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## 4. Building of a Habitable Planet

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**Abstract.** Except the old Jack Hills zircon crystals, it does not exist direct record of the first 500 Ma of the Earth history. Consequently, the succession of events that took place during this period is only indirectly known through geochemistry, comparison with other telluric planets, and numerical modelling. Just after planetary accretion several episodes were necessary in order to make life apparition and development possible and to make the Earth surface habitable. Among these stages are: the core differentiation, the formation of a magma ocean, the apparition of the first atmosphere, oceans and continents as well as the development of magnetic field and of plate tectonics. In the same time, Earth has been subject to extra-terrestrial events such as the Late Heavy Bombardment (LHB) between 3.95 and 3.8 Ga. Since 4.4–4.3 Ga, the conditions for pre-biotic chemistry and appearance of life were already met (liquid water, continental crust, no strong meteoritic bombardment, etc...). This does not mean that life existed as early, but this demonstrates that all necessary conditions assumed for life development were already present on Earth.

**Keywords:** Hadean, Archaean, continental growth, atmosphere and ocean formation, Late Heavy Bombardment

After planetary accretion several stages were necessary in order to make life apparition and development possible, in other words to make the Earth surface habitable. Among these stages are: the differentiation of Earth surface, the apparition of the first atmosphere, oceans and continents as well as the development of magnetic field and of plate tectonics.

#### 4.1. Terrestrial Differentiation

FRANCIS ALBARÈDE

The Earth's primordial mineralogical composition and structure as well as the petrological nature of its surface are totally unknown. Plate tectonics, mountain building and erosion have long ago destroyed any geological record of this period. As developed in part 4.3, the oldest terrestrial material is a mineral, a zircon from Jack Hills (Australia), dated at 4.4 Ga, the oldest rock we can hold in our hand is a 4.1 Ga old gneiss from Acasta (Canada) and the oldest terrestrial swath of continental crust large enough for a field geologist to pace is 3.8 Ga old and located at Isua (Greenland), (Figure 4.1 and part 4.3). In order to understand when and how quickly the modern dichotomy between continental and oceanic crusts has emerged and whether it is relevant to the dynamics of the early Earth and the origin of life, we need to understand the structure of the planet left to us at the end of planetary accretion. To assist us in this task, we can rely on the oldest terrestrial

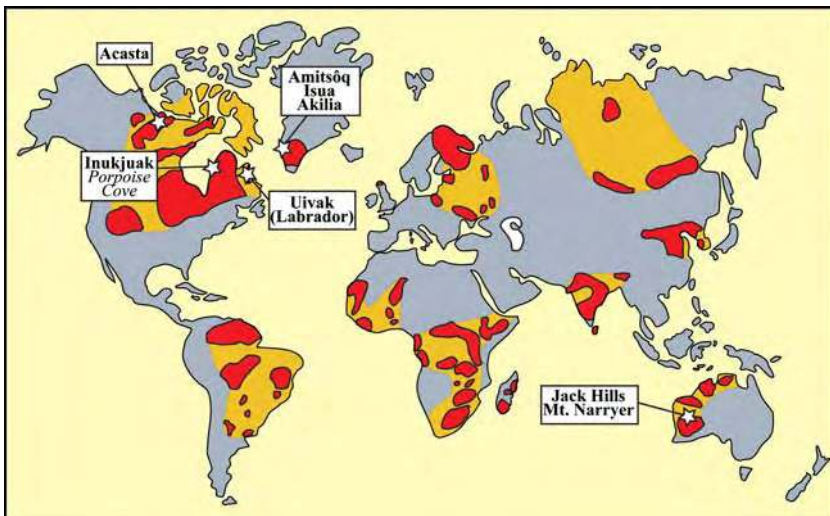


Figure 4.1. Simplified map showing the emplacement of the localities where very old continental crust has been dated. Exposed Archaean terranes are in red, and areas underlain by Archaean rocks are in orange.

material, but as explained in part 4.3, the record until 700 Ma after the Earth's formation comes out rather blurred. We can also proceed by comparison with other planets which have not apparently been as completely resurfaced as the Earth. First and foremost, intense cratering attests to the antiquity of the surface of both Mars and the Moon, while under similar standard, Venus's surface is young. Radiometric ages of Martian and Lunar samples are occasionally old, which supports cratering evidence, similarly chronological data on extinct radioactivities also supported the early Earth differentiation hypothesis. The parent body of some basaltic meteorites (Eucrites Parent Body = EPB) is also a particularly old object that can provide valuable information on the early inner solar system.

#### 4.1.1. BULK COMPOSITION OF THE EARTH ( $\sim 4.568 \text{ GA}^1$ )

In order to understand how the Earth formed, it is first necessary to estimate 'what' our planet is made of. Our current knowledge of the Earth's composition is based on a number of observations and constrained by a number of deductions from our understanding of solar system formation processes:

- The composition of the most primitive carbonaceous chondrites (CI) is (except for gas, mainly H and He) identical to that of the solar photosphere. Any other type of meteorite has lost a substantial fraction of volatile elements (i.e.  $\text{H}_2\text{O}$ , K, Cl, S) due to the radiative activity of the young Sun, (most likely during its T-Tauri phase), and during the metamorphic alteration of the meteorite parent body.
- Planetary accretion is a quick process: the giant planets (Jupiter-type) are essentially gaseous and must form before the end of the T-Tauri phase (few Ma) which blew off all the nebular gas. Modern meteorite chronology using U-Pb and extinct radioactivity supports this scenario.
- Exchange of material across the solar system is very active, notably fed by the destabilization of planetary embryo orbits by Jupiter.
- Primordial material cruising around the Earth has a very limited life expectancy in orbit ( $< 100 \text{ Ma}$ ).

These simple guidelines lead to the conclusion that, if the Earth accreted mostly from local material, our planet must be strongly depleted in volatile elements and consequently its interior must be particularly dry. Such depletion can be illustrated using alkali element ratio: in CI carbonaceous chondrites,  $\text{K}/\text{U} = 60,000$  (refractory U is used as a reference), compared with 12,000 in the Earth, and 3000 in the Moon (Taylor, 2001). On the other hand, since a long time, it has been noticed that the modern  $^{87}\text{Sr}/^{86}\text{Sr}$  of the Earth ( $\sim 0.7045$ ) is much too unradiogenic with respect to  $^{87}\text{Rb}/^{86}\text{Sr}$  in

<sup>1</sup> The age of Earth formation ( $t_0$ ) has been chosen as  $4568 \pm 1 \text{ Ma}$  (Amelin et al., 2002; Bouvier et al., 2005).

chondrites; which points to Earth depletion in Rb (Gast, 1960). The Earth mainly formed from dry, volatile-element depleted indigenous material which is no longer available for analysis. Undepleted ‘wet’ material (ice-covered asteroids, comets) occasionally thrown off out of the outer solar system by Jupiter has been added providing the ‘vener’ required by the geochemistry of platinum group elements and adding at the same time the water necessary to form the terrestrial ocean. Consequently, Earth probably formed by accumulation of planetary embryos of different sizes; the ultimate collision being the Moon-forming event resulting of the impact of the Mars-size embryo with the Earth.

In addition, oxygen isotopic ratios indicate that Earth’s brew was a special one (Clayton, 1993). From one object to another, isotopic abundances can vary for three reasons:

- (1) Thermodynamic fractionation, due to a temperature-dependent population of vibrational modes, in a common stock and which shows a smooth dependence with mass; the consistency of  $\delta^{17}\text{O}$ – $\delta^{18}\text{O}$  values is the base for assigning different meteorites to a single planetary body, notably Mars (SNC) and the eucrite–howardite–diogenite parent body;
- (2) The survival of poorly mixed different nucleosynthetic components, as in refractory inclusions;
- (3) Radiogenic ingrowths in systems with different parent/daughter ratios.

Both cases (1) and (2) are very clearly shown in a  $\delta^{17}\text{O}$ – $\delta^{18}\text{O}$  plot (Figure 4.2). There, the Earth and the Moon lie on a same fractionation line with the predicted slope of 0.5. This coincidence is one of the strongest arguments in favour of the two bodies having accreted on adjacent orbits. Only few CI carbonaceous chondrites and the enstatite ordinary chondrites lie on the terrestrial fractionation line, which gave rise to the conjecture that the Earth may be made of enstatite chondrites (Javoy, 1995). The  $\Delta^{17}\text{O}$  elevation of the points representing the different planetary objects above the Earth–Moon fractionation line is a measure of their nucleosynthetic  $^{16}\text{O}$  excess and indicates by how much their constituting material differed from Earth: oxygen being the most abundant element in the rocky planets, this difference should not be taken lightly.

#### 4.1.2. ENERGETIC OF PLANETARY DIFFERENTIATION PROCESSES

Upon contraction of the solar nebula and collapse of the disk onto its equatorial plane, dust and particles collide with each other. Shock waves emitted by the contracting Sun are now thought to be largely responsible for the melting of chondrules (Hood and Horanyi, 1993). The presence of the

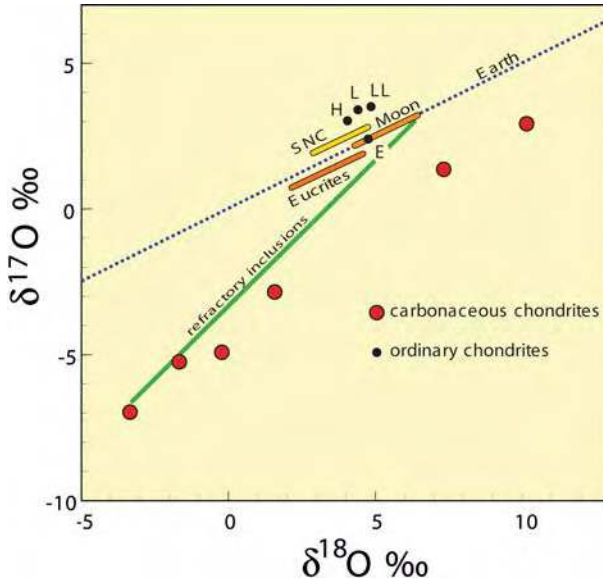


Figure 4.2. Plot of  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  in different planetary materials. These numbers represent excesses or deficits of  $^{17}\text{O}$  and  $^{18}\text{O}$  with respect to  $^{16}\text{O}$  in a reference material, which is seawater. Thermodynamic isotopic fractionation is mass-dependent and moves the points representing actual samples along lines with a slope equal to  $(17-16)/(18-16) = 0.5$ . The most visible of these lines is the Earth-Moon common fractionation trend.  $\delta^{17}\text{O}$  represents the elevation of a point above this line. Different planetary objects (planets or groups of meteorites) have different  $\delta^{17}\text{O}$  values and therefore were created from material with a very different history in the solar nebula or even prior to the isolation of the nebula. SNC = Martian meteorites.

decay products of the short-lived  $^{60}\text{Fe}$  in meteorites attests to the explosion of supernova(e) in the neighbourhood of the solar nebula (Wasserburg and Busso 1998). However, the energy emitted by all these sources has been largely re-irradiated into space and consequently it did not efficiently contribute to planetary differentiation.

Gravitational energy appears to be the main source of planetary energy for Mars-size objects and larger: the temperature increment associated with gravitational energy released by material falling at the surface of a planet with radius  $R$ , mean density  $\rho$ , and specific heat  $C_p$  is  $(3/5)G\pi\rho R^2/C_p$  in which  $G$  is the universal constant of gravitation. This increment is  $\sim 1600$  K for the Moon, 7600 K for Mars and 38,000 K for the Earth. Most of this energy is, however, irradiated back into space by the molten material and impact vapour and for most of the growth history of the planet, much smaller numbers should be considered. Another related source of energy is core formation, which, for the Earth, induced a temperature increase of worth more than 1500 K, and that remains largely buried into the planet. Whether

core segregation took place once in an essentially finished Earth or took place in several planetary bodies that eventually agglomerated to make the Earth should not make significant difference in terms of energy budget.

Two main short-lived radioactive sources of energy played a prominent role in the early solar system as well as in stars:  $^{26}\text{Al}$ , which decays into  $^{26}\text{Mg}$  with a half-life of 0.75 Ma (Gray and Compston, 1974; Lee et al., 1976), and  $^{60}\text{Fe}$ , which decays into  $^{60}\text{Ni}$  with a half-life of 1.5 Ma (Shukolyukov and Lugmair, 1993). The abundance of  $^{26}\text{Al}$  at the outset of planetary formation is well-known, whereas much uncertainty remains about the abundance of  $^{60}\text{Fe}$ : the overall heating power of  $^{26}\text{Al}$  is 9500 K, while that of  $^{60}\text{Fe}$  could be as high as 6000 K. The growth history of planets entirely conditions its thermal history and differentiation: if the radius of a planetary body becomes larger than the thickness of the conductive boundary layer, deep heat will only slowly diffuse and escape and the body will extensively melt and differentiate. Slowly growing objects would form out of material devoid of  $^{26}\text{Al}$  and  $^{60}\text{Fe}$  and indefinitely remain a pile of porous rubble with no internal structure.

The early stages of planetary formation must have therefore seen a relatively large population of small (1–100 km) to medium-sized (100–1000 km) objects orbiting the Sun and colliding with each other. Some of these planetary objects, even the smallest, were molten and differentiated into a metallic core, an ultramafic mantle and a basaltic crust. We can think of the EPB as one of these. Others were only warm porous objects. The later stages differ from one planet to the other. The largest planets (Earth, Venus and Mars) were certainly large enough for the release of accretion energy to induce wholesale melting of their upper 500–2000 km giving rise to a magma ocean.

#### 4.1.3. THE CHRONOMETERS OF ACCRETION AND DIFFERENTIATION

The last decade watched the emergence of powerful dating techniques (see part 2.2). In addition to substantial improvements on Secondary Ionization Mass Spectrometry (SIMS) and traditional Thermal Ionization Mass Spectrometry (TIMS), the advent of Multiple Collector Inductively Coupled Plasma Mass Spectrometry (MC ICP MS) produced most significant advances. For ‘absolute’ U-Pb dating, it is now possible to obtain U-Pb ages with a precision of a fraction of a million years. Similar precisions hold for extinct radioactivities such as  $^{26}\text{Al}$ – $^{26}\text{Mg}$ ,  $^{60}\text{Fe}$ – $^{60}\text{Ni}$ , and  $^{182}\text{Hf}$ – $^{182}\text{W}$ .

In fact measuring ‘absolute’ ages in a rock or in a mineral consist in reality, in obtaining a cooling age. For instance in the U-Pb system the measured date is the time at which a particular phase stops exchanging Pb with surrounding minerals. Lead exchange stops at  $\sim 800^\circ\text{C}$  in pyroxene and at  $\sim 500^\circ\text{C}$  in phosphate (Cherniak et al., 1991; Cherniak, 2001). As discussed in part 4.1.4., planetary bodies went through a stage of

metamorphic heating or even wholesale melting which may have lasted several million years. External (whole-rock) Pb–Pb isochrons potentially date the original U/Pb fractionation stage, such as the segregation of metal (core) from the silicate minerals and melts (mantle and crust) or the differentiation of different objects in the planet (mantle, crust). This technique however relies on a stringent assumption not necessarily met in natural objects: all the samples dated must have formed at precisely the same time and they had the same Pb isotope composition at that time, which is only likely to happen for samples with strong genetic relationships.

In contrast, extinct radioactivities date the extraction of material from the nebula (see part 2.2). Observing in a particular mineral an excess or a deficit with respect to the chondritic reference of a radiogenic nuclide, (i.e.  $^{26}\text{Al} \rightarrow ^{26}\text{Mg}$ ), signals that the host rock picked up Al from the solar nebula at the time  $^{26}\text{Al}$  still existed. The excess may vanish during metamorphic perturbation or melting, but it cannot be created after  $^{26}\text{Al}$  has disappeared.

Because of the distinctive geochemical behaviour of the parent and daughter isotopes, different extinct radioactivities reflect different planetary events:

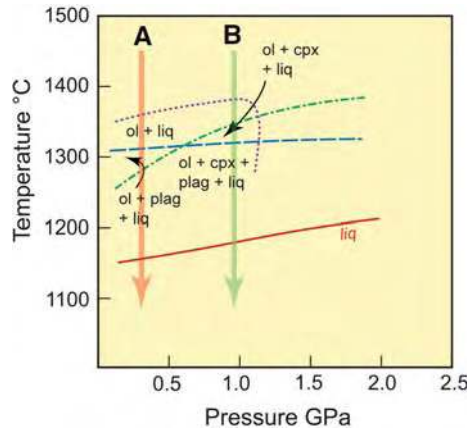
- The fastest accretion chronometers  $^{26}\text{Al}$ – $^{26}\text{Mg}$  ( $T_{1/2} = 0.75$  Ma) and  $^{60}\text{Fe}$ – $^{60}\text{Ni}$  ( $T_{1/2} = 1.5$  Ma) date extraction of the planetary material from the nebula.
- Preferential uptake of W and Ag by metal makes the  $^{182}\text{Hf}$ – $^{182}\text{W}$  ( $T_{1/2} = 8.9$  Ma) and  $^{107}\text{Pd}$ – $^{107}\text{Ag}$  ( $T_{1/2} = 6.5$  Ma) pairs ideal to date planetary core formation.
- Fractionation of the lithophile (silicate-loving) elements makes the  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  chronometer ( $T_{1/2} = 103$  Ma) suitable for the first 100's of Ma of planetary evolution, in particular with respect to the existence of a magma ocean (see below).

#### 4.1.4. PETROLOGY OF PLANETARY DIFFERENTIATION

The Earth, Moon, Mars, Venus are all differentiated planets, which indicates that they went through a molten stage with ensuing core-mantle mantle-crust segregation. Planetary differentiation is the outcome of phase separation, metal-silicate first, then mineral-liquid silicates. Regardless of the composition of the molten planets, the mineral phases in equilibrium with most melts are fortunately few: olivine, three pyroxenes, an Al-bearing phase, and ilmenite. At higher pressures typical of the terrestrial mid-mantle, other phases such as perovskite may be present but their incidence on planetary differentiation is unclear.

Plagioclase stability is a parameter that plays a prominent role in planetary differentiation (Figure 4.3). Among Al-bearing phases stable in mantle





*Figure 4.3.* Solubility of minerals in a basaltic melt as a function of temperature and pressure. Pressure is proportional to depth, but also to the acceleration of the planet gravity ( $g$ ). Cooling at low pressure (arrow A), on Vesta or the Moon, for example, leads to the formation of large volumes of buoyant plagioclase (plagioclase crystallizes before pyroxene) whereas cooling at higher pressure (arrow B), as in the Earth, where pyroxene crystallizes before plagioclase favours crystallization of dense olivine and pyroxene.

conditions, plagioclase is the only one stable at the lower pressure and consequently at shallowest depth. Plagioclase has three important properties related to its loose structure: (a) contrary to any other mantle phase, it is less dense than the parent melt where it crystallizes and therefore it floats to the surface instead of sinking; (b) it is fairly compressible and for that reason becomes more soluble in melt as pressure increases; (c) it more likely precipitates in dry melts rather than in hydrous melts. On a planet, plagioclase stability is first modulated by gravity: pressure is proportional to gravity acceleration  $g$  and  $g = (4/3)G\pi\rho R$ : in the Earth, plagioclase production in dry melts extends down to 30 km whereas in the Moon plagioclase is stable up to 180 km. In addition, by cutting Si–O–Si bonds to produce Si–OH groups, water breaks down the plagioclase component in melts. Hence, a planet with a strong gravity field (Earth) retained water whereas weak gravity field planets (Moon) are almost dry. Consequently, a molten planet with a deep plagioclase production zone such as the Moon, will produce a thick lithosphere of buoyant plagioclase-bearing rocks (gabbros, anorthosites), which will not be possible on bigger planets (Earth).

A different consequence of a strong gravity and of a wet surface is the high-temperature reaction of water with hot mantle and melts. The most abundant mineral dominating the shallow mantle and precipitating from magmatic liquids is olivine. It reacts with water to give serpentine at 500 °C, talc and other hydrous minerals at higher temperature. The density of all these minerals is remarkably low and tends to form a wet lid on top of the hot

mantle (Boyet et al., 2003). This process also produces enormous quantities of hydrogen by damp oxidation of the ferrous component of olivine (fayalite + water  $\rightarrow$  magnetite + silica + hydrogen) (Barnes and O'Neil, 1969; Sleep et al., 2004).

