

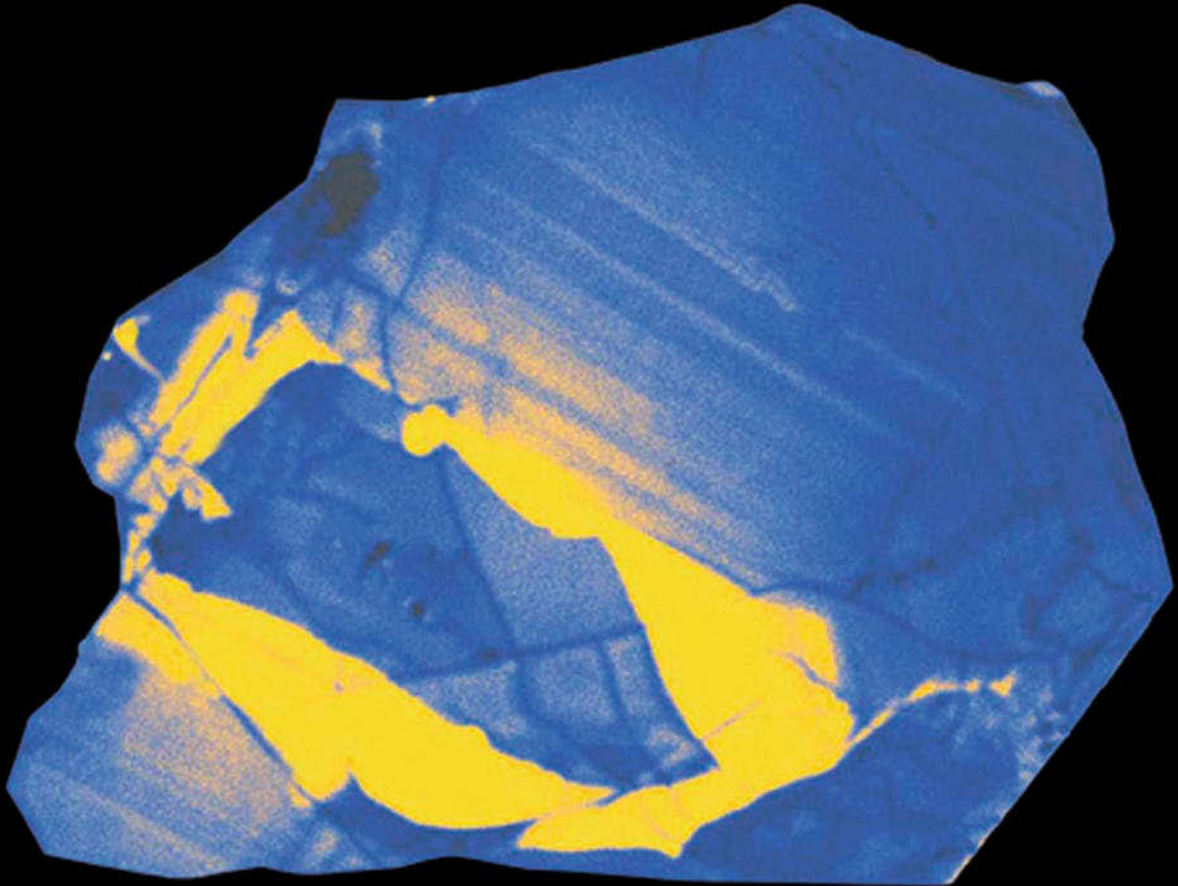
# Water, Continents, and Organic Matter...

## From 4.4 to 4.0 Ga: A Potentially Habitable Planet?

From 4.4 billion years BP (4.4 Ga), the Earth took a more familiar appearance: Its surface was covered with oceans from which a few continents emerged.

Its atmosphere probably contained enough greenhouse gases, such that, despite a “cold” Sun, its surface temperature remained above 0 °C.

The Earth was thus ready for life: It was potentially habitable, although it is not possible for anyone to know, yes or no, whether it was then inhabited.



■ **The oldest terrestrial material yet known:** A zircon crystal discovered in Jack Hills (in Western Australia). Its age is 4.4 billion years. (Photo: John Valley, University of Wisconsin, Madison, United States.)

The image of our planet such as seen by an astronaut nowadays is that of a mosaic of brown continents and blue oceans, occasionally hidden by a veil of white clouds (■ Fig. 3.1). But the Earth has not always presented such an appearance – far from it! Consequently, the question that may legitimately be asked is at what period in its history it acquired these features that, since then, have been so familiar to us.

At the end of the last chapter, we have seen that 4.4 Ga ago, the Earth's surface was already covered by one or more oceans. How have geologists acquired such certainty? By conducting what amounts to a real police investigation, during which they have had to carry out enquiries and gain information from the smallest clues. These clues, as we have already said, are simple crystals of a rather common mineral, zircon. But these particular zircons are exceptional! Discovered at Jack Hills in Western Australia, they are the oldest terrestrial material



■ Fig. 3.1 The Earth photographed during the *Apollo 17* mission on 7 December 1972: a mosaic of brown continents and dark-blue oceans, partly hidden by a veil of white clouds. When did our planet

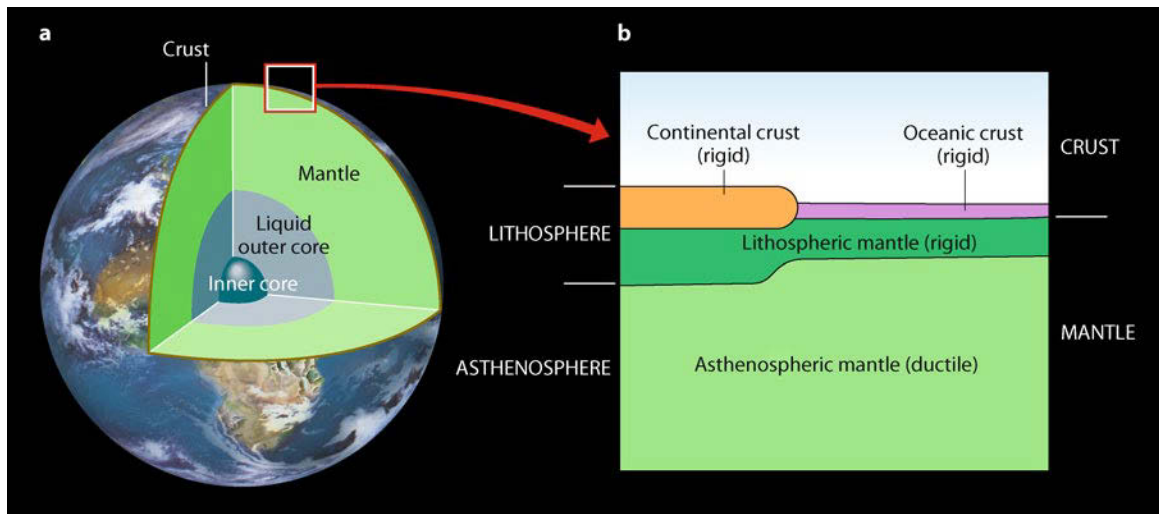
first gain this face that is so familiar to us today? Geologists are conducting the enquiry...

yet identified. The oldest of them has been dated at 4.4 Ga, which means that it crystallized hardly later than 170 Ma after the beginning of our planet's formation.

In this chapter, we shall discover how the analysis of the isotopic composition of oxygen in the Jack Hills zircons (the  $^{18}\text{O}/^{16}\text{O}$  ratio) has allowed us to affirm that liquid water already existed on Earth 4.4 Ga ago. We shall also see that these same crystals have allowed us to answer another fundamental question concerning the history of the Earth: when did the first continents form? We shall finish our sketch of the Hadean Earth between 4.4 and 4.0 Ga by attempting to decipher the physical and chemical conditions that prevailed at the surface: what was the composition of the atmosphere? When, where, and how did prebiotic chemistry, the set of reactions that leads to the synthesis of the more or less complex organic molecules necessary for the appearance of life, begin and then develop?

## The Two Faces of the Earth's Crust

The Earth's structure is “onion-like” (■ Fig. 3.2a): it consists of concentric layers which, going from the center outwards, successively are a metallic core (where the inner portion is solid, and the outer is liquid), then a solid, silicate mantle and, finally, a solid crust. The crust and the rigid outer portion of the mantle form the lithosphere (■ Fig. 3.2b). The latter is divided into plates that move over the subjacent, more viscous, mantle, called the asthenosphere. The movement of plates is described and explained by a theory known as plate tectonics, whose driving force is mantle convection, a process that results from the internal production of heat (■ Box 3.1). This internal structure is obviously not visible to an external observer who, like our astronaut, only sees oceans and continents. This is why, initially, we shall discuss the links that unite the oceans and the continents to the deep structure and the internal dynamics of the planet.



■ **Fig. 3.2 The Earth's internal structure.** a. Schematic section of the Earth, showing its “onion-like” internal structure. Only the outer core is liquid, the inner core, the mantle, the oceanic crust, and the continental crust are solid. b. Schematic section of the oceanic crust,

the continental crust, and the upper portion of the mantle. The crust (rigid) and the rigid portion of the mantle form the lithosphere, while the deeper portions of the mantle are ductile and form the asthenosphere.

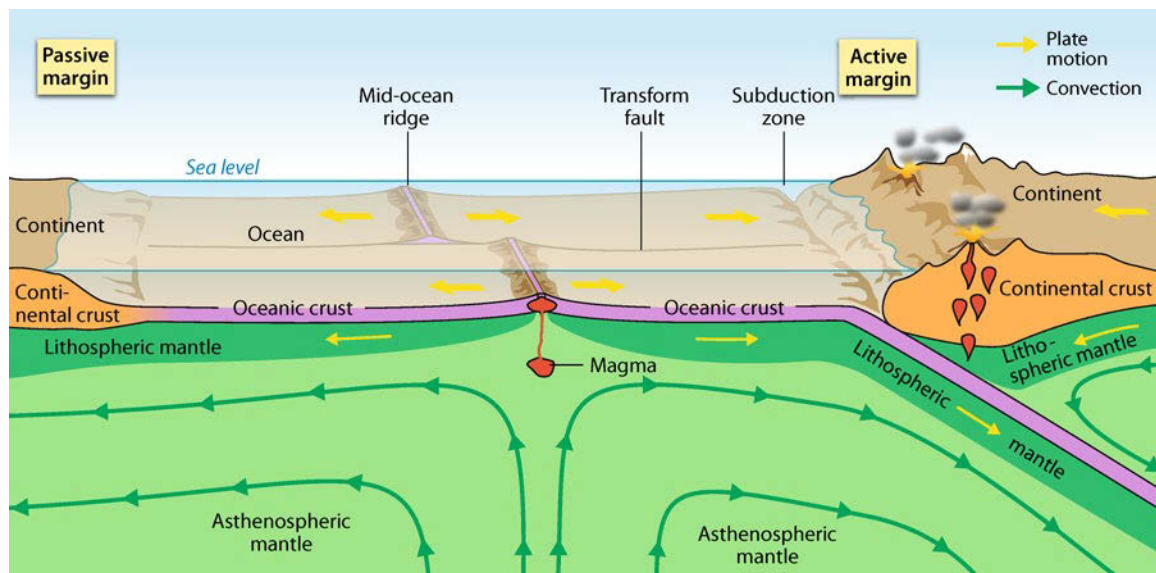


## Oceans and Oceanic Crust

An ocean consists of a layer of water, whose depth averages 5 km and that is located above an oceanic crust. With a typical thickness of 7 km, this crust mostly consists of mafic igneous rocks, basaltic in composition. It is generated at divergent lithospheric plate margins, that is in mid-ocean ridge systems (■ Fig. 3.3). There, the basaltic lavas erupt at temperatures of about 1250 °C. After the crystallization of these lavas, the mantle convection (■ Box 3.1), progressively moves the newly generated oceanic crust away from the ridge, where, due to its contact with the cold oceanic water, it slowly cools. As cooling progresses, the lava density ( $d$ ) that is about 3.1 initially, slowly increases such that, inexorably, the oceanic crust becomes denser than the underlying mantle ( $d \sim 3.3$ ). As a result, the dense oceanic crust sinks and returns (“subducts”) into the mantle, thus giving rise to what geologists call a subduction zone.

Nowadays, this cycle takes, on average, 60 Ma, and no oceanic crust older than 180 Ma is known. Put simplistically, at present the oceanic crust’s cycle does not significantly modify the chemical composition of the mantle. Indeed, most chemical elements that are extracted from the mantle to generate the oceanic crust in mid-ocean ridge systems, are reincorporated into this mantle, on average, 60 Ma later, in subduction zones.

The time when this cycle of oceanic crust started is still the subject of debate and animated controversy. It is highly probable that it could not start until the magma ocean had cooled, which happened 4.4 Ga ago (see ► Chapter 2). In addition, in 2007 scientists discovered, in Greenland, remnants of an oceanic crust dated at 3.86 Ga, preserved in a segment of continental crust, thus demonstrating that the cycle was already active at that date. Consequently, it started very early in the lifetime of our planet.



■ Fig. 3.3 Schematic block diagram showing the different types of relative movement between lithospheric plates. The mid-ocean ridges are situated vertically above the ascending branches of the convection cells in the asthenospheric mantle; they correspond to divergent plate boundaries. There, the mantle peridotites undergo adiabatic decompression which causes them to melt. This process gives rise to the basalts of the mid-ocean ridges and of the oceanic crust. As it moves away from the ridge, the latter gradually cools, becoming progressively denser, such that it sinks and returns down into the

mantle, forming what is known as a subduction zone (a convergent plate boundary). Such a zone corresponds to the descending branch of the convective cells in the asthenospheric mantle. In this scheme, subduction takes place beneath continental crust, but it may also occur beneath oceanic crust. In subduction zones, the magmatic activity results from dehydration of the subducted oceanic lithosphere. Finally, along transform faults, slip movements are observed. It should be noted that most terrestrial volcanic activity is localized along plate boundaries, whether they are convergent or divergent.

