

# A case for landing on the moon's farside to test nitrogen abundances

J. Chela-Flores

*The Abdus Salam ICTP, I-34151, Trieste, Italy and Instituto de Estudios Avanzados, Caracas, República Bolivariana de Venezuela*  
e-mail: chelaf@ictp.it

**Abstract:** A high research priority in astrobiology is the search and eventual identification of biomarkers in the Solar System. In spite of numerous steps forward, lunar science remains largely disjoint from the main stream of astrobiology, but in recent years the Moon has begun to emerge as a novel target for astrobiologists. We discuss an overlap between lunar geology and terrestrial geomicrobiology that arises from analysis of lunar soils and some uncertainties in chemical evolution and the origin of life scenarios. Unexpected isotopic heterogeneity of nitrogen (N) was found to be remarkable in samples from Apollo and the Luna programme. Both the stable isotope geochemical data of the biogenic elements, as well as the noble gases trapped in lunar soils added valuable new and relevant data. These discoveries are potential sources of information on early Earth evolution. The elusive ratio of N's two stable isotopes  $^{15}\text{N}/^{14}\text{N}$  has played a fundamental role in this research. The analysis of individual grains of ilmenite suggests that 90% of all the trapped N does not originate from solar wind (SW). We discuss the significance of these stable isotopes from the point of view of astrobiology in the light of the next generation of lunar exploration. We underline the high priority of testing the origin of non-solar N source trapped in the regolith of the lunar farside. In the proposals of new lunar missions, the characterization of the geochemistry at several lunar sites is a major objective. Some arguments are presented in favour of using novel space technologies in a search for biomarkers in geographical distinct lunar landing sites. We restrict our attention to one aspect of the science requirements for the forthcoming missions by focusing on a very limited objective: to take a closer look at the geochemical characterization of the chemical element N on the soils of the lunar farside.

*Received 7 September 2011, accepted 27 October 2011, first published online 29 November 2011*

**Keywords:** astrobiology, kinetic micro-penetrator technologies, lunar science, next generation of lunar exploration, stable nitrogen isotope geochemistry.

## The Hadean Earth holds a key for understanding the origin of life on Earth

The geologic period between the origin of the Earth and 3.8 billion years (Ga) before the present (BP) is called the Hadean (cf. 'Glossary' section). This eon has left very few traces on the evolving Earth. A fundamental ingredient in our current understanding of the origin of life is centred on chemical evolution scenarios going back to the pioneers John Haldane and Alexander Oparin, in the earlier part of last century. They assumed the Earth once had a more hydrogen (H)-rich atmosphere (called a 'reducing' atmosphere), where the production of organic molecules would have been possible. This was the standard hypothesis in earlier chemical evolution scenarios ever since the classic organic chemistry experiments of the 1950s and early 1960s of Stanley Miller, Sidney Fox, Cyril Ponnampereuma and John Oro (cf., Ponnampereuma & Chela-Flores 1994; 1995, for the corresponding reviews). However, in contrast to this approach to the origin of life it has been recognized that the early Earth atmosphere was dominated by carbon dioxide ( $\text{CO}_2$ ). This alternative view of the early atmosphere arose from taking into account that solar luminosity at that time was an estimated 30% lower compared

to the present time. This early atmosphere would have produced a mean global temperature of approximately 85 °C (Kasting & Ackerman 1986). This, in turn, is supported by geochemical data retrieved from South African Archean cherts (Knauth & Lowe 2003).

The exact composition of the primitive terrestrial atmosphere remains a controversial issue. Besides the major volatiles (nitrogen (N), oxygen (O), water and  $\text{CO}_2$ ), a second group – the noble gases – helium (He), neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe) form a minor component of the paleoatmosphere. As reviewed below, we can understand with the noble gases, our own planet in terms of the early Earth. More significantly we can infer some of the key steps in the origin and evolution of life (cf. the reviews in Chela-Flores & Raulin 1998; Chela-Flores *et al.* 2001). Some general considerations help us to constrain the possible chemical elements that may have been present on the early Earth. For instance, volatiles would not have been captured as gases by the gravitational force (unlike the case of Jupiter; cf. subsection 'Lunar N and the earth nitrogenous atmosphere'). Otherwise this mechanism would have also captured more noble gases ( $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$  and  $^{84}\text{Kr}$ ) that are known to be present as components of the terrestrial atmosphere (Kasting 1993).

Indeed, we would not expect any natural phenomenon to remove these gases throughout geologic time. Such phenomena would also remove other volatiles that are known to be present in the contemporary atmosphere. Small bodies of the Solar System falling on the Earth, such as meteorites and comets, would have implanted volatiles to make the bulk of oceans and atmosphere.

A remarkable role for these small bodies is the transport to the Earth of some of the molecules corresponding to the early stages of chemical evolution. By these means a wide range of lipids, monomers of proteins and nucleic acids reached the terrestrial surface. Samples of such meteorites are labelled according to their composition and petrography (CI group, CM group and CR group; cf. ‘Glossary’ section). They go beyond the well-studied Murchison (CM2) and Orgueil (CI1) meteorites. The other meteorites that have been analysed from this point of view are: Meteorite Hills (MET) 01070 (CM1), Scott Glacier (SCO) 06043 (CM1), Allan Hills (ALH) 83100 (CM1/2), Lewis Cliff (LEW) 90500 (CM2), Lonewolf Nunataks (LON) 94102 (CM2), Murchison (CM2), Grosvenor Mountains (GRO) 95577 (CR1), Elephant Moraine (EET) 92042 (CR2), Graves Nunataks (GRA) 95229 (CR2), Queen Alexandra Range (QUE) 99177 (CR3) and an urelite Almahata Sitta meteorite fragment (Callahan *et al.* 2011).

But this is too simple a scenario, as we still have to take into account the consequences of the Moon-forming event (Halliday 2000; Schultz & Crawford 2011), or even more than one event (Jutzi & Asphaug 2011). To incorporate the consequences of the Moon formation, additional detailed scenarios have to be built to take into account subsequent resupply of volatiles by later collisions of meteorites and comets. It would be necessary to include the effects of out-gassing, due to the additional collisions with the Earth of these small bodies of the Solar System throughout the Hadean. These arguments underline the relevance of any information that may be available on the nature of the original atmosphere. We dwell on a possible way of directly retrieve information of the Hadean atmosphere by renewed lunar exploration, thus providing some precious certainties in the nature of the terrestrial paleoatmosphere.

