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Formation and early evolution of the atmosphere

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Abstract: The tectonic activity of the Earth allowed exchange of volatile elements (H, C, N, rare gases) between the surface of the Earth (atmosphere, crust, sediments, oceans) and the mantle. However, some of these elements still present elemental and isotopic heterogeneities that allow us to reconstruct the volatile composition of the terrestrial mantle. The protosolar nebula supplied a significant fraction of helium and neon, which were presumably trapped during the major phase of the Earth's accretion and were possibly hosted by accreting dust and/or small porous planetesimals. Surprisingly, volatile elements are in chondritic proportion despite their drastic (10^{-3}) depletion in the mantle relative to chondrites, in a way that recalls the case of highly siderophile elements. From stable isotope systematics, we find that the contribution of comets to the volatile inventory of the Earth was very limited. The integrated flux of chondritic-like material necessary to provide water, carbon and nitrogen is consistent with that required for the formation of the lunar craters as well as that necessary to account for the inventory of siderophile elements in the mantle. A consequence of this scenario is that the Earth's surface was oxidized very early. Alternatively, volatile and siderophile elements of the mantle could be the remnant of small patches of chondritic material that did not equilibrate with the core nor drastically degas.

Introduction

The development of life required adequate environmental conditions at the Earth's surface during the Hadean eon. Investigating these conditions and by consequence the origin and early evolution of the atmosphere is necessary to understand which chemical path and metabolism had been favoured during this period. As a result of the Earth's tectonics, the geological record during the Hadean Eon has been completely erased, and most of our knowledge on atmospheric evolution is indirect. Volatile elements in the present-day atmosphere have elemental and isotopic compositions (those of live and extinct radioactivity products) that provide information on the timing of atmospheric evolution. The mantle contains volatile elements that were trapped during Earth's accretion and might have been preserved since then. However, this reservoir exchanged volatile elements with the atmosphere through volcanism and subduction (Fig. 1) and only few elements still keep a record of the volatile component trapped in accreting silicates. Independently, the analysis of extra-terrestrial bodies and of solar wind allows us to infer the composition of potential contributors and to compare it with compositions observed

in terrestrial reservoirs. One of the problems of this comparative approach is that the knowledge of these precursors is still limited. For example, the composition of comets is mainly known through remote sensing and in few instances through direct measurements (and possibly through the analysis of interplanetary dust particles (IDPs) but the origin of these objects remains to be established firmly). Other extremely important sources of information are the compositions of planetary atmospheres. The composition of the Jovian, Martian and Venusian atmospheres have been already measured and there is no doubt that missions planned for the next two decades will allow significant advances in this field. In this paper we focus on the case of the Earth and its early environment.

The terrestrial atmosphere cannot derive directly from the protosolar nebula (hereafter labelled PSN): (1) the abundance of atmospheric rare gases (normalized to a non-volatile element such as Si) is 6–10 orders of magnitude lower than solar (Brown 1952); (2) the isotopic compositions of rare gases (e.g. Ozima & Podosek 1983) and nitrogen (Hashizume *et al.* 2000) are drastically different from those of solar gases. The depletion of rare gases in the Earth resulted in high parent/daughter ratios (where the parent

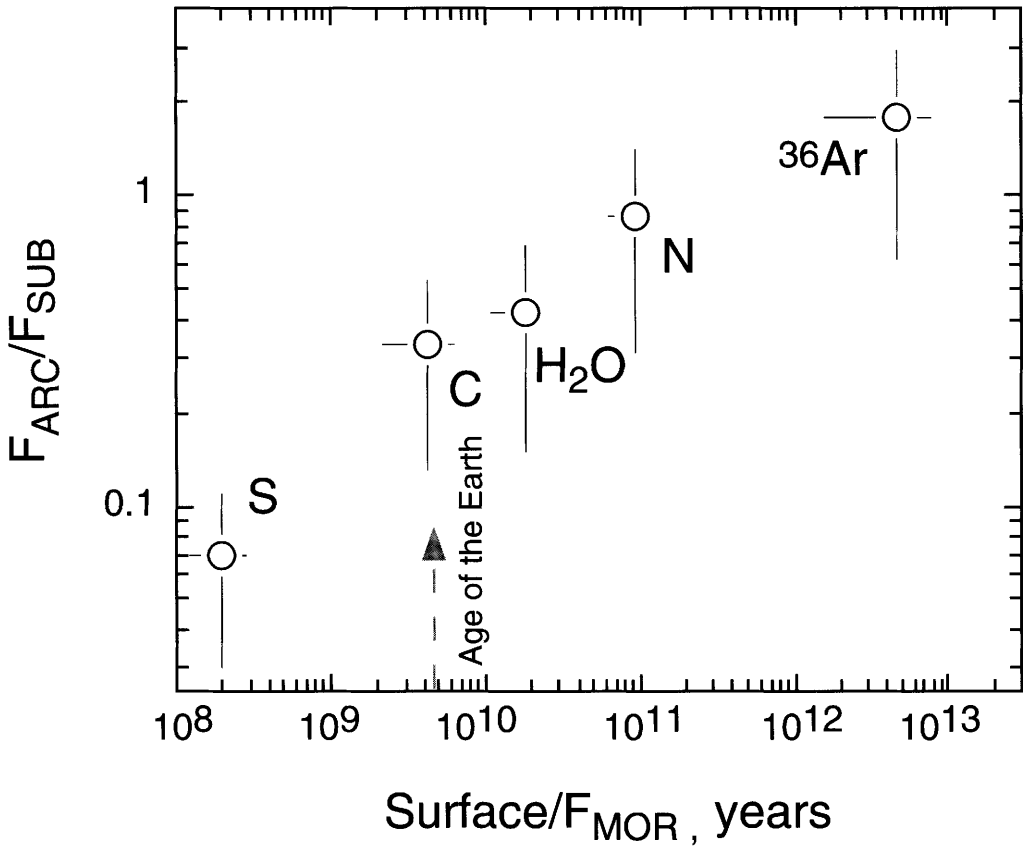


Fig. 1. Recycling of volatile elements in the Earth. The x -axis is the ratio of the surface (atmosphere, oceans, crust, sediments) inventory divided by the present-day flux at ridges. The y -axis is the amount of volatile elements carried by the oceanic crust and sediments to subduction zones by the volcanic flux at arcs. Neon is not represented because its volcanic flux is not known. Data sources: Craig *et al.* (1975), Matsuo *et al.* (1978), Le Guern (1982), Staudacher & Allègre (1988), Staudigel *et al.* (1989), Allard (1992), Marty (1992, 1995), Rea & Ruff (1996), Sano & Williams (1996), Marty & Tolstikhin (1998), Marty & Zimmermann (1999), and references therein.

