

Figure 9.8 Sulfur isotope compositions of marine barites, BaSO_4 , throughout the Cretaceous and the Tertiary (Paytan *et al.*, 2004). The shaded bars represent OAEs (Oceanic Anoxic Events). The sharp changes in $\delta^{34}\text{S}$ reflect strong variations in the burial rates of sedimentary pyrite and global changes in the redox system of the ocean.

Paytan *et al.* (2004) analyzed the sulfur isotope compositions of marine barites (BaSO_4), a mineral oversaturated in the surface ocean but undersaturated at depth. As for most sulfates, sulfur isotope fractionation upon barite precipitation is very small. The obvious advantages of this mineral over more common evaporites are its clearly marine origin and its shown immunity to diagenetic reworking. By about 125 Ma, the $\delta^{34}\text{S}$ decreased by 4 per mil, oscillated up and down for most of the Cretaceous and the Paleocene, and sharply increased to modern marine-sulfate values at about 55 Ma (22‰); it has stayed nearly constant ever since. There is probably no correlation with OAEs. Although such large variations must reflect variable burial rates of sedimentary pyrite, the fast rate of change, in particular at 55 Ma, suggests either very large sulfur fluxes or fairly low sulfate concentrations in the ocean.

9.2 The rise of atmospheric oxygen

9.2.1 The 2.1 Ga crisis

Charles Lyell's uniformitarianism states that "the present is key to the past," which asserts that fundamentally the same geological processes operate today as in the distant past. In modern language, we could simply state that the Earth has long since reached some form of steady state. Although this view proved helpful to elucidate some geological observations, the memory of the first geological times did not just disappear overnight. If there is a

domain in which this principle is worth questioning, it is for the study of the distant past for which observations bear testimony that many geological phenomena were different in the Archean and the Proterozoic. Probably one of the changes that so uniquely affected the surface of the Earth and allowed terrestrial life to thrive was the increase of atmospheric oxygen pressure. Overall, the modern chain of events is as follows: (i) photosynthesis dissociates carbon dioxide to produce reduced biological carbon, (ii) burial and subduction of biological matter remove reduced carbon to the mantle, and (iii) the residual oxygen builds up in the atmosphere. To this should be added the dissociation of atmospheric water by solar ultraviolet radiation in the upper atmosphere: loss of hydrogen, too light to be held back by terrestrial gravitation, contributes to the increase of atmospheric oxygen. We will return to this process in [Chapter 12](#). The modern biological processes by which oxygen is released into the atmosphere probably appeared with cyanobacteria (now fossilized as stromatolites) before 3.0 Ga ago. The atmosphere before that time was characterized by a low level of oxygen as attested to by three observations:

1. Banded iron formations (BIF) are known from Archean terranes of all continents. The archetypal 2.5 Ga old Hamersley formation in Australia is one of the largest iron deposits in the world. These are sediments made of mm-thick laminae of quartz and magnetite Fe_3O_4 , which can be traced over very long distances and record some distinctive astronomical cycles. Most of these rocks are devoid of detrital minerals, which also hints at a pelagic depositional environment. As $\text{Fe}(\text{OH})_3$ is essentially insoluble in oxic waters, it has been suggested that the deep ocean was rich in soluble Fe^{2+} and silica, most likely introduced by submarine geothermal activity, and that locally oxidizing conditions, possibly biologically mediated, would lead to massive precipitation of iron hydroxides and silica (Holland, 1973). Banded iron formations are rare after 1.8 Ga but make a remarkable comeback in the late Proterozoic ($\approx 600\text{--}800$ Ma).
2. Paleosols, 2.2 to 2.4 Ga old, which are rich in chlorite, sericite (a mica similar to muscovite produced by weathering), and quartz are known in Canada and South Africa. They show a characteristic loss of iron unknown in modern soils, which demonstrates that groundwater was oxygen depleted and that Fe was in its soluble ferrous form.
3. Minerals prone to atmospheric oxidation and subsequent dissolution, most conspicuously uraninite UO_2 , are essentially absent from detrital rocks. Large uraninite deposits, however, are common in Archean rocks such as the 3.0-Ga-old Witwatersrand conglomerates (South Africa). They demonstrate that the atmospheric oxygen level must have been low.

