3 The Origin and Evolution of the Oceans

Daniele L. Pinti

3.1 Introduction

Oceans play a key role in the evolution of life. The first organic molecules on Earth have been likely synthesized in aqueous solutions and primitive biota possibly survived near oceanic hydrothermal systems (Stetter 1998, Holm and Andersson 1998, Nisbet and Sleep 2001). The oceans shielded organic molecules from the massive UV radiation (Cleaves and Miller 1998) and protected living organisms from the heavy cometary and meteoritic bombardment of our planet (Sleep et al. 2001, Nisbet and Sleep 2001).

Nonetheless, our knowledge of the origin and the evolution of the oceans is rather poor and a universally accepted model of formation for the terrestrial oceans is not yet available. The main reason is that the atmosphere–ocean system formed during the first 700 Ma of the history of the Earth (Fig. 3.1). During this period, called "Hadean" (from "Hadeus", the Greek god of Hell) and that extends from the Earth accretion to the end of the heavy meteoritic bombardment, 3.9 Ga (Ga = billion years), the geological record has been mostly wiped out by the intense tectonic activity of the young Earth.

The Hadean geological record is reduced to a handful of detrital zircons found in Western Australia (Wilde et al. 2001, Mojzsis et al. 2001). These zircons contain precious information on the presence of liquid water, very early in the history of the Earth, and their study is revolutionizing our geological view on the primitive Earth (Peck et al. 2001, Valley et al. 2002). Perhaps, liquid water occurred at the surface of the Earth 50 Ma after the end of the accretion. A few tens of millions of years later, the oceans may have reached the conditions of temperature, salinity and pH suitable for the survival of living organisms, probably extremophiles (Rothschild and Mancinelli 2001), and this well before the end of the heavy meteoritic bombardment of the Earth. Occasionally, the impact of large asteroids could have boiled the ocean and momentarily sterilized the Earth (Nisbet and Sleep 2001)

In this chapter, I will summarize the current state of knowledge on the origin of the oceans on the basis of theoretical models and the few geochemical and isotopic records that the primitive oceans have left in Precambrian rocks.
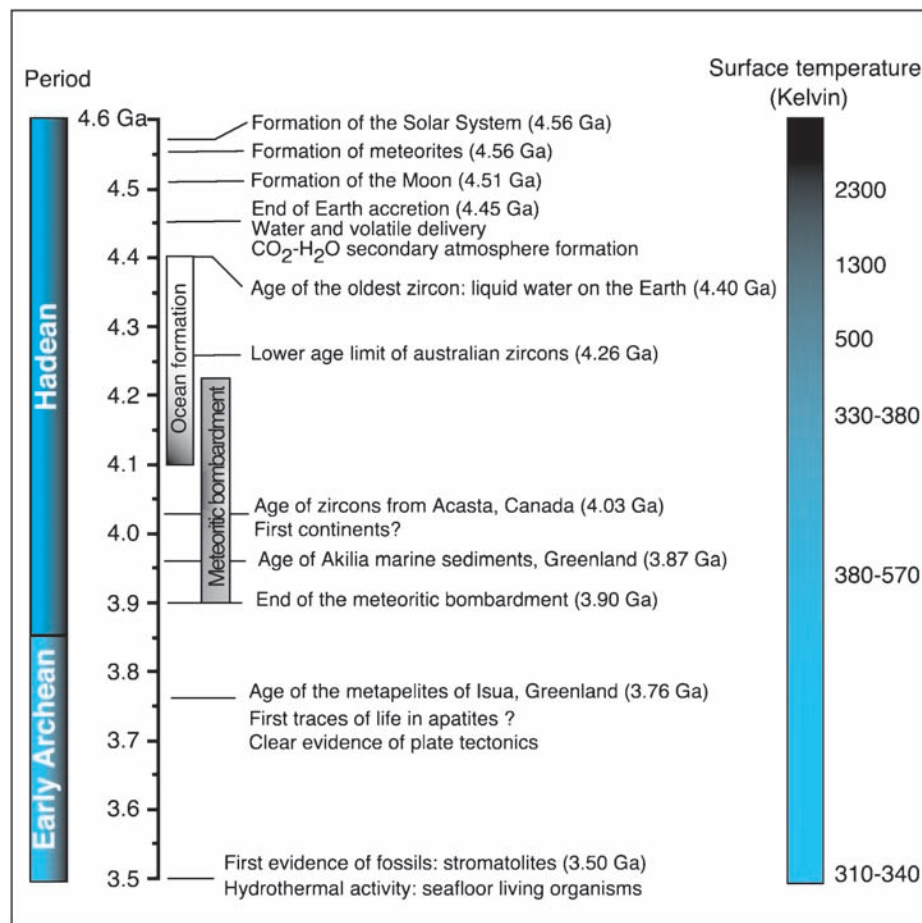
Fig. 3.1. Sketch showing the chronology of the first events that resulted in the formation of the oceans. Surface temperatures are indicative because the transition from uninhabitable hot to uncomfortably cold Hadean climates has been also suggested for the Hadean period (e.g. Sleep and Zahnle 2001). The first traces of life in apatite at 3.8 Ga are graphite particles of possible organic origin found in Isua metasediments (Mojzsis et al. 1996). Recently, van Zuilen et al. (2002) questioned this result, suggesting an inorganic origin for the carbon. The age of Acasta orthogneisses are from Bowring and Williams (1999)

3.2 The Origin of Water

All theoretical models of formation of the oceans need a clear answer to a basic question: when and how water was delivered to our planet. However, the origin of water remains one of the most important subjects of debate and controversy in geosciences and astrophysics.

Knowing the timing of water delivery to the Earth may allow a choice to be made among the possible scenarios of the ocean formation proposed until now: (1) an early delivery of water during the accretion of the Earth, which implies that the oceanic water inventory was available since the beginning (Dauphas et al. 2000, Morbidelli et al. 2000, Robert et al. 2000); or (2) a continuous delivery of water through eons, which implies expanding oceans (Frank 1986, Deming 1999). Currently, the most accepted hypothesis is the former, but the extraterrestrial carrier of the water (chondritic vs. cometary) and the precise moment of the delivery (during the planetary growth or at the end of accretion), are still matters of debate (Owen 1998, Delsemme 1999, Morbidelli et al. 2000, Dauphas et al. 2000, Dauphas 2003).

I would like to briefly discuss the long-standing hypothesis of a constant delivery of water throughout the history of the Earth, which implies an expanding ocean, if we assume that there is not a return of water to the mantle. It is mainly based on the theory of Frank et al. (1986) who showed, through a series of measurements on spacecrafts, that the Earth is annually hit by a large number of small cometary bodies. Their calculations indicated that about 2.2–8.5×10^{21} kg of water has reached the Earth since its formation, if the influx rate is assumed constant. This is equivalent to three times the mass of water in the present-day oceans (1.4×10^{21} kg). More recent data of Frank and Sigwarth (1997) collected by the ultraviolet imagery of the POLAR spacecraft confirmed this finding. The cometary hypothesis is not universally accepted. Harrison (1999) showed, using models of the variations of the continental freeboard, that the constant addition of large quantities of water (comparable to the present-day ocean volume) throughout the history of the Earth is an unlikely process. His conclusion is also supported by geological evidence of a deep water table at the surface of the Earth, since the Archean. The minimum water depth needed to form the 3.2 Ga Ironstone Pods in the Barberton greenstone belt is 982 m (de Ronde et al. 1997). Volcanic massive sulfides are also common in Archean terrains. Some of them are analogous to sulfide deposits produced at present-day midocean ridges. To produce such a deposit, the ocean-floor pressure should be higher than the critical pressure, which is equivalent to an ocean depth of about 3 km (Harrison, 1999).

The universally accepted hypothesis is that the terrestrial water inventory (Table 3.1) was available soon after the Earth formation. A first hypothesis suggests that water and other volatiles degassed from the interior of the Earth, at the moment of its formation (Rubey 1951). The second hypothesis suggests that a few planetary embryos accreted by the Earth at the final stage of its formation carried the bulk of water presently on Earth (Morbidelli et al. 2000). These planetary embryos may have had a chondritic composition and be originally formed in the outer asteroid belt (as the Trojan-class asteroids) (Morbidelli et al. 2000). Several authors challenged this interpretation, proposing alternative carriers of water such as chondritic micrometeorites (Engrand et al. 1999, Maurette et al. 2000) or comets (Delsemme 1999).

Table 3.1. Concentration of water and D/H ratios in terrestrial and extraterrestrial reservoirs

Reservoirs	Mass or concentration of H_2O [kg]	$(\times 10^{-6})$ D/H	δD [‰ SMOW]	Ref.
Whole Earth	$2.2-6.7 \times 10^{21}$	$149-153$	-40 to -20	1
Primitive Earth	$-$	$128-136$	-180 to $+130$	1, 2
Mantle	$5-50 \times 10^{20}$	$143-149$	-80 to -40	3
Oceans	1.40×10^{21}	155.7	0	3
Organic matter	1.36×10^{18}	$135-145$	-130 to -70	3
Metamorphic rocks	3.60×10^{19}	$140-146$	-100 to -60	3
Sedimentary rocks	2.32×10^{20}	$143-145$	-80 to -70	3
PSN	$-$	21 ± 5	-865	4
Carbonaceous chondrites[a]	$6-22$	$128-181$	-180 to $+160$	$5-8$
Antarctic micrometeorites[a]	$2-4$	$120-200$	-229 to $+285$	9, 10
Comets[a]	$58-65$	$298-324$	$+900$ to $+1080$	3, 4, 8

[a] H_2O concentration in wt%.
References: [1] Dauphas et al. 2000, [2] Déloule et al. 1991; [3] Lécuyer et al. 1998; [4] Robert 2001; [5] Boato 1954; [6] Robert and Epstein 1982; [7] Kerridge 1985; [8] Morbidelli et al. 2000; [9] Engrand et al. 1999; [10] Maurette et al. 2000.

In a pioneering work on the origin of the oceans, Rubey (1951) tested different hypotheses. First, he argued that water derived from the weathering of the continental crust, which is known to contain large amounts of water, mostly in the form of hydrated minerals. However, using a simple mass balance, Rubey showed that the amount of water contained in the silicate rocks is insufficient to deliver water to the oceans. The continental crust has a mass of 2.4×10^{22} kg and it contains about 1% of H_2O (Krauskopf and Bird 1995). Even assuming that all the continental crust has been weathered, only 10% of the terrestrial water inventory could have been delivered through this mechanism. Rubey considered another potential source of volatiles, i.e. volcanism. He observed that gas emissions from volcanoes are mainly composed of H_2O and CO_2 with minor amount of sulfates, nitrogen and rare gases. This corresponds to the volatile composition of the atmosphere, oceans and sediments. He argued that the degassing of the volatiles trapped during the Earth accretion, via the volcanism, could explain the formation of the atmosphere and the oceans.

The degassing of the Earth's interior has been largely demonstrated by noble gas studies (e.g., Allègre et al. 1986, Ozima and Podosek 2001). During the first oceanographic cruises at Galapagos and EPR midocean ridges, at the end of the 1970s, an anomalous enrichment of the primordial isotope helium-3 was detected from deep water sampled at the axis of the ridge (Craig et al. 1975). The ratio between the primordial and the radiogenic isotope of helium, namely ^{3}He/^{4}He ratio, was higher than that expected in seawater, which should correspond to the atmospheric one. The degassing of primordial volatiles from the upper mantle was the cause of the observed enrichment of ^{3}He. The analyses of primordial noble gases in mantle rocks such as MORBs (midocean-ridge basalts), diamonds, xenoliths (e.g., Sarda et al. 1988, Staudacher et al. 1989, Ozima and Zashu 1988, Poreda and Farley 1992) and the discovery of extinct radionuclides, such as the Pu-I-Xe system (Butler et al. 1963, Staudacher and Allègre 1982, Marty 1989) has clearly demonstrated a catastrophic degassing that took place in the first 100 Ma after the Earth accretion. The observations of noble gas having a clear "solar" isotopic composition, such as neon, was another piece of evidence supporting the degassing of primordial gases trapped during the formation of the Earth from the solar nebula (Honda et al. 1991). It has been often considered, by comparison with noble gases, that the major volatiles (N, C, O, H) had the same origin.