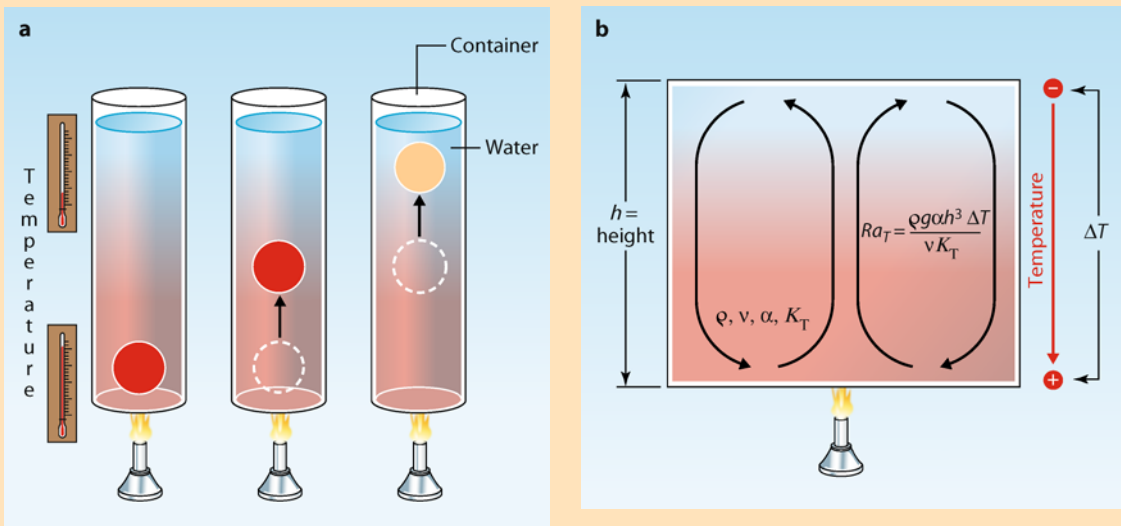
### Box 3.1 Thermal Convection

There are three ways by which thermal energy can be transported: conduction, convection, and radiation. Convection represents by far the most effective mechanism for dissipating the internal thermal energy of the Earth; it consists in a displacement of matter, which, in a way, transports its heat with it.

As we shall see, the process involved in convection is very simple. The only requirement is that the fluid under consideration has a temperature gradient: its base must be hotter than its top. Let us take the familiar example of a container filled with water and that is placed on a hotplate: it is thus heated from below. If we consider a small volume of water located at the bottom (■ Fig. 3.4a), being heated, it will expand and will, as a result, experience a decrease in its density (mass per unit volume). Being less dense, it will then be “lighter” and will ascend towards the top of the container. As it ascends, it will exchange energy with the surrounding medium and will progressively cool. Conversely, the colder water at the top of the container will be “heavier” and will sink. This is how vertical motions are initiated (■ Fig. 3.4b). The driving force is the Archimedes force and opposing forces are the fluid viscosity and thermal diffusivity. A dimensionless number, the thermal

Rayleigh number ( $Ra_T$ ) may be used to quantify the strength of convection. It expresses the relationships between the Archimedean force (the numerator), and the viscosity and thermal diffusivity of the fluid (the denominator).

In any system, convection is initiated for  $Ra_T > \sim 1700$ , and will be turbulent when  $Ra_T > 10^6$ . The planet Earth is internally heated by radioactive sources, while in the same time; it is cooled at its outer surface; which results in a temperature gradient: the Earth's surface being colder than its interior. On geological timescales ( $10^7$  to  $10^8$  years) the asthenospheric mantle rocks are plastic, they behave like fluids, and their  $Ra_T$  is about  $10^8$ : the terrestrial mantle is thus the site of a vigorous and efficient convection. Although the coupling between the mantle's convection and the lithospheric plates is still not well-understood and is the subject of spirited debate and controversy amongst the scientific community, there is an undoubted link between the presence of the mid-ocean ridges and the rising branches of the convection cells, as well as between the subduction zones and the descending branches of the convection cells (■ Fig. 3.3).



■ **Fig. 3.4 Convection.** **a. Principles:** in a container, a fluid is heated from below. When heated, a small volume of this fluid, initially located at the bottom, will expand and consequently, its mass per volume unit will decrease. Being less dense, it will be “lighter” and will ascend in the container. During its rise it will exchange energy with the surrounding medium and will thus progressively cool. **b. Schematic representation of a convection**

**cell:** the hot fluid (which is thus less dense) lying at the base of the container ascends, while the cold fluid (which is thus denser) sinks, and therefore initiates a vertical circulation of the fluids (a convection cell).  $\rho$  = mass density,  $g$  = gravitational acceleration,  $\alpha$  = Thermal expansion coefficient,  $h$  = height of the convection cell,  $\Delta T$  = difference in temperature between the top and bottom of the convection cell,  $\nu$  = dynamic viscosity,  $K_T$  = thermal diffusivity.

## Continents and Continental Crust

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A continent is a portion of continental crust that generally emerges above the sea level. Just like the oceanic crust, the continental crust “floats” on the asthenospheric mantle. Nowadays, this crust has an average thickness of 30 km, but it may reach 70 km beneath mountain ranges. Granitic to granodioritic in composition, the continental crust nowadays is generated at relatively low temperatures (around 800 °C) in subduction zones, as a result of melting of mantle rocks located above the subducted oceanic slab (see ► Chapter 6). Even after its complete cooling, the density of the continental crust ( $d = 2.76$ ) is always less than that of the mantle. As a result, and unlike the oceanic crust, it cannot be returned and recycled into the mantle, in any significant amount. This quasi-indestructibility has two fundamental consequences. The first is that the continental crust records all the important events that have occurred on the surface of the planet, whence its essential role in recording the Earth’s history. The second is that the chemical elements (Si, Al, K, Na, U, Th, etc.), that constitute the continental crust were extracted from the mantle in what may be termed a “definitive” manner, giving rise to sustainable modification in the composition of the upper regions of the latter.

This mechanism of continental crustal growth by subtracting elements that were initially in the mantle has been termed “juvenile”. It results in an increase in the volume of the continental crust. The counterpart of this stability lies in the fact that the continental crust is affected by numerous mechanisms involving the surface (erosion, alteration, etc.) or deeper regions (metamorphism, anatexis = partial melting, etc.) which redistribute elements within it without any addition of new material: the volume of the crust remains unchanged. These mechanisms that operate in a closed system are generally termed “recycling”. It is obvious that recycling of continental crust implies that the latter exists and that it is stable. This is the reason why, at any given location, juvenile mechanisms always precede recycling. As already mentioned earlier, one of the questions asked by geologists, is to know when the first stable continental crust appeared on Earth.

## The Fabulous Story Told by the Jack Hills Zircons

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Until very recently, the oldest terrestrial materials known were the Acasta gneisses, dated to 4.031 Ga, and the Nuvvuagittuq greenstone belt, with an age greater or equal to 4.0 Ga (see ► Chapter 6). In the absence of older rock materials, the most diverse theories concerning the first 500 million years in the Earth’s history (the Hadean) had been proposed. In particular, it had often been stated that if rocks older than 4.031 Ga had never been found, that was because they had never existed or that they had been completely destroyed at the inhospitable and constantly reworked surface of the Earth (existence of a magma ocean, heavy meteoritic bombardment (see ► Chapter 5), etc.). That said, isotopic analysis undertaken since the 1980s on the oldest terrestrial rocks had led researchers to predict that a continental crust formed before 4.0 Ga (► Box 3.2). It was, nevertheless, always thought that this crust only had an ephemeral existence: it had undoubtedly been rapidly destroyed, either through return into the mantle, or by vaporization by the intense meteoritic bombardment. This view of the Earth’s Hadean history was completely called into question in 2001, when zircon crystals much older than 4.0 Ga were discovered, analyzed and studied in detail.

## The World’s Oldest Continental Crust

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Zircon is a mineral whose chemical formula is  $\text{ZrSiO}_4$ ; it is widely used in geochronology, and this for three main reasons. First, it is abundant in felsic magmatic and metamorphic rocks.

Second, it is a very hard mineral (with a hardness of 7–7.5 on the Mohs scale, which runs from 1 to 10) and is thus very resistant to erosion and alteration. Finally, when it crystallizes, its crystal lattice incorporates uranium and thorium, whose radioactive isotopes ( $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$ ) decay into lead over periods of time that are far greater than the lifetime of the Solar System. For this reason, old zircon crystals are easily datable by radiochronology using the U–Pb pair (■ Box 2.2).

The zircon crystals that we are about to describe were discovered in Western Australia, at Jack Hills (■ Fig. 3.5) and at Mount Narryer, in detrital sedimentary rocks (quartzites and conglomerates), deposited at about 3.0 Ga. These rocks were generated by the destruction of other, more ancient rocks, of which the zircons are the only relicts that have resisted erosion and alteration.

A zircon crystal extracted from the Jack Hills quartzites has been analyzed by the U–Pb method, and the age of crystallization that has been thus calculated is  $4.404 \pm 0.008$  Ga (■ Fig. 3.7). This is the oldest terrestrial material known to date. This canonical age is not an exception and several other crystals, derived from the same region, have been systematically dated between 4.4 and 4.0 Ga (■ Fig. 3.8). It is important to emphasize, however, that the age of these detrital zircon crystals is, in no case, that of the rock that contains them today. In other words, we still do not know any rock that older than 4.031 Ga.

Although the rock within which the Jack Hills zircons crystallized has completely disappeared, the latter have, at least partially, preserved its fingerprints and its geochemical signature. These are the clues that enable us to reconstruct, not just the zircon's parent rock, but also the conditions that prevailed when it has been generated.

As a general rule, zircon is one of the first minerals to crystallize, at high temperature, in acid magmas; it is, by contrast, very rare in basic magmas. Acid magmas are silicon-rich and magnesium-poor, whereas the opposite applies to basic magmas. In acid magmas, silicon



■ Fig. 3.5 The Jack Hills range in Western Australia. The outcropping rocks are conglomerates and quartzites deposited about 3.0 Ga ago. They contain the oldest terrestrial materials so far reported: detrital zircon crystals whose ages go back as far as 4.4 Ga. (Photo: N. Eby, University of Massachusetts, U.S.A.)



### Box 3.2 Tracking Down the Most Ancient Continents: The Message from Neodymium

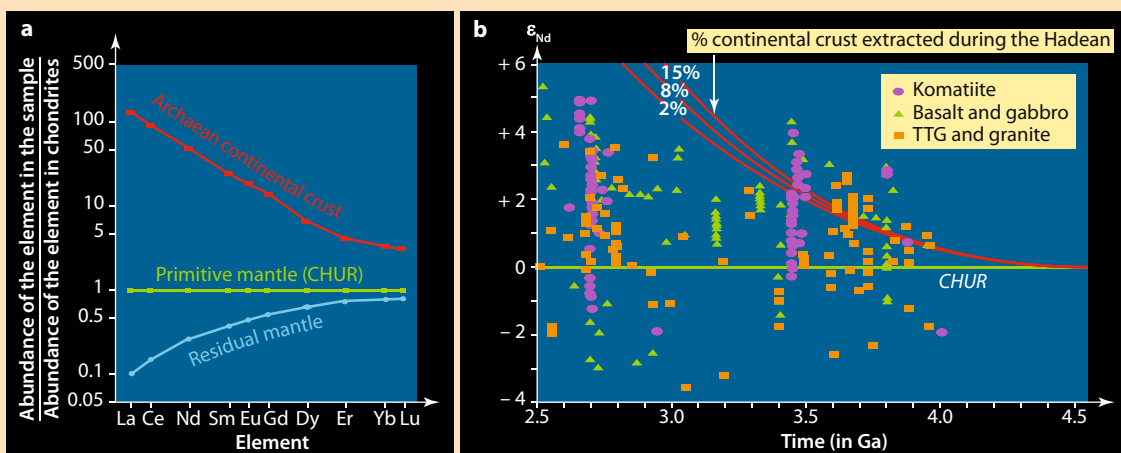
The zircons that have been recently discovered in Western Australia, at Jack Hills and Mount Narryer, and whose ages range from 4.0 to 4.4 Ga, demonstrate in an unquestionable manner the existence of a Hadean continental crust, that is to say older than 4.0 Ga. However, the presence of the latter had been predicted long before. Indeed, juvenile continental crust derives from the mantle through partial melting mechanisms. Consequently, as crust and mantle have totally different compositions, the extraction of the continental crust from the mantle has necessarily modified the composition of the latter (■ Fig. 3.6a); the greater the volume of extracted continental crust, the more significant change in mantle composition. The theories regarding the terrestrial accretion process that have been described in Chapter 1 consider that the primitive mantle of our planet had the same composition as chondritic meteorites. That means, in particular, that the relative abundances of the isotopes of an element (here, for example, neodymium, Nd) were identical in the primitive mantle and in chondrites. Thus, it is possible to quantify the volume of the continental crust extracted from the mantle, thanks to a parameter that geochemists denote  $\epsilon_{\text{Nd}}$ , whose value is proportional to the difference between the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio measured in chondrites and the value measured from the rock being studied.

■ Fig. 3.6b, is a diagram where  $\epsilon_{\text{Nd}}$  is plotted vs. time. An  $\epsilon_{\text{Nd}} = 0$  corresponds to what is known as the CHondritic Uniform Reservoir (CHUR), in other words a mantle that has not been modified by the extraction of the continental crust.

An  $\epsilon_{\text{Nd}} > 0$  indicates that the analyzed rock has been generated from a mantle source previously depleted by the extraction of continental crust, whereas  $\epsilon_{\text{Nd}} < 0$  reflects a crustal source or an enriched mantle source.

■ Fig. 3.6b shows that even the oldest rocks (4.0 Ga) have  $\epsilon_{\text{Nd}} > 0$ ; which proves that huge volumes of continental crust were extracted from the mantle before 4.0 Ga. This conclusion remains true whatever the nature of the rocks being considered: ultrabasic (komatiite), basic (basalt or gabbro), or acid (TTG or granite) (see the description of these rocks in ► Chapter 6, and the classification of rocks on p. 269).

From the early 1990s, simple calculations were able to show that about 10 per cent of the volume of the present-day continental crust must have been extracted from the mantle during the course of the Hadean (i.e., between 4.568 and 4.0 Ga). More recently, similar work, but this time based on hafnium (Hf) isotope behavior has led to perfectly identical conclusions.