### **The Moon’s gradual emergence as a leading target for several space agencies**

We restrict our attention to one aspect of the science requirements for LunarNet (cf. ‘Glossary’ section) and other forthcoming missions by focusing on a limited objective, the geochemical characterization of N on the lunar farside. Recent reviews of the history of lunar science demonstrate the considerable progress that has been achieved since the dawn of lunar exploration in the 20th century (Heiken *et al.* 1991; Jolliff *et al.* 2006). Yet, in spite of all these remarkable and up-to-date steps forward in our understanding of our satellite, they largely remain disjoint from the main stream of astrobiology. As briefly mentioned in section ‘The Hadean Earth holds a key for understanding the origin of life on Earth’, to solve

the problem of life’s origin remains elusive to this day. The difficulty is due to many changes forced upon us by our dynamical Earth that has sadly eradicated all traces of geophysical and biological data that would have been cherished by astrobiologists. Indeed, direct observation of the traces of the earliest life is not possible, due to several geophysical factors, including plate tectonics and volcanism. Especially relevant in this context is the change in the mineralogical characteristics of rocks. This phenomenon is due to the combined effects of heat and pressure (metamorphism). For further insights, we must look elsewhere.

Progress in this context would be to go beyond modelling the primitive atmosphere by retrieving some of its earliest traces. Indeed, there is a possible way to achieve this aim by focusing on N in time. The range that concerns us spans from its interstellar to its proto-solar values, right up to the solar values. We were able to obtain a first relevant measurement by the Galileo Mission during the period from 1995 till 2003. The values were obtained from the Jovian atmosphere (cf. subsection ‘Lunar N and the earth nitrogenous atmosphere’ for a careful discussion). To go beyond, we require new missions that would be in a position to focus on possible rationalization of the heterogeneous N in lunar soils. We argue that some recent proposals for Moon exploration in the coming decade (cf. section ‘Discussion: A case for returning to the Moon with kinetic micro-penetrators’) are, in principle, in a position to take up the question of the source of lunar N and, consequently, to provide some of the missing clues of life’s origin that were lost during the Hadean.

### **N in the ascent of life: the synthesis of lipids, proteins and nucleic acids**

In the early Earth, solar radiation played a major role in the evolution of life through the natural selection of micro-organisms that had developed a certain number of pigments. These included chlorophylls, and other pigments, such as phycobilins that absorb in the yellow and orange wavelengths. One of the earliest micro-organisms to emerge in the Archean were the cyanobacteria. These prokaryotes contain only one form of chlorophyll, namely chlorophyll a, which is a green pigment. In addition, cyanobacteria may contain firstly, various carotenoids, which absorb in the blue and green wavelengths, and secondly, phycobilins, such as the blue phycocyanin and the red phycoerythrin (Frank & Cogdell 1996). The most common species gave the earlier name to cyanobacteria (blue-green ‘algae’, a misnomer as these are really prokaryotes); the colouring arose due to its contents that include phycobilin and chlorophyll. But other species – red microbes – favour phycoerythrin. These red-coloured cyanobacteria provide examples of micro-organisms that use these pigments to survive in low light conditions. Cyanobacteria take advantage of phycobilins’ molecules that are able to turn light into chemical energy to be used for splitting atmospheric molecules, such as ammonia (NH<sub>3</sub>) and hydrogen sulphide (H<sub>2</sub>S) (Glazer 1985). Abundant sources of H were a significant advantage for the earliest stages of the evolution of life.

Photosynthesis turns inorganic into organic molecules that are needed by micro-organisms. This process emerged in the Archean. It allows water to be split, taking advantage of a larger, and more easily accessible source of free H – the oceans – for reacting with CO<sub>2</sub> in the atmosphere to make organic molecules (CH<sub>2</sub>O)<sub>x</sub> that are needed by micro-organisms.

These organic molecules are precursors of sugars and lipids. The role of atmospheric N was an essential additional element for the synthesis of the remaining molecules needed in the living process. In fact, N played a vital role in the synthesis of the monomers of proteins and the monomers of nucleic acids. These processes occurred both inside meteorites, as mentioned in section ‘The Hadean Earth holds a key for understanding the origin of life on Earth’ or on the terrestrial biosphere. One significant case involving N concerns hydrogen cyanide (HCN). This molecule is a precursor of the purines (adenine and guanine; cf. Chela-Flores 2011). One of the factors that have to be overcome to understand the origin of life on Earth is precisely our inability to have reliable clues regarding the early atmosphere, wherever life may have emerged.

Modelling the atmosphere has guided us in the chemical evolution scenarios of a prebiotic atmosphere. Since most geophysical records that could orient us in a model-independent way have disappeared from the Earth surface, it is pertinent to insist with the search for traces of the early atmosphere. Fortunately, as described in detail in section ‘The Moon’s gradual emergence as a leading target for several space agencies’, lunar soils have become available as a target for research. This possibility was amply explored since the retrieval of the lunar material from the early missions. As we shall discuss in the next section, N was soon recognized to be a unique volatile element that carried valuable information of the lunar history, due to the large isotopic variations in ilmenite grains (cf. ‘Glossary’ section) that were studied.

### Is lunar N contemporaneous with a nitrogenous Hadean atmosphere?

#### *Final stages of the accretion process*

Among all the small bodies, chondrites have incorporated interstellar grains from a time before the formation of the Solar System. By careful study of these ancient and primitive rocks, both breccias and basalts (cf. ‘Glossary’ section), we may infer some information on the nature of the isotopes of the chemical elements. We know there were N isotopic inhomogeneities in the early Solar System (Clayton *et al.* 1973a). In particular, we know that N isotopes are synthesized in different astrophysical processes (Prombo & Clayton 1985). For this reason, we expect N to be heterogeneous in interstellar matter (ISM).

The chemical pathways of the biogenic elements can be traced to some extent from the heterogeneous suite of molecules identified with radio astronomy in ISM from which we can infer the probable composition of the gases and grains accreted by the solar nebula (Fegley 1993). But at the present, we are more concerned to focus our attention on

the final stages of the accretion process, when the planetesimals began to accumulate to form the proto-Earth that, in turn, generated the Earth – Moon system. The value for the ratio of N’s two stable isotopes <sup>15</sup>N/<sup>14</sup>N has been the focus of diverse interpretations (discussed in detail in subsection ‘Lunar N and the earth nitrogenous atmosphere’). Especially remarkable though is the 30% variation in the N isotopic composition found in the lunar soils (Hashizume *et al.* 2000). More significant still is the implication of analysis of individual grains of lunar soils suggesting that 90% of all the trapped N does not originate from solar wind (SW) at all (Wieler *et al.* 1999).