#### 4.1.5. PLANETARY MAGMA OCEANS AND THE SURFACE OF THE PLANETS AT THE END OF ACCRETION ( $\sim 4.56$ TO $\sim 4.45$ GA)

The chronological framework emerging from recent data is tightening up. The first planetary objects probably formed shortly before 4.568 Ga (Amelin et al., 2002): the time from the condensation of the first refractory grains to the accretion of  $\sim 100$  km size objects did not last more than a few Ma (Bizzarro et al., 2004). The smallest objects, such as the parent body of H and L ordinary chondrites, took 5–15 Ma to cool below the phosphate closure temperature ( $\sim 500$  °C) of Pb (Göpel et al., 1994). From  $^{182}\text{Hf}$ – $^{182}\text{W}$  evidence, terrestrial core formation was nearly complete within 30 Ma after solar system isolation (Kleine et al., 2002; Yin et al., 2002b).

By then, most of the terrestrial upper mantle was probably molten as a result of impacts on a high-gravity planet. The concept of a widespread magma ocean, however, goes back to the Moon and the Apollo missions (Wood et al., 1970). The first geochemical observations on lunar basalts indicated that they formed from a mantle source with an apparent deficit in two elements concentrated in plagioclase, Eu and Sr. Such a deficit could not result from solid-state processes and therefore it was argued that the lunar mantle went through a stage of wholesale melting during which enormous amounts of buoyant plagioclase-rich cumulates were floated towards the surface. Apollo 14 and subsequent missions brought back samples of anorthosite from the highlands which were identified with these buoyant cumulates. Since then, similar observations were made in eucrites. Other arguments, notably the ubiquity of ilmenite in soil minerals, have been successfully used to strengthen the hypothesis of a lunar magma ocean.

For decades, the existence of a terrestrial magma ocean met a strong resistance. The main reason was that the mineral assemblage that would crystallize in such a gigantic pool of magma would be less rich in plagioclase than the lunar highlands and would mostly contain minerals whose density is greater than magma density; therefore it would sink as it forms, letting heat escape so fast that the magma ocean would freeze on time scales of  $10^4$ – $10^6$  years. This interpretation, however, ignores the existence of Earth's hydrosphere, a term which loosely bounds liquid water, vapour and gas. It is a modern concept based on orbital dynamics and on D/H ratios across the solar system that water was added to the surface from the outer solar system (Morbidelli et al., 2000). The interior of the Earth was nearly dry. Reaction

between any form of water with rocks of mantle or even basaltic composition forms buoyant hydrous minerals (i.e. serpentine). These rocks, transformed into serpentinite, form rafts covering the magma surface and drastically reducing heat radiation into space. In 2003, the case for a terrestrial magma ocean was bolstered by the discovery of  $^{142}\text{Nd}$  anomalies in 3.8 Ga old basalts at Isua (Greenland) (Boyet et al., 2003; Caro et al., 2003). These anomalies indicate that, 3.8 Ga ago, the mantle source of Isua basalts was still preserving the record of a major Sm/Nd fractionation event that took place within the first 100 Ma of the Earth's history. As for the Moon, such a fractionation can only be achieved by melt/mineral segregation: the current interpretation of these hard-won results is therefore that the  $^{142}\text{Nd}$  excess records the wholesale melting and crystallization of the terrestrial upper mantle. The case of the magma ocean was further strengthened by Boyet and Carlson (2005) who identified a difference of  $^{142}\text{Nd}$  abundances between the Earth's mantle and crust on the one hand, and chondrites on the other hand; this finding not only demonstrates that the terrestrial mantle was largely molten  $\sim 30$  Ma after the formation of the solar system, but also that this event was accompanied by the irreversible segregation at the base of the mantle of some material with properties distinct from those of the rest of the mantle. It is remarkable that  $^{142}\text{Nd}$  exists in lunar rocks (Nyquist et al., 1995) but they are more subdued than those found for the Isua mantle source, which suggests that, as expected from experimental data, Sm/Nd fractionation was reduced by the saturation of the magma with plagioclase and probably that the magma ocean lasted longer in the Moon than in the Earth.

#### 4.1.6. THE EARLY CRUST: TOWARD PLATE TECTONICS AND CONTINENTS (4.5–4.4 GA)

The nature of the earliest Earth surface is still in the eye of the beholder. Boyet and Carlson (2005) argue that the difference of  $^{142}\text{Nd}$  abundances between the Earth's mantle and chondrites correspond to the foundering of the primordial crust at the core-mantle boundary where it may have formed the D'' seismic layer. By 4.5–4.4 Ga, plate tectonics was probably nowhere to be seen and continental crust in the modern sense could not form. In order to create plates, a relatively rigid mantle is needed, which, upon upwelling creates oceanic crust and its underlying lithosphere. Progressive cooling of the lithosphere creates negative buoyancy, which is resisted by plate bending and mantle viscous drag (Conrad and Hager, 1999). Even if we forget about the details of crust formation, dewatering and /or melting of the sinking plates seem to be required to form a  $\text{SiO}_2$ -rich crust. None of these characteristics are likely to exist on top of a cooling magma ocean overlain by a lithospheric lid rich in hydrous Mg-bearing minerals. Stronger constraints on

the evolution of the terrestrial magma ocean are a prerequisite to the understanding of the initiation of the plate tectonics regime.

To wrap up with some speculations with what the earliest Earth's surface may have looked like, it was probably a mixed bag of basaltic to komatiitic flows erupted over or intruded into hydrous mafic and ultramafic rocks (serpentinite and amphibolite). The topographic lows were covered by whichever liquid water could condense from the thick dense atmosphere, in which nitrogen, ammonia, methane, and water gas dominated. Ammonia and methane were permanently destroyed by solar irradiation of the upper atmosphere but also permanently produced by widespread serpentinization of freshly erupted magma. Wet rocks flow more easily than their dry equivalent: arguably, by softening the underlying mantle, continuous foundering of lithosphere and its hydrous surface rocks, was instrumental into the transition to plate tectonics. Wet melts are not prone to plagioclase crystallization: occasional patches of more differentiated rocks (granites and granodiorite) would occur produced by melting of amphibolites sinking locally in the underlying mantle. They may represent parent rocks for the rare 4.4 Ga old Jack Hill zircons (Wilde et al., 2001): such rocks certainly herald the upcoming plate tectonic regime. The precise timing of the transition is not well understood but substantial progress is being made. The unique 4.4 Ga old zircon from Jack Hill has typical mantle  $^{18}\text{O}$  abundances and may have formed from mantle-derived magmas (similar zircons are present in Icelandic rhyolites and even in lunar soils). In contrast, most of the  $\delta^{18}\text{O}$  values of the 'younger' 4.3 Ga-old crystals are indistinguishable from those of the modern continents and bear the imprint of a source affected by low-temperature geological processes (Cavosie et al., 2005). In order to resolve this conundrum, Harrison et al. (2005) measured the Hf isotope compositions of the oldest Jack Hill zircons; they found evidence of Lu/Hf fractionation typical of continental crust extraction and concluded that the earliest crust formation events took place between 4.3 and 4.4 Ga ago. Although the transition between the magma ocean stage and plate tectonics may have lasted tens or even hundreds of million years, the oldest continental crust therefore formed in less than 150–200 Ma after the accretion of the planet.

## 4.2. Late Contributions

### 4.2.1. ATMOSPHERE

BERNARD MARTY

#### 4.2.1.1. *The origin of terrestrial volatiles*

The Earth is highly depleted in volatile elements when compared to bodies located further away from the Sun, like giant planets or comets. Even

asteroids located 2–3 AU from the Sun (the Earth is by definition located at 1 AU from the Sun) and which are sampled by meteorites falling onto the Earth are richer in volatile elements like water, carbon, nitrogen, halogens and noble gases. The scarcity of volatile elements may result from the combination of several factors. The classical condensation model for the formation of the solar system stipulates that the existence of a temperature gradient in the protosolar nebula would have prohibited condensation of volatile elements in the inner solar system. Volatile elements such as rare gases, carbon and nitrogen found in carbonaceous chondrites are mostly hosted by carbonaceous phases which are prone to destruction during high temperature processes ( $<1300$  K in laboratory experiments under low oxygen fugacity ( $fO_2$ ) and  $<800$  K in oxidizing condition). A fraction of volatile elements found in primitive meteorites is implanted from the solar corpuscular irradiation, presumably at an early stage of solar activity. These surface-sited components are also released at relatively low temperature. This view is consistent with the apparent concentration gradient of moderately volatile elements (e.g., alkali elements) among the Earth, Mars, Vesta, ordinary chondrites and carbonaceous chondrites (see part 4.1.1). However, recent models for the formation of the solar system propose that terrestrial planets grew up from multiple collisions with smaller bodies, the planetesimals. These later, originated from areas much wider than those specific of the different terrestrial planets (Morbidelli, 2002). Thus volatile elements including water could have been carried by impacting bodies originating from area “wetter” than the 1 AU one (Morbidelli et al., 2000) like the outer asteroid belt, and the Kuiper belt. In such a case, the volatile element gradient could be somewhat coincidental. The Earth is highly volatile-depleted, which could be the result of the giant lunar impact (see below), Mars could represent an Earth that did not experience such a giant impact, ordinary chondrites could represent non differentiated bodies whereas carbonaceous chondrites could originate from region beyond giant planets like comets. This scenario is not without problems. The most important is the similar oxygen isotopic compositions of both the Moon and the Earth, which can hardly result from mixing by any collisional process. If we take into account the diversity of O isotopic signatures among planetary bodies, it seems difficult to achieve such a similarity for two bodies formed by a random mix of smaller bodies from different regions of the mid plane.

The energy released by the Moon-forming impact might have degassed vigorously the proto-mantle. Indeed, lunar basalts are desperately dry and do not contain fluid inclusions even in their most refractory minerals, and the potassium content of the Moon is only half that of the Earth, which is itself about half of the chondritic abundance. This event took place within a few tens of Ma after the solar system started to form. Hence, the fate of terrestrial volatiles is linked to this destruction, which probably resulted in the blow off

of any primitive atmosphere and in degassing of the proto-mantle. However, this degassing might not have been perfect as in the case of the Moon. Some primordial volatiles (i.e. volatile elements that were never at the Earth's surface) remain in the mantle, such as the rare isotope  $^3\text{He}$  (Clarke et al., 1969; Mamyrin et al., 1969), and a neon component different from atmospheric neon and which isotopically resembles to solar neon (Sarda et al., 1988; Marty et al., 1989). The trapping of volatile elements in planetary bodies might have occurred when gas-rich dust coalesced and when it was buried by newly accreting material. Alternatively, these elements could have been "ingassed" from a massive atmosphere into a melted proto-mantle (Mizuno et al., 1980). A third, and not exclusive, possibility is that volatile elements were contributed at a late stage of terrestrial accretion to an essentially volatile-free proto-Earth after the lunar cataclysm. Each type of model has its advantage and inconvenient; in the following we present arguments mainly based on isotopic signatures, which allow further insight into both the source of terrestrial volatiles and the timing of their trapping.

Volatile elements in the solar system present a large variety of isotopic and elemental abundances that probably reflects processing in the solar nebula of an original gas, which is best preserved in the Sun, to some extent in the atmosphere of giant planets, and possibly in some cometary families. For hydrogen and nitrogen, isotopic variations are so large (a factor 7 for D/H and a factor 3 for  $^{15}\text{N}/^{14}\text{N}$ ) that mass-dependent fractionation seems difficult to advocate as the main source of isotopic variations. Nucleosynthetic anomalies with much larger effects are found in specific micro-phases of primitive meteorites but they cannot account for the mentioned large-scale isotopic variations in the solar system. Thus, D/H and N isotope variations measured among different reservoirs of the solar system are attributed by default to mixing with exotic components isotopically fractionated at very low temperature during e.g., ion-molecule exchanges in the interstellar medium.

The diversity of isotopic components for some of the key volatile elements presents the advantage of allowing insight into the origin of volatile elements trapped in planetary bodies and their atmospheres. Important advances in our understanding of the origin of atmospheric volatiles have stem from the ability to identify volatile elements in the terrestrial system in term of solar versus planetary origin. A pre-requisite for this approach is a good knowledge of the isotopic composition of volatile elements in the gas from which the solar system formed. The best analogue to this is probably the Sun itself, but our knowledge in this field is still very limited. The isotopic composition of light noble gases (He, Ne and Ar) has been measured in lunar soils implanted by the solar corpuscular irradiation (the low energy solar wind –  $\sim 1$  keV/amu – and more energetic emissions such as solar energetic particle – SEP, up to 1 MeV/amu) and in aluminium foils exposed by Apollo astronauts. These experiments have shown that the solar  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio is



30% lower than the atmospheric  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio. The isotopic composition of other volatile elements is not well known and measuring the isotopic composition of the solar wind was the goal of the Genesis mission which collected the solar wind for 27 months and returned (brutally) irradiated targets to the Earth on Sept. 8th, 2004 (to date, the samples have not yet been analyzed). The pre-deuterium burning hydrogen isotopic composition of the solar nebula is known from the D/H and  $^3\text{He}/^4\text{He}$  analyses of the atmosphere of Jupiter by the Galileo project (Mahaffy et al., 1998). Studies show that the solar nebula is depleted by 87% in D relative to terrestrial oceans. Recently, depth profiling analysis of lunar soil grains by ion probe together with single grain laser analysis of lunar soils by static mass spectrometry allowed Hashizume et al. (2000) to propose that solar nitrogen is depleted by at least 24% in  $^{15}\text{N}$  relative to terrestrial atmospheric N, a result subsequently confirmed by Galileo data analysis (Owen et al., 2001). These experiments corroborate that planetary bodies like the Earth and primitive meteorites (see below) are enriched in heavy, and rare, isotopes of H, N and Ne relative to the proto-solar nebula, thus making these elements important tracers of provenance for these elements.

A remarkable advance in our knowledge was the discovery of a mantle neon end-member having an isotopic composition similar to that inferred for the solar nebula (Sarda et al., 1988; Marty et al., 1989; Honda et al., 1991). Solar gas could have been trapped in accreting dust and buried during terrestrial accretion (Trieloff et al., 2000). However, the efficiency of this process appears too small (by several orders of magnitude) to supply the terrestrial inventory (Podosek and Cassen, 1994). Alternatively, nebular gas could have been trapped in the terrestrial mantle by dissolution of a massive, hydrogen-rich, solar-like atmosphere into a melted proto-mantle (Mizuno et al., 1980). The atmospheric pressure necessary to account for the noble gas inventory of the mantle is reasonable (few bars up to 100 bars, depending on models – Sasaki and Nakazawa, 1984; Porcelli and Pepin, 2000), and total or partial melting of the proto-mantle, under a massive atmosphere during accretion appears as realistic. In such a case, the limitation of the process is the lifetime of the solar nebula, less than 10 Ma at best (Podosek and Cassen, 1994), which imposes the Earth to have grown at a size sufficient enough to retain a massive hydrogen-rich atmosphere during this time interval. It also requires the proto-mantle to keep at least partially dissolved solar gases during the lunar cataclysm, despite extensive degassing of lunar material. Dissolution of solar noble gases in the core (Tolstikhin and Marty, 1998; Porcelli and Halliday, 2001) might have offered such an harvest and may also account for the association of solar-like neon with mantle plumes, which source is considered as very deep-seated, at the core-mantle boundary.

Recently, the isotopic composition of neon in the convective mantle which is the source of mid-ocean ridge basalts has been found to be similar to that

of gas-rich meteorites, suggesting a mantle-scaled Ne isotope heterogeneity (Ballentine et al., 2005). It also indicates that a major fraction of terrestrial volatiles were contributed by chondritic matter, possibly after the Moon-forming event. Dust irradiated by the Sun in the early solar system and snowing gently at the Earth's surface could have been the vector of such contribution, but in this case, a process able to subduct this dust into the mantle without degassing it has to be found. Cold subduction in the Hadean could have done the job (Tolstikhin and Hofmann, 2005), but the occurrence for such a process is highly speculative.

Other sources than the solar nebula, are also required in order to match the isotopic composition of hydrogen and nitrogen in both terrestrial atmosphere and oceans. The D/H ratio of the oceans water ( $150 \times 10^{-6}$ ) coincides with the average value of primitive meteorites and is 7 times the nebular ratio (Robert et al., 2000). In addition, the atmosphere is enriched in  $^{15}\text{N}$  relative to what has been claimed to be the signature of the proto-solar nebula (Hashizume et al., 2000). Such isotopic ratios are inconsistent with direct derivation from the solar nebula, but are consistent with a chondritic origin (Dauphas et al., 2000). Thus, in addition to a solar nebula contribution whose remnant is found in the deep mantle, another component likely carried by planetary bodies such as meteorites has contributed to the mantle inventory of volatile elements. It seems logical to consider that this contribution took place after the Moon-forming event because, as argued above, such event resulted in a drastic degassing of the mantle, only its deepest regions or the core having kept a record of the solar nebula.

#### 4.2.1.2. *Early evolution of the atmosphere*

Atmospheric erosion due to large impacts could have played a significant role in reducing the atmospheric reservoir. Indeed, the speed of ground on the other side of the Earth due to a major collision might have exceeded the liberation speed of 11 km/s for the Earth and therefore triggered major atmosphere (and ocean) loss. However, the efficiency of this process in the Hadean is subject to discussion as it is unclear if the contribution of volatile elements by the impactors exceeded or not the loss of these elements. A potentially efficient process consists in gravitational escape of light elements, enhanced by the photo-dissociation of water by UV from the young sun, into molecular hydrogen and atomic H, and escape of the latter (Hunten et al., 1987). The so-called hydrodynamic escape process is able to drag atoms and molecules heavier than H, so that the escape of volatile elements from the atmosphere will last during the enhanced UV flux period, which could have lasted up to 150 Ma in the case of weak T-Tauri phase (Pepin, 1991). Atmospheric escape takes place when the velocity of gaseous atoms exceeds the liberation velocity for the planet, and is therefore favoured by high atmospheric temperature. Here too, giant collisions might have played a role by increasing the latter.



The study of extinct radioactivities provides evidence that the atmosphere was open to loss to space during the Hadean. The amount of radiogenic  $^{129}\text{Xe}$  generated by decay of  $^{129}\text{I}$  and of  $^{131-136}\text{Xe}$  from the fission of  $^{244}\text{Pu}$  only represents a fraction of the total Xe isotopes generated by the decays of these elements in bulk Earth. Degassing of the mantle during the Hadean can perfectly account for the depletion of this reservoir in Xe isotopes. However, the atmosphere must also have lost most of radiogenic and fissionogenic Xe isotopes. Taking into account the half-life of  $^{244}\text{Pu}$  (82 Ma), such a loss must have lasted for at least 200 Ma, possibly up to 600 Ma (Tolstikhin and Marty, 1998). Some of the atmospheric noble gases are severely isotopically mass fractionated compared to potential precursors (solar or asteroidal components), which suggests independently escape from the atmosphere that favoured light isotopes relative to heavy ones. As discussed above, atmospheric neon is depleted by 30% in the light  $^{20}\text{Ne}$  isotope relative to  $^{22}\text{Ne}$  when compared to mantle neon, a difference that might have arisen from mass fractionation during atmospheric loss. However, several meteoritic Ne data encompass the atmospheric isotopic ratio, leaving open the possibility that air Ne was contributed by asteroidal bodies (Marty, 1989). Xenon, which is the heaviest noble gas, is severely fractionated by 3% per amu relative to solar or asteroidal precursors, which is fully consistent with isotope fractionation during hydrodynamic escape (Sasaki and Nakasawa, 1988). However, the problem with this element is that it is also elementally depleted relative to lighter noble gases, e.g., the atmospheric Xe/Kr ratio is 5 times lower than the chondritic Kr/Xe ratio, exactly the opposite of what would be expected from Xe isotopes. This long-standing problem, known as the xenon paradox, indicates that the early evolution of the atmosphere was probably very complex and involved several episodes of exchanges between the mantle, the atmosphere, the outer space and some of the precursors (Pepin, 1991; Tolstikhin and Marty, 1998). In this respect, comets that may be depleted in Xe might have contributed lighter volatile elements whereas a residue of isotopically fractionated Xe attested previous episodes of atmospheric loss (Dauphas, 2003).