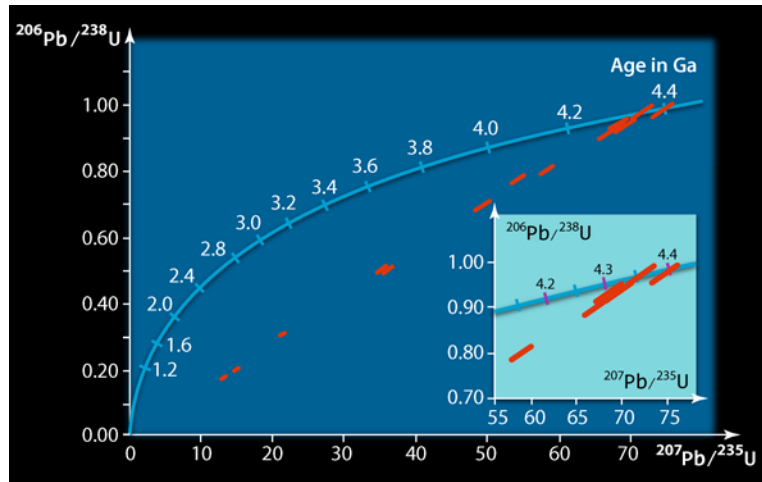


■ Fig. 3.6 Geochemical markers of the early production of the continental crust from the mantle. **a.** Rare Earth Element (REE) patterns, showing how the extraction of a REE-rich continental crust (red curve) from a primitive mantle (green curve) impoverished the latter in this type of elements (residual mantle, blue curve). The degree of mantle impoverishment in a given REE is proportional to the content of the latter in the extracted continental crust. For instance, the residual mantle is strongly impoverished in lanthanum (La), because this element is very abundant in the continental crust. In contrast, the continental crust has relatively low lutetium (Lu) content, consequently, its differentiation had almost no effect on the Lu content of the residual mantle. The

compositions of the continental crust and of the residual mantle are complementary. CHUR = CHondritic Uniform Reservoir, where the value 1 corresponds to the average composition of chondrites. **b.**  $\epsilon_{\text{Nd}}$  vs. age diagram for Archean terrestrial rocks. Even the oldest rocks known on Earth have  $\epsilon_{\text{Nd}} > 0$ , characteristic of a mantle source whose composition has been modified by the extraction of continental crust; which proves that this extraction started before 4.0 Ga, that is, during the Hadean. The red curves represent the theoretical evolution of  $\epsilon_{\text{Nd}}$  in the mantle for the extraction, during Hadean times, of 2, 8 and 15 volume per cent of continental crust. Komatiites and TTG are ultrabasic and acid rocks, respectively, that are typical of the Archean Earth (see ► Chap. 6)



■ **Fig. 3.7** Age of zircon crystals from Jack Hills;  $^{206}\text{Pb}/^{238}\text{U}$  vs.  $^{207}\text{Pb}/^{235}\text{U}$  diagram. The Concordia curve (■ Box 2.2) is drawn in blue and its age scale is given in Ga. Each red line corresponds to the isotopic composition of one of the analyzed zircon crystals. Among these, some are concordant, they lie on the Concordia curve for ages between 4.3 and 4.4 Ga. Others are discordant and all fall on the Discordia straight line, whose intersection with the Concordia curve also gives an age between 4.3 and 4.4 Ga. In other words, the oldest Jack Hills zircons crystallized scarcely any later than 170 million years after the start of the Earth's accretion.



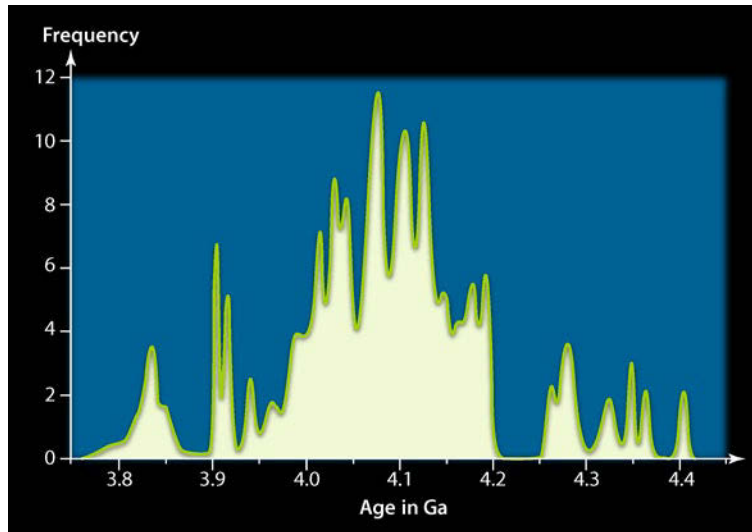
richness results in the crystallization of quartz ( $\text{SiO}_2$ ). The acid magmatic rocks that crystallized at depth (i.e., plutonic rocks; see the classification of rocks on p. 269) are referred to as the granitoid group. This group includes the granites, the granodiorites, the tonalites, and the trondhjemitic rocks, rocks that all contain quartz, but which differ one from another in their relative abundances of plagioclase feldspar and alkali feldspar.

Taken alone, the presence of zircon crystals in the Jack Hills rocks would be enough to assume that granitoids already existed on Earth 4.4 Ga ago. This assumption is corroborated by the study of mineral inclusions within these crystals. Indeed, like all magmatic minerals, the zircons did, during the course of their growth, incorporate within their structure some of the minerals that contemporaneously crystallized in the same magma. The Jack Hills zircons contain inclusions of quartz, plagioclase feldspar, potassium feldspar, hornblende, biotite, chlorite, muscovite, rutile, apatite, pyrite, and monazite (■ Fig. 3.9). All these minerals are characteristic of granitoids. This irrefutably demonstrates that these zircons crystallized from an acid magma. This information is crucial, because granitoids are the main component of the continental crust...

The zircons from Jack Hills therefore allow us to conclude that a continental crust existed 4.4 Ga ago, less than 170 Ma after the start of the accretion of our planet. Another conclusion – a trivial one – is that this crust has not been completely destroyed during the Hadean, because relicts of it still remain today.

We shall now try to determine in more detail the characteristics of the acid magmas that gave rise to the Hadean continental crust. A magmatic liquid contains a mixture of practically all the chemical elements of the periodic table. Some are abundant ( $> 0.1$  per cent): these are the major elements (Si, Al, Fe, Mg, Ca, Na, K, and Ti) whose polymerization gave rise to the minerals. The others are present in trace amounts (a few ppm), which often appear as trapped in mineral lattice defects. Among these, geochemists are particularly fond of the rare-earths or lanthanides. Indeed, these elements, whose atomic numbers range from 57 (lanthanum) to 71 (lutetium), are particularly sensitive to the magmatic mechanisms of crystallization and fusion (■ Box 6.1). In contrast, they are less affected by alteration and metamorphism of their host rock. They are, therefore, excellent tracers of the magma history.

So the Jack Hills zircons incorporated within their crystal lattices some of the rare earths available in the magma from which they were crystallized. Today, the analysis of their rare-earth contents shows that there are two families: those that have preserved all their magmatic characteristics (type 1) – which are those that interest us – and those that have lost them due to late hydrothermal processes (type 2). The Jack Hills zircons of type 1 have the same



■ Fig. 3.8 Frequency histogram for the age of 88 detrital zircon crystals from Western Australia (Jack Hills, Mount Narryer, and the Barlee Range). The zircon ages are more-or-less evenly distributed between 4.4 and 3.8 Ga. Most of them are older than 4.0 Ga, the age of the oldest known terrestrial rocks (the Acasta gneiss, see ► Chap. 6). These zircons bear witness to episodes of genesis or recycling of continental crust, which occurred regularly between 4.4 and 4.0 Ga, with perhaps a few peaks between 4.4 and 4.3 Ga, and between 4.2 and 4.0 Ga.

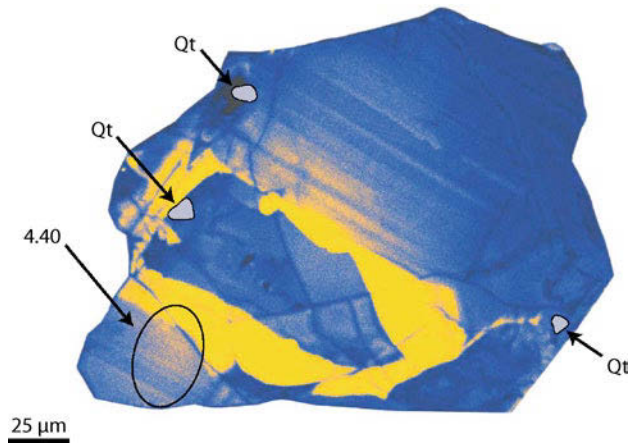
rare-earth contents as that of the zircons extracted from the Acasta gneisses. And we know that the latter crystallized from magmas called “TTG” magmas (tonalite, trondhjemite and granodiorite; see ► Chapter 6), typical of the Archaean continental crust, which was generated between 4.0 Ga and 2.5 Ga. In addition, based on the chemical laws that govern the distribution of rare earths between a zircon crystal and the magma within which it forms, it is possible to determine the latter’s rare-earth content. The result of this calculation shows that the host magma for the Jack Hills zircons was extremely rich in light rare earths and, in contrast, strongly impoverished in heavy rare earths – a character symptomatic of TTG magmas that gave rise to the Archaean continental crust.

An exhaustive study carried out on numerous zircon crystals extracted from the detrital sediments from Jack Hills, Mount Narryer and the Barlee Range, all in Western Australia, shows that these zircon ages spread more or less regularly between 4.4 and 4.0 Ga (■ Fig. 3.8). That means that the episode of crustal growth at 4.4 Ga was not unique but that, on the contrary, several phases of growth or recycling of continental crust took place between 4.4 and 4.0 Ga, with possibly several growth peaks at 4.4 Ga, 4.3 Ga, and between 4.2 and 4.0 Ga. This leads to one obvious conclusion: the genesis of continental crust at 4.4 Ga was not an isolated or accidental event; the crust differentiated over a long period of time between 4.4 and 4.0 Ga, even if this had occurred in an episodic manner rather than continuously. This conclusion has recently been confirmed by the fact that some samples of the Acasta gneisses in Canada that crystallized 4.03 Ga ago, contain inherited zircon cores that have been dated at 4.2 Ga, thus demonstrating that the Acasta rocks were generated by melting of older Hadean crustal materials.

## Earth: A Blue Planet since its Earliest Infancy

During mineral crystallization within a magma, oxygen isotopes 16 and 18 ( $^{16}\text{O}$  and  $^{18}\text{O}$ ) segregate differently between the liquid and crystalline phases. If we know the law that governs the chemical fractionation (in other words, if we know how to determine the partition coefficient of the isotopes between two phases), it is then possible to calculate, from the  $\delta^{18}\text{O}$  ratio (the  $^{18}\text{O}/^{16}\text{O}$  ratio in the sample, normalized to a standard: sea water) measured in a mineral, the  $\delta^{18}\text{O}$  of the parent magma. Zircon crystals from Jack Hills with ages ranging from 4.35 to 4.0 Ga have been analyzed with an ion microprobe. It turns out that the  $\delta^{18}\text{O}$  ratios measured vary between 5.3‰ and 7.3‰, which enables an  $\delta^{18}\text{O}$  of 6.8‰ to 9‰ to be

■ **Fig. 3.9 The oldest zircon on Earth:** a (false-color) cathodoluminescence image of the zircon crystal W74/2-36 hosted in the Jack Hills conglomerate (Western Australia). Ionic microprobe analyses of U and Pb isotopes were performed at the place marked with an ellipse, they enabled the computation of an age of  $4.404 \pm 0.008$  Ga. This zircon crystal also contains small quartz (Qt) inclusions, which bears witness to its crystallization in a granitic magma and that consequently, also attests to the existence of a stable continental crust at 4.4 Ga. (Photo: John Valley, University of Wisconsin, Madison, U.S.A.).

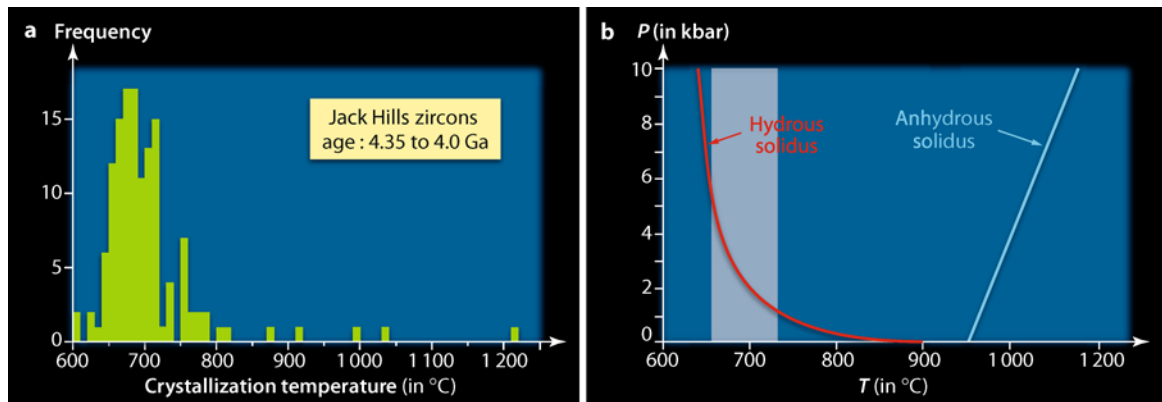


calculated for the parent granitic magma. Typically, the average  $\delta^{18}\text{O}$  of the mantle is  $5.3 \pm 0.3\%$ . Consequently, the high  $\delta^{18}\text{O}$  values of the parental magmas of the Jack Hills zircons, preclude their derivation from any non-contaminated or altered mantle source. On the contrary, these values are characteristic of magmas that have reacted, either at or very close to the surface (i.e., subsurface), with liquid water. This conclusion is extremely important, because it implies that liquid water must have been stable and available in huge amounts at the surface of our planet by 4.35 Ga (and very probably by 4.4 Ga as well). In other words, about 170 Ma after the beginning of its accretion, the Earth already harbored one or more oceans of liquid water.

Several indirect arguments also indicate that a hydrosphere was present at the surface of our planet by 4.4 Ga. Indeed, zircon crystals extracted from continental rocks emplaced between 4.0 and 2.5 Ga (TTG, see ► Chapter 6) display  $\delta^{18}\text{O}$  values that range between 5.0‰ and 7.5‰, values that are identical to those measured in the Jack Hills zircons. The study of the distribution of rare-earths in the zircons from Archaean TTG and the Jack Hills zircons have also led us to conclude on a probable analogy between the TTG and the parental magma of the Jack Hills zircons. TTG are generated through partial melting at high-pressure of a hydrated basalt, and, based on what we currently observe in the mid-ocean ridge systems, basalt hydration requires the presence of huge volumes of liquid water at the surface of the planet.

Another clue has allowed geologists to evaluate the abundance of water in the magma from which the Jack Hills zircons crystallized: their titanium (Ti) content. Indeed, it has been empirically shown that this latter is proportional to the zircon's crystallization temperature, which itself depends on the degree of hydration of the parental magma: the presence of water greatly decreasing the temperature of the magma's solidus (that is, the temperature at which a rock begins to melt or ceases to crystallize; ■ Box 6.1). For example, at a depth of 15 km (~5 kbar), the solidus temperature for a granitic magma will be slightly greater than 1000 °C if it is anhydrous and just 660 °C if it is water-saturated. In 2005, a study of the Ti content of 54 zircon crystals from Jack Hills, dated between 4.35 and 4.0 Ga was carried out. It enabled determination that these minerals crystallized at  $696 \pm 33$  °C (■ Fig. 3.10a). Such low crystallization temperatures can only be achieved in water saturated magmas (■ Fig. 3.10b). This conclusion is, moreover, perfectly consistent with the presence, in the same zircon crystals, of inclusions of hydrated minerals such as biotite or amphibole.

A sheaf of independent arguments thus converges on the same conclusion: large volumes of liquid water – oceans – formed very early on the surface of our planet, definitely by 4.35 Ga, but also very probably by 4.4 Ga.



