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Linda C. Kah^a; Julie K. Bartley^b

^a Department of Earth and Planetary Sciences, University of Tennessee, 1412 Circle Drive, Knoxville, TN, USA ^b Department of Geology, Gustavus Adolphus College, 800 West College Avenue, Saint Peter, MN, USA

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Protracted oxygenation of the Proterozoic biosphere

Linda C. Kah^{a*} and Julie K. Bartley^b

^aDepartment of Earth and Planetary Sciences, University of Tennessee, 1412 Circle Drive, Knoxville, TN 37996 USA; ^bDepartment of Geology, Gustavus Adolphus College, 800 West College Avenue, Saint Peter, MN 56082, USA

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Our current understanding of Proterozoic (2.5–0.54 Ga) biospheric evolution highlights the critical role played by the progressive oxygenation of Earth's surface environments and its effect on oceanic redox potential, nutrient availability, carbon isotopic change, and the evolution of life. The most obvious changes occurred in the first 200 million years of the Proterozoic aeon, with the irreversible oxidation of surface environments, and in the last 200 million years of the Proterozoic, when oxygen reached levels sufficient for the diversification of Metazoa. Although the impact of these events cannot be denied, it remains uncertain to what extent these events represent abrupt, large-scale changes in Earth oxygenation versus points of critical threshold along a continuum of biospheric evolution. In this article, we review the current understanding of ocean-atmosphere oxygenation and explore how a view of Earth's oxygenation as a protracted event, spanning nearly 2 billion years, suggests that Phanerozoic-style models might be inadequate to describe the Proterozoic carbon and sulphur cycles and their resultant isotopic records. Furthermore, Proterozoic evolutionary patterns may be better interpreted to reflect localized environmental conditions, rather than abrupt global environmental shifts.

Keywords: Proterozoic; oxygenation; ocean redox; carbon; sulphur; iron

Mechanisms of Earth oxygenation

The oxidation state of Earth's early biosphere was likely affected by a combination of irreversible oxidation of the mantle reservoir (Kump *et al.* 2001; Holland 2002) resulting from the loss to space of upper atmospheric hydrogen (Kasting *et al.* 1993; Catling *et al.* 2001), fundamental changes in the composition of volcanic gases associated with growth and stabilization of the continental crust (Kump and Barley 2007; Holland 2009), and changes in the rate of oxygen production via sedimentary removal of organic matter derived from oxygenic photosynthesis (Des Marais *et al.* 1992; Canfield 2005). The timing and the relative contribution of each of these influences remain unknown. It is clear, however, that widespread biospheric oxygenation could not have occurred until photosynthetic oxygen production exceeded scavenging of available oxygen by the Earth's reduced atmosphere and mantle reservoirs (Catling and Claire 2005).

Once this threshold was reached, presumably in the late Palaeoproterozoic, deciphering Earth's oxygenation history becomes only slightly less complex, inasmuch as the concentration of biospheric oxygen became increasingly regulated by the geochemical cycles of carbon and sulphur (Berner *et al.* 2003; Canfield 2005). In this scenario, oxygen released via organic carbon burial was largely

consumed by oxidative weathering of exposed crustal components. During this weathering process, pyrite oxidation consumed oxygen and delivered sulphate to the oceans. Oceanic sulphate, with organic carbon as a reductant, was then utilized during bacterial sulphate reduction (BSR), producing H₂S that could be either re-oxidized or removed from the system via reaction with ferrous iron and burial as pyrite. Thus, the amount of oxygen released to the biosphere ultimately reflects the linked processes of the carbon and sulphur cycles. Furthermore, because the biogeochemical cycling of both carbon and sulphur is associated with substantial isotopic fractionation, the extent of organic carbon and pyrite burial can be estimated from the isotopic composition of oxidized and reduced phases preserved in marine sediments. Although feedbacks between production and burial of reduced carbon and sulphur species have been used extensively to infer Phanerozoic oxygen levels (Berner 1987, 2001, 2006; Berner *et al.* 2003) and the behaviour of associated biogeochemical cycles (Canfield and Raiswell 1999; Bergman *et al.* 2004; Algeo and Ingall 2007), there are substantial limitations to using such models to reconstruct the oxygenation history of the early Earth, because these models assume that the exogenic cycle had already assumed a modern complement of feedback mechanisms.

*Corresponding author. Email: lckah@utk.edu

Biospheric oxygen availability also plays a crucial role in biotic evolution, principally because anoxia serves as a significant environmental barrier to the diversification of eukaryotic life – and specifically to the evolution of large, metabolically active animals (Knoll and Carroll 1999). Traditionally, biospheric oxygenation has been constrained by evolutionary landmarks, and is perceived to have occurred in discrete oxygenation events in the Palaeoproterozoic (~2.3 Ga) and the Neoproterozoic (~750 Ma). Four physiological ‘thresholds’ have provided an evolutionary context for estimating the concentration of oxygen in the biosphere: (1) that eukaryotic biosynthesis of sterols, which stiffen cell membranes and are preserved as biomarkers called steranes, requires molecular oxygen (Jahnke and Klein 1983); (2) that macroscopic eukaryotes such as *Grypania* and similar morphotypes likely had metabolic requirements of at least 1% of present atmospheric levels (PALs) of oxygen (Han and Runnegar 1992); (3) that oxygen uptake by metazoans lacking a structured circulatory system, such as the Ediacaran *Dickinsonia*, would require 1–3% PAL, if specifically adapted to living under dysaerobic conditions (Runnegar 1991), or perhaps as high as 10% PAL, based on theoretical calculation of metabolic energy yields (Catling *et al.* 2005); and (4) that biosynthesis of collagens critical for biomineralization likely required biospheric oxygen levels > 10% PAL (Towe 1970).

