The oxygenation of the atmosphere and oceans

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The last 3.85 Gyr of Earth history have been divided into five stages. During stage 1 (3.85–2.45 Gyr ago (Ga)) the atmosphere was largely or entirely anoxic, as were the oceans, with the possible exception of oxygen oases in the shallow oceans.

During stage 2 (2.45–1.85 Ga) atmospheric oxygen levels rose to values estimated to have been between 0.02 and 0.04 atm. The shallow oceans became mildly oxygenated, while the deep oceans continued anoxic.

Stage 3 (1.85–0.85 Ga) was apparently rather 'boring'. Atmospheric oxygen levels did not change significantly. Most of the surface oceans were mildly oxygenated, as were the deep oceans.

Stage 4 (0.85–0.54 Ga) saw a rise in atmospheric oxygen to values not much less than 0.2 atm. The shallow oceans followed suit, but the deep oceans were anoxic, at least during the intense Neoproterozoic ice ages. Atmospheric oxygen levels during stage 5 (0.54 Ga–present) probably rose to a maximum value of *ca* 0.3 atm during the Carboniferous before returning to its present value. The shallow oceans were oxygenated, while the oxygenation of the deep oceans fluctuated considerably, perhaps on rather geologically short time-scales.

Keywords: atmosphere; oceans; oxygen; mass-independent fractionation; great oxidation event; oceanic anoxic events

1. INTRODUCTION

The broad outlines of the oxygenation history of the atmosphere and oceans are now reasonably well known; but there are still significant lacunae in the record, especially for the oxygenation of the oceans, and many of the processes that were responsible for the major transitions in the oxidation state of the atmosphere–ocean system are still poorly defined. This paper attempts to summarize what is reasonably well established regarding the oxygenation of the atmosphere and oceans, to offer some suggestions regarding the state of the system during time periods when its oxygenation is still in dispute, and to propose mechanisms for the major oxygenation transitions. Some sections of the paper are rather speculative, perhaps more so than is warranted or desirable, but excusable because they are part of a scientific discussion meeting of the Royal Society, and therefore intended to encourage debate rather than simply to marshal the certainties of the field. The paper begins with the state of the ocean–atmosphere system during the deposition of the earliest known (meta)sediments. The boundaries of the succeeding stages of Earth history are defined by the times of significant change in the redox state of the system.

2. STAGE 1: 3.85–2.45 Ga

During the second half of the twentieth century evidence from several lines of investigation confirmed that the oxygen level in the atmosphere and oceans was very low during the Archaean and Early Palaeoproterozoic (see for instance Holland 1994). This conclusion was confirmed and extended by the discovery of large degrees of mass-independent fractionation (MIF) of the sulphur isotopes in sulphides and sulphates in pre-2.45 Gyr sedimentary rocks. These measurements indicate that the O_2 content of the Archaean atmosphere was generally less than *ca* 10^{-5} present atmospheric level (PAL) (2 p.p.m.v.; Kasting *et al.* 2001; Pavlov & Kasting 2002). At the time of writing, there is no defensible alternative to this interpretation of the pre-2.45 Gyr MIF-S signals. Figure 1 is a recent compilation of MIF-S data. Large MIF-S values are present in all time periods prior to 2.45 Gyr ago (Ga) except between *ca* 2.8 and 3.0 Ga. In this time interval, MIF-S values are small but non-zero (Watanabe *et al.* 2005). This may indicate that atmospheric O_2 was present in quantities greater than 10^{-5} PAL between *ca* 2.8 and 3.0 Ga, but elevated concentrations of other gases in the atmosphere may also have depressed the MIF-S signal during this period. If O_2 was present in the atmosphere, its concentration was too low (less than *ca* 10^{-3} atm) to be registered by other, less-sensitive indicators of the level of atmospheric O_2. The appearance of even small amounts of O_2 in the atmosphere would have been accompanied by a large decrease in its CH_4 content, and this decrease could have been responsible for the onset of the earliest known ice age at 2.9 Ga (Young *et al.* 1998; Kasting & Ono 2006). Although this connection is suggestive, it does not prove that O_2 was present in the atmosphere at 2.9 Ga, because processes other than a decrease in P_{CH_4} could have been responsible for the 2.9 Ga ice age.

Not a great deal is known about the pre-3.0 Ga biosphere. Photosynthetic bacteria almost certainly

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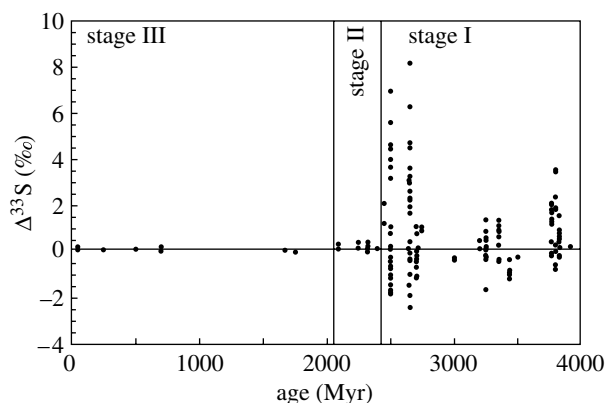
Figure 1. The values of $\Delta^{33}S$, indicator of mass-independent fractionation (MIF) of sulphur in pyrite and barite during the past 4000 Myr. The data were compiled by S. Ono from (Farquhar *et al.* 2000, 2002; Ono *et al.* 2003, Mojzsis *et al.* 2003; Hu *et al.* 2003).

employed photosystem-I (PS-I) and used H_2, H_2S and/or Fe^{2+} to reduce CO_2 to organic matter (Pierson 1994). The simplest explanation for the appearance of O_2 in the atmosphere at concentrations in excess of *ca* 2 p.p.m. at *ca* 2.45 Ga is that cyanobacteria using photosystem-II evolved at that time. However, this is unlikely. The presence of 2 α-methyl hopanes in sedimentary rocks more than 2.7 Gyr suggests that cyanobacteria were important primary producers well before 2.45 Ga (Brocks *et al.* 2003; Summons *et al.* 2006). Debate continues regarding the age of the oldest cyanobacteria (Schopf 1994, 2005; Brasier 2005), but it is likely that they were present at least 300 Myr before the end of the large MIF-S signals.