The hypothesis of Rubey implies that the volatiles trapped during the formation of the Earth derive from the gas and dust of the protosolar nebula (PSN hereafter). However, the proximity of the Earth to the Sun implies high condensation temperatures that cannot allow incorporation of highly volatile elements such as N, C, O, H. Furthermore, the redox conditions that prevailed in this sector of the Solar System did not allow water to form, suggesting a source different from PSN for the oceans. This is confirmed by the isotopic signature of water and particularly by the isotopic ratio of hydrogen (D/H) measured in modern seawater (value of the standard mean ocean water, SMOW), which is equal to 155.7×10^{-6} ($\delta D_{SMOW} = 0‰$; Table 3.1). The D/H ratio is highly variable in the Solar System, but in a general way, it increases moving outward the Solar System due to a progressive enrichment of deuterium. This enrichment is produced by ion–molecule interactions in the interstellar medium (Robert et al. 2000). The D/H ratio in the PSN has been estimated to be $21 \pm 5 \times 10^{-6}$ using as reference the isotopic composition of helium in the Sun (Geiss and Gloecker 1998) and the isotopic composition of molecular hydrogen in the high atmosphere of the giant planets (Gautier and Owen 1983). The value of $21 \pm 5 \times 10^{-6}$ is more than seven times less than the D/H ratio measured in the oceans. Using appropriate models of the solar nebula, Drouart et al. (1999) showed that only planetesimals formed in the region of Jupiter–Saturn and in the outer asteroid belt could contain water with a D/H ratio similar to that of the oceans. Only two types of planetary bodies could be the source of this water: comets and hydrous carbonaceous chondrites (Morbidelli and Benest 2001).

Comets are bodies composed of ices (mainly H_2O and in minor amounts CH_3OH, CO and CO_2) together with particles of silicates, carbon and organic matter. The comets actually observed, such as Halley or Hale-Bopp, likely come from the Oort Cloud, a distant cloud of comet material located in the outer region of the Solar System, itself populated mostly by planetesimals that were originally in the Uranus–Neptune region and in the primordial Kuiper Belt.

Among the most primitive meteorites, carbonaceous chondrites contain a large amount of water (up to 22 g of H_2O per 100 g of rock; Kerridge 1985). Currently, these meteorites are rare and only 4% of the falls on Earth corresponds to carbonaceous chondrites (Dauphas and Marty 2001). However, hydrous carbonaceous chondrites seem to be a large reservoir of extraterrestrial material: the outer asteroid belt, located between Mars and Jupiter at 2 UA and that is the major source region of the meteorites arriving currently on Earth, seems to be dominated by carbonaceous chondrites; the lunar soil contains from 1 to 2% of such material; the Antarctic micrometeorites (AMM), that constitute the highest flux of extraterrestrial material actually reaching the Earth (40 000 tons per year), are hydrous carbonaceous chondrites (Engrand et al. 1999, Maurette et al. 2000).

To choose between these two potential candidates, we have a strong isotopic constraint, which is the ratio between deuterium and hydrogen (D/H ratio) in the water molecule. The values of the D/H ratios in the terrestrial and extraterrestrial reservoirs (PSN, AMM, carbonaceous chondrites, comets) are reported in Fig. 3.2 and Table 3.1. The water of the oceans has a D/H ratio of 155.7×10^{-6}, while the whole Earth has a D/H ratio of $149-153 \times 10^{-6}$ (Lecuyer et al. 1998). These values are close to those measured in the carbonaceous chondrites ($128-180 \times 10^{-6}$, average $149 \pm 6 \times 10^{-6}$; Boato 1954, Robert and Epstein 1982, Kerridge 1985, Robert 2001) and those measured in the Antarctic micrometeorites AMM ($140-200 \times 10^{-6}$, average $154 \pm 16 \times 10^{-6}$, Engrand et al. 1999, Maurette et al. 2000). The D/H ratio in the water of comets has been measured only in Comet Halley ($316 \pm 34 \times 10^{-6}$, Eberhardt et al. 1995), in Comet Hyakutake ($290 \pm 100 \times 10^{-6}$, Bockelée-Morvan 1998) and in Comet Hale-Bopp ($320 \pm 120 \times 10^{-6}$, Meier et al. 1998). The obtained values are $10-20$ times larger than the D/H ratio of molecular hydrogen in the PSN and $2-3$ times larger than the value found for modern seawater, suggesting that comets did not contribute significantly to the delivery of water to Earth.

A simple mass and isotopic balance shows that the amount of water delivered by comets on Earth is around 10% of the total (Dauphas et al. 2000). This is in agreement with independent estimates, based on the mean collision probability with Earth of comets coming from the giant planet region calculated by Morbidelli et al. (2000). This calculation indicates that $\sim 5 \times 10^{-5} M_T$ (M_T is the mass of the Earth $= 6 \times 10^{24}$ kg) of cometary material from the trans-Uranian region could have been accreted to Earth. Even assuming a 100% water composition of material and a 100% impact efficiency, this would imply the delivery of only $10-15\%$ of the terrestrial water inventory.

The defenders of a cometary origin of water observed that the comets in which we measure the D/H ratio are "long-period" comets, probably formed in the Uranus–Neptune region or in the trans-Uranian region (Delsemme 1999). Accepting the model of D/H enrichment in the PSN (Robert et al. 2000), it is understandable to find D/H ratios 10 times higher than that of the PSN in the outer regions of the Solar System. Owen and Bar-Nun (1995) and Delsemme (1999) suggested that comets delivering water on Earth were those formed in the Jupiter region. These comets would have formed at relatively high temperature (100 K) and consequently they would exhibit a lower D/H ratio due to exchange with protosolar hydrogen. Morbidelli et al. (2000) showed that the lifetime of comets from this region is extremely short (estimated lifetime of 1.5×10^5 y), lowering the impact probability of these comets with an accreting Earth. They concluded that the contribution of cometesimals to the terrestrial water inventory was negligible.
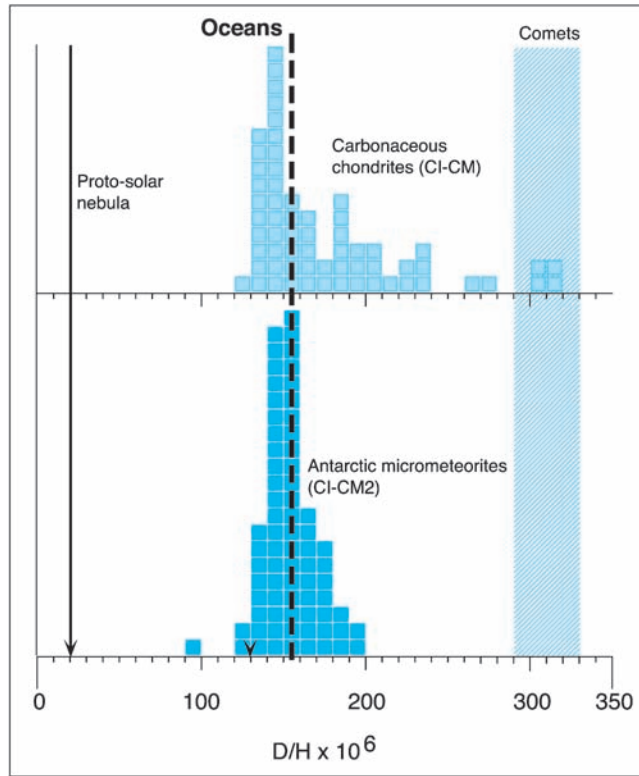

Fig. 3.2. Frequency distribution of the D/H ratios measured in carbonaceous chondrites and Antarctic micrometeorites compared to values for the PSN, Earth oceans and comets. Data: Déloule et al. 1991, Engrand et al. 1999, Maurette et al. 2000, Robert et al. 2000

We can understand from these studies that the debate is far from settled. The accepted hypothesis is that 90% or more of the water has been delivered to Earth by small asteroids having a chondritic composition and coming from the outer asteroidal belt (Morbidelli et al. 2000). The timing of delivery is likely at the end of the accretion of the Earth (Dauphas 2003). This is suggested by the presence of anomalous amounts of siderophile elements in the mantle (Dauphas and Marty 2001).

The siderophiles are elements (such as those of the platinum group) that should have migrated to the core during the Earth primary differentiation, together with Ni-Fe alloy. However, a non-negligible amount of these elements is still present in the mantle and this can only be explained by a late addition, after the core formation and the mantle separation. The core formation is estimated at 50 Ma after the condensation of the PSN (Allègre et al. 1995). The relative abundance of siderophiles in the mantle is very similar to that of the primitive meteorites, such as the hydrous carbonaceous chondrites. Mass-balance calculations suggest that a meteoric flux equivalent to $4.5 \times 10^{-3} M_T$ could explain the late delivery of siderophiles to the mantle (Dauphas and Marty 2001). The same carbonaceous chondrite-like bodies, containing from 6 to 22 $wt\%$ of water (Table 3.1), could have delivered $1.6 - 6.0 \times 10^{21}$ kg of water to Earth, from 1 to 4 times the mass of the present-day oceans (1.4×10^{21} kg).

3.3 Formation of the Oceans: the Geological Record

If different views exist on the origin of water, there is a general consensus that the total oceanic water inventory was available soon after the end of the Earth accretion. The question is when did water condense on the surface to form stable oceans, habitable for life. The chronology of the ocean formation is mostly unknown and it depends on the physical parameters used for the different models of formation and the scarce geological records of the presence of liquid water at the surface of the Earth. The oldest marine sediments found so far are BIF (banded iron formation) in a layered body of amphibolite and ultramafic rocks, crosscut by a quartz-dioritic dyke having a U-Pb age of 3.865 ± 11 Ma, at Akilia, West Greenland (Nutman et al. 1997). Other traces of ancient marine sediments have been found at the Isua Supracrustal Belt, Southern West Greenland and consist of metamorphosed pelagic sediments, probably turbidites, dated at 3.7 Ga (Rosing et al. 1996).

New geological evidence of liquid water comes from the recent U-Pb dating of individual detrital zircons ($ZrSiO_4$) from the Mt. Narryer quartzite and from Jack Hills metaconglomerate, Western Australia (Mojzsis et al. 2001, Wilde et al. 2001). Zircon is a common U-rich trace mineral in granitic rocks that preserves a detailed record of the magma genesis (Pidgeon and Wilde 1998). Furthermore, the radioactive parent nuclides ^{235,238}U decay into the stable daughter products ^{206,207}Pb. Both the parent nuclides and the daughter products can be preserved

in zircons, even when a crystal has been removed from its host rock by weathering, transported as a detrital grain, deposited, hydrothermally altered and metamorphosed (e.g. Valley et al. 1994). This makes zircon a reliable geochronometer for very ancient rocks. The U-Pb ages obtained for the Mt. Narryer and Jack Hills zircons range from 4.28 to 4.40 Ga (Wilde et al. 2001). Because zircons are silicate minerals occurring in intermediate and acid rocks (such as granites), their presence strongly suggests that a differentiated continental crust existed less than 150 Ma after the end of the Earth accretion.

But the most intriguing feature of these zircons is their oxygen isotopic signature (Peck et al. 2001, Fig. 3.3). The $^{18}O/^{16}O$ ratios (denoted as $\delta^{18}O$) of the Jack Hills zircons range from values of $5.0\%_0$, which is close to the primitive value of the Earth mantle ($\delta^{18}O = 5.3 \pm 0.3\%_0$, Valley et al. 1998) to $\delta^{18}O$ of $7.4 \pm 0.7\%_0$. This value can be explained only by a mixing between the mantle source of the zircons and a source enriched in ^{18}O.