#### *Had the Hadean Earth already a nitrogenous atmosphere?*

The standard models of the early Earth include N, water, CO<sub>2</sub> and CO, leaving O as a gas that accumulated to significant proportions only at a later stage, due to the emergence of the living process itself, closely linked to the emergence of the earliest cyanobacteria. The fossil evidence suggests that biomarkers typical of eukaryotes (and hence of the rising presence of an oxygenic atmosphere) are already present in the 2.7 Ga shales in Western Australia – the Pilbara Block’s Fortescue Group (Brocks *et al.* 1999). The subsequent Great Oxidation Event, between 2.3 and 2.4 Ga BP, was the result of the discovery of water as the source of H by purple and green photosynthetic micro-organisms. Free oxygen (O<sub>2</sub>) was liberated in the Earth’s atmosphere after the Earth rusted. The presence of O<sub>2</sub> was evidenced by iron-oxide-rich banded iron formations (BIF). These are reliable geologic indicators, as iron from the deep ocean oxidized. When the rusting process came to an end with the deposition of the last BIFs, the atmospheric level of O was raised from less than 1% to about 15% of the present atmospheric level (PAL; Schopf 1999).

Among the volatiles other than O, N is singular since it is mainly confined to the outer reservoirs of the Earth: its atmosphere, its oceans and its sediments. Water and C are different, due to a large fraction that is also contained in the mantle. As a testimony of the existence of a possible ancient nitrogenous atmosphere, it was suggested that soon after accretion N was degassed reaching the PAL rapidly in some 200 million years, possibly remaining constant since these early times (Zhang & Zindler 1993). This suggestion is further supported by the view that the ratio N/<sup>36</sup>Ar is different between the terrestrial mantle and its atmosphere, N being preferentially partitioned in the terrestrial core with respect to <sup>36</sup>Ar. These arguments rationalize the present values of N/<sup>36</sup>Ar in the atmosphere (~ 10<sup>4</sup>) and the mantle (> 10<sup>6</sup>) (Miyazaki *et al.* 2004). An important ingredient in the chemical evolution scenarios is the presence of NH<sub>3</sub>. After release in outgassing, two possibilities have been discussed. It may have been photo-oxidized to N<sub>2</sub> in a short period of time (Kuhn & Atreya 1979), or the presence of sulphur (S) in the atmosphere could have prevented UV radiation substantially, and thus NH<sub>3</sub> could have remained as an important atmospheric component for a longer period (Kasting 1982).

The mainly biological flux of N is restricted to the atmosphere, oceans and sediments as follows: in the process

of N fixation (cf. ‘Glossary’ section) bacteria may fix N as  $\text{NH}_3$ . Then the N cycle is followed by a combined process of nitrification – by autotrophs – and denitrification (cf. ‘Glossary’ section) that returns N to the atmosphere.

The additional contribution of replenishing of the atmosphere by volcanic activity is negligible by comparison (Fischer *et al.* 2002). The biologically driven N flux replenishes the atmosphere in about 10 million years (Mather *et al.* 2004). The emergence of the biologically driven N flux has been reviewed, including the ongoing debates regarding whether N takes part in additional fluxes, such as being cycled into the mantle by subduction (Rollinson 2007). It is likely that the early Earth had a nitrogenous atmosphere that has been maintained ever since the Hadean.

### Geochemistry of lunar N as a tracer of the Earth’s earliest atmosphere

#### *Stable isotope geochemistry of N*

Isotope variations of N can be retrieved from lunar samples, providing a key to understand the evolution of the Earth–Moon system. A powerful tool available is stable isotope geochemistry. Through this window we can glance at events that occurred prior to the formation of the Sun itself, based on several works (Dahmen *et al.* 1993; Owen *et al.* 2001). This is the case of grains that have been found inside meteorites, such as grains of carbide (Bernatowicz *et al.* 1991) and diamond (Daulton *et al.* 1996).

#### *Why are the lunar biogenic elements heterogeneous?*

By interaction with the solar nebula, small objects of the Solar System – primitive meteorites and comets – acquired their isotopic composition. Thus, they bear an imprint of the primordial isotopic heterogeneities of the early Solar System. However, we do not expect to observe these heterogeneities either on Earth, or on the Moon, because high-temperature processes have obliterated them (Hoefs 2009).

The case of O underlines this remark: measuring small isotope variations in  $^{16}\text{O}$ ,  $^{17}\text{O}$  and  $^{18}\text{O}$  abundances in lunar samples suggests that there is no isotope heterogeneity between the Earth, before and after colliding with the large impactor that eventually gave rise to the Moon, while retaining a fraction of its mass (Wiechert *et al.* 2001). The dispersion of the  $\delta^{18}\text{O}$  parameter for lunar rocks is relevant, where

$$\delta^{18}\text{O}\text{‰} = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{std}}}{(^{18}\text{O}/^{16}\text{O})_{\text{std}}} \times 1000$$

where std is VSMOW, which stands for the Vienna Standard Mean Ocean Water (a water standard defining the isotopic composition of water). The  $\delta^{18}\text{O}$  lunar values are very small and were measured from rocks retrieved by Apollo 15 (Hadley Rille-Appenine site, 26°7′55.99″N 3°38′1.90″E), Apollo 16 (Descartes Highlands, 8°58′22.84″S 15°30′0.68″E) and Apollo 17 (Taurus-Littrow, 20°11′26.88″N 30°46′18.05″E). However, rocks returned from Apollo 14 (the rugged Fra Mauro Highlands, south of Copernicus Crater near Cone Crater)

were, in addition, included in the general study (Clayton *et al.* 1973b).