The role of comets in supplying volatile elements to the early Earth has been often advocated. Indeed, it seems that, when compared to inner regions of the solar system, the Kuiper belt has a mass deficit, which is interpreted as reflecting a depletion of bodies due to gravitational perturbations by giant planets, or to the existence of a yet undiscovered Mars-sized planet that later on disaggregated, or to external factors like the transit of a nearby star. Small bodies caught in resonance from nearby giant planets are ejected and part of them falls towards the inner solar system. As a result, one would expect the inner solar system to be battered by cometary objects ejected from outer regions of the solar system and providing volatile elements to terrestrial planets. Cometary data prone to investigate quantitatively this possibility are

scarce, but some tentative inferences can be made in the case of noble gases, water and nitrogen. First, the hydrogen isotopic ratio measured by remote sensing in a few comets indicates that these objects are richer in D than both the oceans and chondrites, with a D/H ratio about 2 times that of the former. Thus, the contribution of cometary material seems to be very limited. A budget for argon, hydrogen and platinum group elements (which are believed to have been added by asteroidal bodies after the major metal-silicate differentiation), as well as the lunar cratering record led Dauphas et al. (2000) to conclude that the fraction of cometary material in the late contributing veneer (here the amount of undifferentiated material that fell onto Earth after metal-silicate differentiation) was lower than 1%. A similar conclusion is derived from N isotope systematics, indeed, cometary N seems to be depleted in  $^{15}\text{N}$  (Jewitt et al., 1997) as the Sun is. However, recent data for cometary CN show that some of the N compounds are enriched in  $^{15}\text{N}$  (Arpigny et al., 2003), and no definite conclusion can be proposed for this element.

#### 4.2.1.3. *A tentative scenario*

The formation of the atmosphere was a multi-stage process during which several cosmochemical reservoirs contributed volatile elements. There is strong evidence that some of them derived from the solar nebula, possibly through dissolution of a massive solar-like atmosphere. Accumulation of such a massive atmosphere occurred when the nebular gas was present, that is,  $\leq 10$  Ma after start of solar system condensation (ASSC) at most. Therefore, planetary bodies large enough to retain a hydrogen-rich, probably transient, atmosphere existed already within this timeframe. This is in full agreement with time ranges provided by extinct radioactivity products measured in differentiated meteorites (particularly in Martian meteorites which show evidence for metal-silicate-melt differentiation within the first 9 Ma; Halliday et al., 2001) on one hand, and with planetary build up modelling showing the existence of Mars-sized bodies and of giant planets within few Ma ASSC.

The occurrence of a massive hydrogen-rich atmosphere had several important consequences for the thermal and chemical state and evolution of the proto-Earth. During the magma ocean stage (part 4.1.5.) solar-like gases could dissolve into magmas. The low oxygen fugacity ( $f\text{O}_2$ ) imposed by hydrogen might have played a major role in metal reduction that led to the formation of the core, in an active magma ocean where the oxygen fugacity would be buffered by atmospheric hydrogen. The remnant of the solar component might have been kept in the deep mantle or in the core where it might have survived the last giant impact forming the Moon. The  $^{182}\text{Hf}$ - $^{182}\text{W}$  extinct radioactivity system indicates that this event took place at about 30 Ma after Earth accretion, within a possible range of 11–50 Ma (Kleine et al., 2002; Yin et al., 2002a). A magma ocean episode on the Moon might

have lasted 45 Ma, and on Earth, it might have been much longer from obvious thermal consideration. The  $^{129}\text{I}$ - $^{244}\text{Pu}$ - $^{129}\text{Xe}$ - $^{136}\text{Xe}$  systems have recorded a mantle closure time at about 60–70 Ma ASSC (Yokochi et al., 2005) which might correspond to a strong decline in large-scale magma ocean episodes.

Presumably, later on, the proto-mantle was contributed by meteoritic Ne, water, nitrogen and other volatile elements (C, other noble gases). Compared to sun, planetary material (e.g., meteorites, asteroids) is highly depleted in noble gases (relative to H, C, N etc.), such that contribution of this material would dominate the budget of major volatiles without overprinting noble gas characteristics inherited from previous processes. Thus, isotopic fractionation related to atmospheric escape is recorded in noble gases whereas the major volatile element isotopic ratios (e.g., D/H,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$ ) have kept a less disturbed record of their chondritic origin.

The study of extinct radioactivities involving volatile elements like Xe demonstrates that the early atmosphere was open to loss in space during long time intervals, possibly covering the whole Hadean. The Hadean mantle was also very active, convecting at a rate one order of magnitude or more higher than at Present, as indicated by the extensive loss of fissionogenic Xe from  $^{244}\text{Pu}$  (half-life of 82 Ma) which occurred well before the loss of isotopes produced by long-lived radioactivities like  $^{40}\text{Ar}$  or  $^4\text{He}$  (Yokochi et al., 2005).

The amount of nitrogen and water that was supplied by “late” contribution (i.e. after the last global metal-silicate segregation) of asteroidal material, as estimated from the platinum group element (PGE) budget of the mantle, is consistent, (within a 2–3 times range) with the terrestrial inventory of oceans and atmosphere (Dauphas et al., 2000; Dauphas and Marty, 2002). Part of water and nitrogen might have been cycled through time between the mantle and the surface, so that the match between the PGE budget and the surface inventory is fairly good (Figure 4.4). This implies that the main volatile elements that are present in the atmosphere and in the oceans could have been carried by “late” veneer contributions having taken place presumably after the Moon-forming event. It is unclear if these contributions were the product of big impacts or were delivered by snowing dust. The latter could have been efficient in providing part of (Marty et al., 2005), or even most of, volatile elements present in the atmosphere and the oceans (Maurette, 1998).

The amount of  $\text{CO}_2$  assumed to be contributed by this veneer is comparable to the quantity of carbonates trapped in sediments. The latter is probably a lower limit of the carbon inventory since today, due to recycling; the Earth mantle contains a significant fraction of carbon. The calculated equivalent partial pressure of  $\text{CO}_2$  is about 100 atmospheres, which is comparable to that observed today in Venus atmosphere. Such  $\text{CO}_2$  partial

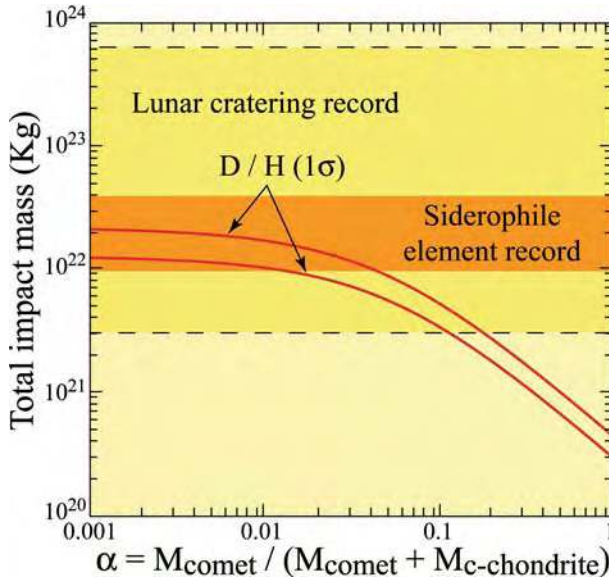


Figure 4.4. The total mass of impacting bodies on Earth after the Lunar cataclysm as a function of the fraction of cometary material in the impacting bodies (cometary plus asteroidal). The lines represent solutions constrained by the D/H ratios of the different end-members. The orange area represents the mass flux constrained by the Lunar cratering record, and the light orange area is the mass fraction constrained by the highly siderophile element (HSE) content of the terrestrial mantle. The latter is not equilibrated with the terrestrial core; it is attributed to addition of chondritic material after core formation. The D/H ratio of comets 3 times larger than that of chondrites imposes that the cometary fraction cannot be higher than 10% at best to be compatible with the mass flux recorded on the Lunar surface, and about ~1% to be consistent with the mass flux constrained by the HSE record. Taking into account the amount of noble gases present in the atmosphere will reduce the cometary contribution to about 0.1% or less (Dauphas et al., 2000; Dauphas and Marty, 2002).

pressure would lead to a greenhouse surface temperature of several hundreds of °C. This scenario implies that a very efficient process of condensation of the oceans and of carbonation of atmospheric CO<sub>2</sub> took place in the early Hadean such that the Earth reached temperatures below the water boiling temperature at about 4.4 Ga. Indeed, oxygen isotope data of some 4.4 Ga old zircons point to water–rock interaction below 100 °C (see part 4.3.4.).

#### 4.2.1.4. Contributions from accretion stages to present

Independent lines of evidence such as the prominence of carbonaceous chondrites over ordinary chondrites in the asteroid belt (Gradie et al., 1989), the occurrence of carbonaceous chondrite debris in the lunar regolith (Keays et al., 1970) and in meteorites (Zolensky et al., 1996; Gounelle et al., 2002),

remnants of a cometary shower in terrestrial sediments (Farley et al., 1998), strongly suggest that extraterrestrial material delivered volatile elements to the surface of the Earth from accretionary stages to Present (e.g. Chyba, 1990; Morbidelli et al., 2000). Mass balance considerations based on hydrogen isotopes, on noble metal and noble gas abundances indicate that this flux was dominated by chondritic material, the mass fraction of comets being  $\sim 10^{-3}$  or less (Dauphas et al., 2000; Dauphas and Marty, 2002). Carbonaceous chondrites, comets and interplanetary dust particles (IDPs) are rich in organic molecules and might have contributed directly to the pre-biotic inventory of the Earth (Anders, 1989; Maurette, 1998).

The flux of cosmic dust measured before atmospheric entry in the near-Earth interplanetary space yields a value of  $30,000 \pm 20,000$  tons/yr (Love and Brownlee, 1993). Cosmic dust represents the largest contribution of extraterrestrial matter to the Earth's surface at present, as the meteorite mass flux over the  $10 \text{ g}^{-1} \text{ kg}$  interval accounts for only  $\sim 3\text{--}7$  tons/yr (Bland et al., 1996). IDPs collected in the stratosphere by NASA have typical sizes below  $50 \mu\text{m}$ . They probably sample a mixed population of debris originating from the asteroidal belt and from the Edgeworth–Kuiper belt (e.g. Brownlee, 1985; Brownlee et al., 1993), with possible contribution from silicates and organics of interstellar origin (Messenger, 2000; Aléon et al., 2001; Messenger et al., 2002, 2003; Aleon et al., 2003).

Objects in the size range  $25\text{--}200 \mu\text{m}$  (exceptionally up to  $400 \mu\text{m}$  and larger), labelled micrometeorites (MMs), dominate the mass flux of cosmic dust onto Earth (e.g. Love and Brownlee, 1993). Micrometeorites share mineralogical and chemical similarities with CM and/or CR chondrites (Kurat et al., 1994; Engrand and Maurette, 1998), and D/H ratios of MMs point to an extraterrestrial, likely to be asteroidal (CM-CI-type), origin of trapped water (Engrand et al., 1999).

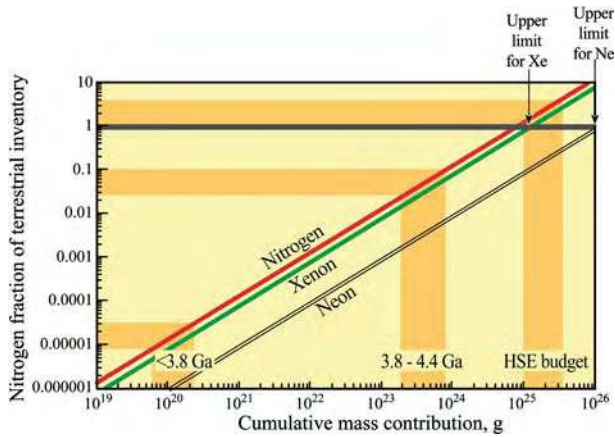
In the following, we make an estimate of the nitrogen contribution by cosmic dust to the atmosphere through time, following a recent study (Marty et al., 2005). The case of nitrogen perfectly illustrates the fate of other atmosphere elements; it can be extended to that of water as far as orders of magnitude are concerned. An estimate of the nitrogen delivery flux can be assessed by assuming a N content of  $\sim 1000$  ppm characteristic of carbonaceous chondrites and in particular of CM chondrites. This value may be a lower limit since some of the micrometeorites might contain a larger initial N content as suggested by the sometimes high trapped noble gas content (see preceding section), although the frequency of such particles is unknown. IDPs can contain N at the percent level (Aleon et al., 2003). However the IDP mass flux is  $\sim 0.01$  times that of micrometeorites, (Love and Brownlee, 1993), so that their nitrogen contribution appears limited, perhaps at the same level as the one from MMs. Comets contain about  $10,000\text{--}40,000$  ppm N (see Dauphas and Marty, 2002, and references herein) and might have

contributed significantly to cosmic dust. However, mass balance considerations involving volatile and siderophile elements together with D/H ratios of the terrestrial oceans suggest that the bulk cometary contribution to the terrestrial inventory of volatile elements was very limited, of the order of  $10^{-3}$  relative to the total mass of contributors (Dauphas et al., 2000; Dauphas and Marty, 2002). It must be noted that the nitrogen content of cosmic dust necessary to account for N isotope variations in lunar soils has been estimated at  $\sim 1000$  ppm on average over most of the lunar history (Hashizume et al., 2002).

The cosmic dust flux might not have varied dramatically since 3.8 Ga ago, except for a significant increase in the last 0.5 Ga (Grieve and Shoemaker, 1994; Culler et al., 2000; Hashizume et al., 2002). A near-constant planetary contribution within a factor of 2 since 3.8 Ga ago is also consistent with the cratering record at the lunar surface (Hartmann et al., 2000). Thus, we assume, as done previously (Chyba and Sagan, 1992), that the cosmic dust flux remained constant since 3.8 Ga at a rate similar to the present-day one. Another important question is the flux ratio between dust and larger objects. The present-day mass ratio between dust and meteorites is of the order of  $10^2$ – $10^3$ . Although highly imprecise, the mass contribution due to large objects, which is dominated by rare events of km (or more) sized objects, might have been comparable to the cosmic dust flux, averaged over the last 3 Ga (Kyte and Wasson, 1986; Anders, 1989; Trull, 1994). A constant cosmic dust flux similar to the present-day one ( $\sim 30,000$  tons/yr) integrated over 3.8 Ga could have supplied  $\sim 4 \times 10^{15}$  mol  $N_2$ , to the atmosphere, which makes only  $\sim 3 \times 10^{-5}$  times the atmospheric  $N_2$  amount ( $1.38 \times 10^{20}$  mol  $N_2$ , (Ozima and Podosek, 2002) (Figure 4.5). Such a limited contribution is unlikely to have had discernable isotopic effects on atmospheric nitrogen. This view is consistent with available data for Archaean and Proterozoic sediments indicating that the atmospheric N isotope composition has been near-constant since 3.5 Ga (Sano and Pillinger, 1990; Pinti, 2002).

Some argue a steep decline of the cratering rate between 4.5 and 3.8 Ga, there is compelling evidence that a spike of bombardment took place 4.0–3.8 Ga ago and that in the time interval 4.4–4.0 Ga ago the impacting flux was not dramatically high (Hartmann et al., 2000, part 4.5). The total mass of impactors during the last spike of bombardment around 3.9 Ga is  $\sim 6 \times 10^{21}$  g (Hartmann et al., 2000). The content of siderophile elements in the ancient highlands suggests that the amount of interplanetary mass accumulated by the Moon in the 4.4–4.0 Ga period is about the same as that required in order to form the 3.9 Ga basins. Consequently, the post 4.4 Ga contribution to the lunar surface might have been  $\sim 1.2 \times 10^{22}$  g (Hartmann et al., 2000). This contribution included both bolides (evidenced by remnants of the lunar cataclysm) and cosmic dust, all of them being integrated in the siderophile element record. A lower limit for the Earth's efficiency over Moon





*Figure 4.5.* ET nitrogen contribution to the terrestrial N inventory (atmosphere, crust and mantle, as a function of the cumulative mass contribution to the Earth. A mean N content of 1000 ppm is assumed for contributing material. A  $\gamma$ -value of 1 (horizontal grey bar) means that the total terrestrial budget can be supplied by contributing material. Cosmic dust contribution from the Archaean (<3.8 Ga) to Present is likely to be negligible for the nitrogen budget. Contributions during the Hadean (3.8–4.4 Ga ago) could have been significant (up to 10%). The highly siderophile element (HSE) budget is based on the amount of these elements in the mantle that did not equilibrate with the core and presumably were supplied after terrestrial differentiation (data from Chyba, 1991). The lower limit of this contribution allows to supply the total amount of nitrogen present in the atmosphere, the crust and the mantle, showing that the case of nitrogen parallels that of HSE. The xenon and neon potential contributions are computed assuming a chondritic composition (Mazor et al., 1970) and put constraints on the total delivery of nitrogen. Assuming mixing between a pre-existing, isotopically fractionated atmosphere and a chondritic-like delivery, the amounts of Xe and Ne that can be brought cannot exceed those of the pre-existing atmosphere because their isotopic compositions differ markedly. Xenon is particularly sensitive to this effect and confirms that the total amount of nitrogen that was delivered after terrestrial differentiation is compatible with the lower limit of the HSE budget.

to collect cosmic dust is given by the ratio between the surfaces of the two bodies (13). Gravitational focusing of cosmic dust (Kortenkamp et al., 2001) possibly increases the collection efficiency of the Earth by a factor of  $\sim 3$  relative to the Moon (Hashizume et al., 2002). Therefore, the range of extraterrestrial material collected by Earth between 4.4 and 3.8 Ga might have been  $\sim (2.4\text{--}7.2) \times 10^{23}$  g. This represents a contribution of  $(0.07\text{--}2.1) \times 10^{19}$  mol  $\text{N}_2$ , that is, 6–18% of present-day atmospheric nitrogen. Nitrogen has been actively exchanged between the surface and the mantle (Marty and Dauphas, 2003), so that it is more appropriate to consider the total nitrogen budget of the Earth, which is  $2.8 \pm 1.0 \times 10^{20}$  mol  $\text{N}_2$  (Marty, 1995; Marty and Dauphas, 2003). Thus, the total post-4.4 Ga contribution of nitrogen to Earth might have been  $\sim 10\%$  of total terrestrial N (Figure 4.5). An upper limit of the nitrogen contribution by extraterrestrial matter to Earth can be

set from the highly siderophile element (HSE) budget of our planet which might have been delivered after metal/silicate differentiation towards the end of terrestrial accretion (e.g. Chyba, 1991, and references herein). If nitrogen is a siderophile element as recently argued (Hashizume et al., 1997), the amount now measured in both mantle and atmosphere might have been delivered after core formation during “late veneer” events. The amount of HSE present in the mantle corresponds to the contribution of  $1 \times 10^{25}$ – $4 \times 10^{25}$  g of chondritic material (Chyba, 1991), thus to a delivery of  $(3\text{--}14) \times 10^{20}$  mol  $\text{N}_2$ . This is clearly in the range of the nitrogen budget of the Earth ( $3 \times 10^{20}$  mol  $\text{N}_2$ ), thus suggesting that cosmic dust, which dominates now the extraterrestrial flux of matter to Earth, could have supplied nitrogen present in the atmosphere, but only during the late building stages of our planet. A summary of nitrogen delivery through time is given in (Figure 4.4).

#### 4.2.2. OCEAN

DANIELE L. PINTI

The establishment of a precise chronology of the formation of the terrestrial oceans depends on the ability to answer two fundamental questions: (1) how and when did water arrive on the Earth? (2) when did internal heat flow from the accreting Earth decreased to a critical threshold allowing water to be liquid on its surface?

The origin of water on Earth has been at the centre of much debate in the last decades, yet few models have been formulated on the origin of the oceans (Abe, 1993; Sleep et al., 2001; Pinti, 2005) because of the evident lack of geological record. Actually, the scientific community agrees with the hypothesis that water was brought very early in the history of the solar system, possibly during the last phases of the Earth accretion, which implies that the oceanic water inventory was available since the beginning (e.g. Morbidelli et al., 2000). Theories on an “expanding ocean”, with water delivered all along the Earth history seem to be implausible and not supported by the geological record (de Ronde et al., 1997; Harrison, 1999), although several authors still claim its existence to account for climate and sea-level variations during eons (Deming, 1999). These variations are likely the result of plate tectonics, continental drifting and the opening of new oceanic basins, rather than variations of the volume of the oceans.