The best explanation is that the mantle source of the Jack Hills zircons interacted, directly or indirectly, with surface waters. The products of weathering and low-temperature alteration (such as oceanic crust) have indeed higher $\delta^{18}O$ values ($> 10\%_0$, Valley et al. 2002). The $\delta^{18}O$ signature measured in the Hadean, Archean and Proterozoic zircons shows a progressive increase towards values up to $10\%_0$ (Fig. 3.3). This can be explained by an increase of the amount of supracrustal high-$\delta^{18}O$ material available for melting and assimilation, as the "wet" continental crust evolved and matured during the Precambrian (Peck et al. 2000). The presence of $\delta^{18}O$ of $7.4 \pm 0.7\%_0$ in a 4.404 ± 0.008-Ga old detrital

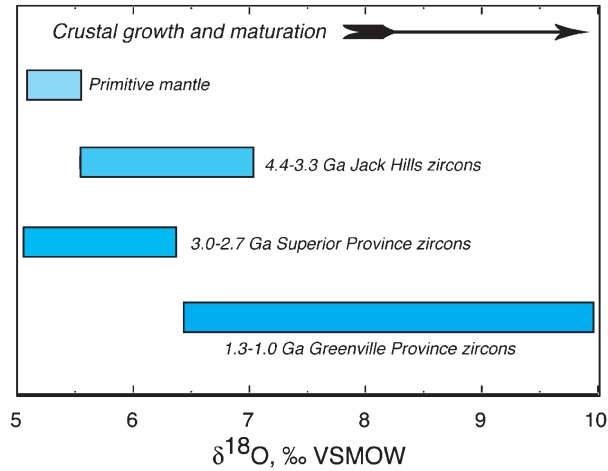**Fig. 3.3.** Variations of the $\delta^{18}O$ measured in zircons of different ages. The progressive increase of the $\delta^{18}O$ with age is due to contamination of high $\delta^{18}O$-supracrustal material from a growing and maturing continental crust. Oxygen isotopic ratios are average values. Oxygen data for zircons: King et al. 1998, Peck et al. 2000, 2001. Data for primitive mantle: Valley et al. 1998

zircon of Jack Hills could thus be the indirect and oldest record of interaction of a magmatic source with liquid water at the surface of the Earth (Peck et al. 2001).

There are several other lines of evidence that liquid water was present very early in the history of the Earth. Among others, we can cite the isotopic signatures of Neodymium (Nd) and Strontium (Sr) obtained in ancient minerals and rocks of ages ranging from 4.04 to 3.80 Ga. The Nd and Sr isotopic ratios suggest that between 10 and 15% of the volume of the present-day continental crust were formed at that period (Taylor and McLennan 1995). This crust has a TTG (Trondhjemite-Tonalite-Granodiorite) composition, which is derived directly by partial melting of hydrated basalt (Martin and Moyen 2002). This means that large volumes of water were available on Earth well before 4 Ga.

In the next section, I will illustrate the formation of the ocean based on the model proposed by Abe (1993) and particularly that of Sleep et al. (2001), which integrated the new evidence coming from the Australian zircons for extensive surface water at indeterminate temperature and long-lived continental crust, 4.40 Ga ago.

3.4 Formation of the Oceans: Chronology and Processes

The formation of the oceans can be summarized in four steps, here represented by the cartoons of Figs. 3.4.1a to 3.4.4d. The first step is from the start of the Earth accretion (4.56 Ga ago) to the segregation of the core and the end of the interior degassing, estimated at $4.45-4.50$ Ga (Allègre et al. 1995, Halliday 2001). During this period, carbonaceous chondrites likely delivered water (and possibly organic molecules) to the Earth.

During impacts, the asteroids vaporized, dispersing the trapped volatiles in the atmosphere. A small part of them has been probably partitioned in the melt (the surface of the Earth was in a molten state) and re-gassed successively (Fig. 3.4.1). The total amount of water delivered to Earth was certainly higher than that in the present-day oceans, because the losses of volatiles were important at the beginning. Pepin (1991) suggested that at least 50% of the water delivered to Earth could have been dissociated in hydrogen and oxygen by the strong UV radiation that the Earth suffered. Further losses could have derived from impact erosion of the atmosphere by part of the arriving planetary bodies.

During the first chaotic moments of the Earth history, at about 4.50 Ga (Halliday 2001), a collision with a planetoid having a size comparable with that of Mars affected our planet (Canup and Asfaugh 2001, Fig. 3.4.1). The accretion of the debris formed the Moon. The energy of the collision has been estimated to be 4×10^{31} J (Sleep et al. 2001). This value, divided by the mass of the Earth, is 7×10^6 J kg^{-1}, an energy comparable to that needed for the vaporization of silicates at the surface of the Earth ($6-14 \times 10^6$ J kg^{-1}). After the
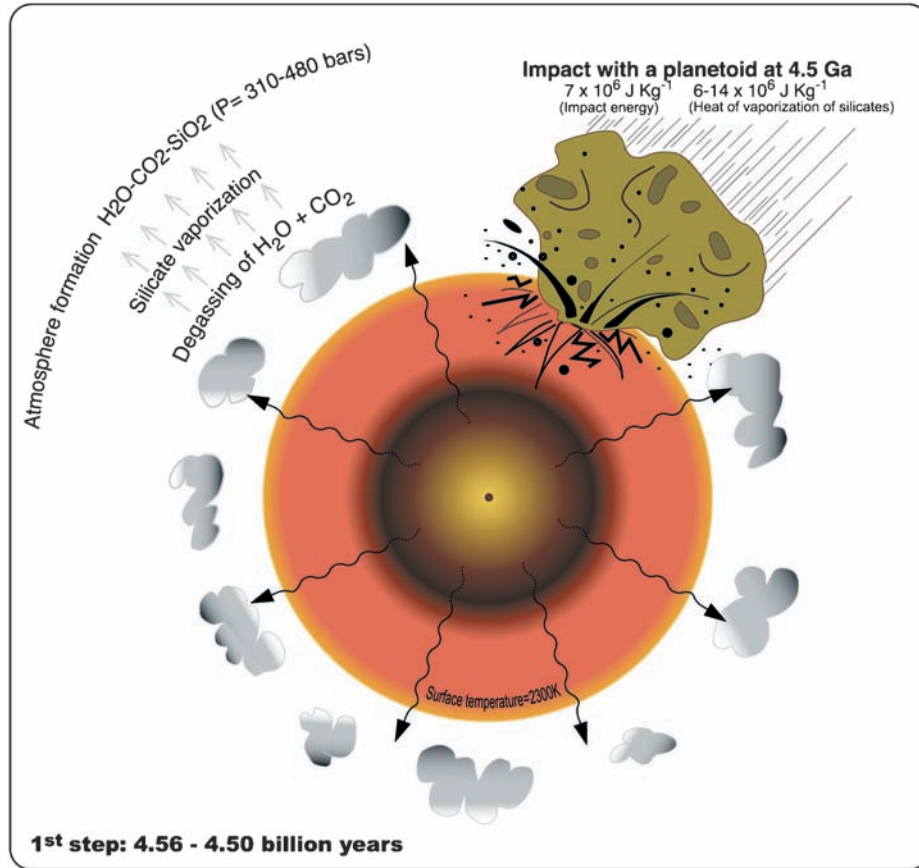
Fig. 3.4.1. Sketch representing the main phases of the formation of the terrestrial oceans [TS30]

collision, the temperature increased to 2300K ($\sim 2000\,°C$), causing melting of the surface of the Earth. If some liquid water existed at that time, it was vaporized together with silicates (Sleep et al. 2001). The age of $4.50-4.45\,$Ga can be assumed as the initial time (T_0) of the ocean formation. The collision of this planetoid caused the formation of a dense atmosphere of gaseous silicates that rapidly cooled down and precipitated after a few thousand years (Sleep et al. 2001).

The residual atmosphere was constituted mainly of water vapor and CO_2 (nitrogen was close to 1% of the total volume and thus negligible, Kasting 1993). If we assume that all the water of the present oceans ($1.4 \times 10^{21}\,kg\,H_2O$) was in the atmosphere, the atmospheric partial pressure would be 270 bars. To this pressure, we must add the partial pressure of CO_2. The CO_2 in the primordial atmosphere was equivalent to the amount of carbon actually preserved in car-
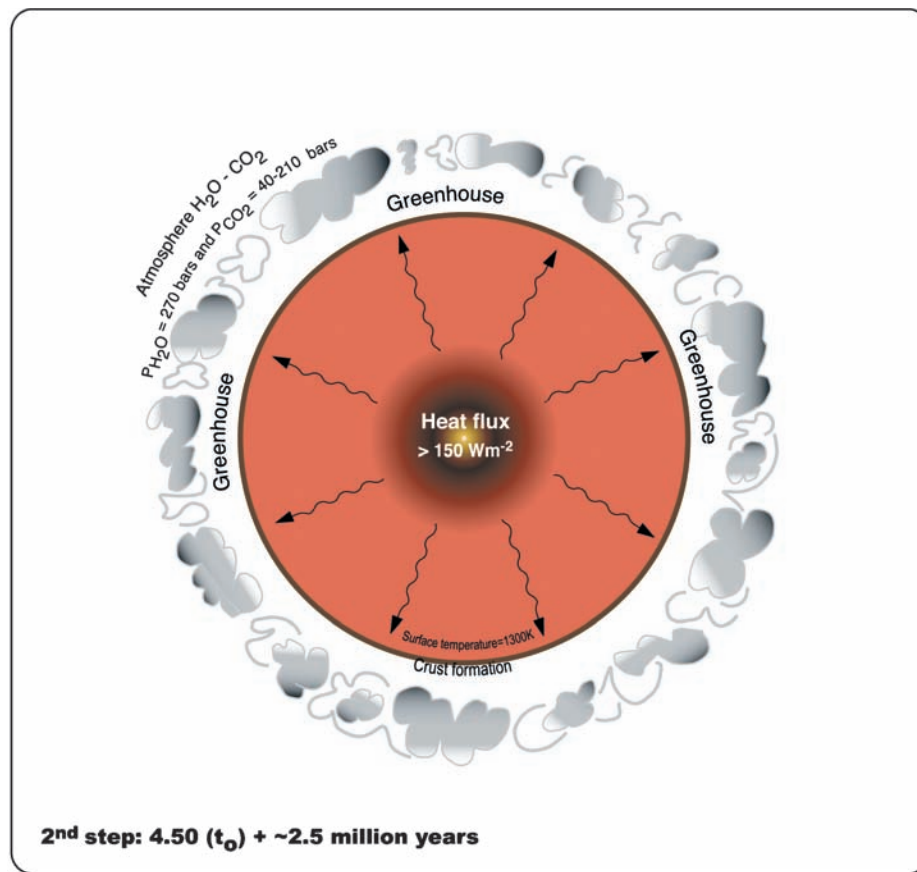
Fig. 3.4.2. Ibid

bonates (3.65×10^{21} moles, Li 2000), in continental sediments (1.12×10^{21} moles, Li 2000) and in the biosphere (2.6×10^{17} moles, Faure 1991). This amount would produce an atmospheric CO_2 partial pressure of 40 bars. Recently, Sleep et al. (2001) proposed that the total inventory of CO_2 in the present mantle (2.5×10^{22} moles, Zhang and Zindler 1993) was concentrated in the primordial atmosphere. This amount is equivalent to a partial pressure of 170 bars. The primordial atmosphere could have been a dense mixture of 270 bars of H_2O and 40–210 bars of CO_2, an atmospheric composition somewhat similar to that of Venus.

