EARTH SYSTEM SHIFT 12-1 The Great Oxidation Event

There is abundant evidence that until about 2.3 billion years ago, chemical sinks were soaking up oxygen so effectively that the concentration of oxygen in the atmosphere remained at only 1 or 2 percent of its modern level. Some of this evidence comes in the form of iron minerals in early Proterozoic rocks. About 2.3 billion years ago a dramatic change occurred. It is known as the Great Oxidation Event.

Recall from Chapter 11 that in the modern world, the iron sulfide mineral pyrite (FeS_2) disintegrates readily by oxidation when exposed to the atmosphere. Nonetheless, pyrite is relatively common in Archean sedimentary rocks. In contrast, it is rare as a detrital component in sandstones deposited after about 2.3 billion years ago. Highly oxidized redbeds older than 2.3 billion years are also rare. This pattern suggests that atmospheric oxygen had by then risen above its Archean level.

The first economically valuable phosphate deposits and the first extensive sulfate evaporite deposits formed at the end of the Great Oxidation Event. Both phosphates and sulfates contain oxygen and require a substantial concentration of oxygen in natural waters to precipitate from them.

Precambrian soils, though rarely preserved, offer a more detailed picture of change in atmospheric oxygen concentrations. These thin units reveal the chemical nature of weathering during the time when the soils formed. In moist soils, iron exposed to abundant oxygen precipitates as hematite and other highly oxidized minerals that are relatively insoluble in water. In contrast, when little oxygen is present, iron that weathers from rocks remains in solution and is carried away by moving water. It is striking that soils that formed on basaltic rocks before about 1.9 billion years ago lost nearly all of their abundant iron. Thus there was still not enough oxygen in the atmosphere to precipitate the iron in these soils as highly oxidized minerals. In contrast, all Proterozoic soils younger than 1.9 billion years accumulated highly oxidized iron. The heavy oxidation of one well-preserved soil that formed 1.9 billion years ago in South Africa indicates that by this time atmospheric oxygen had built up to at least 15 percent of its present level.

FIGURE 1 **Banded iron formations rarely formed after about 1.85 billion years ago.** This weakly metamorphosed banded iron formation in northern Michigan is about 1.875 billion years old. Banded iron formations are among the oldest known rocks on Earth and are quite common in Archean terranes. Most of them accumulated between about 3.5 billion and 1.85 billion years ago. The term *banded iron formation* refers to a bedding configuration in which layers of chert, often contaminated by iron that gives them a red or reddish brown color, alternate with layers of other minerals that are richer in iron than the chert. The iron in these formations may occur in a variety of minerals, and in many cases the mineralogy of the iron has changed over time in ways that cannot be reconstructed. Banded iron formations account for most of the iron ore mined in the world today. Those with great economic value contain iron in the form of magnetite (Fe_3O_4), whose oxygen-to-iron ratio is lower than that of hematite (Fe_2O_3), but most of these rocks contain both magnetite and hematite.

Most banded iron formations accumulated in offshore waters, sometimes in association with turbidites. Some, on the other hand, accumulated in relatively shallow seas. Both the iron and the silica in these sediments appear to have come mainly from hot, watery (hydrothermal) emissions from the seafloor associated with igneous activity along rifting zones. The kind of layer that was deposited at any time probably depended on the chemical composition of nearby watery emissions. The transport of iron in solution indicates that deep and even moderately deep waters of the ocean were poorly supplied with oxygen. When iron-rich waters moved into waters containing more oxygen, the iron precipitated as iron oxide. When more silica than iron was emitted from hydrothermal vents, chert was deposited on top of an iron oxide mineral. Banded iron formations virtually ceased to form about 1.85 billion years ago, perhaps partly because the concentration of oxygen built up in the waters of the deep ocean, reflecting a buildup of oxygen in Earth's atmosphere, but perhaps also partly because hydrothermal activity in the deep sea declined. (Bruce Simonson, Oberlin College.)

