Formation and Early Infancy of the Earth

Between 4.568 and 4.4 Ga: An Uninhabitable Planet?

Immediately after its formation, the surface of the Earth was particularly inhospitable: no continents, no liquid water, but instead, a magma ocean subjected to intense meteoritic bombardment. The period between 4.57 and 4.4 billion years before the present (4.57–4.4 Ga BP) nevertheless saw the progressive establishment of the environmental elements that, later, would allow both the prebiotic chemistry to begin, and the emergence of life.



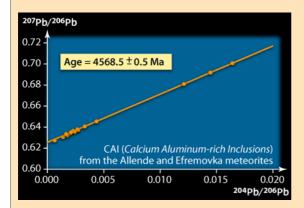
An artist's impression of the magma ocean that covered the very early Earth.

The Earth is a living planet: its surface is perpetually remodeled by plate tectonics as well as by the surface mechanisms of alteration and erosion. As a result, unlike "dead" bodies such as the Moon, where all the stages of their primitive history have been preserved, practically all the traces of the first 500 million years (Ma) of the Earth's history have been obliterated. We know almost nothing about either the mineralogical and petrographic composition, or the surface structure of the primitive Earth.

The oldest rocks currently known outcrop in Canada. They are the Acasta gneisses, dated to 4.031 Ga, and the Nuvvuagittuq greenstone belt, whose age is greater or equal of 4.0 Ga ($see \triangleright Chap. 6$). Only a few minerals, zircon crystals ($ZrSiO_4$), recently discovered at Jack Hills in Western Australia, are older (4.404 Ga, $see \triangleright Chap. 3$), but the rocks that contained them have been eroded away and have completely disappeared long ago. The period of time between the Solar System's " t_0 " (4.568 Ga, $see \triangleright Chap. 1$ and below) and the origin of the Acasta gneisses (4.031 Ga), has been called the Hadean aeon. This chapter will concentrate on the first 170 million years of the Hadean, up to the time when the Jack-Hills zircons crystallized, thus corroborating the presence on our planet of a continental crust and liquid water ($see \triangleright Chap. 3$). In the absence of tangible markers such as rocks or minerals, we shall try to recon-

Box 2.1 The Age of the Earth

Determining the age of the Earth has always been one of Mankind's preoccupations. The first attempts during the Middle Ages, were based on biblical texts and on the lifetimes of successive patriarchs. They led to the conclusion that our planet had been formed 4000 years B.C. – James Ussher (1581–1656) even calculated that the Earth had been created on 23 October 4004 B.C. (but without specifying the time of day!) It was only in the 18th and 19th centuries that scientists such as Georges-Louis Leclerc, Comte de Buffon (1707–1788) or Lord Kelvin (1824–1907) tried a physical approach. Assuming that the Earth formed as a



■ Fig. 2.1 (207 Pb/ 206 Pb) versus (204 Pb/ 206 Pb) isochron diagram for CAI (Calcium Aluminum-rich Inclusions) extracted from the Efremovka and Allende carbonaceous chondrites (■ Box 2.2 and ■ Fig. 2.6 for the description of the dating method). In such a diagram, the age is proportional to the slope of the straight-line isochron. Here, the calculated age, is 4568.5 \pm 0.5 Ma; by convention, this age is considered to be the starting point, "time zero" (t_0), for the formation of the Solar System. (After Bouvier et al., 2007.)

red-hot body and by calculating the time required for it to cool, Kelvin concluded that our planet was between 20 and 400 Ma years old. At the same period, basing their view on the thickness of sedimentary deposits, geologists dated the formation of the Earth as between 3 Ma and 3.5 Ga. The real revolution did not appear until the 20th century with the establishment of dating methods based on the radioactive decay of certain natural elements such as uranium (Box 2.2).

These so-called "absolute" dating methods are capable of attaining an accuracy better than 1 Ma on ages over 4500 Ma. The problem is then one of knowing exactly what event is being dated. In the case of a granite body, for example, is the age obtained that of the melting event that generated the granitic magma? That at which magma was emplaced? Or its age of crystallization? In fact, the isotopic clock will trigger when the object to be dated ceases to exchange isotopes with its environment (gas, fluids, other rocks, etc.), that is, when it starts to behave as an isolated system. Such exchanges operate through chemical diffusion, a mechanism whose rate (and thus efficiency) is strongly temperature dependent. What is known as the closure temperature for an isotopic system is the temperature below which the rate of diffusion of the isotopes under consideration becomes too low to allow redistribution (homogenization) of the parent and daughter isotopes. In fact, most of the ages measured by long-period isotopic systems are crystallization ages or cooling ages. In other words, what we are measuring is the time that has passed since the system dropped below its closure temperature.

In the case of the age of the Earth, the problem is complicated by the fact that, as we have seen in Chapstruct the early Hadean history of our planet from the data given by global geochemistry, the study of meteorites, and comparative planetology.

Before starting on this history, it seems useful to define as clearly as possible the chronological landmarks that will be used. By convention, astronomers and geologists are in agreement with regard to an initial time (t_0) that they have adopted as being the age of the Solar System. We note that this age of 4.568 Ga, has been measured from refractory inclusions (the CAI, *Calcium Aluminum-rich Inclusions*) inside carbonaceous chondrites; the CAI are, at present, the most ancient, dated materials in the Solar System, which condensed at high temperatures (> 1800 K) from the gases in the primitive planetary nebula ($see \triangleright$ Chap. 1 and the box below). It is, however, necessary to remember that all the stages of stellar formation occurred before t_0 .

It was only after t_0 that the planets began to take shape, through successive collisions between small bodies. These collisions extended over a period of several million years in the case of the giant planets and probably over several tens of millions of years for the Earth. This phase in the construction of the planets, often called the accretion phase by geologists, was not therefore a punctual event, but rather lasted a long period of time, whence the difficulty in

ter 1, its formation was not some instantaneous phenomenon, but was, on the contrary, spread over several tens of millions of years.

In a rather arbitrary manner, purely by convention, the age of the carbonaceous chondrites is ascribed to the Earth. These meteorites have, in fact, not undergone any differentiation, and possess the same composition as the solar photosphere: They are primitive meteorites formed early in the Solar System's history. Moreover, in general these meteorites are of small size (when compared to the planets) such that they may be considered to have cooled extremely rapidly. These carbonaceous chondrites do not just consist of chondrules in a matrix, but also contain refractory inclusions that are rich in calcium and aluminum, known as CAI (Calcium Aluminumrich Inclusions). These inclusions are thus older than the chondrules and the matrix (because they condensed at higher temperatures). The CAI are among the oldest materials currently known in the Solar System. Extremely precise measurements using lead isotopes have enabled the chondrules to be dated to 4564.7 \pm 0.6 Ma and the CAI to 4568.5 ± 0.5 Ma (Fig. 2.1). Thus, 3.8 Ma elapsed between CAI condensation and chondrule formation. This difference is in perfect agreement with the relative chronology of the different elements in carbonaceous chondrites, which shows that the CAI are older than the chondrules. An approach based on the now extinct radioactive isotope ²⁶Al (Box 2.2), confirms these results, because it gives an age difference of about 3 Ma.

It is this age of 4568 Ma that is considered to be "time zero" (t_0) for our Solar System (and thus for the Earth). It is, in fact, that of the first solid particles that condensed at high temperatures from the gases in the protoplanetary nebula. It is essential, however, to remember that this reference t_0 does not actually correspond to the age at which the Sun was formed, nor to that of the

Earth. Indeed, terrestrial accretion did actually occur through collisions between small bodies that formed after the condensation of the CAI and the chondrule formation, a process which could have required several tens of millions of years. It was only after this accretion had finished that the Earth could begin its life as an "autonomous" planet (see \triangleright Chapter 1). In addition, all the stages of stellar formation (in other words, the birth of the Sun) occurred before the condensation of the CAI, that is, before t_0 .

So the chronology based on extinct radioactivity (182 Hf, 26 Al, 53 Mn, 60 Fe, 41 Ca, 7 Be, etc...) does, in fact, refer to an event that precedes t_0 . Indeed, these isotopes could not have arisen except as the result of nuclear reactions earlier or, at the best, contemporary with the formation of the CAI (\bullet Box 1.3). We may recall that two mechanisms have currently been proposed to account for their presence in the most primitive meteorites:

- the explosion of a supernova, the shockwave induced the gravitational collapse of a presolar molecular cloud. With this hypothesis, a portion of the supernova's products is injected into the presolar cloud. This mechanism primarily concerns ⁶⁰Fe (which is extremely rich in neutrons, and thus, by necessity the result of explosive nucleosynthesis) and ²⁶Al. In this scenario, the time between the explosion and the formation of the CAI, (t_0), would be, at most, about one million years;
- powerful X-radiation of the protoplanetary disk by the extremely violent eruptions of the young Sun in its TTauri phase. This mechanism includes all the isotopes mentioned above, with the exception of 60 Fe. In this case, the CAI and $(t_{\rm o})$ would be more-or-less contemporary with the explosion.

giving a precise age for the planet's accretion. Be that as it may, it was only after this accretion had finished that the Earth could begin its life as an independent planet, and its geological history began.