Oxygenation of the early Earth

The Palaeoproterozoic Great Oxidation Event (GOE; Holland 2002) represents perhaps the most significant change in Earth’s oxygenation history. This event is marked by strongly ^{13}C -enriched isotopic signatures in carbonates (Karhu and Holland 1996) broadly coeval with (1) the replacement of redox-sensitive detrital minerals, such as pyrite and uraninite, in terrigenous sediments by iron oxide-bearing ‘red beds’ (Cloud 1968; Holland 1999); (2) a change in the composition of palaeosols suggesting decreased mobility of ferrous iron and increased retention of ferric iron (Rye and Holland 1998); and (3) a substantial increase in the observed range of S-isotope compositions (Cameron 1982) implying that marine sulphate levels were high enough to permit expression of biological fractionation during sulphate reduction. More recently, mass-independent S-isotope data ($\Delta^{33}\text{S}$; Farquhar and Wing 2003) confirm an oxygenation event in the early Proterozoic. By 2.32 Ga (Bekker *et al.* 2004), biospheric oxygen levels rose above 0.001% PAL, the level at which homogenization of mass-independent fractionation occurs (Pavlov and Kasting 2002).

Levels of sustained biospheric oxygen during and immediately following the GOE, however, are unknown. The early evolutionary history of oxygenic photosynthesis

is, at present, poorly constrained. Reports of biomarkers including 2α -methylhopanes in 2.7 Ga sediments were originally interpreted to record the presence of oxygenic photosynthetic cyanobacteria in coeval oceans (Summons *et al.* 1999). More recently, though, anoxygenic photosynthetic bacteria have been shown to synthesize 2-methylhopanes (Rashby *et al.* 2007), making the biomarker case for oxygenic photosynthesis somewhat tenuous. Reports of 2.7 Ga steranes, inferred to be eukaryotic in origin (Brocks *et al.* 2003), have also been reinterpreted as post-Archaeal contaminants (Rasmussen *et al.* 2008), although late Archaeal steranes biomarkers may prove to be syngenetic (Waldbauer *et al.* 2009). Microfossil data are similarly equivocal; although Archaeal units preserve possible or probable microfossils (e.g. Schopf 1993; Ueno *et al.* 2006; Javaux *et al.* 2010), none of the morphotypes is diagnostically cyanobacterial or eukaryotic and biogenicity is difficult to establish (Ueno *et al.* 2006; Marshall *et al.* 2007). Recent approaches using molecular phylogenetics and molecular clock models suggest an early origin for oxygenic photosynthesis, but perhaps a delayed expansion into widespread marine habitats (Blank and Sánchez-Baracaldo 2010). Taken together, the Archaeal biosphere may have had the capacity for oxygen production and hence localized presence of oxygenated conditions 200–400 million years prior to the GOE (cf. Anbar *et al.* 2007; Kaufman *et al.* 2007), even as the record of mass-independent fractionation of sulphur demands that the global levels of oxygenation remain < 0.001% PAL.

Resolution of these seemingly contradictory lines of evidence – that of oxygen production without clear evidence of oxygen accumulation – lies in the growing appreciation of the complex geochemical cycling of carbon, sulphur, iron, and additional elements that compose our geologic proxies for biospheric oxygenation. Karhu and Holland (1996) inferred a substantial increase in biospheric oxygen at the time of the GOE based on estimates of the release of 12–22 \times the present atmospheric oxygen inventory derived from organic carbon burial, and linked this oxygenation to the disappearance of banded iron formations via the oxidative removal of ferrous iron from the oceans (Holland 1999). In a competing hypothesis, Canfield (1998) suggested that even a modest increase in biospheric oxygen could effectively remove ferrous iron from the ocean system via increased sulphate delivery to the oceans, enhanced rates of BSR, sulphide production, and concomitant removal of ferrous iron from the ocean as pyrite. This hypothesis, known as the ‘Canfield Ocean’, predicts that deep-ocean anoxia, driven by still low atmospheric levels of oxygen, persisted long after the GOE, and that increased BSR and hydrogen sulphide production would result in deep-ocean euxinia.

The ‘Canfield Ocean’ model is consistent with recent data suggesting relatively small increases in marine sulphate concentration in the aftermath of the GOE, as well

as the development of sulphidic deep-water conditions. Prior to the GOE, oceanic sulphate concentrations are inferred to have been < 1 mM and possibly less than < 200 mM, on the basis of limited isotopic range preserved in sedimentary sulphides and experimental data showing suppressed isotopic fractionation at low sulphate concentrations (Canfield *et al.* 2000; Habicht *et al.* 2002). S-isotope records show a rapid change in the isotopic composition of marine sulphate coincident with the disappearance of mass-independent fractionation (MIF) signatures, suggesting reorganization of the sulphur cycle with initial oxygenation of Earth's surface (Guo *et al.* 2009). Rapid variation in the isotopic composition of marine sulphate in later Palaeoproterozoic strata (Gellatly and Lyons 2005; Chu *et al.* 2007), however, remains consistent with low atmospheric oxygen levels and a limited oceanic sulphate reservoir (Kah *et al.* 2004).

