THE EARLY HISTORY OF ATMOSPHERIC OXYGEN:
Homage to Robert M. Garrels

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■ **Abstract** This paper reviews the Precambrian history of atmospheric oxygen, beginning with a brief discussion of the possible nature and magnitude of life before the evolution of oxygenic photosynthesis. This is followed by a summary of the various lines of evidence constraining oxygen levels through time, resulting in a suggested history of atmospheric oxygen concentrations. Also reviewed are the various processes regulating oxygen concentrations, and several models of Precambrian oxygen evolution are presented. A sparse geologic record, combined with uncertainties as to its interpretation, yields only a fragmentary and imprecise reading of atmospheric oxygen evolution. Nevertheless, oxygen levels have increased through time, but not monotonically, with major and fascinating swings to both lower and higher levels.

DEDICATION

This manuscript is dedicated to the memory of Robert M. Garrels, one of the fathers of modern low-temperature geochemistry. His accomplishments were extraordinary (consult Berner 1992), but of importance here were his pioneering insights into global biogeochemical cycles and oxygen regulation. The landmark book *Evolution of Sedimentary Rocks* (Garrels & Mackenzie 1971) carefully documented and quantified the processes involved in sediment and rock cycling at Earth's surface. The approach forwarded in the book inspired a generation of global biogeochemical models. The processes controlling atmospheric oxygen (O_2) concentrations were also eloquently developed by Garrels & Perry (1974), who also include a precise presentation of the controlling reactions. Rather presciently, Garrels et al. (1973) predicted the occurrence of anoxygenic phototrophic Fe-oxidizing bacteria, later discovered by Widdel et al. (1993). Garrels et al. (1973) furthermore described a complete carbon cycle based on Fe, a topic explored in more detail below.

Sadly, my contact with a number of bright young geobiology students reveals that much of Garrels' work has slipped from view. I blame this on the evolution of scholarship and the heavy reliance of young workers (and indeed all of us)

on internet-accessible reference sources, which have a limited memory. This dedication is directed toward putting the name Garrels back on the table where it belongs.

INTRODUCTION

The evolution of oxygen-producing cyanobacteria was arguably the most significant event in the history of life after the evolution of life itself. Oxygen is a potent oxidant whose accumulation into the atmosphere forever changed the surface chemistry of Earth (e.g., Cloud 1972; Garrels & Perry 1973; Holland 1984, 2002, 2004). Oxygen is also a favorable electron acceptor used in the respiration of countless different organisms that conduct a wide variety of different metabolisms. None of these could have prospered before the evolution of cyanobacteria. Furthermore, as explored below, the evolution of oxygen production dramatically increased the magnitude of primary production on the Earth, further expanding the realm of life (e.g., Knoll & Bauld 1989, Canfield & Raiswell 1999). Thus, relationships between life, oxygen, and the surface chemistry of the Earth are clear (see Knoll 2003). Less clear is the exact nature of these relationships. This requires an accurate understanding of the history of metabolic evolution, including knowledge of when cyanobacteria evolved, as well as a faithful reconstruction of the history of Earth surface oxidation and oxygen accumulation. There are great uncertainties in both areas, but the subject has energized the scientific community with much recent progress. It is the purpose here to review the current ideas regarding the early history of oxygen accumulation, with special reference to the history of biological innovation and the processes controlling oxygen concentration.

LIFE BEFORE CYANOBACTERIA

We briefly consider here the nature and magnitude of life before cyanobacterial evolution. This provides a counterpoint to the world emerging after widespread oxygen production by cyanobacteria. It seems self-evident that before the evolution of cyanobacteria, life on Earth was anaerobic, i.e., not using oxygen. However, phylogenetic reconstructions from the molecular sequences of cytochrome oxidase proteins, which catalyze the reduction of O_2 to H_2O in aerobic respiration, show an early origin of aerobic respiration (Castresana & Saraste 1995). Indeed, aerobic respiration seems to predate the evolution of cyanobacteria and may even predate the split between the two prokaryote domains, the *Bacteria* and the *Archaea* (Castresana & Saraste 1995). Pereira et al. (2001) extended these early studies with structural analyses of cytochrome oxidase complexes and concluded, as before, that these enzymes predate the evolution of cyanobacteria. In contrast to Castresana & Saraste (1995), Pereira et al. (2001) favor the lateral transfer of cytochrome oxidases from the gram-positive bacteria to the *Archaea*. In both scenarios, however,

organisms seemingly evolved the ability to respire oxygen before the evolution of oxygen-producing cyanobacteria.

If true, this rather paradoxical conclusion requires the identification of early nonphototrophic O_2 sources. One possible early source of O_2 could have been the disproportion of atmospherically derived H_2O_2 ($2H_2O_2 \rightarrow 2H_2O$ and O_2) by early catalase enzymes, which, as in modern organisms, remove H_2O_2 to combat the toxic effects of H_2O_2 reaction products (such as hydroxyl radicals) (Blankenship & Hartman 1998, Lane 2002, Canfield et al. 2004). Kasting et al. (1984) have calculated that H_2O_2 fluxes of 1 to 10 μmol m^{-2} day^{-1} could have rained to the surface early in Earth's history, generating O_2 fluxes and potential rates of O_2 respiration of the same magnitude. These potential rates of O_2 respiration are extremely small compared with the modern average rate of soil respiration of about 1.7×10^5 μmol m^{-2} day^{-1} (Raich & Potter 1995). As a result of low production rates, the concentrations of O_2 in the cell would have been very low. However, terminal oxidases in oxygen respiration can have very low half-saturation constants (K_m values) in the 3 to 8 nM range (e.g., D'mello et al. 1996, Preisig et al. 1996, Contreras & Escamilla 1999), so they are capable of utilizing only trace concentrations of O_2.

There may be some vestige of early oxygen utilization in modern "strictly" anaerobic prokaryotes. For example, the anaerobe *Bacteroides fragilis* can use and even benefit from O_2 concentrations of less than 300 nM (Baughn & Malamy 2004). This organism utilizes a cytochrome *db* oxidase that, from whole-genome sequence analysis, is also present in a variety of other strict "anaerobes" such as the sulfate reducer *Archaeoglobus fulgidus* and the methanogen *Methanosarcina bakeri* (Baughn & Malamy 2004). *B. fragilis* (and presumably other strict anaerobes with cyctochrome *bd* oxidase enzymes) cannot tolerate O_2 concentrations of greater than 1 μM. However, its tolerance, and even beneficial utilization of O_2 at low concentrations, reinforces a possible role for ancient oxygen reductase enzymes, predating the evolution of O_2 photosynthesis.

Despite an apparent early evolution of oxygen utilization, the earliest life would have been dominated by anaerobic metabolisms. Important early energy sources, originating from deep-sea and terrestrial hydrothermal systems, would have included H_2, H_2S, and S^o (Des Marais 1997, Canfield & Raiswell 1999, Nisbet & Sleep 2001). The S^o could have originated during the rapid cooling of volcanic gases containing H_2S and SO_2 ($SO_2 + 2H_2S \leftrightarrow 3S^o + 2H_2O$; Grinenko & Thode 1970), whereas the H_2S would have come directly from hydrothermal emanations and would have been used by sulfide-oxidizing anoxygenic phototrophs in terrestrial hydrothermal settings. Assuming all primary reduced gas emissions from hydrothermal sources were used to fuel primary production, Des Marais (2000, 2001) estimated preoxygenic photosynthetic primary carbon production rates of about 2 to 20×10^{12} mol year^{-1}, assuming further that hydrothermal fluxes were 10 times greater than those of today. This rate is 450 to 4500 times lower than the present global primary production rate of about 9000×10^{12} mol year^{-1} (Field et al. 1998), which includes approximately equal terrestrial and marine contributions.

From this comparison the fluxes of reduced gases from the mantle can support only a fraction of the primary production by oxygenic photosynthesis.

This estimate of preoxygenic photosynthetic primary production is made, however, without considering additional production fueled by the recycling of sulfur during organic matter diagenesis. Thus, we can imagine that the sulfide from hydrothermal sources supported the accumulation of microbial mats fueled by sulfide-oxidizing anoxygenic phototrophs. However, beneath the photic zone the mats would undergo extensive decomposition, fueled in part by sulfate reduction (with the sulfate coming from the sulfide oxidized by anoxygenic phototrophs). The sulfide from sulfate reduction could considerably augment the hydrothermal sulfide source, increasing the primary production rate of the photosynthetic community. Indeed, the total primary production (PP, mol C cm^{-2} day^{-1}) of the mat is related to the hydrothermal sulfide flux (HS, mol C cm^{-2} day^{-1}) by the following relationship, assuming that all organic carbon mineralization is channeled through sulfate reduction, that all of the available sulfide is used in anoxygenic photosynthesis, and that the thickness of the active mat is constant:

$$PP = 2HS/y. \tag{1}$$

Here, y is the proportion of PP escaping oxidation and preserved, and 2 is the stoichiometric relationship between the carbon produced and the sulfide oxidized during anoxygenic photosynthesis. With a y value of 0.1, which is reasonable for a microbial mat (Canfield & Des Marais 1993), PP = 20HS, a value 10 times higher than that supported by the hydrothermal flux alone. Thus, rates of primary production might have been even higher on the early Earth than hydrothermal input rates would indicate.

Permissive ocean chemistry could have supported additional and even higher rates of primary production. The most important electron donors for anoxygenic phototrophs are H_2, H_2S, S^o, and Fe^{2+} (e.g., Canfield et al. 2004), and of these, H_2S and Fe^{2+} can dissolve in seawater to concentrations at which, in principle, significant anoxygenic photosynthesis can be fueled. Early in Earth's history, sulfide was an unlikely major persistent component of marine waters, as non-sulfidic Fe phases are common constituents of Archean and early Proterozoic banded iron formations (BIFs) (e.g., James 1966, Beukes et al. 1990, Beukes & Klein 1992, Bjerrum & Canfield 2002). Had sulfide been dissolved in marine waters, Fe sulfides would instead have dominated the authigenic sedimentary Fe mineralogy. Sulfide phases are found among BIFs, particularly those of the Algoma type (James 1966), but these are believed to have formed from locally derived hydrothermal sulfide emissions or sediment-hosted sulfate reduction (e.g., Goodwin et al. 1976). Thus, the rather common precipitation of nonsulfidic Fe phases in Archean BIFs, including the 3.8 Ga BIFs from the Isua Supracrustal Belt, West Greenland (Dymek & Klein 1988), indicates the presence of dissolved Fe in seawater.

