CHAPTER TWO

In the Beginning

The Origins and Importance of Oxygen

IN THE BEGINNING THERE WAS NO OXYGEN. Four billion years ago, the air probably contained about one part in a million of oxygen. Today, the atmosphere is just less than 21 per cent oxygen, or 208 500 parts per million. However this change might have come about, it is pollution without parallel in the history of life on Earth. We do not think of it as pollution, because for us, oxygen is necessary and life-giving. For the tiny single-celled organisms that lived on the early Earth, however, oxygen was anything but life-giving. It was a poison that could kill, even at trace levels. A lot of oxygen-hating organisms still exist, living in stagnant swamps or beneath the seabed, even in our own guts. Many of these die if exposed to an oxygen level above 0.1 per cent of present atmospheric levels. For their ancestors, who ruled the ancient world, pollution with oxygen must have been calamitous. From dominating the world they shrank back to a reclusive existence at the margins.

Oxygen-hating organisms are said to be *anaerobic* — they cannot use oxygen and, in many cases, can only live in its absence. Their problem is that they have nothing to protect them against oxygen poisoning: they possess few, if any, antioxidants. In contrast, most living things today tolerate so much oxygen in the air because they are stuffed full of antioxidants. There is a paradox hidden in this progression. How did modern organisms evolve their antioxidant protection? According to the standard textbook view, antioxidants could not have been present in the first cells that began emitting oxygen as a toxic waste product: how could they have adapted to a gas that had not existed before? Yet if this assumption is true — that antioxidants evolved after the rise in atmospheric oxygen — then the huge rise in atmospheric oxygen must have posed a very serious challenge to early life. If oxygen had anything like the effect on the first anaerobic cells that it does on their descendants today, then there ought to have been a mass extinction of anaerobic organisms that would put the fall of the dinosaurs in the shade.

Why should we care? According to the free-radical theory of ageing discussed in Chapter 1, oxygen toxicity sets limits on our lives. If this is true, the ways in which life has adapted to oxygen over evolutionary time should be revealing. Did the rise in atmospheric oxygen really cause a mass extinction? How did life adapt? If ageing and death are caused by an ultimate failure to adapt, can we learn anything from how the survivors of this putative holocaust coped? Can we somehow 'do more' of whatever they did? In the next few chapters, we will attempt to answer some of these questions by charting the response of organisms to changing oxygen levels over the aeons.

The origins and early history of life have attracted renewed research interest in the past few decades. Some of our most basic ideas about the genesis of life have been turned on their heads. Yet so persuasive and ingrained was the old view that even recent biology textbooks cling to its tenets. Many scientists working in other fields seem oblivious to the rewriting of their gospels. The old story is worth recounting here because the role ascribed to oxygen emphasizes its toxicity.

In the 1920s, J. B. S. Haldane in England and Alexander Oparin in Russia independently began to think about the possible composition of the Earth's original atmosphere, on the basis of gases known to be present in the atmosphere of Jupiter (which could be detected by their optical spectra). Haldane and Oparin argued that if the Earth condensed from a cloud of gas and dust, along with Jupiter and all the other planets, then the original atmosphere of the Earth ought to have contained a similarly noxious mixture of hydrogen, methane and ammonia. Their ideas stood the test of time, and formed the basis of a famous series of experiments by Stanley Miller and Harold Urey in the United States during the 1950s.

Miller and Urey passed electric sparks (simulating lightning) through a gaseous atmosphere comprising the three Jupiter gases, and collected the end-products. They found a complex mixture of organic compounds, including a high proportion of amino acids (from which all living things make proteins, the building blocks of life). Such reactions, they said, could have turned the early oceans into a thin organic soup containing all the precursors of life. The only other ingredients needed for life to congeal out of this soup were chance and time, both of which seemed to be virtually limitless: the planet is 4.5 billion years old, and the first fossils of large animals date from half a billion years ago. Four billion years should have been long enough.

The choice of the gases to work with made good practical as well as theoretical sense. Hydrogen, methane and ammonia do not last long in the presence of oxygen and light. The mixture becomes oxidized, and when this happens the yield of organic compounds quickly falls off. Chemically speaking, *oxidation* refers to the removal of electrons from an atom or molecule. The reverse process is called *reduction*, which involves the addition of electrons.