For reasons which still remain to be explained, these features vanished by 2.1–1.9 Ga; this is broadly interpreted as indicating an abrupt rise in atmospheric oxygen pressure. This idea recently received strong support from sulfur isotope analyses in Archean sediments. Mass fractionation of the 32, 33, 34, and 36 isotopes of sulfur in recent rocks back to 2.1 Ga is perfectly mass-dependent, which means that, for example, variations of the $^{34}\text{S}/^{32}\text{S}$ ratio are twice the variations of $^{33}\text{S}/^{32}\text{S}$. In other words, the quantity $\Delta^{33}\text{S}$ calculated as

$$\Delta^{33}\text{S} = \delta^{33}\text{S} - 0.5 \delta^{34}\text{S} \quad (9.1)$$

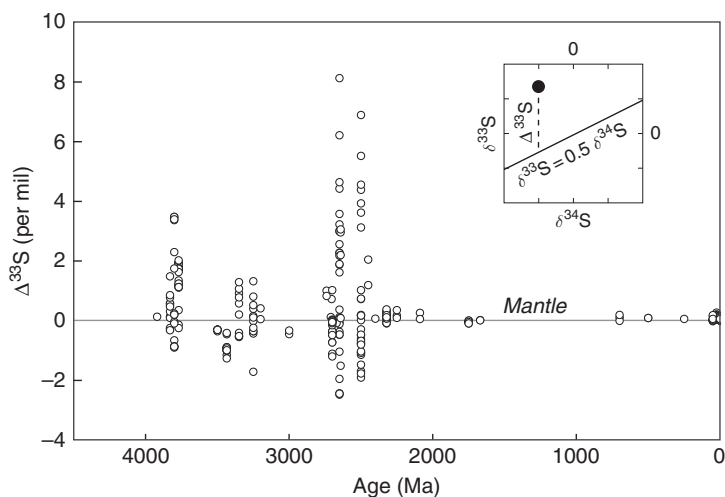


Figure 9.9

Evidence for mass-independent isotope fractionation of sulfur isotopes in sediments (Farquhar *et al.*, 2000). The value of $\Delta^{33}\text{S} = \delta^{33}\text{S} - 0.5 \delta^{34}\text{S}$ is a measure of the deviation from the normal mass-dependent isotope fractionation behavior. Mass-independent isotope fractionations prior to ≈ 2.45 Ga indicate photolysis of atmospheric SO_2 by ultraviolet radiation and disproportionation of sulfur compounds into reduced and oxidized species. After that time, the rise of atmospheric P_{O_2} led to the formation of the ozone layer at the base of the stratosphere and protected SO_2 from UV photolysis.

is very near zero. It was shown by Farquhar *et al.* (2000) (Fig. 9.9) that prior to 2.45 Ga, the S isotopic abundances deviated very substantially from the mass-dependent conditions or, in other words, that $\Delta^{33}\text{S}$ was very different from zero. The interpretation calls for different sulfur and oxygen cycles over geological times. In the modern atmosphere, ultraviolet radiation does not reach the lower atmosphere: it is absorbed by the ozone layer located in the stratosphere at ≈ 25 km above the ground before SO_2 pressure becomes significant. Modern atmospheric SO_2 is therefore oxidized to sulfate and is washed down with precipitation, all the reactions being characterized by regular mass-dependent isotope fractionations. In contrast, prior to 2.45 Ga, the oxygen atmospheric pressure was too low to produce a significant ozone layer. As shown by experiments, mass-independent isotope fractionation results from the breakdown of SO_2 by ultraviolet radiation (UV photolysis) and its subsequent recombination as reduced and oxidized compounds. The UV photolysis of Archean atmospheric SO_2 therefore produced a variety of compounds that do not follow a mass-dependent fractionation behavior, hence making non-zero $\Delta^{33}\text{S}$ values a strong marker of the ozone layer and therefore of the total oxygen pressure. It was recently found that $\Delta^{36}\text{S}$ correlates with $\Delta^{33}\text{S}$, which makes the case of mass-independent fractionation even stronger.