If this water was at saturation with both siderite and calcite, as suggested by Holland (2003) for the Archean, then, as also pointed out by Holland (2003), limits

can be placed on the concentration of dissolved Fe^{2+}. Thus, ignoring differences in activity coefficients, the molar ratio of Fe^{2+} and Ca^{2+} is equivalent to the ratio of the solubility product of siderite and calcite (from Holland 2003):

$$m_{Fe^{2+}}/m_{Ca^{2+}} = K_{sid}/K_{cal} = 10^{-10.8}/10^{-8.4} = 4 \times 10^{-3}. \tag{2}$$

Through the Phanerozoic, Ca^{2+} concentrations have varied from 10 to 30 mM (Horita et al. 2002), and a similar range of variability in early Earth history would yield Fe^{2+} concentrations of 40 to 120 μM. This is a possible bracket for marine dissolved Fe^{2+} concentrations before the evolution of oxygenic photosynthesis.

This brings us back to Garrels, who surmised (Garrels et al. 1973) that in a dissolved Fe^{2+}-containing ocean, photosynthetic prokaryotes would oxidize the Fe^{2+} advecting and diffusing into the photic zone (see Figure 1). Indeed, over the last 10 years a variety of Fe-oxidizing phototrophs from the purple sulfur bacteria (Widdel et al. 1993) and the green sulfur bacteria (Heising et al. 1999) have been isolated. How productive might an early ocean have been that contained 40 to 120 μM Fe^{2+}? This is difficult to answer precisely, but sensible limits can be offered. From Reaction 3, four moles of Fe^{2+} are used to fix one mole of CO_2 into organic carbon.

$$7H_2O + 4Fe^{2+} + CO_2 \leftrightarrow CH_2O + 4FeOOH + 8H^+. \tag{3}$$
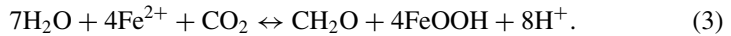
Furthermore, one mole of organic matter is associated, presently, with about 1/106 moles of P and 1/16 moles of nitrogen, with these nutrients used in biomolecule synthesis (Redfield 1958). We assume similar average nutrient distributions in Fe-oxidizing anoxygenic phototrophs. Therefore, focusing on phosphorus (P),
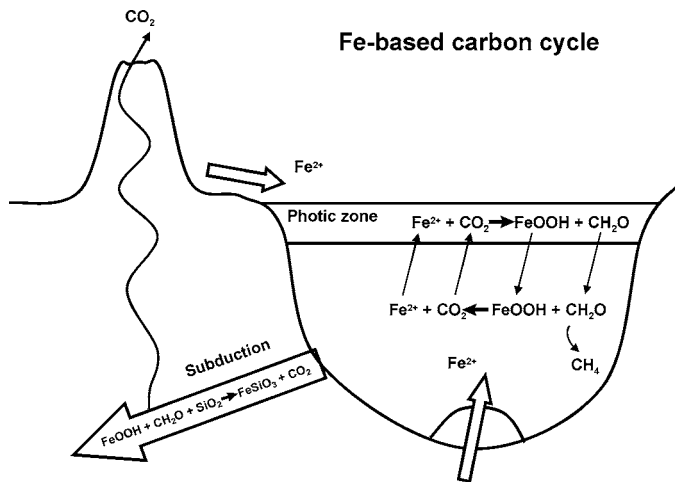

Figure 1 Cartoon showing an Fe-based carbon cycle as imagined before the evolution of oxygenic photosynthesis. See text for details.

TABLE 1 Rates of primary production (PP) before oxygenic photosynthesis

Process supporting PP	Rate ($\times 10^{12}$ mol C year^{-1})	Reference
Hydrothermal flux	2 to 20	(Des Marais 2001)
Hydrothermal flux with recycling	20 to 200	Present study
Anoxygenic photosynthesis in Fe-containing ocean	180 to 560	Present study
Present marine	4040	(Field et al. 1998)
Present terrestrial	4700	(Field et al. 1998)

one mole of P is needed in the utilization of 424 moles of Fe^{2+} in phototrophic carbon fixation. This means that 40 to 120 μM Fe^{2+} would be fully utilized with an accompanying 0.094 to 0.28 μM phosphate. This amount of P utilization is about 8 to 25 times lower than the modern deep-water average of 2.3 μM (Broecker & Peng 1982). Assuming ocean circulation and nutrient utilization patterns similar to today, we can also predict that using 7 to 22 times less P in primary production would translate into rates of primary production that are 7 to 22 times lower. Thus, ocean productivity driven by Fe cycling would be lower than today's O_2-driven carbon cycle, but would still be equally as productive, if not more productive, as a carbon cycle driven solely by hydrothermal reduced species input (Table 1).

Such a pre-oxygen carbon cycle would be complete. Organic matter mineralization would be driven by Fe reduction (Reaction 3 written backward) and methanogenesis, both of which have ancient roots (Vargas et al. 2000, Stetter 1996; but also see House et al. 2003 for a different view on the antiquity of methanogensis). Furthermore, as Garrels & Perry (1974) point out, deeply buried Fe_2O_3 and associated CH_2O would react under metamorphic conditions to form Fe(II) silicates and liberate CO_2 (Reaction 4) (Figure 1):

$$2Fe_2O_3 + CH_2O + 4SiO_2 \rightarrow 4FeSiO_3 + CO_2 + H_2O. \qquad (4)$$

In this case, the metamorphic reduction of Fe_2O_3 serves the function of oxidative weathering by O_2 in the modern carbon cycle, accomplishing both the substantial breakdown of organic matter and the regeneration of the electron donor.

THE EMERGENCE OF CYANOBACTERIA

The timing of cyanobacterial evolution is central to reconstructing the history of Earth surface oxidation (see review by Knoll 2003). From molecular and biochemical considerations, some insights into the relative timing of cyanobacterial evolution can be offered. Thus, from phylogenies constructed from the small subunit (SSU) of the RNA molecule, cyanobacteria are relative latecomers in the history of

prokaryote evolution (Woese 1987, Pace 1997), postdating the emergence of a variety of lineages presently associated with sulfate reduction (*Thermodesulfobacteriales*), anoxygenic photosynthesis (*Chloroflexales*), fermentation (*Thermotogales*), chemolithoautotrophy (*Aquaficales*), and organic matter respiration with Fe oxides (Vargas et al. 2000). Other lines of evidence place the evolution of oxygenic photosynthesis after the evolution of anoxygenic phototrophic bacteria. One line comes from the nature of the coupled photosystems used in oxygenic photosynthesis, in which light energy is converted into ATP and reducing equivalents and H_2O is oxidized to O_2 (e.g., Blankenship 1992). Each of the individual photosystems used in oxygenic photosynthesis bares a strong resemblance to the two main types of photosystems existing among anoxygenic phototrophs, which suggests that each of these was coopted by the ancestral oxygenic phototroph (Blankenship 1992). Furthermore, recent phylogenic reconstructions show that the genes involved in the synthesis of bacteriochlorophyll (used by anoxygenic phototrophs) predate those used to produce the chlorophyll used by oxygenic phototrophs (Xiong et al. 2000). Even so, when did the evolution of oxygenic photosynthesis occur?

A body of converging evidence suggests that cyanobacteria were present in the environment by 2.7 Ga. The most direct evidence comes from the isolation of 2α-methylhopanes (2 Me-hopanes) from 2.7 Ga organic-rich shales from Western Australia (Brocks et al. 1999). These compounds are derived from 2-methylbacteriohopanepolyol (2-MeBHP), which, with extended side chains and >31 carbon atoms, are, as far as is known, only synthesized by cyanobacteria (Summons et al. 1999), although not by all cyanobacteria. In a separate line of evidence, Hayes (1992) highlighted the preponderance of highly ^{13}C-depleted organic matter occurring around 2.7 Ga. No single-step, carbon-fixation process is known to produce such ^{13}C-depleted organic carbon, and Hayes (1992) suggested multiple carbon inputs and, in particular, the contribution from aerobic methanotrophs. These organisms incorporate ^{13}C-depleted carbon into their biomass as they oxidize methane with oxygen. Finally, on the basis of morphological grounds and by analogy with modern stromatolites, Buick (1992) noted that the occurrence of 2.7 Ga lacustrine stromatolites from Australia were most likely formed in association with phototrophic organisms. Anoxygenic phototrophs were ruled out, as no sign of reduced sulfide or Fe compounds could be found, leaving oxygenic phototrophs as the most likely stromatolite builder.

Can we identify cyanobacteria further back in time? Cyanobacterial-like microfossils from the 3.45 Apex Chert from Western Australia (Schopf & Packer 1987, Schopf 1993) have long stood as possible evidence for the early emergence of cyanobacteria. However, the microfossils themselves are not uniquely cyanobacterial (see Knoll 2003) and their biogenicity has recently been brought into question (Brasier et al. 2002). Graphite depleted in ^{13}C from the 3.8 Ga Amitsoq Gneiss from Southwestern Greenland (Rosing 1999) has an isotopic composition consistent with the Rubisco pathway used by cyanobacteria. From sedimentalogical grounds, Rosing (1999) also argued that the organic carbon originated from a pelagic source. However, water column methanogens (oxidizing

H_2 from the atmosphere?), for example, using the reductive acetyl Co-A pathway, would produce fractionations rivaling or even exceeding those from Rubisco (see Knoll & Canfield 1998), and many other bacterial photoautotrophs also use the Rubisco pathway (see Canfield et al., 2004 for a review). Thus, by itself the isotope evidence cannot be uniquely ascribed to a cyanobacterial source.

Rosing & Frei (2004), however, have recently presented other evidence for oxygen production in the early Archean. In particular they have argued that >3.7 Ga sediments from the Isua Supracrustal Belt in West Greenland were enriched in uranium at the time of sediment deposition. Uranium enrichment indicates mobilization and transport of uranium at the time of deposition, which further indicates oxidizing conditions as uranium is only mobilized as the uranyl ion (UO_2^{2-}) under such conditions. Rosing & Frei (2004) argue for an oxidizing surface environment (at least an oxidizing surface ocean) at the time of Isua sediment deposition, implying also the evolution of cyanobacteria. Conflicting with this conclusion is the occurrence of mass-independent S isotope fractionations in Isua sedimentary rocks, implying no ozone shield and very low O_2 concentrations (Mojzsis et al. 2003; see below for a discussion of S isotope systematics). These observations, however, need not be mutually exclusive. In principle, an oxidizing surface ocean could mobilize uranium from shallow water sediments without involving an oxygenated atmosphere.