Oxidation is named after oxygen, which is good at stripping electrons from molecules; to help you remember, think of oxygen as being caustic or destructive, like a paint-stripper. Oxidation strips off the electron paint, whereas reduction has the blanketing effect of a fresh coat of paint.[1] The point is that oxygen can strip organic molecules of electrons, often shredding the molecules, which give up their own electrons as a sacrificial offering, in the process. Today, cells counter this kind of damage with antioxidants, but in the beginning there were no antioxidants. Free oxygen would have been an insurmountable problem, because any organic molecules, or incipient forms of life, would have been shredded if much oxygen was present. The fact that life did start can only mean that oxygen was not present in any abundance.

The first cells, then, presumably evolved in an oxygen-free atmosphere, and in turn must have generated energy without the aid of oxygen. This seemed a reasonable proposal, as at the close of the nineteenth century Louis Pasteur had described fermentation as 'life without oxygen', and subsequent research had proved him right. Because yeasts and many other single-celled organisms depend on fermentation for their

[1] There is also an old mnemonic, 'LEO the lion says GER': **L**oss of **E**lectrons is **O**xidation, **G**ain of **E**lectrons is **R**eduction).

energy, and are simple in structure, it was an easy extrapolation to assume that they were relics of ancient life. This single-celled life must have lived by fermenting organic compounds dissolved in the oceans, the theory went, until they were superseded by the evolution of the first oxygen-evolving photosynthetic bacteria — the cyanobacteria (once, inaccurately but poetically, called the blue-green algae).

The cyanobacteria learnt to harness the energy of the Sun. Microscopic they may have been, but as the aeons ticked away, inconceivably large numbers of cyanobacteria (several billion fit in a droplet of water) silently polluted their environment with toxic oxygen waste. To begin with, this oxygen would have reacted with minerals dissolved in the oceans or eroded from the rocks, oxidizing them and locking up the oxygen in mineral compounds. These enormous natural resources acted as a buffer against free oxygen for hundreds of millions of years. In the end, however, the buffer became completely oxidized. With nothing left to take up the slack, the atmosphere and oceans became abruptly (in geological terms) contaminated with excess oxygen. The cost was terrible — an oxygen holocaust. Here is Lynn Margulis, distinguished professor of biology at the University of Massachusetts, Amherst, writing in 1986:

> This was by far the greatest crisis the earth has ever endured. Many kinds of microbes were immediately wiped out. Microbial life had no defence against this cataclysm except the standard way of DNA replication and duplication, gene transfer and mutation. From multiple deaths and an enhanced bacterial sexuality that is characteristic of bacteria exposed to toxins came a reorganisation of the superorganism we call the microcosm. The newly resistant bacteria multiplied, and quickly replaced those sensitive to oxygen on the Earth's surface as other bacteria survived beneath them in the anaerobic layers of mud and soil. From a holocaust that rivals the nuclear one we fear today came one of the most spectacular and important revolutions in the history of life.

According to this view, the success of the new world order stemmed not just from the ability of microorganisms to withstand oxygen toxicity, but from a stunning evolutionary *tour de force* in which cells became dependent on the very substance that had been a deadly poison. The inhabitants of this brave new world were energized by oxygen.

The old theory continues: our dependency on oxygen obscures the fact that it is a toxic gas, intimately linked with ageing and death, to say nothing of being a serious fire risk. Over evolutionary time, the reactivity of oxygen has served to modulate its own accumulation in the atmosphere. We are told that ever since the explosion of multicellular life, some 550 million years ago, atmospheric oxygen has hovered around 21 per cent, the outcome of a sustainable natural balance. If its concentration strays too high, then oxygen toxicity suppresses plant growth. As a result, the amount of oxygen produced by photosynthesis falls, and this lowers atmospheric levels again. In an atmosphere with more than about 25 per cent oxygen, we are told, even wet rain forests would flare up in vast conflagrations. Conversely, if oxygen levels were to fall below about 15 per cent, animals would suffocate and even dry twigs would fail to light. The continuous record of fossil charcoal in sedimentary rocks over the past 350 million years suggests that fires have continuously swept the Earth. If so, then oxygen levels could never have fallen below 15 per cent. Thus, the biosphere has regulated atmospheric oxygen at a level congenial to itself throughout the modern age of plants and animals.

This is the story I grew up with, and much of it is still widely accepted, or at least unquestioned. Although based on somewhat limited evidence, most of the claims sound biologically plausible. To summarize: life evolved through chemical evolution in a primordial soup, formed from a planetary atmosphere containing methane, ammonia and hydrogen. The first cells fermented this soup until they were displaced by cyanobacteria, which used solar energy to power photosynthesis, giving off oxygen as a toxic waste product. This poisonous gas oxidized the rocks and oceans, and finally accumulated in the atmosphere, causing an apocalyptic extinction, an oxygen holocaust. From the ashes a new world order emerged, which depended on the very gas that had wiped out most of its ancestors. The new order was energized by oxygen. Even so, the toxicity and reactivity of oxygen constrained the biosphere to regulate its atmospheric content at 21 per cent.