However, contrasting opinions subsist on the extraterrestrial carrier that brought water on Earth, splitting in two the scientific community. Some authors propose a dominant cometary origin (Frank et al., 1986; Delsemme, 1999), which has found much credit among the biologists because comets contain plenty of organic molecules that could be considered as the



primordial “bricks” of life. The other part of the community, supported by strong isotopic evidence and dynamical models of the solar system evolution (Dauphas et al., 2000; Morbidelli et al., 2000; Robert, 2001; Dauphas and Marty, 2002; Dauphas, 2003; Robert, 2003), proposes that a few asteroidal embryos of chondritic composition are the water deliverers.

#### 4.2.2.1. *Water accretion to Earth (4.56–4.49 Ga = $t_0$ + 11–70 Ma)*

The prevailing opinion on the origin of the oceans is that the water comes from the outer solar system, brought by comets or asteroids colliding the freshly formed Earth, the usually called “late veneer scenario” (e.g. Javoy, 1998; Javoy, 2005 and references therein) (Figure 4.6). Isotopic and mass balance calculations, based respectively on the hydrogen isotopic ratio of water (D/H), the amount of water in different extraterrestrial reservoirs (e.g., meteorites, comets) and numerical simulations of extraterrestrial fluxes suggests that delivery of water by comets is less than 10% of the total (Dauphas et al., 2000; Robert, 2001). Compilation of the isotopic ratio of hydrogen

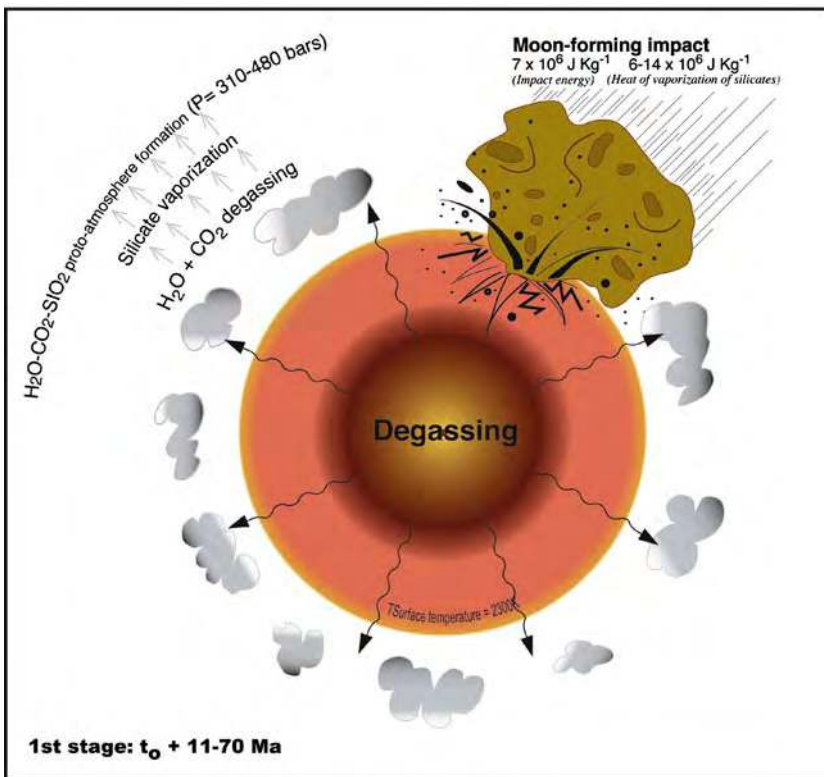


Figure 4.6. Sketch representing the main phases of the formation of the terrestrial oceans ( $t_0 + 11-70$  Ma).

(D/H) measured in different extraterrestrial reservoirs and compared with that of the modern seawater ( $D/H = 155.7 \times 10^{-6}$  or  $\delta D = 0$  by definition) suggests that few embryos of asteroids (with a  $D/H = 149 \pm 6 \times 10^{-6}$ , Morbidelli et al., 2000; Robert, 2003) or alternatively consistent fluxes of large IDPs (AMM, Antarctic Micrometeorites with a  $D/H = 154 \pm 16 \times 10^{-6}$ , Maurette et al., 2000) could be the carrier of water on Earth. The chemical and isotopic composition of both these two reservoirs is close to that of the carbonaceous chondrites (Robert, 2003), the latter ranging from that of Orgueil (CI; fully hydrated) to that of Murchinson (CM; containing about 40% of hydrated minerals). Independent estimates based on the excess of siderophile elements of the platinum group in the mantle suggest that contribution from comets could be less than  $10^{-3}$  by mass of the total (Dauphas and Marty, 2002). Numerical simulations indicate that impact probability of comets is too low to supply all of the terrestrial water (Zahnle and Dones, 1998; Morbidelli et al., 2000). Very recently, new simulations have been carried out in order to explain the cataclysmic Late Heavy Bombardment (LHB) period that lasted between 10 and 150 Ma, at around 4.0–3.8 Ga ago (Gomes et al., 2005, see part 4.5). In these simulations, the rapid migration of the giant planets destabilized the planetesimal disk thus resulting in a sudden massive delivery of these planetesimals to the inner solar system. During this burst, the total amount of cometary material delivered to the Earth is  $1.8 \times 10^{23}$  g, which corresponds to about 6% of the current ocean mass.

The hypothesis of Maurette et al. (2000) of adding water to Earth's oceans by accreting cosmic dust (AMM) is interesting but it fails against the unknown fluxes of extraterrestrial particles hitting the early Earth and the capacity of AMM to furnish the total Earth's water inventory. This latter includes both the mass of the oceans ( $1.37 \times 10^{24}$  g; 98% of the total surface water inventory) and an unknown amount of water that could reside in the Earth's mantle, as suggested by its high degree of oxidation. Water masses up to 50 times the amount in the modern ocean have been postulated for the primitive mantle (Abe et al., 2000), while high-pressure experiments in hydrous mineral phases suggest that Earth's lower mantle may actually store about five times more water than the oceans (Murakami et al., 2002). The minimum estimation for the whole mantle is of  $1.93 \times 10^{24}$  g, only 1.4 times the present-day oceanic inventory (Dreibus and Wanke, 1989). Accepted values of the volume of water for the most "wet" mantle scenarios are from 5 to 10 times that of the modern oceans.

Best estimates of the present-day accretion rate of cosmic dust measured before atmospheric entry yields a value of  $30,000 \pm 20,000$  tons/yr (see part 4.2.1.) while initially Love and Brownlee (1993) gave a slightly higher value of  $40,000 \pm 20,000$  tons/yr. On Earth surface, the flux is much less and estimates obtained from abundance of cosmic dust from Antarctic cores yields values from  $5300 \pm 3,100$ – $16,000 \pm 9300$  tons/yr with a global average of

14,000 tons/yr (Yada et al., 2004). The amount of water in the AMM has been measured to range from 2 to 8 wt.% (Engrand et al., 1999). Assuming a cosmic dust accretion rate ranging from 2200 to 60,000 tons/yr, integrated to the whole Earth history (4.5 Ga), the total amount of water would be between 1000 and 100,000 times less than the present-day oceanic inventory.

Cosmic dust accretion rate has been relatively constant in the last 3.8 Ga within 2 times the present flux (Hartmann et al., 2000). However, the fluxes in the period between 4.5 and 3.8 Ga are unknown and highly debated. Marty et al. (2005) propose that the total amount of collected cosmic dust might have been  $2.4\text{--}7.2 \times 10^{23}$  g, between 4.4 and 3.8 Ga. In term of added water, this represents a contribution of 0.3–4% of the present-day oceanic inventory. Integrating 2 times the present flux over the remaining 3.8 Ga, does not significantly change the figure. Theoretical extrapolations of Hartmann et al. (2000) indicated a declining flux since the start of the Earth accretion, with an initial flux of planetesimal impactors at  $t_0$ , on the order of  $2 \times 10^9$  the present flux. Assuming a ratio of 100–1000 between meteorites and the cosmic dust, as at the present-day, the initial flux of cosmic dust could have been as high as  $10^6 \times$  the present flux (Maurette, 2001). Assuming a present flux ranging from 20,000 to 60,000 tons/yr, a water content of 2–8 wt%, a dust/planetary ratio of 100–1000 and integrating accretion rates from Hartmann (Hartmann et al., 2000) (Figure 4.7), we can calculate the “age” of the oceans (i.e. the time needed to add water to the Earth). Assuming maximum rates of cosmic dust accretion and water contents, our computations give us a minimum time of 70 Ma to collect the present ocean inventory ( $1.37 \times 10^{24}$  g; Figure 4.7) since the time  $t_0$  of the Earth formation. The total maximum amount of water that could be brought to Earth in  $4568 \pm 1$  Ma by cosmic dust however, is only 116% of the present oceanic inventory ( $1.59 \times 10^{24}$  g; Figure 4.7), which means that other sources are needed to account for the whole Earth water content (hydrosphere + mantle =  $3.3\text{--}15.1 \times 10^{24}$  g). If we assume minimum fluxes of AMM hitting the Earth, after 70 Ma from the solar system formation, only 0.8% of the total oceanic inventory will be delivered. This latter figure strongly supports the existence of alternative carriers of terrestrial water. The above calculation does not take into account the peak of the so-called LHB, which lasted from between 10 and 150 Ma, at 4.0–3.8 Ga (Gomes et al., 2005, see part 4.5). During this spike, the amount of asteroidal material that struck the Moon is calculated to be  $3\text{--}8 \times 10^{21}$  g (Hartmann et al., 2000; Gomes et al., 2005), which corresponds to an amount on Earth of  $0.6\text{--}1.7 \times 10^{23}$  g. Assuming again an asteroid/cosmic dust ratio of 100–1000, the total amount of water added during the spike varies from 1.3 to  $130 \times 10^{18}$  g, which can be considered as negligible.

Based on dynamical models of primordial evolution of the solar system, Morbidelli et al. (2000) calculated the orbits and timescales of all possible

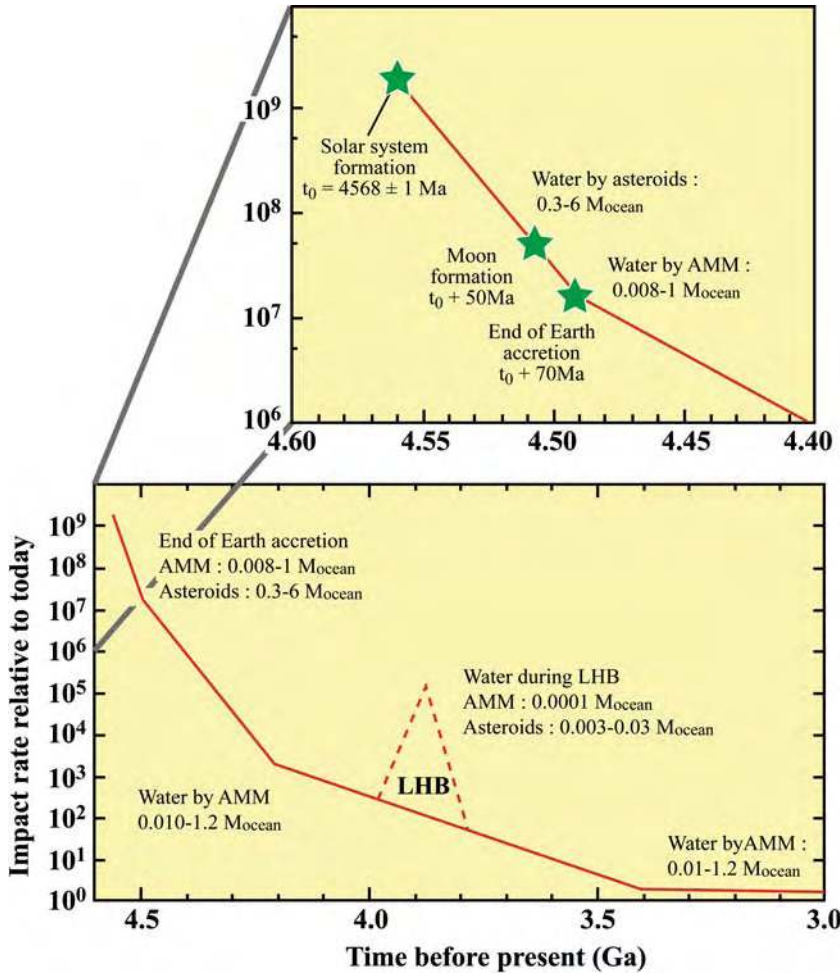


Figure 4.7. Empirical curve of impact declining flux during Hadean, as reported by Hartmann et al. (2000), modified. The cumulated amount of water transported by a minimum and maximum flux of cosmic dust composed principally of AMM of chondritic composition (Engrand et al., 1999) is calculated for each segment of the curve. The total amount of water delivered by asteroids and AMM during the LHB have been also reported. Small figure top-right is a zoom on the first period of Earth's accretion. It is possible to note that most of the oceanic and mantle water has been likely transported within the first 100 Ma of the Earth history.

water carriers in the primordial solar system. They concluded that towards the end of the solar system formation (several tenths of millions years), the Earth began to accrete few planetary embryos originally formed in the outer asteroid belt, heavily hydrated with a water content of about 10 wt.% deduced from average contents of hydrated carbonaceous chondrites (Boato, 1954; Robert and Epstein, 1982; Kerridge, 1985; Robert, 2003). A 10% of the Earth mass ( $6 \times 10^{27}$  g) could derive from this late accretion of primitive

material, which means that at least 5 times the present oceanic water inventory could have been brought by these planetary embryos, satisfying the “wet Earth” geochemical models. The timescale of this late water accretion can be supposed from the argumentations of Dauphas and Marty (2002). They assumed that highly siderophile element (HFSE) excess in the mantle might have been delivered by a late veneer of chondritic composition, after the metal/silicate differentiation of the Earth. The total amount of planetary embryos that struck the Earth was of  $0.7\text{--}4 \times 10^{25}$  g (Chyba, 1991; Dauphas and Marty, 2002). Assuming a 6–22 wt% of water content of these objects, between 0.3 and 6 times oceanic water inventory was delivered after the core formation by this chondritic veneer. Hf-W chronology indicates that the core formation occurred during the first 10–50 million years of the life of the solar system (Kleine et al., 2002; Yin et al., 2002a; Yin and Ozima, 2003), prior of the giant impact from which originated the Moon (Jacobsen and Yin, 2003). This impact is dated at 50 Ma after the differentiation of the earliest planetesimal in the solar system (Canup and Asphaug, 2001).

Recent simulations of the loss of the primary solar-type atmosphere of the primitive Earth show that an ocean-covered Earth might have existed well before the Moon-forming giant impact (Genda and Abe, 2005). The presence of an ocean significantly enhances the loss of atmosphere during a giant impact owing two effects: evaporation of the ocean and lower shock impedance of the ocean compared to the ground. Morbidelli et al. (2000) proposed that hydrated asteroids from the outer belt could have delivered an amount of water comparable to the present ocean, at time  $t_0 + 10$  Ma, but they concluded that only tiny amounts of this water survived to stripping by giant impacts. Genda and Abe (2005) simulations suggest that a giant impact could have stripped out 70% of a proto-atmosphere of solar composition, with essentially no loss for the ocean. Thus the initial hydrated planetesimals of Morbidelli et al. (2000) could have survived the giant impact period and participated to the oceanic water budget. It is interesting to note that for all these models, the time of water accretion is within the time of the Earth formation. Both hydrated planetary embryos and AMM could have sustained the water flux on Earth between  $t_0 + 10$  and 70 Ma.

#### 4.2.2.2. *Ocean formation (4.49–4.39 Ga = $t_0 + 70\text{--}165$ Ma)*

If water arrived very early on the accreting Earth, it does not mean necessarily that a stable and cold ocean existed in a very early period of its history. Earth became potentially habitable once it developed a solid proto-crust to separate the hot interior of the planet from a cooler surface environment featuring liquid water. Giant impacts such as the Moon-forming one has likely molten the Earth surface and vaporized proto-oceans to form a thick

$\text{CO}_2\text{-H}_2\text{O}$  proto-atmosphere (Pinti, 2005), yet this stage lasted likely less than 1 Ma (Abe, 1993). A molten surface can be sustained only by the blanketing effect of a massive proto-atmosphere. Yet, a hot runaway water greenhouse maintained by interior temperatures could have existed only for a short geological time (Sleep et al., 2001) (Figure 4.8). The Earth's interior would cool down, in the presence of a runaway water greenhouse, of 700 K in only 1.8 Ma (Sleep et al., 2001). During this very short period, after the Moon-forming impact, molten surface might have facilitated the exchange of volatiles with the Earth interior and part of the accreted water would be partitioned to the mantle, leaving at the surface the amount needed to form the present oceanic inventory.

The second stage of formation of the ocean is the production of a tiny basaltic proto-crust covering the Earth surface. This could have took place when the interior heat flow, produced by the gravitational energy flux released by accretion of the Earth, decreased to a threshold value of  $150\text{-}160 \text{ W m}^{-2}$  (Abe, 1993; Sleep et al., 2001). This could have been reached

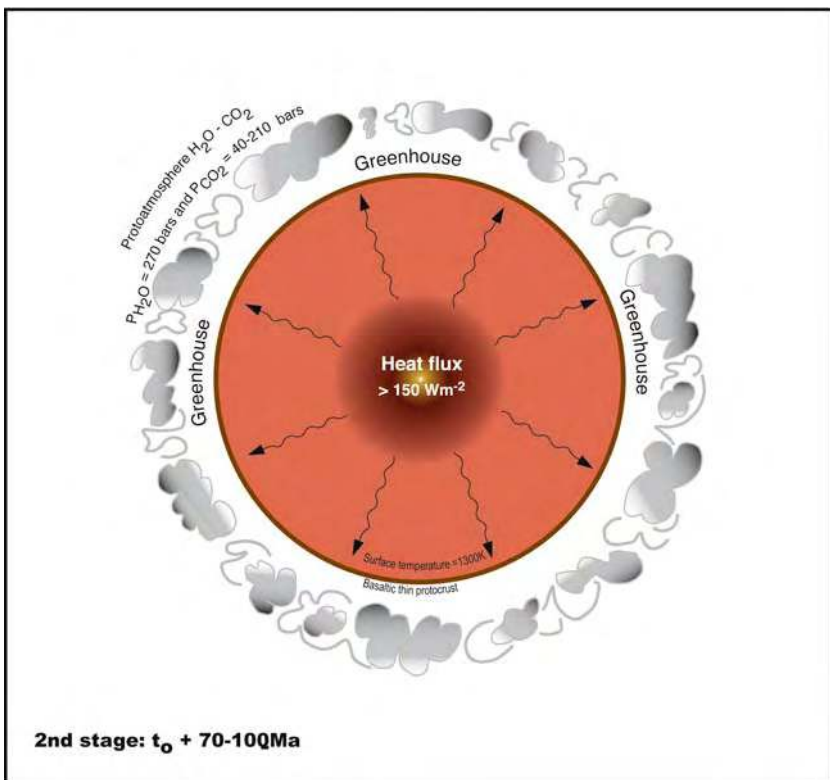


Figure 4.8. Sketch representing the main phases of the formation of the terrestrial oceans ( $t_0 + 70\text{-}100$  Ma).



at the end of the Earth accretion, when the Earth radius was 97% of the present size (Abe, 1993).

The ending stage of the Earth accretion, at  $t_0 + 50\text{--}70\text{Ma}$ , was characterized by a mechanically fragile proto-crust that was partially molten and resurfaced by meteoritic impacts and extensive volcanism. Assuming an atmospheric pressure at the surface of several hundred bars (270 bars of  $\text{H}_2\text{O}$  and  $\approx 40$  bars of  $\text{CO}_2$ , Pinti, 2005), water starts to condense and precipitates when the surface temperatures were below 600 K. Condensation of the oceans could have been a very rapid process, lasted few thousand years (Abe, 1993) (Figure 4.9). Although formed, the oceans were not yet habitable. Temperatures were too high for the survival of any form of life, and large-scale hydrothermal alteration of the proto-crust produced very saline water (halite-dominated brines, Sleep et al., 2001), where few forms of life could have survived.