#### *Lunar N and the Earth nitrogenous atmosphere*

Elemental N (PAL of almost 80%) has two isotopes with the composition  $^{14}\text{N}$  (99.63%) and  $^{15}\text{N}$  (0.37%) (Rosman & Taylor 1998).  $\text{N}_2$  is used for  $^{15}\text{N}/^{14}\text{N}$  measurements relative to standard terrestrial atmospheric N. Isotopic variations are reported in terms of:

$$\delta^{15}\text{N}\text{‰} = \frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}} - (^{15}\text{N}/^{14}\text{N})_{\text{std}}}{(^{15}\text{N}/^{14}\text{N})_{\text{std}}} \times 1000$$

where std denotes standard atmospheric  $\text{N}_2$ . The terrestrial atmospheric value of  $^{15}\text{N}/^{14}\text{N}$  is  $3.66 \times 10^{-3}$  (Anders & Grevesse 1989). To get insights into the early atmosphere (and hence to have a better appreciation of chemical evolution as a precursor to the origin of life on Earth), we must obtain a deeper understanding of the stable isotope geochemistry of N, both in our own planet, as well as on the Moon, and elsewhere. The above-mentioned atmospheric value of N is somewhat higher than, for instance, its value in dense molecular clouds in the galactic disk. For this specific case of N in molecules of HCN,  $^{15}\text{N}/^{14}\text{N}$  is closer to  $2.2 \times 10^{-3}$  (Dahmen *et al.* 1993).

The Galileo Mission allowed the Jovian atmosphere to provide an estimate of the protosolar value of  $^{15}\text{N}/^{14}\text{N} = (2.3 \pm 0.3) \times 10^{-3}$  (Owen *et al.* 2001). In that work, Jupiter was considered to be a surrogate of the Sun. This was a robust assumption, since for the Jovian large mass (about twice the mass of the rest of the Solar System bodies excluding the Sun), there is a corresponding large gravitational force that has retained elements and gases since its formation. Thus, Jupiter provides a reliable sample of the original contents of the solar nebula. We should remark that additional missions are nevertheless needed to strengthen our confidence on the protosolar value of  $^{15}\text{N}/^{14}\text{N}$  by using Jupiter as a surrogate of the Sun, since the Galileo Mission was only able to probe the Jovian upper atmosphere. Fortunately, though the reliability of our present understanding of the value of Solar/Jovian N content will be tested in 2016 by the current National Aeronautics and Space.

Administration (NASA) Juno Mission to the Jovian system.

On the other hand, the sample-return missions of Apollo demonstrated that while the stable isotope chemistry of the noble gases did not show any significant difference from sample to sample, in the case of  $^{15}\text{N}/^{14}\text{N}$  there was an unexpected and significant temporal increase, since about 1.7 Ga BP (Kerridge 1975, 1993). The SW (cf. ‘Glossary’ section) is expelled from the Sun isotropically at supersonic speeds (several hundred km/s close to the Earth). At the boundary of the Solar System, the SW eventually slows in the presence of ISM.

In particular, supersonic SW has bombarded the Moon since its formation. Its flow is not diverted. The reason is that our satellite has no ionosphere (Bagenal 2009) and it has a very low surface conductivity. As a consequence of such lack of an ionosphere, the Moon is incapable of diverting the SW.



The lack of lunar atmosphere is an additional factor contributing to the modification of lunar soils by SW. The result is that the SW impinges directly on the lunar surface and is, thereby, absorbed in its soils. Noble gases that have been retained by the lunar soils can be used as tracers of the isotopic abundances in the SW throughout the Sun's existence (Wieler *et al.* 1996).

This phenomenon is a surprising and valuable gift to astrobiology, since by careful analysis of the lunar soils we can retrieve a complete archive of data of the changing Sun. Such information can be shown to be another source of valuable information on the emergence of life on Earth (Messerotti & Chela-Flores 2009). Indeed, with lunar soil we are able to infer, not only the current solar characteristics, but more importantly, we can infer features of the ancient Sun.

N is present in lunar soils and there is some evidence that most of the N on the lunar soils has not been delivered by SW (cf. subsection 'Final stages of the accretion process' for references). This remark has been rationalized by the observation that there are significant changes in the ratio of  $^{14}\text{N}/^{36}\text{Ar}$  in the different ilmenite grains that have been studied. This measurement is in sharp contrast with the ratios of Ar/Kr and Kr/Xe, which do not vary in the various grains that were considered.

### The relevance for astrobiology of the emergence of the Earth geomagnetic field (GMF)

#### *N in chemical evolution: scenarios of life's origin*

As discussed in previous sections, N is anomalous in its distribution in lunar soils compared with the other biogenic elements. As a consequence, it has been suggested that it may provide a significant window into the nature of the earliest terrestrial atmosphere (Ozima *et al.* 2005, 2008). Such 'Earth wind' (EW; cf. 'Glossary' section) adds another piece to the puzzle of life's origin, as we may have in lunar N a measurable component of our early atmosphere through the lunar N isotopic anomaly. To a large extent, the evolution of life on Earth depends on the origin of the GMF (cf. 'Glossary' section). Various dynamo theories (cf. 'Glossary' section) have been reviewed in the literature (Buffett 2000), in which a source of energy in the core of the Earth causes a self-sustaining magnetic field.

A detailed reconstruction of the formation and evolution of the Earth core is not possible, although some of the processes that may have taken place can be identified. The GMF would have shielded potential terrestrial surface proto-biota emerging from the ocean's hydrothermal-vent environment. The GMF virtually provided a protection to the early life from the damaging effects of SW, and other extraterrestrial sources of radiation, including cosmic rays. It is possible that there was an overlap between the period when the GMF was evolving and the Moon had a stable regolith (Buffett 2003; Dunlop 2007). This would have allowed ions around the terrestrial ionopause to be exposed to the incoming SW and, hence, eventually to leave the terrestrial atmosphere forming part of the SW that

can at present be recorded on the Moon soils, where they may have been implanted before the GMF emerged.

This hypothesis is significant, since it is subject to verification during the next generation of lunar missions: the EW would not influence the Moon's farside. Absence of N anomalies that would be due to the EW would give us a possibility to have a direct handle on one component of the early Earth atmosphere. This is relevant. Detailed discussions with specific hypotheses on the nature of the terrestrial paleoatmosphere have been fed into the chemical evolution scenarios of the origin of the molecules of life. These arguments have led to controversies (Kasting 1987, Stribling & Miller 1987).