The isotopic record of sulfur and nitrogen provides additional clues about the evolution of the pre-Phanerozoic atmosphere:

1. Average values of sulfur isotopes of sedimentary pyrite show mantle-like $\delta^{34}\text{S}$ values (~ 0) from the oldest samples well into the late Proterozoic (≈ 600 Ma). This reflects the

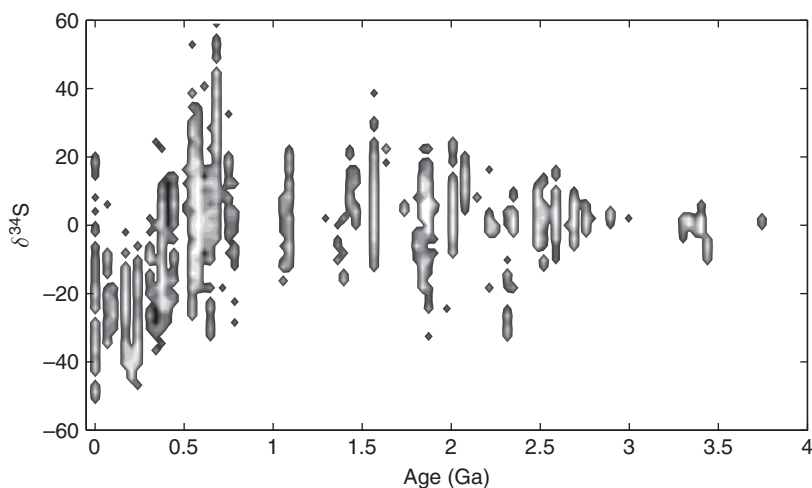


Figure 9.10 Evolution of the $\delta^{34}\text{S}$ values in pyrites from sediments (compilation courtesy of Don Canfield) over the geological ages. The values remain close to zero until ≈ 600 Ma, which suggests that until then the bulk of oceanic sulfur was dominantly in the form of sulfide. The rise of P_{O_2} in the late Proterozoic shifted sulfur speciation in seawater from sulfide to sulfate, yet the incoming fluxes maintained the $\delta^{34}\text{S}$ of this reservoir at mantle values. Sulfur isotopes in < 600 -Ma-old pyrite are substantially fractionated with respect to marine sulfate (Canfield, 2004).

fact that oceanic sulfur is dominantly of mantle origin (volcanic eruptions, hydrothermal activity). Because sulfur isotopes fractionate between sulfates and sulfides by about 20 per mil (Chapter 3), this record indicates the lack of competing reservoirs of sulfate and sulfur (Fig. 9.10) prior to the Phanerozoic. This suggests that, prior to the Phanerozoic, most of the oceanic sulfur was not present as sulfate but was dominantly in the form of sulfide delivered by magmas and hydrothermal activity and went to the sediments with no isotopic fractionation.

2. The nitrogen isotopes of sedimentary kerogen show a strong increase in $\delta^{15}\text{N}$ values from slightly negative mantle-like values prior to 2.7 Ga to positive values (up to + 10) over the late Archean, Precambrian, and Proterozoic. These data can be interpreted as indicating that nitrification and denitrification did not operate in the early Archean the way they operate today.
3. In contrast, the $\delta^{13}\text{C}$ values of ancient kerogen are in the range of their modern counterparts.

9.2.2 The Snowball Earth and the emergence of Metazoans

A second major oxygen crisis leading to another major increase in atmospheric P_{O_2} took place during the Late Proterozoic. The BIFs that had disappeared from the surface of the Earth after 1.85 Ga returned on different continents between 800 and 600 Ma, at localities such as Rapitan, Canada, and Urucum, Brazil, and give the first indication that