Perhaps more importantly, in the aftermath of the GOE, open marine shelf settings have been found to record highly reactive iron (FeHR), total iron (FeT), and pyrite iron (FePY) values consistent with deposition under anoxic (FeHR/FeT > 0.38) and sulphidic (FePY/FeHR > 0.8) waters (Poulton *et al.* 2004). Iron speciation data are particularly useful in determining redox conditions because FeHR (i.e. iron bound in pyrite, magnetite, and ferric oxides) is limited under oxic conditions and the extent to which reactive iron is converted to pyrite defines sulphide availability in the water column (Raiswell and Canfield 1998). Molybdenum, as well, is sensitive to both the degree of anoxia and the extent of euxinia in bottom waters (Barling *et al.* 2001), although complexity of feedbacks within the system requires independent constraint on local redox conditions (Gordon *et al.* 2009). In the aftermath of the GOE, low molybdenum concentrations combined with low isotopic ratios indicates limited oxidative weathering on land and enhanced drawdown of molybdenum via oceanic euxinia (Arnold *et al.* 2004; Siebert *et al.* 2005; Scott *et al.* 2008). Because the relative importance of oxidative weathering, thus atmospheric oxygen concentrations, and euxinic drawdown on marine Mo content cannot be uniquely determined, chromium isotopes have been examined with the aim of gathering complementary information. In the absence of atmospheric oxygen, chromium remains immobile in crustal rocks; under conditions of oxidative weathering, however, chromium experiences shifts in mobility, redox state, and isotopic composition, which permits exploration into the initiation of the oxidative weathering process. Recent chromium-isotope profiles from rocks deposited in the aftermath of the GOE are consistent with initiation of oxidative weathering immediately followed by a decline in the degree of oxidative weathering and potential return to reducing conditions (Frei *et al.* 2009).

Together, these lines of evidence suggest limited oxygenation of the biosphere in the aftermath of the GOE.

Combined with a growing inventory of chemical data suggesting that locally oxygenated environments may have occurred nearly 200 million years prior to the GOE (Ono *et al.* 2003; Anbar *et al.* 2007; Kaufman *et al.* 2007; Frei *et al.* 2009; Reinhard *et al.* 2009), our view of the GOE changes dramatically. In this emerging picture, the GOE represents a transition in the oxidation state of Earth's biosphere that has critical implications for the cycling of redox-sensitive elements and for the trajectory of life on Earth, but which likely represented only the first small step in a protracted interval of biospheric oxygenation.

Neoproterozoic rise in oxygen

If, as postulated above, the GOE represents only limited oxygenation of the biosphere, then when does a 'modern' ocean-atmosphere system emerge? That is, when did Earth establish a persistently ventilated deep ocean, with a stable reservoir of dissolved sulphate and oxygen conditions suitable to sustain animal life throughout the ocean? The traditional view that modern biogeochemical cycling was established in the Neoproterozoic, concomitant with biospheric oxygen levels ≥ 10 –20% PAL (Canfield 2005; Holland 2006), is based on (1) the presence of elevated marine C-isotope ratios associated with increased organic carbon burial and inferred oxygen release (Knoll *et al.* 1986; Des Marais *et al.* 1992; Logan *et al.* 1995); (2) appearance of diverse animal life (Knoll and Carroll 1999; Chen *et al.* 2004; Narbonne 2005; Xiao *et al.* 2007); and (3) estimated physiological constraints for early metazoans (Towe 1970; Runnegar 1991; Catling *et al.* 2005). Estimates of oxygen levels up to 18% PAL are potentially supported by the preservation of sulphur isotope fractionations exceeding $\sim 46\text{‰}$, interpreted to record intermediate sulphur oxidation and disproportionation within the sulphur cycle. These sulphur isotopic data have been interpreted to record the origin of aerobic sulphur-oxidizing bacteria (Canfield and Teske 1996). Because modern sulphur-disproportionating bacteria are spatially restricted to habitats characterized by steep and opposing gradients of oxygen and sulphide (Jørgensen 1982), Canfield and Teske (1996) estimate a minimum of 5% PAL (to as much as 18% PAL) for this evolutionary transition, and this level of biospheric oxygen would result in oxygenation of 10–50% of the benthic marine substrate.

More recent data, however, suggest that Neoproterozoic oxygenation may be as complex as our emerging views of the GOE. The first complexity lies in the extreme volatility of the marine carbon-isotope record, wherein rocks younger than ~ 800 Ma consistently record highly positive C-isotope values punctuated by strongly negative excursions (Halverson *et al.* 2005). Although the origin of these negative excursions is debated (e.g. mixing of a stratified deep-ocean reservoir containing byproducts of organic decomposition, Grotzinger and

Knoll 1995; Kaufman *et al.* 1997; build-up and mixing of mantle-derived carbon, Hoffman *et al.* 1998; or decomposition and release of isotopically light carbon from methane clathrate build-ups, Kennedy *et al.* 2001; Schrag *et al.* 2002), most of these mechanisms call on an abrupt input of isotopically light material into surface oceans. The short residence time of carbon in well-mixed surface oceans would require, at steady state, rapid recovery from these isotopic excursions. However, improved chronology of the Neoproterozoic C-isotope record (Halverson *et al.* 2005; Le Guerroué *et al.* 2006) indicates that isotopic recovery from these negative excursions may have required 10–50 million years. The most parsimonious explanation for such long recovery times consists of episodic oxidation of a distinct, isotopically light pool of dissolved organic carbon (DOC; Rothman *et al.* 2003). Existence of a large (100–1000 times greater than that observed in the modern oceanic system; Rothman *et al.* 2003) reduced organic pool, however, demands weak mixing of the water column and low levels of marine oxygen likely well below 20% PAL.

Low-oxygen conditions in the Neoproterozoic are also supported by S-isotope data that show rapid variation in isotopic composition and remarkably heavy isotopic ratios of both marine sulphate and sulphide, implying nearly complete reduction of a limited sulphate reservoir (Hurtgen *et al.* 2002, 2004; Gorjan *et al.* 2003). Furthermore, spatial heterogeneity in isotopic composition has been used to suggest the potential for a strongly stratified water column that was periodically homogenized during post-glacial mixing (Hurtgen *et al.* 2006; Shen *et al.* 2008). Additional complexity in the S-isotope record broadly supports C-isotope evidence for substantial oxidation of a deep-ocean carbon reservoir in the terminal Neoproterozoic (Fike *et al.* 2006; Le Guerroué *et al.* 2006). For instance, terminal Neoproterozoic strata from the western USA reveal an increase in the concentration of carbonate-associated sulphate (CAS) coincident with a fall in the isotopic composition of this CAS, which has been interpreted to reflect increased biospheric oxygen, oceanic ventilation, oxidation of deep-water sulphides, and enlargement of the marine sulphate reservoir (Kaufman *et al.* 2007). Similarly, successions from Namibia and Oman record increases in the difference in isotopic composition between coeval pyrite and sulphate consistent with an increase in marine sulphate concentrations and the delayed onset of active bacterial sulphur disproportionation (Fike *et al.* 2006; Halverson and Hurtgen 2007).