A stable oceanic habitat took place when surface heat flow was less than  $1\text{ W m}^{-2}$ , and best estimates following the model of Abe (1993)

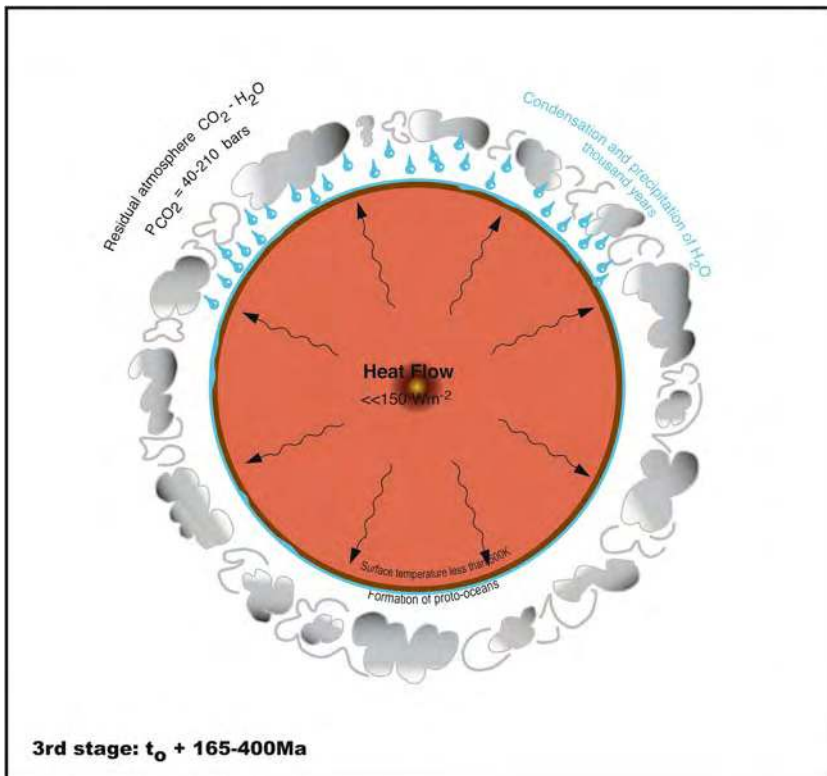


Figure 4.9. Sketch representing the main phases of the formation of the terrestrial oceans ( $t_0 + 165\text{--}400\text{ Ma}$ ).

indicate that such a situation was reached at  $t_0 + 400$  Ma (Figure 4.10). Independent estimates can be obtained by assuming that the temperature of the ocean was controlled by the greenhouse effect of a  $\text{CO}_2$  residual atmosphere, after the condensation of water in the oceans (Sleep et al., 2001). The maximum temperature acceptable for living organism is  $\leq 110^\circ\text{C}$  (thermophiles, Lopez-Garcia, 2005). This can be taken as one of the minimum conditions acceptable for a habitable ocean. This temperature is reached at equilibrium with a residual atmosphere of 25 bars of  $\text{CO}_2$  (Sleep et al., 2001). The initial atmosphere might have contained from 40 to 210 bars of  $\text{CO}_2$  (Pinti, 2005). The most effective way to remove  $\text{CO}_2$  from the primitive atmosphere is weathering of silicates in the proto-crust (during Hadean, weathering could have been a fast process, at rates of 10,000 times higher than the present ones, Abe, 1993), formation of carbonates and recycling of produced  $\text{CaCO}_3$  to the mantle. Zhang and Zindler (1993) proposed a maximum initial recycling rate of  $\text{CO}_2$  in the mantle of  $1.5 \times 10^{14}$  mol/yr. At this rate, 15–185 bars of  $\text{CO}_2$  could have

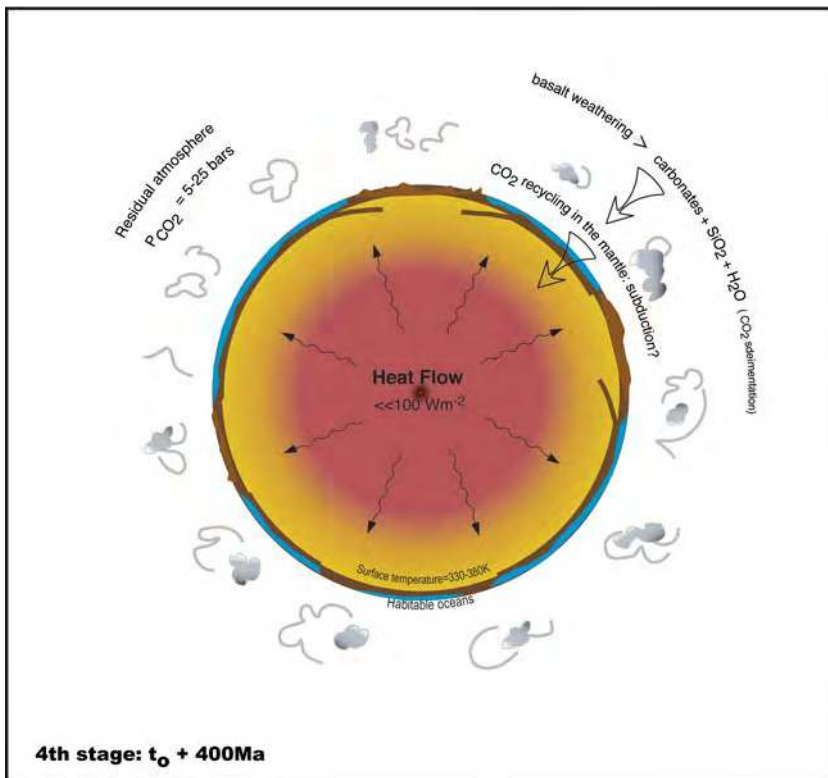


Figure 4.10. Sketch representing the main phases of the formation of the terrestrial oceans ( $t_0 + 400$  Ma).



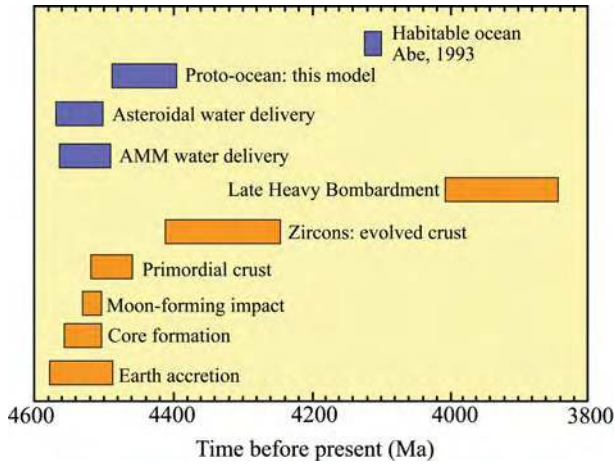


Figure 4.11. Chronology of the main phases of the Earth formation and differentiation, together with the phases of extraterrestrial water delivery and ocean formation.

been removed from the atmosphere in a span of time ranging from 19 to 140 Ma. The upper limit is close to a  $t_0 + 165$  Ma age, which corresponds to the minimum age of an evolved continental proto-crust containing liquid water, as suggested by the Jack Hills detrital zircon W74/2–36 Pb-Pb age ( $4404 \pm 4$  Ma, Wilde et al., 2001) (Figure 4.11). Clement conditions for the establishment of a habitable ocean were thus possibly in place at  $t_0 + 165$  Ma.

### 4.3. The First Continents

HERVÉ MARTIN

On Earth, plate tectonics is a powerful set of mechanisms that continuously rebuilds the planet surface; indeed oceanic crust is generated in mid ocean ridge systems and due to its relatively high density, it returns into the mantle through subduction zones, the average time for such a cycle is 60 Ma and no ocean older than 200 Ma is known today. In other words oceanic crust is not able to constitute an efficient archive of Earth history. On the opposite, continental crust has a lower density such that it is not easily recycled into the mantle. Consequently, continental crust is able to undergo and to record most of the episodes of Earth history. In addition, continental crust average composition is granodioritic, such that, contrarily to oceanic basalts, minerals such as zircon can easily crystallize in it. These minerals are extremely important in geochronology and this for two reasons: (1) zircon is a silicate of zirconium ( $ZrSiO_4$ ) where sometimes Th and

U can replace Zr. Due to the radioactivity of these elements zircon is “easy” to date. (2) zircon is extremely resistant to weathering and metamorphism, consequently it can resist to mechanisms as alteration, erosion and even sometimes to partial melting. This resistance allows it to efficiently record ages of old events.

#### 4.3.1. THE 3.8–3.9 GA ARCHAEOAN CRUST

##### 4.3.1.1. *Amitsôq TTG (Greenland)*

Since the field work of McGregor (1968; 1973) it has been recognized that Greenland Archaean terrains were among the oldest in the world. The oldest components of this craton were called the Amitsôq gneisses, which were first dated by Rb–Sr whole rock isochron method at  $3.98 \pm 0.17$  Ga (Black et al., 1971) and  $3.74 \pm 0.1$  Ga (Moorbath et al., 1972). More recent works showed that the so-called Amitsôq gneisses were not homogeneous, but on the contrary very diverse, and in order to account for this heterogeneity, Nutman et al. (2004) proposed to refer these formations as “Itsaq Gneiss Complex”; both denominations are used in geological literature. Zircon dating allowed to more precisely determine the ages of the genesis of these gneisses which range between 3.88 and 3.60 Ga. A statistical analyse performed on ca. 2000 zircons from this area pointed to the existence of 3 main episodes of continental crust genesis at Amitsôq: at  $\sim 3.80$  Ga;  $\sim 3.7$  Ga and  $\sim 3.65$  Ga. Even if rarer, ages older than 3.85 Ga were also measured. A zircon extracted from a gneiss sample, tonalitic in composition, gives the oldest reliable age obtained in this area:  $3.872 \pm 0.010$  Ga (Nutman et al., 1996). This age is interpreted as being that of crystallisation and emplacement of the tonalitic magma. The same authors (Nutman et al., 2000) also obtained an age of  $3.883 \pm 0.009$  Ga on a zircon core, whereas the main part of the mineral was dated at  $3.861 \pm 0.022$  Ga; here too these ages are supposed to give the time of crystallization of the parental magma.

Amitsôq gneisses outcrop over about 3000 km<sup>2</sup>; they are well exposed and generally well preserved of weathering (Figure 4.12). They derived from magmatic rocks Tonalitic, Trondhjemitic and Granodioritic (TTG) in composition (Nutman and Bridgwater, 1986; Nutman et al., 1996). TTG is the widespread composition of the Archaean crust between 3.8 and 2.5 Ga, crust which is considered as generated by hydrous basalt melting, possibly in subduction like environment (Martin et al., 2005). The ages obtained on the Amitsôq gneisses indicate that as early as 3.87 Ga ago, these mechanisms were already active and efficient, able to generate the huge volumes of continental crust observed at Amitsôq.



Figure 4.12. 3.87 Ga old Amitsôq gneisses (Greenland) that emplaced as TTG (Tonalite, Trondhjemite, Granodiorite) magmas. On this picture they are cut by a pegmatitic dyke related to later granitic intrusion. (Photo G. Gruau)

#### 4.3.1.2. *Isua and Akilia greenstone belt (Greenland)*

Supracrustal rocks (i.e. volcanic and sedimentary) also outcrop as lenses into the Amitsôq gneisses. Some lenses as at Isua can be big (~35 km long), but they are generally less than 1km long (Akilia Island for instance). Contrarily to TTG that emplaced deep into the crust, supracrustal deposited or erupted at the surface of the Earth (Figure 4.13). At Isua, zircons gave an age of  $3.812 \pm 0.014$  Ga (Baadsgaard et al., 1984). In Akilia Island, the Amitsôq tonalite dated at  $3.872 \pm 0.010$  Ga by Nutman et al. (Nutman et al., 1996) is intrusive (dyke) into a banded iron formation (BIF) thus demonstrating that this sedimentary rock is older than 3.872 Ga.



Figure 4.13. Isua (Greenland) gneisses, these rocks emplaced as sediments more than 3.87 Ga ago; they represent the oldest known terrestrial sediment (Photo G. Gruau).

The Isua and Akilia supracrustal rocks are extremely important, first of course because they represent the oldest huge volumes of rocks so far recognized, but also because:

- They contain sediments, thus demonstrating the existence of a hydrosphere (ocean) as old as 3.87 Ga.
- The origin of sediments has been subject to active discussion, some authors consider them as mostly of pure chemical origin, or even due to transformation (metasomatism) of pre-existing magmatic rocks (Rose et al., 1996; Fedo, 2000; Fedo et al., 2001; Myers, 2001; Fedo and Whitehouse, 2002; Bolhar et al., 2004). However, recent work (Bolhar et al., 2005) clearly demonstrates that at least some parts of Isua supracrustals correspond to true clastic sediments of mixed mafic and felsic provenance. The weathering, erosion and transport of the clasts are strong arguments in favour of emerged continents as early as 3.87 Ga.
- Both Isua and Akilia sediments contain carbonaceous inclusions, (generally into apatite crystals) whose  $\delta^{13}\text{C}$  average isotopic constitution of  $-30$  to  $-35$  could be interpreted as biological signature (Mojzsis et al., 1996). More recently, U-rich sediments from the same locality were interpreted as indicators of oxidized ocean water resulting of oxygenic photosynthesis (Rosing and Frei, 2004). However the reliability of these biological signatures is still subject to a very active controversy and the so-called bacteria *Isuasphaera Isua* as well as *Appellella ferrifera* are now considered as artefacts (Appel et al., 2002; Westall and Folk, 2003).
- Since at least 30 years, evidence of horizontal tectonics have been recognized in Amitsôq area (Bridgwater et al., 1974) and more recently it has been proposed that the early Archaean crustal accretion in Greenland proceeded by assemblage and collage of terranes (Nutman and Collerson, 1991; Nutman et al., 2004). All these arguments militate in favour of plate tectonic like processes operating since the Early Archaean.
- Investigation performed on the mafic magmatic components of Isua and Akilia greenstone belts, and based on lead (Kamber et al., 2003) or short-life isotopes (Boyet et al., 2003; Caro et al., 2003) conclude to a very early differentiation of a proto-crust, probably during the magma ocean stage and its long-lived preservation during the Hadean.

#### 4.3.1.3. *Uivak gneisses and Inukjuak (Porpoise Cove) greenstone belt (Canada)*

Along the northern Labrador coast, metamorphic rocks very similar to Amitsôq and Isua gneisses are exposed; there, they are called the Uivak

gneisses. Zircons analysed in these tonalitic (TTG) gneisses yield ages of  $3.733 \pm 0.009$  Ga, however they also contain rounded cores dated at  $3.863 \pm 0.012$  Ga (Schiøtte et al., 1989). However, in Labrador these rocks suffered a NeoArchaean granulite facies metamorphism (Collerson and Bridgwater, 1979) which is not the case in Greenland. Very recently, a volcano-sedimentary formation very similar to Isua was discovered in Hudson Bay (Canada) at Inukjuak (it was earlier called Porpoise Cove) and dated at  $3.825 \pm 0.016$  Ga (David et al., 2002; Stevenson, 2003). The wide repartition of these early Archaean crustal components militates in favour of the existence of a big continent (or of many small) older than 3.8 Ga in this part of the northern hemisphere.

#### 4.3.2. THE 4.0 GA ARCHAEOAN CRUST

At Acasta, in Northern Territories (Canada) small amounts (20 km<sup>2</sup>) of Archaean rocks are exposed. They mainly consist in banded tonalite and granodiorite (TTG) associated with subordinate amphibolite and ultramafic rocks. Most of these outcrops are strongly deformed, such that in these high strain zones all lithologies are juxtaposed and parallelized, resulting in banded rocks. However, small low strain zones exist; there, zircons measured in TTG samples gave ages of  $4.031 \pm 0.003$  Ga (Bowring and Williams, 1999). Moreover, in a tonalitic sample, zircons contain cores that have been dated at  $4.065 \pm 0.008$  Ga. Bowring and Williams (1999) interpret these cores as reflecting the incorporation in the tonalitic magma of remnants of older continental crust. Consequently, the Acasta TTG, not only represent the oldest rocks (continental crust) so far discovered, but they also demonstrate the existence of even older continental crust.

Ages measured on Amitsôq and Uivak gneisses, lead to the conclusion that the mechanisms of TTG genesis by hydrous basalt melting were active at 3.87 Ga. In the light of Acasta data, this conclusion can be extended back in time until 4.03 Ga and very probably until 4.06 Ga.

#### 4.3.3. THE PRE-4.0 GA HADEAN CRUST

Until recently, Acasta rocks were the oldest known terrestrial materials, and the question was to know if continental crust existed or not before 4.0 Ga. Consequently, isotopic compositions of the oldest rocks were used in order to indirectly discuss the possible existence and nature of the Hadean continental crust.

##### 4.3.3.1. *Indirect evidences*

The basic idea on which are based these hypothesis is that continental crust has been extracted from the mantle through partial melting processes. As the

composition of the crust is drastically different of that of the mantle, its extraction would have modified the mantle composition such that greater the continental crust volume greater the mantle composition change. The primordial Earth mantle is assumed to have the same Nd isotopic ratios as chondritic meteorites. In Figure 4.14,  $\epsilon_{Nd}$  represents the difference between the  $^{143}\text{Nd}/^{144}\text{Nd}$  of a rock and that of chondrites; consequently a  $\epsilon_{Nd} = 0$  will reflect a mantle source not affected by the extraction of the continental crust (CHUR = Chondritic Uniform Reservoir), whereas  $\epsilon_{Nd} > 0$  indicates a mantle impoverished by crust extraction;  $\epsilon_{Nd} < 0$  would rather reflect crustal source or contamination.

Even the oldest known rocks already display positive  $\epsilon_{Nd}$ , thus demonstrating that important volumes of continental crust were formed before 4.0 Ga. Simple calculations (McCulloch and Bennet, 1993; Bowring and Houst, 1995) showed that about 10% of the volume of the present day continental crust formed during Hadean times. Investigations performed on Hf (Vervoort et al., 1996; Albarède et al., 2000) and Pb (Kamber et al., 2003) isotopes led to the same conclusion. If all authors agree that continental crust differentiation started early in Earth history, they diverge about the rate and efficiency of this mechanism. For instance, Moorbath (1977) and Vervoort et al. (1996) estimate a relatively low degree of differentiation during the Hadean which could imply a constant crustal growth rate throughout the

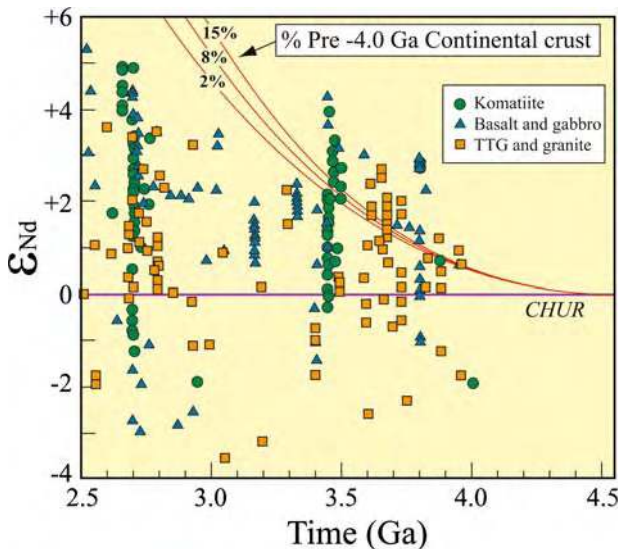


Figure 4.14.  $\epsilon_{Nd}$  vs. time diagram showing that even the oldest known rocks possess  $\epsilon_{Nd} > 0$  characteristic of mantle composition impoverished by extraction of continental crust prior to 4.0 Ga. Red curves are theoretical mantle Nd isotopic composition assuming 2, 8 and 15% extraction of Hadean continental crust. Data are from McCulloch and Bennet (1993), Jahn (1997) and personal data. CHUR (Purple line) = Chondritic Uniform Reservoir.



whole Earth history (Moorbath, 1977). On the contrary, more recent researches militate in favour of important rates of Hadean crust extraction (Collerson et al., 1991; Bennet et al., 1993; McCulloch and Bennet, 1993; Albarède et al., 2000). Similarly, studies of  $^{142}\text{Nd}$  (produced by decay of  $^{146}\text{Sm}$ , half-life = 0.103 Ga) points to an important crust differentiation during the very early stages of Earth history, probably during the magma ocean stage (Boyet et al., 2003; Caro et al., 2003). It has been proposed (McCulloch and Bennet, 1994) that the early depletion of the mantle has been buffered after 3.75 Ga by changes in the mantle convective regime resulting in mixing between depleted mantle and underlying less depleted lower mantle. Results presented by Albarède et al. (2000) are in agreement with this model.