Figure 2 shows a large compilation of data for the isotopic composition of carbon in limestones, dolomites and calcitic fossils (Shields & Veizer 2002). Although there is a considerable amount of scatter in $\delta^{13}C$ at any given time, the dataset as a whole can be divided into segments where the $\delta^{13}C$ of marine carbonates was close to 0‰ and segments where large excursions occur. During the first type of segment the atmosphere–ocean–crust system was apparently at or close to steady state. If, as seems likely, the $\delta^{13}C$ value of CO_2 injected into the atmosphere from mantle degassing has been close to -5‰ during much of Earth history, segments of time during which the $\delta^{13}C$ value of marine carbonates was close to 0‰ were periods during which the deposition of organic matter drove the $\delta^{13}C$ value of seawater to *ca* 0‰. The $\delta^{13}C$ of organic matter buried with sediments has been somewhat variable both in time and space. Hayes (1994) has shown that a good deal of Archaean organic matter had $\delta^{13}C$ values between -30 and -40‰. If organic matter and carbonate minerals were the only important sinks of volcanic and hydrothermal carbon, roughly 14% of the degassed carbon was converted to organic matter during the Archaean; the rest became part of carbonate sediments. These percentages are consistent with the removal of most or all of the volcanic H_2 from the atmosphere via the overall reaction (Holland 2002)

$$2H_2 + CO_2 \rightarrow C_{org} + 2H_2O. \qquad (2.1)$$
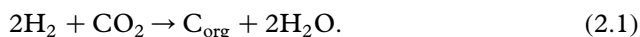
This result suggests that steady state during much, if not all, of the Archaean was achieved while the

atmosphere contained no or essentially no O_2. The O_2 generated by cyanobacteria using photosystem-II was apparently insufficient to outweigh the reducing effect of H_2 and other reductants on the atmosphere–ocean system.

The quantity of organic matter buried during any given period of Earth history has been the difference between the quantity of organic matter generated and the quantity of organic matter destroyed prior to burial. Today the quantity of organic matter that is buried is considerably less than 1% of the quantity of organic matter that is generated. It is likely that this percentage was somewhat larger during the Archaean, since oxygenic degradation of organic matter is so rapid; but the quantity of organic matter buried was almost certainly much smaller than the quantity that was generated. Then, as now, the role of the generation and the rate of destruction of organic matter both depended on the redox state of the atmosphere–ocean system. The rate of organic matter generation by PS-I organisms was probably limited by the availability of H_2, H_2S and Fe^{2+} in the photic zone. The rate of generation of organic matter by cyanobacteria was probably limited by the quantity of nutrients remaining after their depletion by PS-I organisms. It seems likely that phosphate was usually limiting, since nitrogen-fixing organisms existed, and denitrification was limited in a largely anoxic ocean. The destruction of organic matter was probably dominated by methanogenesis and SO_4^{2-} reduction. In the absence of quantitative data for the rate of these processes during the Archaean, it seems premature to construct quantitative models to define the redox state of the atmosphere–ocean system. All that can be said with some assurance is that steady state during much, if not all of the Archaean was maintained without the enhancing effect of atmospheric O_2 on the decomposition rate of organic matter.

The deeper oceans were almost certainly anoxic but not euxinic during the Archaean. This is indicated most clearly by the widespread occurrence of oxide facies banded iron formation (BIF; figure 3). The occurrence of large marine manganese deposits (figure 4 and table 1) during the Archaean almost certainly demands the presence of reducing conditions in the deeper oceans, where Mn^{2+} was able to accumulate, upwell into the shallow oceans, and be precipitated there as a constituent of Mn carbonates and/or Mn oxides (Roy 1997). Much of the shallow ocean was probably anoxic as well. However, there is some biomarker evidence for the presence of oxygen oases where the rate of oxygen production by cyanobacteria outweighed the downward mixing of reduced gases from the atmosphere.

There are no known Archaean phosphorite deposits (Cook & Shergold 1986). Later erosion of such deposits cannot be ruled out, but their entire absence suggests that one or more of the ingredients that are required for the formation of phosphorites were missing during the Archaean. A likely candidate is too minor a downward transport of organic matter into the deeper oceans. Today *ca* 10% of the organic matter that is generated in the photic zone sinks into the deeper oceans and is destroyed there, largely by oxygenic decomposition. The phosphate that is released during
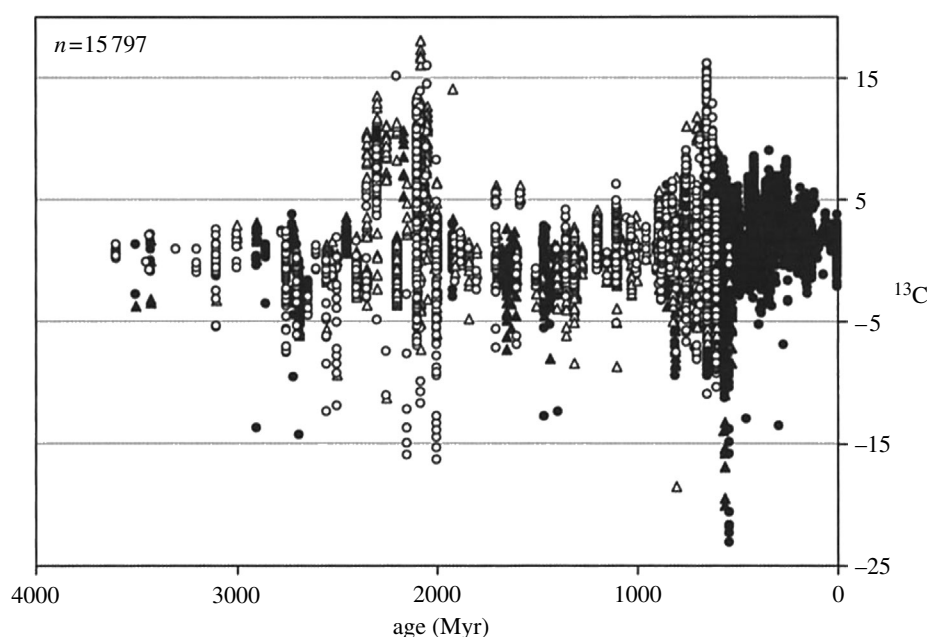
Figure 2. Carbon isotopic evolution of marine carbonate based on published analyses of limestones (circles), dolostones (triangles) and Phanerozoic calcitic fossils. Poorly time-constrained samples (more than ± 50 Ma) are shown as open symbols (Shields & Veizer 2002).
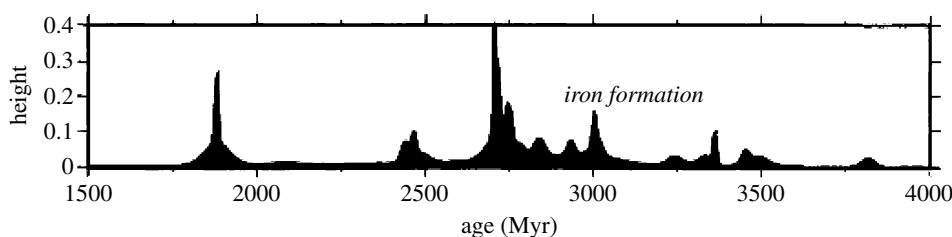

Figure 3. Time-series of occurrences of iron formation generated by summing Gaussian distributions of unit area in the compilation by Isley & Abbott (1999).

this decomposition raises the phosphate concentration of deep ocean water. During upwelling this phosphate-enriched seawater hosts intense biologic activity, which can give rise to the formation of phosphorites. Today much of the organic matter that sinks is packaged in faecal pellets which are ballasted by $CaCO_3$ and SiO_2. Such ballasting was very minor during the Archaean. Hence, the fraction of organic matter that sank into the deep ocean was almost certainly very much smaller than today (Logan *et al.* 1995). Adsorption of organic matter and dissolved phosphate on $Fe(OH)_3$ generated in the near surface oceans by the effect of UVC on Fe^{2+} and by photosynthetic organisms which used Fe^{2+} as a reductant for CO_2 must have transported some PO_4^{3-} into the deep oceans, but apparently in quantities that were insufficient to generate phosphorite deposition.