It is likely, despite evidence for increasing marine oxygenation in the latest Neoproterozoic, that oxygen levels remained substantially below PALs. Constraints from the marine S-isotope record indicate marine sulphate concentrations of 3–5 mM or ~10–15% of present oceanic levels of 28 mM (Hurtgen *et al.* 2004; Kah *et al.* 2004). Secular variation in the isotopic composition of pyrite and

sulphate during the Neoproterozoic is interpreted to reflect rapid fluctuation in isotopic composition due to restricted sulphate availability, unrelated to the advent of sulphur disproportionation (Hurtgen *et al.* 2005). Low sulphate concentrations may also restrict isotopic discrimination within the sulphur cycle. It is well documented that sulphate concentrations > 200 μM permit the expression of 25–35‰ isotopic fractionation during BSR (Habicht *et al.* 2002), and it has been hypothesized that greater isotopic fractionation (> 46‰) will occur only after the evolution of sulphur-disproportionating bacteria (Canfield and Teske 1996; Halverson and Hurtgen 2007). Experimental evidence from paired ^{33}S – ^{34}S isotopic data, however, reveals resolvable differences in isotopic fractionation associated with sulphur disproportionation (Farquhar *et al.* 2003) and indicates that sulphur-disproportionating communities were an active part of the oceanic sulphur cycle from at least 1300 Ma (Johnston *et al.* 2005). These results suggest that the absence of isotopic fractionation > 46‰ results from limited expression of isotopic fractionation driven by oceanic sulphate reservoir size (Kah *et al.* 2001), and the appearance of greater fractionations at ~580 Ma reflects, at minimum, a moderate increase in oceanic sulphate concentrations.

Continuation of low levels of biospheric oxygen through much of the Neoproterozoic followed by a moderate rise of oxygen in the terminal Neoproterozoic is also supported by iron speciation data (Canfield *et al.* 2007, 2008). FeHR/FeT ratios indicate predominantly anoxic deep waters through much of the Neoproterozoic, until ~580 Ma, when a large proportion of deep-basinal sediments show FeHR/FeT indicative of deposition under oxic conditions. This transition suggests the first widespread ventilation of deep-ocean waters and biospheric oxygen levels of perhaps 15% PAL (Canfield *et al.* 2007). Evidence that Neoproterozoic deep waters may have been alternately sulphidic or ferruginous (Canfield *et al.* 2007) is also consistent with a protracted oxygenation of the biosphere, resulting in temporally and spatially heterogeneous oceanic redox conditions subject to environmental overprinting resulting from changing oceanographic conditions, such as during the Neoproterozoic ‘snowball’ glaciation events. For instance, even low levels of biospheric oxygen are expected to result in dominantly sulphidic oceanic conditions (Canfield 1998). The intermittent presence of ferruginous conditions may therefore reflect either limited riverine delivery of sulphate to the oceans or enhanced delivery of ferrous iron from mid-ocean ridges or via continental weathering. It is possible that, if sulphate is delivered predominantly from continental run-off and iron delivered via mid-ocean ridge activity, a dynamically maintained compositional stratification could occur. In this case, the degree to which ferrous iron in the deep ocean is converted to pyrite will ultimately depend on riverine input of sulphate and the continued drawdown of sulphate, via BSR and

pyrite burial, will maintain low levels of marine sulphate. Such a scenario potentially explains both the widespread nature of ferruginous conditions in the Neoproterozoic and the S-isotope values that imply the near-complete reduction of the oceanic sulphate reservoir, and suggests that climate-driven oceanographic effects (e.g. upwelling of deeper marine waters onto continental shelves and concomitant changes in water column chemistry) cannot be overlooked when deciphering long-term trends in biospheric oxygenation.

Clearly, the history of Earth surface oxidation is not as simple as tradition would suggest. A critical threshold of oxygenation, necessary to initiate sequestration of a vast oceanic reservoir of ferrous iron via oxidation or precipitation as sedimentary sulphide, was clearly surpassed at the GOE. Yet a second threshold of oxygenation, necessary to reduce chemical stratification of the oceans and bring a large portion of the oceanic substrate into the oxidative realm, may not have been surpassed until, perhaps, the final days of the Proterozoic. Potentially unique climatic and oceanographic conditions of the latter Neoproterozoic, however, lend uncertainty to the long-term meaning of Neoproterozoic oxygenation records. To better define the role that Palaeoproterozoic and Neoproterozoic oxygenation events may have played in defining the long-term history of biospheric oxygenation, it is necessary as well to explore potential indications of biospheric oxygenation from the nearly 1.5 billion year interval between these two events.

A view from the Mesoproterozoic

The Mesoproterozoic (1.6–1.0 Ga) has long been assumed to be a time of geologic and ecologic stasis (Buick *et al.* 1995; Brasier and Lindsay 1998), based on the relatively subdued C-isotope variability preserved in many Mesoproterozoic sedimentary successions. Yet the latter half of the Mesoproterozoic also contains multiple lines of evidence that suggest potentially measurable changes in the extent of biospheric oxygenation. These changes include (1) an abrupt increase in the C-isotopic composition of marine carbonates (Kah *et al.* 1999; Bartley *et al.* 2001), potentially reflecting increased release of oxidizing potential; (2) the first appearance of widespread bedded marine gypsum (Whelan *et al.* 1990; Kah *et al.* 2001), indicating a growing oceanic sulphate reservoir; and (3) the divergence of major eukaryotic clades (Butterfield 2000; Knoll *et al.* 2006), suggesting that oxygen availability reached an important geochemical and biological threshold.