the atmospheric system was severely tipped out of balance with the return of oxygen deficiency. These layers are overlain by rather poorly dated Neoproterozoic glacial deposits. These cold spells are known as the Sturtian (≈ 730 Ma), Marinoan (≈ 640 Ma), and Gaskiers (≈ 590 Ma) glaciations and are of worldwide extension. The deposits are characterized by laminated layers of fine clays and siltstones, known as diamictites, in which are embedded large clastic fragments; some of them are angular, others rounded and decorated with striations. These rocks are identified beyond doubt as glacial deposits. Above the diamictites occur discordant massive layers of dolomite-rich carbonates, known as the cap-carbonates. Associated with these dolostones, or on top of them, phosphorites are commonly found, which contain wonderfully preserved multicellular organisms, e.g. in Doushantuo in China. These are the first incontrovertible Metazoans, also endowed with body symmetry and motility. With these layers began the Ediacaran radiation and the advent of multicellular life. Although its members were unequally successful with respect to their descendance, the Ediacaran fauna was incredibly rich and seemed to bloom very rapidly in the aftermath of the Gaskiers event.

Although many of these geological observations were made up to 40 years ago, it is only during the last decade that we have been able to start making sense of them. In the late 1980s, paleomagnetic data on some of the iron-rich glacial layers showed that glaciers reached sea level even under tropical and even equatorial latitudes. Such a surprising observation is unlikely to reflect a tilted terrestrial spin axis, because the equatorial bulge of our planet, like the bulge of a top, is stabilized near its current position by the attraction of the Moon. The term of Snowball Earth was coined in 1992 by Joe Kirschvink to reflect the extensive glaciation of the planet to very low latitudes, possibly sealing off most of the ocean surface from sunlight. With extensive ice blanketing, increased reflection of the solar radiation cooled the Earth even more (in jargon, the albedo became very high), and if it were not for the greenhouse effect, the Earth could have remained frozen for eons. These glacial bouts probably lasted millions of years, long enough for most previous life forms to become extinct. It is believed that volcanic emissions of CO_2 saved our planet from the ice doom: by progressively building up in the atmosphere, CO_2 captured more and more of the solar radiation, surface temperature increased and the ice quickly melted. Weathering under high atmospheric P_{CO_2} acting on a barren crust triggered an alkalinity rush to the ocean and led to the massive sedimentation of carbonates.

Carbon isotopic compositions of the cap-carbonates were found to be quite informative. The $\delta^{13}\text{C}$ values nose-dive by more than 15 per mil over a very narrow sedimentary interval (Fig. 9.11). One of the early interpretations appealed to the nearly complete cessation of photosynthetic activity and to the demise of the biomass as a result of the ice blocking sunlight. Carbon would have the isotopic composition of mantle inputs, i.e. ≈ -7 per mil. The discovery of $\delta^{13}\text{C}$ lower than mantle values rather suggests that an oceanic reservoir of isotopic light carbon was being oxidized. Destabilization of gas hydrates has been suggested to provide enough carbon with very negative $\delta^{13}\text{C}$ values, but such speculation still remains to be tested. Regardless of which process caused the carbon isotope shift, it left the terrestrial ocean and the atmosphere much more oxidized than in the pre-glacial times. It is believed that access to higher P_{O_2} allowed multicellular organisms to increase their metabolism and their motility so as to lead the way to the thriving Phanerozoic life.