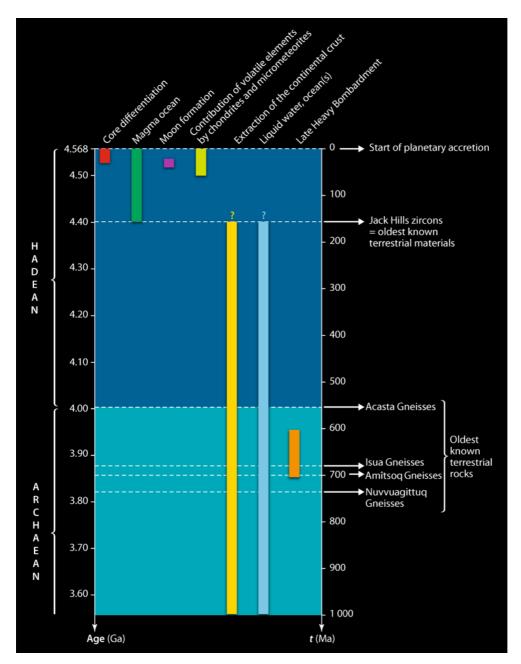
The Rapid Differentiation of a Metallic Nucleus: The Core

Unlike the formation of the continental crust, which as we shall discover later in the book (see ▶ Chaps. 6 and 7), has been extracted progressively from the mantle throughout the last 4.4 Ga, the segregation of the core (consisting of an iron/nickel alloy) and of the mantle (consisting of silicates), as shown in Chap. 3 (Fig. 3.2), was a far more rapid and dramatic event. The age of this differentiation has recently been measured using the extinct radioactivity of hafnium, ¹⁸²Hf (Box 2.2). In fact, ¹⁸²Hf decays into tungsten ¹⁸²W, with a half-life of 9 Ma, which implies that all the 182Hf would have disappeared less than 60 Ma after the beginning of the condensation of the Solar System (t_0) . Consequently, the ¹⁸²Hf/¹⁸²W pair is a chronological marker particularly well adapted to the earliest stages of the Solar System. In addition, it is particularly well suited to the study of the mantle/core differentiation, because Hf and W have contrasting geochemical behaviors: W is a siderophile element, which means that it concentrates within a metallic phase, such as the core, whereas Hf is lithophilic, and concentrates within a silicate phase such as the mantle. If the mantle/core separation took place more than 60 Ma after the Solar System condensation began, it would have taken place when all the ¹⁸²Hf had already been transformed into ¹⁸²W. Under such conditions, the ¹⁸²W should now be found solely within the core. However, recent measurements have revealed an excess of 182W in the mantle. This means that 182Hf still existed when the mantle and core separated, and that this element, being lithophilic, remained within the silicates. It subsequently decayed to produce the excess 182W measured today in rocks from the mantle. We may therefore conclude that the mantle/core differentiation occurred less than 60 Ma after the start of the Solar System's condensation. More precise calculations based on the amount of the ¹⁸²W in excess in the Earth mantle has enabled the determination of the age of this differentiation as being between 11 and 50 Ma, with an average value of 30 Ma, if the event was unique and global (Fig. 2.2).

What mechanisms governed the mantle/core separation? Although the general principle of the process is simple – the metallic phase is far denser that the silicate phase and, as a result, the force of gravity will attract it towards the center of the planet – the details remain complex and largely speculative. Most researchers agree on the fact that the metal was in liquid form when it migrated to the center of the planet. But although some believe that the metallic liquid percolated between solid silicate grains, others consider that the sedimentation took place from two immiscible liquid phases (molten metal and silicates) within the terrestrial magma ocean (see later).

The type of planetary body in which this differentiation occurred is also subject to debate. According to certain researchers, the process took place at high pressure, at the end of the accretion phase, in an Earth whose size was close to the one it currently has. In this theory, the ages averaging 30 Ma measured by the ¹⁸²Hf/¹⁸²W system disagree with the recent data from theoretical modeling of the accretion of the terrestrial planets, which all indicate that the latter formed in several tens of millions of years, probably between 50 and 100 Ma (*see* Chap. 1). According to others, the differentiation began earlier, at low pressure and in the interior of planetesimals. It may be noted that in the context of this second theory, the Earth's core would be the result of the agglomeration of the cores of several planetesimals, which would imply that a second migration phase would have brought these "mini-cores" together in the center of the Earth.

Currently, the Earth's core consists of two parts: a solid inner core surrounded by a liquid outer core. As the Earth is slowly cooling, the solid core is growing at the expense of the liquid outer core.



■ Fig. 2.2 Simplified geological time scale showing a possible succession of the different geological events that took place during the first billion years of the Earth's history. The separation into a metallic core and a silicate mantle was rapid and dramatic in comparison with the growth of the continental crust, which has taken place in a continuous manner since 4.4 Ga, at least ($see \triangleright$ Chap. 3). Moreover, several arguments indicate that the mantle of the very young Earth underwent an episode of general melting. In other words, the surface of our planet was completely molten, forming what geologists term a magma ocean (which persisted until 4.4 Ga at the latest). Between $t_0 + 10$ Ma (the minimum age for the differentiation of the core) and $t_0 + 70$ Ma, carbonaceous chondrites and micrometeorites contributed a significant proportion of terrestrial water, such that at 4.4 Ga, liquid water was stable on the surface of our planet ($see \triangleright$ Chap. 3). The meteoritic bombardment, a cataclysmic event that affected the Earth about 3.9 Ga ago, will be discussed in Chap. 5.

■ Box 2.2 Geochronology

The isotopes of an element are atoms that have the same number of protons (and electrons), but a different number of neutrons. Stellar nucleosynthesis gives rise to several stable or unstable isotopes, the latter decaying over the course of time into another element. For example, rubidium has, in total, 24 isotopes of which one of the most abundant is $^{87}_{37}$ Rb, which has 37 protons and 50 neutrons. $^{85}_{37}$ Rb is the stable form of rubidium; it has 37 protons and 48 neutrons, giving a total of 85 nucleons. $^{87}_{37}$ Rb is unstable and decays into $^{87}_{37}$ Sr (which is stable) according to the following reaction:

$$^{87}_{37}\text{Rb} \longrightarrow ^{87}_{38}\text{Sr} + e^-$$
 (2.1)

This reaction, which emits an electron (e⁻), corresponds to what is known as β -decay. There are other types of radioactive decay (α , β ⁺, and ϵ), but in every case the rate of decay is totally independent of the nature and history of the object being considered. For example, the time required for the decay of half of the atoms of $^{87}_{37}$ Rb that are present in the system into $^{87}_{38}$ Sr will always be 48.81 Ga: this period of time is also known as the half-life ($T_{1/2}$) ($^{\odot}$ Fig. 2.3).

In a more general case, if we consider a nuclear reaction of the form:

$$P \rightarrow D$$

where P = number of parent atoms ($_{37}^{87}$ Rb in our example) and D = the number of daughter atoms ($_{38}^{87}$ Sr in our

■ Fig. 2.3 Diagram showing the temporal evolution of the number of parent atoms P and daughter atoms D in a decaying radioactive system. The half-life $T_{1/2}$ is the time required for half of the parent atoms that are present to decay. At the end of $t = T_{1/2}$, half of the initial 20 parent atoms have decayed, so only 10 remain. At $t = 2T_{1/2}$, just half of the parent atoms present at $t = T_{1/2}$ remain, i.e., 5 parent atoms, etc. The half-life $t = T_{1/2}$ is a characteristic constant of any given radioactive isotope.

example), then the proportion of parent atoms that decay per time unit *t* is a constant:

$$\frac{dP}{Pdt} = -\lambda \tag{2.2}$$

where λ is the decay constant and corresponds to the probability of a decay event per time unit. The half-life may thus also be expressed as a function of λ :

$$T_{1/2} = \frac{\ln 2}{\lambda} \tag{2.3}$$

 $T_{1/2}$ being expressed in years and λ in yr⁻¹.

If, at a time t_0 , a system (such as a rock) contains a number P_0 of parent atoms, then the integration of equation (2.2) may be expressed as follows:

$$P = P_0 e^{-\lambda t} \Rightarrow P_0 = P e^{\lambda t} \tag{2.4}$$

In the same way, at time t_0 , the system may also contain some amounts D_0 of daughter atoms (\square Fig. 2.4), which means that at time t, the total number of daughter atoms D will be:

$$D = D_0 + D^* (2.5)$$

 D^* being the number of daughter atoms produced through decay since t_0 ; D^* is thus equal to the number of parent atoms that have disappeared:

$$D^* = P_0 - P (2.6)$$

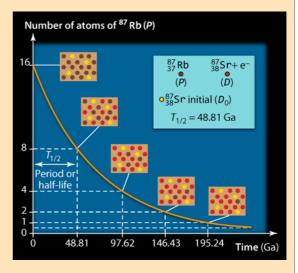


Fig. 2.4 Diagram showing the evolution of the number of parent atoms ($^{87}_{37}$ Rb; maroon circles) and daughter atoms ($^{87}_{37}$ SF; red circles) versus time. The daughter atoms derived from the decay of $^{87}_{37}$ Rb. The yellow circles represent atoms of $^{87}_{38}$ Sr initially present in the system (at time t_0). As these atoms were stable, their number remains constant over the course of time. The number of parent atoms decreases in accordance with an exponential law: $P = P_0 e^{-\lambda t}$.