A runaway greenhouse effect produced by the massive H_2O–CO_2 atmosphere dominates the second phase of formation of the oceans (Fig. 3.4.2). This runaway greenhouse maintained the surface of the Earth at the melting temperature, while the heat flow from the interior was greater than 150 W/m^2 (Abe 1993). This is the critical surface heat flow that corresponds to the difference between the
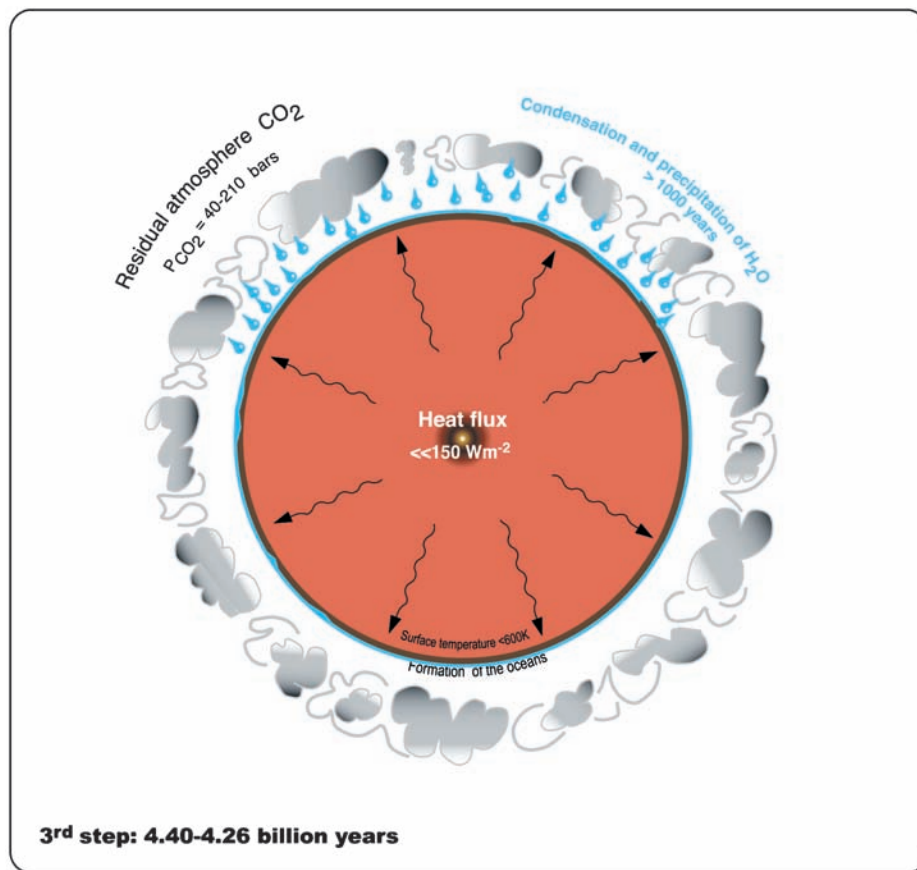
Fig. 3.4.3. Ibid

critical greenhouse threshold and the heat supply by the Sun. For a surface heat flow lower than $150\,\text{W/m}^2$, the runaway greenhouse cannot be maintained longer and the surface of the Earth rapidly cooled down. In a few million years, the surface reached a temperature of around $1,300\,\text{K}$, sufficiently cold to produce a solid rim of basaltic composition, which separated the atmosphere from the hot interior of the Earth. The surface of the Earth cooled down rapidly, allowing the condensation of water (Fig. 3.4.3).

The oceans formed by a sort of "universal deluge" due to the condensation of the atmospheric water vapor (Fig. 3.4.3). Abe (1993) suggested that the terrestrial oceans were produced in less than 1000 years, due to heavy rains. The raining rates were $7000\,\text{mm/year}$, which corresponds to 10 times the present-day raining rates at the tropical latitudes. Assuming an atmospheric pressure at the surface of several hundred bars, water starts to condense and precipitates at $600\,\text{K}$. The presence of stable liquid water at relatively low temperatures at

Residual atmosphere P CO₂ = 5-25 bars

Basalt weathering → carbonates + SiO2 + H2O (Sedimentation of CO2)

Recycling of CO₂ in the mantle:subduction?

Heat flux $\ll 100$ Wm^{-2}

Surface temperature=330-380K

Habitable oceans

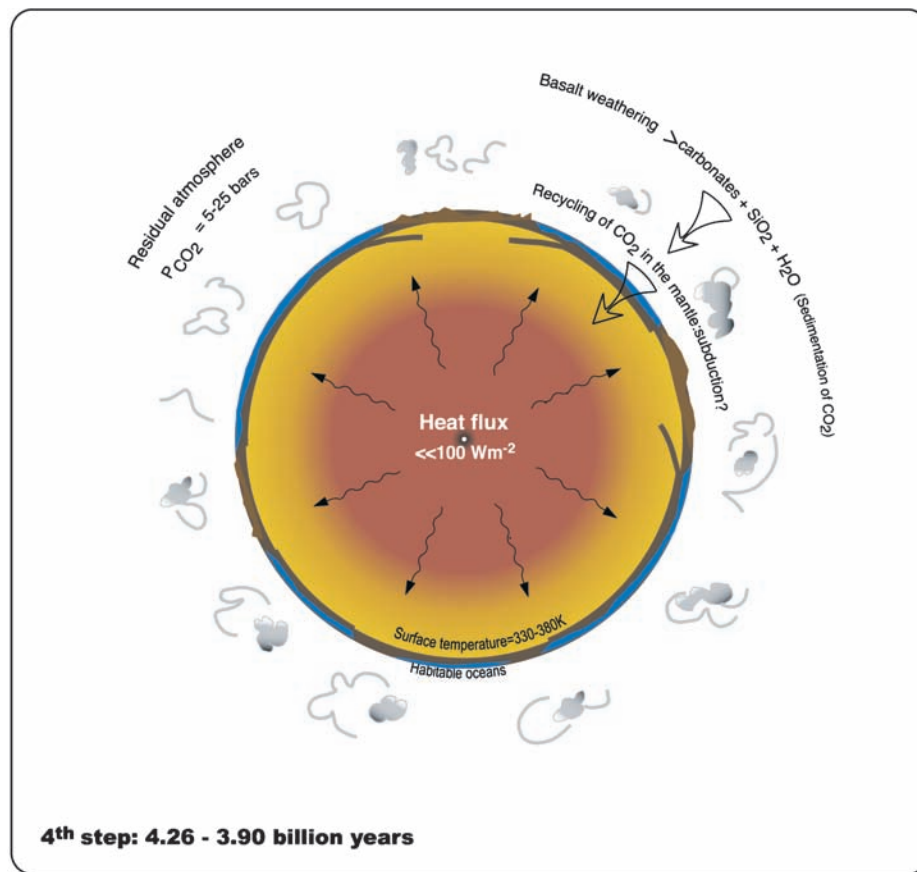**4ᵗʰ step: 4.26 - 3.90 billion years**

Fig. 3.4.4. Ibid

4.40–4.35 Ga, as suggested by the oxygen isotopic composition of zircons, indicates that the Earth cooling was a relatively rapid process (Valley et al. 2002). Temperatures lower than 600 K were probably available between 50 to 150 Ma after the formation of the Earth.

The neoformed oceans were too hot for the development of life. From our knowledge of extremophiles, the maximum temperature allowed for the survival of "hyperthemophiles" (heat-loving organisms) is from 80 to 110 °C (Rothschild and Mancinelli 2001). When the terrestrial heat flux decreased to a value of 100 W/m^2, the greenhouse effect directly controlled the temperature of the oceans. Temperatures of 60 to 110 °C canbe reached at equilibrium with a residual atmosphere of 5 to 25 bars of CO_2. If we assume an initial CO_2 partial pressure of 210 bars, this means that we must be able to recycle efficiently 185–205 bars of CO_2 into the mantle. Sleep et al. (2001) proposed the carbonation of the oceanic basaltic protocrust as the most efficient process of extraction of CO_2

from the atmosphere. The most common reaction of carbonation is (Holland 1984):

$$CaSiO_3 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2 \tag{3.1}$$

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2CO_3 \tag{3.2}$$
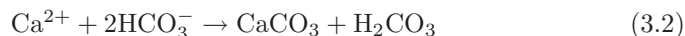
The so-formed carbonates 3.2 could have been recycled to the interior of the Earth, by subduction (Fig. 3.4.4). This implies that plate tectonics was active since 4.4–4.3 Ga, which cannot be excluded but for which we have no direct evidence, because of the scarce geological record. Taking into account the instability of a young and thin protocrust, its partial melting caused by the impact of meteoritic bodies could have permitted a sort of crustal recycling. Zhang and Zindler (1993) showed that the present-day CO_2 recycling rate is 2.3×10^{13} mol/y. This means that from 40 to 210 bars of CO_2 can be removed from the atmosphere in a span of time ranging from 200 Ma to 1.0 Ga. The generation and recycling of oceanic crust was probably higher in the Hadean, because of the larger amount of heat to be evacuated from the interior of a very hot early Earth, helped by vigorous mantle convection (Nisbet et al. 1993, Pinti 2002). Bickle (1986) estimated an Archean plate generation 2–3 times higher than at modern MOR, which means a 2–3 times higher crustal recycling. Zhang and Zindler (1993) proposed a maximum initial recycling rate of 150×10^{12} mol/y. At this rate, the atmospheric CO_2 could have been recycled in a shorter time, between 30 and 160 Ma.

This means that at 4.3–4.2 Ga, the oceans were stable and cold enough to assure the survival of the first living communities, possibly hyperthemophiles. It is likely that the temperature of the oceans was not stable in this period but successive impacts of asteroids and comets may have locally increased temperatures up to 110°C, or higher (≥ 300°C) causing the partial evaporation of the oceans and their recondensation (Nisbet and Sleep 2001). Oceans were stable at the end of the Hadean (3.9 Ga) when the massive meteoritic bombardment of the Earth ended.

3.5 Chemical Composition of the Primitive Oceans

If the volume of the oceans has not likely changed in the last 4 billion years, its chemistry certainly has. Here, I present an overview of the evolution of the physical and chemical conditions that operated in the primitive oceans and where the first living organisms developed. For a complete treatment on the subject, the reader can consult the excellent book of Heinrich Holland "The Chemical Evolution of the Atmospheres and the Oceans" (Holland 1984). The physical and chemical parameters of the oceans discussed here, which can have an impact on the development of life, are the temperature, the pH, the redox and the salinity. This is based both on thermodynamical modeling and, also, on the few traces that oceans left in the Precambrian marine sediments.

3.5.1 Temperature

In the last 4 billion years, the temperature of the oceans decreases from an initial value of $230\,^{\circ}$C (calculated at equilibrium with a massive CO_2 atmosphere, Sleep et al. 2001) to the present-day average of $20\,^{\circ}$C at the surface. The temperature decrease is linked to the progressive decline of the CO_2 amount in the atmosphere and the consequent weakening of the related greenhouse effect (Abe 1993, Kasting 1987, 1993, Tajika and Matsui 1993, Fig. 3.5). The evolution of the ocean temperature can be compared with the geological record. A measurement of the past ocean temperatures could be that recorded by the isotopic ratio of the oxygen (^{18}O/^{16}O expressed as δ^{18}O) measured in cherts, a hard rock composed of very fine-grained silica (Knauth 1994). Of particular interest is that $\delta^{18}O_{\text{water-rock}}$ in cherts decreases as the temperature of the ocean increases, due to isotopic fractionation during precipitation of silica in the ocean (Knauth and Lowe 1978). Therefore, from the δ^{18}O values recorded by cherts of different ages we can provide a measure of the oceanic temperature at any time (Fig. 3.5). The variation of the δ^{18}O measured in the cherts of Archean age suggests that these rocks precipitated in an ocean that was $50\,^{\circ}$C warmer than today. This result has been contested because it could simply reflect isotopic variations of the δ^{18}O of the ancient oceans. However, measurements of the $\delta^{18}O_{\text{SMOW}}$ of $0 \pm 3\,\permil$ in Early Proterozoic seawater suggest that the isotopic signature of the ocean has not changed significantly during eons (Knauth and Robert 1991). The problem with this paleothermometer is the doubtful origin of Archean cherts. Most of them seem to be silica gel precipitated from hydrothermal fluids (Sugitani 1992, Nijman et al. 1998, Pinti et al. 2001). Consequently, the temperature curve of Knauth and Lowe (1978) may reflect the temperature of silica precipitation from hot hydrothermal fluids, rather than that of ambient seawater.