**Fig. 3.10 Investigation of the crystallization temperature of the Jack Hills zircons.** **a.** Frequency histogram of the crystallization temperature of 54 zircon crystals from Jack Hills (the temperatures being estimated from their Ti content). **b.** A diagram of pressure versus temperature, showing curves for the beginning of melting (solidus) for hydrated granite (in red) and anhydrous granite (in blue). The grey zone on the diagram corresponds to the range of crystal-

lization temperature of the Jack Hills zircons (average crystallization temperature:  $696 \pm 33$  °C). Only magmas oversaturated in water (hydrous granites) can crystallize at such a low temperature. This oversaturation in water (in other words, the fact that the Jack Hills zircons crystallized from a magma rich in water), bears witness to the presence of large volumes of liquid water on the Hadean Earth.

### A stable Continental Crust at 4.4 Ga!

The decryption of the history of the old zircons from Jack Hills is not confined solely to the detailed study of their chemical composition. It also involves a detailed analysis of the structure of these minerals.

A number of these zircons consist of an ancient core rimmed by a younger zone. For example, the core of a zircon crystal (poetically called “54–90” ...) gives an age of  $4.263 \pm 0.004$  Ga, while its outer rim was formed  $4.030 \pm 0.006$  Ga ago. Another crystal (54–66) has a large, rounded core,  $4.195 \pm 0.004$  Ga old, surrounded by a zone that is dated to  $4.158 \pm 0.004$  Ga. These figures bear witness to a complex history. They are common in more recent terranes, where they are interpreted as an evidence for at least two magmatic episodes, often linked to continental crust recycling. The ancient core is called “relict” or “inherited”, because it is a remnant of an older rock that, except for the zircon crystals, has totally melted to form a new magma. And it was when the latter crystallized that the younger outer rim grew. Crustal recycling can proceed through direct melting of the ancient rock itself (direct recycling) or the latter could have been first altered and eroded, giving rise to sediments which, subsequently, almost completely melted thus generating a new magma – the crustal recycling was thus indirect, via a sedimentary stage. Whichever the recycling process, these figures imply reworking and internal rearrangement of the continental crust.

Other clues are provided by the mineral inclusions within the zircon crystals. Among these are muscovite and potassium feldspar. Muscovite is an aluminum-rich mineral ( $\text{KAl}_2[\text{Si}_3\text{AlO}_{10}(\text{OH})_2]$ ), which crystallizes only within peraluminous magmas. A peraluminous magma is such that its Al content is high enough for allowing muscovite growth after all the feldspars ( $\text{K[AlSi}_3\text{O}_8]$ ) have completed their crystallization. However, magmas generated directly (by melting of mantle peridotite) or indirectly (by melting of basalt) from the terrestrial mantle are not peraluminous. These magmas (known as juvenile magmas) are meta-luminous and, as a result, they cannot contain muscovite, unlike magmas generated through sediment melting, which are peraluminous. The presence of muscovite inclusions inside the Jack Hills zircons is therefore a strong evidence that during Hadean times, mechanisms of crustal recycling through a sedimentary cycle were already efficiently operating on Earth. The potassium feldspar inclusions reinforce this conclusion, indeed, juvenile magmas are rather



poor in this mineral (tonalitic or granodioritic in composition), in contrast to those generated by crustal recycling (granitic in composition).

All these clues that geologists have unearthed therefore show that the Hadean continental crust had not only been relatively regularly (or even continuously) extracted from the mantle since 4.4 Ga, but also that this crust was stable. The recycling of a juvenile crust requires, in fact, that it had remained stable over a sufficiently long period thus giving time for the mechanisms of erosion and alteration to operate. The latter could then have led to the formation of detrital sediments, whose melting generated the continental crust of which the Jack Hills crystals are the ultimate remnants.

In conclusion it appears that, contrarily to what was believed, the Hadean continental crust was not ephemeral; it was not destroyed immediately after its genesis, but it was sufficiently stable to undergo these processes of maturation and recycling. Finally we may note that all these mechanisms – the genesis of juvenile hydrated magmas and their recycling – imply the availability of huge volumes of liquid water throughout the Hadean, which requires the oceans to have been permanent, and to have also remained stable throughout this whole period.

## The Atmosphere Between 4.4 and 4.0 Ga: An Outline

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Water, earth (the continents), fire (volcanism)... In our quest to reconstruct the face of the Earth during the Hadean, between 4.4 and 4.0 Ga, one element is missing: air, i.e., the atmosphere. Apart from the Jack Hills zircons, there are, as we already wrote earlier, no vestiges of the Hadean Earth. Although these precious minerals have revealed so much to geologists, they do not contain any clues about the composition of the primitive Earth's atmosphere. Despite this, might it be possible to outline some of its characteristics?

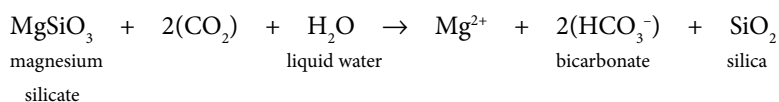
To start with, let us recall that nowadays the oceans and the atmosphere only represent a tiny fraction of the mass of our planet (0.022 and 0.0001 per cent, respectively). This means that a significant portion of the oceanic and, above all, atmospheric components is trapped into both the crust and the mantle – by way of example, today, all the ocean water represents only two thirds of the Earth's water. Determining the composition of the Earth's atmosphere at any given period in its history therefore assumes being able to draw up an overall balance-sheet, taking account, not only of the chemical species present at the surface, but also those that are buried in the interior. It must also be remembered that the current composition of the atmosphere is the result of intense interaction with the biosphere, that is with living beings that populate the planet for several billion years. Could the composition of the Earth's primitive atmosphere be deduced from that of the present-day atmosphere, after removing the contribution from living beings? No, because in attempting to do so, one would neglect the influence of processes that are currently masked by lifeforms, and particularly the role played by prebiotic chemistry (*see later*). Moreover, no planet that is currently accessible for analysis provides us with an analogous model for the primitive Earth. In addition, any reconstruction from details currently observed elsewhere in the universe on a body provided with an atmosphere – for example, Titan, one of Saturn's satellites – would appear to be a difficult task. A model based on a certain number of assumptions thus remains, for the time being, the only method that can be envisaged.

We have seen in the preceding chapter that the degassing of the magma ocean and the chemical species contributed by external bodies (comets, asteroids, and meteorites) enabled the formation of an initial atmosphere lying above a superheated Earth, and consisting of all of the volatile chemical species. Immediately after the condensation of the oceans (around 4.4 Ga if we believe the Jack Hills zircons), the models predict that the terrestrial atmosphere mainly consisted of carbon dioxide (CO<sub>2</sub>), together with a still significant amount of water vapor (H<sub>2</sub>O), as well as with other components in lesser abundance – but not of lesser impor-

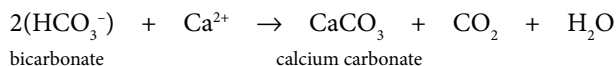
tance – such as molecular hydrogen ( $\text{H}_2$ ), molecular nitrogen ( $\text{N}_2$ ), and methane ( $\text{CH}_4$ ). How did this atmospheric composition evolve between 4.4 and 4.0 Ga?

### Carbon Dioxide Takes Control of the Climate

After the condensation of the oceans,  $\text{CO}_2$  became the principal component of the atmosphere, with a partial pressure that, depending on the estimations, ranges between 40 and 210 bars. This produced a significant greenhouse effect which resulted in a surface temperature of 200 to 250 °C. Under these conditions, siliceous rocks (basalts of the oceanic crust or granitoids of the continental crust) underwent leaching (at the bottom of the oceans and, where appropriate, through erosion of any emergent surface), resulting in the release of silica and bicarbonate in a reaction as follows:



The bicarbonate  $\text{HCO}_3^-$  subsequently precipitated in the form of insoluble calcium carbonate  $\text{CaCO}_3$ :



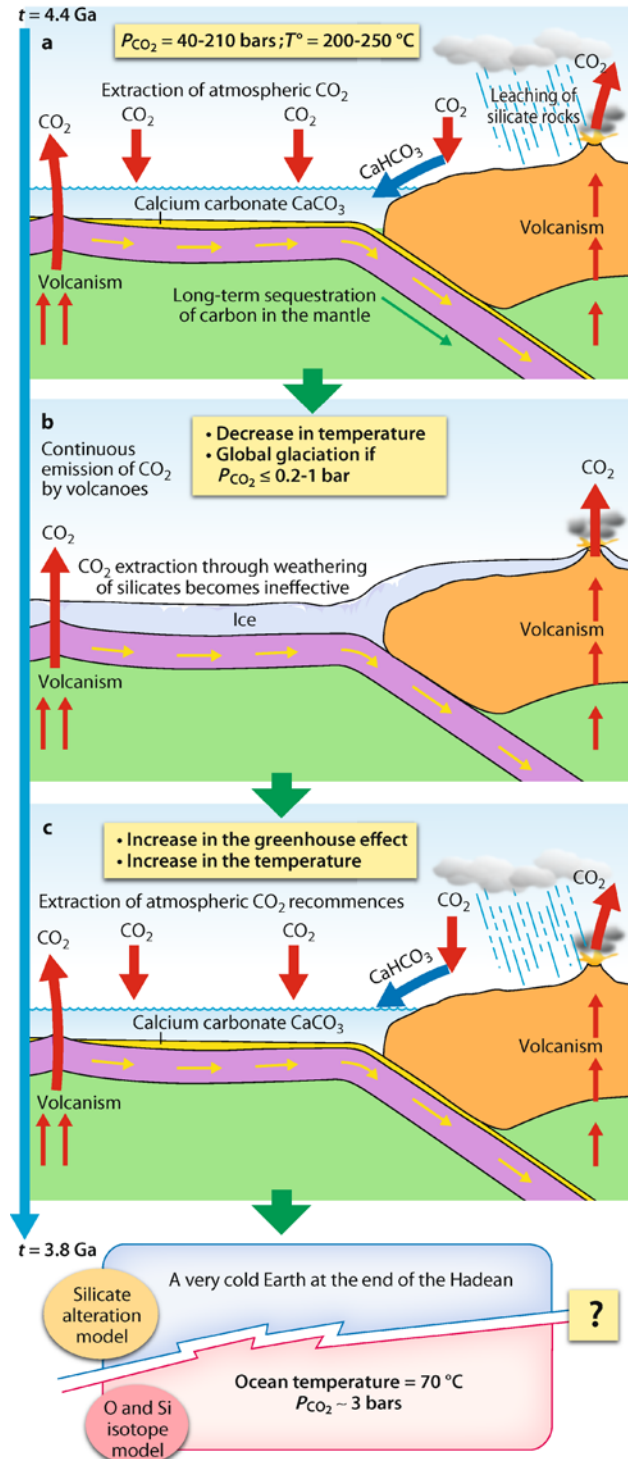
The overall outcome of these two reactions is that a molecule of atmospheric  $\text{CO}_2$  (or of  $\text{CO}_2$  dissolved in the ocean) was trapped in a mineral (carbonate). To prime this  $\text{CO}_2$  “pump”, all that was required was that liquid water should be available at the planet’s surface. However, a very significant reduction of the atmospheric partial pressure of  $\text{CO}_2$ , required a sufficient cooling of the oceanic crust such that subduction was able to start, allowing the recycling of significant volumes of carbonate sedimentary rocks into the mantle, and consequently the long-term sequestration of the carbon that they contained. The Jack Hills zircons show us that fragments of continental crust, undoubtedly generated in a subduction geodynamic environment, existed since 4.4 Ga, and in huge amounts from 4.2–4.3 Ga onwards. From then on, the atmospheric  $\text{CO}_2$  partial pressure decreased, leading to a diminution of the greenhouse effect, such that the temperature at the surface of the Earth became compatible with life. Depending on the scenario adopted, this process took between 10 and more than 100 Ma. However, once the subduction process had become active, trapping of  $\text{CO}_2$  in carbonate sediments could have become so efficient that the average surface temperature of the Earth was capable of dropping below the fateful threshold of 0 °C, resulting in a global glaciation (the “Snowball Earth”). Given the low luminosity of the young Sun (about 75 per cent of its current value, [Box 6.2](#)), only an efficient greenhouse effect could then have prevented such a global glaciation. The most recent atmospheric models predict that the  $\text{CO}_2$  partial pressure, below which such an event could have occurred on Earth, would be between 0.2 and 1 bar. It must be noted that at present the total atmospheric pressure is 1 bar, of which only  $3.5 \times 10^{-4}$  bar is  $\text{CO}_2$ . Nothing can rule out the fact that such glacial episodes may indeed have taken place.

It should, however, be noted that on a totally frozen Earth, trapping of  $\text{CO}_2$  by alteration of silicates becomes ineffective, because this gas continues to be emitted continuously through volcanic activity. This then induces an increase in  $\text{CO}_2$  atmospheric content and a correlated increase of the greenhouse effect, which enables the Earth to rapidly escape – on a geological time-scale – from the global glaciation. The  $\text{CO}_2$  pump responsible for the altera-

tion of silicates could then restart, eventually leading to a new “Snowball Earth” episode, or in a less extreme fashion, to variation around a state where the two constraints remained in balance (■ Fig. 3.11).

We can therefore see how climate regulation through carbon dioxide and episodes of glaciation – partial or total – could come to arise on the Hadean Earth. Under such conditions, it is hard to see how temperate climatic conditions could have been maintained on the Earth's

■ **Fig. 3.11 Regulation of the surface temperature of the Earth through weathering of silicate rocks.** From 4.4 Ga, as soon as liquid water was available at the surface of our planet, leaching of silicate rocks absorbed atmospheric  $\text{CO}_2$  (a). The decrease in the partial pressure of atmospheric  $\text{CO}_2$  caused a reduction in the greenhouse effect and consequently, a reduction in the surface temperature, which could have resulted in a global glaciation. However, on a completely frozen Earth, trapping of  $\text{CO}_2$  would be ineffective, while the gas was continuously released by volcanoes (b). Then the  $\text{CO}_2$  partial pressure would have risen, together with the greenhouse effect and the surface temperature (c). Models based on this system of exchange between silicates and carbonates predict that, at the end of the Hadean, about 3.8 Ga ago, the Earth was extremely cold worldwide... which contradicts the analysis of oxygen and silicon isotopes in rocks of that period, which points to an ocean temperature of about  $70^\circ\text{C}$ .



surface. In this scenario, the temperatures hospitable to life could only have arisen very temporarily and episodically, either during the initial cooling corresponding to the period when the CO<sub>2</sub> started to be trapped through silicate alteration, or in the wake of reheating possibly induced by large-size meteoritic impacts. However, a frozen Earth is not an insurmountable obstacle to the emergence of life. Indeed, liquid water may circulate beneath an ice-cap, and this latter is even liable to melt at the surface when close to regions with a high geothermal flux. In addition, the possible presence, within the ice, of pockets of water laden with organic substances and remaining liquid at low temperature could equally have become a very propitious factor in the development of life.