Presumably part of the reason for the buildup of atmospheric oxygen about 2 billion years ago was that chemical sinks for oxygen, including reduced iron compounds, were filling up. As they did so, more of the oxygen produced by photosynthesis accumulated in the atmosphere. In addition, however, a large amount of organic carbon was apparently buried in marine sediments. Oxygen that would have been used up in the decomposition of this organic matter was left to accumulate in the atmosphere (see Figure 10-6). The evidence for this burial of organic carbon is a marked shift toward heavier carbon isotope ratios in limestones throughout the world between about 2.2 billion and 2.0 billion years ago. Recall that the burial of large volumes of organic carbon, which is isotopically light, leaves isotopically heavy carbon behind in the ocean. This heavy carbon ends up in limestones that are precipitated from the seawater (see Figures 10-11 and 10-14).

The buildup of atmospheric oxygen early in Proterozoic time had major ramifications for life on Earth, setting the stage for animals to evolve.

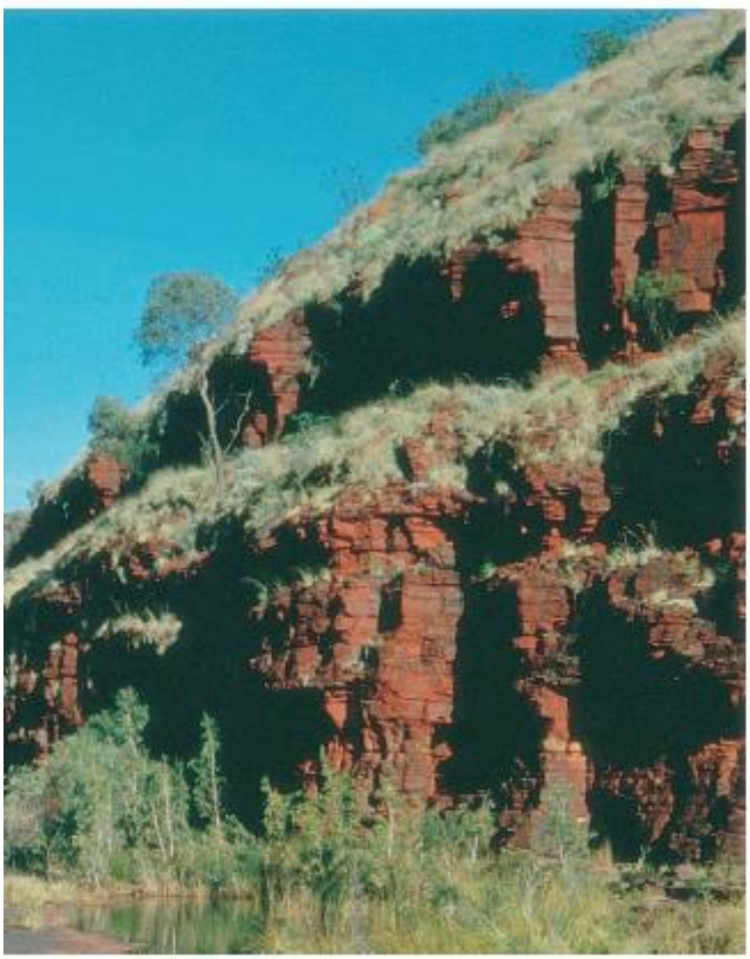

FIGURE 2 **Red beds are seldom found in terranes older than 2.3 billion years.** In other words, their pattern is the opposite of that displayed by banded iron formations. These highly oxidized iron-rich sediments are in the Proterozoic Hamersley Group in Western Australia. Hematite, a highly oxidized iron mineral, gives red beds their color. Often the hematite found in red beds has formed secondarily by oxidation of other iron minerals that accumulated with the sediments. Oxygen has been plentiful in Earth's atmosphere during Phanerozoic time, so this secondary oxidation has often occurred within a few millions or tens of millions of years after the sediments were deposited. It would appear that oxidation of this type did not occur early in Earth's history. (Cornelius Klein, The University of New Mexico.)