element is a non-volatile element and the daughter is a rare gas isotope), allowing us to use natural radioactivity products to quantify the evolution of the terrestrial atmosphere. The first significant observation in the field was by Von Weizsacker, who proposed in 1937 the decay of ^{40}K ($T_{1/2} = 1.25$ Ga) to ^{40}Ar to explain the relatively high content of argon in the atmosphere (0.934%) compared with other rare gases (e.g. 0.0016% Ne). As the major reservoir of terrestrial potassium is the silicate Earth (mantle + crust), this observation implies transfer of radiogenic ^{40}Ar from the K-bearing silicates to the atmosphere through time by magmatism and metamorphism. Rubey (1951) showed that the alteration of rocks at the Earth's surface could not account for the budget of atmospheric gases

and, noting that the composition of volatiles present at the Earth's surface (atmosphere + sediments + oceans) resembled to that of volcanic gases, proposed that the atmosphere was formed by volcanic degassing. This view is fully consistent with the potassium-argon budget of the Earth: approximately half of radiogenic argon produced by the decay of ^{40}K is now in the atmosphere. The timing of this transfer was investigated when the analysis of oceanic basalts, presumably derived from the convective mantle, showed that the radioactive/primordial, $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of the mantle was much higher than that of the atmosphere. To obtain such a high isotopic ratio in the mantle relative to that of the atmosphere, it is necessary to transfer primordial ^{36}Ar from the mantle to the atmosphere 'before' significant

radiogenic in-growth of ^{40}Ar in the mantle from the decay of ^{40}K . Models quantifying this observation led to the concept of 'catastrophic' degassing early in the Earth's history, a major event that was thought to have occurred in the Hadean Eon and might have been linked with the formation of the core (Ozima 1975; Alexander & Schwartzman 1976; Allègre *et al.* 1983; Ozima & Podosek 1983; Sarda *et al.* 1985).

Another major advance in the field was the discovery of ^{129}Xe excess (relative to Xe isotopic composition of the atmosphere) in a few CO_2 -rich natural gases (Zartman *et al.* 1961; Phinney *et al.* 1978) and in mantle-derived, mid-ocean ridge basalts (MORB) (Staudacher & Allègre 1982; Marty 1989; Staudacher *et al.* 1989). ^{129}Xe is the radioactive daughter of ^{129}I ($T_{1/2} = 17$ Ma), a now extinct radioactive isotope that was synthesized before formation of the Solar System. Assuming that the atmosphere was derived from the mantle, the existence of higher $^{129}\text{Xe}/^{130}\text{Xe}$ ratios (where ^{130}Xe is a non-radiogenic Xe isotope used as a reference) in the mantle than in the atmosphere implied that the catastrophic degassing of the Earth occurred before ^{129}I of the mantle was completely decayed, that is, within a few half-lives of ^{129}I . The study of xenon isotopes ('terrestrial xenology') allowed model ages of the atmosphere to be computed within the range of 0.1–0.2 Ga after the start of condensation in the Solar System (Staudacher & Allègre 1982; Allègre *et al.* 1987; Pepin 1991; Tolstikhin & Marty 1998). It is important to note that the concept of rapid atmospheric formation is still valid even though the starting assumptions have failed to reproduce all rare gas observations.

The first problem with the concept of catastrophic degassing as a source of atmospheric gases came from other radioactive decays that produced Xe isotopes. $^{131}\text{--}^{136}\text{Xe}$ are produced by two radioactivities, the spontaneous fission of still existing ^{238}U ($T_{1/2} = 4.46$ Ga), and that of ^{244}Pu ($T_{1/2} = 82$ Ma). These two decays produce Xe isotopes in proportions that are fairly close, but precise analysis of Xe isotopes of natural gases and of MORB has allowed computation of the fraction of fissionogenic Xe in the mantle produced by plutonium-244 (Ozima *et al.* 1985; Kunz *et al.* 1998) and therefore the $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}^*$ ratio (where the asterisk indicates radiogenic or fissionogenic and ^{136}Xe is taken as an example among the $^{131}\text{--}^{136}\text{Xe}$ isotopes) resulting from the decays of ^{129}I and ^{244}Pu in the mantle (Marty 1989). The atmosphere contains also Xe isotopes produced by extinct radioactivities and the $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}^*$ ratio of the atmospheric source could also be computed (Pepin & Phinney 1979;

Igarashi 1986). It turned out that there was more plutonium-derived Xe relative to iodine-derived Xe in the atmosphere than in the mantle (Ozima *et al.* 1985; Marty 1989). Degassing of the atmosphere after formation of the mantle would have produced the opposite situation, as the half-life of ^{244}Pu is longer than that of ^{129}I . This comparison was at odds with the classical view of simple derivation of atmospheric gases from the mantle reservoir early in the Earth's history: for a common I–Pu geochemical source, the atmosphere as a geochemical reservoir would have been formed before the mantle, which is logically absurd. A way round this problem is to consider that the hypothesis of a common I–Pu geochemical source is not adequate and that two different geochemical sources contributed xenon in the mantle and in the atmosphere, respectively (Marty 1989). This implies either (1) heterogeneous accretion of bodies with contrasted compositions having different I/Pu ratios (Marty 1989) and/or (2) active exchange between atmosphere and mantle while atmospheric xenon was fractionated during escape to space (Pepin 1991; Tolstikhin & Marty 1998). It must be noted, however, that the identification of xenon components in the Earth–atmosphere is not yet definitive, as the isotopic composition of primitive Xe that was presumably trapped during the Earth's formation has not been measured directly in extraterrestrial samples but has been inferred from a statistical treatment of meteoritic data (Pepin & Phinney 1979; Igarashi 1986), making the terrestrial budget of $^{129}\text{Xe}^*$ and $^{136}\text{Xe}_{\text{Pu}}^*$ model dependent. Moreover, the non-radiogenic isotopic composition of xenon in the mantle, necessary to compute these two values, is not precisely known, although CO_2 -well gas studies suggest that there exists a non-atmospheric Xe component in the Earth (Caffee *et al.* 1999).

The aim of this study is to identify the volatile (H, C, N, rare gases) components present at the Earth's surface and in its interior. We then use such compositions to infer the potential contributing sources and processes that resulted in the surface and the mantle inventory of volatile elements.

Reservoirs and potential contributors

Identification of volatile components in the Earth–atmosphere

As a result of plate tectonics, plume activity and volcanism, volatile elements are continuously exchanged between the surface and the mantle.