An alternative method for measuring the past ocean temperatures could be the homogenization temperature of seawater inclusions preserved in ancient rocks. de Ronde et al. (1997) have shown that ancient seawater was preserved in bodies of iron oxide (Ironstone Pods) from the 3.5–3.2 Ga Barberton greenstone belt, South Africa. These rocks have been interpreted as deposits of Archean seafloor hydrothermal vents (de Ronde et al. 1997). It is to be noted that Donald Lowe of Stanford University and Gary Byerly of Louisiana State University have recently contested this interpretation, showing that the ironstone pods are composed largely of goethite (a thermally unstable hydrated iron oxide mineral), deriving from quaternary dissolution of the Archean siderite (Lowe and Byerly 2003). They concluded that these pods are deposits of young subaerial springs and contain no record of Archean environments. Although a remobilization of iron could have been produced during quaternary weathering, selected fluid inclusions by de Ronde et al. (1997) show primary textures and geochemical information can be considered genuine for Archean times (F. Westall, personal communication).

If the fluids contained in the inclusions are preserved at different physical conditions of temperature and pressure (i.e. depth) than the original fluid, phase
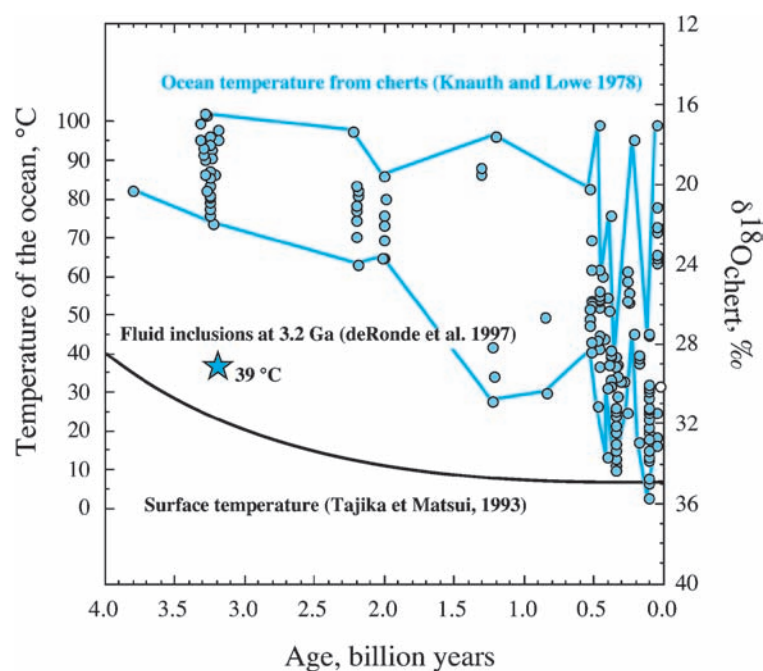
Fig. 3.5. Isotopic variations of oxygen (expressed as $\delta^{18}O$) measured in cherts of different ages compared to the ocean temperatures where the cherts precipitated. Data: Knauth and Lowe (1978). The *lower curve* represents the surface temperature variations as calculated by the model of Tajika and Matsui (1993). The *star* indicates the temperature at 3.2 Ga, obtained from homogenization temperatures of primary seawater inclusions from Ironstone Pods, South Africa (de Ronde et al. 1997)

separation will take place in inclusions. In the case of seawater, the change of temperature and pressure can produce the separation of a saline phase from the liquid. Heating or cooling down the sample homogenizes the phases contained in the inclusions and thus we can know the temperature of formation (Roedder 1984). In the case of the Ironstone pods, de Ronde et al. (1997) calculated an oceanic surface temperature of 39°C, which is lower than the 70°C proposed by Knauth and Lowe (1978) on the basis of the $\delta^{18}O$ in cherts (Fig. 3.5).

3.5.2 The pH and the Redox State

Archean ocean was probably acid. This hypothesis is based on the fact that the primitive ocean was in equilibrium with an atmosphere mainly composed of CO_2. At the present time, the pH of the ocean is controlled by its equilibrium with the carbonates (dissolution and precipitation of $CaCO_3$) and the CO_2 fugacity in the atmosphere (Ottonello 1997). The equation relating the CO_2 fugacity in the atmosphere and the pH of the ocean at equilibrium is:

$$10^{9.38} \cdot f_{CO_{2(g)}}^{-1} \cdot \left[H^+\right]^4 + \left[H^+\right]^3 - \left(10^{-7.82} \cdot f_{CO_{2(g)}} + 10^{-14}\right)$$
$$\cdot \left[H^+\right] - 10^{-17.85} \cdot f_{CO_{2(g)}} = 0 \tag{3.3}$$

The curve of variation of CO_2 in the atmosphere, as calculated by Tajika and Matsui (1993), is reported in Fig. 3.6 together with the curve of variation of the pH in the ocean, calculated from (??[TS][31]). The ocean was probably acid until 2 Ga to become progressively basic until the present-day value of 8.2 (Fig. 3.6). The chosen model for the CO_2-level variation in the atmosphere predicts an initial value of 10 bars (Tajika and Matsui 1993). In the Hadean, the CO_2 level could have been much higher (40–210 bars, Sleep et al. 2001) and the ocean pH directly controlled by the equilibrium of carbonation of the oceanic crust rather than by the precipitation of carbonates. More complicated thermodynamic models are thus needed to predict the pH of the Hadean ocean. Sleep et al. (2001) considered the carbonation reactions produced at equilibrium (??[TS][31] and ??[TS][31]). The pH fixed by these reactions is controlled directly by the pCO_2. Sleep et al. (2001) calculated the theoretical pH from the reactions and consequently that of oceans at initial temperatures of 200–230°C. The obtained pH ranges from 4.8 and 6.5, supporting the idea of an acid Hadean ocean.

Kempe and Degens (1985) proposed an alternative model for the Hadean ocean, based on their observations of the soda lakes of the east African rift.
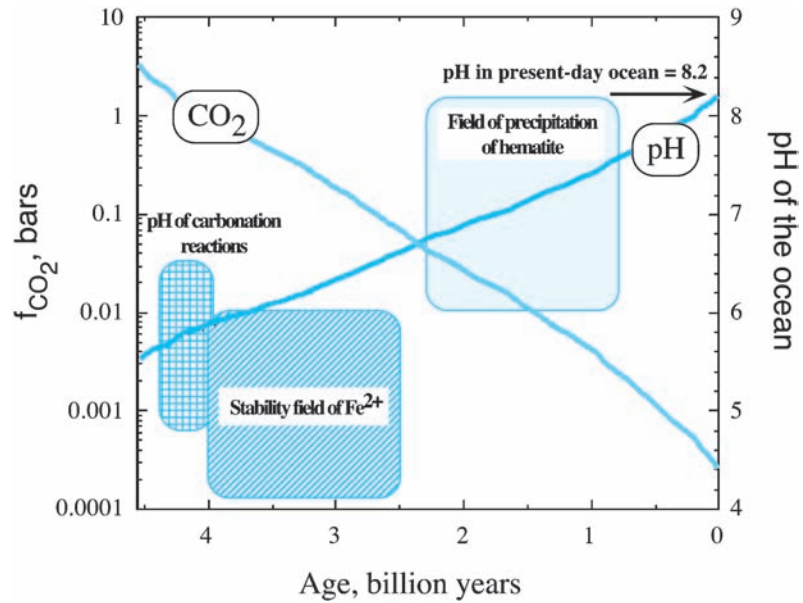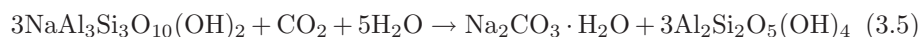

Fig. 3.6. Variations of the partial pressure of CO_2 in the atmosphere and change of pH of the ocean, at equilibrium. The different fields represent the variations of the pH of the ocean as obtained from different thermodynamic calculations. See text for more details

They suggested an early soda ocean, saturated in sodium carbonate (thermo-natrolite: $Na_2CO_3 \cdot H_2O$). The resulting ocean would be alkaline, with pH ranging from 9 to 10.5. Thermo-natrolite could have been produced by reactions between sodium-rich rocks (such as those of the TTG, that constitute the primitive crust) and the CO_2 in the atmosphere:

$$\text{CE}^{32}\ 2NaAlSi_3O_8 + CO_2 + 3H_2O \rightarrow Na_2CO_3 \cdot H_2O + Al_2Si_2O_5(OH)_4 + 4SiO_2 \quad (3.4)$$

$$3NaAl_3Si_3O_{10}(OH)_2 + CO_2 + 5H_2O \rightarrow Na_2CO_3 \cdot H_2O + 3Al_2Si_2O_5(OH)_4 \quad (3.5)$$

Sleep et al. (2001) argued against an early soda ocean, based on thermodynamic and mass balance. Reactions ??$_{TS}{}^{31}$ and ??$_{TS}{}^{31}$ at temperatures between 20 and 200°C take place only for pCO_2 comprised between 3 kbar up to 6 Gbar, while only 40 bars to 210 bars were probably available in the Hadean atmosphere. Mass balance indicates that the Na/Al ratio in the weathered crust should be of 1:1, while the most sodium-rich rocks, the magmatic suite TTG, has a Na/Al ratio of 1:2. In other terms, there was not enough sodium to saturate the ocean in $Na_2CO_3 \cdot H_2O$.

The hypothesis of an Archean acid ocean is supported by the large deposition, at the start of the Proterozoic era, of BIF, rocks composed by a succession of cherts, siderite ($FeCO_3$) and hematite (Fe_2O_3) (Morris 1993, Isley 1995). The amount of iron is between 30 and 45 wt%. The precipitation of most of BIF at the start of the Proterozoic can be explained by a progressive accumulation of Fe in its reduced form (Fe^{2+}) in the ocean during the Hadean and the Archean (Holland 1984). The Fe^{2+} ion is indeed soluble in water in an anoxic, reduced environment and for pH ranging from 0 up to 6. In an alkaline and oxygenated ocean, as modern seawater, the Fe^{3+} is precipitated as hydroxide $Fe(OH)_3$. The accumulation of iron during the Archean and its precipitation as BIF in the Proterozoic is thus a clear indication of a major change in the pH and redox conditions of seawater and particularly the evolution from an anoxic and acid ocean to a basic and oxygenated one.

There are several other lines of evidence of the redox state of the ocean (Holland 2002). The study of rare-earth elements in marine sediments shows this change due to the progressive oxygenation of the atmosphere and of the ocean (the Great Oxidation Event, Holland 2002, Murakami et al. 2001, Yang et al. 2002). For example, Archean microbialites (laminated limestones), found at the 2.52-Ga Campbellrand carbonate Platform, South Africa, show an excess of cerium (Ce) that cannot be found in the present-day microbialites (Kamber and Webb 2001). Ce^{3+} is easily oxidized to Ce^{4+} in the presence of O_2 and is scavenged by iron hydroxides, as in the present-day ocean. The presence of a cerium positive anomaly in the Archean marine sediments could thus be another sign of an anoxic ocean (Yang et al. 2002).