#### *Evidence suggesting life's origin in the Hadean*

During the period known as the late heavy bombardment (LHB) from around 4.0 till 3.9 Ga BP, there was intense traffic among Solar System bodies, including the Earth–Moon system (Sleep *et al.* 1989). It is most relevant to constrain the time window in which the Moon was already formed in the Hadean, since as a consequence, the Earth mantle began to cool to temperatures that were going to be eventually compatible with life. This cooling off period seems to have been brief on a geologic scale. Zircons (cf. 'Glossary' section) dating back to 4.4 Ga BP have signatures of the presence of liquid water at that time (Wilde *et al.* 2001).

From the point of view of astrobiology there is an important implication of having discovered the earliest piece of the Earth in Jack Hills Australia – the mineral zirconium silicate. After the Mars-size object collided with the proto-Earth, the terrestrial surface must have cooled off very quickly. This remark rationalizes the possibility that has been raised by molecular biology that an early branch of the phylogenetic tree emerged in the Hadean (Battistuzzi *et al.* 2004). This early emergence of life is compatible with the accumulating evidence from geochemical data which suggest that the origin of life may have occurred even before the LHB was over by about 3.9 Ga BP (Nisbet 2000; Nisbet & Sleep 2001). This means that practically before the time when the Solar System had completed the incorporation of planetesimals into the suite of planets, the living process may have already emerged on Earth. In this early environment the first steps of evolution were to be taken, soon after the Moon-forming cataclysmic event.

#### *Relation between a late onset of the GMF and n-isotopes*

The analysis of lunar ilmenite grains has been interpreted in terms of a GMF that was null, or very weak, before about 3.9 Ga BP (Ozima *et al.* 2005). This assumption is compatible with information from silicate crystals of a dome of ancient rock in the Kaapvaal craton in South Africa with ages between 2.5 and 3.6 Ga BP (Tarduno *et al.* 2007). This result has an important implication, namely that the onset of the GMF had already taken place by 3.2 Ga BP. Older rocks that could carry the signature of the Earth magnetic field are known, but the harsh changes that metamorphism has implanted in them does not allow a reliable date to be inferred for the onset of the GMF. This makes the possible EW implanted on the lunar soils a valid tracer of the GMF that could be studied in

forthcoming missions to the lunar farside, where the EW would not have had any effect on the regolith. However, it is worth pointing out that the next generation of lunar exploration should not be limited only to the proposed measurements in the Moon's farside. It is reasonable to suggest that additional measurements of nearside regoliths should also be included in the future mission objectives to allow more reliable comparisons with the farside results.

These are small steps forward in gaining more direct evidence of some environmental conditions that prevailed on the Hadean Earth at a time when life first emerged. These considerations justify, as we shall discuss in the next section, to be kept in mind in our current plans for returning to the Moon, especially when probing the soils of the Moon's farside with one kinetic micro-penetrator of the possible suite out of at least four such instruments, as we shall discuss in the following section.

### Discussion: a case for returning to the Moon with kinetic micro-penetrators

Continued research and exploration will provide further insights that are hidden in both the lunar regolith, and especially its paleoregolith (Crawford *et al.* 2007, 2008, 2010). Increasing experience that is being provided by the penetrator technology will become gradually a more compelling instrument that will prove its worth as a complement to human exploration of the Moon. The SW has irradiated the lunar regolith for over 4 Ga. But more significant still is the fact that an indication of isotopic fractionation of the light biogenic elements on the Moon was already evident from analyses of the lunar samples retrieved by the Apollo and Luna Programme sample-return missions. This geochemical phenomenon is illustrated by the deviation of the  $\delta^{34}\text{S}$  parameter:

$$\delta^{34}\text{S}\text{‰} = \frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}} - (^{34}\text{S}/^{32}\text{S})_{\text{std}}}{(^{34}\text{S}/^{32}\text{S})_{\text{std}}} \times 1000,$$

where the standard (std) for the S isotope scale is the meteorite troilite (FeS) of Cañon Diablo troilite (CDT). The isotopic fractionation in lunar soils is further evidenced in terms of the  $\delta^{13}\text{C}$  parameter:

$$\delta^{13}\text{C}\text{‰} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{std}}}{(^{13}\text{C}/^{12}\text{C})_{\text{std}}} \times 1000$$

where the standard (std) is the Pee Dee Belemnite (PDB) based on a Cretaceous marine fossil, *Belemnitella americana* from the Pee Dee Formation in South Carolina. Data from the Apollo 11 lunar bulk fines, breccias and fine-grained basalts excluded biogenic origin, but demonstrated that S and C isotopic fractionation had occurred due to SW impinging on the lunar soils (Kaplan 1975).

Additional, and significant progress in our knowledge of the Moon and the rest of the Solar System, will depend on the adoption of new space technologies. One particularly relevant example is the kinetic micro-penetrator technology. The UK Lunar Penetrator Consortium (cf. 'Glossary' section) is preparing to demonstrate the penetrator versatility with the potential identification of biomarkers robotically. Two

possibilities are being followed up. An eventual return to the Moon (Smith *et al.* 2011), as well as the exploration of the Jovian Moon Europa (Gowen *et al.* 2011). We have argued that support would not only be economically more feasible with penetrators, but that the reward of increasing our data of the lunar regolith and its paleoregolith is full of promising astrobiological returns that are no longer accessible on terrestrial locations.

We have argued that significant relevant data for astrobiology may remain accessible on the Moon soils, due to the total lack of lunar erosion or plate tectonics. Since the predictions that EW may have implanted relics of the earliest terrestrial atmosphere exclusively on the nearside of the Moon, the case for returning to the farside of our natural satellite with penetrator technology is compelling. The chief motivation for the renewed lunar exploration from what we have discussed above is to ascertain that no traces of EW were ever implanted on the Moon's farside.

This task of exploring the lunar surface is feasible by the emplacement of kinetic micro-penetrators bearing a suite of instruments. These would include miniaturized mass spectrometers and miniaturized mass analysers. These instruments are already available for *in situ* elemental analysis of a variety of Solar System bodies in the next generation of planetary missions (Rohner *et al.* 2004; Tulej *et al.* 2011). The exciting forthcoming new age of space exploration is expected to probe the S patches on Europa's icy surface, in analogy with terrestrial S patches (Chela-Flores 2006, 2010; Gleeson *et al.* 2010; Gowen *et al.* 2011). Secondly, as we have argued persistently in the present paper, the next generation of space exploration (Smith *et al.* 2011) should give a high priority to characterizing the geochemistry of Moon soils, especially the N abundances on the lunar farside, which should have remarkable implications on overlapping areas of the early Earth geophysics and the science of astrobiology.