#### 4.3.3.2. Jack Hills zircons

Recently, zircon crystals, extracted from Jack Hills meta-quartzites in Australia gave an age of  $4.404 \pm 0.008$  Ga (Wilde et al., 2001), which is the oldest age so far obtained on terrestrial material (Figure 4.15). However, it must be noted that many detrital zircons from Jack Hills and Mont Narryer in Australia already gave a great variety of ages ranging between 4.3 and 4.0 Ga (Froude et al., 1983; Compston and Pidgeon, 1986; Cavosie et al., 2004), which demonstrates that Hadean crust existed but also that it developed and grew all along Hadean times.

- Zircons predominantly crystallize in granitic (*s.l.*) melts, so it can be reasonably concluded that granitoids already formed at 4.4 Ga. This conclusion is reinforced by the presence, into the zircon crystals of

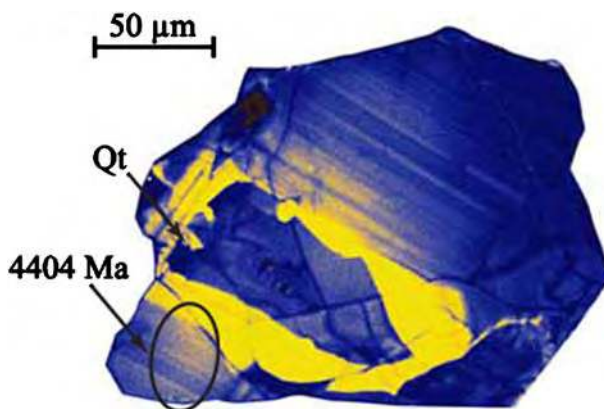


Figure 4.15. Cathodoluminescence image of zircon W74/2-36 from the Jack Hills metaconglomerate (Western Australia). An age of 4.404 Ga has been determined by ion microprobe from the place shown by an ellipse. This crystal also contains quartz (Qt) inclusions indicating that it crystallized in a granite-like magma (Photo: John Valley, University of Wisconsin, Madison).

inclusions of quartz, feldspars, hornblende, biotite and monazite; these minerals crystallized together with the zircon and are typical of granitoids (Maas et al., 1992; Wilde et al., 2001; Cavosie et al., 2004). Consequently, as granitoids are the main components of continental crust, it can be concluded that continental crust existed at 4.4 Ga. Based on a hafnium isotope studies in these zircon crystals, Harrison et al. (2005) concluded that both continental crust genesis and plate tectonics began during the first 100–150 Ma of Earth history.

- From Rare Earth Element (REE) content in zircons, and based on partition coefficients between felsic melts and zircon, it is possible to estimate the REE content of the host magma. The melt compositions calculated from older zircons have REE patterns enriched in Light REE (LREE: La to Sm) and depleted in Heavy REE (HREE: Gd to Lu) (Wilde et al., 2001); which are characteristics of Archaean granites (TTG, Martin et al., 2005). Similarly, *Type-1* zircons from Jack Hills have the same REE patterns as Acasta gneiss ones that are TTG in composition (Hoskin, 2005). Consequently, very probably Jack Hills crystallized in TTG-type felsic magma.
- The population of Jack Hills zircons not only recorded ages of 4.4 Ga, but on the contrary, they recorded several continental crust genesis events. Cavosie et al. (2004), evidenced several picks of crustal growth at 4.4, 4.25, 4.2, 4.0 Ga (Figure 4.16). It can be concluded that the Hadean continental crust grew over a time range of about 400 Ma, even if the process could have been episodic (as it is since 4.0 Ga).

Jack Hills zircons also possess rims that indicate that during the 4.4–4.0 time interval, they underwent reworking (re-melting). Such mechanism signifies that this Hadean continental has been stable enough to be re-worked, by both

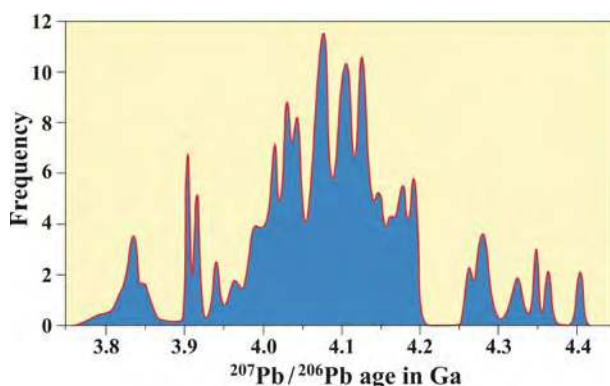


Figure 4.16. Histogram of age frequency of 88 zircons from Jack Hills, Mont Narryer and Barlee terrane (Cavosie et al., 2004).



magmatic and sedimentary processes. Similarly, the fact that these zircons exist implies that the early continental crust was enough stable (and consequently with a sufficiently huge volume) to resist at least partly to the Late Heavy Bombardment.

- Oxygen isotope measurements performed on Jack Hills zircons ( $\delta^{18}\text{O} = 5.4$  to 15) allow to calculate the isotopic composition of their host magma which ranges between  $\delta^{18}\text{O} = 7$  and  $\delta^{18}\text{O} = 11$  (Mojzsis et al., 2001; Peck et al., 2001; Wilde et al., 2001). These authors conclude that the zircons contain crustal material that had interacted with liquid water under surface or near surface conditions. These data are extremely important as they imply that liquid water (ocean?) was probably available on Earth surface as early as 4.4 Ga. In addition, the genesis of TTG like magmas results of hydrous melting of metamorphosed basalts, in the stability field of garnet (Martin, 1986; Martin et al., 2005); which, in turn, also implies the existence of an hydrosphere.

In conclusion, Jack Hills zircons, demonstrate that a TTG like continental crust existed as early as 4.4 Ga ago and that it more or less regularly continued to be generated and re-worked during the whole Hadean. This crust can be considered as stable, such that it can resist to meteoritic bombardment. In addition, Hadean crust composition (TTG) as well as zircons oxygen isotopic composition militate in favour of liquid water on Earth surface during Hadean, which could constitute a strong argument for discussing possible life existence and development.

#### 4.3.3.3. *Discussion of zircon data*

Jack Hills zircons are subject to several extensive studies and recent papers (Utsunomiya et al., 2004; Hoskin, 2005) seem to moderate the enthusiasm provoked by the oxygen isotopes data. Indeed, based on REE, Hoskin (2005) showed that it exists two populations of zircons in Jack Hills population; one group is considered as having recorded primary magmatic composition (type-1), whereas the other (type-2) displays typical hydrothermal features. The hydrothermalism is supposed to have occurred 130 Ma after zircon crystallization. The group, which evidenced hydrothermalism, is also the one with the higher  $\delta^{18}\text{O}$ . The author consider that this hydrothermalism did not necessarily required huge amounts of liquid water, but that it could have developed with small volumes of ephemeral fluid. The conclusion of the author is that, their results do not provide any evidence that ocean did not exist during Hadean times, but on the other hand, most high  $\delta^{18}\text{O}$  in Jack Hills zircons do not prove that liquid water was permanently available on Hadean Earth surface or near surface.

#### 4.4. Late Heavy Bombardment (LHB)

PHILIPPE CLAEYS, ALESSANDRO MORBIDELLI

##### 4.4.1. THE LATE HEAVY BOMBARDMENT (LHB)

The oldest known terrestrial rocks are represented by the gneisses outcropping in Amitsôq and Isua (Greenland) that are dated between 3.82 and 3.85 Ga and by small enclaves of older (4.03 Ga) gneisses in Acasta, Canada (Martin, 2001). An older formation age of 4.4 Ga has been measured in the cores of a few detrital zircon crystals recovered from Jack Hill (Australia) (Wilde et al., 2001; Valley et al., 2002). On Earth, the period comprised between the end of the accretion and the first occurrence of terrestrial rocks is commonly referred to as the Hadean Eon (Harland et al., 1989). The definition of this first division of the stratigraphic timescale is somewhat ambiguous because it is not sustained by a chronostratigraphic unit, which is a body of rock established to serve as reference for the lithologies formed during this span of time. The Hadean is not even represented on the recently published International Stratigraphic Chart that considers the Archaean as the first Eon, which “lower limit is not defined” (Gradstein et al., 2004). The Hadean covers the interval between the end of the accretion and 4.0 Ga. If there is almost no rock of Hadean age on Earth, this time interval is well represented by the Pre-Nectarian period and the Nectarian period on the Moon (Wilhems, 1987) or by the Early Noachian period on Mars (Figure 4.17). This stratigraphy places the LHB period in the beginning of the Archaean (in the Eoarchaeon Era according to (Gradstein et al., 2004), coeval or slightly older than the oldest metamorphosed sediments found in Isua (Greenland).

The lack of lithological record on Earth between 4.5 and 3.9 Ga is explained by the LHB, which almost completely resurfaced the planet (Ryder et al., 2000) coupled with active geological processes such as plate tectonic and erosion, which continuously recycled the most ancient lithologies. The ancient surface of the Moon provides the best evidence for intense collisions in the period centred around 3.9 Ga. Its anorthositic (only made of feldspars) crust crystallized around 4.45 Ga, and the morphology of the highlands recorded a dense concentration of impact craters excavated prior to the emplacement of the first volcanic flows of the mare plains around 3.8 Ga (Wilhems, 1987; Snyder et al., 1996) (Figure 4.18). The LHB is now clearly established all over the inner solar system (Kring and Cohen, 2002). However, the magnitude and frequency of the collisions between 4.5 and 4 Ga remains a topic of controversy. Two explanations have been proposed (Figure 4.19). The frequency of impacts declined slowly and progressively since the end of

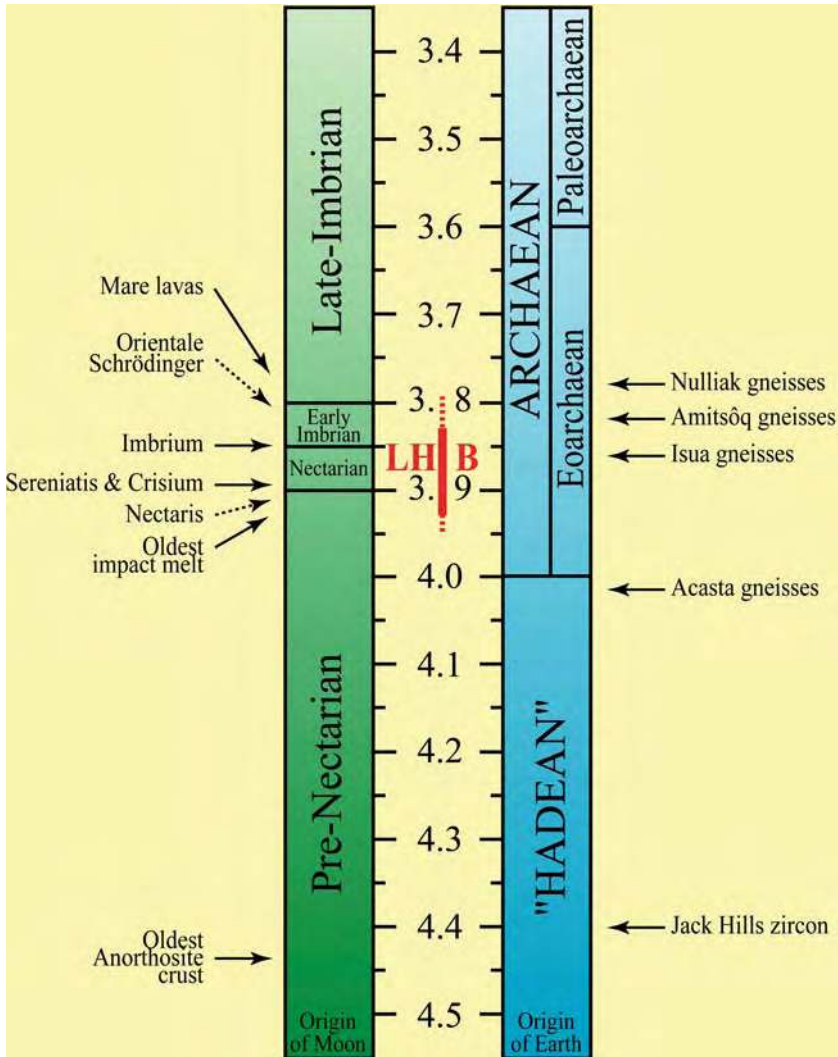
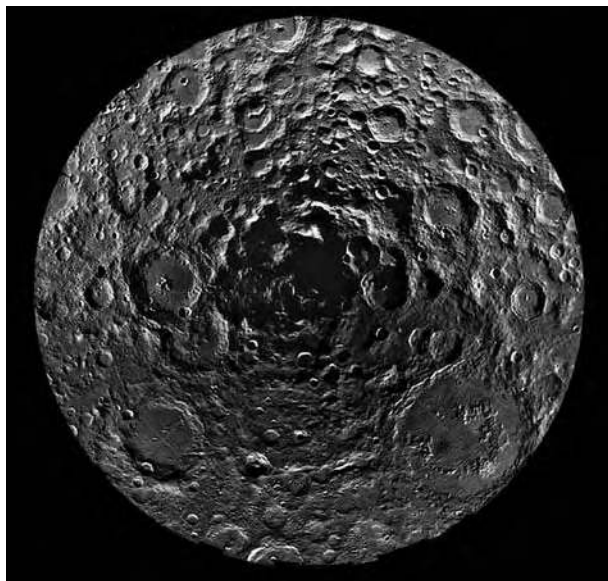


Figure 4.17. Comparative stratigraphy of the first 1.5 Ga on Earth and on the Moon. The full arrows are isotopic dates, the dotted-line arrows are dates based on relative chronology (modified after Ryder et al., 2000).

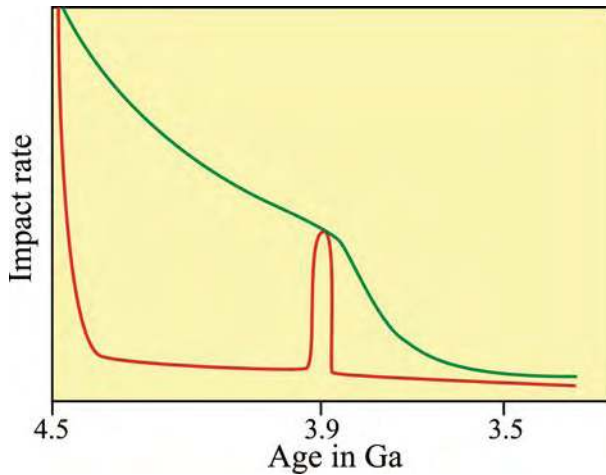
the accretion period explaining why the bombardment is still important around 3.9 Ga (Hartmann, 1975; Wilhems, 1987; Hartmann et al., 2000). According to these authors, the so-called LHB is not an exceptional event. Rather it is the tail end of a 600 million year period, during which the Earth was subject to major and devastating collisions, with seminal consequences such as the chronic melting of the crust and the vaporization of the oceans. Another view advocates a rapid decline in the frequency of impacts after the formation of the Moon to a value only slightly higher than today ( $\sim 2X$ ). The



*Figure 4.18.* View of the Moon's South Polar Region (mosaic of 1500 images) showing a great number of impact craters of all sizes (Image NASA, Clementine mission) mostly formed during the LHB. The Schrödinger crater (320 km in diameter) is clearly visible on the lower right.

period between 4.0 and 3.80 represents thus an exceptional and cataclysmic event marked by an extraordinarily high rate of collisions (Tera et al., 1974; Ryder, 1990; Cohen et al., 2000; Ryder et al., 2000; Ryder, 2002).

Today, most authors favour the LHB cataclysmic scenario around 3.9 Ga. It is supported by a series of arguments; one of these arguments being that some 600 million years of continual impacts should have left an obvious trace on the Moon. So far such trace has not been found. The isotopic dating of both the samples returned by the various Apollo and Luna missions revealed no impact melt-rock older than 3.92 Ga (Ryder, 1990; Ryder et al., 2000; Stoeffler and Ryder, 2001). The lunar meteorites confirm this age limit; they provide a particularly strong argument because they likely originated from random locations on the Moon (Cohen et al., 2000). A complete resetting of all older ages all over the Moon is possible but highly unlikely taking into account the difficulties of a complete reset of all isotopic ages at the scale of a planet (Deutsch and Schrarer, 1994). The U–Pb and Rb–Sr isochrones of lunar highland samples indicate a single disruption by a metamorphic event at 3.9 Ga and between 3.85 and 4 Ga, respectively, after the formation of the crust around 4.4 Ga (Tera et al., 1974). There is no evidence for a re-setting of these isotopic systems by intense collisions between 4.4 and 3.9 Ga. The old upper crustal lithologies of the Moon do not show the expected enrichment in siderophile elements (in particular the



*Figure 4.19.* Schematic representation of the flux of projectile on Earth between 4.5 and 3.5 Ga (modified after Kring, 2003). The green curve shows a slow decrease of the bombardment, the red curve illustrates the leading hypothesis of a rapid decrease of the flux followed by an unexplained peak, the Late Heavy Bombardment, around 4.0–3.9 Ga. The duration of this high flux period varies (20 and 200 Ma); the slope of the decrease after 3.9 Ga is also poorly constrained. It cannot be excluded that other cataclysmic events took place between 4.5 and 4.0 Ga, but their traces must have been fully erased by the complete resetting of the Earth surface caused by the last event.

Platinum Group Elements, PGE) implied by an extended period of intense collisions (Ryder et al., 2000). Moreover, if the elevated mass accretion documented in the period around 3.9 Ga is considered to be the tail end of an extended period of collisions, the whole Moon should have accreted at about 4.1 Ga instead of 4.5 Ga (Ryder, 2002; Koeberl, 2004). On Earth, the oxygen isotopic signature ( $\delta^{18}\text{O}$ ) of the oldest known zircons (4.4 Ga) indicates formation temperatures compatible with the existence of liquid water (Valley et al., 2002). This argument seems contradictory with an extended period of intense collisions. It can thus be concluded that today, there is strong evidence for a cataclysmic LHB event in the inner solar system around 3.9 Ga; in other words a short and intense peak in the cratering rate rather than a prolonged post-accretionary bombardment lasting  $\sim 600$  Ma.

On planets, whose surface was not re-modelled by erosion, sedimentation and plate tectonics (Moon, Mars, Venus...) the ancient impact structures frequently exceed 1000 km in diameter (Stoeffler and Ryder, 2001). The battered old surfaces of these planets witness past collisions which frequency and scale were 2 to perhaps 3 orders of magnitude higher than the Phanerozoic values. It seems highly unlikely that a target the size of Earth would have been spared, even if active geological processes have obliterated the record of these past impacts. Their traces are perhaps to be found in the

existence of elevated concentrations of shocked minerals, tektites or PGE in sedimentary sequences at the very base of the Archaean. So far, most searches have failed to yield convincing evidence (Koeberl et al., 2000; Ryder et al., 2000). Assuming that the bombardment was proportional with that on the Moon, several explanations account for the lack of impact signatures in Earth's oldest lithologies. First, it can be due to the relative small number and the limited type of samples available. Second, a high sedimentation rate could have diluted the meteoritic signal. Third, the LHB and the rocks from Isua may not overlap. A much younger age of 3.65 Ga has also been proposed by some authors for the Amitsôq gneisses (Rosing et al., 1996; Kamber and Moorbath, 1998). Such younger age based on whole rock Pb–Pb, Rb–Sr and Sm–Nd dating seems less accurate than the chronology obtained on single zircon crystals (Mojzsis and Harrison, 2000). Even considering the commonly accepted age of 3.80 Ga for the metasediments in Isua, it is possible that the LHB had already ended when deposition occurred. This is particularly likely if the bombardment rate declined rapidly after a short peak period. However, based on  $^{182}\text{W}/^{183}\text{W}$  isotopic ratios, (Schoenberg et al., 2002) have detected a possible meteoritic signal in four out of six samples of metamorphosed sediments from Isua (Greenland) and Nulliak in Northern Labrador (Canada) dated between 3.8 and 3.7 Ga. These analyses should be replicated but they probably provide the first evidence of the existence of the LHB on Earth (Figure 4.20). However, recently a chromium isotope study carried out on similar lithologies at Isua failed to detect an extraterrestrial component (Frei and Rosing, 2005).