Stromatolites are attached lithified sedimentary structures, usually with conspicuous layering, and they often exhibit complex growth patterns such as the formation of columns and domes (see Grotzinger & Knoll 1999 for a review). They have often been associated with microbial biofilms and, in particular, the activities of cyanobacteria (e.g., Arwamik 1992). The oldest well-preserved pseudocolumnar stromatolites, which show preferred vertical elongation of the cones and may be associated with microbial accretion, are from the 3.45 Ga Warrawoona Group in Western Australia (Hofmann et al. 1999; also see Lowe 1980, Walter et al. 1980). Morphologically complex stromatolites are also found in similarly aged rocks from the Swaziland Supergroup, South Africa (Byerly et al. 1986). Furthermore, a variety of morphologically different stromatolites, which range from columnar to stratiform and are all finely laminated, are found in tidally dominated near-shore sediments preserved in the 3.0 Ga Pongola Supergroup in South Africa (Beukes & Lowe 1989). Here, each morphologic type is preserved in an environment comparable to morphologically similar stromatolites in the modern Shark Bay, Australia (Logan et al. 1974). Beukes & Lowe (1989) argued that these 3.0 Ga stromatolites were formed by microbial mediation and, in particular, by the activities of cyanobacteria.

However, Grotzinger & Rothman (1996) and Grotzinger & Knoll (1999) have introduced a large measure of caution into the interpretation of Archean stromatolites. Thus, many of the features associated with stromatolites, including laminations and columnar structures, can be formed by abiotic process. Furthermore, the demonstrable function of cyanobacteria in stromatolite growth is the trapping
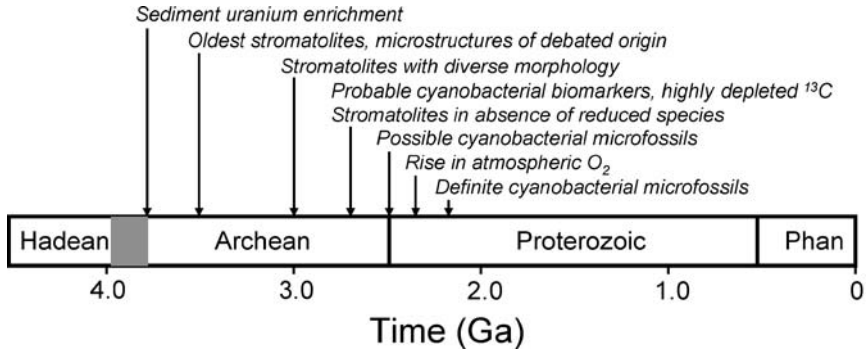
Figure 2 A summary of the geologic evidence pointing to the early emergence of cyanobacteria. Concept modified after figure 2 in Knoll (2003). See text for details.

and binding of sediment particles. Trapping and binding, however, is rare in Archean stromatolites and is not apparent in those Archean examples discussed above. Therefore, neither the association of cyanobacteria in the growth of the earliest examples of Archean stromatolites nor their biogenicity can be proven. As a counterpoint, Awramik (1992) argues that "stromatolites with wavy-laminated stratiform shapes, domes, columns (especially branching columns), possessing laminae 5 or 10 μm thick that show gradational boundaries between the dark and light lamina, and which formed on the surface at the sediment/water interface in an aqueous setting (sea, lake, stream, thermal spring) are known to be the products of phototrophic microbial activity." Therefore, some early Archean examples of stromatolites may have been formed by the activities of cyanobacteria, but with what we presently know, this cannot be demonstrated with absolute certainty. Therefore, 2.7 Ga stands as the earliest time we can speak of cyanobacterial evolution with a high degree of confidence. The various lines of evidence pertinent to early cyanobacterial evolution are shown in Figure 2.

It is clear, as we shall see below, that the evolution and emergence of cyanobacteria had a minimal immediate impact on the surface chemistry of Earth. Other processes, many of them related to geological and geochemical controls on element cycling, significantly influenced the history of oxygen accumulation.

EVIDENCE FOR EARTH SURFACE OXYGENATION

Much has been written over the last several decades about the history of Earth surface oxygenation (e.g., Holland 1962, 1984; Berkner & Marshall 1965; Cloud 1972; Garrels et al. 1973, 1974; Dimroth & Kimberley 1976; Clemmey & Badham 1982; Ohmoto 1997; Holland 2003). A great deal of controversy still exists (e.g., compare Ohmoto 1997 with Holland 1999), and our understanding is still rather primitive. Nevertheless, multiple lines of evidence (see recent review by

Holland 2003) paint a rather consistent picture of low Archean and early Protero-
zoic atmospheric O_2 concentrations, yielding to higher concentrations around 2.3
Ga (the Great Oxidation Event of Holland 2002), and higher levels yet ushering in
the Phanerozoic (Rye & Holland 1998). This outline is expanded upon below and
includes aspects of the chemical evolution of ocean chemistry, which is influenced
by atmospheric O_2.

Redox-Sensitive Elements

The differential preservation of redox-sensitive elements through Earth's history
frames the classic arguments related to the history of atmospheric oxygenation
(e.g., Holland 1962, 1984, 1994; Clemmey & Badham 1982; Cloud 1972). This
evidence has been thoroughly reviewed by Holland (1984, 1994, 2003) and is only
briefly addressed here. Central to this argument is the preservation of uraninite
(UO_2), pyrite (FeS_2), and siderite ($FeCO_3$) as detrital placers in river deposits
older than about 2.3 Ga. All these phases are redox sensitive and readily oxi-
dize with present atmospheric O_2 concentrations, although the oxygen level at
which preservation occurs is difficult to constrain (Holland 1984, 2003). Detrital
uraninites are known from the approximate 2.7 Ga Witwatersrand quartz-pebble
conglomerates of South Africa (e.g., Smith & Minter 1980; Schidlowski 1981),
the approximate 2.3 Ga conglomerates from Eliot Lake, Canada (e.g., Roscoe
1957), and from terrestrial sandstones and conglomerates from the Pilbara Block,
Australia, ranging in age from 2.75 to 3.25 Ga (Rasmussen & Buick 1999). A
possible hydrothermal source for the Witwatersrand uraninites has been discussed
(Barnicoat et al. 1997). However, rounded uraninite and pyrite grains yield U-Pb
and Re-Os ages of around 3.0 Ga, considerably older than the depositional age
of the conglomerate (Minter 2002), reinforcing a placer interpretation. Uraninite,
pyrite, and siderite placers are rare in fluvial systems younger than 2.3 Ga. They are
also rare in modern rivers, except under cold conditions, and in high relief terrains
where weathering and burial is extremely rapid (Maynard et al. 1991). Maynard et
al. (1991) and Rasmussen & Buick (1999) argue that the Archean and early Pro-
terozoic examples cited above do not reflect especially cold conditions, nor were
they deposited in high relief terrains, and therefore reduced oxygen concentrations
before 2.3 Ga are indicated.

The differential retention of Fe in ancient soils, known as paleosols, has been
widely used as an indicator of atmospheric O_2 (e.g., Gay & Grandstaff 1979,
Holland 1984, Pinto & Holland 1988, Rye & Holland 1998, Beukes et al. 2002,
Yang & Holland 2003). In general, under low O_2 conditions, Fe is mobilized during
weathering, whereas it is oxidized and retained when O_2 levels are high. Rye &
Holland (1998) report no Fe oxidation and substantial Fe remobilization for a large
number of Precambrian paleosols older than about 2.2 to 2.3 Ga. The O_2 levels
implied by this lack of oxidative weathering depend on the composition of the
paleosol and the model assumptions regarding the sources and transport vectors of
O_2 and CO_2 into the ancient weathering environment (e.g., Holland 1984, Pinto &

Holland 1988, Rye & Holland 1998). Values of O_2 less than 0.1% to 1% of present day values (PAL) are advanced by Rye & Holland (1998).

The 2.2 Ga Hekpoort paleosol of the Transvaal Supergroup, South Africa, is the earliest paleosol to show evidence for oxidative weathering, although substantial Fe remobilization is also indicated (Beukes et al. 2002, Yang & Holland 2003). There is considerable disagreement as to how this paleosol should be viewed. Beukes et al. (2002) draw comparisons between the Hekpoort paleosol and modern laterites and therefore raise the prospect that when this soil formed atmospheric O_2 concentrations were similar to those of today. Yang & Holland (2003) feel that the comparison with modern laterites is unlikely; for one, a substantial source of organic reductant is not easy to identify. Instead, they advocate O_2 levels somewhat elevated, but not exceeding about 5% PAL. In any event, other lines of evidence suggest Earth surface oxidation by this time (see below), and after about 2.2 Ga paleosols show high degrees of Fe oxidation and retention. Oxygen concentrations modeled from paleosols formed after 2.2 Ga are all greater than 1% PAL (Rye & Holland 1998). Associated with the initiation of substantial oxidative weathering in soils is the appearance of red bed deposits around 2.2 Ga, providing further evidence for an oxygenated atmosphere (Cloud 1968; Holland 1984, 1994).

Sulfur Isotopes

There are four stable isotopes of sulfur (S), with the following abundance in the sulfur reference standard V-CDT: ^{32}S (95.04%), ^{33}S (0.749%), ^{34}S (4.20%), and ^{36}S (0.0146%) (Ding et al. 2001). When fractionations occur through biological and most geological processes, they are mass dependent (the magnitude of the fractionation depends on the mass of the isotope), with ^{33}S fractionating about half as much as ^{34}S from ^{32}S and ^{36}S fractionating about twice as much as ^{34}S from ^{32}S (Hulston & Thode 1965). The magnitude of the mass dependency of the fractionation, however, is not constant and depends somewhat on the processes by which fractionation occurs (see Farquhar et al. 2003). Nonmass-dependent S isotope fractionation is also observed under some circumstances (Farquhar et al. 2000), and both mass-dependent and nonmass-dependent S isotope fractionations are relevant for unraveling the history of Earth surface oxygenation.