Yet despite the occurrence of these traditional hallmarks of biospheric oxygenation, geochemical analyses on proxies such as sulphur, iron, and molybdenum indicate that biospheric oxygen levels remained substantially below current levels. S-isotope data from gypsum (Kah *et al.*

2001) and CAS (Kah *et al.* 2004) show rapid isotopic variation that, along with comparatively high S-isotope ratios of sedimentary sulphide (Lyons *et al.* 2000, 2006; Shen *et al.* 2002, 2003), are consistent with a small marine sulphate reservoir. Although oceanic sulphate levels appear to have remained low throughout the Mesoproterozoic, time-dependent modelling of S-isotopic change suggests that oceanic sulphate levels were likely < 2 mM (or 5–7% present oceanic levels) in the earlier Mesoproterozoic and may have risen to levels > 3 mM (or 10% present oceanic levels) between 1.3 and 1.2 Ga (Kah *et al.* 2004). Interestingly, within this time interval paired ^{33}S – ^{34}S isotopes record the earliest evidence for microbial sulphur disproportionation (Johnston *et al.* 2005), suggesting increased oxygenation of the marine substrate and availability of intermediate sulphur compounds (Canfield and Teske 1996). The absence, however, of large isotopic fractionations associated with disproportionation suggests that the expression of isotopic fractionation was limited by low sulphate concentrations.

Iron and molybdenum systematics also indicate low biospheric oxygen levels through the Mesoproterozoic. Elevated FeHR/FeT and FePY/FeHR in various units are indicative of at least local euxinia and, in, at minimum, one instance, Fe–S systematics indicate a distinct shelf-to-basin transition from oxic to euxinic environments (Shen *et al.* 2002, 2003). Molybdenum data (Arnold *et al.* 2004; Scott *et al.* 2008) show relatively low isotopic ratios and moderate concentrations, consistent with both moderate amounts of oxidative weathering and a greater proportion of molybdenum uptake under euxinic conditions. The occurrence of widespread euxinia in the early Mesoproterozoic is also supported by a decrease in Fe-isotope fractionation that has been interpreted to reflect the widespread disappearance of dissolved iron from the deep oceans (Rouxel *et al.* 2005). These events are broadly coincident with both development of voluminous SEDEX (Sedimentary Exhalative) mineralization (Lyons *et al.* 2006) and initiation of MVT-type mineralization (Kesler and Reich 2006), which is consistent with an increase in oceanic sulphate concentration and the rise of sulphide-dominated deep-ocean conditions.

Whereas euxinic conditions appear to be common in the Mesoproterozoic, the nature and extent of these environments appears to be substantially more variable. For instance, molecular fossils from early Mesoproterozoic strata of Australia provide evidence for ecologically significant populations of green and purple sulphur bacteria (Brocks *et al.* 2005). Both green and purple sulphur bacteria are anaerobic sulphur-oxidizing bacteria, which constrains their presence to euxinic environments. Furthermore, both groups are obligate phototrophs that commonly occur in water depths < 20 m, suggesting that euxinic conditions may have been present even in the shallowest Mesoproterozoic environments. Euxinia itself may

have played a role in restricting the expansion of oxygenated environments. In the absence of pyrite formation within the water column, hydrogen sulphide in contact with an overlying oxic to suboxic water column would be readily re-oxidized and made available, once again, for BSR. A continuous cycle of sulphur re-oxidation, followed by BSR, could thus result in substantial drawdown of biospheric oxygen.

Interpretation of molybdenum concentration and isotopic data, however, suggests that the extent of oceanic euxinia may have been less than 10 times that of the modern ocean (Arnold *et al.* 2004). Such levels of euxinia are inconsistent with both ubiquitous euxinia predicted by the 'Canfield Ocean' model (Canfield 1998) and evidence for shallow-ocean euxinic conditions (Brocks *et al.* 2005), but might be explained, in part, by a Mesoproterozoic expansion of suboxic environments. In modern suboxic environments, which contain little dissolved oxygen but in which the presence of hydrogen sulphide is restricted to substrate pore waters, the concentration and isotopic composition of molybdenum is typically intermediate between that observed for oxic and that for euxinic environments (Poulson *et al.* 2006; Siebert *et al.* 2006). Mesoproterozoic values may thus reflect a substantially more complex system that included both widespread suboxic environments and limited regions of euxinia. In fact, a variety of data sets ranging from Fe–S relationships (Lyons *et al.* 2000), to molybdenum (Scott *et al.* 2008), to the redox behaviour of rare earth elements (Slack *et al.* 2007), support an interpretation of suboxic conditions in a variety of deep-to-shallow water environments in the Mesoproterozoic. Under conditions of suboxia and restricted mixing, it is also possible to imagine that even shallow-water substrates may have developed euxinic pore waters suitable for the proliferation of anaerobic sulphur-oxidizing bacteria, in which case the molecular data may represent a feature of widespread suboxic conditions, rather than shallow-water euxinia. Restriction of euxinia to substrate pore waters would also construct a diffusional barrier to the chemical re-oxidation of hydrogen sulphide, thus slowing drawdown of biospheric oxygen via the sulphur cycle.

Implications of an intermediate redox state

Collectively, the data presented in this review suggest that the time between the GOE and the terminal Neoproterozoic deep-water oxygenation events represented a protracted state of intermediate redox potential, wherein widespread suboxic to anoxic conditions and variable availability of ferrous iron resulted in a complex distribution of euxinic and ferruginous marine conditions (Figure 1). Such a scenario prompts two questions: What impact did protracted oxygenation of Earth's surface environments have on biological evolution? And how does a protracted period of

low oxygen affect our understanding of the mechanisms of biospheric oxygenation?