So firmly entrenched was this story in my own mind that I was exasperated to hear a claim on television that oxygen levels once reached 35 per cent — during the Carboniferous period, around 300 million years ago. Nonsense, I thought! Everything would burn! Plants wouldn't grow! I was not alone. The idea, although advanced seriously by geochemists of international standing, had at first been derided by the wider geological and biological communities. It was not until I began to research the subject that I became convinced that the revisionists were right. Many of the ideas are still controversial, and most of the individual pieces of evidence are flawed, but they have one redeeming feature: in the last two decades we have stepped from the realms of 'geopoetry' into a new era of molecular evidence, which underpins the new models of global change. Taken together, I find the weight of evidence convincing, even if the new story flies in the face of oxygen toxicity and indeed, sometimes, common sense.

Before examining the evidence, and asking how it affects the lives we lead today, we should reorientate ourselves to the emerging picture. Almost every step of my previous summary has been reversed. Far from coalescing from a primordial soup, the new story goes, life might have begun in hot sulphurous vents known as black smokers, deep in the mid-ocean trenches. Paradoxically, the last common ancestor of all known life, tenderly known as LUCA (the Last Universal Common Ancestor), is thought to have used trace amounts of oxygen to respire, even before her descendants learnt to photosynthesize (at least to generate oxygen). Instead of muddling along by fermentation, the first cells are thought to have extracted energy from a range of inorganic elements and compounds including nitrate, nitrite, sulphate and sulphite — and oxygen. If so, LUCA was already resistant to oxygen toxicity before there was any free oxygen in the air. Presumably, her descendants, such as the cyanobacteria, were similarly protected against their own waste product, and so did not succumb to an oxygen holocaust.

In fact, there is no solid evidence that oxygen ever caused a mass extinction. Instead of rising swiftly to reach an equilibrium controlled by the biosphere, the oxygenation of the Earth seems to have proceeded in a series of sharp jerks or pulses, each one precipitated by non-biological factors such as plate tectonics and glaciation. Each rise in atmospheric oxygen has been linked with prolific biological 'radiations', in which life expanded to fill vacant ecological niches, in much the same way that the empty prairies propelled the colonization of the American West. An injection of oxygen into the air immediately preceded the rise of single-celled *eukaryotes* — cells containing a nucleus — which are the cellular ancestors of all multicellular organisms, including ourselves. Similar oxygen injections preceded the explosion of multicellular plants and animals at the beginning of the Cambrian period (which began 543 million years ago), and the evolution of giant insects and plants during the Carboniferous and early Permian (320–270 million years ago); perhaps even the rise of the dinosaurs. Conversely, several mass extinctions are associated with periods of falling oxygen levels, including the 'mother of all extinctions' at the end of the Permian (around 250 million years ago). The inescapable conclusion, that oxygen is a Good Thing, may give few people a sleepless night, but will certainly help constrain our ideas of oxygen toxicity in ageing and disease.

The first sacred cow to be sacrificed was the Jupiter-like composition of Earth's primordial atmosphere. In fact, life must have evolved under an atmosphere that contained very little methane, hydrogen or ammonia. The evidence for this is direct and comes from geology.

The Earth and the Moon were formed just over 4.5 billion years ago. The age of the craters on the Moon, dated from rock samples brought back by the Apollo astronauts, suggests that our planetary system was bombarded by meteorites for at least 500 million years. The bombardment ended around 3.8 to 4 billion years ago. The oldest sedimentary rocks on Earth, which were laid down along what is now the west coast of Greenland, have been reliably dated to an age of 3.85 billion years — a mere 700 million years after the formation of the Earth and certainly not long after the end of the bombardment.

