmistry, Volume 10, 2nd Edition. Elsevier, pp 499-558

Schildkroft M, Eichmann R, Junge CE (1976) Carbon isotope geochemistry of the Precambrian Lomagundi carbonate province, Rhodesia. Geochemistry et Cosmochimica Acta 40: 449-455

Stagno V, Fei Y (2020) The redox boundary of Earth's interior. Elements 16: 167-172

Tyrrell T (1999) The relative influences of nitrogen and phosphorus on oceanic primary production. Nature 400: 532-534

Van Cappellen P, Ingall ED (1994) Benthic phosphorus regeneration, net primary production, and ocean anoxia: a model of the coupled marine biogeochemical cycles of carbon and phosphorus. Paleocenography and Paleoclimatology 9: 677-692

Zahnle K, Claire M, Catling D (2006) The loss of mass-independent fractionation in sulfur due to a Palaeoproterozoic collapse of atmospheric methane. Geobiology 4: 271-283

Zahnle KJ, Gacesa M, Catling DC (2019) Strange messenger: a new history of hydrogen on Earth, as told by xenon. Geochimica et Cosmochimica Acta 244: 56-85

Zhang S and 9 coauthors (2016) Sufficient oxygen for animal respiration 1,400 million years ago. Proceedings of the National Academy of Sciences of the United States of America 113: 1731-1736

Zhang M, Reinhard CT, Planavsky N (2018) Terrestrial methane fluxes and Proterozoic climate. Geology 46: 139-142

**Elements**

**JUNE 2020**