Stromatolites

Archean rocks are often rich in minerals, and Archean regions have been well explored geologically for economic reasons. The Pilbara region of Northwest Australia is a remote and inhospitable area that originally attracted geological attention because it is rich in the mineral barite. It is now famous for more academic reasons.

Pilbara rocks include the Warrawoona Series, dated to about 3300 to 3550 Ma. The Warrawoona rocks are mainly volcanic lavas erupted in shallow water, or nearby on shore, but there are sedimentary rocks too. The sediments include storm-disturbed mudflakes, wave-washed sands, and minerals formed by evaporation in very shallow pools. The rocks have not been tilted, folded, or heated very much, and the environment can be reconstructed accurately. The rocks formed along shorelines that we can interpret clearly because we can match them to modern environments.

The Warrawoona rocks contain structures called **stromatolites**, which are low mounds or domes of finely laminated sediment (Fig. 2.8). We know what stromatolites are because they are still forming today in a few places. Thus we can study the living forms to try to understand the fossil structures (Fig. 2.9).

Stromatolites are formed by mat-like masses of abundant microbes, usually including photosynthetic cyanobacteria. Stromatolites live today in Shark Bay, Western Australia, in warm salty waters in long shallow inlets along a desert coast (Fig. 2.10). They form from the highest tide level down to subtidal levels, but the higher ones close to shore have been better studied (sea snakes, not sharks, are the problem).

The cyanobacteria that grow and photosynthesize in Shark Bay so luxuriantly thrive in water that is too salty for grazing animals such as snails and sea urchins that would otherwise eat them. Like most bacteria, they secrete slime, and can also move a little in a gliding motion. Sediment thrown up in the waves may stick to the slime and cover up some of the bacteria. But they quickly slide and grow through the sediment back into the light, trapping sediment as they do so. As the cycle repeats itself, sediment is built up under the growing mats. Eventually the mats grow as high as the highest tide, but cannot grow higher without becoming too hot and dry. Some mats harden because the photosynthetic activity of the bacteria helps carbonate to precipitate from seawater, binding the sediment into a rocklike consistency that resists wave action (Fig. 2.11). However, sediment stabilization in stromatolites today works best in the light. Stromatolites placed experimentally in the dark lose stability (Paterson et al. 2008). This implies that all stromatolites, ancient and modern, formed and built rock-like trace fossils through photosynthesis.

Some cyanobacterial mats are so dense that light may penetrate only 1 mm. The topmost layer of cyanobacteria absorbs about 95% of the blue and green light, but just underneath is a zone where light is dimmer but exposure to UV radiation and heat is also less. Green and purple bacteria live here in huge numbers and also contribute to the growth of the mat. Deeper still in the mat, light is too low for photosynthesis, and there heterotrophic bacteria absorb and process the dying and dead remains of the bacteria above them. Oxygen diffuses down into the mat

Banded Iron Formations: BIF

From the beginning of the Archaean (around 3800 Ma) we find increasing accumulations of a peculiar rock type. **BIF** or **Banded Iron Formations** are sedimentary rocks found mainly in sequences older than 1800 Ma. The bands are alternations of iron oxide and chert (Fig. 2.14), sometimes repeated millions of times in microscopic bands (Fig. 2.15). No iron deposits like this are forming now, but we can

Figure 2.14 Block of banded iron. Image by André Karwath, and placed into Wikimedia.

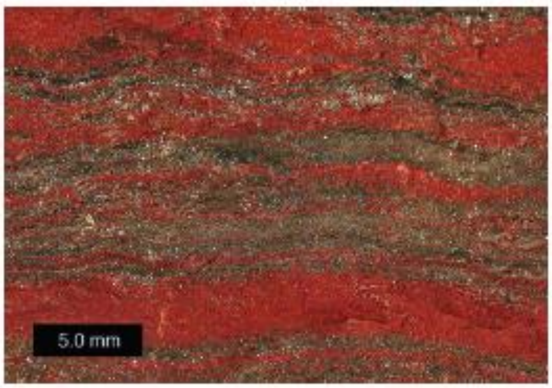

Figure 2.15 Close up of banding in BIF specimen from the Proterozoic of Michigan. Scale bar is 5 mm. Photograph by Mark Wilson of the College of Wooster, and placed into Wikimedia.

make intelligent deductions about the conditions in which BIF were laid down.