Despite their antiquity, these ancient rocks speak of an atmosphere and a hydrological cycle surprisingly similar to our own. The fact that these rocks were once sediments implies that they were laid down under a large body of water. The sediments were presumably eroded by rainwater from a land mass. This constrains the possible temperatures to within a range compatible with evaporation, cloud formation and precipitation. The mineral content of the rocks allows an informed guess about the composition of the air at the time. There are carbonates present, which probably formed from carbon dioxide reacting with silicate rocks, as happens today; we may presume then that carbon dioxide was present. There are also various iron oxides in the rocks, which from a chemical point of view could not have formed under Jupiter-like conditions, but equally could not exist if more than a trace of oxygen was present. We may take it that oxygen was no more than a trace gas at the time. Finally, we must assume that nitrogen was the main component of the air then, as today, because nitrogen is almost inert as a gas and cannot be generated in large amounts by life. No known chemical or biological process could have produced an atmosphere so rich in nitrogen, so it must have been there all along. Thus, the Earth's atmosphere, nearly 4 billion years ago, probably consisted mostly of nitrogen, as today, with some carbon dioxide and water vapour, and trace amounts of other gases including oxygen. There was essentially no methane, no ammonia, and no hydrogen.

These predictions, based on the composition of early rocks, are supported by a second line of evidence, which provides a clue to the origin of this early atmosphere. This is the rarity of inert unreactive gases, particularly neon, in the Earth's atmosphere today. Neon is the seventh most abundant element in the Universe. It was abundant in the clouds of dust and gas from which the Earth and the other planets of the Solar System condensed. As an inert gas, neon is even more unreactive than nitrogen. If any of the Earth's original atmosphere had survived the meteorite bombardment, it should have contained about the same amount of neon as nitrogen. In fact, the ratio of neon to nitrogen is 1 to 60 000. If there ever had been a Jupiter-like atmosphere on Earth, then it must have been swept away during that first ferocious period of meteorite bombardment.

Where, then, did our modern atmosphere come from? The answer seems to be volcanoes. As well as emitting sulphurous fumes (which would have precipitated in the rain), volcanic gases include nitrogen and carbon dioxide (in about the right balance), tiny amounts of neon, and almost no methane, ammonia or oxygen.

Where did the oxygen come from? There are only two possible sources of the oxygen in the air. By far the most important is *photosynthesis*, the process in which plants, algae and cyanobacteria use the energy of sunlight captured by the green pigment chlorophyll to 'split' water. The splitting of water releases oxygen, which is discharged into the atmosphere as a waste product, while the energy rich compounds derived from the split (by the absorption of light energy) are used to bind carbon dioxide from the air and package it into the sugars, fats, proteins and nucleic acids that make up organic matter. Photosynthesis therefore uses sunlight, water and carbon dioxide to produce organic matter. It gives off oxygen as a waste product.

If photosynthesis were the only living process on the planet, oxygen would continue to build up in the air until the plants used up all the available carbon dioxide. Then everything would grind to a halt. Clearly this has not been the case. In fact, there are a number of processes that can consume oxygen, including reactions with minerals in the rocks and oceans and with volcanic gases. Today, however, almost all the oxygen produced by plants is used up by the *respiration* of animals, fungi and bacteria, which use oxygen to 'burn up' or oxidize the organic material they take in as food, extracting energy for the organism's use and releasing carbon dioxide back into the air.[2] Because animals, bacteria and fungi all consume organic matter that comes from another organism, they can be classed together as *consumers*. By definition, consumers gain their energy through the respiration (the controlled burning) of the sugars, fats and proteins made by the primary photosynthetic *producers*. The overall reaction of respiration, in which oxygen and sugars are consumed and the waste products carbon dioxide and water are produced, is almost exactly the opposite of photosynthesis, and consumes essentially the same amount of oxygen that is being produced by photosynthesis. As well as using up oxygen, burning the food we eat regenerates the carbon dioxide needed for photosynthesis to continue; however much we may feel like parasites, the plants need us as much as we need them.

If the consumers were to devour all the organic matter made by primary producers, then all the oxygen released into the air would be consumed by respiration. Perhaps surprisingly, this is very close to what actually happens. The oxygen released by the photosynthesizers is almost completely (99.99 per cent) used up by the animals, fungi and bacteria which feed on the remains of the producers, or on each other. The apparently trivial 0.01 per cent discrepancy, however, is in fact responsible for all life as we know it. It represents the organic matter that is not burnt, but is instead buried under sediments. Over several billion years, this adds up to a vast amount of buried organic matter.

If organic remains are buried rather than eaten, then the complete re-uptake of oxygen by consumers is prevented.[3] The left-over oxygen accumulates in the atmosphere. Almost all our precious oxygen is derived from a 3-billion-year mismatch between the amount of oxygen generated by the primary producers and the amount used up by consumers. The vast amount of dead organic matter buried in the rocks dwarfs the total carbon content of the living world. The Yale University geochemist Robert Berner estimates that there is 26 000 times more carbon buried in

[2] Plants, algae and cyanobacteria also respire, using some of the oxygen released during photosynthesis to burn the carbohydrates produced by photosynthesis and extract the stored energy from them.