But, in fact, the problem does not lie there. Rather, it arises from the fact that this vision of an extremely cold Earth at the end of the Hadean is in complete contradiction with the values found for palaeotemperatures of surface ocean water. These latter have been determined from oxygen- and silicon-isotope measurements in sedimentary rocks dated from the very beginning of the Archaean, i.e., 3.8 Ga: these temperatures are, in fact, of about 70 °C, which, depending of the models used, corresponds to a greenhouse effect resulting of an atmospheric CO<sub>2</sub> partial pressure of about 3 bars. We are forced, therefore, to recognize that several elements and clues are missing when studying such a distant period in the Earth's history...

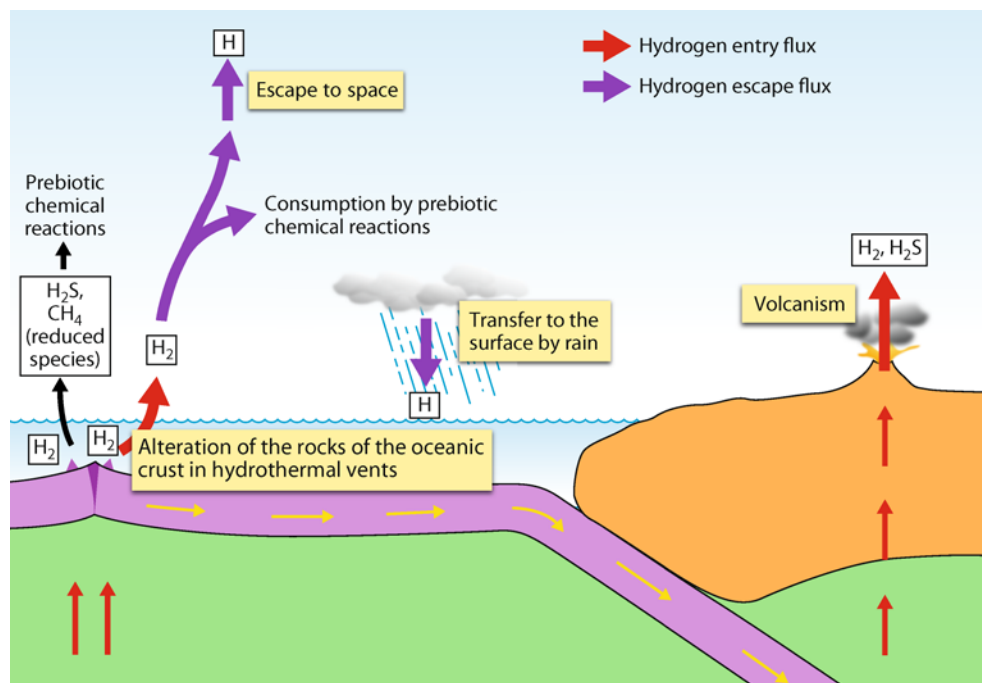
How can we explain this hiatus? A first hypothesis is that we can imagine that the CO<sub>2</sub> trapping through silicate alteration at the bottom of the oceans could have been less effective than in the scenario just described above. A strong cooling leading to glaciation would then require large-scale alteration of emerged continents. A second hypothesis, which we shall discuss again in details in Chap. 6, consists in assuming that the high temperatures that prevailed during the early Archaean resulted from the metabolism of methanogenic organisms capable of enriching the atmosphere in powerful greenhouse gas. As such, life would have already been present by 3.8 Ga and its action on the environment would have caused the first drastic alteration in the atmosphere composition. Another hypothesis might be the abiotic production of atmospheric methane. Nevertheless, both the early existence of methanogenic *Archaea* and the effects of high atmospheric methane content (■ Box 6.2) are the subject of debate. Undoubtedly, years of research will be required before being able to decide, all the more, as we shall see in Chap. 6, the situation in the Archaean is by no means simpler, because once again we do not have any direct record of the atmospheric composition at that time.

In the end, all that we can say about the composition of the atmosphere between 4.4 and 2.5 Ga solely rests on models that are liable to significantly evolve and change as our overall picture of the primitive Earth improves.

### A Critical and Debatable Question: The Hydrogen Content

Although from a strictly quantitative aspect, hydrogen is a minor component of the atmosphere, this element nevertheless remains an essential player in the evolution of the Hadean Earth. Indeed – and we shall return to this point in some detail later – the efficiency in the production of organic substances in the atmosphere is strongly dependent on its oxidizing or reducing characteristics or, in other words, its redox potential. An atmosphere that is relatively rich in hydrogen is reducing and forms an environment that is favorable to the synthesis of organic molecules whereas, conversely, a hydrogen-poor atmosphere is neutral from the redox point of view. The determination of the hydrogen content of the primitive Earth's atmosphere is thus an essential parameter for anyone who is trying to understand how our planet became enriched in organic molecules: a question that is not unconnected with that of the origin of life. Molecular hydrogen (H<sub>2</sub>) is released into the atmosphere through the serpentinization of the basalts of the oceanic crust, that is, through the alteration of their miner-





■ **Fig. 3.12 Hydrogen flux in the atmosphere of the Hadean Earth.** The composition of the atmosphere evolved until a stable state, where the hydrogen flux (and that of other reducing gases) entering and leaving the atmosphere were in balance. The significance of hydrogen escape to space has recently been revised downwards. As a result the atmosphere of the Hadean Earth was perhaps richer in hydrogen than thought, thus being more reducing.

als by high-temperature water in submarine hydrothermal systems, The reaction is described on p. 53 and involves the transformation of an iron silicate, fayalite ( $\text{Fe}_2[\text{SiO}_4]$ ), into silica ( $\text{SiO}_2$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ) and molecular hydrogen ( $\text{H}_2$ ). These contributions are difficult to quantify, but they were undoubtedly significant during the Hadean, in an environment where there was intense volcanic activity and thus efficient hydrothermal processes on the ocean floor (■ Fig. 3.12).

Even before its escape, hydrogen could have contributed to atmospheric chemistry by participating to the synthesis of reduced species ( $\text{H}_2\text{S}$ ,  $\text{CH}_4$ , etc.) which would have been transported to the outermost layers of the planet. The photolysis of  $\text{H}_2$  molecules, converted them into atomic hydrogen that would reach interplanetary space through simple gravitational escape. For a long time, it was assumed that this mechanism had played a major role in the evolution of the Earth's Hadean atmosphere. Nowadays, this idea is challenged.

Indeed, escape is more efficient the higher the temperature. For instance, on Earth today, because of the presence of molecular oxygen ( $\text{O}_2$ ), which absorbs solar ultraviolet radiation, the temperature of the atmosphere's outer layer (exosphere) is very high (about 1000 K) and the atoms of hydrogen that form there by photolysis of water primarily escape into interplanetary space. But if we consider that during the Hadean aeon, the upper atmosphere had a low oxygen content (limiting the absorption of ultraviolet radiation) and a high  $\text{CO}_2$  content (able to disperse the radiative energy received from the Sun), this would imply that the exosphere was probably far less hot than nowadays. The escape mechanism would then have been very much less efficient. Under such conditions, the atmospheric hydrogen content would have evolved towards a stable state where the entering and outgoing energy fluxes were balanced. In drawing up this balance sheet, it is worth noting that prebiotic chemistry initiated in the atmosphere (*see later*) could have consumed a significant amount of hydrogen, as well as of other reducing chemical species required for the formation of organic molecules.

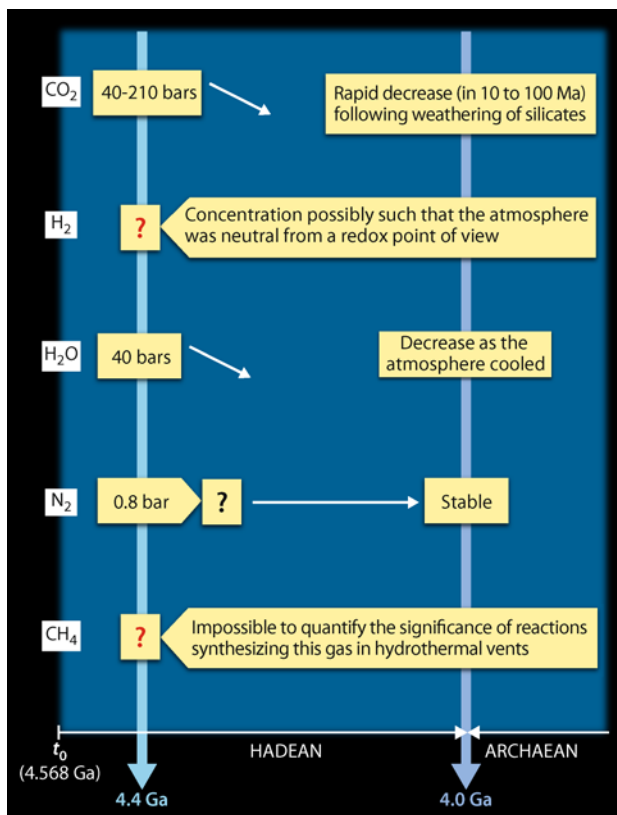
Be that as it may, we cannot exclude the fact that, contrary to what was believed, the Hadean atmosphere was not neutral, but was reducing.

### Water, Nitrogen and Methane

**Water.** The atmosphere's water content depends on the temperature that prevails at the Earth's surface. After condensation of the oceans, the huge amounts of atmospheric  $\text{CO}_2$  resulted in an intense greenhouse effect: the atmosphere was hot. As a result the partial pressure of water was raised (up to 40 bars), which reinforced the greenhouse effect. Subsequently, until the end of the Hadean, the global cooling caused by the alteration of silicates and the trapping of  $\text{CO}_2$  in carbonates, was accompanied by a decrease in the atmospheric water content. In addition, throughout this period, the presence of water in the atmosphere resulted in meteorological phenomena, in particular precipitation, which then, as today, led to variable atmospheric water content, depending on location and altitude.

**Nitrogen.** Usually, researchers consider that the partial pressure of  $\text{N}_2$  in the atmosphere has remained stable from the Hadean to the present day, where it amounts to 0.8 bar, due to early mantle degassing and other early contributions to the primitive Earth (see ► Chap. 2). But currently a significant amount of nitrogen remains trapped in the continental crust after burial of organic material originating from living beings. Nothing therefore excludes the fact that the initial  $\text{N}_2$  content of the atmosphere may have been twice or three times as high or, on the other hand, that the atmosphere may have been impoverished by the absence of biochemical processes converting organic nitrogen into  $\text{N}_2$ .

**Methane.** Like other hydrocarbons and even some lipids, methane could have been produced through the alteration of magmatic rocks in the Hadean oceanic crust by  $\text{CO}_2$ -rich



■ Fig. 3.13 The evolution of Earth's atmosphere between 4.4 and 4.0 Ga. All our understanding of the composition of the Hadean atmosphere rests solely on models that are susceptible to change substantially as our knowledge of the primitive Earth improves. The question marks on this diagram should therefore come as no surprise.

hydrothermal fluids (via Fischer-Tropsch reaction, *see later*). However, it is almost impossible to determine to what extent these reactions have been actually active and efficient between 4.4 and 4.0 Ga. This point is, however, a key point. Indeed, on the one hand, methane is a very powerful greenhouse gas (far more powerful than CO<sub>2</sub>) which could have contributed to prevent episodes of global glaciation, and, on the other hand, the hydrocarbons or lipids that were formed could (as we shall discuss later) have participated in the emergence or in the development of life.

## From the Atmosphere to the Bottom of the Oceans: Was the Earth Rich in Organic Matter?

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Oceans, continents, atmosphere, and climate: we now have a reasonably complete picture – even if there are still numerous dark areas – of the Hadean Earth. But there remains one essential critical question: was our planet already capable of sheltering life? Before trying to reply to this question, let us ask whether, in the scenario that we have just described, the chemistry of life and, in particular, the reactions that allow the synthesis of organic molecules that form the basis of living beings, could have taken place and, if so, where, and for the production of what kinds of molecules.

### Abiotic Chemistry or Prebiotic Chemistry?

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During the period that preceded the onset of biological evolution, simple organic molecules as well as more elaborate structures arose through a group of processes that are known as *prebiotic chemistry*. Behind this label are hidden the chemical pathways that could have led to the origin of life on Earth ... or elsewhere in the Universe. Organic matter and life ... to many of us, the link between the two seems to imply that they are inseparable. However, the formation of organic molecules is not necessarily synonymous with the presence of life. Organic matter is permanently synthesized in the interstellar medium, which is difficult to imagine as favorable to the emergence of life. Nevertheless, and perhaps because of the survival of vitalist ideas (■ Box 3.3), many people still consider the mere presence of organic matter as a clue of the presence of life. Imagine, for example, the consequences that would arise from the discovery of amino acids during a mission to a planetary body of the Solar-System. It is a good bet that this would rapidly be interpreted as a clue for either current or past life, whereas we already know that these compounds have been present for more than four billion years in some meteorites, objects, which as far as we know, never hosted life. This is why we make a distinction between prebiotic chemistry and *abiotic chemistry*, the latter covering the synthesis of organic matter that was produced in the past, and which is still produced today, under conditions that are not specially propitious for the emergence of life.

However, the matter is not that simple. First, because frequently the formation of organic matter on some bodies of the Solar-System or in the interstellar medium, is referred as “prebiotic chemistry”, while these places are most unlikely to host life. Second, because even the definition of “prebiotic” characteristics remains very subjective, because it is linked to the conditions under which the only example of life that we know – those on planet Earth – have developed.

The organic chemistry that will be described here is prebiotic, in the sense that it takes place in an environment where, at an indeterminate time and through mechanisms that are just as uncertain (*see* ► Chap. 4) some of the reactions that we are about to describe could not have occurred, in a context that was not linked to the development of living systems. In other

### Box 3.3 A Glimpse of the Evolution of Ideas About the Formation of Organic Matter

From antiquity until the end of the 18<sup>th</sup> century, vitalist ideas dominated: organic and mineral matter were fundamentally different, the former being always associated with a “vital force”. Things were to change in the 19<sup>th</sup> century. In 1828, the German chemist Friedrich Wöhler showed that urea (organic molecule) can be easily synthesized from ammonium cyanate (mineral). Subsequently, during the course of the 19<sup>th</sup> and then the 20<sup>th</sup> century, thanks to the development of organic chemistry, it was realized that the most complex biomolecules that are found in living beings were not inaccessible to laboratory synthesis techniques. In the last decades of the 19<sup>th</sup> century, the vitalist concepts were thus severely discredited. Nevertheless, it took nearly a century for the abundance of abiotic organic matter in the universe to be recognized and accepted. The presence of organic matter in certain meteorites, an assumption held by some 19<sup>th</sup>-century chemists (including Friedrich Wöhler himself, and also many others, such as the Swede Jöns Jacob Berzelius and the Frenchman Marcellin Berthelot, who examined the meteorites that fell in 1806 near Alès and in 1864 at Orgueil), was still seriously doubted in the first half of the 20<sup>th</sup> century. In particular, it took the analyses carried out after the fall of the Murchison meteorite in 1969, for there to be no possible argument about the matter.