Other geochemical evidences of an anoxic ocean during the Archean are the nitrogen isotopic signatures of kerogens (polymerized organic matter) preserved in ancient cherts (Beaumont and Robert 1999, Boyd 2001a, Pinti et al. 2001, Pinti 2002). The average isotopic composition of N in present-day marine organic

matter differs significantly from that of the atmosphere. The average value of the $\delta^{15}N$ in marine organic matter is $+6\%_0$(Peters et al. 1978, Boyd 2001b), while that of the atmosphere is assumed to be $0\%_0$. The difference between the $\delta^{15}N$ values in the organic matter and in the atmosphere is due to the isotopic fractionation during the process of denitrification of NO_3^- caused by anaerobic microorganisms (denitrifiers) (Peters et al. 1978).

In Early Archean kerogens, the $\delta^{15}N$ ranges from close to $0\%_0$ down to $-8.1\%_0$ (Beaumont and Robert 1999, Pinti et al. 2001, 2003). At the start of the Proterozoic, the $\delta^{15}N$ values in kerogens shift from negative values to positive values (Boyd and Philippot 1998). This shift could well be related to the Great Oxidation Event (Holland 2002). The oxygenation of the upper parts of the oceans at that time was almost certainly accompanied by a shift in the marine chemistry of N from NH_4^+-dominated to NO_3^--dominated.

In the absence of O_2 in the water column, NH_4^+ must have been the N-dominant containing species (Boyd 2001a). The NH_4^+ ion probably cycled efficiently between photosynthesizers, decomposers, and the water column. The most likely metabolic pathway for N in an anoxic ocean was N fixation or NH_4^+ uptake caused by bacteria, which could be able to produce the observed negative shift in the $\delta^{15}N$ values of Archean kerogens (Beaumont and Robert 1999, Pinti and Hashizume 2001). The situation changed drastically when the concentration of O_2 in the water column increased. Nitrifying chemoautotrophs were then able to oxidize NH_4^+ to NO_2^- and subsequently to NO_3^-. These N-species were convertible to N_2 in anaerobic settings by denitrifiers, producing the positive shift of $\delta^{15}N$ observed in the present-day marine organic matter.

The hypothesis of an anoxic primitive ocean demands that all or nearly all of the sulfur in volatiles added to the ocean–atmosphere system in Archean time was removed as a constituent of sulfides, mainly pyrite. This seems to be true. Anhydrite is known only as a replacement mineral before 2.3 Ga. The earliest significant anhydrite deposits are at 2.2 Ga. Barite is reasonably common in Archean and early Proterozoic sediments. Its quantity is very small compared to that of contemporaneous pyrite, but its presence does indicate that SO_4^{-2} has been present in surface ocean water during the past 3.45 Ga. This is not surprising. Volcanic SO_2 reacts with H_2O at temperatures below $400\,^{\circ}C$ to give H_2S and H_2SO_4, without requiring the presence of oxygen (Holland 2002).

3.5.3 Salinity

The salinity of the oceans derives from two distinct sources: weathering of the continental crust and oceanic hydrothermalism. In the present-day ocean, weathering is the dominant source of salinity, but during the Hadean and the Archean period, it was likely the oceanic hydrothermalism that was dominant (Derry and Jacobsen 1988). The volume of the continents was lower than today (10–15% of the present-day volume) and the surface of the Earth was composed by a larger amount of small plates. Models suggest that the extension of the midocean ridges

during Archean was 10 times longer and production of new oceanic crust at MOR was 2–3 times higher than the present-day (Bickle 1986). The input of dissolved species from hydrothermal activity at MOR and from interactions of hot fluids with oceanic crust was predominant during this period. The occurrence of large amounts of iron from the ridge crests, as a source of iron in BIF (Isley 1995), is the evidence that the mantle buffered the chemistry of the ocean.

The Proterozoic era marks the end of an ocean salinity dominated by hydrothermal sources and the beginning of a salinity produced by the weathering of continents. Measuring the isotopic variation of the Sr and Nd ratios in the Archean and the Proterozoic marine sediments have permitted observation of the change in the salinity sources of the ocean. The continental crust is enriched in rubidium (Rb) because this element is incompatible (which means that it tends to remain in the residual melt during magma crystallization, the melt forming the crust). The isotope ^{87}Rb decays to the isotope of mass 87 of strontium (^{87}Sr) and consequently, the isotopic ratio ^{87}Sr/^{86}Sr increases in the crust compared to the values observed in the mantle, which is correlatively depleted in Rb. Veizer and Compston (1976) measured the strontium isotopic ratios ^{87}Sr/^{86}Sr in Archean carbonates and found values of 0.7025 ± 0.0015 to 0.7031 ± 0.0008. These values are close to that characteristic of the mantle during the Archean (< 0.703). The present-day carbonates show strontium isotopic ratios higher than 0.715, indicating that the source of Sr in the ocean evolved with a progressive enrichment in ^{87}Sr due to the continental input (Veizer et al. 1989).

Isotopic studies of neodymium (Nd) and Sr in Archean microbialites of the Campbellrand carbonate Platform, South Africa, allowed to constrain the ratio between the hydrothermal and the continental sources of salinity (Kamber and Webb 2001). Figure 3.7 shows the isotopic ratios of Nd ($^{143}Nd/^{144}Nd$) and Sr(^{87}Sr/^{86}Sr) measured in the 2.52-Ga microbialites. The Nd and Sr ratios show a mixing between the mantle and the continental crust reservoirs of Nd and Sr. From a simultaneous mass and isotopic balance, we can estimate the mantle and the continental flux ratio for the elements dissolved in the ocean at the transition between the Archean and Proterozoic (2.5 Ga). The results suggest that the mantle flux of elements to the oceans was 3 times higher than the continental flux, while now the ratio between the mantle and the continental inputs is of 0.3 to 0.5 (Kamber and Webb 2001).

The change in salinity sources, pH and redox state of the ocean has likely altered the relative concentration of dissolved species in ancient seawater. However, the salinity of the oceans was likely dominated, since the beginning, by halite (NaCl). A NaCl brine largely similar to modern seawater could have been produced by water–rock reactions at midoceanic ridges since Hadean (Sleep et al. 2001). Finding traces of preserved seawater in ancient rocks would be, of course, helpful for determining its chemistry. de Ronde et al. (1997) found primary inclusions at the 3.2-Ga Ironstone Pods of the Barberton greenstone belt, South Africa, containing two fluids mixed up. The first is seawater having a NaCl–CaCl$_2$–H$_2$O composition. The second fluid is of hydrothermal origin
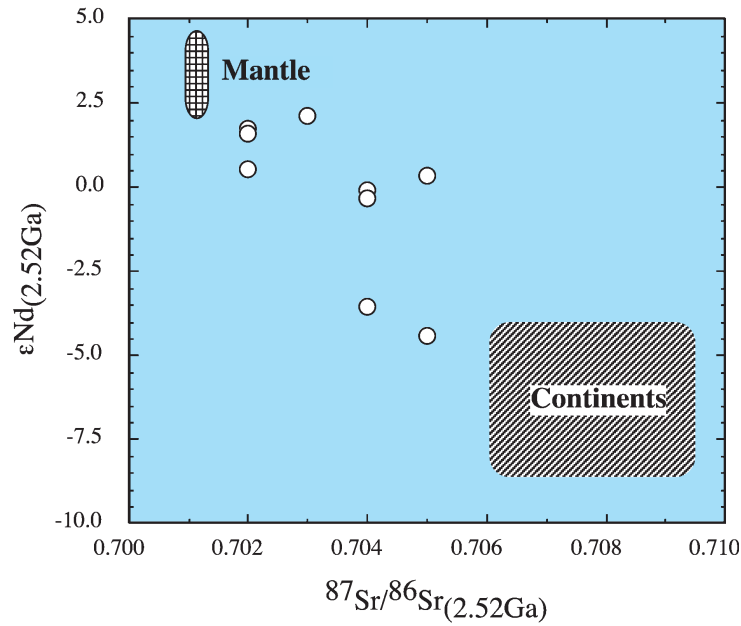
Fig. 3.7. Isotopic variations of Nd and Sr measured in 2.52-Ga microbialites from South Africa (Kamber and Webb 2001). The variations can be explained by a mixing between a mantle and a continental input of dissolved species in the ancient ocean

and has a $CaCl_2$–$FeCl_2$–H_2O composition. Recent studies on primary fluid inclusions found in intrapillow quartz at the 3.5-Ga North Pole Dome, Western Australia, show the presence of ancient seawater having a NaCl–$CaCl_2$–H_2O composition similar to that found by de Ronde and his colleagues (Foriel et al. 2003).

The concentration of the major cations and anions dissolved in the Archean fluids found in the Ironstone Pods is reported in Table 3.2 and Fig. 3.8. The Na/Cl ratio in the Archean seawater is the same as the present-day ocean (0.858), but the total amount of sodium and chlorine is 165% higher than that of modern seawater. The concentrations of Ca^{2+} and Sr^{2+} are 22 and 50 times higher than the present-day ocean. The higher Ca and Sr concentrations could derive from reactions with carbonates (the seawater end-member fluid is a NaCl–$CaCl_2$–H_2O brine). The concentration of Mg^{2+} is mostly the same as that of modern seawater, while K^+ is 87% higher (Fig. 3.8). The concentration of SO_4^{2-} is lower than in modern seawater. This could be explained by reactions between calcium sulfates and hydrothermal fluids (de Ronde et al. 1997) or alternatively by reactions of these fluids with the oceanic crust (Bischoff and Dickson 1991). However, these reactions would reduce considerably the Mg amount, which is not the case. Finally, the amount of halogens Br and I are 2.6 and 74 times higher, respectively, than what is observed in modern seawater.

Table 3.2. Concentrations of the main dissolved species in the Archean ocean (in mmole/L). Data are from de Ronde et al. 1997

Cl^-	Br^-	I^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}
				Archean seawater				
920	2.25	0.037	2.3	789	18.9	50.9	232	4.52
				Modern seawater				
556	0.86	0.0005	28.7	477	10.1	54.2	10.5	0.09

The Br/Cl ratio in the Archean seawater is estimated at 2.5×10^{-3} (de Ronde et al. 1997), which is close to the mantle value of 2.9×10^{-3} (McDonough and Sun 1995), but higher than what is measured in modern seawater of 1.54×10^{-3}. The I/Cl ratio in the Archean seawater is 40×10^{-6} (de Ronde et al. 1997), which is higher than that of modern seawater (0.9×10^{-6}) but lower than that estimated for the mantle of 190×10^{-6}. Two hypotheses can explain the enrichment of halogens. The first is that the Archean ocean chemistry was controlled by large-scale hydrothermal interaction between the oceanic crust/volcano-sedimentary pile and seawater. In other words, the ocean chemistry was buffered by the mantle, that is the source of I and Br. The second
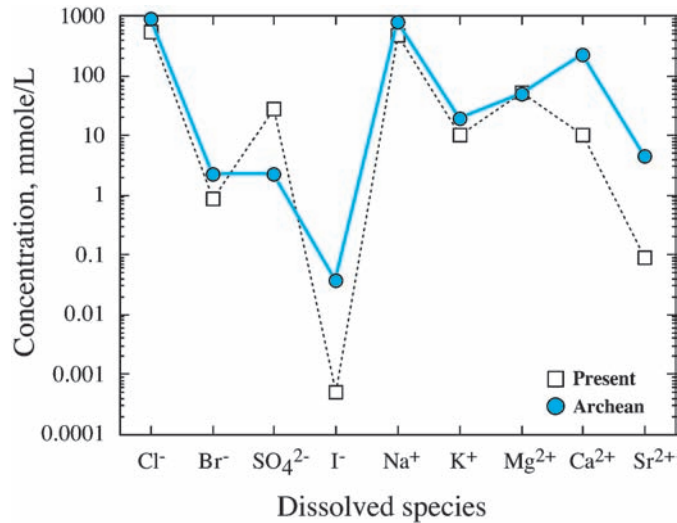
Fig. 3.8. Variations of the concentration of the main dissolved species in Archean seawater and in modern seawater. Data from de Ronde et al. (1997)

hypothesis assumes the role of the biosphere in the uptake of halogens from seawater. In modern seawater, Br and I are depleted because they are fixed in plankton (they are metabolites for plankton). The burial of organic matter with sediments causes the scavenging of halogens from the ocean (Krauskopf and Bird 1995). Channer et al. (1997) explained the enrichment of Br and I in Archean seawater by two different hypotheses. The first is the presence of an ancient biosphere that interacted differently with halogens (absence of plankton or different metabolic pathways) and preserved halogens to be scavenged from the ocean. The second suggests that the carbon burial rate in the Archean was lower than today. The carbon burial rate is indeed controlled by the rate of sedimentation, which in turn depends on the continental surface available for erosion. Smaller continents dominated the Archean period and it is likely that sedimentation and carbon burial were reduced to a minimum value compared to the present-day (Des Marais et al. 1992), preserving high halogens concentrations in the water column.