 $lue{}$ **Table 2.1** Half-life $T_{1/2}$ of the main isotopic systems used in geochronology.

Parent nuclide = P	Daughter nuclide = D	Half-life = T _{1/2}
⁷ Be	⁷ Li	53.1 days
²²⁸ Th	²²⁴ Ra	1.91 years
²²⁶ Ra	²²² Rn	1602 years
¹⁴ C	¹⁴ N	5730 years
⁵⁹ Ni	⁵⁹ Co	76 000 years
⁴¹ Ca	⁴¹ K	100 000 years
³⁶ Cl	³⁶ Ar	301 000 years
²⁶ Al	²⁶ Mg	707 000 years
⁶⁰ Fe	⁶⁰ Ni	1.5 Ma
¹⁰ Be	¹⁰ B	1.51 Ma
¹⁸² Hf	¹⁸² W	9.0 Ma
129	¹²⁹ Xe	15.7 Ma
⁵³ Mn	⁵³ Cr	37.1 Ma
¹⁴⁶ Sm	¹⁴² Nd	103 Ma
²³⁵ U	²⁰⁷ Pb	704 Ma
⁴⁰ K	⁴⁰ Ar	1.31 Ga
²³⁸ U	²⁰⁶ Pb	4.47 Ga
²³² Th	²⁰⁸ Pb	14.0 Ga
¹⁷⁶ Lu	¹⁷⁶ Hf	35.9 Ga
¹⁸⁷ Re	¹⁸⁷ Os	42.3 Ga
⁸⁷ Rb	⁸⁷ Sr	48.81 Ga
¹⁴⁷ Sm	¹⁴³ Nd	106 Ga

Combining equations (2.4), (2.5) and (2.6) gives:

$$D = D_0 + P_0 - P$$

$$D = D_0 + Pe^{\lambda t} - P$$

$$D = D_0 + P(e^{\lambda t} - 1) (2.7)$$

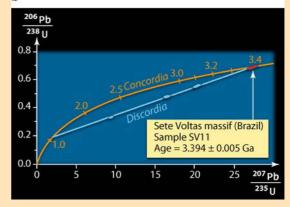
The age *t* of the system may therefore be obtained as follows:

$$t = \frac{1}{\lambda} \ln \left(1 + \frac{D - D_0}{P} \right) \tag{2.8}$$

Although the parameters P and D are measured directly from the rock or mineral, D_0 itself is unknown, so the equation (2.8) cannot be used directly. The solution employed is different depending on the radioactive



b



■ Fig. 2.5 Zircon crystal extracted from a gneiss (SV11) from the Sete Voltas massif in Brazil (a) and the 206 Pb/ 238 U against 207 Pb/ 235 U diagram that enabled it to be dated (b). The Concordia curve (orange) is calibrated in Ga; the Discordia straight line is shown in blue. One of the zircon crystals analyzed (red dot) lies on the Concordia curve whereas the others (blue dots) have partly lost their lead such that they plot on a Discordia straight line. The intersection of the Discordia straight line with the Concordia curve at top right gives the age of the zircon population (3.394 \pm 0.005 Ga). (Dating after Martin *et al.*, 1997; photo: H. Martin.)

element being considered (Table 2.1). A distinction is made between elements that have a short half-life (< 500 Ma; short-period radioactivity) and those where the half-life far exceeds 500 Ma (long-period radioactivity).

1. Long-period Radioactivity

Here, two cases should be considered:

- D_0 is negligible relative to $D(D_0 \ll D)$

This is basically the case with the uranium-lead systems $^{235}\text{U} \rightarrow ^{207}\text{Pb}$ and $^{238}\text{U} \rightarrow ^{206}\text{Pb}$ used for dating the zircons. Because during their crystallization, natural zircons are practically unable to incorporate lead into their crystalline lattice, the initial quantities of ^{207}Pb and ^{206}Pb are utterly negligible relative to the quantity of lead produced by the decay of the uranium. Equation (2.8) may thus be written:

$$t = \frac{1}{\lambda} \ln \left(1 + \frac{D}{P} \right)$$
 that is: $t = \frac{1}{\lambda_{235_U}} \ln \left(1 + \frac{207}{235} \text{U} \right)$

or
$$t = \frac{1}{\lambda_{238_{U}}} \ln \left(1 + \frac{^{206} \text{Pb}}{^{238} \text{U}} \right)$$

Classically, the two isotopes ²³⁵U and ²³⁸U are plotted in a 206Pb/238U versus 207Pb/235U diagram (■ Fig. 2.5). In such a diagram, the identical ages, independently calculated from the two isotopic systems lie along a curve known as Concordia. If a zircon crystal has evolved as a closed system (without any loss of lead), then its isotopic composition will lie exactly on the Concordia curve, which enables its age to be determined directly (the zircon is said to be concordant). However, it may happen that a zircon crystal loses lead over the course of its geological history (during a metamorphic event, for example); then the two isotopic systems give different (discordant) ages. In this case, the population of studied zircons lies on a line known as Discordia and located below the Concordia curve. The intersection of the Discordia and Concordia curves at top right (called upper intercept) then gives the crystallization age of the zircon (Fig. 2.5).

$-D_0$ is not negligible relative to D

In the case where D_0 is not negligible relative to D, a computation method based of the principle of isotopic homogenization is used. For example, during melting or crystallization processes, the chemical elements may have different behavior with respect to the solid and liquid phases; in contrast, the isotopes of a single element do not undergo any fractionation. The ratio of two isotopes of a specific nuclide remains constant. In this case, at a time t, equation (2.7) may be written as:

$$\left(\frac{D}{D'}\right)_{t} = \left(\frac{D}{D'}\right)_{0} + \left(\frac{P}{D'}\right)_{t} (e^{\lambda t} - 1)$$
(2.9)

where *D*' represents the number of atoms of a stable isotope of *D*. In a closed system, *D*' remains constant.

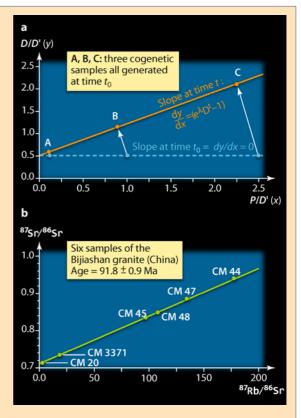
Taking as an example the rubidium-strontium (Rb-Sr) system and taking ⁸⁶Sr as the stable isotope, equation (2.9) may be written:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{t} = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{0} + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_{t} (e^{\lambda_{87_{Rb}}t} - 1)$$

Several cogenetic samples (generated, for example, from the same magma) may have different (87Rb/86Sr)_t ratios (because of magma fractionation; Box 6.1), and identical (87Sr/86Sr)₀ ratios. In a (87Sr/86Sr)_t versus (87Rb/86Sr)_t diagram, the isotopic composition of each sample evolves following a linear law (1 Fig. 2.6),

defining a straight line called an *isochron*, whose slope a is equal to $e^{\lambda_{87_{\rm Rb}}t}-1$. This enables determination of t:

$$t = \frac{1}{\lambda_{87_{Rh}}} \ln a$$

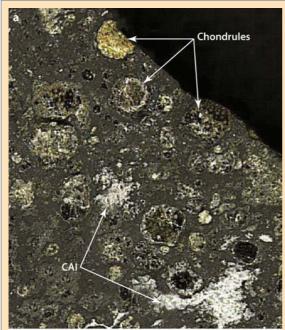


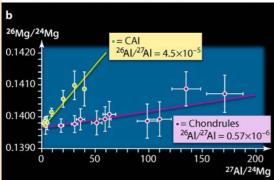
■ Fig. 2.6 a. (*D/D'*) versus (*P/D'*) diagram: the age of a set of samples is proportional to the slope of the straight-line isochron, (see equation 2.9); b. Example of a ⁸⁷Sr/⁸⁶Sr versus ⁸⁷Rb/⁸⁶Sr diagram: the straight-line isochron obtained from six granite samples from the Bijiashan Massif in China gives an age of 91.8 ± 0.9 Ma. (Isochron for the Bijiashan granite after Martin *et al.*, 1994.)

In order to determine as accurately as possible the equation of the isochron, several samples must be analyzed.