Even today, the mineral world and the organic world appear to be utterly distinct – as witness the fact that organic chemistry and inorganic chemistry are still disciplines that are taught within separate, watertight compartments. This is undoubtedly because, in our terrestrial environment, the omnipresence of lifeforms

makes them appear as the almost unique source of organic molecules (whether past or present). However, the exploration of several objects in the Solar System (such as comets and Titan), as well as the progress achieved in identifying organic molecules within the interstellar medium, lead to the conclusion that the abundance of abiotic organic matter in the universe is a certainty. On the present-day Earth, the processes that produce such abiotic organic matter are difficult to detect, because of the overwhelming influence of lifeforms and because of the presence of oxygen (which, it is worth remembering, is not an element that favors the synthesis and stability of organic matter). However, it is possible that such processes do play a minor role in the synthesis of hydrocarbons through abiotic geochemical pathways.

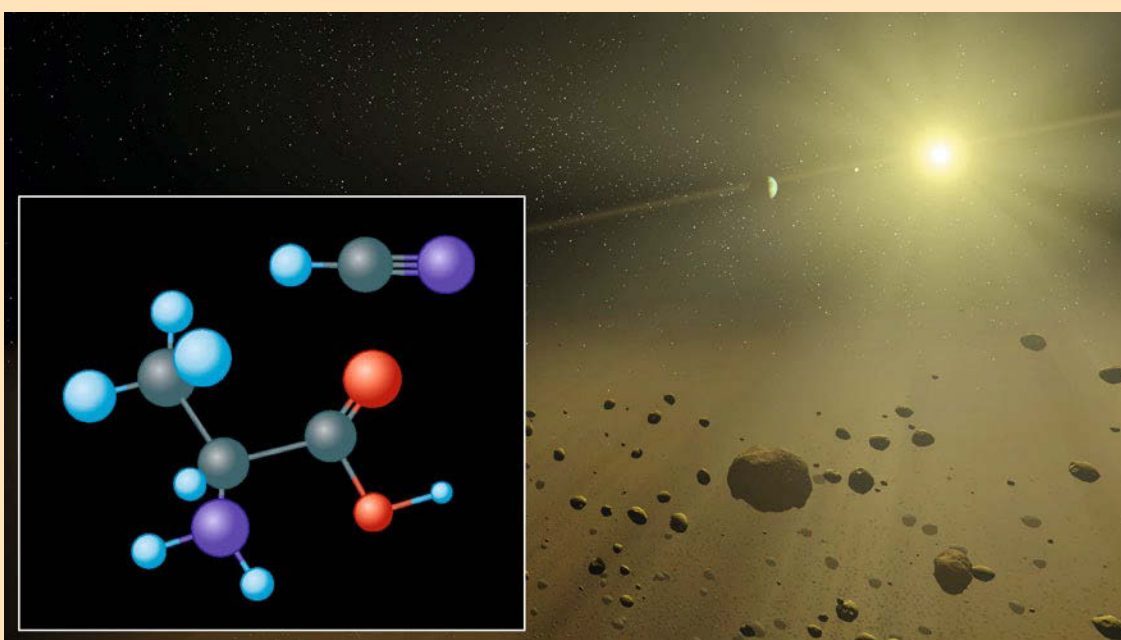
Let us return to the end of the 19<sup>th</sup> century. The exclusion of “spontaneous generation” by Louis Pasteur’s experiments accompanied the progressive disbelief in theories that assigned a “special character” to organic molecules. At the same time, these experiments ran counter to the idea that organic molecules formed in an abiotic manner could be the basis for the birth of life, because such a scenario undoubtedly formed *an exception to the impossibility of spontaneous generation*. These changes in scientific thought did, however, occur at the same time as the development of Darwinian theory which predicted the existence of a common ancestor to all living beings and thus raised the question of the origin of life. All these contradictions resulted at the beginning of the 20<sup>th</sup> century, that this question of the origin of life was, so to speak, taboo. At the beginning

words, certain reactions that we will discuss here also belong to the domain of abiotic chemistry, just as much in the interstellar medium as on Earth. So, this is almost a methodological or conventional necessity: because life arose on Earth, we shall term prebiotic chemistry, the abiotic organic chemistry that took place on Earth before the emergence of life.

## Organic Matter Likes Reducing Environments

Not all environments are favorable for the abiotic formation of organic molecules. And if there is one that is not favorable, this is undoubtedly, and paradoxically, that of the present-day Earth. As inhabitants of this planet, we empirically know that, on the present day Earth, organic molecules are unstable: a number of them oxidize, degrade, and may even burn in the presence of air. In fact, the formation of organic matter is strongly disfavored in an oxidizing atmosphere, oxygen-rich like that of the Earth nowadays. So, in such an environment, these are mainly the living systems that produce organic matter, because they have acquired, through biological evolution and at the price of a significant expenditure of energy, the capacity to carry out those reactions that are disadvantaged from a thermodynamical point of view. This is probably our experience of terrestrial life that leads us, more or less consciously,





■ **Fig. 3.14 Organic molecules in space.** Two organic molecules that are common in meteorites and in the interstellar medium, hydrogen cyanide, HCN, and an amino acid, alanine, are shown superimposed on an artist's view of planetary objects, accreting within the protoplanetary disk around a young star (see ► Chap. 1).

Indeed, contrary to a vitalist concept that is often unconsciously present in our minds, organic matter is not inseparable from life, and the Universe is rich with organic matter, formed under abiotic conditions.

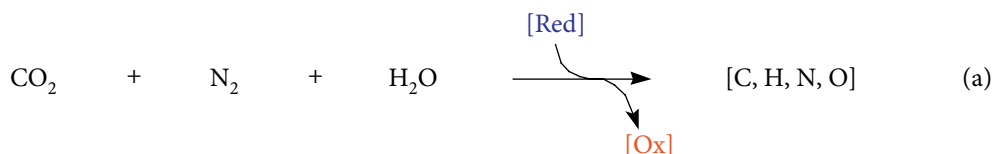
of the 1930s, Alexander I. Oparin and J. B. S. Haldane opened new avenues for research by formulating the theory – which, as will be understood, was daring at the time – that, in a reducing atmosphere, biomolecules formed by abiotic means could have supplied the first

living organisms with organic matter and energy. This intuition has been confirmed only in 1953, after Miller's experiment revealed the formation of amino acids from the action of electrical discharges in a reducing atmosphere (■ Fig. 3.17).

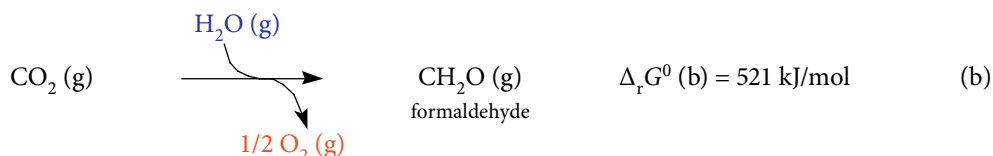
to associate life with organic matter. But the latter may be formed in a manner that is perfectly independent of living systems in reducing environments, where oxygen is absent.

Let us examine in greater detail the link between the formation of organic molecules and the reducing character of the environment. So doing, we will then come to understand why the question of the redox characteristics of the Earth's atmosphere during the Hadean is so significant for prebiotic chemistry.

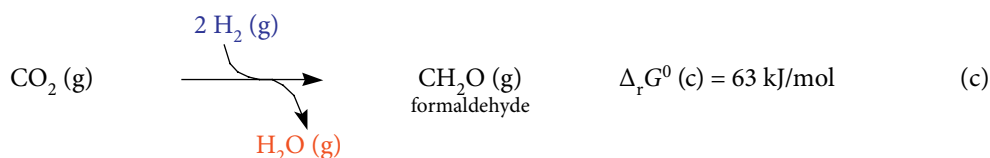
The organic molecules correspond to a combination of atoms of carbon, hydrogen, nitrogen and oxygen [C,H,N,O], in a systematically reduced form (richer in hydrogen) relative to a mixture of CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O. Using these three gases as the ultimate sources of carbon, nitrogen, hydrogen and oxygen for the formation of organic molecules requires not only a lot of energy but also a reducing agent, in accordance with the general reduction reaction (a):



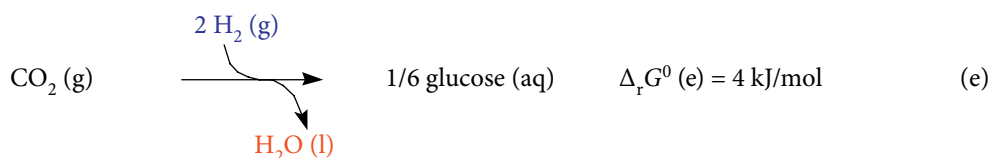
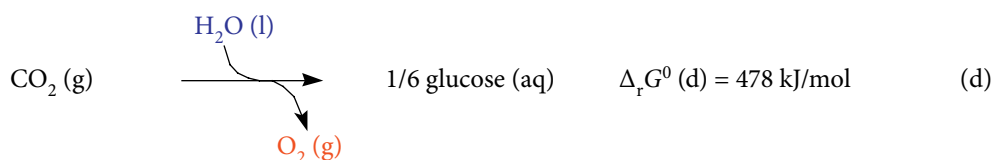
This reduction is most frequently energetically disfavored. This is quantified by using the standard Gibbs free energy of reaction,  $\Delta_r G^0$ , which expresses the possibility that a reaction may occur spontaneously: the more  $\Delta_r G^0$  is negative, the greater the likelihood of the reaction occurring; the more  $\Delta_r G^0$  is positive, the more the reaction is unfavored. For example, the formation, in a gaseous phase, of formaldehyde  $\text{CH}_2\text{O}$  (the simplest of carbohydrates: it is related to sugars) from  $\text{H}_2\text{O}$  and  $\text{CO}_2$  (b) is highly unlikely:



The synthesis of formaldehyde here is accompanied by the formation of oxygen from the decomposition of water. Replacing water by hydrogen as the hydrogen source – in other words, carrying out this synthesis in a more reducing environment – facilitates the reaction. This latter, although it remains unfavorable, benefits from the energy liberated by the formation of water, the amount of which, being very high, contributes to the reaction (c). On the contrary, in reaction (b), the conversion of the atom of oxygen from the water into dioxygen ( $\text{O}_2$ ) acts against the synthesis of formaldehyde due to its energetic cost.



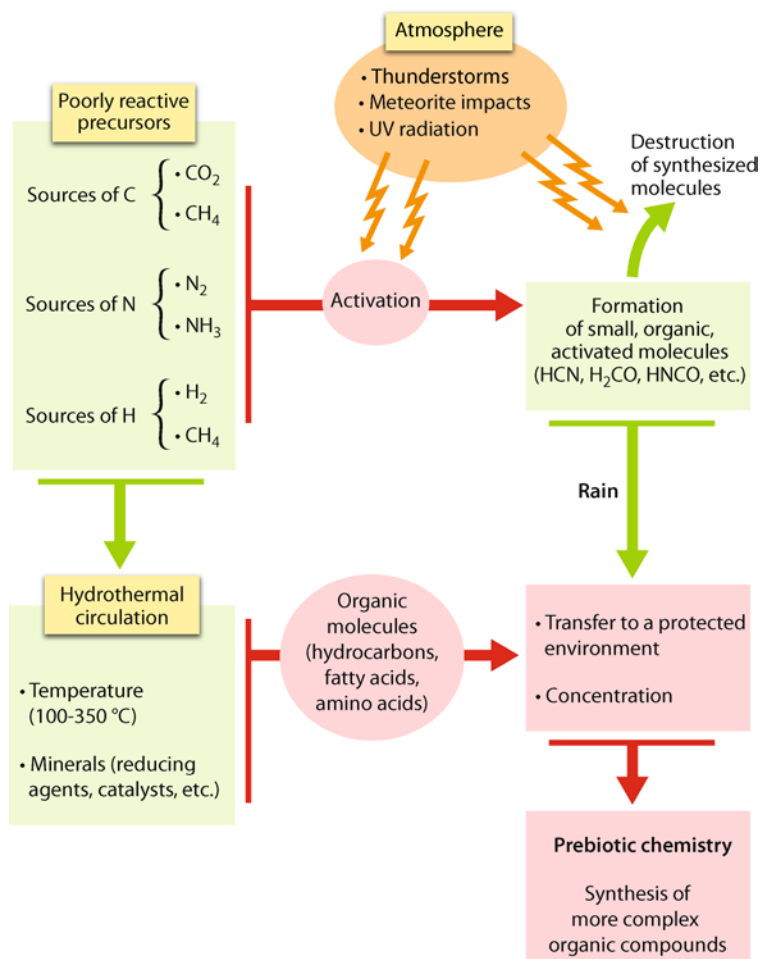
It is the same for the synthesis of glucose, which is energetically disfavored when it requires the conversion of water into oxygen (d), but the formation of which is, in theory, near thermodynamical equilibrium in the presence of a high hydrogen concentration (e). (In practice, this reaction is not, however, necessarily attainable through simple biochemical pathways.)



Of course, nowadays, the synthesis of glucose from  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (reaction d) is one of the most commonplace. But it is the prerogative of the living beings that possess a sophisticated photosynthesis equipment, which allows them to use the energy provided by light as the driving force and water as the source of hydrogen and consequently as a reducing agent. This optimum system is the result of a long biological evolution. Prebiotic chemistry was utterly incapable of attaining such a feat in the environment of the Hadean Earth. On the other hand, our present view of the Hadean environment is that of a reducing medium, which could have been far more efficient in synthesizing organic molecules.

## Heat or Radiation: Activators for the Synthesis of Organic Matter

Quite apart from the fact that it is dependent on the reducing nature of the environment (the thermodynamic factor), the synthesis of organic molecules from sources of carbon such as  $\text{CO}_2$  or  $\text{CH}_4$ ; of hydrogen such as  $\text{H}_2$  or  $\text{CH}_4$ ; or of nitrogen such as  $\text{N}_2$  or  $\text{NH}_3$  is not spontaneous. These precursors are themselves poorly reactive. Synthesis can, therefore, proceed only through some activation, either thermal in nature (through lightning during thunderstorms, through the impact of meteorites with the Earth, at hydrothermal vents, etc.) or photochemical in nature (provided that the photons should carry sufficient energy to make up for the bonds to be broken). Under such conditions, transient, highly reactive species are formed, and random recombinations yield small organic molecules within the activated mixture.