3. STAGE 2: 2.45–1.85 Ga

The age of the youngest sediments in which sulphur has a large MIF signal is 2.41 Gyr (see figure 1). Thereafter, the record is rather spotty until 2.32 Ga, when the pyrite of the Timeball Hill–Rooihogte Formations in South Africa was deposited. These contain no significant MIF-S signal (Bekker *et al.* 2004), and large MIF-S signals do not reappear thereafter. Atmospheric O_2 seems to have appeared irreversibly between 2.41 and 2.32 Ga.

The reasons for the change in atmospheric chemistry during stage 2 have been debated widely but inconclusively (Canfield 2005). The near-coincidence of the end of Archaean BIF deposition and the appearance of atmospheric O_2 is striking. The end of BIF deposition was followed by a *ca* 360 Myr hiatus before the resumption of major BIF deposition at *ca* 2.08 Ga. Complete erosion of a BIF record between 2.44 and 2.08 Ga is possible but unlikely. It is much more likely that *ca* 2.45 Ga a real change in the operation of the Earth system ushered in the oxygenated atmosphere (Barley *et al.* 2005). The decrease in the deposition rate of BIFs must have contributed to the change. Archaean BIFs contain on the average *ca* 0.3×10^{-2} mol P per mol Fe (Bjerrum & Canfield 2002). The estimated minimum rate of Fe deposition in the very large Hamersley BIFs is *ca* 5×10^{11} mol yr^{-1} (Holland 1984). The total worldwide Fe output with BIFs during the deposition of the Hamersley BIFs was surely larger, but probably less than *ca* 3×10^{12} mol yr^{-1}, which is *ca* 10 times the estimated present hydrothermal Fe^{2+} flux. The output of P with BIFs at that time was therefore probably more than 1.5×10^9 mol yr^{-1} but less than 9×10^9 mol yr^{-1}. The most recent estimate of the input of P to the oceans today is *ca* 30×10^9 mol yr^{-1} (Colman & Holland 2000). The P input during the Late Archaean was
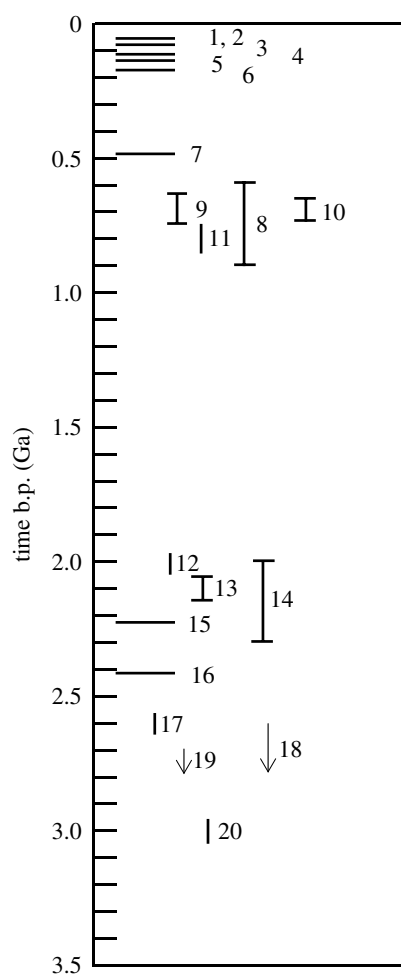
Figure 4. Marine manganese deposits (Roy 1997).

probably several times larger. A complete cessation of BIF formation could therefore have had a minor but possibly significant effect on the P budget of the oceans. More P would have become available for photosynthesis, and more organic matter could have been buried. It is not clear, however, whether the excess O_2 generated in this way was sufficient to usher in the oxygenated atmosphere.

The precipitation of BIF consisting largely of Fe_3O_4 requires the oxidation of two-thirds of the parent Fe^{2+} to Fe^{3+} via the overall reaction

$$6\,'FeO' + O_2 \rightarrow 2Fe_3O_4. \qquad (3.1)$$

The oxidation of 5×10^{11} mol Fe^{2+} yr^{-1} therefore requires 0.8×10^{11} mol yr^{-1} O_2. The oxidation of the likely maximum Fe^{2+} flux of 3×10^{12} mol yr^{-1} requires 5×10^{11} mol O_2 yr^{-1}. This is trivial compared to the *ca* 4×10^{14} mol O_2 generated annually today by marine photosynthesis, but it represents several percent of the *ca* 120×10^{11} mol of O_2 generated by the burial of organic matter (see for instance Holland 2002). The cessation of BIF deposition therefore reduced or eliminated a minor O_2 sink and, in a small way, contributed to the transition of the atmosphere to an oxygenated state. However, other potentially important changes in the Earth's redox system, including a decrease in the hydrothermal flux of H_2 and H_2S, and changes in the biosphere and in the nutrient flux to

the oceans could have been as or more important than these relatively minor shifts.

The period between 2.4 and 2.0 Ga has become known as the Great Oxidation Event (GOE). The large positive excursion in the $\delta^{13}C$ of marine carbonates between *ca* 2.3 and 2.0 Gyr shows that during this period the carbon cycle was not in steady state (Karhu & Holland 1996). Some of the excess carbon that was buried during this period raised the O_2 content of the atmosphere, but most of the excess O_2 was used to transform the geochemical cycle of Fe and of S. In our study of the composition of Precambrian shales, the average $Fe_2O_3 : FeO$ weight ratio of 190 pre-2.3 Ga shales was *ca* 0.25, and very few shales had Fe_2O_3/FeO weight ratios in excess of 1.0 (Bekker *et al.* 2003, see also Yamaguchi 2002). On the other hand, the average $Fe_2O_3 : FeO$ weight ratio of 317 2.3–2.1 Ga shales in our dataset was 0.83 and some 25% of the shales had Fe_2O_3/FeO ratios in excess of 1.0. This indicates a major change in the redox state of Fe during the course of the GOE.