3.6 Conclusions

The most recent models of ocean formation (Sleep et al. 2001) and recent geological findings (Mojzsis et al. 2001, Wilde et al. 2001) suggest that liquid water was present at the surface of the Earth soon after the accretion of our planet. The total oceanic water inventory was available since the beginning, delivered by hydrous carbonaceous chondrites and, in minor amount, by comets (Morbidelli et al. 2000, Dauphas and Marty 2001, Dauphas 2003). Probably 50 to 150 Ma later, the water vapor composing the secondary atmosphere of the Earth condensed to the surface to form the oceans (Abe 1993). However, their temperature was still too high ($\geq 230\,^{\circ}$C) to allow the survival of living organisms. Probably in a few tens of millions of years, the temperature of the oceans cooled down enough ($80-110\,^{\circ}$C) to allow the development of hyperthermophiles organisms, living on the oceanic floor or close to hydrothermal vents. At the beginning of the Archean (3.9 Ga ago), the presence of marine sediments clearly indicates a stable oceanic environment. The ocean was probably more acid and anoxic than the modern one, being in equilibrium with a CO_2-dominated atmosphere (Kasting 1991). The chemistry of the Archean ocean was dominated by halite, as in modern seawater, but the total concentrations were higher, especially for elements such as halogens. This can be explained by an ocean chemistry buffered by the mantle, through large-scale hydrothermal interactions with the oceanic crust.

CE 33 Places of publication of books missing

Editor's or typesetter's annotations (will be removed before the final TEX run)

CEREGE gave valuable suggestions. Genevieve Roche is thanked for the color plates illustrating the birth of the oceans. Research work on Archean is supported by French national funding CNRS-GDR Exobiology; CNRS-PNP; MAE. This is the LGMT contribution no. 45.

References[CE33]

Abe, Y. (1993). Physical state of the very early Earth. *Lithos*, **30**, 223–235.

Allègre, C.J., Manhès, G., Gopel, C. (1995). The age of the Earth. *Geochim. Cosmochim. Acta*, **59**, 1445–1456.

Allègre, C.J., Staudacher, T., Sarda, P. (1986/87). Rare gas systematic: formation of the atmosphere, evolution and structure of the Earth's mantle. *Earth Planet. Sci. Lett.*, **81**, 127–150.

Beaumont, V., Robert, F. (1999). Nitrogen isotope ratios of kerogens in Precambrian cherts: a record of the evolution of atmosphere chemistry? *Precamb. Res.*, **96**, 63–82.

Bickle, M.J. (1986). Implications of melting for stabilisation of the litosphere and heat loss in the Archaean. *Earth Planet. Sci. Lett.*, **80**, 314–324.

Bischoff, J.L., Dickson, F.W. (1991). Seawater-basalt interaction at $200\,°C$ and $500\,bar$. Implications for the origin of heavy-metal deposits and regulation of sewater chemistry. *Earth Planet. Sci. Lett.*, **25**, 385–397.

Boato, G. (1954). The isotopic composition of hydrogen and carbon in the carbonaceous chondrites. *Geochim. Cosmochim. Acta*, **6**, 209–220.

Bockelée-Morvan, D. et al. (1988). Deuterated water in comet C/1996 B2 (Hyakutake) and its implications for the origin of comets. *Icarus*, **193**, 147–162.

Bowring, S.A., Williams, I.S. (1999). Priscoan (4.00–4.03 Ga) orthogneisses from northwestern Canada. *Contrib. Mineral. Petrol.*, **134**, 3–16.

Boyd, S.R. (2001a). Ammonium as a biomarker in Precambrian metasediments. *Precamb. Res.*, **108**, 159–173.

Boyd, S.R. (2001b). Nitrogen in future biosphere studies. *Chem. Geol.*, **176**, 1–30.

Boyd, S.R., Philippot, P. (1998). Precambrian ammonium biogeochemistry: a study of the Moine metasediments, Scotland. *Chem. Geol.*, **144**, 257–268.

Butler, W.A., Jeffery, P.M., Reynolds, J.H., Wasserburg, G.J. (1963). Isotopic variations in terrestrial xenon. *J. Geophys. Res.*, **68**, 3283–3291.

Canup, R.M., Asphaug, E. (2001). Origin of Moon in a giant impact near the end of the Earth's formation. *Nature*, **412**, 708–712.

Channer, D.M.D.R., de Ronde, C.E.J., Spooner, E.T.C. (1997). The Cl-Br-I composition of ∼3.23 Ga modified seawater: implications for the geological evolution of ocean halide chemistry. *Earth Planet. Sci. Lett.*, **150**, 325–335.

Cleaves, H.J., Miller, S.L. (1998). Oceanic protection of prebiotic organic compounds from UV radiation. *Proc. Natl. Acad. Sci. USA*, **95**, 7260–7263.

Craig, H., Clarke, W.B., Beg, M.A. (1975). Excess ^{3}He in deep water on the East Pacific Rise. *Earth Planet. Sci. Lett.*, **26**, 125–132.

Dauphas, N. (2003). The dual origin of the terrestrial atmosphere. *Icarus*, **165**, 326–339.

Dauphas, N., Marty, B. (2001). Inference on the nature and the mass of Earth's late veneer from noble metals and gases. *J. Geophys. Res.*, **107**, 12–1[TS34].

Dauphas, N., Robert, F., Marty, B. (2000). The late asteroidal and cometary bombardment of Earth as recorded in water deuterium to protium ratio. *Icarus*, **148**, 508–512.

de Ronde, C.E.J., Channer, D.M.D.R., Faure, K., Bray, C. J., Spooner, T. C. (1997). Fluid chemistry of Archean seafloor hydrothermal vents: Implications for the composition of circa 3.2 Ga seawater. *Geochim. Cosmochim. Acta*, **61**, 4025–4042.

Deloule, E., Albarede, F., Sheppard, S.M.F. (1991). Hydrogen isotope heterogeneities in the mantle from ion probe analysis of amphiboles from ultramafic rocks. *Earth Planetary Science Letters*, **105**, 543–553.

Delsemme, A.H. (1999). The deuterium enrichment observed in recent comets is consistent with the cometary origin of seawater. *Planet. Space Sci.*, **47**, 125–131.

Deming, D. (1999). On the possible influence of extraterrestrial volatiles on Earth's climate and the origin of the oceans. *Palaeogeogr. Palaeoclim. Palaeoecol.*, **146**, 33–51.

Derry, L.A., Jacobsen, S.B. (1988). The Nd and Sr evolution of Proterozoic seawater. *Geophys. Res. Lett.*, **15**, 397–400.

Des Marais, J., Strauss, H., Summons, R.E., Hayes, J.M. (1992). Carbon isotope evidence for the stepwise oxidation of the Proterozoic environment. *Nature*, **359**, 605–609.

Drouart, A., Dubrulle, B., Gautier, D., Robert, F. (1999). Structure and transport in the solar nebula from constraints on deuterium enrichment and giant planets formation. *Icarus*, **140**, 59–76.

Eberhardt, P., Reber, M., Krankowski, D., Hodges, R.R. (1995). The D/H and $^{18}O/^{16}O$ ratios in water from comet P/Haley. *Astron. Astrophys.*, **302**, 301–316.

Engrand, C., Deloule, E., Robert, F., Maurette, M., Kurat, G. (1999). Extraterrestrial water in micrometeorites and cosmic spherules from Antarctica: An ion microprobe study. *Meteor. Planet. Sci.*, **34**, 773–786.

Faure, G. (1991) *Principles and Applications of Inorganic Geochemistry: a Comprehensive Textbook for Geology Students.* Maxwell Macmillan International.

Foriel, J., Philippot, P., Banks, D., Rey, P., Cauzid, J., Somogyi, A. (2003). Composition of a 3.5 Gyr shallow seawater from the North Pole Dome, Western Australia. *Geochim. Cosmochim. Acta*, **67**, A100.

Frank, L.A., Sigwarth, J.B. (1997). Trails of OH emissions from small comets near Earth. *Geophys. Res. Lett.*, **24**, 2435–2438.

Frank, L.A., Sigwarth, J.B., Craven, J.D. (1986). On the influx of small comets into the Earth's atmosphere I. Observations. *Geophys. Res. Lett.*, **13**, 303–306.

Gautier, D., Owen, T. (1983). Cosmological implication of helium and deuterium abundances of Jupiter and Saturn. *Nature*, **302**, 215–218.

Geiss, J., Gloecker, G. (1998). Abundance of Deuterium and Helium in the protosolar Cloud. *Space Science Rev.*, **84**, 239–250.

Halliday, A.N. (2001). Earth science – In the beginning. *Nature*, **409**, 144–145.

Harrison, C.G.A. (1999). Constraints on ocean volume change since the *Archean. Geophys. Res. Lett.*, **26**, 1913–1916.

Holland, H.D. (1984) *The Chemical Evolution of the Atmosphere and Oceans.* Princeton University Press.

Holland, H.D. (2002). Volcanic gases, black smokers, and the great oxidation event. Geochim. *Cosmochim. Acta*, **66**, 3811–3826.

Holm, N.G., Andersson, E.M. (1998) Hydrothermal systems. *In The Molecular Origins of Life. Assembling Pieces of the Puzzle*, ed. Brack, A., p. 86–99, Cambridge Universty Press.

Honda, M., McDougall, I., Patterson, D.B., Doulgeris, A., Clague, D.A. (1991). Possible solar noble gas component in Hawaiian basalts. *Nature*, **349**, 149–151.

Isley, A.E. (1995). Hydrothermal plumes and the delivery of iron to Banded Iron Formation. *J. Geol.*, **103**, 169–185.

Kamber, B.S., Webb, G.E. (2001). The geochemistry of late Archaean microbial carbonate: Implications for ocean chemistry and continental erosion history. *Geochim. Cosmochim. Acta*, **65**, 2509–2525.

Kasting, J.F. (1987). Theoretical constraints on oxygen and carbon dioxide concentrations in the precambrian atmosphere. *Precamb. Res.*, **34**, 205–229.

Kasting, J.F. (1991). Box models for the evolution of atmospheric oxygen: An update. *Palaeogeogr. Palaeoclim. Palaeoecol.*, **97**, 125–131.

Kasting, J.F. (1993). Earth's early atmosphere. *Science*, **259**, 920–926.

Kempe, S, Degens, E.T. (1985). An early soda ocean? *Chem. Geol.*, **53**, 95–108.

Kerridge, J.F. (1985). Carbon, hydrogen and nitrogen in carbonaceous chondrites: Abundances and isotopic compositions in bulk samples. *Geochim. Cosmochim. Acta*, **49**, 1707–1714.

King, E.M., Valley, J.W., Davis, D.W., Edwards, G.R. (1998). Oxygen isotope ratios of Archean plutonic zircons from granite-greenstone belts of the Superior Province: indicator of magmatic source. *Precamb. Res.*, **92**, 365–387.

Knauth, L.P., Lowe, D.R. (1978). Oxygen isotope geochemistry of cherts from the Onverwatch Group (3.4 billion years), Transvaal Group, South Africa, with implications for secular variations in the isotopic composition of cherts. *J. Geol.*, **41**, 209–222.