2 Short-period Radioactivity or Extinct Radioactivity

The basic principle is that the nucleosynthesis of these radionuclides was caused by a supernova explosion at the very beginning of the formation of the Solar System, 4.568 Ga ago, and that they were homogeneously distributed within the solar nebula. This latter hypothesis is fundamental and indispensable, because it allows the assumption that different objects (meteorites, for example), which, *a priori*, were generated in different places in the Solar System, have identical initial isotopic ratios. As explained in the • Box 1.3, there is currently a debate about their origin, which is doubtless to be found in some "accommodation" between the two





■ Fig. 2.7 a. The Allende meteorite (a carbonaceous chondrite): note the distribution of chondrules and the CAI (Calcium-Aluminum-rich Inclusions; photo. M. Chaussidon). b. Isochron diagram of ²⁶Mg/²⁴Mg versus ²⁷Al/²⁴Mg: the slope of the regression lines is equal to the ratio (²⁶Al/²⁷Al), which is itself dependent on time. The Δt calculated from equation (2.12) is 2.02 Ma. (After Chaussidon, 2005.)

mechanisms: X-ray radiation within the solar nebula by eruptions from the young star in its pre-T Tauri phase, and "pollution" by nuclei produced by the explosive nucleosynthesis in a nearby supernova.

Given their short half-lives, all the parent atoms have now completely decayed into daughter atoms (P = 0 and $D^* = P_0$). Equation (2.9) may thus be written in the following form:

$$\left(\frac{D}{D'}\right)_t = \left(\frac{D}{D'}\right)_0 + \left(\frac{P}{D'}\right)_0 \tag{2.10}$$

To be able to use this equation as a chronometer, it is necessary to input a stable isotope P_2 of the parent, short-lived radionuclide P:

$$\left(\frac{D}{D'}\right)_{t} = \left(\frac{D}{D'}\right)_{0} + \left(\frac{P}{P_{2}}\right)_{0} \left(\frac{P_{2}}{D'}\right) \tag{2.11}$$

When this equation (2.11) is applied to the $^{26}\text{Al} \rightarrow ^{26}\text{Mg}$ system (where $T_{1/2} = 707\,000$ years), and where ^{27}Al is taken as the stable isotope of aluminum (P_2), this becomes:

$$\left(\frac{{}^{26}\text{Mg}}{{}^{24}\text{Mg}}\right)_{t} = \left(\frac{{}^{26}\text{Mg}}{{}^{24}\text{Mg}}\right)_{0} + \left(\frac{{}^{26}\text{Al}}{{}^{27}\text{Al}}\right)_{0} \cdot \left(\frac{{}^{27}\text{Al}}{{}^{24}\text{Mg}}\right)$$

In this short-period system, the isotopic composition of the parent nuclide 26 Al will vary very swiftly: the 26 Al/ 27 Al ratio dwindles to half in 707 000 years. As a consequence, the temporal accuracy of such a chronometer is excellent. If we know the value of this ratio in the solar nebula at t_0 , then this chronometer may be used to calculate the age t of a sample. Indeed, we have:

$$\left(\frac{{}^{26}\text{AI}}{{}^{27}\text{AI}}\right)_{t} = \left(\frac{{}^{26}\text{AI}}{{}^{27}\text{AI}}\right)_{0} e^{-\lambda.t}$$

In fact, extinct radioactivity is most frequently used to measure the age difference between two samples generated from a single reservoir, at times t_1 and t_2 ($\Delta t = t_1 - t_2$). This difference in age may thus be expressed in the following manner (\square Fig. 2.7):

$$\frac{(^{26}AI/^{27}AI)_{t_1}}{(^{26}AI/^{27}AI)_{t_2}} = e^{-\lambda.\Delta t}$$

$$\Delta t = \frac{1}{-\lambda} \cdot \ln \left(\frac{(^{26}AI/^{27}AI)_{t_1}}{(^{26}AI/^{27}AI)_{t_2}} \right)$$
 (2.12)

The formation of the metal core could have had several consequences for the overall evolution of the Earth. First, the differentiation between metal and silicates liberated a huge amount of gravitational energy, which, if it was released in a single episode, would have been capable of raising the overall temperature of the planet by about 1500 K, thus contributing in a substantial manner to the melting of the silicate rocks and the formation of a magma ocean (*see later*). Second, the differentiation of the core could have played a part in the birth of the Earth's magnetic field. It is this second point on which we will now focus the discussion.

Opening a Protective Umbrella: the Birth of the Earth's Magnetic Field

The formation of a metallic core is one of the conditions necessary for the appearance of a magnetic field. In fact, the movements affecting the liquid core (they result both from the phenomenon of convection and from the Coriolis forces that are linked to the rotation of the Earth), induce electrical currents which produce a magnetic field: this is known as the geodynamo. This geodynamo is self-sustaining: the magnetic field itself produces induced electrical currents, producing a magnetic field, etc.

However, there is nothing to prove that the appearance of the terrestrial magnetic field was concomitant with the core/mantle differentiation, nor even that it followed shortly after. In other words, no one knows precisely when the magnetic field appeared! Some minerals can record, in the form of remanent magnetism, the presence and the characteristics of a magnetic field that existed at the time they crystallized. Unfortunately, if they are heated (through a metamorphic process, for example), they can lose this magnetic memory, and record the magnetic field present at the time of reheating. At present, the oldest trace of a magnetic field preserved by minerals has been discovered in 3.6 Ga-old rocks in South-Africa; however, in any case, in the absence of rocks older than 4.0 Ga, the search for a fossil magnetic field is difficult to apply to the Hadean. Nevertheless, preliminary studies carried out on the Australian zircons from Jack Hills (4.4 Ga) appear to indicate that these oldest terrestrial materials, recorded the marks of a magnetic field contemporary with their formation. If these results are confirmed, that would indicate that the magnetic field appeared very early in the Earth's history, between 4.568 and 4.4 Ga. Moreover, analyses carried out on the martian meteorite ALH84001 have been able to establish that it possesses remanent magnetism that was acquired between the time of its formation (between 4.5 and 4.4 Ga) and 4.0 Ga. So, it seems that a geodynamo has been active extremely early on the planet Mars, which suggests that the magnetic fields of the terrestrial planets were established shortly after the separation of their mantles and cores.

The time when the Earth's magnetic field arose is significant, both for the history of life and for that of the atmosphere. Indeed, on the Earth, the magnetic field has always played a fundamental protective role, by deflecting the ionized particles of the solar wind, the effects of which would be lethal to living organisms. In addition, before the magnetic field was established it is highly likely that, on the primitive Earth, the solar-wind particles would have "swept away" light elements from the atmosphere, by providing them with the energy necessary to escape from the Earth's gravitational attraction.

A Partially Molten Earth: the Magma Ocean Assumption

The idea of a global magma ocean, that is, the idea that the outer layer of the primitive Earth could have been completely molten to a depth of several hundred kilometers (or even more), is a legacy of the first explorations of the Moon (Fig. 2.8).

In 1969, the *Apollo 11* mission returned to Earth a large number of lunar rocks. Among them were samples from the maria, the dark areas on the surface of our satellite that may be seen by the naked eye from Earth. Their analysis showed that these were basalts generated from a differentiated mantle, that is to say that have been previously depleted in certain chemical elements such as strontium (Sr) and europium (Eu) (Fig. 2.9g). Because these elements are, on Earth, particularly abundant in plagioclase feldspar, it has been concluded that the lunar mantle underwent plagioclase extraction. This theory has been confirmed three years later, when the *Apollo 16* mission returned to Earth samples of anorthosites,

19 Fig. 2.8 The Moon, photographed by the *Galileo* probe on 7 December 1992. This image shows the two main components of the lunar surface. The light areas, known as the highlands, are richer in craters and are thus considered to be older. These primarily consist of anorthosites and correspond to the lunar crust formed by the accumulation (by floatation) of plagioclase at the surface of a magma ocean. The dark areas are known as the maria. They are less cratered and are thus younger than the highlands. They consist of basalts that originated from the melting of a differentiated mantle.



dated at 4.456 Ga. In 2011, one sample of lunar anorthosites (FAN 60025) has been dated using multiple chronometers (207Pb-206Pb, 147Sm-143Nd and 146Sm-142Nd). All these isotopic systems give a crystallization age of 4.360 ± 0.003 Ga, which could mean that the moon solidified later (~100 Ma) than supposed. These rocks formed through the accumulation of plagioclase crystals, and because of this, are rich in Sr and Eu (Fig. 2.9b to d). So the geochemical signatures of the anorthosites and of the basalts from the lunar maria have proved to be perfectly complementary. For example, • Fig. 2.9d shows that where the anorthosites have a positive Eu anomaly, which is characteristic of the accumulation of plagioclase crystals, the maria basalts exhibit a negative anomaly, indicative of the loss of plagioclase (Fig. 2.9g). This complementary nature is a solid argument in favor of the differentiation of the anorthosites and the maria basalts from one and the same magma. More recent space missions (the Clementine and Galileo probes) have established that the anorthositic signature is found almost everywhere on the Moon (particularly as regards the highlands, which are the light areas of the Moon's surface, visible from Earth), and thus bear witness to the global character of their petrogenetic mechanism. But how should these observations be interpreted?