[3] For the chemically minded, the overall equation for photosynthesis can be given as $CO_2 + H_2O \rightarrow CH_2O$ (organic carbon in the form of carbohydrate) + O_2; respiration can be given as the reverse reaction. This means that for every molecule of CH_2O (or its equivalent in other organic matter) that is buried and not burned up by respiration, one molecule of O_2 is left in the air.

the crust than is present in the entire living biosphere. Put another way, this means that the entire living world accounts for just 0.004 per cent of the organic carbon currently present on or in the Earth. If all this organic matter reacted with oxygen, then there would be no oxygen left at all. If a mere 0.004 per cent of total organic carbon — in other words, just the living biosphere — reacted with oxygen, then 99.996 per cent of the atmospheric oxygen would be left over. Thus, even the most foolhardy destruction of world forests could hardly dint our oxygen supply, though in other respects such short-sighted idiocy is an unspeakable tragedy.

Buried organic matter takes the form of coal, oil and natural gas, as well as less obvious remains mixed with sediments and minerals such as iron pyrites or fool's gold. Ordinary sandstone rocks, which do not appear to have any trapped carbon at all, typically contain a few per cent organic carbon by weight. Because these rocks are so abundant, they actually account for most of the organic carbon buried in the Earth's crust. Only a small proportion of buried matter is accessible in the form of fossil fuels. This means that, even if we succeeded in burning all the coal, oil and gas trapped in the Earth's crust, we would still only deplete a few per cent of atmospheric oxygen.

The original source of oxygen in the atmosphere was not biological photosynthesis, however, but a chemical equivalent. Few processes show more vividly the importance of the *rate* of a reaction, and the difference that life can make. Solar energy, especially the ultraviolet rays, can split water to form hydrogen and oxygen without the aid of a biological catalyst. Hydrogen gas is light enough to escape the Earth's gravity. Oxygen, a much heavier gas, is retained in the atmosphere by gravity. On the early Earth, most of the oxygen formed in this way reacted with iron in the rocks and oceans, locking it permanently into crust. The net result was that water was lost, because after it had been split, the hydrogen seeped into space and the oxygen was consumed by the crust instead of accumulating in the air.

Over billions of years, the loss of water through the effects of ultraviolet radiation is thought to have cost Mars and Venus their oceans.[4]

[4] The Mars Global Surveyor, which has been orbiting the red planet since April 1999, has sent back detailed pictures of sedimentary rocks that NASA scientists say probably formed in lakes and shallow seas. Erosional channels suggesting the presence of flowing water on Mars sometime in the past were described long ago, but the new images provide the first solid evidence that oceans once existed on Mars. Whether these oceans drained away under the surface of the planet or evaporated into space, or both, is as yet unknown.

Today, both are dry and sterile, their crusts oxidized and their atmospheres filled with carbon dioxide. Both planets oxidized slowly, and never accumulated more than a trace of free oxygen in their atmospheres. Why did this happen on Mars and Venus, but not on Earth? The critical difference may have been the rate of oxygen formation. If oxygen is formed slowly, no faster than the rate at which new rocks, minerals and gases are exposed by weathering and volcanic acitivity, then all this oxygen will be consumed by the crust instead of accumulating in the air. The crust will slowly oxidize, but oxygen will never accumulate in the air. Only if oxygen is generated faster than the rate at which new rocks and minerals are exposed can it begin to accumulate in the air.

Life itself saved the Earth from the sterile fate of Mars and Venus. The injection of oxygen from photosynthesis overwhelmed the available exposed reactants in the Earth's crust and oceans, allowing free oxygen to accumulate in the atmosphere. Once present, free oxygen stops the loss of water. The reason is that it reacts with most of the hydrogen split from water to regenerate water, so preserving the oceans on Earth. James Lovelock, father of the Gaia hypothesis and a rare scientific mind, estimates that today, with oxygen in the air, the rate of hydrogen loss to space is about 300 000 tons per year. This equates to an annual loss of nearly 3 million tons of water. Although this may sound alarming, Lovelock calculates that at this rate it would take 4.5 billion years to lose just 1 per cent of the Earth's oceans. We can thank photosynthesis for this protection. If ever life existed on Mars or Venus, we can be sure that it never learnt the trick of photosynthesis. In a very real sense, our existence today is attributable to the early invention of photosynthesis on Earth, and the rapid injection of oxygen into the atmosphere through the action of a biological catalyst.