The efficiency of these homogenizing processes is illustrated in Figure 1 which compares the 'mean degassing duration' (MDD) of the atmosphere for several volatile elements with the efficiency of recycling at arcs. The former is defined as the surface inventory (the total amount of a given volatile element, whatever its chemical state, in the crust, the sediments, the oceans and the atmosphere) divided by its degassing rate from the mantle, thought to occur mainly at mid-ocean ridges (degassing at plumes is minor compared with that at ridges; see, e.g. Marty & Tolstikhin 1998). MDD lower than the age of the Earth would imply fast recycling whereas MDD greater than the age of the Earth would suggest either decreasing degassing rate with time or the occurrence of a volatile component at the Earth's surface not derived from the mantle, or both. The y -axis of Figure 1 is the ratio $F_{\text{ARC}}/F_{\text{SUB}}$ between the volatile flux through arc volcanism and the amount of volatiles carried by plates towards subduction zones ($F_{\text{ARC}}/F_{\text{SUB}}$ values close to unity imply no recycling). The correlation between $F_{\text{ARC}}/F_{\text{SUB}}$ and MDD strongly suggests a recycling and mantle-atmosphere exchange efficiency decreasing from sulphur (MDD *c.* 200 Ma) to carbon (MDD *c.* 4 Ga), H₂O, N and finally to rare gases. The isotopic compositions of these volatiles between the mantle and the surface follow this logic well, as both S and C isotopic ratios are similar in the mantle and in the surface inventory, whereas water (δD *c.* -80‰ relative to ocean water in the upper mantle), nitrogen ($\delta^{15}\text{N}$ *c.* -4‰ in the upper mantle relative to atmospheric N; e.g. Marty & Humbert 1997) and neon ($\delta^{22}\text{Ne} \leq -200\%$ relative to atmospheric N; e.g. Sarda *et al.* 1988) present isotopic heterogeneities that probably represent different volatile sources that were not fully homogenized. Hence it is possible to distinguish partly a mantle reservoir from the 'atmosphere' (surface inventory) one and to explore the origins of both.

The potential components that might have delivered volatile elements to the Earth are the PSN (the major reservoir in the Solar System) and solid matter bodies such as meteorites and comets. The composition of meteoritic volatiles is thought to have been derived from the PSN through elemental and isotopic fractionation. Contributions from sources outside the Solar System such as pre-solar grains or species affected by interstellar chemistry are attested by the discovery of pre-solar grains in primitive meteorites on one hand, and by the large variation of the D/H ratio in the Solar System on another hand, but their extent is a matter of debate. A comparison of the abundances of

He, Ne, Ar, C and N between cosmochemical potential precursors (PSN and chondrites) and terrestrial reservoirs (the atmosphere and the mantle source of MORB) is given in Figure 2. Volatile abundances are normalized to ²⁰Ne and the Sun, which, in this figure, results in a flat pattern for the solar abundance. Neon is used for normalization as its isotopic (non-radiogenic) composition in the mantle is clearly different from that of the atmosphere (see below).

Meteorites

Figure 2 illustrates the large difference in abundance pattern between primitive meteorites and the PSN, which presumably reflects different trapping efficiency during condensation of the Solar System material and further exchange between gas and solid in the forming Solar System. The chondritic excesses of C and N relative to solar may have resulted from preferential trapping of C and N compounds, which were stable in the reducing conditions of the hydrogen-rich PSN. The origin of these compounds is unclear: the large heterogeneity of the nitrogen isotopic composition among Solar System objects (Kerridge & Swindle 1988) is not compatible with a single homogeneous source such as a well-mixed solar nebula, but rather suggests mixing between different components (Hashizume *et al.* 2000). It is likely that a major fraction of H and N (and C by analogy, although in this case the isotope argument is less straightforward) was incorporated as compounds and that the ultimate origin of these elements could be partly interstellar. Notably, rare gases are also fractionated in meteorites and the origin of such fractionation is a matter of debate (Pepin 1991; Ozima *et al.* 1998).

Terrestrial mantle

The analysis of rare gases together with C and N of mantle-derived samples allows us to investigate the volatile composition of the mantle. However, data need to be corrected for surficial processes such as partial melting, fractional crystallization, degassing and atmospheric contamination, and we have developed in the past few years analytical and correction techniques that allow reconstruction of the elemental and isotopic composition of the mantle for He, C, N and Ar (Marty & Jambon 1987; Marty 1995; Marty & Humbert 1997; Marty & Zimmermann 1999). The data used in Figure 1 were summarized by

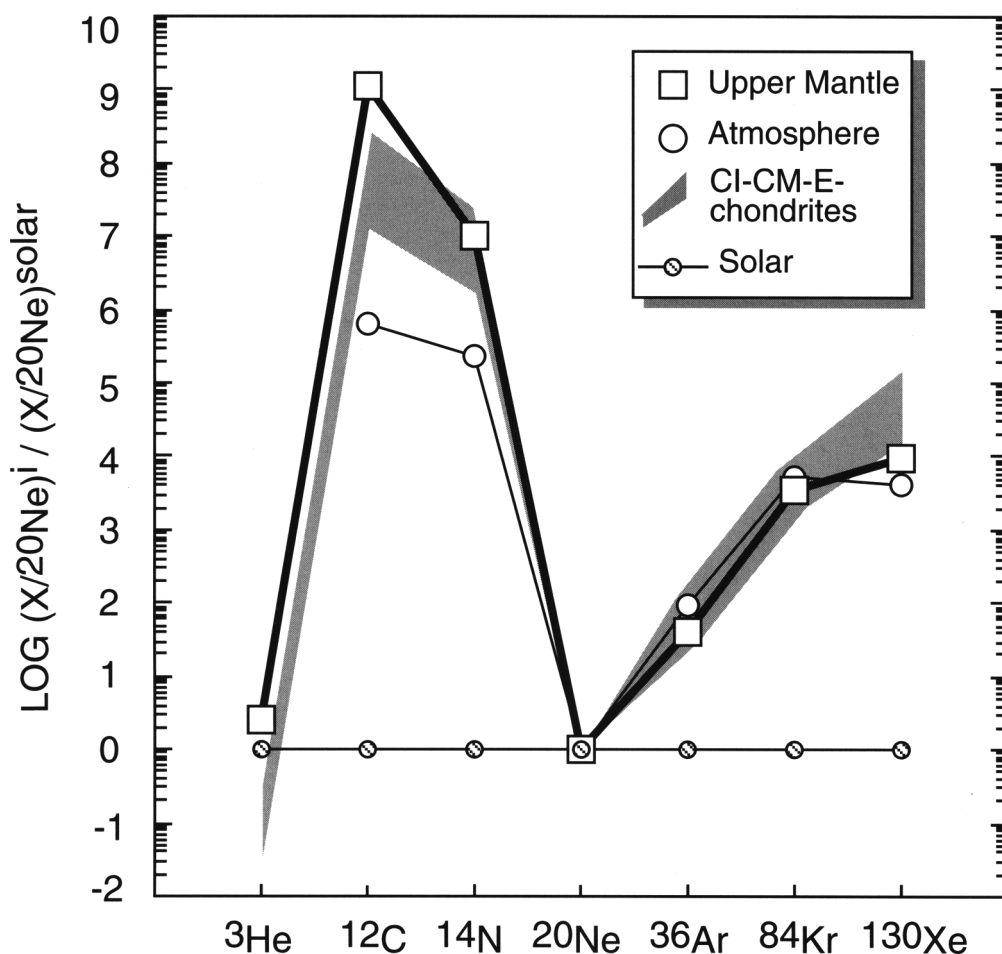


Fig. 2. Comparison of volatile abundance data in protosolar nebula (PSN), primitive chondrites, terrestrial mantle and 'atmosphere' (atmosphere *sensu stricto*, crust, sediments, oceans). Data are normalized to ^{20}Ne and PSN, so that the PSN pattern is flat. The choice of ^{20}Ne as a normalizing isotope is based on the observation that recycling of atmospheric neon in the mantle is limited as indicated by its isotopic composition. Data sources: Mazor *et al.* (1970), Marty & Jambon (1987), Anders & Grevesse (1989), Pepin (1991), Moreira *et al.* (1998), Ozima *et al.* (1998), Marty & Zimmermann (1999).