Biological evolution

Clearly the greatest impact of Earth's protracted oxygenation history is the equally protracted evolution of the biota. Although both oxygenic photosynthesis and eukaryotic organization may date to the Archaean (Pace 1997; Summons *et al.* 1999; Eigenbrode *et al.* 2008; Waldbauer *et al.* 2009), prokaryotic metabolisms appear to dominate at least some shallow marine environments well into the Mesoproterozoic (Dutkiewicz *et al.* 2003; Brocks *et al.* 2005), and eukaryotic assemblages reflect a generally muted diversity (Javaux *et al.* 2004; Knoll *et al.* 2006). Despite low overall eukaryotic diversity, a growing body of evidence suggests minor increases in acritarch disparity (Huntley *et al.* 2006) during the Mesoproterozoic, the advent of multicellular algae by the late Mesoproterozoic (Butterfield 2000), and multicellular Metazoa by the early Neoproterozoic (Neuweiler *et al.* 2009). Muted eukaryotic diversity continues until the latest Neoproterozoic, when increased rates of evolutionary turnover (Knoll 1994) and diversification of numerous clades (Knoll *et al.* 2006) presage the rise of the Ediacara fauna (Narbonne 2005) and the first indication of deep-water oxygenation (Canfield *et al.* 2007).

A key point in understanding the trajectories of biotic evolution in the Proterozoic lies in both the antiquity of eukaryotes, in general, and the preservation of moderately diverse eukaryotic morphologies throughout the Proterozoic (Javaux *et al.* 2004), which suggest that diversification trends have less to do with evolutionary origins than with environmental change. Anbar and Knoll (2002) explored the potential link between the geochemical evolution of the oceans and the delayed radiation of eukaryotic life, in which observed patterns of eukaryotic evolution were intimately tied to biospheric redox conditions via environmental depletion of bioessential nutrients. Specifically, bioessential nutrients such as molybdenum and iron are critical components of nitrogenase enzymes responsible for microbial nitrogen fixation that would have been readily stripped from the ocean during sulphide precipitation in a euxinic ocean. Open marine environments may thus have experienced nitrogen-limiting conditions and resultant reduction in eukaryotic productivity, which may have extended even to nearshore environments during widespread episodes of euxinia.

The idea that eukaryotic evolution suffered from nutrient limitation, driven by oxygenation, is intriguing, particularly in light of investigations that suggest a diversity of oxygen-influenced nutrients, including nitrogen, copper, and phosphorus. In the presence of moderately oxic surface environments, ammonia produced by nitrogen fixation would have been rapidly oxidized to nitrate (Fennel

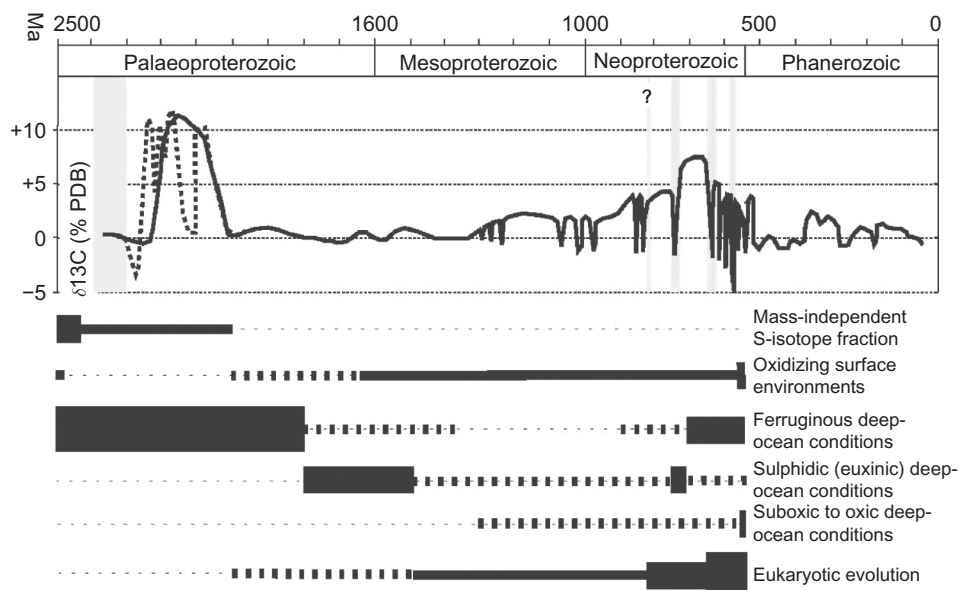


Figure 1. Summary of biogeochemical evidence for Earth oxygenation during the Proterozoic. The marine carbon isotope curve (black line after Bartley and Kah 2004; with alternative interpretation of the isotopic signal during the GOE, after Melezhik *et al.* 2005) is superimposed upon the geologic record of ‘Snowball Earth’ glaciation events (after Bekker *et al.* 2005; Melezhik *et al.* 2005; Halverson *et al.* 2005). Together these events mark the traditional timing of biospheric oxygenation. The disappearance of MIF sulphur signals at 2.32 Ma, however, indicates oxygen levels of only $> 0.001\%$ PAL, and the apparent oxidation of deep-marine environments at ~ 580 Ma suggests oxygen levels of only $\sim 15\%$ PAL. These constraints, combined with geochemical evidence for alternately ferruginous or sulphidic (euxinic) deep-marine conditions, suggest that Earth surface oxygenation was a protracted event that was governed primarily by the long-term process of oxidizing Earth’s crustal reservoirs, and substantially delayed biotic evolution. See details in text.