### Glossary

**Basalt:** These are fine-grained igneous rocks that are derived from the process of melting in the mantles of planets or satellites. From basalts we are able to investigate the nature – geochemical and thermal – of planets or satellites.

**Breccia:** A rock that has been formed from fragments of pre-existing rocks, normally with fragments that are larger than about 2 mm.

**CI:** A group of carbonaceous chondrites named after the Ivuna meteorite, have chemical compositions that are close to that measured in the solar photosphere.

**CM:** A group of carbonaceous chondrites named after Mighei. They contain a rich mix of complex organic compounds.

**CR:** A group of carbonaceous chondrites named after Renazzo (Italy). The parent body has been assumed to be the asteroid 2 Pallas, a large asteroid to have been discovered, by Heinrich W.M. Olbers in 1802.

**Denitrification:** This is an important step in the N cycle on Earth, by means of which micro-organisms reduce nitrate to

produce molecular nitrogen (N<sub>2</sub>) through a series of intermediate steps.

**Dynamo theory of the generation of a magnetic field:** A theory that attempts to identify the internal generation of a magnetic field of a body in the cosmos. The theory includes hypotheses for various observed properties of the terrestrial geomagnetic field, such as the maintenance over geologic time of a magnetic field by the physical phenomena of convection, rotation and electrical conductivity.

**Earth wind:** Interplanetary particles that impinge on Solar System bodies (including the Moon), whose origin is the Earth, in contrast to SW.

**Geomagnetic field:** It is the magnetic field in the vicinity of the Earth, first conjectured by G.F. Gauss. To a first approximation it has two poles. Away from the surface, the dipole becomes distorted and its strength and shape change over time.

**Hadean:** A geologic period lasting some 0.75 Ga, spanning from the formation of the Earth till 3.8 Ga BP. It has to be understood before we are certain of the conditions that led to the origin of life.

**Ilmenite:** FeTiO<sub>3</sub> an oxide mineral, iron titanium oxide. This mineral is known to be present on the Moon; although it is a common component of mare basalts, it is not a significant component of highland anorthositic regolith. It is known to have the highest retentivity for implanted noble gases (Ozima *et al.* 2008). With a hydrogen reduction process it has been proposed for the production of O at a future lunar settlement (Gibson & Chang 1992).

**Ionopause:** The top of the ionosphere.

**Ionosphere:** That part of the upper atmosphere that is ionized by solar radiation.

**Kinetic Micro-Penetrator:** Planetary (kinetic) Micro-Penetrators are instruments consisting of small projectiles that can be delivered at high velocity to reach just beneath the surface of planets or their satellites for probing samples of surficial chemical elements, among other investigations (cf. below, UK Lunar Penetrator Consortium).

**Lunar Net:** A mission proposed by the UK Lunar Penetrator Consortium for the emplacement of at least four kinetic micro-penetrators geographically distributed over the lunar surface (Smith *et al.* 2011).

**Nitrate:** It is a group of atoms (RONO<sub>2</sub>, where R stands for any organic residue) within molecules that are responsible for the characteristic chemical reactions of those molecules.

**Nitrification:** It is an important step in the N cycle on Earth: a multi-step oxidation process (oxidation of NH<sub>3</sub> with O into nitrite, followed by the oxidation of these nitrites into nitrates). Autotrophic organisms mediate this process.

**N (biological) fixation:** An atmospheric process in the N cycle on Earth that is driven by the enzyme nitrogenase, by means of which N is converted to NH<sub>3</sub>.

**Petrography:** It is a branch of geology that studies rocks, especially focusing on the conditions in which rocks form.

**Regolith:** A layer of loose, heterogeneous material covering solid underlying base that can be rock or solid ice.

**Solar nebula:** The standard model of the origin of the solar system, in which a gaseous cloud from which, the Solar System formed by condensation.

**UK Lunar Penetrator Consortium:** An UK consortium to develop kinetic micro-penetrators for the exploration of the Moon and beyond.

**Zircon:** A mineral (zirconium silicate) with chemical formula ZrSiO<sub>4</sub>. It is found in various contexts such as igneous, metamorphic and in sedimentary rocks.

## References

- Anders, E. & Grevesse, N. (1989). Abundances of the elements – meteoritic and solar. *Geochim. Cosmochim. Acta* **53**, 197–214.
- Bagenal, F. (2009). Comparative planetary environments. In *Heliophysics: Plasma Physics of the Local Cosmos*, ed. Schrijver, C.J. & Siscoe, G.L., pp. 360–398. Cambridge University Press, Cambridge.
- Battistuzzi, F., Feijao, U. & Hedges, S.B. (2004). A genomic timescale of prokaryote evolution: insights into the origin of methanogenesis, phototrophy, and the colonization of land. *MC Evol. Biol.* **4**, 44–60.
- Bernatowicz, T., Amari, S., Zinner, E. & Lewis, R. (1991). Presolar grains within presolar grains. *Astrophys. J. Lett.* **373**, L73.
- Brocks, J.J., Logan, G.A. & Summons, R.E. (1999). Archean molecular fossils and the early rise of eukaryotes. *Science* **285**, 1033–1036.
- Buffet, B.A. (2003). The thermal state of the Earth's core. *Science* **299**, 1675–1677.
- Buffett, G.A. (2000). Earth core and the geodynamo. *Science* **288**, 2007–2012.
- Callahan, M.P., Smith, K.E., Cleaves, H.J. II, Ruzicka, J., Stern, J.C., Glavin, D.P., House, C.H. & Dworkin, J.P. (2011). Carbonaceous meteorites contain a wide range of extraterrestrial nucleobases. *Proc. Natl. Acad. Sci. U.S.A.* **108**, 13995–13998.
- Chela-Flores, J. (2006). The sulphur dilemma: are there biosignatures on Europa's icy and patchy surface? *Int. J. Astrobiol.* **5**, 17–22 (copyright holder: Cambridge University Press; <http://www.ictp.it/~chelaf/sulphurdilemma.pdf>).
- Chela-Flores, J. (2010). Instrumentation for the search of habitable ecosystems in the future exploration of Europa and Ganymede. *Int. J. Astrobiol.* **9**, 101–108 ([http://www.ictp.it/~chelaf/jcf\\_IJA\\_2010.pdf](http://www.ictp.it/~chelaf/jcf_IJA_2010.pdf)).
- Chela-Flores, J. (2011). *The Science of Astrobiology A Personal Point of View on Learning to Read the Book of Life*, 2nd edn, Book Series: Cellular Origin, Life in Extreme Habitats and Astrobiology, Springer, Dordrecht, The Netherlands, Chapter 4, especially p. 86. <http://www.ictp.it/~chelaf/ss220.html>.
- Chela-Flores, J., Owen, T. & Raulin, F. (eds) (2001). *The First Steps of Life in the Universe*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Chela-Flores, J. & Raulin, F. (eds) (1998). *Exobiology: Matter, Energy, and Information in the Origin and Evolution of Life in the Universe*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Clayton, R.N., Grossman, L. & Mayeda, T.K. (1973a). A component of primitive nuclear composition in carbonaceous chondrites. *Science* **182**, 485–488.
- Clayton, R.N., Hurd, J.M. & Mayeda, T.K. (1973b). Oxygen isotopic compositions of Apollo 15, 16, and 17 samples, and their bearing on lunar origin and petrogenesis. *Proc. Lunar Sci. Conf.* **4**, 1535–1542.
- Crawford, I.A., Baldwin, C., Taylor, E.A., Bailey, J.A. & Tsembeles, K. (2008). On the survivability and detectability of terrestrial meteorites on the Moon. *Astrobiology* **8**, 242–252.
- Crawford, I.A., Fagents, S.A. & Joy, K.H. (2007). Full Moon exploration. *Astron. Geophys.* **48**, 3.18–3.21.
- Crawford, I.A., Fagents, S.A., Joy, K.H. & Rumpf, M.E. (2010). Lunar palaeoregolith deposits as recorders of the galactic environment of the solar system and implications for astrobiology. *Earth Moon Planets* **107**, 75–85.