Marty & Zimmermann (1999) and, for heavy rare gases, we have also used the best available estimates of the upper-mantle composition (Moreira *et al.* 1998).

The mantle displays a chondritic pattern, and this similarity provides important information on the process of delivery, as it suggests that the bulk fraction of these volatiles was delivered with minimal fractionation to the Earth by chondritic-like material. In fact, it is very surprising that such a chondritic pattern could have been preserved despite the severe fractionating processes that are likely to have occurred

during formation of the Earth, such as impact degassing, core formation or atmospheric escape. Indeed, the Earth's mantle is extremely depleted in volatile elements, by a factor of 10^{-3} relative to carbonaceous chondrites in the case of nitrogen (1 ± 0.4 ppm N for the mantle, based on K–Ar–N systematics (Marty 1995; Dauphas & Marty 1999), compared with about $(1-3) \times 10^3$ ppm for carbonaceous chondrites). The situation resembles that of highly siderophile elements for which a chondritic pattern is found in the mantle despite drastic depletion (e.g. Righter & Drake 1997). These elements should have

been largely partitioned into the core, leaving the mantle much more depleted than is at present observed, and largely fractionated relative to the chondritic pattern. The late addition of a chondritic veneer (after core formation) is frequently advocated for siderophile elements (see 'The case of major volatiles', below). Could it be also the case for volatile elements? We discuss this possibility below for H and possibly C and N but it seems doubtful that rare gases could have been preserved in silicates during late impact shocks. The observation that volatile elements seem to be in chondritic proportion (and isotopic ratios for at least H, N and Ar) despite their drastic depletion is enigmatic at present and will certainly put strong constraints on future models of volatile geochemistry.

There are two notable exceptions to the chondrite analogy. First, carbon is enriched in the mantle relative to other cosmochemical reservoirs, and this difference is likely to reflect preferential recycling of carbon from the surface, as carbon at the Earth's surface is mainly present in sediments as carbonates and organic matter (Javoy *et al.* 1986). This view is consistent with the first-order homogeneity of C isotopes in the mantle and at the Earth's surface, as mentioned above (part of surface nitrogen has probably been recycled also and its fate will be discussed below). Second, the He/Ne ratio of the mantle is similar to the solar ratio within a factor of two (Honda & McDougall 1997; Marty *et al.* 1998; Moreira *et al.* 1998), strongly suggesting that a major fraction of light rare gases in the mantle is derived from the PSN with limited fractionation.

The possibility that light rare gases originated partly from the PSN is confirmed by Ne isotopic ratios in mantle-derived rocks (Fig. 3). In the now classical three-isotope diagram for neon ($^{20}\text{Ne}/^{22}\text{Ne}$ v. $^{21}\text{Ne}/^{22}\text{Ne}$), the mantle differs from atmospheric neon by excesses of ^{20}Ne and ^{21}Ne relative to ^{22}Ne (Sarda *et al.* 1988; Marty 1989; Staudacher *et al.* 1989; Honda *et al.* 1991, 1993a, b; Hiyagon *et al.* 1992; Marty *et al.* 1998; Moreira *et al.* 1998). In this diagram format, mixing between two Ne components translates into a straight line joining dots representing these components. Excesses of ^{21}Ne result from nuclear reactions such as neutron activation of oxygen in the mantle or spallation reactions by cosmic rays and are not a primordial character. In contrast, high $^{20}\text{Ne}/^{22}\text{Ne}$ ratios in the mantle relative to the air composition require the presence of a primordial Ne component different from that present in the atmosphere, as no known nuclear process can produce the observed excesses of ^{20}Ne . $^{20}\text{Ne}/^{22}\text{Ne}$ ratios observed for

some of the mantle-derived rocks analysed so far are higher than those of neon-Q ($^{20}\text{Ne}/^{22}\text{Ne} = 10.7$), a meteoritic component thought to characterize best rare gases trapped in chondrites (Wieler *et al.* 1992), or SEP neon ($^{20}\text{Ne}/^{22}\text{Ne} = 11.2$) (e.g. Ozima *et al.* 1998), a high-energy component of the solar corpuscular emission. Therefore, mantle samples display Ne isotope variations that are best explained by mixing between atmospheric neon ($^{20}\text{Ne}/^{22}\text{Ne} = 9.80$) and a ^{20}Ne -rich component such as neon ($^{20}\text{Ne}/^{22}\text{Ne} = 13.8$) as measured in solar-wind irradiated lunar soils (e.g. Ozima *et al.* 1998). The observation that the abundance pattern of volatiles normalized to ^{20}Ne reproduces a chondritic pattern despite a presumably solar origin for Ne is not problematic. Indeed, neon in the mantle seems to include also a meteoritic-like component (Trieloff *et al.* 2000). Trieloff *et al.* remarked that very few, if any, Ne isotope data with good accuracy have $^{20}\text{Ne}/^{22}\text{Ne}$ higher than 12.5 and proposed that neon in the mantle was not exactly solar but included a component of the type found in some gas-rich chondrites. In addition, as the solar pattern of rare gases is highly enriched in He and Ne relative to the chondritic pattern, mixing of the two results in He/Ne ratio close to solar together with a near-chondritic-like Ar/N ratio. The fact that the N/Ne ratio is also chondritic is the result of the extreme relative depletion of nitrogen in the solar composition (N/Ne = 0.8) relative to the chondritic pattern (N/Ne *c.* 10^7).

The case of trapping light rare gases in the terrestrial mantle from the PSN with little fractionation requires the presence of the PSN and gas-dust exchange during the early stage of accretion of terrestrial planets. The process of trapping is unclear and could be adsorption on accreting dust. However, such a process would probably result in elemental He-Ne fractionation (although the lack of adsorption data for light rare gases prevents quantitative evaluation of this possibility). PSN gases could also have been occluded in pores of accreting material, a process that would have been able to prevent elemental fractionation. Further compaction would have then resulted in occlusion of pores and subsequent trapping into mantle-forming silicates. Another possibility is gas exchange between the PSN and the Earth in a molten stage; for example, during episodes of magma ocean in the presence of a thick proto-atmosphere derived from the PSN (Abe & Matsui 1986). Equilibrium dissolution of rare gases into silicate melts would have resulted in He-Ne fractionation by a factor of *c.* 2 (e.g. Jambon *et al.* 1986) which is within the uncertainty of the mantle He/Ne ratio.