We begin with biologically induced mass-dependent fractionations. In particular, sulfate-reducing prokaryotes fractionate during sulfate reduction by amounts that depend on the organism involved (Detmers et al. 2001) and, more importantly, by environmental conditions. With high sulfate concentrations, independent of temperature and rate, natural populations of sulfate reducers typically fractionate between around 20% and 40% ($\delta^{34}S_{SO_4}$-$\delta^{34}S_{H_2S}$) (Habicht & Canfield 1996, Canfield et al. 2000, Canfield 2001). As recognized originally by Harrison & Thode (1958), fractionations are greatly reduced at low sulfate concentrations, and Habicht et al. (2002) have found that the transition between high and low fractionation is sharply defined at around 200 μM sulfate. Turning to the isotope record (Figure 3), generally low fractionations are preserved until around 2.5 Ga and, as
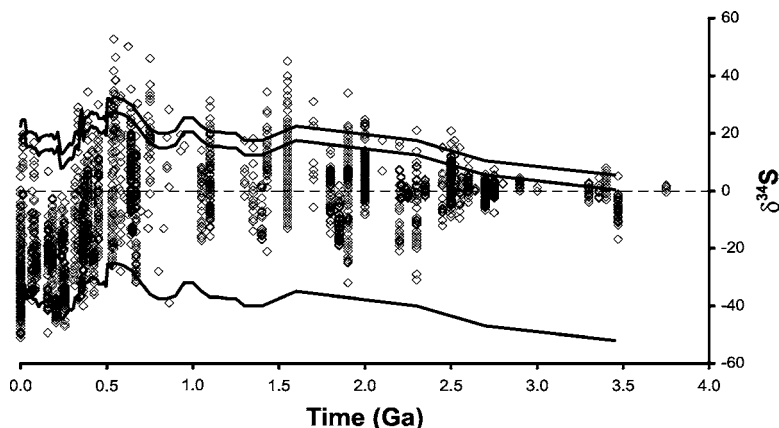
Figure 3   Compilation of the isotopic composition of sedimentary sulfides (*diamonds*)
through time. Also shown is a reconstruction of the isotopic composition of sulfate
(upper line) and, as a guide, the isotopic composition of sulfate offset by 55% (lower
line). The plot is modified after figure 13 in Canfield (2001).

first observed by Cameron (1982), they increase dramatically from around 2.3 to
2.4 Ga to values expected for microbial sulfate reduction with nonlimiting sulfate
concentrations (Figure 3). It follows then, as argued by Habicht et al. (2002), that
the lower fractionations preserved in pre-2.4 Ga sulfides were produced by sulfate
reducers metabolizing sulfate at concentrations less than 200 μM (compared with
28 mM today). High fractionations, however, are observed in the 3.5 Ga North Pole
Quartz-barite deposits, a locally sulfate-rich environment, providing the earliest
evidence for microbial sulfate reduction (Shen et al. 2001).

The most likely explanation for such low Archean concentrations of sulfate
is the limited oxidative weathering of pyrite on land under reduced concentra-
tions of atmospheric O_2. Limited oxidative weathering is also observed from the
preservation of detrital pyrites in Archean and early Proterozoic riverine systems
as discussed above. Canfield et al. (2000; see footnote 5 in this reference) calcu-
lated that the complete oxidation of 100 μm pyrite grains in soils (sedimentary
pyrites are typically this size or smaller, although much larger pyrites can also be
found) should occur with water containing greater than 1 μM O_2. This amount
of O_2, at 25°C, is in equilibrium with 0.4% PAL. Thus, as a rough estimate, the
S isotope record is consistent with atmospheric O_2 concentrations of <0.4% PAL
before 2.4 Ga. This upper limit on pre-2.4 Ga O_2 concentrations is in line with the
concentrations predicted from the paleosol data discussed above.

The S isotope record (Figure 3) records another large increase in fractionations
around 0.7 Ga. Indeed, the highest of these fractionations is greater than can be
explained by sulfate reduction alone, and Canfield & Teske (1996) argued that they
represent additional fractionations produced by the disproportionation of sulfur-
containing species s such as elemental sulfur (S^o), sulfite (SO_3^{2-}), and thiosulfate

($S_2O_3^{2-}$). The disproportionation of each of these produces sulfate and sulfide, in which the sulfide is ^{34}S-depleted compared with the isotopic composition of the original compound (Canfield & Thamdrup 1994, Habicht et al. 1997, Cypionka et al. 1998, Canfield et al. 2000). It appears, then, that around 0.7 Ga the isotope record records the significant expression of S compound disproportionation reactions, but probably not the evolution of disproportionating organisms. Canfield & Teske (1996) argue that the sulfur isotope data are most consistent with an increase in atmospheric O_2 concentrations to levels high enough to substantially oxidize the surface seafloor in near-shore settings, accelerating the formation of S intermediate compounds and the disproportionation process. They calculate that atmospheric O_2 in excess of 5% to 18% PAL could do this. The implication is that O_2 levels were lower than this amount when disproportionation reactions were not expressed in the isotope record.

When the minor isotopes of S are considered (^{33}S and ^{36}S), the mass dependency of the fractionation can be evaluated. The isotope record of the mass dependence of ^{33}S fractionation ($\Delta^{33}S$) is shown in Figure 4, where $\Delta^{33}S$ expresses the isotopic difference between the $\delta^{33}S$ expected and the $\delta^{33}S$ measured, assuming a mass-dependent relationship between ^{33}S and ^{34}S (Farquhar et al. 2000, Farquhar & Wing 2003). This isotope record shows mass-independent fractionations before about 2.45 Ga and generally mass-dependent fractionations after this. The only
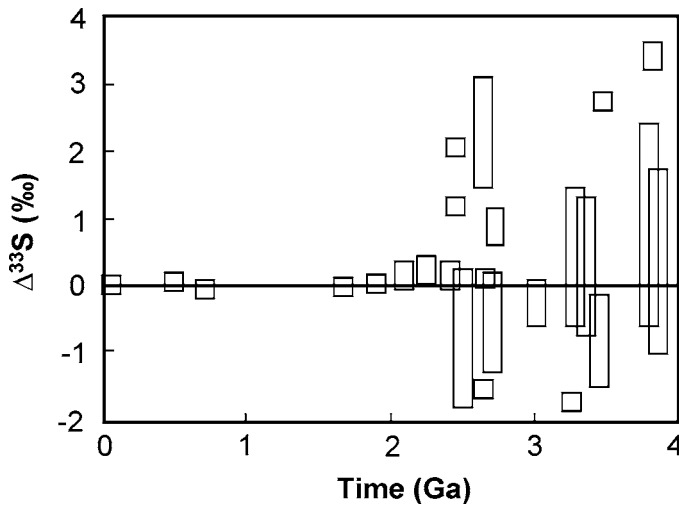

Figure 4   A summary of the mass dependency of sulfur isotope fractionation through time as preserved in sedimentary sulfides and sulfates. $\Delta^{33}S$ expresses the difference between the $\delta^{33}S$ measured in the sample and the expected $\delta^{33}S$ based on a mass-dependent relationship between $\delta^{33}S$ and $\delta^{32}S$. Values of $\Delta^{33}S$ that diverge from 0 indicate mass-independent fractionations, whereas mass-dependent fractionations are observed if $\Delta^{33}S$ is 0. The graph is abstracted from figure 1 in Farquhar & Wing (2003).

known reactions producing mass-independent fractionations of the nature seen before 2.45 Ga are atmospheric reactions involving SO_2 and SO photolysis with deep UV radiation of <220 nm (Farquhar et al. 2001, Farquhar & Wing 2003). The source of SO_2 would have been volcanic, and the penetration of deep UV radiation requires the absence of ozone and a nearly anoxic atmosphere. Pavlov & Kasting (2002) have constructed a combined photochemical and isotope model for atmospheric S reactions and conclude that the preservation of the isotope signal produced from SO_2 and SO photolysis requires atmospheric O_2 levels of $<10^{-5}$ PAL. If true, the Archean atmosphere was very low in oxygen indeed, with an increase to higher oxygen levels of probably $>1\%$ PAL after 2.45 Ga. Recent work shows that mass-dependent fractionations were preserved in pyrites from the 2.32 Ga Rooi-hoogte and Timeball Hill formations, South Africa (Bekker et al. 2004). Thus, a significant rise in O_2 occurred between 2.45 and 2.32 Ga.

Banded Iron Formations

Banded iron formations (BIFs) are common in Archean and early Proterozoic sedimentary sequences, and their genesis has been briefly discussed above. They have no modern analogs, but it seems most likely that they deposited in an ocean containing dissolved Fe(II) (e.g., Holland 1984, 2003), which is consistent with low Archean concentrations of atmospheric O_2 and low concentrations of seawater sulfate (see above). The former would allow for an anoxic deep ocean (more on this below), whereas the latter would suppress rates of sulfate reduction and hence sulfide production, allowing dissolved Fe to persist (see Canfield 1998).

Of immediate interest here, however, is the absence of BIFs in the geologic record. The frequency distribution of BIFs through time has been compiled by Isley & Abbott (1999) and is shown in Figure 5 for the time before 1.5 Ga. While BIFs are common in sedimentary rocks before 2.4 Ga, they are largely absent from the geologic record between 2.4 and 2.0 Ga. A lack of BIFs after about 2.4 Ga might be consistent with the evidence cited above for oxygenation of the surface environment around this time. One might suspect that atmospheric O_2 became high
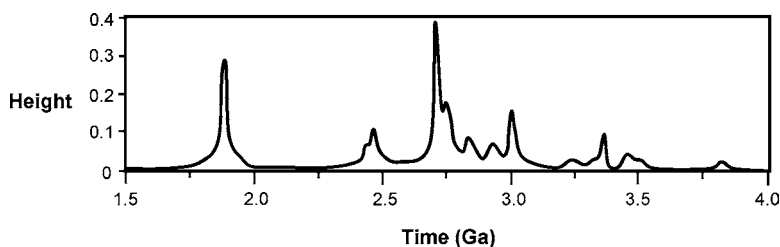

Figure 5   The abundance of BIFs through time. The Y-axis (height) is a measure of relative abundance of BIFs, depending on the frequency of their occurrence and the uncertainty in their age. The graph is modified after Isley & Abbott (1999).

enough to oxygenate the oceans or, alternatively, that increasing sulfate concentrations (in response to elevated oxygen levels) increased rates of sulfate reduction, and the resulting sulfide titrated the Fe from solution (see Bjerrum & Canfield 2002). This latter hypothesis is explored below for a somewhat later period in Earth's history. The important point here is the prospect that increasing oxygen levels profoundly influenced ocean chemistry between 2.4 and 2.0 Ga, and that Fe-containing ocean bottom water returned between 2.0 and 1.8 Ga. If increasing oxygen levels led to the removal of Fe from the oceans, then the reappearance of BIFs might logically imply a decrease in oxygen levels between 2.0 and 1.8 Ga.