- Dahmen, G., Wilson, T.L. & Matteucci, F. (1993). The nitrogen isotope abundance in the galaxy. 1: The galactic disk gradient. *Astron. and Astrophys.* **295**, 194–198.
- Daulton, T.L., Eisenhour, D.D., Bernatowicz, T.J., Lewis, R.S. & Buseck, P.R. (1996). Genesis of presolar diamonds: Comparative high-resolution transmission electron microscopy study of meteoritic and terrestrial nano-diamonds. *Geochim. Cosmochim. Acta* **60**(23), 4853–4872.
- Dunlop, D. (2007). A more ancient shield. *Nature* **446**, 623–625.
- Fegley, B. Jr. (1993). Chemistry of the Solar Nebula. In *The Chemistry of Life's Origin*, ed. Greenberg, J.M., Mendoza-Gomez, C.X. & Pirronello V., pp. 75–147. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Fischer, T.P., Hilton, D.R., Zimmer, M.M., Shaw, A.M., Sharp, Z.D. & Walker, J.A. (2002). Subduction and recycling of nitrogen along the Central American margin. *Science* **297**, 1154–1157.
- Frank, H.A. & Cogdell, R.J. (1996). Carotenoids in photosynthesis. *Photochem. Photobiol.* **63**, 257–264.
- Gibson, E.K. Jr. & Chang, S. (1992). The Moon: Biogenic elements. In *Exobiology in Solar System Exploration*, ed. Carle, G.C., Schwartz D.E. & Huntington, J.L., vol. 512, pp. 29–43. NASA Ames Research Center Moffett Field, CA, USA.
- Glazer, A.N. (1985). Light harvesting by phycobilisomes. *Annu. Rev. Biophys. Chem.* **14**, 47–77.
- Gleeson, D., Pappalardo, R.T., Grasby, S.E., Anderson, M.S., Beauchamp, B., Castano, R., Chien, S., Doggett, T., Mandrake, L. & Wagstaff, K. (2010). Characterization of a sulfur-rich, Arctic spring site and field analog of Europa using hyperspectral data. *Remote Sens. Environ.* **114**, 1297–1311.
- Gowen, R.A., Smith, A., Fortes, A.D., Barber, S., Brown, P., Church, P., Collinson, G., Coates, A.J., Collins, G., Crawford, I.A. *et al.* (2011). Penetrators for *in situ* sub-surface investigations of Europa. *Adv. Space Res.* **48**, 725–742 (<http://www.ictp.it/~chelaf/ScienceDirect.pdf>).
- Halliday, A.N. (2000). Terrestrial accretion rates and the origin of the Moon. *Earth Planet. Sci. Lett.* **176**, 17–30.
- Hashizume, K., Chaussidon, M., Marty, B. & Robert, F. (2000). Solar wind record on the Moon: deciphering presolar from planetary nitrogen. *Science* **290**, 1142–1145.
- Heiken, G.H., Vaniman, D.T. & French, B.M. (1991). *The Lunar Sourcebook*. Cambridge University Press, Cambridge.
- Hoefs, J. (2009). *Stable Isotope Geochemistry*. Springer, Dordrecht, The Netherlands p. 93.
- Jolliff, B.L., Wieczorek, M.A., Shearer, C.K. & Neal, C.R. (eds) (2006). *New Views of the Moon. Reviews in Mineralogy and Geochemistry*, vol. 60, Mineralogical Society of America, Chantilly, VA, 721 pp.
- Jutzi, M. & Asphaug, E. (2011). Forming the lunar farside highlands by accretion of a companion Moon. *Nature* **476**, 69–72.
- Kaplan, I.R. (1975). Stable isotopes as a guide to biogeochemical processes. *Proc. R. Soc. Lond. B* **189**, 183–211 (cf. pp. 202–205).
- Kasting, J.F. (1982). Stability of ammonia in the primitive terrestrial atmosphere. *J. Geophys. Res.* **87**, 3091–3098.
- Kasting, J.F. (1987). Theoretical constraints on oxygen and carbon dioxide concentrations in the Precambrian atmosphere. *Precambrian Res.* **34**, 205–229.
- Kasting, J.F. (1993). Early evolution of the atmosphere and ocean. In *The Chemistry of Life's Origin*, ed. Greenberg, J.M., Mendoza-Gomez, C.X. & Pirronello, V., pp. 149–176. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Kasting, J.F. & Ackerman, T.P. (1986). Climate consequences of very high carbon dioxide levels in the Earth's early atmosphere. *Science* **234**, 1383–1385.
- Kerridge, J.F. (1975). Solar nitrogen: evidence for a secular increase in the ratio of nitrogen-15 to nitrogen-14. *Science* **18**, 162–164.
- Kerridge, J.F. (1993). Long-term compositional variation in solar corpuscular radiation – evidence from nitrogen isotopes in the lunar regolith. *Rev. Geophys.* **31**, 423–437.
- Knauth, L.P. & Lowe, D.R. (2003). High Archean climatic temperature inferred from oxygen isotope geochemistry of cherts in the 3.5 Ga Swaziland Supergroup, South Africa. *Geol. Soc. Am. Bull.* **115**, 566–580.
- Kuhn, W.R. & Atreya, S.K. (1979). Ammonia photolysis and the greenhouse effect in the primordial atmosphere of the Earth. *Icarus*, **37**, 207–213.
- Mather, T.A., Pyle, D.M. & Allen, A.G. (2004). Volcanic source for fixed nitrogen in the early Earth's atmosphere. *Geology* **32**, 905–908.