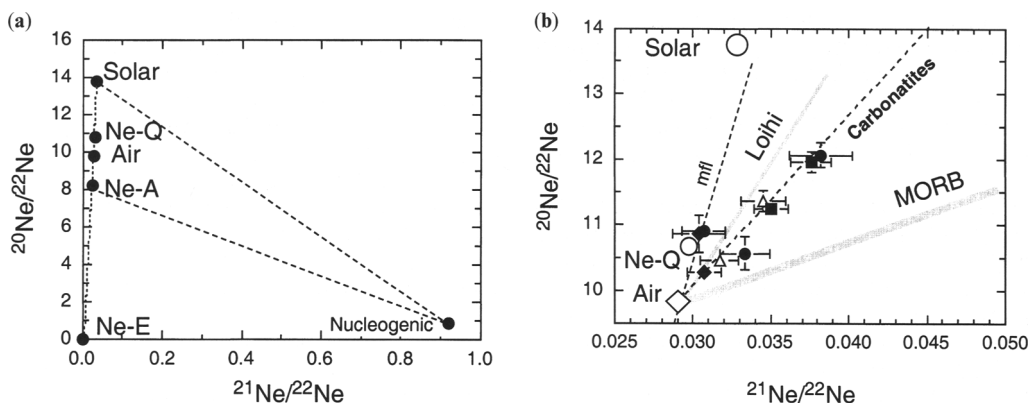


Fig. 3. Diagrams of three neon isotopes. In this format, mixing between end-members is represented by straight lines. **(a)** Overall variations of Ne isotopes in nature. ^{21}Ne and ^{22}Ne are produced significantly by natural nuclear reactions such as neutron activation of oxygen and fluorine, and spallation by cosmic rays. The PSN component is represented by the analysis of solar wind and displays the highest $^{20}\text{Ne}/^{22}\text{Ne}$ ratio measured so far. Neon-Q is a ubiquitous rare gas component trapped in primitive meteorites (Wieler *et al.* 1992); neon-A, often called planetary neon, is another meteoritic end-member but it is not clear if it represents a single, well-individualized component or a mixture between other neon components; neon-E is almost pure ^{22}Ne of nucleosynthetic origin. It should be noted that atmospheric neon presents a $^{20}\text{Ne}/^{22}\text{Ne}$ ratio intermediate between solar and Ne-A. Dashed lines between Ne-A, solar and nucleogenic Ne represent the field of values observed in meteorites. **(b)** Ne isotope variations in mantle-derived samples. Mid-ocean ridge basalts (MORB) are thought to derived directly from the convective mantle driving plate tectonics and are represented by an array between atmospheric neon and a mantle component enriched in both ^{20}Ne and ^{21}Ne (Sarda *et al.* 1988). The latter enrichment is accounted for by production and accumulation of nucleogenic neon in the mantle whereas the ^{20}Ne enrichment is regarded as representing the occurrence of solar-type neon in the mantle. A similar situation is observed for samples linked with mantle plumes such as Hawaii (Loihi Seamount is the youngest volcano of the Hawaiian chain (Honda *et al.* 1991; Hiyagon *et al.* 1992)) or carbonates and associated minerals from the Kola Peninsula (data points are represented to illustrate their spread and uncertainties (Marty *et al.* 1998)). mfl (Mass fractionation line) represents the effect of isotopic mass fractionation on neon isotopes.

Atmosphere and volatile recycling

The atmosphere presents a fractionated rare gas pattern somewhat similar to that of chondrites, but there are also two major differences. First, C and N are underabundant relative to chondritic pattern (Fig. 2). We have advocated recycling through time for carbon and possibly for nitrogen as a net sink for surface C and N. For carbon, this would make the mantle and 'atmosphere' patterns converge towards the shaded zone representing the field of chondrites. A similar effect is also expected for nitrogen. The 'atmosphere' reservoir and the mantle reservoir contain approximately the same amount of nitrogen (Marty 1995), equivalent to 1 ppm when normalized to the mass of the mantle. Contrary to the case of carbon, the two reservoirs differ isotopically by *c.* 5%, which is significant for the Earth, but not for extraterrestrial reservoirs. Therefore, we postulate that nitrogen was exchanged actively between the surface and the mantle, but not to a point erasing isotopic differ-

ences (the isotopic difference may alternatively result from isotopic fractionation, a possibility that will be discussed in another paper). It must be emphasized that most of nitrogen recycling must have taken place before *c.* 3 Ga ago, as both mid-ocean-ridge basalts, sampling the present-day upper mantle, and diamonds (Cartigny *et al.* 1997), which sampled the ancient (for some of them Archaean) subcontinental lithospheric mantle, present a similar distribution of $\delta^{15}\text{N}$ values centred around -4% . A further argument for nitrogen recycling is based on the N_2/Ar ratio of the upper mantle (Marty 1995). The $\text{N}_2/^{40}\text{Ar}$ ratio of this reservoir is comparable with that of the atmosphere and, as ^{40}Ar is produced by ^{40}K , this similarity suggests a similar behaviour of N and K. Nitrogen can substitute for K^+ in the form of NH_4^+ , which make these two elements potentially recyclable at similar rates. In contrast, the $\text{N}_2/^{36}\text{Ar}$ ratio of the mantle is two orders of magnitude higher than that of the atmosphere, exactly what is expected if nitrogen is recycled and ^{36}Ar is not.