The nature of Fe depositing in BIFs between 1.8 and 2.0 Ga provides further insight into atmospheric O_2 levels. If we look at the 1.88 Ga Gunflint Iron Formation from Ontario, Canada, Fe oxides precipitated in the high-energy region of shoaling waves and near the seashore (Pufahl & Fralick 2000). A similar situation for the approximate 1.8 Ga Frere Formation of the Nabberu Basin, Western Australia, is also described (Goode et al. 1983). Furthermore, for the Gunflint, some subtidal upper shoreface stromatolites are reddened with precipitated Fe oxides, and this Fe was likely incorporated during stromatolite growth, as sediment infill is Fe free. Thus, dissolved Fe was delivered well over the shelf and occasionally into the surf zone of the Gunflint paleoshore. Similarly reddened stromatolites are also found in the approximate 2.0 Ga Tulomozerskaya Formation of the Onega Lake area, Russia (Melezhik et al. 1999). The O_2 levels required to allow for Fe^{2+} transport into near-shore environments are difficult to constrain, but Holland (2003) calculates O_2 levels of about 0.1% PAL in explaining similar phenomena in the 2.49 Ga Griquatown Fe formation from South Africa. This estimate may be too low for oxygen concentrations between 2.0 and 1.8 Ga, but relatively low oxygen concentrations are nonetheless indicated.

BIFs again stopped depositing after about 1.8 Ga, and one can surmise that oxygen again increased. A critical question is, to what level did oxygen rise? It has generally been thought that oxygen levels rose to the point at which the deep oceans became oxygenated and dissolved Fe could, therefore, not persist (Cloud 1972, Holland 2003). Canfield (1998) suggested, as described above, that increased oxygen levels gave rise to higher concentrations of seawater sulfate. Increased rates of sulfide production by sulfate reduction resulted and this sulfide titrated dissolved Fe from solution. Thus, the oceans may have gone from Fe-containing to sulfidic. Canfield (1998) calculated that an anoxic deep ocean could be maintained with atmospheric O_2 concentrations less than around 40% PAL. There has been a growing body of recent evidence to support this model. For example, the Fe-S-C systematics in those Mesoproterozoic basins studied to date suggests euxinic conditions, although this alone does not prove that the global ocean was sulfidic (Shen et al. 2002, 2003). Furthermore, the isotopic composition of Mo in sediments deposited in the MacArthur Basin, Australia, indicates extensive global anoxia (Arnold et al. 2004). Finally, work by our own group has revealed a transition from Fe-containing marine bottom water to sulfidic conditions in going from the 1.88 Ga Gunflint Iron Formation to the overlying shales of the Rove Formation

(Poulton et al. 2004). We have apparently caught the ocean in an important chemical transition at around 1.84 Ga. We can conclude, then, that the global ocean probably experienced extensive periods of anoxic sulfidic conditions during the middle Proterozoic. This puts an upper limit on O_2 of around 40% PAL (see above for other constraints on O_2 levels through the Mesoproterozoic).

Summary

Multiple lines of evidence are consistent with low Archean levels of atmospheric O_2, probably lower than 0.1% PAL (Figure 6). Geochemical proxies record oxygenation of the surface environment after about 2.45 Ga (the Great Oxidation Event; Holland 2002) to levels that are difficult to constrain. A focused effort exploring the nature of ocean chemistry (i.e., were ocean bottom waters oxygenated or sulfidic?) during this time would be most instructive. There is an apparent return to low oxygen conditions between around 2.0 and 1.8 Ga, to levels that are also difficult to constrain, but possibly to concentrations as low as those before 2.4 Ga. After 1.8 Ga the oceans apparently become sulfidic, with atmospheric O_2 levels still less than the present day and possibly in the range of 5% to 18% PAL. An increase in oxygen concentrations in the late Neoproterozoic to values >10% PAL is also indicated. The history of atmospheric O_2 concentrations was certainly more dynamic than this simple reconstruction suggests, and complexity will be added as new and better insights emerge. Furthermore, as is hopefully obvious from the above discussion, it is difficult to constrain absolutely the levels of atmospheric O_2 through time. Hopefully, new and insightful geochemical, biological, and geological constraints will bear on this problem.
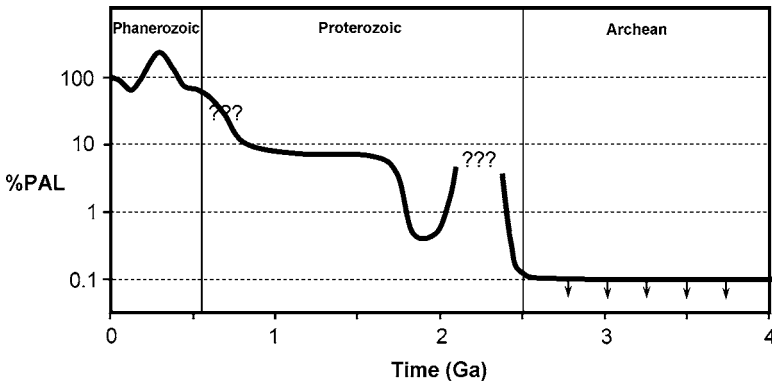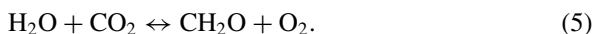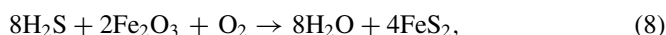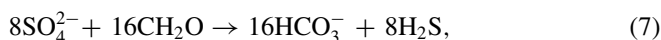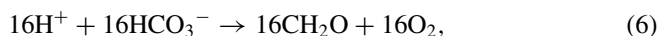

Figure 6 A proposed reconstruction of the concentrations of atmospheric O_2 through geologic time. The values for the Phanerozoic are taken from Berner et al. (2003). The question marks indicate periods when oxygen concentrations are particularly uncertain. This reconstruction is far less certain than the relatively few question marks would seem to indicate. See text for details.

OXYGEN REGULATION

The concentration of oxygen in the atmosphere is a kinetic balance between the rates of processes producing oxygen and the rates of processes consuming it. As described originally by Ebelmen (1845; also see Berner & Maasch 1996, Berner et al. 2003), and re-emphasized by Garrels & Perry (1974) and Holland (1973), the accumulation of oxygen into the atmosphere is controlled by the burial of organic carbon and pyrite sulfur into sediments. For carbon the situation is quite straightforward; in a perfect balance, in which respiration exactly matches photosynthesis, no oxygen would accumulate. However, the burial of organic carbon into sediments frees oxygen to accumulate into the atmosphere (Reaction 5) and to react with reduced species such as Fe(II) and sulfide.

$$H_2O + CO_2 \leftrightarrow CH_2O + O_2. \tag{5}$$

For S we must consider the following series of reactions:

$$16H^+ + 16HCO_3^- \rightarrow 16CH_2O + 16O_2, \tag{6}$$

$$8SO_4^{2-} + 16CH_2O \rightarrow 16HCO_3^- + 8H_2S, \tag{7}$$

$$8H_2S + 2Fe_2O_3 + O_2 \rightarrow 8H_2O + 4FeS_2, \tag{8}$$

Sum:

$$16H^+ + 8SO_4^{2-} + 2Fe_2O_3 \leftrightarrow 8H_2O + 4FeS_2 + 15O_2. \tag{9}$$

Thus, the organic matter produced by oxygenic photosynthesis (Reaction 6) drives sulfate reduction (Reaction 7), which produces sulfide that reacts with Fe oxides and some oxygen, producing pyrite (Reaction 8). In sum, pyrite burial liberates O_2 to the atmosphere (Reaction 9).

Oxygen is consumed during the weathering of organic matter and pyrite-containing rocks exposed at the Earth's surface during uplift and denudation, as well as during the oxidation of reduced C and S gases generated during deep burial diagenesis and metamorphism (see Berner et al. 2003). In addition, magmatism and associated volcanism generate reduced gases such as H_2, SO_2, H_2S, and CO, which also react with O_2. A simple cartoon depicting the geochemical cycle of O_2 is shown in Figure 7, and these processes can be expressed in the following formulation (modified from Garrels & Lerman 1984, Berner & Canfield 1989):

$$\frac{dO_2}{dt} = Fborg - Fworg + 15/8(Fbpy - Fwpy) - Fv, \tag{10}$$

where *Fborg* is the O_2 produced during organic carbon burial, and *Fworg* is the O_2 consumed during weathering and reactions with reduced gases originating from
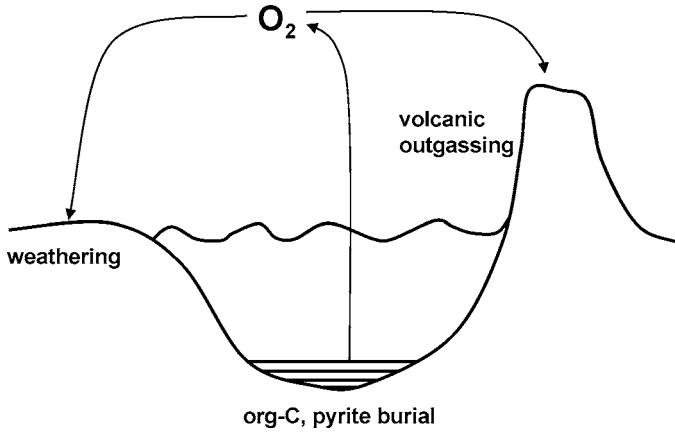
Figure 7   A cartoon of the oxygen cycle showing oxygen sources and oxygen sinks.

organic decomposition during late burial diagenesis and metamorphism (collectively called weathering, see Berner et al. 2003). Oxygen sources and sinks during pyrite burial and weathering are also shown (*Fbpy* and *Fwpy*), as well as O_2 used in the oxidation of reduced gases originating from the mantle, *Fv*. Through the Phanerozoic, O_2 concentrations have apparently been stabilized by a variety of feedbacks that regulate, as functions of O_2 concentration, the burial and weathering rates of organic carbon and pyrite (e.g., Berner & Canfield 1989, Berner et al. 2000, Lenton & Watson 2000; see review in Berner et al. 2003). Similar feedbacks may also have been important in early oxygen regulation, but there may be additional considerations. In the following section we evaluate the magnitudes of the various O_2 sources and sinks.