The first evaporitic sediments known to contain gypsum or anhydrite were deposited during the GOE. (Melezhik *et al.* 2005). This indicates that the concentration of SO_4^{2-} in seawater increased during the GOE, although $m_{SO_4^{2-}}$ at 2.0 Ga was almost certainly much less than today (Gellatly & Lyons 2005). This is corroborated by the observation that the average $\delta^{34}S$ value of S in pyrite remained close to 0‰ until near the end of the Proterozoic (figure 5), indicating that most of the SO_4^{2-} input to the oceans continued to be removed as a constituent of pyrite until the Neoproterozoic. During the GOE, the surface oceans must have been mildly, but progressively more oxygenated. On the other hand, the formation of very large marine Mn deposits such as that of the Hotazel Formation in South Africa during the GOE indicates that the deep oceans continued to be anoxic

Marine phosphorite deposits made their first appearance during the GOE (Cook & Shergold 1986, see table 2). If these deposits owed their origin to the same processes that were responsible for the formation of Phanerozoic phosphorites, the transport of phosphate into the deep oceans in the absence of ballasting of organic matter by $CaCO_3$ and SiO_2 must be explained. The most likely mechanism is the downward transport of PO_4^{3-} adsorbed on $Fe(OH)_3$. In the Black Sea today Fe^{2+} is oxidized to Fe^{3+} close to the H_2S–O_2 boundary. It is then precipitated as $Fe(OH)_3$, sinks into the reduced, deeper part of the sea, and becomes reduced there. PO_4^{3-} is adsorbed on the $Fe(OH)_3$ precipitates and is released into the water column during the reduction of $Fe(OH)_3$ below the chemocline (Shaffer 1986).

Although it is difficult to model the operation of this process quantitatively in the ocean during the GOE, it can be shown that it is a feasible mechanism for transporting significant quantities of PO_4^{3-} into the deeper oceans. At the present rate of seawater hydrothermal fluxing some 3×10^{11} mol of Fe^{2+} are added annually to the oceans at high-temperature vents. If this Fe^{2+} were mixed toward the surface oceans, oxidized to Fe^{3+}, and precipitated as $Fe(OH)_3$,

Table 1. Marine manganese deposits (Roy 1997).

|		age	geological sequence	deposits
Phanerozoic	1	Early Oligocene	Early Kharkovian	Nikopol, Ukraine
	2		Early Kharkovian	Chiatura, Georgia
	3	Late Cretaceous		Imini-Tasdremt, Morocco
	4	Middle Cretaceous	Mullaman beds	Groote Eylandt, Australia
	5	Late Jurassic	Taman Fm, Chipoco facies	Molango, Mexico
	6	Early Jurassic		Urkut, Hungary
	7	Middle Ordovician	Modaoxi	Taojiang, China
Late Proterozoic	8	900–600 Ma	Santa Cruz Fm, Jacadigo Group	Urucum, Brazil
	9	*ca* 750–650 Ma	Chuos Fm, Damara Sequence	Otjosondu, Namibia
	10	*ca* 720–680 Ma	Datangpo Sequence, Nantuo ice age	Xiangtan, Minle, Datangpo, Tangganshan, China
	11	*ca* 800 Ma	Penganga Group	Tamsi, Guda, Kanpa, India
	12	*ca* 2.0 Ga	Sausar Group	Mansar, Chikla, Tirodi, India
Early Proterozoic	13	*ca* 2.1 Ga	Francevillian Series	Okouma and Bangombe Plateaus, Gabon
	14	*ca* 2.3–2.0 Ga	Birimian Supergroup	Nsuta, Ghana; Mokta, Ivory Coast; Tambao, Burkina Faso
	15	*ca* 2.24 Ga	Hotazel Fm Postmasburg Group Transvaal Supergroup	Mamatwan, Wessels, South Africa
	16	2.42	Koegas	South Africa
	17	*ca* 2.6 Ga	Chitradurga Group	Chitradurga–Tumkur Kumsi–Hornhalli, Karnataka, India
Archaean	18	*ca* > 2.6 Ga	Eastern Ghats Sequence	Kodur, Garividi, Garbham, Andhra Pradesh, India
	19	*ca* > 2.7 Ga	Rio das Velhas Supergroup	Morro do Mina, Minas Gerais, Brazil
	20	*ca* 3.0 Ga	Iron Ore Group	Joda, Kalimati, Gurda Phagua, Mahulsukha, Orissa, India
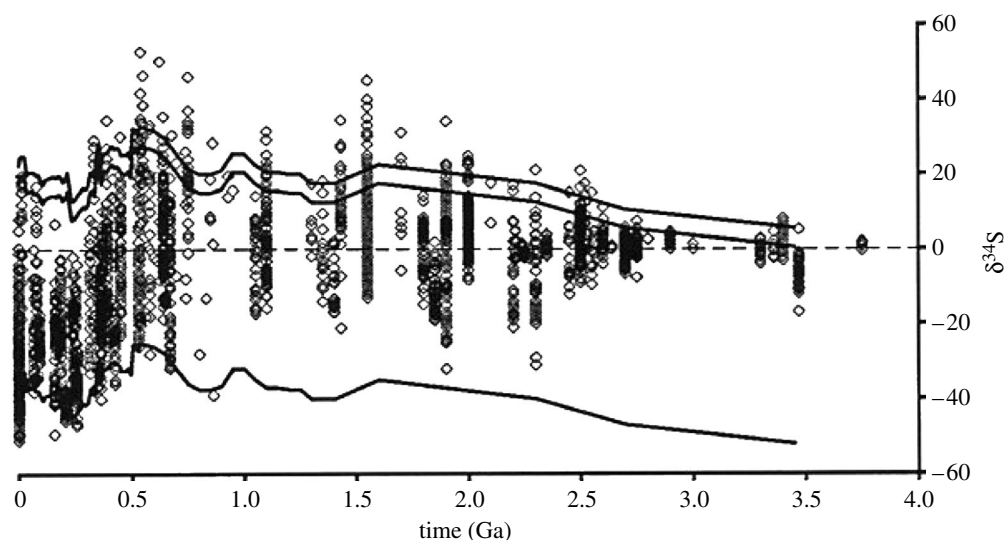
Figure 5. Compilation of the isotopic composition of sedimentary sulphides (diamonds) through time. Also shown is a reconstruction of the isotopic composition of sulphate (upper line) and, as a guide, the isotopic composition of sulphate offset by 55% (lower line) (Canfield 2005).

the P : Fe mol ratio of the precipitate would have been

$$\frac{P}{Fe} \sim 0.018 + 0.060 m_{PO_4^{3-}}, \qquad (3.2)$$

where $m_{PO_4^{3-}}$ is the total P concentration in $\mu mol\, l^{-1}$ in the local seawater (Wheat *et al.* 1996; Feely *et al.* 1998). The PO_4^{3-} concentration of surface seawater was probably very low, but increased toward the base of the photic zone. $Fe(OH)_3$ precipitation probably occurred near the chemocline, where $m_{PO_4^{3-}}$ was probably in the μmol range. The P : Fe ratio in the sinking $Fe(OH)_3$ may therefore have been between *ca* 0.08 and 0.14. A single pass of all hydrothermal Fe^{2+} would then have removed between 0.2×10^{11} and 0.4×10^{11} mol PO_4^{3-}

Table 2. Palaeoproterozoic phosphorites (Nothold & Sheldon 1986).

North America	Marquette Range Supergroup Animikie Group
Europe	Lower Proterozoic Schist belt, Finland
Korea	Mach' onnyang Series
China	Dongjian Group
India	Bijawar Group
Australia	Pine Creek Geosyncline, Rum Jungle District, Northern Territory

from the surface into the deep ocean. This accounts for 3–6% of the estimated present day PO_4^{3-} flux into the oceans. Larger quantities of PO_4^{3-} could have been moved into the deeper oceans if the hydrothermal Fe^{2+} made several redox passes through the surface oceans.