The chemistry of seawater on an Earth without oxygen differed greatly from today's situation. Today there is practically no dissolved iron in the ocean, but iron dissolves readily in water without oxygen. Even today, in oxygen-poor water on the floor of the Red Sea, iron is enriched 5000 times above normal levels. So Archean oceans must have contained a great deal of dissolved iron as well as silica.

Silica would have been depositing more or less continuously on an Archean seafloor to form chert beds, especially in areas that did not receive much silt and sand from the land. But iron oxide can only have precipitated out of seawater in such massive amounts by a chemical reaction that included oxygen.

Therefore, to form the iron oxide layers in BIF, there must have been occasional or regular oxidation events to produce iron ore, against a background of regular chert formation. Between oxidation events, dissolved iron was replenished from erosion down rivers or from deep-sea volcanic vents. What were these oxidation events, and what started them? The most likely hypothesis to explain BIF formation calls on seasonal changes in sunlight and temperature that in turn affect bacterial action and mineral deposition.

Lake Matano, on the Indonesian island of Sulawesi, gives us an idea of how an Archaean ocean may have worked (Crowe et al. 2008). The lake is small but very deep. The tropical climate means that the surface waters are always warm, so they never sink or mix with the deeper water below. The surface waters are well-lit, and floating cyanobacteria photosynthesize there. But the lake water has few nutrients, so these surface bacteria are not important, except that they keep the surface layers of the lake oxygenated.

Below the surface layer is water with no oxygen, rich in dissolved iron, just as we imagine the Archaean ocean to have been. Sunlight reaches the top layer of this deeper water, but the light is too dim for cyanobacteria to photosynthesise. Instead, huge numbers of green sulfur bacteria, with a variety of chlorophyll that works better in dim light, operate lithotrophy (Chapter 1) about 120 meters down in Lake Matano. They break down water, use the oxygen to oxidise the dissolved iron, and make a metabolic profit from the reaction. Oxidized iron sinks to the lake floor in large quantities.

Laboratory experiments suggest that in this situation, iron oxidation would work fastest in a narrow temperature range, with silica depositing faster at higher or lower temperatures. Using the evidence from Lake Matano, it looks as if sulfur bacteria could also have formed the alternating mineral bands in Archaean BIF. Although they involve oxidation, the reactions occur in environments without oxygen, and they do not produce any. Since sulfur bacteria are very ancient, there is no problem in suggesting that they were involved in producing the first BIF in the Isua rocks at 3800 Ma.

In an extensive Archaean ocean, rather than a small tropical lake like Lake Matano, we would expect that iron oxidation would occur over a large area. Indeed, BIF were often deposited in bands that can be traced for hundreds of kilometers.

Today we probably see only a small fraction of the BIF that once formed on Archean sea floors, because most ocean crust has since been recycled back into the Earth. But even the amounts remaining are staggering. BIF make up thousands of meters of rocks in some areas and they contain by far the greatest deposits of iron ore on Earth. At least 640 billion tonnes of BIF were laid down in the early Proterozoic between 2500 Ma and 2000 Ma (that's an average of half a million tonnes of iron per year). [The

Edicaran, Burgess Shale

oxygen. Several new studies have revealed how the physical and biological world changed during the Ediacaran, though there is no convenient summary yet.

Large Ediacaran Animals

Many Ediacaran fossils belong to an extinct group called **rangeomorphs**, but there are Ediacaran sponges, cnidarians and bilaterians, too. Rangeomorphs became extinct at the end of the Ediacaran, at or before 543 Ma, but the others were the ancestors of the Cambrian animals that followed.