The "Textbook Case" for a Lunar Magma Ocean

To take account of all these characteristic features, it has been proposed that just after the formation of our satellite (as a result of the collision of a planetoid called Theia with the Earth, followed by the accretion of debris; • Box 1.5), a very large proportion of the lunar mantle melted, so giving rise to a magma ocean. The latter subsequently steadily cooled and progressively solidified. The minerals that crystallized are olivine, orthopyroxene, clinopyroxene and plagioclase. With the exception of plagioclase, all these minerals have a higher density than that of the magma within which they formed (• Table 2.2). They therefore slowly sank and



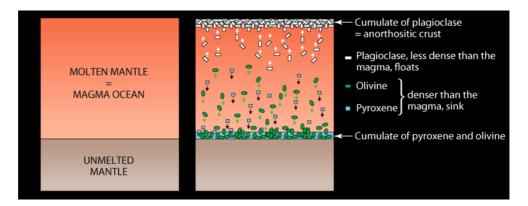
■ Fig. 2.9 Close-up on the lunar rocks. In a, the geologist Harrison Schmitt is in the process of collecting lunar rocks during the Apollo 17 mission. Among the samples returned to Earth were anorthosites (b) and basalts from the lunar maria (e). The anorthosites are almost exclusively made up of plagioclase crystals (c; in this thin section, appearing as grey and white minerals, occasionally showing alternating white and black bands). The basalts also contain a small amount of plagioclase, but in addition, they include pyroxene crystals (deep orange in thin section f) and sometimes olivine, as well as iron and titanium oxides (black crystals in f). The rare earth in the anorthosites (d) and in the maria basalts (g) display comple-

mentary patterns: for instance, where the anorthosites have a positive Eu anomaly, characteristic of plagioclase accumulation, the basalts show a negative anomaly, indicative of plagioclase extraction. The complementary nature of the geochemical signatures of the anorthosites and the basalts from the lunar maria provides a strong argument in favor of their differentiation from a single magma. These characteristics may be explained if we assume that the lunar mantle melted shortly after the formation of our satellite, giving rise to a magma ocean, whose cooling would have led to the formation of an anorthositic crust.

■ Table 2.2 Chemical composition and density of minerals likely to have crystallized from the magma ocean.		
Mineral	Chemical formula	Density
Olivine	(Mg,Fe) ₂ SiO ₄	3.32
Orthopyroxene	(Mg,Fe) ₂ Si ₂ O ₆	3.55
Clinopyroxene	Ca(Mg,Fe)Si ₂ O ₆	3.4
Garnet majorite	$\mathrm{Mg_3(Fe^{3+},Al)}_2\mathrm{(SiO_4)}_3$	3.9
Plagioclase	CaAl ₂ Si ₂ O ₈	2.65
Talc	$\mathrm{Mg_3Si_4O_{10}(OH)}_2$	2.7
Serpentine	${\rm Mg_{e}Si_{4}O_{10}(OH)}_{8}$	2.54
Basic magma = basalt		2.85
Ultrabasic magma = komatiite		2.95

accumulated at the base of the magma ocean, giving rise to what would become the lunar mantle. The plagioclase, being less dense than the magma, floated to the surface of the magma ocean, leading to the formation of an anorthositic crust. This mechanism would have had the effect of separating the plagioclase from the other minerals (olivine + orthopyroxene + clinopyroxene). As plagioclase is, unlike olivine and the pyroxenes, a Sr and Eu-rich mineral, the anorthositic crust became enriched in Sr and Eu relative to the mantle, which itself became impoverished in these same elements (Fig. 2.9 d and g).

The formation of this crust and the chemical differentiation between the basalts and anorthosites that followed became possible because the mass of the Moon is one 80th of that of the Earth, which means that when the surface gravity on the Earth is 9.78 m.s⁻², it is just 1.62 m.s⁻² on the Moon. As a consequence, and when compared with the Earth, the pressure inside the Moon rises with depth far more slowly and whereas plagioclase is stable on Earth only down to depths of 30 km, it remains stable down to depths of 180 km on our satellite. The crystallization of the lunar magma ocean is therefore able to generate huge volumes of plagioclase that accumulated through flotation, thus giving rise to a thick anorthositic crust (Fig. 2.10). The latter formed an insulating layer, through which heat could escape only by way of conduction, a mechanism that is of low efficiency (i.e., slow); as a result it was undoubtedly the presence of this anorthositic crust that slowed down and delayed cooling – and thus the crystallization and solidification – of the Moon's magma ocean. As far as the basalts of the lunar maria are concerned, they formed later, with their ages reaching 3.2 Ga. They arose through a new episode of melting in the lunar mantle as a result of the release of radioactive heat or through the heat created by meteoritic impacts.



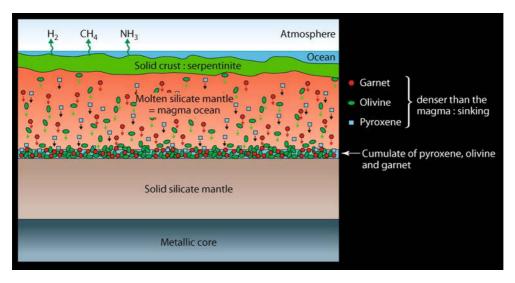
■ Fig. 2.10 Differentiation in the lunar magma ocean. The left side illustrates the initial state, where the upper portion of the lunar mantle is molten, forming what is known as a magma ocean, whereas the lower portion, unmelted, remains in a solid state. The right side illustrates the crystallization of the magma ocean. The crystals of pyroxene and olivine, denser than the magma, accumulate at the base of the magma ocean, whilst the crystals of plagioclase, being lighter, float and accumulate at the surface, forming the lunar anorthositic crust.

And on Earth?

The generalized melting of the lunar mantle was, basically, the result of the gravitational energy liberated through the accretion of this planetary body. But what was it like on the Earth? Given that our planet is far more massive than the Moon, the gravitational energy released during its accretion was far greater. Assuming that the release was instantaneous (which was obviously not the case), the increase in temperature could have been around 38 000 K (as against 1600 K for the Moon under similar conditions). To this source of heat, we may add the equivalent of 1500 K resulting from the core/mantle differentiation (see above). Finally, the decay of radioactive elements also significantly contributed to the heating of the young planet Earth. This was particularly the case with certain short-period radionuclides (i.e., through extinct radioactivity) such as ²⁶Al, which decays into ²⁶Mg with a half-life of 0.75 Ma. Taking account of the mass of ²⁶Al available at the time of the Earth's formation, it is possible to calculate that the thermal contribution given by its decay is 9500 K. As for the decay of 60Fe into 60Ni (half-life 1.5 Ma), it would have contributed to the extent of 6000 K. So the amount of energy available at the end of the Earth's accretion was considerable, and even if a significant amount was dissipated by radiation to space, it would have been more than sufficient to melt completely a large part of the mantle. The formation of a magma ocean was therefore potentially possible on Earth, but, once again, before concluding that it existed, we need to try to find witnesses and proofs of its existence.

As we have seen earlier, unlike the Moon, to this day the Earth has not yielded any rock that is older than 4.0 Ga. Consequently, there is no existing direct witness of the existence of a possible terrestrial magma ocean. On Earth, nothing indicates that the most ancient rocks known, might have been formed from a mantle source that had been previously depleted in Sr and Eu by the loss of plagioclase.

However, if the matter is considered more closely, this last observation is not very surprising. Indeed, as we have already mentioned, the lunar gravity corresponds to only 17 per cent of the Earth's gravity, which means that on our planet plagioclase is stable only down to a depth of 30 km. In other words, a very simple calculation shows that a hypothetical terrestrial anorthositic crust would have been about six times less thick than on the Moon. In addition, contrarily to the Moon where, under the low-pressure conditions that reign in the lunar mantle, and consequently where plagioclase was the first phase to crystallize after

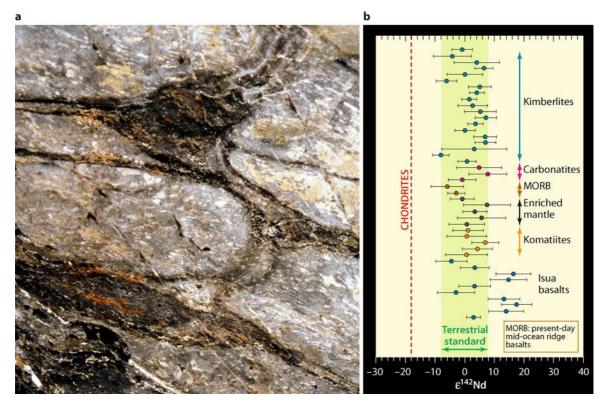


■ Fig. 2.11 Schematic section of the terrestrial magma ocean. The release of gravitational energy during accretion and the decay of radioactive elements was sufficient to lead to the complete melting of the outer region of the terrestrial mantle, thus giving rise to a magma ocean which must have covered the whole surface of the planet. As it cooled, olivine, pyroxenes and garnet crystallized. Because of their high density, these crystals sank to the bottom of the magma ocean, where they accumulated. The surface of the magma ocean cooled and solidified first. When in contact with the hydrosphere (with the water either in liquid or vapor state), anhydrous minerals such as olivine and pyroxenes were altered into hydrated minerals (talc, serpentine). They thus formed a superficial crust (less dense than the underlying magma). The serpentinization reactions liberated molecular hydrogen (H₂) which would have been able to combine with the carbon dioxide (CO₂) and molecular nitrogen (N₂) in the primitive atmosphere to form methane, (CH₂), and ammonia, (NH₃).

olivine (and before clinopyroxene), on Earth it was clinopyroxene that formed after olivine (and before plagioclase). So even if a small amount of plagioclase did crystallize in the terrestrial magma ocean, it was never in sufficient quantity to generate an anorthositic crust. The conclusion is that, even if it did really take place, the differentiation of the terrestrial mantle from a primitive magma ocean is not the result of plagioclase segregation. Other possible geochemical markers have thus been investigated.