Knauth, P.L. (1994). Petrogenesis of chert. *Review Mineral.*, **29**, 233–258.

Knauth, P.L., Roberts, S.K. (1991) The hydrogen and oxygen isotope history of the Silurian-Permian hydrosphere as determined by direct measurement of fossil water. In *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*, Vol. Special Publication No. 3, eds. Taylor, H.P., O'Neil, J.R., Kaplan, I.R., p. 91–104, The Geochemical Society.

Krauskopf, K.B., Bird, D.K. (1995) *Introduction to Geochemistry.* McGraw-Hill.

Lecuyer, C., Gillet, P., Robert, F. (1998). The hydrogen isotope composition of seawater and the global water cycle. *Chem. Geol.*, **145**, 249–261.

Li, Y.-H. (2000) *A Compendium of Geochemistry; from Solar Nebula to Human Brain.* Princeton University Press.

Lowe, D.R., Byerly, G.R. (2003). Ironstone pods in the Archean Barberton greenstone belt, South Africa: Earth's oldest seafloor hydrothermal vents reinterpreted as Quaternary subaerial springs. *Geology*, **31**, 909–912.

Martin, H., Moyen, J.-F. (2002). Secular changes in tonalite-trondhjemite-granodiorite composition as markers of the progressive cooling of Earth. *Geology*, **30**, 319–322.

Marty, B. (1989). Neon and xenon isotopes in MORB: implications for the earth-atmosphere evolution. *Earth Planet. Sci. Lett.*, **94**, 45–56.

Maurette, M., Duprat, J., Engrand, C., Gounelle, M., Kurat, G., Matrajt, G., Toppani, A. (2000). Accretion of neon, organics, CO_2, nitrogen and water from large interplanetary dust particles on the early Earth. *Planet. Space Sci.*, **48**, 1117–1137.

Meier, R., Owen, T.C., Matthews, H.E., Jewitt, D.C., Bockelée-Morvan, D., Biver, N., Crovisier, J., Gautier, D. (1998). A determination of the DH_2O/H_2O ratio in Comet C/1995 O1 (Hale-Bopp). *Science*, **279**, 842–844.

Mojzsis, S.L., Arrhenius, G., Friend, C.R.L. (1996). Evidence for life on Earth before 3,800 million years ago. *Nature*, **384**, 55–57.

Mojzsis, S.J., Harrison, M.T., Pidgeon, R.T. (2001). Oxygen-isotope evidence from ancient zircons for liquid water at the Earth's surface 4,300 Myr ago. *Nature*, **409**, 178–181.

Morbidelli, A., Chambers, J., Lunine, J.I., Petit, J.M., Robert, F. (2000). Source regions and timescales for the delivery of water to the Earth. *Meteoritics Planet. Sci.*, **35**, 1309–1320.

Morris, R.C. (1993). Genetic modelling for banded iron-formation of the Hamersley Group, Pilbara Craton, Western Australia. *Precamb. Res.*, **60**, 243–286.

Murakami, T., Utsunomiya, S., Imazu, Y., Prasad, N. (2001). Direct evidence of late Archean to early Proterozoic anoxic atmosphere from a product of 2.5 Ga old weathering. *Earth Planet. Sci. Lett.*, **184**, 523–528.

Nijman, W., de Bruijne, H., Valkering, M.E. (1998). Growth fault control of Early Archean cherts, barite mounds and chert-barite veins, North Pole Dome, Eastern Pilbara, Western Australia. *Precamb. Res.*, **88**, 25–52.

Nisbet, E.G., Cheadle, M.J., Arndt, N.T., Bickle, M.J. (1993). Constraining the potential temperature of the archaean mantle – a review of the evidence from komatiites. *Lithos*, **30**, 291–307.

Nisbet, E.G., Sleep, N.H. (2001). The habitat and nature of early life. *Nature*, **409**, 1083–1091.

Nutman, A.P., Mojzsis, S.J., Friend, C.R.L. (1997). Recognition of $\geq$ 850 Ma water-lain sediments in West Greenland and their significance for the early Archean Earth. *Geochim. Cosmochim. Acta*, **61**, 2575–2484.

Ottonello, G. (1997) *Principles of Geochemistry*. Columbia University Press.

Owen, T.C. (1998) The origin of the atmosphere. In *The Molecular Origins of Life*, ed. Brack, A., p. 13–34, Cambridge University Press.

Owen, T.C., Bar-Nun, A. (1995). Comets, impacts, and atmospheres. *Icarus*, **116**, 215–226.

Ozima, M., Podosek, F.A. (2001) *Noble Gas Geochemistry*. 2nd edition. Cambridge University Press.

Ozima, M., Zanshu, S. (1988). Solar-type Ne in Zaire cubic diamonds. *Geochim. Cosmochim. Acta*, **52**, 19–25.

Peck, W.H., King, E.M., Valley, J.W. (2000). Oxygen isotope perspective on Precambrian crustal growth and maturation. *Geology*, **28**, 363–366.

Peck, W.H., Valley, J.W., Wilde, S.A., Graham, C.M. (2001). Oxygen isotope ratios and rare earth elements in 3.3 to 4.4 Ga zircons: Ion microprobe evidence for high $\delta^{18}O$ continental crust and oceans in the Early Archean. *Geochim. Cosmochim. Acta*, **65**, 4215–4229.

Pepin, R.O. (1991). On the origin and ealy evolution of terrestrial planetray atmospheres and meteoritic volatiles. [CE35] *Icarus*, 92.

Peters, K.E., Sweeney, R.E., Kaplan, I.R. (1978). Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. *Limnol. Oceanogr.*, **23**, 598–604.

Pidgeon, R.T., Wilde, S.A. (1998). The interpretation of complex zircon U-Pb systems in Archaean granitoids and gneisses from the Jack Hills, Narryer gneiss Terrane, Western Australia. *Precamb. Res.*, **91**, 309–332.

Pinti, D.L. (2002). The isotopic record of Archean nitrogen and the evolution of the early earth. *Trends in Geochemistry*, **2**, 1–17.

Pinti, D.L. Hashizume, K. (2001). N-15-depleted nitrogen in Early Archean kerogens: clues on ancient marine chemosynthetic-based ecosystems? A comment to Beaumont, V., Robert, F., 1999. Precambrian Res., 96, 62–82. *Precamb. Res.*, **105**, 85–88.

Pinti, D.L., Hashizume, K., Matsuda, J. (2001). Nitrogen and argon signatures in 3.8 to 2.8 Ga metasediments: Clues on the chemical state of the Archean ocean and the deep biosphere. *Geochim. Cosmochim. Acta*, **65**, 2301–2315.

Pinti, D.L., Hashizume, K., Philippot, P., Foriel, J., Rey, P. (2003). Nitrogen quest in Archean metasediments of Pilbara, Australia. *Geochim. Comochim. Acta*, **67**, A379.

Poreda, R.J., Farley, K.A. (1992). Rare gases in Samoan xenoliths. *Earth Planetary Science Letters*, **113**, 129–144.

Robert, F. (2001) L'origine de l'eau dans le Système Solaire telle qu'elle est enregistrée par son rapport isotopique *D/H*. In *L'environnement de la Terre Primitive*, eds. Gargaud, M., Despois, D., Parisot, J.-P., p. 79–90, Presses Universitaires de Bordeaux.

Robert, F., Epstein, S. (1982). The concentration and isotopic composition of hydrogen, carbon and nitrogen in the carbonaceous meteorites. *Geochim. Cosmochim. Acta*, **46**, 81–95.

Robert, F., Gautier, D., Dubrulle, B. (2000). The solar system *D/H* ratio: Observations and theories. *Space Sci. Rev.*, **92**, 201–224.

Roedder, E. (1984) *Fluid Inclusions*. Mineralogical Society of America.

Rosing, M.T., Rose, N.M., Bridgwater, D., Thomsen, H.S. (1996). Earliest part of Earth's stratigraphic record: A reappraisal of the > 3.7 Ga Isua (Greenland) supracrustal sequence. *Geology*, **24**, 43–46.

Rothschild, L.J., Mancinelli, R.L. (2001). Life in extreme environments. *Nature*, **409**, 1092–1101.

Rubey, W.W. (1951). Geologic history of seawater: An attempt to state the problem. *GSA Bull.*, **62**, 1111–1147.

Sarda, P., Staudacher, Th., Allègre, C.J. (1988). Neon isotopes in submarine basalts. *Earth Planet. Sci. Lett.*, **91**, 73–88.

Sleep, N.H., Zahnle, K. (2001). Carbon dioxide cycling and implications for climate on ancient Earth. *J. Geophys. Res.*, **106**, 1373–1399.

Sleep, N.H., Zahnle, K., Neuhoff, P.S. (2001). Initiation of clement surface conditions on the earliest Earth. *Proc. Natl. Acad. Sci. USA*, **98**, 3666–3672.

Staudacher, T., Allegre, C.J. (1982). Terrestrial xenology. *Earth Planet. Sci. Lett.*, **60**, 389–406.

Staudacher, T., Sarda, P., Richardson, S.H., Allègre, C.J., Sagna, I., Dmitriev, L.V. (1989). Noble gases in basalt glasses from a Mid-Atlantic Ridge topographic high at 14∘N: geodynamic consequences. *Earth Planet. Sci. Lett.*, **96**, 119–133.

Stetter, K.O. (1998) Hyperthermophiles and their possible role as ancestors of modern life. In *The Molecular Origins of Life*, ed. Brack, A., p. 315–335, Cambridge University Press.

Sugitani, K. (1992). Geochemical characteristics of Archean cherts and other sedimentary rocks in the Pilbara Block, Western Australia: evidence for Archean seawater enriched in hydrothermally-derived iron and silica. *Precamb. Res.*, **57**, 21–47.

Tajika, E., Matsui, T. (1993). Degassing history and carbon cycle of the Earth: From an impact-induced steam atmosphere to the present atmosphere. *Lithos*, **30**, 267–280.

Taylor, S.R., McLennan, S.M. (1995). The geochemical evolution of the continental crust. *Rev. Geophys.*, **33**, 241–265.

van Zuilen, M.A., Lepland, A., Arrhenius, G. (2002) Reassessing the evidence for the earliest traces of life, *Nature*, **418**, 627–630.

Valley, J.W., Chiarenzelli, J.R., McLelland, J.M. (1994). Oxygen isotope geochemistry of zircon. *Earth Planet. Sci. Lett.*, **126**, 187–206.

Valley, J.W., Kinny, P.D., Shulze, D., Spicuzza, M.J. (1998). Zircon megacrysts from kimberlite: Oxygen isotope variability among mantle melts. *Contrib. Mineral. Petrol.*, **133**, 1–11.

Valley, J.W., Peck, W.H., King, E.M., Wilde, S.A. (2002). A cool early Earth. *Geology*, **30**, 351–354.

Veizer, J., Compston, W. (1976). $^{87}Sr/^{86}Sr$ in Precambrian carbonates as an index of crustal evolution. *Geochim. Cosmochim. Acta*, **40**, 905–914.

Veizer, J., Hoefs, J., Ridler, R.H., Jensen, L.S., Lowe, D.R. (1989). Geochemistry of Precambrian carbonates: I. Archean hydrothermal systems. *Geochim. Cosmochim. Acta*, **53**, 845–857.

Wilde, S.A., Valley, J.W., Peck, W.H., Graham, C.M. (2001). Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature*, **409**, 175–178.

Yang, W., Holland, H.D., Rye, R. (2002). Evidence for low or no oxygen in the late Archean atmosphere from the ∼2.76 Ga Mt. Roe #2 paleosol, Western Australia: Part 3. *Geochim. Cosmochim. Acta*, **66**, 3707–3718.

Zhang, Y.X., Zindler, A. (1993). Distribution and evolution of carbon and nitrogen in earth. *Earth Planet. Sci. Lett.*, **117**, 331–345.