Apart from the case of recycling as a source of atmosphere alteration, the isotopic compositions of atmospheric neon (and xenon; see Introduction) do not support a mantle origin. An important feature of the atmosphere is its $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of 9.8, much lower than that of the mantle. Assuming that atmospheric Ne was also solar-like initially, its present-day value requires extensive isotopic fractionation, which might have taken place either in precursors or in the atmosphere itself during early evolution (Zahnle *et al.* 1988). In the first possibility, late accreting material would have released a low $^{20}\text{Ne}/^{22}\text{Ne}$ component (Marty 1989). Indeed, $^{20}\text{Ne}/^{22}\text{Ne}$ ratios as low as eight are observed in bulk chondrites (Mazor *et al.* 1970) and are thought to result from mixing between a nucleosynthetic ^{22}Ne -rich end-member and the well-characterized trapped Ne-Q component (Wieler *et al.* 1992) and/or solar Ne. Alternatively, atmospheric neon could have been isotopically fractionated by hydrodynamic escape of a thick proto-atmosphere (Zahnle *et al.* 1988). Early models required an extremely thick hydrogen-rich atmosphere to start with (Hunten *et al.* 1987; Sasaki & Nakasawa 1988), which faced a serious problem with conventional models of planetary formation in the terrestrial feeding zone. In this type of scenario, a hydrogen-rich atmosphere, either a remnant of the PSN or the result of strong reduction of water by molten iron, possibly ionized by an enhanced solar UV flux, escapes from the terrestrial gravitational field and entrains other volatile species following a distillation process that greatly fractionates isotopes according to their mass difference. Subsequent works showed the role of other atmospheric constituents such as CO, CO₂ and H₂O in increasing significantly the efficiency of isotopic fractionation during escape (Ozima & Zahnle 1993), which removed the need for a very thick proto-atmosphere. Model calculations show that, depending on the atmospheric composition, Ne can be fractionated from the solar composition to the atmospheric composition with limited Ne loss (Ozima & Zahnle 1993). Further models advocated giant impacts to blow off partially the early atmosphere of the Earth (Pepin 1997), but it is not yet clear if such events would have resulted in extensive isotopic fractionation (Melosh & Vickery 1989). Atmospheric escape could also account for the underabundance of C and N in the atmosphere relative to Ne (Fig. 2), provided that these elements were in the form of species lighter than ^{20}Ne , which could be lost more efficiently than neon. The best candidates for these are methane ($m = 16$) and ammonia ($m = 17$), implying escape

when the atmosphere was strongly reducing (a detailed scenario for isotope fractional loss of nitrogen has been developed by Tolstikhin & Marty (1998)).

Atmospheric xenon is also isotopically unique among Xe components in the Solar System (with the possible exception of Martian atmospheric Xe, e.g. Swindle 1995) as it is fractionated by 3% per atomic mass unit (a.m.u.). In addition, atmospheric xenon is depleted relative to the chondritic or solar patterns: the Kr/Xe ratio of air is 25 times the mean ratio of chondrites (Fig. 2). The depletion of xenon is not consistent with its isotopic fractionation because, in the first case, the heavy element (Xe) is depleted relative to the lightest one (Kr) and, in the second case, the light isotopes (e.g. ^{124}Xe) are depleted relative to the heavy ones (e.g. ^{136}Xe). The elemental depletion of Xe could be due to xenon trapping in a terrestrial reservoir, but possibilities exclude ice or sediments, which cannot explain the 25-fold depletion (Podosek *et al.* 1981; Bernatowicz *et al.* 1985). Preferential subduction of Xe trapped in sediments could account qualitatively for it, but is not yet documented.

Timing

In this section we review briefly chronological constraints relevant to atmospheric evolution. The onset of condensation and accretion of the Solar System is well dated at 4.556 Ga from the analysis of primitive meteorites (Allègre *et al.* 1995). Recent accretion models propose that the duration to obtain Mars-sized planets would have been fairly short, less than 10 Ma (see, e.g. Chambers & Wetherhill 1998). The typical time interval indicated by extinct radioactivities to differentiate primitive meteorite parent bodies into metal and silicates is also short, of the order of few million years (e.g. Wetherill 1975; Lee & Halliday 1995). The formation of the giant planets would have also been a relatively short process (<10 Ma), but the process of accretion of terrestrial planets would have slowed down, given the decreasing availability of bodies in the inner Solar System. Recent models postulate a duration of 50–80 Ma to obtain a terrestrial planet of the size of the Earth (Vityazev *et al.* 1990; Weidenschilling *et al.* 1997). Some models postulate that, because of the presence of giant planets, gravitational forces would have deflected bodies formed in colder regions of the Solar System and therefore richer in volatiles to the inner Solar System (e.g. Chambers & Wetherhill 1998; Petit *et al.* 1999). Periodic gravitational forces produced by Jupiter and Saturn could

move bodies from the asteroidal belt located in specific narrow zones known as orbital resonances into elongated orbits crossing the terrestrial region. The efficiency of such a process is so high that such zones would have become quickly exhausted and, recently, Vokrouhlicky & Farinella (2000) have proposed that such zones could be continuously refuelled in meteoritic fragments because of the drag exerted by emission of thermal radiation from objects asymmetrically exposed to the Sun. Linking the efficiency of terrestrial bombardment with the solar radiation presents the exciting possibility of modulating the bombardment of the Earth with solar activity.

The life duration of the PSN, the presence of which is required to feed solar-type Ne in the terrestrial matter forming the mantle, is thought to have not exceeded 10–20 Ma (Montmerle 1999). Hence it is conceivable that, if solar-like light rare gases now seen in the mantle were trapped directly from the PSN during accretion or during exchanges between the proto-mantle and a PSN-rich atmosphere, these processes could not have lasted more than a few tens of million years, and that both waning of the PSN and increasing rate of degassing of bodies impacting on the growing Earth would have prevented further delivery of rare gases to the interior of the Earth. The Hf–W chronometer allows proposal of a time interval of 10–60 Ma to form the core (Lee & Halliday 1995), depending on which type of model (e.g. continuous accretion and differentiation v. single-stage differentiation) is adopted. As stated above, the time required to grow the Earth to its present-day mass is ≤ 100 Ma, and such a duration is in agreement with the lead isotope record of the mantle (Allègre *et al.* 1995). Notably, the age of the Moon-forming event is of the order of 4.46 Ga (e.g. Heiken *et al.* 1991), and the use of the coupled ^{146}Sm – ^{147}Sm system allows us to constrain the initial mantle differentiation yielding the first crustal reservoir to 4.47 Ga (Jacobsen & Harper 1996). Finally, evidence has been reported from zircon analysis that a continental crust existed 4.4 Ga ago (Wilde *et al.* 2001), and that liquid water was present 4.3 Ga ago (Mojzsis *et al.* 2001).

We postulate, in view of these constraints, that rare gases were delivered to the Earth and fractionated in the atmosphere mainly within the first 100 Ma, possibly within 50 Ma, when most of the terrestrial accretion took place. During this period, atmosphere and proto-mantle rare gases were actively exchanged and rare gas fractionation took place following a combination of impact degassing, atmospheric escape and

mantle–atmosphere exchange during magma ocean stages (Sasaki & Nakasawa 1988; Pepin 1997; Tolstikhin & Marty 1998). Rare gas modelling of mantle–atmosphere differentiation suggests that these reservoirs might have remained ‘open’, that is, might have continued to exchange their volatiles between reservoirs or with space during a longer period up to 100 Ma, but also predicts that the corresponding fluxes would have decreased dramatically with time (Pepin 1991; Tolstikhin & Marty 1998).