Towards the end of the 1980s, researchers turned their attention to Archaean komatiites, ultrabasic volcanic rocks, typical and characteristic of the Archaean aeon that ranges from 4.0 to 2.5 Ga (the Archaean), and which we shall speak about in detail in Chap. 6. Study of them has shown that certain characteristics of the lavas that produced them (the content of rare-earths, for example) testify of a global differentiation that would have affected the whole terrestrial mantle before 3.4 Ga. Geochemists have therefore concluded that this was the result of the crystallization and segregation of garnet within the magma ocean. Unlike plagioclase, garnet has a density considerably higher than that of the magma (Table 2.2) and, like olivine and the pyroxenes, it sank and accumulated at the bottom of the magma ocean (Fig. 2.11).

More recently, in 2003, other geochemists have analyzed the isotope 142 of the element called neodymium (¹⁴²Nd) in basalts aged 3.872 Ga, from Isua in Greenland (see ▶ Chap. 6). This isotope is the product of the decay of ¹⁴⁶Sm (samarium, ▶ Box 2.2). During their crystallization, silicates such as the pyroxenes and garnet generally incorporate more Sm than Nd, such that their crystallization modifies (decreases) the Sm/Nd ratio in the magma. Obviously, this fractionation will affect all the isotopes of Nd and Sm, including ¹⁴⁶Sm. In other words, the early crystallization of garnet and pyroxene will first result in a decrease in the content of ¹⁴⁶Sm (the parent isotope) in the magma ocean. As a result when all or part of the ¹⁴⁶Sm had decayed into ¹⁴²Nd, the relative abundance of ¹⁴²Nd in the magma would be less than in the minerals that had accumulated at the bottom of the magma ocean (the cumulate). As the life-time of the isotope ¹⁴⁶Sm is short (its half-life is 103 Ma), the ¹⁴²Nd can be a marker and



IDENTIFY and SET UP: Fig. 2.12 The traces of a magma ocean in the pillow basalts of Isua. These 3.872 Ga old rocks, which outcrop in the Isua region of Greenland (**a**), are among the oldest known on Earth. The diagram (**b**) shows the ¹⁴²Nd content of these basalts, together with that of other terrestrial rocks generated through mantle melting. The quantity marked "ε¹⁴²Nd" is a measure of the ¹⁴²Nd content relative to a standard value (here the average of terrestrial values). It clearly ap-

pears that some Isua basalts have values of $\varepsilon^{142}Nd$ lying between +12 and +20, values that are significantly greater than the range of values from younger samples (-8 < $\varepsilon^{142}Nd$ < +8). This excess in ¹⁴²Nd leads to the conclusion that the Archaean mantle from which they originated recorded and preserved the traces of its primordial chemical differentiation within a magma ocean. (Photo: M. Boyet; diagram: after Boyet *et al.*, 2003.)

a chronometer for such silicate fractionation only if the latter took place during the first hundreds of millions of years of our planet's history. Now the Isua basalts, generated by partial melting of the terrestrial mantle around 3.87 Ga ago, have an excess of ¹⁴²Nd relative to all other, more recent, terrestrial samples (Fig. 2.12). Calculations show that this anomaly may be explained by fractionation of silicates within a magma ocean during the first 100 Ma of the Earth's history.

Contrary to what happened on the Moon, the crystallization of the magma ocean did not lead to plagioclase accumulation through flotation but, on the contrary, it differentiated by precipitation of olivine, pyroxenes, and garnet at the base of the magma ocean (Fig. 2.11). This mechanism led to an early stratification of the Earth's mantle, with a deep layer corresponding to the cumulate made up of garnet, olivine, and pyroxenes, and a shallower layer corresponding to the residual magmatic liquid, which, after cooling, crystallized as a peridotite that was poorer in olivine and garnet. It appears that this early stratification of the mantle disappeared after 3.4 Ga, probably because of efficient mixing caused by mantle convection.

On the Moon the anorthositic crust played the part – to a certain extent – of a lid that slowed down the loss of heat and thus the cooling and then solidification of the magma ocean. On Earth, the accumulation of minerals took place through sedimentation at the bottom of the magma ocean: so there was no such anorthositic lid. Obviously, the upper layer of the magma ocean, in contact with the external, colder medium, cooled and solidified, in a manner very similar to what is observed today, on a much smaller scale, in lava lakes. This

solid crust, set on the surface of the magma ocean, had a density greater than 3, whereas that of the subjacent magma, with the same composition, was about 2.9 (Table 2.2). So it is perfectly logical that under the influence of its own weight, this solid crust rapidly sank into the magma ocean, leaving free space at the surface for fresh magma to rise, and which created a rapid cooling (in a few tens of thousands of years) of the magma ocean.

This scenario of very rapid cooling of the magma ocean, as much seductive it may seem, is probably not the correct one. The time required for an effective separation of the cumulate and thus for a stratified structure for the mantle is, in fact, about several tens of millions of years. In addition, as we shall see later, models for the formation of the Earth lead everyone to believe that water was available, either in liquid or gaseous form, very shortly after the formation of our planet. It could therefore immediately react with the cooled surface of the magma ocean, whose dense, anhydrous minerals (olivine, pyroxenes) it would convert into hydrated and less dense minerals such as talc or serpentine (density < 2.8; ■ Table 2.2). When thus altered, the surface crust would have become less dense than the subjacent magma, such that it would have floated on its surface, creating an insulating layer that would have slowed down the cooling and crystallization of the magma ocean (■ Fig. 2.11). Whatever the case may be, the Jack Hill zircons show that this ocean had completely cooled at 4.4 Ga (see ▶ Chap. 3).

This theory of alteration of the surface crust, proposed in 2006–2007 by the geologist Francis Albarède, is also capable of explaining the reducing nature of the Earth's atmosphere between 4.4 and 4.0 Ga (*see* ▶ Chap. 3). For example, the alteration of the ferrous component of olivine (fayalite) takes place following the reaction:

The silica reacts with forsterite, which is the magnesian component of olivine:

As for the hydrogen that is liberated, it rapidly combines with the carbon dioxide, CO_2 , and the molecular nitrogen, N_2 , in the primitive atmosphere to form methane, CH_4 , and ammonia, NH_3 . These reduced molecules could combine with H_2 and H_2O to form amino acids, as was shown in the famous experiment carried out by Stanley Miller et Harold Clayton Urey in 1953 (see \triangleright Chap. 3).

The Birth of the Outer Shells: The Atmosphere and the Hydrosphere

Nowadays, the atmosphere and the hydrosphere only represent 0.000088 per cent (5.29 \times 10¹⁸ kg) and 0.022 per cent (1.35 \times 10²¹ kg) respectively of the mass of our planet (5.98 \times 10²⁴ kg). They are essentially located at the surface, that is to say at the interface between the solid Earth and interplanetary space. It is also on that surface that life has arisen and, as a consequence, these two envelopes will play a determining role in the emergence and spread of life on Earth. The atmosphere and the hydrosphere very probably had a common origin. Indeed, at the temperatures that reigned at the period at which the Earth accreted, water was in the state of vapor in the atmosphere, and it was only after the formation of the oceans (fol-

lowing the condensation of the atmospheric water, *see* ▶ Chap. 3) that these two outer, fluid envelopes evolved separately.

The Early Degassing of the Primitive Atmosphere

It is traditionally accepted that the very first terrestrial atmosphere had the composition of the solar nebula (the protoplanetary nebula): it primarily consisted of hydrogen and helium. But, due to the turbulent history of the accretion of the Earth, there remains almost nothing of that primordial atmosphere. Indeed, the ratios between the various atmospheric components and their isotopes are very different from those measured in the Sun, which, in essence, retains the elemental and isotopic signature of the nebula that gave it birth. By contrast, the most massive planets and the most distant from the Sun better preserved their primitive atmospheres that arose from the protoplanetary nebula. By way of example, Jupiter's atmosphere consists of 81 per cent hydrogen and 18 per cent helium.