Organic Carbon Burial

Organic carbon burial has been the major source of O_2 through the Phanerozoic (Garrels & Lerman 1984, Berner 1987), and this burial history has been constrained through isotope mass balance models (Berner & Raiswell 1983, Garrels & Lerman 1984, Berner et al. 2000) and through rock abundance data (Berner & Canfield 1989), both giving comparable results. Rock abundance data are of little value in the Precambrian, where so little of the rock record is preserved, so we must rely on the isotope data. Organic carbon depleted in ^{13}C is fixed from dissolved inorganic carbon (DIC) by autotrophic processes. Globally, the more organic carbon removed from the oceans, the more ^{13}C enriched the remaining DIC becomes. This DIC is precipitated into carbonate minerals in the oceans, providing a record of the $\delta^{13}C$ of marine DIC through time and the intensity of organic carbon burial. The following expression is usually used to relate carbon burial to the $\delta^{13}C$ of marine carbonates

(Reaction 11):

$$f = \frac{\delta^{13}C_{carb} - \delta^{13}C_{in}}{\Delta_{org}}, \tag{11}$$

where f is the ratio of organic carbon burial to total carbon burial, $\delta^{13}C_{carb}$ is the isotopic composition of carbonate carbon, $\delta^{13}C_{in}$ is the isotopic composition of DIC input into the oceans, usually taken as the mantle value (-5%; Des Marais 2001), and Δ_{org} is the isotope difference between DIC and the organic carbon buried in sediments ($\delta^{13}C_{carb} - \delta^{13}C_{org-C}$). The data for the isotopic composition of carbonate carbon and organic carbon through the Precambrian are shown in Figure 8a.

Calculations of the f ratio based on these data are shown in the upper curve of Figure 8c. The simple model presented in Reaction 11, however, tells only part of the story. Bjerrum & Canfield (2004) have recently described how the removal of DIC during hydrothermal circulation of ocean bottom water through ocean crust (ocean crust carbonatization, OCC) is an important sink in the carbon cycle, potentially affecting the carbon isotope balance of the oceans. In particular, the isotopic composition of DIC precipitated in marine surface waters can be influenced by OCC if there is an isotope gradient between surface and deep waters. Evidence suggests that deep water may have been $\sim$5% depleted in ^{13}C relative to surface waters at least during parts of the Archean (Beukes et al. 1990, Des Marais 2001). Bjerrum & Canfield (2004) have modified Reaction 11 to account for OCC (Reaction 12):

$$f = \frac{\left(\delta^{13}C_{in} - \delta^{13}C_{surfcarb} - \lambda\Delta_s\right)}{\left(\Delta_{org} - \lambda\Delta_s\right)}, \tag{12}$$

where $\delta^{13}C_{surfcarb}$ is the isotopic composition of surface water carbonates, λ is the proportion of carbonate removed by OCC, and Δ_s is the isotope difference between surface and deep water ($\delta^{13}C_{surf}$-$\delta^{13}C_{deep}$). The influence of OCC on f depends on a number of factors, including the history of λ and the magnitude of Δ_s. An example of model results is shown in Figure 8c, in which λ has a high early Archean value (Figure 8b), and with Δ_s values of 2% (the modern value) and 5% (presumed Archean value). Clearly, the f value (Figure 8c) is not uniquely defined from the isotope mass balance expression as shown in Reaction 11. Very low f values, which imply limited organic carbon burial, are permissible if OCC is an important Archean process and with a significant isotope gradient between surface and deep water. A significant role for OCC in the Archean has been surmised by Walker (1990) and Sleep & Zahnle (2001).

With the exception of the time period around 2.3 Ga, and the Neoproterozoic, all reconstructions reveal Precambrian values of the f ratio to be lower than the present value of 0.2. Particularly low values are reproduced in the Archean. We consider below possible explanations for these trends.
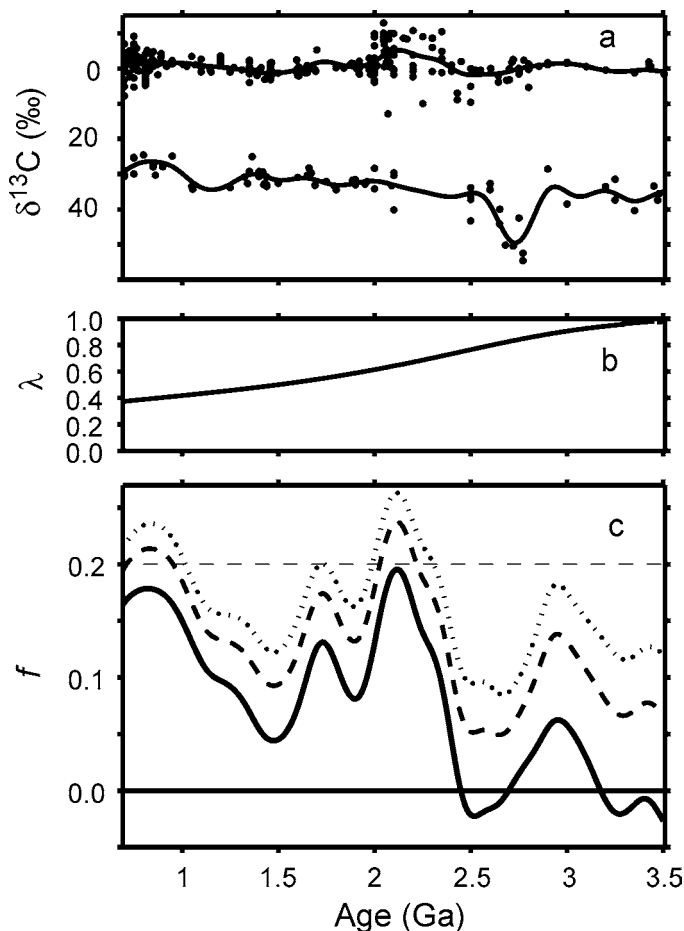
Figure 8   (*A*) A summary of the isotopic composition of inorganic carbon (upper line) and organic carbon (lower line) through geologic time. (*B*) A reconstruction of the relative significance of ocean crust carbonitization (OCC) in removing DIC from the oceans through time. This reconstruction is based on the model of Sleep & Zahnle (2001). (*C*) Reconstructions of the relative significance of organic carbon in total carbon burial through time (*f*). The upper curve is based on standard interpretations of isotope mass balance as shown in Reaction 11. The lower two curves are based on the model incorporating OCC (Reaction 12) with the values of λ (as shown in panel *B*) and with an isotope gradient between the surface and deep oceans of 2% (middle line) and 5% (lower line), respectively. See Bjerrum & Canfield (2004) for details.

Pyrite Burial

Reduced S burial, mainly as pyrite, is also a source of O_2. Canfield (2004) has recently analyzed the isotope record of sedimentary sulfide and sulfate, and has concluded that through most of the Precambrian nearly all the S was buried as pyrite. There is little isotopic evidence for substantial sulfate burial. This contrasts with the last 200 million years, in which pyrite burial only accounts for 30% to 40% of the total S buried, with sulfate making up the rest (e.g., Holland 1973, Berner & Raiswell 1983, Garrels & Lerman 1984).

As discussed above, oxygen levels after about 2.3 Ga were probably sufficient to efficiently weather pyrite to sulfate in soils, producing a significant sulfate input to the oceans. If the oceans were at steady state, meaning that the removal fluxes from the oceans balanced the input fluxes, then the O_2 production from pyrite burial can be written as:

$$O_{2py} = 15/8 f_{py} S_{in}, \tag{13}$$

where O_{2py} is the rate of O_2 production from pyrite burial; f_{py} is the fraction of sulfate flux into the oceans (S_{in}) which is buried as pyrite; and 15/8 expresses the stoichiometric relationship between the burial of pyrite S and O_2 production (Reaction 10). Reaction 13 can be used to provide absolute rates of O_2 production by pyrite burial if f_{py} and S_{in} are known (e.g., Garrels & Lerman 1984, Kump & Garrels 1986, Berner 1987). Uncertainty, however, in the magnitude of S_{in} over time, particularly in the Precambrian, generates significant associated uncertainty in calculations of O_{2py}. Probably better constrained is the relative significance of O_2 production from pyrite burial (O_{2py}) compared with O_2 production from organic carbon burial (O_{2oc} in Reaction 14). This is given in Reaction 15:

$$O_{2oc} = f_{oc} DIC_{in}, \tag{14}$$

$$\frac{O_{2py}}{O_{2oc}} = 15/8 \frac{f_{py}}{f_{oc}} \frac{S_{in}}{DIC_{in}}. \tag{15}$$

In evaluating Reaction 15, f_{py} is varied from 0.75 to 1 through the Precambrian, which accommodates the average and standard deviation of f_{py} values observed (Canfield 2004), except for the Neoproterozoic, in which the S isotope system is apparently out of balance, but this is not discussed further here (see Canfield 2004). For the Phanerozoic, f_{py} values are calculated from S isotope data compilations (e.g., Canfield 2001). The Precambian values for f_{oc} are taken from Bjerrum & Canfield (2004) for the case shown in Figure 8c, with a Δ_s value of 2%, identical to the modern value. For the Phanerozoic, the f_{oc} value is taken from Hayes et al. (1999). A summary of the f_{py} and f_{oc} values used in calculating O_{2py}/O_{2oc} is presented in Table 2. The development of S_{in}/DIC_{in} through time, particularly in the Precambrian, is highly uncertain, but, in the absence of better estimates, a ratio identical to that of today is assumed.