Rare gas models

The fractionation of rare gases in the atmosphere cannot be explained in a straightforward manner and calls for selective fractionation processes. Several sophisticated models have been developed in which each rare gas is affected selectively by a combination of mixing and isotope fractionation during atmospheric escape events. Pepin (1991, 1997) assumed a two-stage hydrodynamic atmospheric escape. In the first stage, a H_2 -rich proto-atmosphere containing CO , N_2 and the noble gases in proportions found in primitive chondrites was driven by intense extreme-ultraviolet (EUV) radiation from the young evolving Sun starting at a solar age of *c.* 50 Ma. This episode was followed by a long (*c.* 80 Ma) period of quiescence, followed by abrupt degassing of remnant H_2 , CO_2 and N_2 from the mantle and of light rare gases trapped deep in the Earth having a solar composition. Hydrodynamic escape resumed with the available H_2 in a waning but still potent EUV flux. Atmospheric volatiles remaining at the end of this second stage, 4.2 Ga ago, formed the bulk of the present-day atmosphere. The role of atmospheric erosion by giant impacts was further considered but did not change the essence of this two-stage scenario (Pepin 1997). Tolstikhin & Marty (1998) attempted to integrate in a global model the formation of the Earth, the differentiation of the mantle and the formation of the atmosphere. They proposed a combination of isotopic fractionation during hydrodynamic atmospheric escape and mantle–atmosphere exchange, with significant differences from Pepin’s models. A gradual, single-stage process in which solar-like rare gases and chondritic N were contributed by impacts in the presence of the PSN was postulated. The selective fractionation of each rare gas took place during ocean magma episodes when rare gases were sorted according to their respective solubilities in basaltic melt during vigorous magma convection. The timing of these processes was derived from the I–Pu–Xe

systematics and the model predicted that the atmosphere was settled for its rare gases and nitrogen >4.3 Ga ago. The models of Pepin (1991) and Tolstikhin & Marty (1998) agree on several important predictions: (1) both the PSN and chondritic-type material contributed terrestrial volatiles; (2) during the first tens of million years the forming mantle and atmosphere exchanged volatiles; (3) the atmosphere (and the mantle) were closed early in the Earth's history around 4.3 Ga ago and the atmospheric composition (but not its chemistry) experienced little change since then; (4) they require intense yet decreasing EUV during a long period, e.g. 100–200 Ma. This also poses the problem of penetration of the EUV radiation in an initially dense region. These models call for very specific conditions and processes, which will need close

examination to confirm or refute. It may also be possible that we still ignore the composition of the contributing sources, and with this respect comets deserve special attention, as the process of rare gas trapping at low temperature in their ice might have resulted in specific fractionation that remains to be documented. The recent discovery that comet C/1995 O1 (Hale Bopp) contains argon in solar proportion (Stern *et al.* 2002) suggests, however, that fractionation of heavy rare gases in comets is unlikely.

The case of major volatiles

The case of major volatiles deserves special attention, as it was these elements that shaped the early terrestrial environment necessary for the

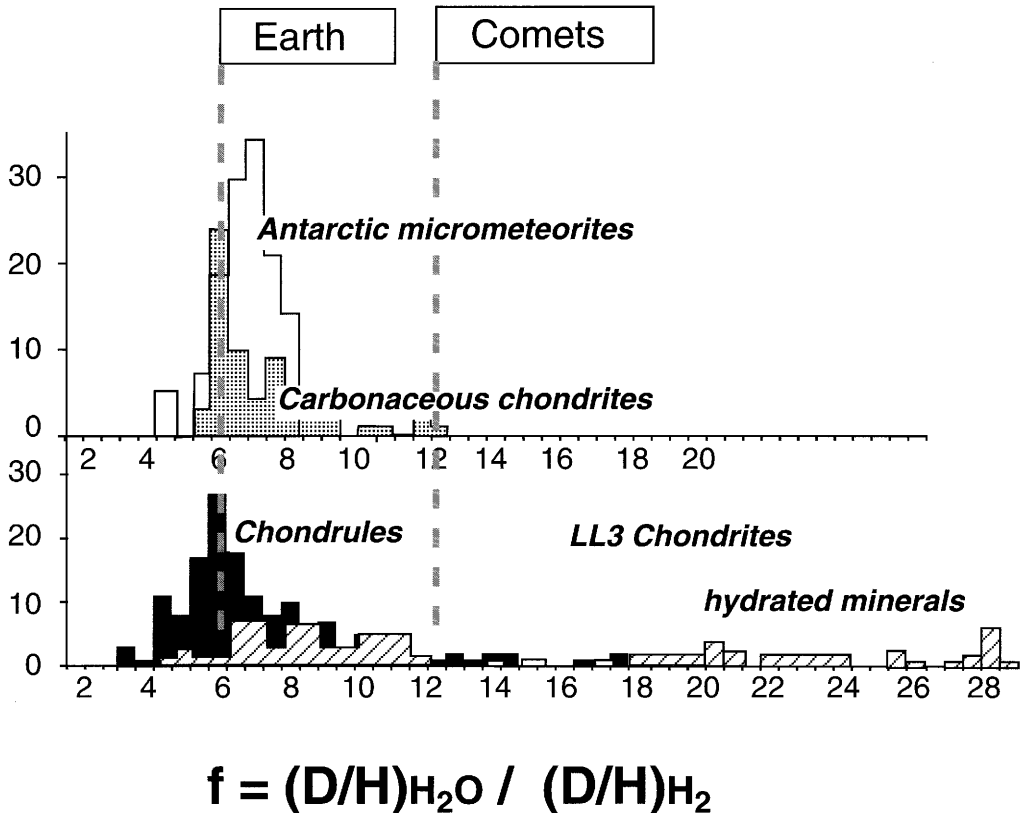


Fig. 4. Isotopic variations of hydrogen in the Solar System (adapted from Robert *et al.* 2000). The deuterium/hydrogen ratio of different components is normalized to the D/H ratio of the Sun (as it was before deuterium burning), which is thought to represent H₂ in the protosolar nebula. Numbers along the y-axis represent the numbers of cases. Terrestrial hydrogen is enriched in deuterium by a factor of about six relative to solar. Among Solar System objects analysed so far, carbonaceous chondrites, Antarctic micrometeorites (Engrand & Maurette 1998) and chondrules from LL3 chondrites present a distribution of D/H values that centre around the terrestrial D/H ratio. Notably, comets analysed so far (Halley, Hale Bopp and Hyakutake, references given by Dauphas *et al.* (2000)) present D/H values about two times higher than the terrestrial value.

development of life. A direct derivation of major volatile elements from the PSN is not supported by abundance data and H, N isotopic ratios, which rather favour a chondritic origin (Fig. 2).