■ Fig. 3.15 Some of the conditions governing the prebiotic synthesis of organic matter. The precursors of organic matter present in a reducing environment are poorly reactive, whence the necessity for their activation. This process of activation may destroy the synthesized molecules, whence the requirement to transfer the reaction products into a protected environment, where a truly prebiotic chemistry may possibly take place.

However, these organic molecules are also sensitive to activation processes: if UV radiation is able to activating mixtures of simple gases, it also has a destructive effect on organic molecules. Similarly, in hydrothermal systems, these same molecules are easily destroyed by high temperature water (often 350 °C, or even more). To be preserved, these freshly synthesized molecules must therefore be isolated from the activation system; for instance, by condensation and rain in the atmosphere, or else by circulation in hydrothermal systems. From this point of view, the different methods of activation are not equivalent (■ Fig. 3.15).

Both the amounts and forms of energy brought into play and the time-scales of activation processes (fractions of a nanosecond for photochemistry, fractions of a second for electrical discharges, and much greater durations for hydrothermal circulations) will affect the nature of the molecules that are formed. In particular, the latter themselves will remain in an activated state if the duration of the activation is short when compared with the rate of the subsequent deactivation reactions, or of the return to an equilibrium state, as well as of the transfer rate. From this point of view, we could schematically say, that molecules formed in the atmosphere are still activated when they reach the ocean, and that they are therefore still reactive. For instance, they could directly take part in a proto-metabolism. On the other hand, molecules formed in hydrothermal systems are close to thermodynamic equilibrium and are no longer reactive, unless there is an external source of energy (for example the form that could be gained from reducing minerals originating from the mantle, see ► Chap. 6.)

In addition, any analysis of the productive or destructive nature of any activation process must take into account the efficiency of these transfers towards a protected environment, where a chemistry that could truly be described as prebiotic could develop. Such an environment would be likely to offer conditions suitable for the synthesis of the building blocks of life (biomolecules) and even for more complex assemblies. It may be noted that, in addition to this transfer, an effective prebiotic chemistry would call for a process of concentration (dilution in the ocean is of such a nature that it would make any subsequent constructive chemistry impossible, simply because any significant encounter between organic molecules would become highly unlikely, and that these latter would be fated only to degrade). It would at least require a sequestration of the molecules that had been formed within a limited space, as is the case with adsorption on the surface of a mineral (thus enabling interactions between them, and as a result, the formation of molecules of a more significant size).

## Prebiotic Chemistry on the Primitive Earth: Where and to What Ends?

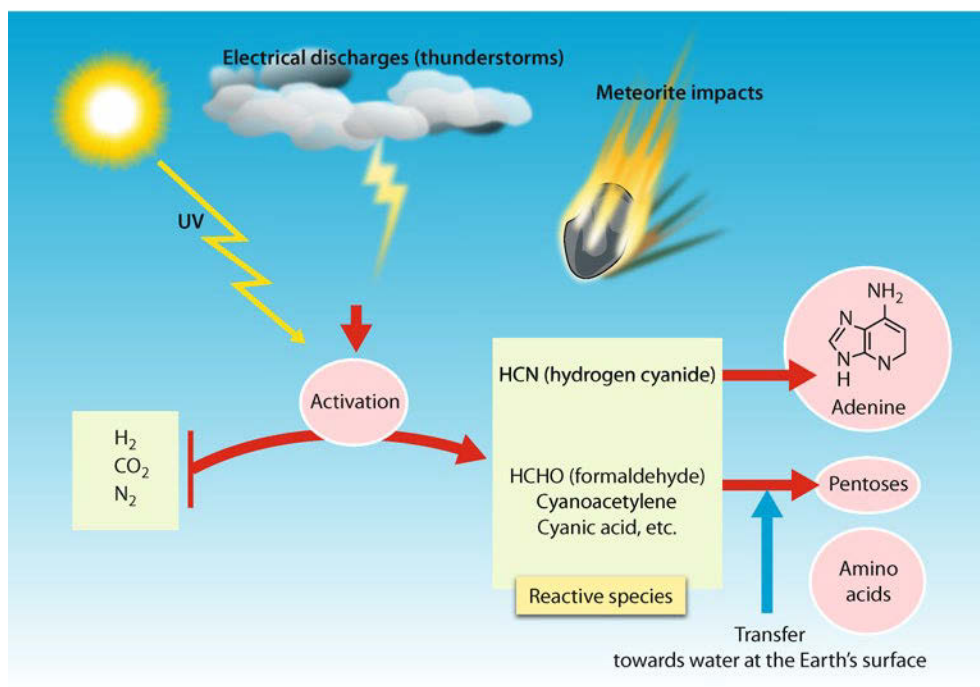
Let us now ask the following question: What were the environments on Earth between 4.4 and 4.0 Ga that possessed the three elements favorable for the synthesis of organic matter? Those three elements being: a reducing nature, the potential for activation of chemical precursors, and the possibility of transferring the products into a protected environment. There is no reason to believe that a unique process was involved, and, on the contrary, several paths were probably active in parallel.

### The Atmosphere

The setting where prebiotic chemistry could have started is the atmosphere, where gas molecules can be activated, either through the effects of UV irradiation, or through processes that momentarily raised the temperature, such as with electrical discharges linked to thunderstorm activity, or through the impact of meteorites (■ Fig. 3.16).

Following on from Alexander I. Oparin and J. B.S. Haldane who, in the 1920s, assumed that the atmosphere of the primitive Earth was reducing, in 1952 the chemist Harold Urey regarded it as primarily consisting of hydrogen  $H_2$ , methane  $CH_4$ , nitrogen  $N_2$ , and ammonia





■ **Fig. 3.16 Prebiotic chemistry in a reducing atmosphere.** Thermal or photochemical activation of mixtures of gases produces highly reactive species capable of subsequently forming amino acids, nitrogenous bases or sugars, and of initiating the formation of far more complex systems.

$\text{NH}_3$ . In an experiment that has become famous, in 1953 his student, Stanley Miller, showed that amino acids were indeed formed by thermal activation of a mixture of hydrogen, methane and ammonia (■ Box 3.4). The publication of these results led scientists to carry out similar experiments, which all showed that a wide range of biomolecules could be produced under these conditions. Among these biomolecules are some nitrogen bases found in nucleic acids. Space exploration proved the relevance of this process by demonstrating that even today, it is still at work in Titan's reducing atmosphere. All this work left its mark on the scientific community; indeed, from these researches, it became conceivable that organic molecules formed in an abiotic manner (or, more exactly, in a prebiotic fashion) could have been used as the source of both matter and energy for the first living beings (■ Box 3.3 and ► Chapter 4).

In fact, for chemists, the activation of gaseous mixtures by UV irradiation or by electrical discharges provided at least two “advantages” in terms of organic synthesis. On the one hand, chemical species that are produced under these conditions by recombination of atoms, ions or radicals (hydrogen cyanide HCN, cyanoacetylene  $\text{C}_3\text{HN}$ , isocyanic acid HNCO, formaldehyde HCHO, other aldehydes, etc.) are very reactive. Thus they could form amino acids, nitrogenous bases (such as adenine) or sugars (such as pentoses), through polymerization of hydrogen cyanide or formaldehyde, thus initiating the formation of far more complex systems, whose study is, nowadays, a major issue in prebiotic chemistry. On the other hand, the lifetimes of these species was sufficiently long for them to be transferred from the atmosphere to the ocean or the ground.

Nevertheless, the theory according to which, on the primitive Earth, the atmosphere was a favorable environment for the prebiotic synthesis of organic molecules has long been neglected by researchers. The composition of the atmosphere proposed by Urey was very quickly disputed, and a consensus arose around the idea that the atmosphere was neutral as far as redox was concerned, and that it primarily consisted of  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Under such

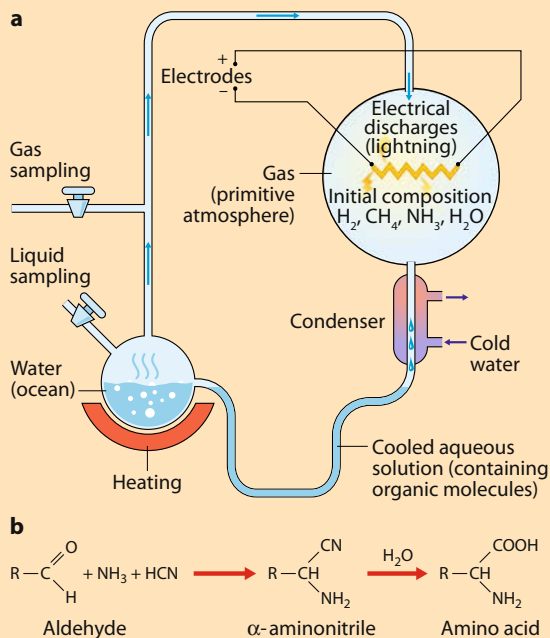
### Box 3.4 The Miller-Urey Experiment

In 1952, the chemist Harold Clayton Urey accepted the idea, advanced at the beginning of the 1930s by Alexander Ivanovich Oparin and John Burdon Sanderson Haldane that the Earth's primitive atmosphere was reducing. He assumed that the latter consisted of hydrogen, methane, nitrogen and ammonia, and theorized that activation of such a system could lead to the synthesis of organic molecules. In 1953, his young student Stanley Miller wanted to test this hypothesis. He devised the equipment shown diagrammatically in Fig. 3.17a. He filled it with a gaseous mixture of hydrogen, methane and ammonia, then brought the aqueous phase (initially containing distilled water, which to a certain extent, mimicked the ocean) to boiling point, thus creating a steam flow. Then, the gaseous mixture was activated by electrical discharges, simulating lightning. Very soon, he identified amino acids among the reaction products. This experiment caused quite a stir because it demonstrated that the synthesis of the basic components for life from simple precursors ( $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{NH}_3$ , and  $\text{CH}_4$ ) was possible by simulating conditions on the primitive Earth. It thus became conceivable that biomolecules formed by an abiotic method could have provided the first living organisms with organic matter and energy.

The amino acids are synthesized in aqueous solution through the Strecker reaction. In this process,  $\alpha$ -aminonitriles (AN) are synthesized from the aldehydes (A) and hydrogen cyanide (HCN) formed in the gaseous phase by electrical discharges and ammonia. These intermediate products are subsequently hydrolyzed into  $\alpha$ -amino acids (AA) (Fig. 3.17b).

Because of progress in understanding the formation of the Earth's gaseous envelope, no one now supports,

as Urey did at the time, the idea that the primitive atmosphere consisted mainly of methane, ammonia, carbon monoxide and water. But the main conclusion of this Miller-Urey experiment remains valid for less reducing ( $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ) or completely neutral ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ) mixtures: amino acids may be formed, though with varying efficiency, by abiotic pathways, as the result of the activation of the primitive atmosphere.



**Fig. 3.17** a. The Miller-Urey experiment: a schematic representation of the equipment. b. The Strecker reaction.

conditions, it was long believed that prebiotic synthesis would have been a very inefficient process. But in the last few years, two new pieces of information have returned atmospheric prebiotic synthesis to the foreground.

The first of these is that the atmosphere remained reducing over quite a long period of time, because, as has been explained earlier, the hydrogen escape to space was overestimated. Second, was a re-examination of the production of organic matter from atmospheres that are neutral from a redox point of view. The experimental approach that concluded that this pathway was inefficient has been called into question by work published in 2008. The “productivity” of gaseous mixtures consisting of  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , has been significantly re-evaluated, even though it still remains lower than that of highly reducing systems ( $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ).

We may therefore conclude that the production of organic molecules did definitely take place in the terrestrial atmosphere during the whole Hadean (except, perhaps, before the condensation of the oceans, because, due to the high temperature and the water-vapor pressure, the lifetime of molecules that had been formed was probably limited), where it could have fed prebiotic chemistry. It may well have equally taken place subsequently, until the end of the

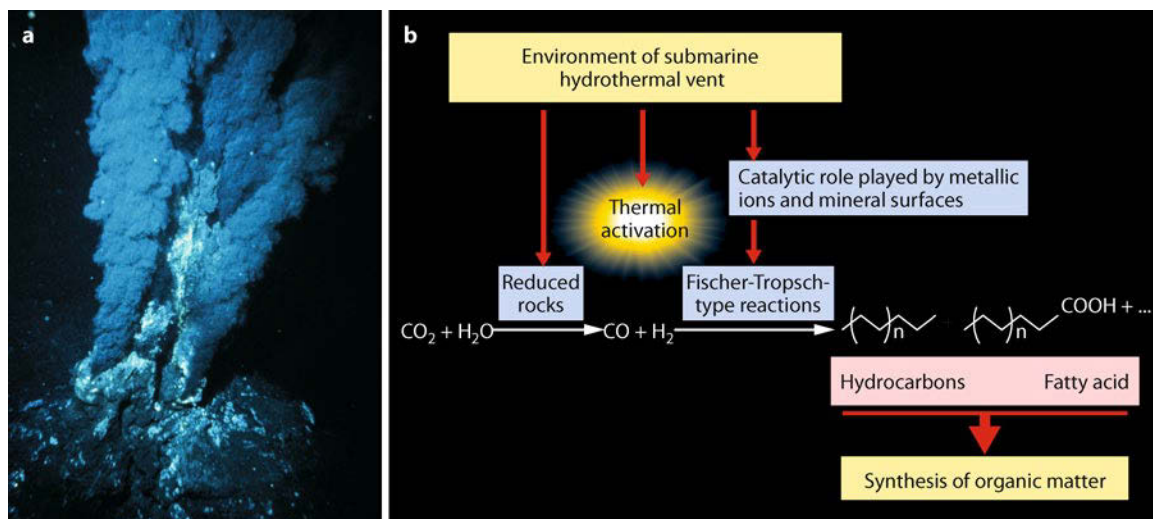
Archaean (2.5 Ga) marked by the increase in the atmosphere's oxygen content, or else, until it was overwhelmed by the extent of production by autotrophic organisms.

### Hydrothermal Systems

The debate relative to the reducing nature of the primitive terrestrial atmosphere and to the efficiency of the formation of organic molecules from neutral atmospheres is not yet completed. But even if one sticks to the hypothesis that prevailed in recent decades that a rapid escape of hydrogen to space led to a non-reducing atmosphere and on the idea that the formation of organic molecules from neutral atmospheres is inefficient, other environments could have been favorable for organic synthesis. Indeed, all the assumptions presented above, only take into account the most superficial layer of the planet. As it is still the case today, the mantle of the Hadean Earth – as well as the oceanic crust derived from it – was reducing, on the whole. The synthesis of organic matter was thus possible in the close vicinity of the hydrothermal systems; indeed, these latter are located at the interface between seawater and the magmatic reducing rocks (with a high content of  $\text{Fe}^{2+}$ ) of the oceanic crust (■ Fig. 3.18).