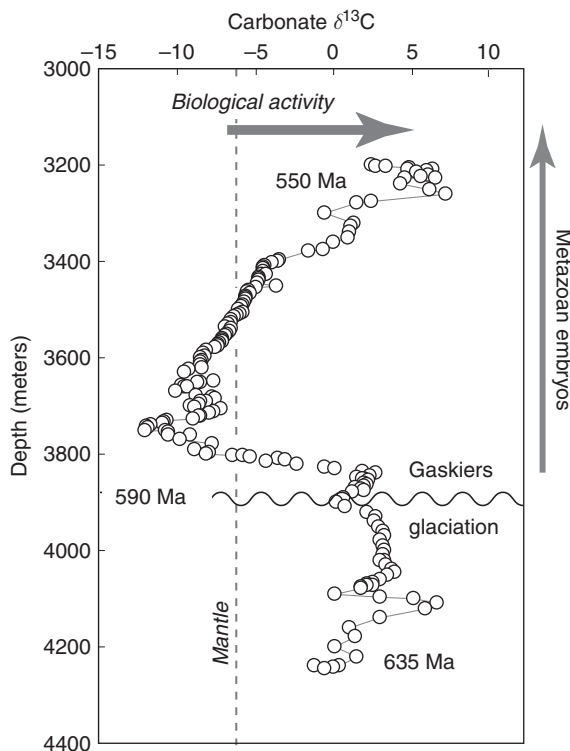


Figure 9.11

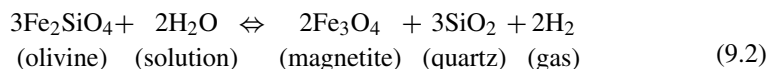
Negative excursion of $\delta^{13}\text{C}$ values after the Gaskiers glaciation in Oman (data from Fike *et al.*, 2006). The sediments are discordant over the Marinoan glacial deposits (≈ 635 Ma). The Gieskes glaciation (≈ 590 Ma) locally misses diamictites but can be recognized with the cap-carbonates in the middle of the section. The $\delta^{13}\text{C}$ values lower than those of the mantle indicate that a carbon reservoir rich in ^{12}C , possibly gas hydrates, was being oxidized. Oxidation coincides with the radiation of multicellular organisms (Metazoan).

As previously alluded to, oxidation of the ocean also resulted in the oxidation of oceanic sulfur into sulfate, which clearly shows in the burial of pyrite with negative $\delta^{34}\text{S}$ values (Fig. 9.10). The reason why such a massive rise of oxygen in the atmosphere and the ocean took place remains so far poorly understood.

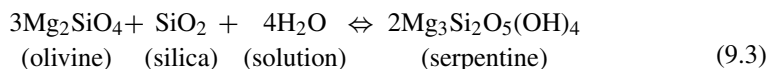
9.3 The geochemical environment of the origin of life

In a famous experiment, Miller and Urey (1959) triggered electrical discharges in a balloon containing ammonia, methane, and liquid water. After a few hours, the solution became very rich in amino acids, which are the building blocks of proteins. After first being hailed as a breakthrough illuminating our understanding of the origin of life, this experiment was heavily criticized for misrepresenting the early Earth atmosphere, which, critics said, was

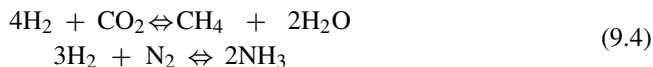
largely dominated by CO₂ and N₂, and therefore too oxidizing to allow for methane and ammonia to be stable. Miller and Urey's work fell into near oblivion for decades. This criticism incorrectly assumes that all atmospheric gases would be well mixed and everywhere in equilibrium. The actual situation is very different since, although the atmosphere was dominated by carbon dioxide and nitrogen, along mid-ocean ridges, hydrogen, methane, and ammonia were produced in abundance by serpentinization reactions. Production of serpentine results from the combination of two reactions between water and olivine, a major mineral of basaltic rocks and a solid solution of Fe and Mg components. First, iron from the Fe-olivine component (fayalite) is oxidized by water to produce silica, magnetite, and hydrogen:



Second, silica liberated in this reaction reacts with water and Mg-olivine to form serpentine:



Hydrogen liberated by serpentinization reacts with CO₂ and N₂ to give methane and ammonia:



The Mid-Atlantic Ridge today shows how this may have happened: reaction of water with hot igneous material at temperatures < 600 °C produces hydrogen, which in turn reacts with CO₂ and N₂ to produce methane and ammonia, respectively. Whether hydrogen was lost from the atmosphere and methane and ammonia oxidized by atmospheric gases is not relevant to such a dynamic system: the source of reducing gas was enormous and steady, and favorable geological sites must have been ubiquitous at the bottom of the ocean. The floor of mid-ocean ridges, and also the ocean floor on top of the magma ocean in the early stages of the Earth's evolution, must have represented major production sites for methane and ammonia. The lack of an ozone layer probably allowed solar ultraviolet radiation to reach the surface of the Earth. Irradiation of the surface of the ocean by solar UV wherever deep oceanic upwellings would degas dissolved methane and ammonia into the atmosphere provided natural conditions for the formation of proteins and the emergence of life.