et al. 2005). Copper is an essential component of enzymes key to denitrification and the component most efficiently scavenged during euxinic sulphide deposition (Saito *et al.* 2003), which would thus have effects on nitrogen limitation similar to the stripping of molybdenum or iron (Buick 2007). Whereas nitrogen limitation will differentially affect the productivity of eukaryotes, which lack the ability to fix nitrogen, phosphorus can also be an effective agent in the limitation of overall productivity. Over long timescales, phosphorus availability is controlled by both terrestrial weathering fluxes and redox-sensitive oceanic recycling (Van Cappellen and Ingall 1996), wherein reactive phosphorus is retained in the substrate by sorption onto iron (hydr)oxides under oxic conditions and released from the substrate under anoxic conditions and returned to the surface ocean via active vertical circulation (Wallmann 2003). The apparent strength of the phosphorus recycling feedback (Van Cappellen and Ingall 1996; Lenton and Watson 2000; Algeo and Ingall 2007) suggests oceanic productivity in the aftermath of the GOE (Bjerrum and Canfield 2002) and through the rest of the Proterozoic may have been affected not only by phosphorus input (Brasier and Lindsay 1998), but also by the degree to which oceanic iron was sequestered through oxic versus sulphidic deposition, and the potential vigorousness of oceanic circulation.

The complex spatial and temporal patterns of environmental oxygenation and nutrient availability likely controlled the degree of spatial restriction, diversity, and dominance of numerous higher taxonomic groups, including cyanobacteria, eukaryotes, sulphur-disproportionating bacteria, and Metazoa. Evidence that these groups have evolutionary origins that significantly predate the widespread existence of the environments in which they thrive suggests that there is a direct relationship between protracted environmental change, linked to biospheric oxygenation, and biotic evolutionary pattern. Viewing biological evolution through this lens leads to the conclusion that the evolutionary landmarks typically associated with the establishment of particular environmental conditions are better interpreted to record the local initiation of such conditions (‘oxygen oases’ of Kasting *et al.* 1992), rather than their global importance.

Biospheric evolution and the carbon isotope record

A picture of extraordinarily protracted oxygenation throughout the Proterozoic, potentially reaching levels of 15% PAL only in the final stages of the Neoproterozoic, suggests a necessary revision of our views of how accurately the marine C-isotopic record reflects the geologic history of Earth surface oxidation. In short, is there any reason to assume that traditional Phanerozoic-style models of

the exogenic cycle, in which atmospheric oxygen levels are controlled by a balance of net photosynthesis, represented by the burial of organic matter and pyrite in sediments, and oxidative consumption during uplift and weathering of the continents (Garrels and Lehrman 1984; Berner *et al.* 2003) is appropriate for the Proterozoic? A closer look at models used to predict variation in atmospheric oxygen over Phanerozoic time would suggest perhaps not, because a complex series of negative feedbacks are required to avoid unreasonable results obtained with the assumption of a straightforward inverse relationship between rates of organic carbon and pyrite burial and atmospheric oxygen. These negative feedbacks include assumptions regarding the role of atmospheric oxygen in nutrient availability (Lenton and Watson 2000), weathering (Berner and Petsch 1998; Chang and Berner 1999), and sedimentary recycling (Berner and Canfield 1989), as well as relationships between atmospheric composition and the isotopic composition of biogenic carbon and sulphur (Berner *et al.* 2000). Arguably, these assumptions work well for the Phanerozoic atmosphere; these relationships are less well constrained in an evolving Proterozoic atmosphere-ocean system.

Two primary considerations that must be a part of any realistic assessment of Proterozoic biospheric oxygenation are missing from this dynamic Phanerozoic view: first, that the biospheric carbon reservoir size [i.e. atmospheric levels of CO₂ and the concentration of dissolved inorganic carbon (DIC) and DOC in the oceans] may have a dramatic effect on the resultant carbon isotopic records (Rothman *et al.* 2003; Bartley and Kah 2004), and second, that long-term changes in the composition of biospheric and crustal reservoirs (Hayes and Waldbauer 2006) may very well have restricted the onset of a dynamic, Phanerozoic-style exogenic balance.

Traditional views of the impact of reservoir size on the Proterozoic C-isotope record have focused on relatively small changes in the extent of isotopic discrimination resulting from changes in metabolic rate under conditions of variable carbon dioxide availability (Hayes *et al.* 1999). By contrast, rather than focusing on the extent of metabolic isotopic discrimination, Bartley and Kah (2004) explored, at a broad scale, the potential effects of marine carbonate saturation state, biologic evolution, and the degree of coupling between organic and inorganic carbon reservoirs on the sensitivity of the carbon isotopic record. In the Palaeoproterozoic, elevated atmospheric carbon dioxide and marine carbonate saturation (Grotzinger and Kasting 1993) likely resulted in a marine system strongly buffered by marine DIC that, despite potentially nutrient-limited productivity (Brasier and Lindsay 1998; Anbar and Knoll 2002), would record only a limited isotopic response to system perturbations. In this model, progressive decline of pCO₂ in the latter Mesoproterozoic and Neoproterozoic (Kasting 1987) results in increased isotopic sensitivity, a progressive onshore shift in the locus of carbonate

deposition, and spatial decoupling of organic and inorganic carbon reservoirs (see also Ridgwell *et al.* 2003; Rothman *et al.* 2003) that further sensitizes the system to isotopic change. The potentially extreme isotopic sensitivity of the Neoproterozoic would be fundamentally changed with the advent of abundant skeleton-forming organisms, which would result in the biological coupling of organic and inorganic carbon reservoirs and a fundamentally more stable isotopic system.