On the Moon, where the record of these collisions is best preserved, some 1700 craters larger than 20 km in diameter are known, among them 15 reach sizes between 300 and 1200 Km. All of them are dated between 4.0 and 3.9 Ga, ages that correspond to the end of the Nectarian and the beginning of the Imbrian periods according to the Lunar stratigraphy (Figure 4.17), (Wilhems, 1987). About 6400 craters with diameters >20 km should have been produced on Mars (Kring and Cohen, 2002). In comparison, the Earth because of its size and larger gravitational cross section represents an easier target to hit. Based on scaling the Moon flux, it would have been impacted by between 13 and 500 times more mass than the Moon according to the size distribution of the projectiles (Zahnle and Sleep, 1997; Hartmann et al., 2000). Using conservative values Kring (2003) estimates the formation of ~22,000 craters with a diameter over 20 km. The number of structures larger than 1000 km would vary between 40 and 200, and it is not impossible that some would reach 5000 km, that is the dimension of an entire continent (Grieve and Shoemaker, 1994; Kring and Cohen, 2002). The duration of the LHB cataclysmic event is difficult to estimate. Based on the cratering record of the Moon, it varies between 20 and 200 Ma, depending on the mass flux estimation used in the calculation. According to the lowest estimation on Earth a collision capable of



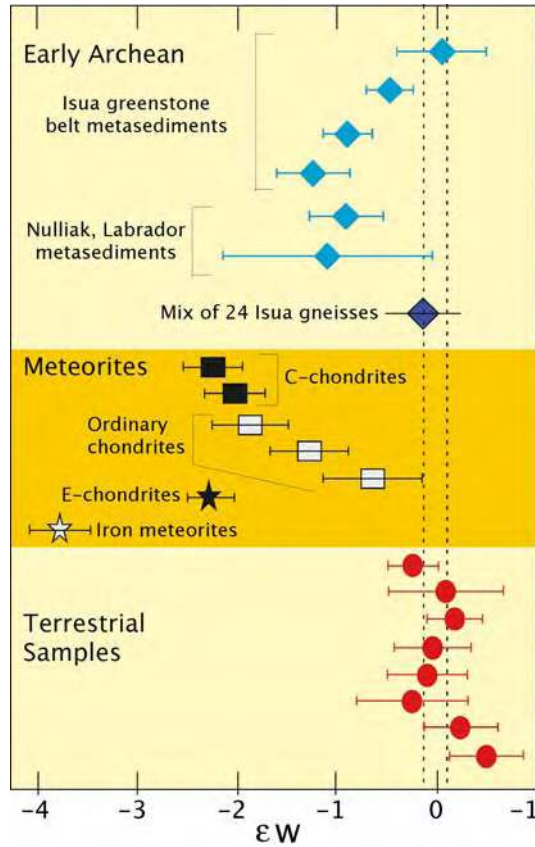


Figure 4.20. Values of  $\epsilon W$  for terrestrial rocks, meteorites and early Archean samples relative to the composition of a tungsten standard, ACQUIRE-W (Figure modified from Schoenberg et al., 2002). Blue diamonds represent early Archean metasediments, which plot outside the terrestrial values. Dashed lines show  $2\sigma$  of mean uncertainty envelope of the standard ( $n = 46$ ). Terrestrial samples are represented by red circles. Open star is an average of published iron meteorites; filled star an average of bulk rock enstatite chondrites; open squares are bulk rock ordinary chondrites; filled squares represent Allende carbonaceous chondrite. Dark blue diamond is an average of early Archean crust samples.

generating a 20 km crater could take place every 10,000 years (Kring, 2003). This would correspond to the impact of a  $\sim 1$  km projectile, an event that presently occurs once every 0.350–1 Ma. If the highest estimation is considered, the frequency increases to such an impact every 20 years!

Based on the lunar cratering record, it seems that around 3.8 Ga the impact frequency had decreased significantly and stabilized close to the present values. However, slope of the decrease is difficult to estimate. The  $^{40}\text{Ar}$ – $^{39}\text{Ar}$  dating of spherules formed by lunar impacts shows that this decrease in the frequency is perhaps more progressive (by factor 2 or 3 between 3.5 and 1 Ga), and that it has increased slightly again some 500 Ma



ago (Culler et al., 2000). This interesting observation based on the dating of spherules collected by the Apollo 14 mission needs to be confirmed by applying the same approach to other sites sampled by Lunar missions.

#### 4.4.2. ORIGIN OF THE LHB

The cause of such a bombardment has remained a puzzle for 30 years. Indeed, to have a cataclysmic spike in the bombardment rate, it is necessary that a massive reservoir of planetesimals remains intact during the planet formation epoch and the subsequent  $\sim 600$  Ma and then, all of a sudden, is destabilized. This seems to be in conflict with the classical view according to which the solar system did not undergo substantial modifications since soon after its formation.

In a recent paper, (Gomes et al., 2005) designed a scenario that explains how the LHB might have been triggered. In their model, the giant planets formed on quasi-circular, coplanar orbits, between approximately 5.5 and 15 AU. This orbital configuration was much more 'compact' than the current one, where the planetary orbits are placed from 5.2 to 30 AU. A massive disk of planetesimals surrounded the planetary system, extending from a few AUs beyond Neptune outwards. The perturbations of the planets allowed the planetesimals from the inner parts of the disk to slowly develop planet-crossing orbits. The encounters of these planetesimals with the planets drove a slow, progressive migration of the planets. Computer simulations show that Saturn, Uranus and Neptune slowly moved outwards, and Jupiter slowly moved inwards. The rate of this migration was governed by the rate at which the planetesimals could leak out of the disk, which was slow because the disk was quite far from the closest planet.

As a consequence of Jupiter and Saturn's migrations in divergent directions, the ratio of the orbital periods of these two planets increased. This ratio is currently slightly smaller than 2.5, and thus it had to be smaller in the past. Gomes et al. (2005) proposed that the orbital period ratio was initially smaller than 2. Their simulations show that with reasonable initial conditions for the planets and the disk, the ratio of the orbital periods could reach the exact value of 2 (the 2:1 mean motion resonance in the jargon of celestial mechanics) quite late: on a time ranging from 350 Ma and 1.2 Ga, an interval that embraces the LHB time,  $\sim 600$  Ma after planet formation.

The 1:2 resonance crossing triggered the LHB. Indeed, when the ratio of orbital periods passed through the value of 2, their orbits of Jupiter and Saturn became eccentric. This abrupt transition temporarily destabilized the system of the 4 giant planets, leading to a short phase of close encounters among Saturn, Uranus and Neptune. Because of these encounters, the orbits of the ice giants became eccentric and the furthest planet penetrated into the

disk. This destabilized the disk completely. All planetesimals were scattered in sequence by the planets. A fraction of them temporarily penetrated into the inner solar system. About  $10^{-7}$  of the original planetesimals hit the Moon and  $10^{-6}$  hit the Earth. About  $10^{-3}$  of the original planetesimals probably remained trapped in the Kuiper belt.

The interaction of the planets with the destabilized disk enhanced planet migration and damped the planetary eccentricities and inclinations. A large number of simulations of this process, made by Tsiganis et al. (2005) show that, if the planetesimal disk contained about 35 Earth masses at the time of the LHB, the planets statistically had to end on orbits very close to those currently observed. A more massive disk would have driven Jupiter and Saturn too far apart, and a less massive disk would not have moved them enough. Interestingly, given this total disk mass, the total mass of the planetesimals hitting the Moon turns out to be consistent with that inferred from the counting of basins formed at the LHB time.

The distant planetesimals were not the sole cause of the LHB though. The migration of Jupiter and Saturn from the 1:2 resonance to their current position destabilized also the asteroid belt. About 90% of the asteroids could develop orbits crossing those of the terrestrial planets, although this fraction is poorly estimated because it depends on the dynamical state of the asteroid belt before the LHB, which is unknown. Given the current mass of the asteroid belt ( $5 \times 10^4$  Earth masses), this implies that  $\sim 5 \times 10^3$  Earth masses of asteroids became Earth crossers. Of these, about  $2 \times 10^{-4}$  hit the Moon, supplying again a mass of projectiles consistent with the LHB constraints. Thus, according to Gomes et al. (2005) model, the projectiles causing the LHB would have been a mixture of comets (from the distant disk) and asteroids, in roughly equal proportions. The exact relative contribution of asteroids and comets to the LHB cannot be stated with precision from the model, at least at the current state. Chemical analyzes on lunar samples collected in the vicinity of basins seem to indicate that asteroids of enstatite or more likely ordinary chondritic type participated in the process (Kring and Cohen, 2002; Tagle, 2005).

The strength of Gomes et al. (2005) model on the origin of the LHB is that it explains not only the main characteristics of the LHB (intensity, duration, abrupt start) but also several other puzzling properties of the solar system. It accounts for the orbital architecture of the giant planets (for what concerns both the mutual spacing, the eccentricities and the mutual inclinations of the orbits, Tsiganis et al., 2005), the population of Jovian Trojans (for what concerns their orbital distribution and total mass, Morbidelli et al., 2005), the absence of numerous asteroid families formed at the LHB time (Gomes et al., 2005).

There do not seem to be many alternatives to Gomes et al. (2005) model. The destabilization of a small body reservoir requires a change in planetary orbits. Planet migration gives such a change, and once it is done, the solar

system has acquired the current state. Thus, to make a cataclysmic LHB planet migration had effectively to start at that time. Two conditions need to be fulfilled in order for a compact planetary system to stay quiet for more than half a billion years. The first is that the planetary orbits had to be quasi-circular. The second is that the region among the planets was essentially depleted of planetesimals. If the planetary orbits had to be quasi-circular, then an event had to excite the eccentricities. Resonance crossing provides eccentricity excitation, but only the 1:2 resonance between Jupiter and Saturn provides the required eccentricity values. Thus, Jupiter and Saturn had to cross this resonance. And these are the basic ingredients of Gomes et al. (2005) model.

### References

- Abe, Y.: 1993, *Lithos* **30**, 223–235.
- Abe, Y., Drake, M., Ohtani, E., Okuchi, T. and Righter, K.: 2000, in K. Righter and R. Canup (eds.), *Origin of the Earth and Moon* (University of Arizona Press, Tucson, Arizona), pp. 413–433.
- Albarède, F., Blichert-Toft, J., Vervoort, J. D., Gleason, J. D. and Rosing, M. T.: 2000, *Nature* **404**, 488–490.
- Aléon, J., Engrand, C., Robert, F. and Chaussidon, M.: 2001, *Geochim. Cosmochim. Acta* **65**, 4399–4412.
- Aleon, J., Robert, F., Chaussidon, M. and Marty, B.: 2003, *Geochim. Cosmochim. Acta* **67**(19), 3773–3783.
- Amelin, Y., Krot, A. N., Hutcheon, I. D. and Ulyanov, A. A.: 2002, *Science* **297**, 1679–1683.
- Anders, E.: 1989, *Nature* **342**, 255–257.
- Appel, P. W. U., Moorbath, S. and Touret, J.: 2002, *Precambrian Res.* **176**, 173–180.
- Arpigny, C., Jehin, E., Manfroid, J., Hutseméker, D., Schulz, R., Stüwe, J. A., Zucconi, J. M. and Ilyin, I.: 2003, *Science* **301**, 1522–1524.
- Baadsgaard, H., Nutman, A. P., Bridgwater, D., Rosing, M. T., McGregor, V. R. and Allaart, J. H.: 1984, *Earth Planet. Sci. Lett.* **68**, 221–228.
- Ballentine, C. J., Marty, B., Lollar, B. S. and Cassidy, M.: 2005, *Nature* **433**(7021), 33–38.
- Barnes, I. and O’Neil, J. R.: 1969, *Geol. Soc. Amer. Bull.* **80**, 1947–1960.
- Bennet, V. C., Nutman, A. P. and McCulloch, M. T.: 1993, *Earth Planet. Sci. Lett.* **119**, 299–317.
- Bizzarro, M., Baker, J. A. and Haack, H.: 2004, *Nature* **431**(7006), 275–278.
- Black, L. P., Gale, N. H., Moorbath, S., Pankhurst, R. J. and McGregor, V. R.: 1971, *Earth Planet. Sci. Lett.* **12**, 245–259.
- Bland, P. A., Smith, T. B., Jull, A. J. T., Berry, F. J., Bewan, A. W. R., Cloudt, S. and Pillinger, C. T.: 1996, *Mon. Not. R. Astron. Soc.* **283**, 551–565.
- Boato, G.: 1954, *Geochim. Cosmochim. Acta* **6**, 209–220.
- Bolhar, R., Kamber, B. S., Moorbath, S., Fedo, C. M. and Whitehouse, M. J.: 2004, *Earth Planet. Sci. Lett.* **222**(1), 43–60.
- Bolhar, R., Kamber, B. S., Moorbath, S., Whitehouse, M. J. and Collerson, K. D.: 2005, *Geochim. Cosmochim. Acta* **69**(6), 1555–1573.
- Bouvier, A., Blichert-Toft, J., Vervoort, J. D. and Albarède, F.: 2005, *Earth Planet. Sci. Lett.* **240**(2), 221–233.

- Bowring, S. A. and Houst, T. B.: 1995, *Science* **269**, 1535–1540.
- Bowring, S. A. and Williams, I. S.: 1999, *Contrib. Mineral. Petrol* **134**, 3–16.
- Boyet, M., Blichert-Toft, J., Rosing, M., Storey, M., Telouk, P. and Albarede, F.: 2003, *Earth Planet. Sci. Lett.* **214**(3–4), 427–442.
- Boyet, M. and Carlson, R. W.: 2005, *Science* **309**, 576–581.
- Bridgwater, D., McGregor, V. R. and Myers, J. S.: 1974, *Precambrian Res.* **1**, 179–197.
- Brownlee, D. E.: 1985, *Ann. Rev. Earth Planet. Sci. Lett.* **13**, 147–173.
- Brownlee, D. E., Joswiak, D. J., Love, S. G., Nier, A. O., Schlutter, D. J. and Bradley, J. P.: 1993, *Lunar Planet. Sci.* **XXIV**, 205–206.
- Canup, R. and Asphaug, E.: 2001, *Nature* **412**, 708–712.
- Caro, G., Bourdon, B., Birck, J.-L. and Moorbath, S.: 2003, *Nature* **423**(6938), 428–432.
- Cavosie, A. J., Valley, J. W. and Wilde, S. A.E. I. M. F.: 2005, *Earth Planet. Sci. Lett.* **235**, 663–681.
- Cavosie, A. J., Wilde, S. A., Liu, D., Weiblen, P. W. and Valley, J. W.: 2004, *Precambrian Res.* **135**(4), 251–279.
- Cherniak, D. J.: 2001, *Chem. Geol.* **177**(3–4), 381–397.
- Cherniak, D. J., Lanford, W. A. and Ryerson, F. J.: 1991, *Geochim. Cosmochim. Acta* **55**, 1663–1673.
- Chyba, C.: 1990, *Nature* **343**, 129–133.
- Chyba, C. and Sagan, C.: 1992, *Nature* **355**, 125–132.
- Chyba, C. F.: 1991, *Icarus* **92**, 217–233.
- Clarke, W. B., Beg, M. A. and Craig, H.: 1969, *Earth Planet. Sci. Lett.* **6**, 213–220.
- Clayton, R. N.: 1993, *Ann. Rev. Earth Planet. Sci. Lett.* **21**, 115–149.
- Cohen, B. A., Swindle, T. D. and Kring, D. A.: 2000, *Science* **290**(5497), 1754–1756.
- Collerson, K. D. and Bridgwater, D.: 1979, in F. Barker (ed.), *Trondhjemites, Dacites and Related Rocks* (Elsevier, Amsterdam), pp. 206–273.
- Collerson, K. D., Campbell, I. H., Weaver, B. L. and Palacz, Z. A.: 1991, *Nature* **349**, 209–214.
- Compston, W. and Pidgeon, R. T.: 1986, *Nature* **321**, 766–769.
- Conrad, C. P. and Hager, B. H.: 1999, *J. Geophys. Res.* **104**, 17551–17571.
- Culler, T. S., Becker, T. A., Muller, R. A. and Renne, P. R.: 2000, *Science* **287**(5459), 1785–1788.
- Dauphas, N.: 2003, *Icarus* **165**(2), 326–339.
- Dauphas, N. and Marty B.: 2002, *J. Geophys. Res. Planets* **107**, E12-1–E12-7.
- Dauphas, N., Robert, F. and Marty, B.: 2000, *Icarus* **148**(2), 508–512.
- David, J., Parent M., Stevenson R., Nadeau P. and Godin L.: 2002. La séquence supracrustale de Porpoise Cove, région d’Inukjuak; un exemple unique de croûte paléo-archéenne (ca. 3.8 Ga) dans la Province du Supérieur. 23<sup>ème</sup> Séminaire d’information sur la recherche géologique, Ministère des ressources naturelles du Québec.(session 2).
- de Ronde, C. E. J., Channer, D. M. d., Faure, K., Bray, C. J. and Spooner, T. C.: 1997, *Geochim. Cosmochim. Acta* **61**(19), 4025–4042.
- Delsemme, A. H.: 1999, *Planet. Space Sci.* **47**, 125–131.
- Deming, D.: 1999, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **146**, 33–51.
- Deutsch, A. and Schrärer, U.: 1994, *Meteoritics* **29**, 301–322.
- Dreibus, G. and Wanke, H.: 1989, in S. K. Atreya, J. B. Pollack and M. S. Matthews (eds.), *Origin and Evolution of Planetary and Satellite Atmospheres* (University of Arizona Press, Tucson), pp. 268–289.
- Engrand, C., Deloule, E., Robert, F., Maurette, M. and Kurat, G.: 1999, *Meteor. Planet. Sci.* **34**, 773–786.
- Engrand, C. and Maurette, M.: 1998, *Meteorit. Planet. Sci.* **33**, 565–580.