How early life could resist oxidizing conditions and find nutrients to keep going is another issue. Today, the main terrestrial productivity is concentrated at the surface of the oceans. The most important nutrients, nitrates and phosphates, are, however, brought to the sea by the rivers. Mid-ocean ridges produce no nitrate, but we do not know which nitrogen source was used by early organisms, presumably dissolved nitrogen or ammonia. In contrast, modern ridges are a net sink for phosphorus, and if rivers were to dry out overnight, this element so critical for life would rapidly disappear from the ocean and, with it, oceanic productivity. It is likely that, at some point, the emergence of continents,

another hallmark of our planet with respect to its neighbors, started carrying renewable resources to the ocean for life to grow stronger and stronger. A water world may not have bred life with the same efficiency as our dual world of oceans and continents which is so unlike other planets. The early emergence of plate tectonics may have been instrumental in defining the conditions for long-lasting biological activity.

Continents may have been paid back for the help they provided life. We have seen and will discuss again in the next chapter that biological activity strongly interferes with diagenesis. It actually increases the efficiency of erosion, helps process more detrital sediments, and in the long run increases the proportion of hydrous material, such as clay minerals, which are much more prone to melting than their anhydrous equivalents. Biological activity may therefore have strengthened the production of orogenic magmas and eventually the amount of continental crust produced. The feedback loop between plate tectonics and the emergence of life is likely to have endowed our planet with the main features of its biogeochemical dynamics.

Exercises

1. In the range 0–20 °C, the vapor pressure of water at saturation $P_{\text{H}_2\text{O}}^{\text{sat}}$ changes with temperature T as $\ln P_{\text{H}_2\text{O}}^{\text{sat}} = -5365.37 T^{-1} + 26.06$, where pressure is in Pa and temperature in K. Assume that atmospheric water vapor forms above the ocean at low latitudes at 15 °C and calculate a relationship between the residual fraction f of water vapor (Table 3.2). Assuming that $1000 \ln \alpha^{18\text{O}} = 1.0779 \cdot 10^6 T^{-2} - 2.796$, infer a relationship between the $\delta^{18\text{O}}$ values of rain water and their precipitation temperature. Find appropriate linear approximations to all these equations.
2. Use the Mg/Ca ratios from Table 9.1 to calculate the sea-surface temperature of the Eastern Tropical Pacific over the last glacial cycle. Use $T(^{\circ}\text{C}) = -0.667x^2 + 7.76x + 8.73$ with $x = \text{Mg/Ca}$. Which cycles can you identify?

Table 9.1 Mg/Ca in *Globigerinoides ruber* from the Eastern Tropical Pacific for different ^{14}C calendar ages (Lea, 2004)

$t(\text{y})$	Mg/Ca	$t(\text{y})$	Mg/Ca	$t(\text{y})$	Mg/Ca	$t(\text{y})$	Mg/Ca
1800	2.99	27800	2.32	73 500	2.61	116 400	2.86
4400	3.07	32200	2.59	78 600	2.79	121 500	3.20
6900	3.16	39800	2.56	83 600	2.78	125 400	3.53
9500	3.06	44100	2.55	88 700	2.55	131 000	3.19
12 000	2.84	50900	2.53	93 700	2.63	134 100	2.79
14 300	2.72	55000	2.63	98 800	2.87	138 000	2.54
16 500	2.52	58600	2.53	101 300	2.95	141 400	2.51
18 800	2.38	65700	2.40	106 300	2.93	144 900	2.52
23 300	2.44	69200	2.45	111 400	2.78	148 400	2.63

3. Use data from Appendices A and F to compute a modern value of the sulfate residence time in the ocean. Draw a sulfur cycle involving erosion, rivers, the ocean, ridges, and the burial of sedimentary pyrite. Examine Fig 9.8 and propose possible interpretations to the fast $\delta^{34}\text{S}$ oscillations in the Cretaceous and the Paleocene.

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