As seen earlier, hydrothermal circulation leads, initially, to the alteration of the rocks of the oceanic crust (serpentinization) and to the release of hydrogen. In addition, in this hot and reducing microenvironment, the  $\text{CO}_2$  dissolved in seawater may be reduced through reactions that involve liquid water (in Fischer-Tropsch-type reactions), which are likely to produce organic molecules such as hydrocarbons and fatty acids. Amino acids may also be formed in such systems.

It is often considered that the wealth of minerals and metallic ions in hydrothermal vents favors the catalysis of these reactions. According to scientists who are studying this type of organic syntheses, the surface and the pores of the minerals do thus play a prominent role. They may, simultaneously, act as catalysts and enable the adsorption of reaction products, thus preventing too great a dilution of the formed chemical species – whereas the equilibrium concentrations are very low: of about  $10^{-6} \text{ mol.L}^{-1}$  for  $\alpha$ -amino acids – and thus favoring subsequent reactions before the molecules are dispersed in the ocean. This adsorption in a local



■ Fig. 3.18 A present-day hydrothermal vent (a) and the prebiotic reactions (Fischer-Tropsch reactions) that could have taken place in such an environment between 4.4 and 4.0 Ga (b). Such reactions could, for example, produce hydrocarbons or fatty acids.

It should be emphasized, however, that it is very difficult to determine to what extent these reactions were actually active on the Hadean Earth.

mineral environment would equally protect the molecules formed against the high temperatures that prevail in hydrothermal systems.

As we shall discuss in the next chapter, organic synthesis at these hydrothermal vents is considered as playing a crucial role by those chemists, biologists and geologists who subscribe to the view that life arose in such an environment, and that the first living systems were autotrophic, that is, that they synthesized their organic matter from mineral molecules. However, we have already emphasized, that it is very difficult to determine to what extent the Fischer-Tropsch reactions were actually efficient. It must also be noted that, within the context of the theory of an autotrophic origin of life, the redox gradient between rocks originating in the mantle and the atmosphere-ocean system does itself constitute a source of energy potentially capable of initiating organic chemistry processes. It could initiate a precursor of a metabolism independent of being an abiotic source of organic matter.

### Meteorites

Let us leave there, the submarine depths for considering a last potential source of organic molecules that could have seeded the Hadean Earth. This source is not hiding in the water, nor in the atmosphere, but ... in space. Indeed, we have already stressed this point: the interstellar medium is a site where organic matter is synthesized and perforce by abiotic paths. Thanks to radiotelescopes and spectroscopy (that is to say, the study of the detailed characteristics of the light that is emitted or absorbed by an object), more than 150 organic species have been detected in the interstellar clouds of gas and dust, from which stars are born (see ► Chap. 1). Most of these are very simple (CO, HCN), but some may contain more than a dozen atoms (such as  $\text{H}(\text{C}\equiv\text{C})_5\text{CN}$ ). In fact, nearly the total amount (99.9 percent) of the organic matter present in the universe is concentrated within these clouds.

Irradiation is the phenomenon that underlies these organic syntheses. Indeed, even before these clouds collapse and are transformed into stellar nurseries, the interstellar medium is exposed to the intense cosmic radiation, which causes the breakdown of simple molecules present in a gaseous state, and leads to the formation of isolated atoms, free radicals, and ions. The latter are then involved in numerous chemical reactions that are studied thanks to theoretical chemistry methods, which appear as perfectly appropriate for computing the progresses of chemical reactions that take place under vacuum.

The surface of grains of dust and ice also plays a significant role in the construction of organic species. Indeed, the energy released during the synthesis of these molecules – which would be such as to cause their rupture if it were not removed – may dissipate within the solid body, which is at a very low temperature (around 10 to 50 K). It is, moreover, likely that when they attain a significant size, the molecules remain inaccessible to observation, because they are trapped within the particles (in particular within ices), whereas any possibility of detection requires their presence in a gaseous state.

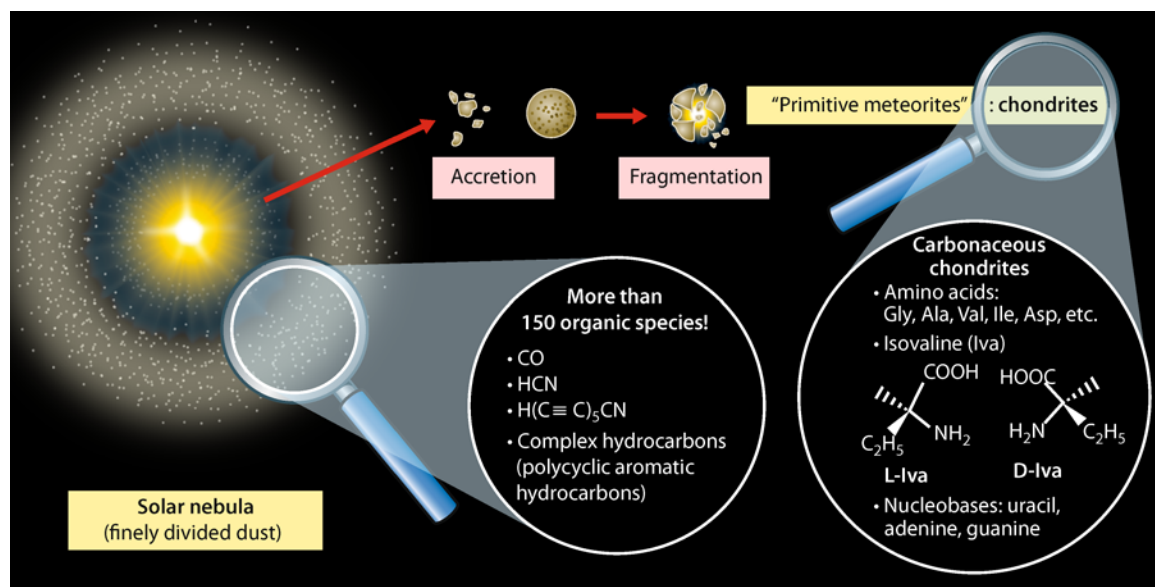
The nebula within which our planet was born (the protosolar nebula) was the site of such an organic synthesis. In the outer regions of the nascent Solar System, the molecules synthesized were subsequently incorporated into comets, whereas in the inner regions, they were involved in the accretion of planetesimals, of which meteorites are the present-day representatives (see ► Chap. 1). The meteorites formed in this way and rich in organic matter are known as carbonaceous chondrites. Although accretion releases heat, the organic molecules included in objects the size of the precursors of the carbonaceous chondrites, could have been simultaneously spared from excessive heating and could have simultaneously encountered liquid water, which would have allowed them to evolve towards families of molecules such as the amino acids. Indeed, these meteorites contain an extremely wide range of organic molecules among which amino acids are well represented as well as alkyl derivatives on the  $\alpha$  carbon, such as isovaline (Iva), whose  $\alpha$  carbon carries a methyl group and an ethyl group (Iva is absent from the set of amino acids encoded by life.)

Both L and R optical isomers of these amino acids have been detected in carbonaceous chondrites. However, the analysis of one of them – the Murchison meteorite, which was collected immediately after its fall in Australia in 1969 – has delivered an extremely intriguing result: The L and R forms are not present in equal amounts. Should this asymmetry – the origin of which is unknown – be seen as an explanation for the fact that the proteins in the living world consist solely of amino acids of the L type (they are “homochiral”)? This is what some researchers have suggested. Be that as it may, it is obvious that the organic matter that survived the fall of meteorites and comets onto the primitive Earth provided a recurring source of basic organic building-blocks, which could have been used subsequently for pre-biotic chemistry.

## Was a Niche for Life Available as Early as This?

At this stage in our story, let us draw up a final summary of the main characteristics of the Earth between 4.4 and 4.0 Ga. First, we find liquid water, that is to say one of the key ingredients for the chemistry of life (■ Box 3.5). Then there are continents, which are probably sufficiently stable to have been altered by erosion. And finally, the Hadean Earth was continuously seeded by the addition of organic matter, whether endogenous – that is synthesized on Earth either from the atmosphere or from submarine hydrothermal vents (or both), - or exogenous, that is the organic materials synthesized in space and delivered to the Earth through the falls of carbonaceous chondrites.

Our ignorance of the diverse range of chemical processes that took place on Earth at that time remains considerable, but there were undoubtedly a great many of them. The presence and availability of liquid water probably allowed the development of both molecular assemblies and reaction systems that were already complex, and as such precursors of “the” transition towards life itself. However, the Earth was certainly very active geologically, which implies continuous destruction of this organic matter by heat, either by sediment burying, or by circulation of seawater in hydrothermal systems and then of the dissolved



■ Fig. 3.19 Interstellar clouds and meteorites: extraterrestrial sources of organic matter for the primitive Earth. It is not just living beings that can synthesize organic matter. The gas and dust clouds

in interstellar space are the site of intense organic synthesis. It was the same for the protosolar nebula.



### Box 3.5 Are Water and Carbon Necessary for Life?

Theoretically, nothing precludes the possibility that life could arise in the absence of water or of a carbon-based chemistry. However, for most researchers, the presence of these two ingredients appears to be essential for the emergence of life. There are good reasons for this.

Carbon is the chemical element that most easily forms molecular scaffolds, because it is able to link with other atoms through several covalent bonds (up to four). This partly arises through its electronic structure (four electrons in its outer shell) and from its ability to become involved in strong covalent bonds with a large number of different atoms (unlike silicon, which is also tetravalent) (■ Fig. 3.20.). So it is not purely by chance that, among all the elements, the carbon is the one that displays the richest chemistry. In addition, this rather unique behavior is associated with a great abundance in the Universe: carbon is the fourth element by abundance in our galaxy, after hydrogen, helium and oxygen. Moreover, by far the majority of molecules detected in interstellar medium by radio astronomy are carbon based : this is not by chance!

Now water... How could one envisage a cell without liquid water? Based on this simple statement, it is often believed to be a self-evident fact that water is indispensable for life. But what is the true scientific basis for such an assertion?

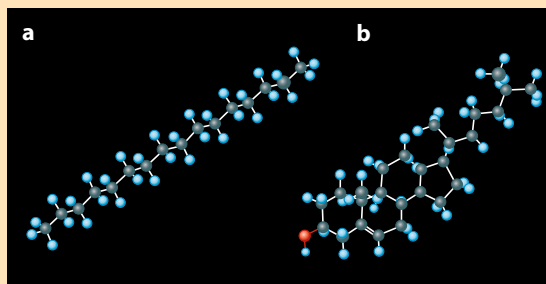
The property that leads some molecules that possess one hydrophobic (non polar) end and another hydrophilic (polar) end to link together into organized, microscopic structures (such as vesicles) can only be observed in a limited number of liquids. In liquid water, this property is due to the strong interactions (known as hydrogen bonds) between the  $H_2O$  molecules (it is these bonds that allow water to remain in the liquid state up to a temperature that is much higher than that of other molecules of similar molecular mass such as ammonia or methane, both of which are gaseous at ambient temperatures). Molecules or portions of molecules that cannot fit easily into this network of hydrogen bonds are repelled by water's structure, which leads them to link together. This occurs independently of the interactions – favorable or unfavorable – that they might otherwise establish between themselves. This type of hydrophobic organization not only governs the formation of membranes, but is equally an essential element in the folding of proteins as well as for the links between molecules in which the latter are involved (the interaction between an enzyme and its substrate, for example).

From this point of view, as we have already said, substitutes for water are few and imperfect. Among the chemical species whose synthesis under prebiotic conditions is plausible, only the formamide (methanamide) is able to give rise to the aggregation of hydrophobic molecules. However the simplicity of the water molecule associated with the abundance of oxygen and hydrogen

in the Universe leads to the logical conclusion that liquid water may be available in great amounts on a non-negligible number of Solar System bodies (and doubtless elsewhere); which is not the case with the other potential substitutes.

Other physical and chemical properties of water undoubtedly played a role in the emergence of life. First, this molecule may be found simultaneously in solid, liquid and gaseous form under moderate temperature conditions. A change in the water's state, either by transformation into vapor or by freezing in the form of pure ice is thus capable of very effectively concentrating solutes into the residual liquid. These concentration mechanisms, difficult to imagine in any other context than that of a change of state, will increase the probability of encounters for the dissolved molecules, thus leading to the production of larger-sized molecules. They are thus undoubtedly the determining factors in the formation of biopolymers. Moreover water possesses a high dissociative power (linked to its dielectric constant) which means that it is an excellent solvent for a great number of salts and, more generally, for chemical species carrying electrical charges. In addition, its structure based on a network of hydrogen bonds makes the proton transfer extremely rapid. This point is important because most of chemical reactions involving biomolecules imply proton migration. Biomolecules are thus more easily formed. Finally, water plays the role of chemical reagent in the numerous biochemical pathways involving hydrolysis of active species (ATP, for example). These metabolisms based on hydrolysis could also have played an important part in the emergence of life (■ Box 4.5).

All these properties mean that, to date, apart from water, no liquid appears to be able to provide, in any credible fashion, an environment favorable for the emergence of life. It is just the same for carbon. The water molecules as well as the carbon chemistry thus appear indispensable for life, although not sufficient by themselves.



■ Fig. 3.20 Examples of molecules based on a carbon skeleton: a saturated linear hydrocarbon consisting of 16 atoms of carbon (a); cholesterol (b).

species. Major meteorite impacts would certainly have also contributed to the destruction of organic matter (*see* ► Chap. 5). This means that we should think of prebiotic chemistry less as the progressive accumulation, over hundreds of millions of years, of a stock of organic matter, subsequently available “for” the appearance of life, but rather as a dynamical molecular system, completely renewed over a time scale of a few million years at the most, and within which complex processes took place. Some of those that led to the emergence of life were undoubtedly already active.

Very early in its history, perhaps from 4.4 Ga, or, more definitely, from 4.3 Ga (the time when the CO<sub>2</sub> pump had allowed the surface temperature to decline sufficiently), the Earth seems to have been ready to accommodate life: it was potentially habitable. However, no one knows – and doubtless no one will ever know – how much time was required for the emergence of life, nor even if it emerged “all at once” or whether it emerged repeatedly. In particular, even if the Hadean was not the hell that its name suggests (Hades was the Greek god who reigned over the underworld and the dead), and even if the Earth’s face gradually evolved during this period, this does not preclude the possibility that cataclysmic events similar to the Late Heavy Bombardment (*see* ► Chapter 5) did take place. Assuming that such cataclysms did supervene, nothing enables us to know whether life could have survived it.

So, if we do not know when and where life appeared, can we at least answer the question “how”? Like Russian dolls, every question raises another, and we must ask an all-important question: What is life? What is a living system? And – something that is not an independent question – how could such a system have been built without an architect? These questions lie at the heart of the next chapter.