The present day oceans are ventilated at a rate of ca. 1×10^{18} kg yr^{-1}. If the PO_4^{3-} absorbed on $Fe(OH)_3$ was released at depth and was added to the PO_4^{3-} which was carried downward with surface waters cycled along the Proterozoic analogue of the modern conveyor belt, the increment of PO_4^{3-} would have been between 0.02 and 0.04 µmol kg^{-1}. This is too small to affect the formation phosphorites. It is likely, however, that the hydrothermal input of Fe^{2+} during the GOE was several times greater than the present rate, and iron could well have cycled several times across the chemocline. If so, the PO_4^{3-} concentration of seawater could have been augmented by as much as 0.5 µmol l^{-1} in its passage along the conveyor belt. An increment of this magnitude could have played a significant role in promoting the formation of the Palaeoproterozoic phosphorites.

The level of atmospheric O_2 during the GOE is still rather uncertain. The mineralogy and chemical composition of the Hekpoort paleosol profile at Gaborone, Botswana, suggests that at 2.25 Ga atmospheric P_{O_2} was between *ca* 0.1 and 5% PAL (Yang & Holland 2003). A 2.2–1.9 Ga palaeoweathering profile in Griqualand West, South Africa, suggests that during the formation of this profile P_{O_2} was greater than *ca* 15% PAL. These estimates are, perforce, rough; they are consistent with the notion that P_{O_2} was much greater at the end than at the beginning of the GOE, but that at 2.0 Ga P_{O_2} was still significantly lower than the present level of 0.21 atm.

The deposition of BIF's resumed *ca* 2.08 Ga and continued until 1.8 Ga (Isley & Abbott 1999). Then it apparently ceased for a billion years, ushering in the long period of environmental stability that has been called the 'boring billion'.

4. STAGE 3: 1.85–0.85 Ga

Some two decades ago, I ascribed the end of BIF deposition at *ca* 1.8 Ga to the oxidation of the deep oceans (Holland 1984). Since then Canfield (1998) has suggested that the end of BIF deposition was due to just the opposite process: the development of sulphidic deep oceans. This model of the Mesoproterozoic oceans has become known as the 'Canfield Ocean'. Canfield (1998) pointed out that the supply of O_2 to the deep oceans during this period was almost certainly much less than it is today, if—as seems likely—the O_2

content of the atmosphere was 10–20% PAL. The O_2 content of seawater would then have become exhausted during its passage from the sea surface downward and along the oceanic conveyor belt. The deep ocean would therefore have become anoxic or euxinic, if all other parameters of the system had remained unchanged. The two most important of these parameters are the annual rate at which organic matter sinks into the deep oceans and the rate at which surface water sinks into the deep oceans. As pointed out earlier in this paper, the flux of sinking organic matter was probably much less during the Mesoproterozoic than today. At present the concentration of O_2 in North Atlantic deep water is *ca* 260 µm. Some 120 µm of this are lost during transit along the conveyor belt (Broecker & Peng 1982), largely due to the oxidation of sinking organic matter. Recent work by Francois *et al.* (2002), Klaas and Archer (2002), and Armstrong *et al.* (2002) has shown that today very little, if any, organic matter sinking from the photic zone reaches depths greater than 2000 m in the absence of ballasting by $CaCO_3$. As far as is known, $CaCO_3$ ballasting did not exist during the Mesoproterozoic. The fraction of organic matter reaching the deep oceans during this period must, therefore, have been much smaller than today. If the quantity of organic matter sinking annually into the deep oceans during the Mesoproterozoic was only one-tenth of the present quantity (J. M. Hayes 2005, personal estimate) the loss of O_2 during passage through the deep oceans would have been only *ca* 12 µmol l^{-1}, all other things being equal. Such a loss would not have been sufficient to eliminate all of the O_2 from sinking surface water at the present rate of ocean ventilation, even if the atmospheric O_2 level was only 10% PAL. This calculation does not prove that the deep Mesoproterozoic oceans were mildly oxygenated, only that anoxic or euxinic deep oceans during this period were not inevitable.

The absence of marine manganese deposits during the entire 'boring billion' (figure 4) suggests that the deep oceans were indeed mildly oxygenated between 1.8 and 0.8 Ga. It is possible that all of the marine manganese deposits from this period have been eroded or are still covered, but this seems unlikely. Their absence from the Mesoproterozoic record extends over a billion years, whereas they are present in the geologic record both before 1.8 and after 0.8 Ga.

The reason for the existence of mildly oxygenated deep oceans may well be a very small delivery rate of organic matter to the deep oceans between 1.8 and 0.8 Ga. The strongest evidence for this is the absence of phosphorites during this entire period. In the absence of significant ballasting, the transfer of organic matter and its contained PO_4^{3-} into the deep oceans must have been very minor. In addition, Fe^{2+} from hydrothermal vents would have been oxidized to Fe^{3+} and precipitated as a constituent of $Fe(OH)_3$ in the deep oceans, and would not have been available to transport PO_4^{3-} downward from the surface ocean during stage 2, as proposed above. The beds of haematitic jasper proximal and distal to the 1.74 Ga volcanogenic massive sulphide (VMS) deposits at Jerome, AZ, are one example of this process (Slack *et al.* 2005). Some of the jaspers contain haematitic

filaments 1–3 μm in diameter and 30–50 μm long that are morphologically similar to remains of Fe^{2+}-oxidizing bacteria in Ordovician and younger VMS-related jaspers. The rare earth element (REE) patterns of the jaspers contain no or small positive Ce anomalies. Another example is supplied by the 1–2 m thick bands of magnetite and/or haematite in the metamorphosed *ca* 1.2 Gyr Gamsberg VMS zinc deposit in the Namaqualand district of the northwestern Cape Province, South Africa (Rozendaal & Stumpfl 1984).

Organic matter generated in the photic zone was nearly completely recycled in the shallow oceans. Where the O_2 minimum zone intersected the sediment–water interface, euxinic areas such as the McArthur Basin in Australia tended to develop (Shen *et al.* 2002). The isotopic composition of Mo in the sediments of these basins indicates that they were major sinks for this element. Deposition of Mo^{6+} with manganese nodules was apparently less extensive than now (Anbar & Knoll 2002; Arnold *et al.* 2004). It is not clear whether this was due to the lower O_2 content of deep ocean waters or to the more widespread removal of Mo in shallow euxinic basins, or to both.

This brings us back to the reasons for the cessation of BIF deposition at *ca* 1.8 Ga. It seems unlikely that the development of a 'Canfield Ocean' was responsible for their absence in sediments between 1.8 and 0.8 Gyr. The end of BIF deposition may well have been related to a decrease in the flux of Fe^{2+} to the oceans, the subsequent elimination of nearly all Fe^{2+} from the oceans, and the beginning of a non-stratified, mildly oxidized ocean. Although this seems likely, other processes may also have contributed to create a higher oceanic oxidation state. Such an increase may then have been responsible for the oxidation of Fe^{2+}, the precipitation of $Fe(OH)_3$ in the deep oceans, and the lack of BIF deposition between 1.8 and 0.8 Ga.