All Ediacaran animals were soft-bodied. It is only when their corpses were colonized after death by layers of bacteria that we see them at all, typically as "ghost" outlines where biofilms of bacteria compacted the sediment. We also see a few tracks and traces where mobile Ediacaran bilaterians moved on or just under the surface sediment. These Ediacaran animals colonized the seafloor, from shallow water to well below the well-lit surface zone.

In the Mistaken Point Formation in Newfoundland, Canada, we find the earliest large organized Ediacaran animals, from about 565 Ma. Here masses of rangeomorphs (and a few other animals) were killed and buried where they lived by very fine-grained volcanic ash falling through the water. The animals are preserved in great detail in three dimensions, giving us a unique opportunity to interpret their mode of life.

Rangeomorphs are animals built from small blade-shaped units ("frondlets") about 1 cm long. Young forms have only a few frondlets, but larger ones have multiple branching supports, each one bearing multiple frondlets, and growing up to a meter long. The animal is fixed to the seafloor by a circular disk or holdfast (Fig. 5.1).

There are no openings in the rangeomorph body wall, and the simplest hypothesis for their biology is **osmotrophy**: taking up dissolved nutrients from the water directly through the skin by osmosis. Each frondlet thus obtains its own nutrition, but clearly there must be some nutrient transport through the body to grow the non-feeding holdfast and the supporting tissues. The fractal arrangement of branches and frondlets approaches a mathematical optimum for an array of osmotrophic collectors (Fig. 5.2).

Many marine invertebrates get some nutrition this way, through skin, gills, or tentacles: jellyfish are just one example. Even a vertebrate, the ghastly hagfish, can burrow inside a whale carcass and absorb dissolved nutrients from the rotting flesh, through its gills and its skin. However, nutrients are not concentrated enough in most environments today to feed larger animals entirely by osmotrophy. Probably Ediacaran seafloors had more dissolved nutrients because there were few organisms eating plankton at the surface, or intercepting and eating dead and dying plankton before they decayed to release nutrients. Rangeomorphs may have died out as larger metazoans radiated at the base of the Cambrian and depleted their nutrient supplies.

Figure 5.1 The rangeomorph *Avalofructus* from the Mistaken Point Formation in Newfoundland. Reconstruction of a large specimen showing branches, frondlets, and the basal holdfast. Image from Narbonne et al. (2009). © Guy Narbonne and The Paleontological Society, used by permission.

Other Ediacaran animals include distinct bilaterians. *Dickinsonia* (Fig. 5.3) is flat and large, and also seems to have fed by osmotrophy through its lower side as it moved across the sea floor. *Kimberella* (Fig. 5.4) may be evolving toward a slug-like early mollusc, and may have grazed on algal mats. Some Ediacaran fossils resist interpretation.

How could these large metazoans survive if Ediacaran environments had low-oxygen conditions, as would certainly have been the case for the rangeomorphs at Mistaken Point? Osmotrophic animals today have very low metabolic rates, so the Ediacaran rangeomorphs, and *Dickinsonia*, probably had the same low oxygen requirements.

However, some Ediacaran animals left trace fossils of their burrowing activity in and on the surface, and these presumably were bilaterians using a coelom to move through the sediment: a relatively high-energy way to move about.

A large coral reef complex lies off the north coast of Venezuela, around the Las Roques islands. Some shallow lagoons are warm and very salty, so that normal marine animals do not live there. Cyanobacterial mats flourish in very shallow water, and produce oxygen by day under the tropical sun. The water immediately around the mats can

Figure 5.3 *Dickinsonia*, a bilaterian from the Ediacaran. Scale in cm. Image by Merikanto, and placed into Wikimedia.

Figure 5.4 *Kimberella*, a bilaterian from the Ediacaran of Russia About 1 cm long. Image by Aleksey Nagovitsyn, and placed into Wikimedia.