TABLE 2 Parameters used to calculate relative O_2 production from pyrite and organic carbon burial

Time (Ga)	f_{py}	f_{oc}
0	0.33	0.20
0.032	0.44	0.28
0.105	0.35	0.25
0.177	0.30	0.25
0.226	0.30	0.27
0.268	0.24	0.32
0.326	0.43	0.26
0.386	0.62	0.20
0.424	0.56	0.25
0.475	0.85	0.13
0.527	0.75 to 1	0.30
0.572	0.75 to 1	0.18
0.65	0.75 to 1	0.30
0.75	0.75 to 1	0.10
0.8	0.75 to 1	0.30
1.0	0.75 to 1	0.20
1.2	0.75 to 1	0.14
1.4	0.75 to 1	0.11
1.6	0.75 to 1	0.14
1.8	0.75 to 1	0.14
2.0	0.75 to 1	0.22
2.2	0.75 to 1	0.2
2.4	0.75 to 1	0.13
[a]DIC_{in}	1.8×10^{13} mol year^{-1}	
[b]S_{in}	2.1×10^{12} mol year^{-1}	

[a]Berner (1991).

[b]Including volcanic outgassing and MOR input (Berner & Berner 1996, Canfield 2004).

The results are rather unexpected (Figure 9). As opposed to most of the Phanerozoic, in which organic carbon burial dominates O_2 production, through most of the Proterozoic, pyrite burial is apparently as important, or more important, than organic carbon burial. This means that through the Proterozoic O_2 productions rates were probably much higher than considerations of organic carbon burial alone would suggest. These results should be tempered by the recognition that the relative
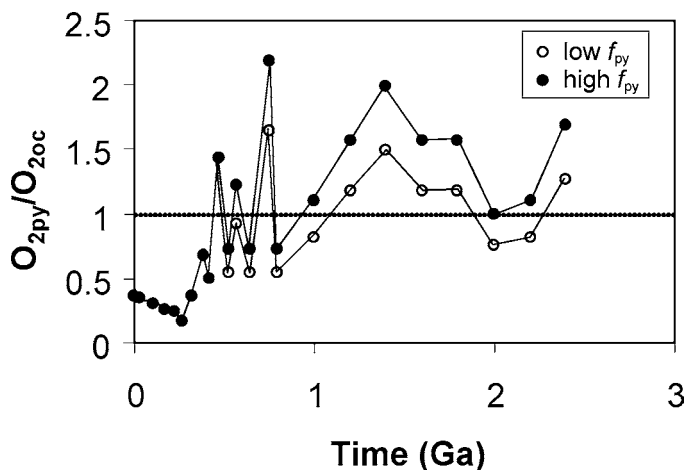
Figure 9 The relative significance of pyrite burial versus organic carbon burial in liberating oxygen to the surface environment. Calculations assuming both high and low estimates for the relative significance of pyrite in total sulfur burial (f_{py}) are shown. See text for details.

input fluxes of sulfate and DIC to the oceans are unknown so far back in time and could have deviated substantially from the modern ratio. Still, a potentially substantial role for pyrite burial in Proterozoic O_2 regulation should be taken seriously.

O_2 Removal

As described in Reaction 10, oxygen is removed either through the oxidation of reduced species in sedimentary rocks on land, mostly organic matter and pyrite, or through the oxidation of reduced gases generated from volcanism, metamorphism, and deep burial diagenesis. The processes controlling O_2 removal during weathering will be discussed immediately below, whereas O_2 removal as a result of gases formed during volcanism will be explored when discussing models for O_2 regulation.

The kinetics associated with O_2 removal exerts a critical control on atmospheric levels of O_2. This is an area about which relatively little is known, but where some insights are emerging. For example, from field observations of weathering shales, pyrite typically weathers faster than organic matter. Also, organic matter oxidation is not always complete, and some rock-derived unoxidized organic matter is delivered to the oceans and buried in sediments (e.g., Dickens et al. 2004). The burial of this recycled organic carbon does not contribute to contemporary oxygen production; its contribution dates back to when the organic matter was first formed. The recycling of organic carbon should have been even more important under low atmospheric O_2. Chang & Berner (1999) have explored directly the kinetics of coal oxidation, and they conclude that coal weathers with a square root

dependency on O_2 concentration. These experiments probably revealed inorganic reaction rates between O_2 and coal (also see Lasaga & Ohmoto 2002). It is also probable that aerobic microorganisms accelerate organic carbon weathering (see Petsch et al. 2001) as they generate oxygen radicals, easily promoting the oxidation of complex organics (see review in Canfield 1994). As discussed above, some aerobes can function under extremely low oxygen concentrations, so the microbial enhancement of weathering is also likely under low oxygen conditions, although the kinetics of this process have not been explored.

On a global scale, weathering is usually represented as a first-order process with respect to the total mass of organic matter or pyrite. For example, the weathering of organic matter is often represented by an expression similar to Reaction 16.

$$\frac{d\text{M}_{OC}}{dt} = -{O_2}^x k\text{M}_{OC}, \tag{16}$$

where M_{OC} is the mass of organic carbon at the Earth surface reservoir, k is a rate constant, O_2 is the concentration of atmospheric oxygen, and x ranges between 0 and 1 depending on the model (Kump & Garrels 1986, Berner 1987, Berner & Canfield 1989, Lasaga & Ohmoto 2002). In some models organic carbon and pyrite are split into slowly recycling and rapidly recycling reservoirs (Berner 1987, Berner & Canfield 1989), expressing the reasonable idea that the most recently deposited sediments become the most susceptible to weathering. Rapid recycling considerably dampens atmospheric O_2 fluctuations. Lasaga & Ohmoto (2002) developed a new model in which organic carbon is weathered during soil formation, and thus the weathering reservoir is the active soil layer at the Earth's surface. With this model real organic matter oxidation kinetics can be used, and rates of oxidation also depend on rates of soil formation. This is an important advancement in modeling global-scale organic carbon oxidation rates.

Nevertheless, modeling rates of O_2 removal in the Precambrian will be plagued by a variety of uncertainties, including (*a*) an accurate description of organic carbon and pyrite oxidation kinetics at low oxygen concentrations, (*b*) constraints on the size of the organic carbon and pyrite reservoirs over time, and (*c*) appropriate choice of model and model parameters to represent global-scale weathering. For example, if a model such as that by Lasaga & Ohmoto (2002) is used, a variety of parameters will need accurate representation including the history of soil formation rates, average soil depth, and any relationships between these parameters and tectonic activity, which scales with heat flow from the mantle (Gurnis & Davies 1986). (*d*) The magnitude of reduced volcanic gas input over time, which is explored in more detail below.

MODELS FOR THE EVOLUTION OF ATMOSPHERIC O_2

No quantitative models exist that attempt to hindcast the evolution of atmospheric O_2 concentrations in the Precambrian. Rather, models are more qualitative, attempting to identify processes that might have significantly influenced oxygen

concentration and that might have encouraged significant change in oxygen concentration as revealed in the geologic record. Explored below are the most prominent models attempting to explain the history of atmospheric O_2 through the Precambrian. Emphasized are models aimed at explaining low concentrations of Archean oxygen and the transition to higher levels around 2.3 Ga. As pointed out by Kump et al. (2001), most explanations for low levels of O_2 in the Archean rely on either low production rates of O_2 or high rates of reduced species input from volcanic sources to titrate the oxygen. As mentioned above, oxygen-producing cyanobacteria were members of the marine ecosystem by 2.7 Ga and possibly much earlier. Thus, in pursuing this discussion we assume that the problem of low Archean levels of oxygen is one of limited O_2 accumulation in the face of biological O_2 production and no distinctions will be drawn between the situation at 2.7 Ga, when we are relatively certain cyanobacteria were present, and times before, when their presence was possible (probable?) but less certain.

In a number of models low Archean levels of atmospheric O_2 resulted from the enhanced delivery of reduced mantle compounds to the Earth's surface, effectively titrating and removing O_2. The enhanced delivery of reduced species may have occurred in association with higher heat flow and tectonic activity (Des Marais 1997) or, alternatively, from a more reducing mantle delivering a higher proportion of reduced gases to the Earth's surface (Kasting et al. 1993, Kump et al. 2001, Holland 2002). In a novel contribution Kump et al. (2001) reasoned that a more reducing early mantle would deliver a higher proportion of reduced gases such as H_2, CO, and CH_4 to the Earth's surface. They argued that if the mantle oxygen fugacity (fO_2) was poised at the Fe-wustite buffer ($fO_2 = 10^{-11.3}$), as opposed to the present fayalite-magnetite-quartz (FMQ) buffer ($fO_2 = 10^{-7.3}$), then the flux of reduced species would have been sufficient to titrate all of the O_2 produced at the Earth's surface by oxygenic photosynthesis. Kump et al. (2001) further noted that H_2 is also produced during the serpentinization of ocean crust, and subduction of this material produces deep-seated relatively oxidizing regions in the lower mantle. The upwelling of this relatively oxidized mantle material in massive plume-related volcanism around 2.45 Ga (Barley et al. 1997, Condie et al. 2001), then, delivered more oxidizing volcanic gases, allowing O_2 to accumulate for the first time. As this deep-seated oxidized material becomes mixed into the upper mantle, the whole mantle becomes more oxidized, approaching the FMQ buffer (also see Lecuyer & Ricard 1999). Thus, the Kump et al. (2001) model offers an explanation for both the low concentrations of atmospheric O_2 in the Archean and the increase in O_2 at around 2.3 to 2.4 Ga.

One possible objection to this model comes from the partitioning of Vanadium and Chromium into Archean mantle-sourced igneous rocks, which shows that the mantle has probably been poised at the FMQ buffer through most of Earth's history (Delano 2001; Canil 1997, 1999). This is not reducing enough to provide the Archean flux of H_2, CO, and CH_4 as envisioned by Kump et al. (2001).

Holland (2002) also reasoned that a more reducing mantle delivered a higher proportion of reduced species, mainly H_2, to the Earth's surface during the Archean. However, in the Holland model, the mantle redox state remains much closer to the

FMQ buffer and thus better satisfies the trace metal constraints on mantle redox evolution over time (see above). Thus, Holland (2002) calculated the proportion of H_2 necessary in volcanic gases to reduce volcanic SO_2 to FeS_2 and 20% of the volcanic CO_2 to organic matter (CH_2O), thereby satisfying isotope constraints on the proportion of carbon buried as organic matter (however, see above). The Holland model makes no assumptions about the process involved in CO_2 reduction to organic matter, but the reduction of the O_2 produced by oxygenic photosynthesis with H_2 is stoichiometrically equivalent to the direct reduction of CO_2 with H_2.