The implications of differential sensitivity of the C-isotope record are critical to any exploration of Proterozoic oxygenation, primarily because positive C-isotope excursions are inexorably linked to the sedimentary removal of organic matter produced by oxygenic photosynthesis and, thus, the release of oxidizing potential (Des Marais *et al.* 1992; Hayes and Waldbauer 2006). For instance, strongly positive C-isotopic compositions in the Neoproterozoic (Halverson *et al.* 2005) plausibly reflect a combination of increased organic carbon burial resulting from exhumation and erosion of Grenvillian orogenic systems (Rainbird *et al.* 1997, 2001) and deposition along new continental margins during the break-up of Rodinia (Halverson *et al.* 2007), and non-steady-state dynamics that reflect the establishment and subsequent interaction of distinct oceanic carbon pools (Rothman *et al.* 2003). Similarly, the transition between isotopic monotony of the early Mesoproterozoic and the establishment of long-term, moderately elevated C-isotope compositions in the latter Mesoproterozoic (Kah *et al.* 1999) are more likely to reflect the complex interactions of the carbon and sulphur cycles in an evolving biosphere, rather than a sustained 50% increase in productivity and organic carbon burial under potentially nutrient-limited conditions (Brasier and Lindsay 1998; Anbar and Knoll 2002). Finally, this model suggests that the strong, protracted positive C-isotope excursion associated with the GOE could represent a much greater release of oxidizing potential than has been currently recognized. However, if the GOE C-isotope excursion does record such a tremendous release of oxidizing potential, it evidently did not result in a large increase in biospheric oxygen.

Combined, these examples suggest that although marine C-isotope records in the Proterozoic may reflect reorganization of Earth's biogeochemical cycles in response to biospheric evolution, they likely provide little quantitative support for increases in atmospheric and marine oxygen. Similar arguments have been recently made by Hayes and Waldbauer (2006), who argued that the oxidation of Earth's crust has proceeded continuously, rather than episodically, and that the canonical C-isotope excursion that marks the GOE may represent the consequence of oxygenation and concomitant biological development, rather than a causal mechanism for oxygen release. Through a careful reexamination of the theoretical release of oxidizing power, the extent of biospheric and crustal sinks, and empirical constraints provided by

the geologic record, Hayes and Waldbauer (2006) stress that the constancy, since at least 2.7 Ga, of plate tectonics and carbon reduction via oxygenic photosynthesis demands a continuous release of oxidizing power through Earth's history.

When considering the history of biospheric oxygenation, the implications of continuous, rather than episodic, release of oxidizing potential are profound. Because ferrous iron reacts rapidly with sulphide to produce pyrite, we would expect that little sulphate would accumulate in oceans until the marine ferrous iron reservoir was substantially depleted. Such a scenario is consistent with both the 'Canfield Ocean' model, wherein sulphate released via oxidative weathering is rapidly reduced via sulphate reduction and serves, instead, as a mechanism for sequestration of ferrous iron, and the empirical data indicating low marine sulphate concentrations throughout the Proterozoic. Furthermore, even under conditions of low iron availability, repeated oxidation and reduction of water column hydrogen sulphide may have also acted to slow the expansion of the oxygenated environments. Thus, drawdown of Earth's oxidative potential would be expected to continue as long as either ferrous iron or sulphidic conditions occurred within the marine water column. Only once the marine iron reservoir was sufficiently depleted and sulphidic conditions became limited to pore-fluids within the sedimentary substrate would the Earth's continual release of oxidizing potential be reflected in growth of the marine sulphur reservoir.

We would further suggest that Earth's surface environments remained incompletely oxidized well into the early Palaeozoic. Although biospheric oxygen may have been sufficient to terminate deep-ocean ferruginous conditions in the terminal Neoproterozoic (Canfield *et al.* 2007), this conservative estimate of 15% PAL is preconditioned on a thermohaline ocean circulation model, which delivers surface-oxygenated waters directly to the deep ocean. Evidence for both a restricted marine sulphate reservoir (Kah and Zhan in preparation) and ferruginous conditions at the shelf-to-basin transition of the Yangtze Platform (Zhan and Jin 2007), however, occurs during Middle Ordovician greenhouse times. These observations suggest that oceanic circulation may play a critical role in regulating the long-term oxidation of crustal sinks and, ultimately, the expansion of the atmospheric oxygen reservoir.

Conclusions

- (1) Earth's biosphere has contained oxygen since the 'Great Oxidation Event' ~2.3 Ga, when oxygen levels surpassed 0.001% PAL. However, oxygen levels likely remained < 5% PAL until the end of the Proterozoic Aeon.

- (2) Low levels of oxygen throughout the Proterozoic suggest weak coupling between the marine carbon isotope record and episodes of environmental oxygenation, reflecting a model of continuous release of oxidizing potential and the buffering of biospheric oxygen via the iron and sulphur reservoirs.
- (3) Low-oxygen conditions in the aftermath of the GOE resulted in dynamic redox stratification in the oceans, with moderately oxidizing surface waters and deep waters that were both anoxic and sulphidic. Deep-ocean euxinia was likely paramount in the sequestration of the marine reduced-iron reservoir.
- (4) Perseverance of low oceanic sulphate into the Neoproterozoic suggests that release of oxidizing potential was balanced either by a marine pool of reduced iron or by repeated oxidation and reduction of marine sulphur within an euxinic water column. A small increase in oceanic sulphate concentration in the late Mesoproterozoic, coincident with evidence for increasingly dysaerobic marine conditions, suggests that the majority of the marine reduced-iron reservoir had been effectively sequestered from the oceans by this time and that euxinia may have shifted largely to within sedimentary pore waters.
- (5) The first evidence for deep-water oxygenation in the latest Neoproterozoic, and a concomitant increase in marine sulphate concentration, may have resulted in part due to vigorous oceanic circulation associated with conditions of global glaciation. Persistence of low-oxygen conditions well into the Ordovician may reflect the importance of oceanic circulation in regulating the oxidation of crustal sinks and, ultimately, the expansion of the atmospheric oxygen reservoir. In light of this protracted history of biospheric oxygenation, traditional interpretations of marine carbon isotopic change as a direct record of environmental oxidation may need to be revised.
- (6) Against this backdrop, the evolutionary landmarks typically associated with the establishment of particular environmental conditions are better interpreted to record the local initiation of such conditions, rather than their global establishment.

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