How life began on earth is beyond the scope of this book. Interested readers should turn to the writings of Paul Davies, Graham Cairns-Smith and Freeman Dyson, listed in Further Reading. Let us accept that life evolved in the oceans of an Earth shrouded in an atmosphere of nitrogen and carbon dioxide, but with as yet only trace amounts of oxygen. Photosynthesis probably evolved early. We will return in Chapter 7 to the theme of how and why this happened. For now, we wish to chart how life responded to the challenge of rising oxygen levels, as photosynthesis

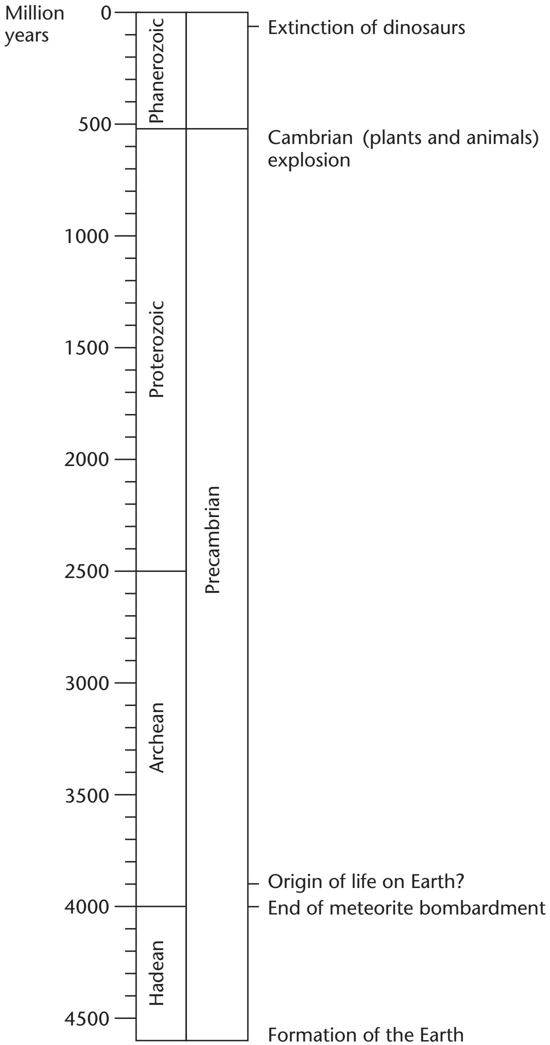

Figure 1: Geological timeline from the formation of the Earth 4.6 billion years ago to the present day. Note the immense duration of the Precambrian era. The first plants and animals appeared around the time of the Cambrian explosion 543 million years ago. The extinction of the dinosaurs was about 65 million years ago.

pumped out oxygen into the air and the oceans. Did oxygen pollution bring about an apocalyptic extinction, as proposed by Lynn Margulis and others, or did it stimulate evolutionary innovations? So long after the event, is there any evidence left to support either interpretation?

The gauntlet was thrown down as long ago as the 1960s by Preston Cloud, one of the pioneers of geochemistry. Even after the large technological strides that the field has taken since then, his work and views still cast a long shadow today. Cloud argued that the major events of early evolution were coupled with changes in the oxygen content of the air. Each time oxygen levels rose, life responded with exuberance. Cloud himself set three criteria to prove this hypothesis: we need to know exactly how and when the oxygen levels changed; we need to show that the adaptations of life happened at exactly the same time; and we need good biological reasons for linking the change in oxygen levels to the evolutionary adaptation. Just how far Cloud's hypothesis is true in the light of new evidence is the focus of the next three chapters.

To make our quest more manageable, we will split Earth's history into three unequal parts (Figure 1). First comes the Precambrian, that long and silent age before there were any visible fossils in the rocks, excepting a faltering experiment in multicellular life in the last few moments. Next comes the so-called Cambrian explosion, when multicellular life exploded into the fossil record like Athena from the head of Zeus, fully formed and wearing armour (shells in their case). Finally the Phanerozoic arrives, our 'modern' age of land plants, animals and fungi, when trilobites, ammonites, dinosaurs and mammals pursued each other in geologically swift succession. The conditions that enabled such an explosion of multicellular life were all set in the Precambrian period. We will deal with this period in Chapter 3, therefore, and with the Cambrian explosion and the Phanerozoic in Chapters 4 and 5, respectively.