5. STAGE 4: 0.85–0.54 Ga

If it is apt to describe stage 3 as boring, then stage 4 was blustery and baleful. Three, perhaps the largest three ice ages, visited the Earth (Hoffman & Schrag 2002; Hoffman in press), and these may all have been followed by unusually hot climates. On the other hand, the period can also be described as burgeoning and blossoming. Evolution proceeded apace and culminated in the appearance of animals and the biological explosion near the Cambrian–Precambrian boundary (Knoll 2005, Conway Morris 2005). The second of the major positive $\delta^{13}C$ excursions of marine carbonates occurred during this period (figures 2 and 6). This signalled the burial of excess carbon and the generation of excess O_2. The O_2 content of the atmosphere (Berner 2004) and the sulphate concentration of seawater (Horita *et al.* 2002) rose to levels that were probably not much lower than those of the present day (Canfield 2005). The sediments of the last 300 Myr of the Proterozoic contain BIFs, marine manganese deposits and evaporites. The BIFs are widespread (figure 7) and are associated with glacial deposits (Hoffman in press). Three of the four major groups of manganese deposits are also associated with
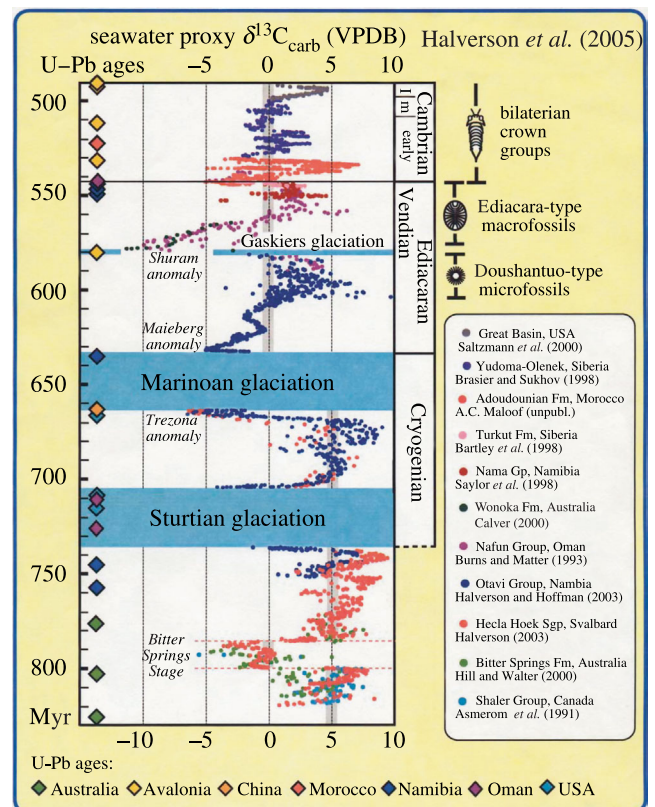

Figure 6. The isotopic composition of carbon in marine carbonates between 490 and 830 Ma (Halverson *et al.* 2005).
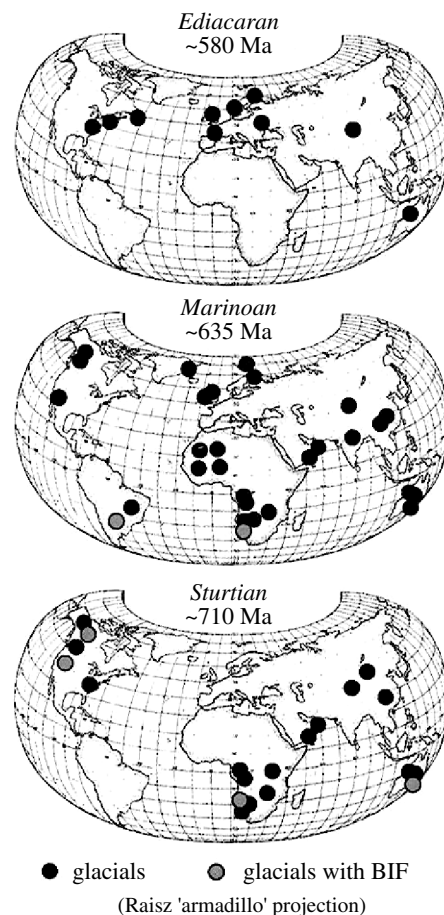

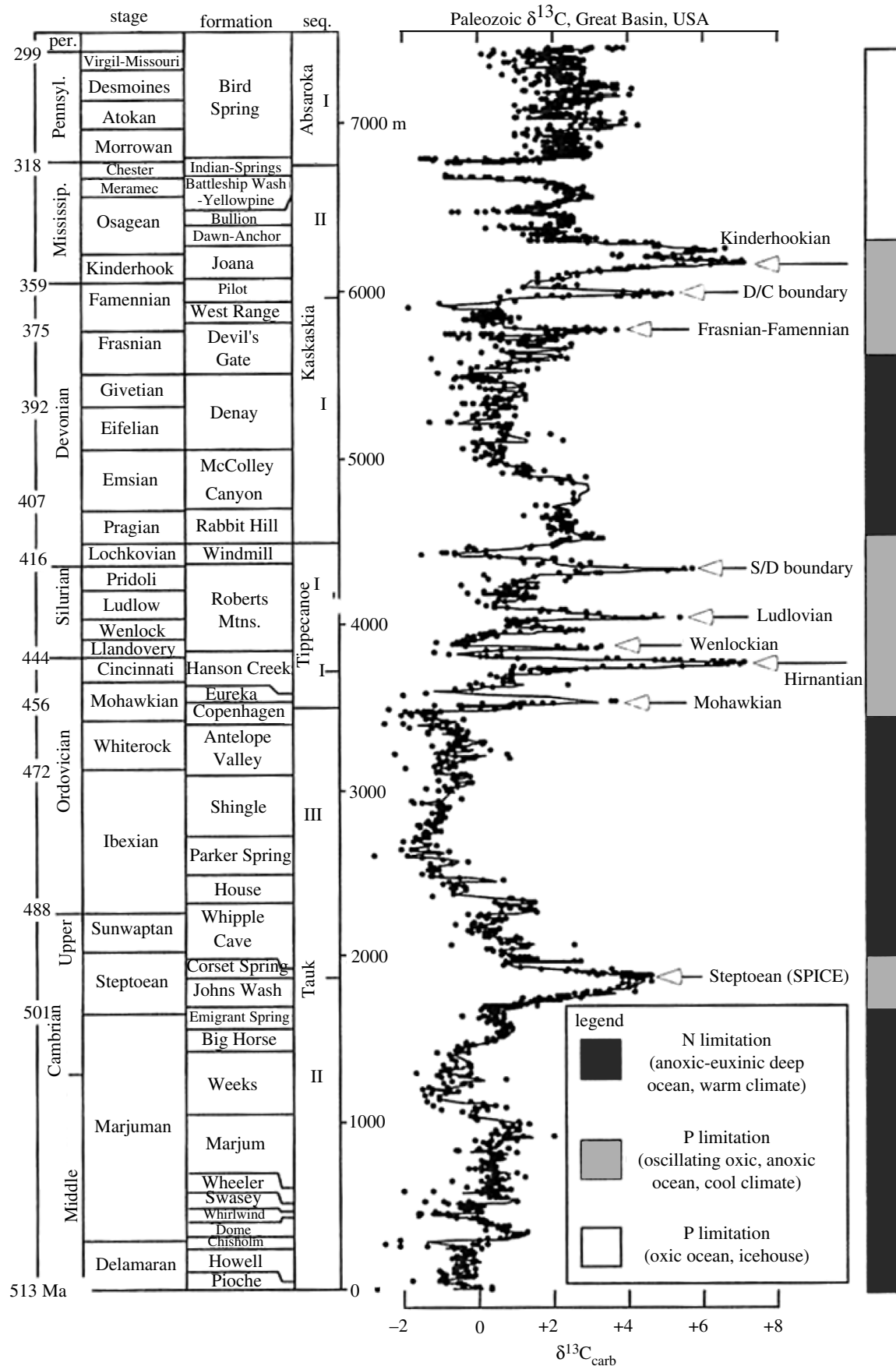Figure 7. The distribution of Neoproterozoic glacial deposits with and without BIFs (Hoffman in press).