Volcanically derived CO_2 likely represented only a small fraction of the total CO_2 fixed during primary production through most of Earth's history (and especially after the evolution of oxygenic photosynthesis; see above). Thus, in the Holland (2002) model the gases produced during deep diagenesis, metamorphism, and the melting of crustal rocks must have had the same reducing power as primary mantle input. According to Holland (2002), the accumulation of atmospheric O_2 around 2.3 Ga resulted from an increase in seawater sulfate concentrations and the removal of sulfate into ocean crust during high-temperature basalt-seawater interaction at mid-ocean ridges. The subducted sulfate acted as an H_2 sink during magma generation in volcanic arc settings, and the gases emitted were more oxidizing, consuming less O_2.

An uncertainty with this model is the oxidation state and fate of secondary gases produced by deep diagenesis, metamorphism, and the melting of crustal rocks. For example, if a large proportion of methane was produced during organic matter heating, which is likely (see Hayes et al. 1983), some of this methane could have been photolyzed in the atmosphere to CO_2 and H_2, with the H_2 escaping to space (Catling et al. 2001). If this occurred, volcanic gases would not have had the oxidizing power envisioned by Holland (2002). Another concern is the fate of sulfate during basalt-seawater interaction. Presently, most of the sulfate removed as anhydrite at high temperatures is redissolved during low-temperature off-axis circulation (Alt et al. 1989, Alt 1994). If this also occurred in the early Proterozoic, when sulfate levels began to increase, then the flux of sulfate into subducted seafloor may have been insufficient to substantially affect the oxidation state of volcanic gases derived from the subduction of ocean crust.

Each of the above models reasons that Archean levels of atmospheric O_2 were low because of an enhanced flux of reduced species from the mantle and that the increase in O_2 at around 2.3 Ga was caused by a change in the oxidation state of volcanic gases. Catling et al. (2001) and Hoehler et al. (2001) both take a reducing Archean atmosphere as a given and focus on the oxidation of the Earth's surface around 2.3 Ga. Catling et al. (2001) considers the potential consequences of an Archean atmosphere rich in CH_4, as some recent models of atmospheric evolution propose (Pavlov et al. 2000). Under such conditions, methane should photolyze in the stratosphere to CO_2 and H_2 with the H_2 escaping to space. The loss of H_2 would result in a net oxidation of the Earth's surface.

In a somewhat similar manner, Hoehler et al. (2001) observed a large and unexpected flux of H_2 at night from active cyanobacterial mats. They argued that

if a similar nighttime H_2 flux occurred in Archean mats, then a large flux of H_2 into the atmosphere could have been sustained. Using the same reasoning as advanced by Catling et al. (2001) this H_2 flux would oxidize the Earth's surface if lost to space. In both the Catling et al. (2001) and the Hoehler et al. (2001) models, the loss of H_2 would be reduced as atmospheric O_2 accumulates, as both CH_4 and H_2 should both readily react with the O_2. The net effect of both models is the accumulation of large oxidized reservoirs of Fe and S, which reduce the O_2 sink during weathering reactions, helping O_2 to accumulate.

There are some associated uncertainties with these models as well. Thus, the flux of H_2 from microbial mats is uncertain now and even more so in the distant geologic past. Furthermore, if organic haze formed as a result of elevated methane concentrations (Pavlov et al. 2001), this would absorb the spectrum of solar radiation required to produce mass-independent isotope fractionations during the photolysis of SO_2 (Farquhar & Wing 2003). Thus, the mass-independent S isotopic compositions preserved in Archean rocks, as discussed above, are not easily explained if organic haze formed from a methane-rich Archean atmosphere.

Other models of early Precambrian oxygen evolution have focused on oxygen production rate. The *f* ratio for organic carbon burial was low in the Archean, and if the model of Bjerrum & Canfield (2004) is correct, very low indeed (Figure 8*c*). A low *f* ratio is consistent with low rates of O_2 production, possibly contributing to low concentrations of atmospheric O_2. Bjerrum & Canfield (2002) proposed that severe P limitation may have reduced rates of marine primary production in the Archean and early Proterzoic, contributing to a low *f* ratio. Indeed, from the P content of Archean and early Proterozoic BIFs they deduced that marine waters had phosphate levels that were 10% to 20% as high as modern levels, which could reduce primary production rates by similar amounts. Phosphorus (P) limitation was apparently caused by substantial adsorption onto the Fe oxides precipitating as BIFs.

According to Bjerrum & Canfield (2002), increasing sulfate levels around 2.4 to 2.5 Ga stimulated sulfate reduction, binding Fe as pyrite. The nature of ocean chemistry after this time is unclear, but if the oceans became sulfidic (see Bjerrum & Canfield 2002 and discussion above), the removal of Fe as pyrite would have been substantial. If the oceans were oxic, Fe oxide deposition may still have been reduced because of elevated sedimentary pyrite formation. In any event, less Fe oxide deposition would have freed P to fuel higher rates of marine primary production. Bjerrum & Canfield (2002) speculated that increased P availability could have partly explained the increase in atmospheric O_2 around 2.3 Ga.

There was an apparent return to low oxygen conditions between 2.0 and 1.8 Ga, as discussed above. This proposed decrease does coincide with a decrease in *f* ratio (see Figure 8*c*) and presumably also decreasing rates of organic carbon burial, and therefore could be a logical consequence of decreasing O_2 production rate. The cause of decreasing carbon burial rate is unclear, although the redeposition of oxide facies BIFs may have again adsorbed P, limiting primary production, and exacerbated low carbon burial rates. It seems that the pre-2.4 Ga situation was reestablished.

An apparent transition to sulfidic conditions at around 1.8 Ga would have ended BIF deposition, and a long period of sulfidic oceans may have ensued. Oxygen levels during this time are difficult to constrain, but they may have been in the range of 8% to 15% PAL (see above). Lower f ratios for carbon burial are indicated from the isotope record (Figure 8), and this would have contributed to lower O_2 production, at least partly explaining the lower O_2 levels. Lower burial rates of organic carbon may also have been a consequence of anoxic marine conditions, but in this case N rather than P may have been the limiting nutrient (Anbar & Knoll 2002). This is because intense denitrification, and associated N loss as N_2, would have been associated with a stratified anoxic water column. Furthermore, nitrogen input by nitrogen fixation may have been hindered by trace metal limitation, as would have occurred with sulfidic marine bottom water (Anbar & Knoll 2002).

The above relationships are outlined in Figure 10 and express the possibility that internal ocean dynamics influenced rates of marine primary production, organic carbon burial, and levels of atmospheric O_2. Two different control regimes are indicated. One regime has low sulfate levels and an Fe-containing ocean. In this case, P removal onto Fe oxides limits primary production and carbon burial. In the other regime, sulfate levels are higher, the ocean is sulfidic, and N limits primary production and carbon burial. In both regimes, ocean anoxia ultimately limits primary production. One potential complicating factor is the elevated rates of O_2 production resulting from high rates of pyrite burial under sulfidic ocean conditions. However, if pyrite is readily oxidized during weathering, then the influence of enhanced pyrite burial on oxygen concentrations may be small except
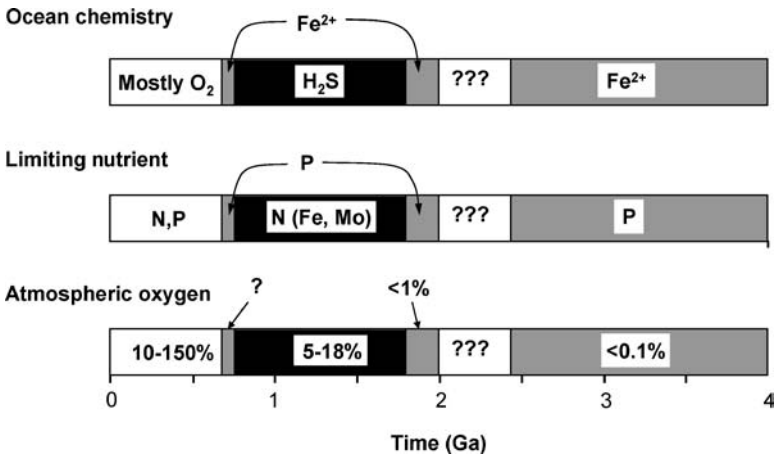

Figure 10   A cartoon summarizing the proposed relationship between atmosphere and ocean chemistry, and the nutrients that may have limited marine primary production through time.

under circumstances when the size of the crustal pyrite reservoir is in flux. This issue needs serious consideration.

There was an apparent rise in atmospheric O_2 near the end of the Neoproterozoic, ushered in quite likely by increased organic carbon burial, possibly linked to continental breakup and high rates of sediment deposition (Knoll et al. 1986, Derry et al. 1992, Kaufman et al. 1997). This rise in O_2 may have spurred the evolution of large animals (Knoll 1992, Knoll & Carroll 1999), but it came about in a time of great environmental instability with at least two, and possibly more, massive, probably global, glaciations (Kirschvink 1992, Hoffman et al. 1998). There was also a return to periodic anoxic Fe-containing ocean water, and low water column sulfate concentrations (Canfield 1998, Hurtgen et al. 2002). Though fascinating, in-depth considerations of O_2 levels and controls through this dynamic period in Earth's history are beyond the scope of the present review.

SUMMARY

The study of Precambrian oxygen evolution has matured into a serious science. It invites contributions from a number of disciplines in new and exciting combinations that would have surely gladdened Bob Garrels and other early pioneers. Yet, even so, we can provide only a sketch of how oxygen concentrations have evolved through the Precambrian, with a handful of compelling, yet uncertain, models of oxygen control. Indeed, we have insufficient understanding to advance realistic quantitative models hindcasting the evolution of Precambrian atmospheric O_2 concentrations. We need much better constraints on the processes that control oxygen production and oxygen removal, and we need more information on the evolution of ocean chemistry through time, as this is an important window into atmospheric evolution. We must provide better constraints on the timing of cyanobacterial evolution. Furthermore, we must better understand the nature of carbon cycling through time and the influence of nutrient limitation on primary production. Finally, we must strive to understand what combination of factors allowed the Earth to accumulate high concentrations of metabolically advantageous O_2. Part of the answer lies with active plate tectonics driving element cycling and a dynamic carbon cycle (see Berner et al. 2003; Berner 2004). However, from the history of O_2 accumulation here on Earth, we also know that an O_2-rich atmosphere is not an inevitable consequence of oxygenic photosynthesis. Our understanding of the processes controlling O_2 through the Precambrian will allow us to better appreciate the prospects for oxygen-rich atmospheres elsewhere in the heavens. There is a great deal of work for new and upcoming generations of geobiologists.

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