The disappearance (the erosion) of the Earth's primordial atmosphere is the result of several phenomena. First, during its accretion, Earth has been impacted by planetesimals or large meteorites (just like Theia, Box 1.5), some of the energy released by the shock was transferred to gas atoms, allowing them to exceed the escape velocity and thus break away from Earth's gravitational attraction. However, as we shall soon see, these "impactors" could equally well have brought volatile elements to our planet. As a result, we have absolutely no idea of the net balance between these collisions and the erosion of the planetary primitive atmosphere. And then, before the terrestrial magnetic field was established, the surface of the Earth was subjected to the solar wind, that is to a flux of very energetic particles that certainly "swept away" the lightest elements (H, He), enabling them to gain the Earth's escape velocity and to escape into interplanetary space. Finally, these same elements could have left the planet through simple gravitational escape. For instance, ultraviolet radiation induces the photodissociation of water and produces molecular hydrogen, H₂, and this latter dissociates into atomic hydrogen, H, which easily escapes from the Earth's gravity.

Relics of the Primitive Atmosphere in the Terrestrial Mantle!

Although most of the Earth's primordial atmosphere has disappeared, an infinitesimal fraction has, despite everything, been preserved by our planet and, as astonishing as it may seem,

■ Box 2.3 How the Isotopes of Xenon Contribute to the Study of Degassing in the Primitive Earth

The study of the isotopes of a rare gas, xenon (Xe), has enabled the early nature of the degassing of the primitive atmosphere to be established. Isotope 129 of xenon (129Xe) results from the radioactive decay of isotope 129 of iodine (129I), the latter originating in the supernova, the explosion of which contributed to the formation of the Solar System (■ Box 1.3). The half-life of 129I is 15.7 Ma, so this element had completely decayed into 129Xe in less than 150 Ma. The xenon emitted today from the mid-oceanic ridges contains an excess of 129Xe relative to the atmosphere. Under mid-ocean ridge systems, the Earth's mantle ascents through convective motion; it undergoes adiabatic decompression – that is, without any exchange of heat – which causes

its partial melting and the emplacement of magmas which, when solidified, will form the oceanic crust. During the course of their crystallization these magmas release the dissolved gases that come from the terrestrial mantle, thus providing information about the volatile content of the Earth's interior. If degassing of the Earth had taken place more than 150 Ma after the start of the Earth's accretion that is to say after all the ¹²⁹I had been transformed into ¹²⁹Xe, then the isotopic composition of atmospheric xenon should be identical to that of the mantle. But this is not the case, and the excess in ¹²⁹Xe in the Earth's mantle indicates that almost all of the degassing had finished while ¹²⁹I still existed, that is, less than 150 Ma after the start of Earth's accretion.

geochemists are nowadays able to find traces of it. Our atmosphere today contains about 5 ppm of helium. The isotope 4He forms most of it, with the isotope 3He amounting to only about 7×10^{-6} ppm (${}^{3}\text{He}/{}^{4}\text{He} = 1.4 \times 10^{-6}$). Although ${}^{4}\text{He}$ primarily results from the decay of heavy radioactive elements such as uranium and thorium, ³He is considered as resulting mainly of the primordial episode of nucleosynthesis; it was thus present in the protosolar nebula. The residence time of He in the terrestrial atmosphere is about one million years, which means that the current atmospheric helium cannot by any means be a "residue" of the primitive atmosphere. However, at the bottom of the oceans, along the mid-ocean ridges (on the mid-ocean spreading centers), the ³He/⁴He ratio is, on average, 8 times higher than that in the atmosphere (in Iceland, a region that corresponds to an emergent portion of the North Atlantic Ridge, it may even be as much as 37 times greater). The only way to explain the excess of ³He measured directly below the ridges is to assume that this gas arises from degassing of the magmas that are being erupted there. In other words, in the absence of any other mantle source, researchers conclude that the ³He being degassed is of primary origin, that is the relict of a primitive atmosphere, trapped within the Earth's mantle. The study of another rare atmospheric gas, neon, leads to an identical conclusion: in these same mid-ocean ridges, the measured ²⁰Ne/²²Ne ratio is closer to that of the Sun than to that of the current atmosphere. This local excess of ²⁰Ne is similarly interpreted as the result of degassing of the mantle, through volcanism. As for the He/Ne ratio within the mantle (measured at the ridges) it is also close to that of the Sun.

All these isotopic data prove that the Earth's mantle has preserved a component of the solar type, and the composition of which is inherited from the protoplanetary nebula. Some authors, proposed that the He and Ne originally from the primitive atmosphere being found today in the mantle, were incorporated, either by being trapped in pores between the minerals, or by being dissolved in the magma ocean.

So it appears that the primordial degassing of the planet (*see later*), although it may have been significant, was not total. Even catastrophic events such as the collision with the "Theia" planetoid about 4.528 Ga ago, did not allow degassing of the deepest parts of the Earth's mantle.

An Extraterrestrial Origin for the Atmosphere of the Very Young Earth?

The smaller and consequently, the less massive planets are, the more difficult it is for them to retain light elements, because they have a lower gravitational attraction. So, as we have seen, the Earth (together with Mercury, Venus, and Mars) completely lost its primordial atmosphere, in contrast to Jupiter, Saturn, Uranus, and Neptune. In addition, the surface temperature of the planets decreases with distance from the Sun. The higher the temperature, the more significant the thermal agitation (the average velocity of the atoms and molecules) becomes, which allows more efficient gravitational escape. The Earth, both small and close to the Sun, thus fulfilled the conditions that favored rapid erosion of the primitive atmosphere.

Nevertheless, our planet still possesses an atmosphere and a hydrosphere. This implies that the light elements of which these two outer envelopes are made up must have been subsequently provided to the surface. The question that then arises is the source of this "late" addition. There are two, competing, but not mutually exclusive, theories.

The Theory of Primordial Degassing

The first theory envisages primordial degassing of the planet. It is based both on the observation of the fact that volcanoes currently release large quantities of volatile elements (mainly $\rm H_2O$, but also $\rm CO_2$, $\rm CO$, $\rm H_2S$, $\rm H_2$, $\rm SO_2$, $\rm N_2$, $\rm Cl$, rare gases, etc.) into the atmosphere, and also on

the discharge of ³He and ²⁰Ne by oceanic ridge systems, proving that even today, degassing of volatile elements originating in the deeper portions of the planet is still active (*see earlier*). By analogy with ³He and ²⁰Ne, it has been proposed that atmospheric gases such as N₂, CO₂ or H₂O also result from significant degassing of the Earth's deep interior. The isotopic analysis of a rare gas, xenon (■ Box 2.3) shows that such an event occurred during the first 150 million years of our planet's existence; the degassing observed today along the mid-oceanic ridges being only a pale relic of this event.

During the Earth's accretion, the hydrated mineral phases could have been destabilized by the shocks occurring between planetesimals, and the volatile elements that they contained could have been released, leading to an intensive and efficient degassing of the planet. Is it possible to suppose that the whole of the terrestrial atmosphere and hydrosphere were generated through such a primordial degassing? The answer to this question very strongly depends on the model considered for planetary formation. If, as in the conventional view, the Earth is considered to consist of 15 per cent of carbonaceous chondrites (containing 5 to 10 per cent of water), and 85 per cent of ordinary chondrites, then the amount of water contributed by these meteorites corresponds to 50–70 times the quantity of water currently present on Earth. On the other hand, if it is believed that 99.5 per cent of our planet was formed from enstatite chondrites, whose water content is only 0.05-0.1 per cent, then that source of water would have contributed only 50 to 100 per cent of the volume of present-day oceans. That is totally insufficient, because, on Earth, water is found not only in the ocean $(1.35 \times 10^{21} \text{ kg})$, but also in the mantle (between 5 and 50×10^{20} kg) and, in addition, the loss of volatile elements during the accretion (erosion of the atmosphere) is generally estimated to be at least 90 per cent of the Earth's initial water budget. Under these conditions, terrestrial water (as well as other volatile elements) could not have exclusively come from the primordial degassing of the planet. So it is necessary to call on extraterrestrial reservoirs.

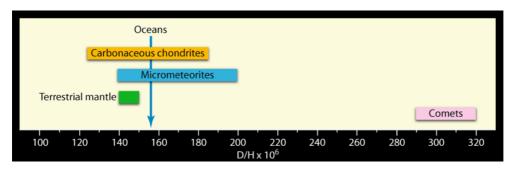
The Theory of Cometary or Meteoritic Contributions

The planetary bodies that formed in the outer zones of the Solar System are rich in volatile elements, because these latter could condense at the low temperatures that prevailed in those regions, very distant from the Sun. Among these objects, there were, of course, the comets, whose mass consists of at least 50 per cent of water and that originate in the Kuiper belt or in the Oort Cloud (beyond the orbit of Neptune, see Chap. 5, Figs. 5.7 and 5.8). They are therefore potentially capable of having contributed a significant portion of terrestrial water. Some researchers consider that this cometary contribution took place very early in the planet's history, while others have suggested a continuous supply, due to a permanent flux of micrometeorites. This latter theory assumes, however, that the volume of the oceans has increased throughout the life of the Earth, which is contradicted by geological data.