Figure 8. Composite diagram of the $\delta^{13}C$ value of Palaeozoic carbonates of the Great Basin, USA (Saltzman 2005).

glacial deposits. Those of the Penganga Group in India are not (Roy 1997).

The Neoproterozoic is one of the most phosphorite rich periods in Earth history. Its sediments host some of

the worlds largest phosphorite deposits (Cook & Shergold 1986). The return of phosphorite deposition after a billion year hiatus is almost certainly due to the increased diversity of acritarchs and other protistan
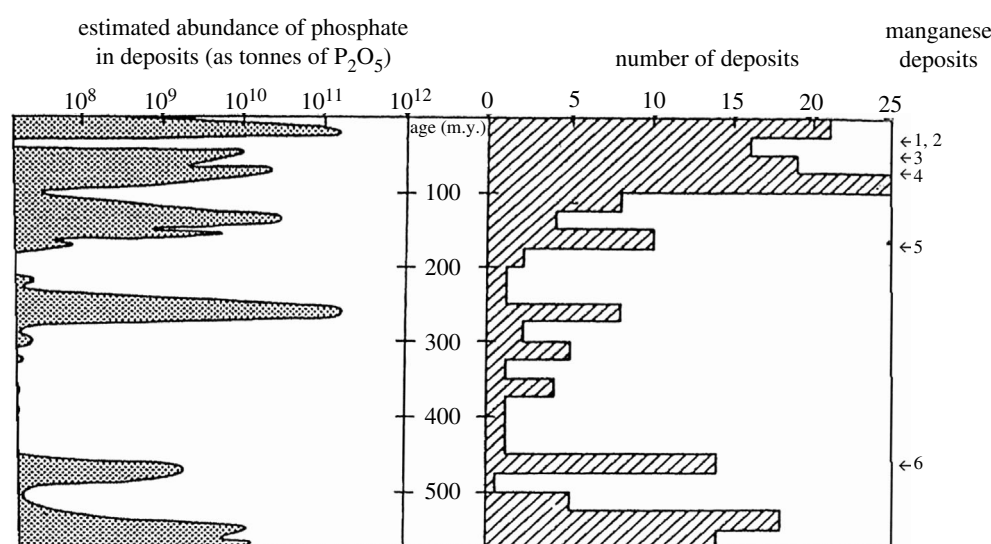
Figure 9. Estimated abundance of phosphate (expressed as metric tons P_2O_5) in phosphate deposits throughout the Phanerozoic. The fixed time interval in the histogram is 25 Myr. It should be noted that a logarithmic scale is used for P_2O_5 abundance (Cook & McElhinny 1979). At the right margin, there is a list of the large Phanerozoic marine manganese deposits (Roy 1997). The numbers identify the following deposits: 1, Nikopol, Ukraine; 2, Chiatura, Georgia; 3, Groote Eylandt, Australia; 4, Molango, Mexico; 5, Úrkút, Hungary; 6, Taojiang, China.

morphotypes (e.g. Butterfield & Rainbird 1998), whose remains sank into the deep ocean. The transport of organic matter into the deep oceans was also augmented by the development of organisms such as the vase-shaped microfossils (VSM) with tests consisting of 1 to more than 10 μm silica scales (Porter & Knoll 2000; Porter *et al.* 2003). The increased downward transport of organic matter with and without ballast was apparently sufficient to return anoxic condition to the deep oceans for at least parts of stage 4. The close association of BIFs and many of the manganese deposits with glacial deposits is striking. Anoxia may have been particularly pronounced during the three major Neoproterozoic glacial periods. The circulation of deep water during these periods may have been particularly intense, and this may have contributed to the close temporal association of BIFs and manganese deposits with the three ice ages.

6. STAGE 5: THE LAST 0.54 Gyr

The level of atmospheric O_2 has probably varied significantly during the Phanerozoic. Improvements in computation schemes from BLAG to SUPERBLAG to GEOCARB to BROD have increased the believability of the results, but additional direct confirmation of the calculated O_2 levels is still needed. The most recent computations (Berner 2004) indicate that atmospheric O_2 may have attained values as high as 0.35 atm during the Permo–Carboniferous (figure 10). This result agrees with the isotopic composition of Permo–Carboniferous fossil plants, the effect of O_2 on photosynthetic carbon isotope fractionation during plant growth, and the development of giant insects during this period of Earth history (Graham *et al.* 1995; Dudley 1998; Lane 2002). The principal cause of the proposed high O_2 levels was probably the evolution of the large vascular land plants that brought about increased O_2 production and increased O_2 levels due to the enhanced global burial of microbially resistant,

lignin-rich organic matter during the Permo–Carboniferous (Berner 2004). The surface oceans must have been oxygenated throughout the Phanerozoic, but the oxidation state of the deeper oceans has fluctuated widely. The Cretaceous oceanic anoxic events (OAEs) are particularly well documented (Arthur *et al.* 1985). They coincided with rising sea level and warm, generally stably stratified oceans. The mechanisms that induced widespread deposition of organic carbon-rich sediments involved some combination of elevated biologic productivity and enhanced organic carbon preservation under oxygen-depleted water masses (Arthur 2005).