- Messerotti, M. & Chela-Flores, J. (2009). Solar activity and life. A Review. *Acta Geophysica* **57**(1), 64–74 (<http://www.ictp.it/~chelaf/MesserottiJCF.pdf>).
- Miyazaki, A., Hiyagon, H., Sugiura, N., Hirose, K. & Takahashi, E. (2004). Solubilities of nitrogen and noble gases in silicate melts under various oxygen fugacities: implications for the origin and degassing history of nitrogen and noble gases in the Earth. *Geochim. Cosmochim. Acta* **68**, 387–401.
- Nisbet, E.G. (2000). The realms of Archaean life. *Nature* **405**, 625–626.
- Nisbet, E.G. & Sleep, N.H. (2001). The habitat and nature of early life. *Nature* **409**, 1083–1091.
- Owen, T., Mahaffy, P.R., Niemann, H.B., Atreya, S. & Wong, M. (2001). Protosolar nitrogen. *Astrophys. J.* **55**, L77–L79.
- Ozima, M., Seki, K., Terada, N., Miura, Y.N., Podosek, F.A. & Shinagawa, H. (2005). Terrestrial nitrogen and noble gases in lunar soils. *Nature* **436**, 655–659.
- Ozima, M., Yin, Q.-Z., Podosek, F.A. & Miura, Y.N. (2008). Toward understanding early Earth evolution: prescription for approach from terrestrial noble gas and light element records in lunar soils. *Proc. Natl. Acad. Sci. USA* **105**(46), 17654–17658.
- Ponnamperuma, C. & Chela-Flores, J. (eds) (1995). *Chemical Evolution: The Structure and Model of the First Cell*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Ponnamperuma, C. & Chela-Flores, J. (Guest Editors) (1994). *J. Biol. Phys.* **120**(1–4).
- Prombo, C.A. & Clayton, R.N. (1985). A striking isotope nitrogen anomaly in the Bencubbin and Weatherford meteorites. *Science* **230**, 935–937.
- Rohner, U., Whitby, J.A. & Wurz, P. (2004). Highly miniaturized laser ablation time-of-flight mass spectrometer for a planetary rover. *Rev. Sci. Instrum.* **75**, 1314–1322.
- Rollinson, H.R. (2007). Chapter 5: The Origin of the Earth's Atmosphere and Oceans. In *Early Earth Systems: A Geochemical Approach*. pp. 184–186. Blackwell Publishing, Oxford, UK.
- Rosman, J.R. & Taylor, P.D. (1998). Isotopic compositions of the elements (technical report): commission on atomic weights and isotopic abundances. *Pure Appl. Chem.* **70**, 217–235.
- Schopf, J.W. (1999). Chapter 6: So far, So fast, so early? In *Cradle of Life*. pp. 171–174. Princeton University Press, Princeton, NJ, USA.
- Schultz, P.H. & Crawford, D. (2011). Origin of nearside structural and geochemical anomalies on the Moon. In *Recent Advances and Current Research Issues in Lunar Stratigraphy*, ed. Ambrose, W.A. & Williams, D.A., pp. 141–159, Geological Society of America, Special Paper 477, Boulder Co, USA.
- Sleep, N., Zahnle, K., Kasting, J. & Morowitz, H. (1989). Annihilation of ecosystems by large asteroid impacts on the early Earth. *Nature* **342**, 139–142.
- Smith, A., Crawford, I.A., Gowen, R.A., Ambrosi, R., Anand, M., Banerdt, B., Bannister, N., Bowles, N., Braithwaite, C., Brown, P. *et al.* (2011). Lunar Net – A proposal in response to an ESA M3 call in 2010 for a medium sized mission. *Exp. Astron.*, published online 1 September doi:10.1007/s10686-011-9250-5.
- Stribling, R. & Miller, S.L. (1987). Energy yields for hydrogen cyanide and formaldehyde syntheses: the HCN an and amino acid concentrations in the primitive ocean. *Orig. Life* **17**, 261–273.
- Tarduno, J.A., Cottrell, R.D., Watkeys, M.K. & Bauch, D. (2007). Geomagnetic field strength 3.2 billion years ago recorded by single silicate crystals. *Nature* **446**, 657–660.
- Tulej, M., Iakovleva, M., Leya, I. & Wurz, P. (2011). A miniature mass analyser for *in-situ* elemental analysis of planetary material-performance studies. *Anal. Bioanal. Chem.* **399**(6), 2185–2200.
- Wiechert, U., Halliday, A.N., Lee, D.-C., Snyder, G.A., Taylor, L.A. & Rumble, D. (2001). Oxygen isotopes and the Moon-forming giant impact. *Science* **294**, 345–348.



- Wieler, R., Humbert, F. & Marty, B. (1999). Evidence for a predominantly non-solar origin of nitrogen in the lunar regolith revealed by single grain analysis. *Earth Planet. Sci. Lett.* **167**, 47–60.
- Wieler, R., Kehm, K., Meshik, A.P. & Hohenberg, C.M. (1996). Secular changes in the xenon and krypton abundances in the solar wind recorded in single lunar grains. *Nature* **384**, 46–49.
- Wilde, S.A., Valley, J.W., Peck, W.H. & Graham, C.M. (2001). Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature* **409**, 175–178.
- Zhang, Y. & Zindler, A. (1993). Distribution and evolution of carbon and nitrogen in the Earth. *Earth Planet. Sci.* **117**, 331–345.