An alternative theory envisages degassing of volatile elements contained within micrometeorites when they enter the Earth's atmosphere. Every year, 40 000 tonnes of such interplanetary dust fall onto the surface of the planet; these micrometeorites have an average size of about 100 μ m, and 50 to 100 per cent of them consists of hydrated minerals,. Assuming that during the first 100 Ma of the Earth's history, the micrometeorite flux was 106 times as great as it is today (i.e., the maximum value envisaged by current models), this dust would have contributed, over that period, between 0.5 to 1.2×10^{21} kg of water to the Earth.

How to Decide?

To decide between these two theories, geochemists have once again had recourse to isotopic analysis. Indeed, they focused their research on the isotopes of hydrogen and, in particular, on the deuterium ($^{2}H = D$)/hydrogen (^{1}H) ratio. In the present-day oceanic water, this D/H ratio is 155.7×10^{-6} , a value that is perfectly consistent with the isotopic composition of carbonaceous chondrites and micrometeorites ($^{\bullet}$ Fig. 2.13). These bodies could, therefore, have



■ Fig. 2.13 Tracking extraterrestrial water with hydrogen isotopes: comparison of the deuterium(²H = D)/hydrogen(¹H) (D/H) ratio in the Earth's ocean and in different reservoirs: comets, carbonaceous chondrites, meteorites, and terrestrial mantle. Clearly, that with values of D/H > 290, comets could not have contributed significantly to the supply of volatile elements to the primitive Earth, unlike the case with the carbonaceous chondrites and micrometeorites.

supplied a substantial part of Earth's water. Yet, with a D/H ratio ranging between 290×10^{-6} and 320×10^{-6} , cometary water could not, by any means, have been the main source of terrestrial water: at the most, the cometary contribution to the Earth's oceans could not have exceeded 10 per cent.

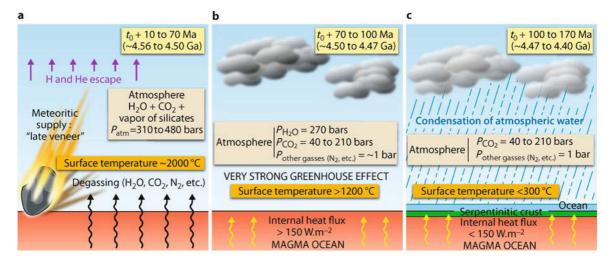
When could extraterrestrial water have been supplied to the surface of the Earth? Here, this is the abundance of siderophile elements and in particular platinum-group elements (platinoids = Pt, Pd, Rh, Ru, Ir and Os) in the Earth's mantle that can help to answer this question. All the siderophile elements that were present in our planet when the core and mantle had segregated, migrated into the metallic core. However, the content of platinum-group metals in the present-day terrestrial mantle is by no means insignificant, which cannot be explained unless these platinoids were added to the mantle after the core/mantle separation. This is what is known as the "late veneer" theory. In addition, and consistently with the previous conclusion, the relative abundance of siderophile elements in the mantle is the same as in primitive meteorites, i.e., those meteorites, such as the carbonaceous chondrites, that have not undergone any differentiation into a metallic and a silicate phase.

The excess of platinum-group metals in the mantle enables the meteoritic flux to be assessed as 0.45 per cent of the Earth's mass. By assuming that these meteorites were chondritic, i.e., that they contained between 6 and 22 weight per cent of water, it is possible to assess their contribution as ranging between 1.6 and $6.0 \times 10^{21}\,$ kg of water, which is more than the current mass of the oceans $(1.35 \times 10^{21}\,$ kg). Models predict that this late contribution of water of extraterrestrial origin took place between $t_0 + 10\,$ Ma (the minimum age for the mantle differentiation) and $t_0 + 70\,$ Ma. However, it is not possible to decide between the theory of a late veneer brought by a few large asteroids and that of a regular sprinkling by micrometeorites. This last theory is only realistic if the flux of micrometeorites onto the early Earth had really been 10^6 greater than its current value.

To Summarize: the Atmosphere Between 4.56 and 4.4 Ga

Primordial degassing of our planet on its own or with contributions of extraterrestrial volatile elements enabled the formation of an atmosphere that replaced the primitive atmosphere inherited from the solar nebula. Initially, the surface temperature was such that water, and also, obviously, other volatile elements (including CO_3), were in the state of vapor (\square Fig. 2.14a).

If all the mass of the current ocean water was in the form of vapor, that would produce a partial atmospheric water pressure of 270 bars (Fig. 2.14b). Similarly, as far as CO₂ is con-



■ Fig. 2.14 Schematic representation of the various episodes in the evolution of the atmosphere and the hydrosphere before 4.4 Ga. a. Between 10 and 70 Ma (after the beginning of the accretion), the metallic core and the silicate mantle became differentiated. The latter was largely molten and the surface of the Earth was covered with an ocean of molten silicates (magma ocean). The primordial atmosphere, inherited from the protosolar nebula (H + He) was rapidly eroded, whereas degassing of the planet and the meteoritic contribution ("late veneer") brought the elements of a new atmosphere to Earth. b. Between 70 and 100 Ma, the internal heat flux remained very high (> 150 W.m⁻²) such that even the very outermost

portion of the magma ocean could not crystallize. The massive atmosphere of water vapor and carbon dioxide created an intense greenhouse effect and the temperature "at the ground" exceeded 1200 °C. c. Between 100 and 170 Ma, the heat flux had decreased such that the formation of a solid crust on the surface of the magma ocean became possible. The Earth's outer envelopes then cooled much faster and the atmospheric water was able to condense: one or several oceans covered the Earth's surface. The concentration of atmospheric CO₂ remained very high and the temperature at the ground became less than 300 °C. (After Pinti, 2002.)

cerned, some researchers consider that all the carbon nowadays present in carbonates was in the atmosphere in the form of CO_2 , from which they conclude that the partial pressure for that molecule was 40 bars. If the carbon that is now in the mantle (where it has been recycled through the subduction zones) is also taken into account, the estimated partial pressure for atmospheric CO_2 reaches 210 bars. By way of comparison, the atmospheric partial pressure of CO_2 is currently 3.5 × 10⁻⁴ bars. In addition to these gases, were both molecular nitrogen (N_2) and other rare gases, but researchers consider that their partial pressure was less than 1 bar.

Water and carbon dioxide being both efficient greenhouse gases, the radiation emitted by the Earth could not have been totally released to space. That would thus contribute to efficiently maintaining a very high surface temperature, such that, immediately after Earth accretion, the very surface layer of the magma ocean would not be able to solidify. When the flux of internal heat decreased (dropping below the threshold of 150 W.m⁻²), a solid crust could form on the surface of the magma ocean (*see above*), resulting in an insulation of the hot magma from the outer envelopes, these latter being then able to cool more rapidly (Fig. 2.14c). It was this atmospheric cooling that allowed water vapor to condense and to give rise to oceans of liquid water. Is it possible to determine when this condensation took place?

All the models relating to the origin of terrestrial water converge towards the following conclusion: on the Earth, about 100 Ma after the start of accretion, the amount of water necessary for the formation of the oceans was available. In addition, as we have already indicated, the Australian Jack Hills zircons prove that liquid water was stable on the surface of the planet, 4.4 Ga ago, that is about 170 Ma after that the accretion started. Finally, the impact of the planetoid Theia, 40 Ma after the beginning of the accretion, liberated enough energy for all the liquid water present on the Earth to be completely vaporized. When taken all together these different data, lead to the conclusion that the condensation of water and the formation

of a liquid ocean occurred between 4.47 and 4.40 Ga. In addition, recent models show that 400 to 700 years were sufficient for all the atmospheric water to condense and fall onto the Earth's surface. This event led to the formation of the oceans and certainly left an atmosphere that was "massive" (with an atmospheric pressure of 40 to 210 bars, depending on the model), basically consisting of CO₂, whose greenhouse effect alone would be sufficient enough for maintaining a surface temperature of around 200 to 250 °C.

The Conclusion: a Planet That Was Undoubtedly Uninhabitable

Our foray into the Earth's infancy has led us from the beginning of its accretion (4.568 Ga) to the period when geologists are certain that the oceans had condensed (4.4 Ga). Is it possible to imagine that life could have appeared on our planet during those 170 Ma? No, that seems highly improbable because the surface conditions resulted in a hostile and unfavorable environment. However, this period did see a transition between a planet that was utterly uninhabitable to a planet that was potentially habitable. Indeed, during the first hundred million years that followed the start of the Earth's accretion, the high temperatures that reigned at the surface of the Earth allowed neither the liquid water to exist, nor the surface of the magma ocean to cool and form a solid crust (and thus no stable, cool substrate). In addition, major meteoritic impacts churned up the planetary surface and vaporized, at least partially, the atmosphere and the hydrosphere. It was only subsequently, in a second stage, that the various environmental elements progressively arose that, later, would permit the start of prebiotic chemistry and the emergence of life: the birth of a magnetic field, the cooling of the magma ocean, and the formation of a solid crust, the condensation of the water and the formation of oceans, and the stabilization of the atmosphere.