As shown in figure 8, the $\delta^{13}C$ data for Palaeozoic carbonates of the Great Basin, USA is extremely 'spikey' (Saltzman 2005), suggesting that between 299 and 513 Myr ago (Ma) the rate of organic carbon burial varied rapidly in this part of the oceans and possibly in the world ocean. Phosphorites are common in the Phanerozoic, but some periods within this era are much richer in phosphorites than others, as shown in figure 9. The correlation between the timing of large phosphorites and manganese deposits is not striking; neither is the correlation between the timing of the large OAEs and that of the large manganese deposits. The Cretaceous anoxic event OAE 1 peaked near the Albian–Aptian boundary, *ca* 115 Ma, whereas the Groote Eylandt giant manganese deposit formed close to 100 Ma in the Late Albian to Early Cenomanian. On the other hand, OAE 2 and the Imini–Tasdremi manganese deposits both occurred *ca* 93 Ma, close to the Cenomanian–Turonian boundary. The lower Oligocene manganese deposits at Nikopol in the Ukraine and at Chiatura in Georgia were deposited during what was no more than a mild positive $\delta^{13}C$ carbonate excursion at 35 Ma (Miller & Fairbanks 1985). These deposits seem to be related to local or regional rather than to oceanic periods of oxygen depletion (Frakes & Bolton 1992). The limited correlation between the occurrence of OAEs,
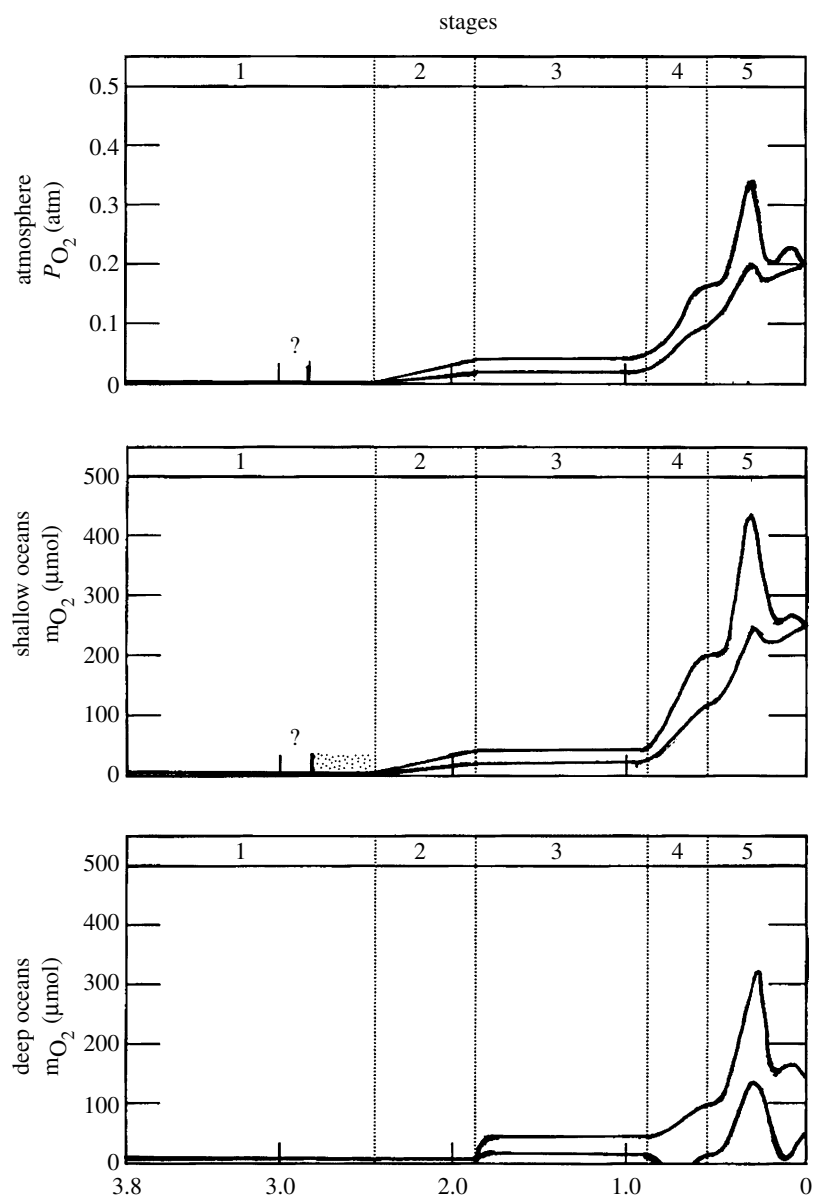
Figure 10. Estimated evolution of atmospheric P_{O_2} and the concentration of O_2 in the shallow and deep oceans.

phosphorites and marine manganese deposits surely reflects the complexity of their development and the incomplete overlap between the factors that control their formation (Roy 1992, 1997).

7. SUMMARY AND CONCLUSIONS

Figure 10 summarizes the proposed evolution of the atmospheric pressure of O_2 and the concentration of O_2 in the shallow and deep oceans during the last 3.8 Gyr of Earth history. During stage 1, from 3.85 to 2.45 Ga, atmospheric O_2 was almost certainly less than a few parts per million, except possibly during the period between 3.0 and 2.8 Ga. The oceans were almost certainly anoxic except perhaps in oxygen oases within the photic zone. Such oases may have been present during the last 200–300 Ma of the Archaean. They probably existed earlier if cyanobacteria evolved before 2.8 Ga. The deep oceans were almost certainly anoxic during all of stage 1.

Atmospheric O_2 rose during the GOE between *ca* 2.4 and 2.0 Ga. Its value at 2.0 Ga is still poorly defined. It was probably higher than 10% PAL (0.02 atm) but significantly lower than 1 PAL (0.2 atm). The concentration of O_2 in much of the shallow oceans was probably close to equilibrium with atmospheric O_2 levels, but the deep oceans were almost certainly anoxic during much, if not all of stage 2 (2.45–1.85 Ga).

Stage 3 (1.85–0.85 Ga) seems to have been rather static. There is no evidence for large changes in the O_2 content of the atmosphere or in the shallow oceans. In some areas, the O_2 minimum zone must, however, have been anoxic or euxinic as indicated, for instance, by the highly reduced *ca* 1.5 Gyr sediments of the McArthur Basin, Australia (Shen *et al.* 2002). Such spatial heterogeneities in the O_2 content of the shallow ocean are not represented in figure 10. The deep oceans appear to have been mildly oxygenated during much, if not all of stage 3.

Stage 4 (0.85–0.54 Ga) saw a further rise in the level of atmospheric O_2 and in the concentration of O_2 in the shallow oceans. However, anoxic and euxinic conditions prevailed in the shallow oceans at least locally, as on the Yangtze Platform at the end of the

Neoproterozoic (Mao *et al.* 2002). Deep ocean water may have been anoxic during most of this stage.

During stage 5 (the last 0.54 Gyr) the level of atmospheric O_2 may have passed through a maximum during the Carboniferous before returning to 0.2 atm, perhaps along a rather irregular path. Shallow ocean water probably followed the same pattern. Deep ocean water apparently had a rather complex history, which included low-O_2 periods such as those during the Cretaceous OAEs. Figure 10 is probably an improvement over previous attempts to represent the oxygenation of the atmosphere and oceans, but it is no more than a step along the long road ahead. The pattern proposed for the oxygenation of the atmosphere and oceans is probably qualitatively correct, but its quantitative aspects should be regarded with a significant degree of scepticism.

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