- Farley, K. A., Montanari, A., Shoemaker, E. M. and Shoemaker, C.: 1998, *Science* **1250**–1253.
- Fedo, C. M.: 2000, *Precambrian Res.* **101**(1), 69–78.
- Fedo, C. M., Myers, J. S. and Appel, P. W. U.: 2001, *Sediment. Geol.* **141–142**, 61–77.
- Fedo, C. M. and Whitehouse, M. J.: 2002, *Science* **296**, 1448–1452.
- Frank, L. A., Sigwarth, J. B. and Craven, J. D.: 1986, *Geophys. Res. Lett.* **13**, 303–306.
- Frank, L. A., Sigwarth, J. B. and Craven, J. D.: 1986, *Geophys. Res. Lett.* **13**, 303–306.
- Frei, R. and Rosing, M. T.: 2005, *Earth Planet. Sci. Lett.* **236**, 28–40.
- Froude, D. O., Ireland, T. R., Kinny, P. D., Williams, I. S., Compston, W., Williams, I. R. and Myers, J. S.: 1983, *Nature* **304**, 616–618.
- Gast, P. W.: 1960, *J. Geophys. Res.* **65**, 1287–1297.
- Genda, H. and Abe, Y.: 2005, *Nature* **433**, 842–844.
- Gomes, R., Levison, H. F., Tsiganis, K. and Morbidelli, A.: 2005, *Nature* **435**, 466–469.
- Göpel, C., Manhès, G. and Allègre, C. J.: 1994, *Earth Planet. Sci. Lett.* **121**, 153–171.
- Gounelle, M., Zolensky, M. and Liou, J. C.: 2002, *Geochim. Cosmochim. Acta* **67**, 507–527.
- Gradie, J. C., Chapman, C. R. and Tedesco, E. F.: 1989, in T. G. M. S. M. R. P. Binzel (ed.), *Asteroids II* (Univ. Arizona Press, Tucson), pp. 316–335.
- Gradstein F. M., Ogg J. G., Smith A. G., Agterberg F. P., Bleeker W., Cooper R. A., Davydov V., Gibbard P., Hinnov L., (†) M. R. H., Lourens L., Luterbacher H.-P., McArthur J., Melchin M. J., Robb L. J., Shergold J., Villeneuve M., Wardlaw B. R., Ali J., Brinkhuis H., Hilgen F. J., Hooker J., Howarth R. J., Knoll A. H., Laskar J., Monechi S., Powell J., Plumb K. A., Raffi I., Röhl U., Sanfilippo A., Schmitz B., Shackleton N. J., Shields G. A., Strauss H., Dam J. V., Veizer J., Kolfschoten T.v. and Wilson D.: 2004, *A Geological Time Scale 2004*. Cambridge University, Cambridge, 610 pp.
- Gray, C. M. and Compston, W.: 1974, *Nature* **251**, 495–497.
- Grieve, R. A. F. and Shoemaker, E. M.: 1994, in T. Gehrels (ed.), *Hazards Due to Comets and Asteroids* (Univ. Arizona Press, Tucson), pp. 417–462.
- Halliday, A. N., Wänke, H., Birck, J. L. and Clayton, R. N.: 2001, *Space Sci. Rev.* **96**, 1–34.
- Harland, W. B., Armstrong, R. L., Cox, A. V., Craig, L. E., Smith, A. G. and Smith, D. G.: 1989, *A Geologic Time Scale*, Cambridge University Press, Cambridge, 263 pp.
- Harrison, C. G. A.: 1999, *Geophys. Res. Lett.* **26**, 1913–1916.
- Harrison, T. M., Blichert-toft, J., Müller, W., Albaredo, F., Holden, P. and Mojzsis, S. J.: 2005, *Science* **310**, 1947–1950.
- Hartmann, W. K.: 1975, *Icarus* **24**, 181–187.
- Hartmann, W. K., Ryder, G., Dones, L. and Grinspoon, D.: 2000, in K. Righter and R. Canup (eds.), *Origin of the Earth and Moon* (University of Arizona Press, Tucson, Arizona), pp. 493–512.
- Hashizume, K., Chaussidon, M., Marty, B. and Robert, F.: 2000, *Science* **290**(5494), 1142–1145.
- Hashizume, K., Kase, T. and Matsuda, J. I.: 1997, *Kazan* **42**, S293–S301.
- Hashizume, K., Marty, B. and Wieler, R.: 2002, *Earth Planet. Sci. Lett.* **202**, 201–216.
- Honda, M., McDougall, I., Patterson, D. B., Douglgeris, A. and Clague, D. A.: 1991, *Nature* **349**, 149–151.
- Hood, L. L. and Horanyi, : 1993, *Icarus* **106**, 179–189.
- Hoskin, P. W. O.: 2005, *Geochim. Cosmochim. Acta* **69**(3), 637–648.
- Hunten, D. M., Pepin, R. O. and Walker, J. C. B.: 1987, *Icarus* **69**, 532–549.
- Jacobsen, S. B. and Yin, Q.: 2003, *Lunar Planet. Sci.* **XXXIV**, 1913 .
- Jahn, B. M.: 1997, in R. Hagemann and M. Treuil (eds.), *Introduction à la Géochimie et ses Applications* (Editions Thierry Parquet), pp. 357–393.
- Javoy, M.: 1995, *J. Geophys. Res. Lett.* **22**, 2219–2222.

- Javoy, M.: 1998, *Chem. Geol.* **147**, 11–25.
- Javoy, M.: 2005, *C. R. Geosci.* **337**(1–2), 139–158.
- Jewitt, D. C., Matthews, H. E., Owen, T. and Meier, R.: 1997, *Science* **278**(5335), 90–93.
- Kamber, B. S., Collerson, K. D., Moorbath, S. and Whitehouse, M. J.: 2003, *Contrib. Mineral. Petrol.* **145**, 25–46.
- Kamber, B. S. and Moorbath, S.: 1998, *Chem. Geol.* **150**, 19–41.
- Keays, R. R., Ganapathy, R., Laul, J. C., Anders, E., Herzog, G. F. and Jeffery, P. M.: 1970, *Science* **167**, 490–493.
- Kerridge, J. F.: 1985, *Geochim. Cosmochim. Acta* **49**, 1707–1714.
- Kleine, T., Münker, C., Mezger, K. and Palme, H.: 2002, *Nature* **418**, 952–955.
- Koerberl, C.: 2004, *Earth Moon Planets* **92**, 79–87.
- Koerberl, C., Reimold, W. U., McDonald, I. and Rosing, M.: 2000, in I. Gilmour and C. Koerberl (eds.), *Impacts and the Early Earth* (Springer, Berlin), pp. 73–97.
- Kortenkamp, S. J., Dermott, S. F., Fogle, D. and Grogan K.: 2001, in: B. P.-E.a.B. Schmitz (ed.), *Accretion of Extraterrestrial Matter Throughout Earth's History* (Kluwer Academic), pp. 13–30.
- Kring, D. A.: 2003, *Astrobiology* **3**(1), 133–152.
- Kring, D. A. and Cohen, B. A.: 2002, *J. Geophys. Res.* **107**(E2), 10.1029/2001JE001529.
- Kurat, G., Koerberl, C., Presper, T., Branstätter, F. and Maurette, M.: 1994, *Geochim. Cosmochim. Acta* **58**, 3879–3904.
- Kyte, F. T. and Wasson, J. T.: 1986, *Science* **232**, 1225–1229.
- Lee, T., Papanastassiou, D. A. and Wasserburg, G. J.: 1976, *Geophys. Res. Lett.* **3**, 109–112.
- Lopez-Garcia, P.: 2005, in M. Gargaud, B. Barbier, H. Martin and J. Reisse (eds.), *Lectures in Astrobiology* (Springer-Verlag, Berlin), pp. 657–676.
- Love, S. G. and Brownlee, D. E.: 1993, *Science* **262**, 550–553.
- Maas, R., Kinny, P. D., Williams, I. S., Froude, D. O. and Compston W.: 1992, *Geochim. Cosmochim. Acta* **56**, (1281–1300).
- Mahaffy, P. R., Donahue, T. M., Atreya, S. K., Owen, T. C. and Niemann, H. B.: 1998, *Space Sci. Rev.* **84**(1–2), 251–263.
- Mamyrin, B. A., Tolstikhin, I. N., Anufriev, G. S. and Kamensky, I. L.: 1969, *Dokkl. Akad. Nauk. SSSR.* **184**, 1197–1199 (In Russian).
- Martin, H.: 1986, *Geology* **14**, 753–756.
- Martin, H.: 2001, in M. Gargaud, D. Despois and J.-P. Parisot (eds.), *L'environnement De la Terre Primitive* (Presses Universitaires de Bordeaux, Bordeaux), pp. 263–286.
- Martin, H., Smithies, R. H., Rapp, R., Moyen, J.-F. and Champion, D.: 2005, *Lithos* **79**(1–2), 1–24.
- Marty, B.: 1989, *Earth Planet. Sci. Lett.* **94**, 45–56.
- Marty, B.: 1995, *Nature* **377**, 326–329.
- Marty, B. and Dauphas, N.: 2003, *Earth Planet. Sci. Lett.* **206**, 397–410.
- Marty, B., Jambon, A. and Sano, Y.: 1989, *Chem. Geol.* **76**, 25–40.
- Marty, B., Robert, P. and Zimmermann, L.: 2005, *Meteorit. Planet. Sci.* **40**, 881–894.
- Maurette, M.: 1998, *Orig. Life Evol. Biosph.* **28**, 385–412.
- Maurette, M.: 2001, in M. Gargaud, D. Despois and J.-P. Parisot (eds.), *L'environnement de la terre primitive* (Presses Universitaires de Bordeaux), pp. 99–130.
- Maurette, M., Duprat, J., Engrand, C., Gounelle, M., Kurat, G., Matrajt, G. and Toppani, A.: 2000, *Planet. Space Sci.* **48**(11), 1117–1137.
- Mazor, E., Heymann, D. and Andus, E.: 1970, *Geochim. Cosmochim. Acta* **34**, 781–824.
- McCulloch, M. T. and Bennet, V. C.: 1993, *Lithos* **30**, 237–255.
- McCulloch, M. T. and Bennet, V. C.: 1994, *Geochim. Cosmochim. Acta* **58**, 4717–4738.
- McGregor, V. R.: 1968, *Rapport Gronlands Geol. Unders* **19**, 31.



- McGregor, V. R.: 1973, *Philos. Trans. R. Soc. Lond. A* **A-273**, 243–258.
- Messenger, S.: 2000, *Nature* **404**, 968–971.
- Messenger, S., Keller, L. P., Stadermann, F. J., Walker, R. M. and Zinner, E.: 2003, *Science* **300**, 105–108.
- Messenger, S., Keller, L. P. and Walker, R. M.: 2002, *Discovery of Abundant Silicates in Cluster IDPs, LPS XXXIII*, LPI, Houston, 1887 pp.
- Mizuno, H., Nakasawa, K. and Hayashi, C.: 1980, *Earth Planet. Sci. Lett.* **50**, 202–210.
- Mojzsis, S. J., Arrhenius, G., Keegan, K. D., Harrison, T. H., Nutman, A. J. and Friend, C. L. R.: 1996, *Nature* **384**, 55–59.
- Mojzsis, S. J., Harrison, M. T. and Pidgeon, R. T.: 2001, *Nature* **409**, 178–181.
- Mojzsis, S. J. and Harrison, T. M.: 2000, *GSA Today* **10**, 1–6.
- Moorbath, S. (ed.), 1977, *Aspects of the geochronology of ancient rocks related to continental evolution. The continental crust and its mineral deposits, 20*. Geological Association of Canada Special Paper, pp. 89–115.
- Moorbath, S., O’Nions, R. K., Pankhurst, R. J., Gale, N. H. and McGregor, V. R.: 1972, *Nature* **240**, 78–82.
- Morbiddelli, A.: 2002, *Ann. Rev. Earth Planet. Sci.* **30**, 89–112.
- Morbiddelli, A., Chambers, J., Lunine, J. I., Petit, J. M., Robert, F., Valsecchi, G. B. and Cyr, K.E.: 2000, *Meteorit. Planet. Sci.* **35**, 1309–1320.
- Morbiddelli, A., Levison, H. F., Tsiganis, K. and Gomes, R.: 2005, *Nature* **435**(7041), 462–465.
- Murakami, M., Hirose, K., Yurimoto, H., Nakashima, S. and Takafuji, N.: 2002, *Science* **295**, 1885–1887.
- Myers, J. S.: 2001, *Precambrian Res.* **105**(2–4), 129–141.
- Nutman, A. J., Bennet, V. C., Friend, C. R. L. and McGregor, V. R.: 2000, *Geochim. Cosmochim. Acta* **64**(17), 3035–3060.
- Nutman, A. J. and Bridgwater, D.: 1986, *Contrib. Mineral. Petrol.* **94**, 137–148.
- Nutman, A. J. and Collerson, K. D.: 1991, *Geology* **19**, 791–794.
- Nutman, A. J., McGregor, V. R., Friend, C. R. L., Bennett, V. C. and Kinny, P. D.: 1996, *Precambrian Res.* **78**, 1–39.
- Nutman, A. P., Friend, C. R. L., Barker, S. L. L. and McGregor, V. R.: 2004, *Precambrian Res.* **135**(4), 281–314.
- Nyquist, L. E., Wiesman, H., Bansal, B., Shih, C.-Y., Keith, J. E. and Harper, C. L.: 1995, *Geochim. Cosmochim. Acta* **59**, 2817–2837.
- Owen, T., Mahaffy, P. R., Niemann, H. B., Atreya, S. and Wong, M.: 2001, *Astrophys. J.* **553**, L77–L79.
- Ozima, M. and Podosek, F. A.: 2002. *Noble Gas Geochemistry*, Cambridge University Press, Cambridge, 286 pp.
- Peck, W. H., Valley, J. W., Wilde, S. A. and Graham, C. M.: 2001, *Geochim. Cosmochim. Acta* **65**(22), 4215–4229.
- Pepin, R. O.: 1991, *Icarus* **92**, 1–79.
- Pinti, D. L.: 2002, *Trends Geochem.* **2**, 1–17.
- Pinti, D. L.: 2005, in M. Gargaud, B. Barbier, H. Martin and J. Reisse (eds.), *Lectures in Astrobiology. Advances in Astrobiology and Biogeophysics* (Springer-Verlag, Berlin), pp. 83–107.
- Podosek, F. A. and Cassen, P.: 1994, *Meteorit. Planet. Sci.* **29**, 6–25.
- Porcelli, D. and Halliday, A. N.: 2001, *Earth Planet. Sci. Lett.* **192**(1), 45–56.
- Porcelli, D. and Pepin, R. O.: 2000, in R. M. Canup and K. Righter (eds.), *Origin of the Earth and Moon* (The University of Arizona Press, Tucson), pp. 435–458.
- Robert, F.: 2001, *Science* **293**(5532), 1056.
- Robert, F.: 2003, *Space Sci. Rev.* **106**(1–4), 87.



- Robert, F. and Epstein, S.: 1982, *Geochim. Cosmochim. Acta* **46**, 81–95.
- Robert, F., Gautier, D. and Dubrulle, B.: 2000, *Space Sci. Rev.* **92**, 201–224.
- Rose, N. M., Rosing, M. T. and Bridgwater, D.: 1996, *Am. J. Sci.* **296**, 1004–1044.
- Rosing, M. T. and Frei, R.: 2004, *Earth Planet. Sci. Lett.* **217**(3–4), 237–244.
- Rosing, M. T., Rose, N. M., Bridgwater, D. and Thomsen, H. S.: 1996, *Geology* **24**, 43–46.
- Ryder, G.: 1990, *Eos Trans AGU* **71**, 313–323.
- Ryder, G.: 2002, *J. Geophys. Res. Planets* **107**, 6–14.
- Ryder, G., Koeberl, C. and Mojzsis, S. J.: 2000, in R. M. Canup and K. Righter (eds.), *Origin of the Earth and Moon* (University of Arizona Press, Tucson, Arizona), pp. 475–492.
- Sano, Y. and Pillinger, C. T.: 1990, *Geochem. J.* **24**, 315–325.
- Sarda, P., Staudacher, T. and Allègre, C. J.: 1988, *Earth Planet. Sci. Lett.* **91**, 73–88.
- Sasaki, S. and Nakasawa, K.: 1988, *Earth Planet. Sci. Lett.* **89**, 323–334.
- Sasaki, S. and Nakazawa, K.: 1984, *Icarus* **59**, 76–86.
- Schiøtte, L., Compston, W. and Bridgwater, D.: 1989, *Can. J. Earth Sci.* **26**, 1533–1556.
- Schoenberg, R., Kamber, B. S., Collerson, K. D. and Moorbath, S.: 2002, *Nature* **418**, 403–405.
- Shukolyukov, A. and Lugmair, G. W.: 1993, *Science* **259**, 1138–1142.
- Sleep, N. H., Meibom, A., Fridriksson, T., Coleman, R. G. and Bird, D. K.: 2004, *Proc. Nat. Acad. Sci.* **101**, 12818–12823.
- Sleep, N. H., Zahnle, K. and Neuhoff, P. S.: 2001, *Proc. Natl. Acad. Sci. U. S. A.* **98**(7), 3666–3672.
- Snyder, G., Hall, C. M., Lee, D. C., Taylor, L. A. and Halliday, A. N.: 1996, *Meteorit. Planet. Sci.* **31**, 328–334.
- Stevenson, R. K.: 2003, *Geochemistry and isotopic evolution (Nd, Hf) of the 3.825 Ga Porpoise Cove sequence, Northeastern Superior Province, Québec.*, Vancouver 2003 GAC – MAC – SEG Meeting, Vancouver, pp. GS6.
- Stoeffler, D. and Ryder, G.: 2001, *Stratigraphy and Isotopic Ages of Lunar Geologic Units: Chronological Standard for the Inner Solar System., The Evolution of Mars. Space Science Reviews*, International Space Science Institute, Bern, Switzerland, 7–53 pp.
- Tagle, R.: 2005, *LL-Ordinary chondrite impact on the Moon: Results from the 3.9 Ga impact melt at the landing site of Apollo 17*, Lunar and Planetary Science Conference, Houston Texas, pp. CD-ROM Abstract # 2008.
- Taylor, S. R.: 2001, *Solar System Evolution: A New Perspective*, Univ. Press, Cambridge, 484 pp.
- Tera, F., Papanastassiou, D. A. and Wasserburg, G. J.: 1974, *Earth Planet. Sci. Lett.* **22**, 1–21.
- Tolstikhin, I. N. and Hofmann, A. W.: 2005, *Phys. Earth Planet. Int.* In press.
- Tolstikhin, I. N. and Marty, B.: 1998, *Chem. Geol.* **147**, 27–52.
- Trieloff, M., Kunz, J., Clague, D. A., Harrison, C. J. and Allègre, C. J.: 2000, *Science* **288**, 1036–1038.
- Trull, T.: 1994, in J. I. Matsuda (ed.), *Noble Gas Geochemistry and Cosmochemistry* (Terra Sci. Pub. Co., Tokyo), pp. 77–88.
- Tsiganis, K., Gomes, R., Morbidelli, A. and Levison, H. F.: 2005, *Nature* **435**(7041), 459–461.
- Utsunomiya, S., Palenik, C. S., Valley, J. W., Cavosie, A. J., Wilde, S. A. and Ewing, R. C.: 2004, *Geochim. Cosmochim. Acta* **68**(22), 4679–4686.
- Valley, J. W., Peck, W. H., King, E. M. and Wilde, S. A.: 2002, *Geology* **30**(4), 351–354.
- Vervoort, J. D., Patchett, P. J., Gehrels, G. E. and Nutman, A. J.: 1996, *Nature* **379**, 624–627.
- Wasserburg, G. J. G. R. and Busso, M.: 1998, *Astroph. J.* **500**, L189–L193.
- Westall, F. and Folk, R. L.: 2003, *Precambrian Res.* **126**, 313–330.
- Wilde, S. A., Valley, J. W., Peck, W. H. and Graham, C. M.: 2001, *Nature* **409**, 175–178.

- Wilhems, D. E.: 1987, *Geologic history of the Moon. Professional Paper, 1348*. US Geological Survey, Reston VA.
- Wood, J. A., Dickey, J. S., Marvin, U. B. and Powell, B. N.: 1970, *Proc. Apollo 11*(Lunar Sci. Conf. 1), 965–988.
- Yada, T., Nakamura, T., Takaoka, N., Noguchi, T., Terada, K., Yano, H., Nakazawa, T. and Kojima, H.: 2004, *Earth Planets Space* **56**, 67–79.
- Yin, Q., Jacobsen, S. B., Yamashita, K., Blichert-Toft, J., Télouk, P. and Albarède, F.: 2002a, *Nature* **418**, 949–952.
- Yin, Q., Jacobsen, S. B., Yamashita, K., B.-T., J., Télouk, P. and Albarède, F.: 2002b, *Nature* **418**, 949–952.
- Yin, Q. Z. and Ozima, M.: 2003, *Geochim. Cosmochim. Acta* **67**(18), A564–A564.
- Yokochi, R., Marty, B., Pik, R. and Burnard, P.: 2005. *Geochem. Geophys. Geosyst.* 6, Q01004.
- Zahnle, K. and Dones L.: 1998. Source of terrestrial volatiles, Origin of the Earth and Moon. LPI Contribution, pp. 55–56.
- Zahnle, K. J. and Sleep, N. H.: 1997, in P. J. Thomas, C. F. Chyba and C. P. McKay (eds.), *Comets and the Origin and Evolution of Life* (Springer, New York), pp. 175–208.
- Zhang, Y. X. and Zindler, A.: 1993, *Earth Planet. Sci. Lett.* **117**(3–4), 331–345.
- Zolensky, M. E., Weisberg, M. K., Buchanan, P. C. and Mittlefehldt, D. W.: 1996, *Meteorit. Planet. Sci.* **31**, 518–537.