The D/H ratio of Solar System reservoirs presents variations over a factor of 30 (Fig. 4), which are thought to result from mixing of PSN-type hydrogen and D-rich compounds (Geiss & Gloecker 1998; Robert *et al.* 2000). The deuterium enrichment of the latter is attributed to trapping of hydrogen-bearing molecules that experienced low-temperature fractionation in molecular clouds during ion–molecule exchanges. This makes the hydrogen isotopic composition a good diagnostic tracer of sources and mixings among Solar System objects (Robert *et al.* 2000). Hydrogen in water of terrestrial oceans is enriched by a factor of six relative to solar (pre-deuterium burn-ing) hydrogen (Fig. 4) and cannot be derived from the PSN directly. It is possible, however, that hydrodynamic escape of PSN hydrogen would have favoured preferential escape of hydrogen, leaving residual hydrogen rich in deuterium. However, the terrestrial D/H ratio is within the range of values found in primitive meteorites, and this similarity strongly suggests a chondritic origin for terrestrial water. It is also important to note that the terrestrial D/H ratio is clearly different from those of comets as far as the few available data are representative of these objects. Therefore hydrogen isotopic data favour a derivation of terrestrial hydrogen from chondrite-like bodies, with limited, if any, fractionation.

A similar scenario emerges from N isotope systematics. Most planetary objects display $^{15}\text{N}/^{14}\text{N}$ ratios around the terrestrial atmospheric value within 50‰. These objects include the Earth, Venus (Mars constitutes an exception as its atmosphere is enriched by >600‰ in ^{15}N , presumably as a result of fractional loss of nitrogen, e.g. Yung & DeMore 1999), carbonaceous chondrites and notably enstatite chondrites, which constitute a building material of reference as their oxygen isotopic compositions lie on the terrestrial fractionation line (Javoy *et al.* 1986). Recently, Hashizume *et al.* (2000) proposed that solar wind nitrogen is enriched in ^{15}N relative to the terrestrial atmosphere ($\delta^{15}\text{N} \leq 240\text{‰}$) based on ion probe analysis of lunar soil grains, and Owen *et al.* (2001) proposed a solar N composition of $\delta^{15}\text{N} = -370 \pm 80\text{‰}$ from Galileo data for the atmosphere of Jupiter. Thus it is conceivable that nitrogen in the Solar System is the result of mixing between gaseous nitrogen of the PSN and a ^{15}N -rich component carried by solid phases and mostly present in planetary bodies. The incorporation of solar nitrogen would have resulted in ^{15}N -poor nitrogen, which is not seen at the Earth's surface although a remnant of it could be still present in the deep Earth (although the N/Ne ratio of the mantle does not support this possibility). Interestingly, mid-ocean ridge lavas are slightly depleted in ^{15}N by 5‰ relative to atmospheric N. There are, however, other possibilities such as enstatite-type nitrogen, which is depleted by 20–40‰ in ^{15}N relative to atmospheric N (Javoy *et al.* 1986).

Table 1. Elemental composition of comets

	Dust (mol g ⁻¹)	Gas (mol g ⁻¹)	Bulk (mol g ⁻¹)
H	0.050 ± 0.010	0.081 ± 0.017	0.067 ± 0.010
C	0.020 ± 0.003	0.009 ± 0.002	0.014 ± 0.002
N	0.0010 ± 0.0003	0.0045 ± 0.0022	0.0029 ± 0.0012
O	0.022 ± 0.002	0.045 ± 0.002	0.034 ± 0.002
Na	0.00025 ± 0.00015	–	0.00012 ± 0.00007
Mg	0.0025 ± 0.0002	–	0.0012 ± 0.0002
Al	0.00017 ± 0.00004	–	0.000079 ± 0.000023
Si	0.0046 ± 0.0005	–	0.0021 ± 0.0004
S	0.0018 ± 0.0006	0.00045 ± 0.00022	0.0011 ± 0.0003
K	0.0000050 ± 0.0000025	–	0.0000023 ± 0.0000012
Ca	0.00016 ± 0.00005	–	0.000073 ± 0.000025
Ti	0.000010 ± 0.000005	–	0.000005 ± 0.0000025
Cr	0.000022 ± 0.000005	–	0.000010 ± 0.000003
Mn	0.000012 ± 0.000005	–	0.0000061 ± 0.0000026
Fe	0.0013 ± 0.0002	–	0.00060 ± 0.00014
Co	0.0000074 ± 0.0000050	–	0.0000034 ± 0.0000024
Ni	0.00010 ± 0.00005	–	0.00005 ± 0.000025

Dust composition is from Jessberger *et al.* (1988), gas composition is from Delsemme (1988). Bulk abundances were calculated assuming that the dust/gas ratio of typical comets is within 0.5–1.3 (Delsemme 1988). Uncertainties were propagated accordingly.

The late bombardment of the Earth

The term late generally refers to addition of material to the growing Earth once its differentiation was completed. It does not quantify any time interval but the term late is used because such addition is thought to have occurred once the Earth had reached a 'significant' size allowing differentiation and internal evolution. Hence material added after the major building period was not in chemical equilibrium with the bulk Earth. Planets formed from the accretion of planetary material, and this process is still going on at present although at a much lower rate than 4.56 Ga ago. The density of lunar craters increases with the age of the exposed surface in a manner indicative of an overall decline with time of the bombardment intensity (e.g. Chyba 1990; Heiken *et al.* 1991). It is interesting to note that this idea was first stated based on the superposition principle cherished by field geologists 7 years before the first lunar samples were collected and brought back to Earth (Shoemaker & Hackman 1962). It is estimated from the lunar impact record that the mass of asteroids and comets that fell during late bombardment on our planet is within 1×10^{21} to 7×10^{23} kg, with a preferred value of 3.2×10^{21} kg as derived from fitting of the cumulative crater density v. age curve (Chyba 1990).

Additional evidence that remnants of planetary formation struck the Earth at a much higher rate in the Hadean Eon than at present comes from highly siderophile elements (Ru, Rh, Pd, Re, Os, Ir, Pt and Au). When the core segregated from the mantle, highly siderophile element should have been partitioned into the core, leaving the mantle depleted and fractionated. The concentrations of highly siderophile elements in the mantle are much higher than those predicted in the case of equilibrium partitioning between metal and silicate. In addition, the highly siderophile element abundance pattern of the mantle is almost unfractionated relative to potential Earth-forming material (e.g. Righter & Drake 1997). A straightforward interpretation is that a late veneer brought highly siderophile elements into the mantle after the core formed. It has been suggested that highly siderophile elements were not in chondritic proportion in the Earth's mantle and were carried by non-chondritic extraterrestrial material or by the entrainment of core material by plumes. Alard *et al.* (2000) measured highly siderophile elements in mantle sulphides and concluded that non-chondritic highly siderophile element abundance patterns directly reflect processes occurring in the upper mantle and are not evidence for the addition of core material

or exotic meteoritic components. The mass of extraterrestrial matter necessary to account for the budget of siderophile elements in the mantle is $(1-4) \times 10^{22}$ kg (Chyba 1991).

Several observations suggest that our planet was struck by volatile-rich bodies. Carbonaceous asteroids are overwhelmingly the most abundant type in the main belt. Whether pieces of C-type asteroids are present in meteorite collections is debatable but it seems that their reflectance spectra best match that of the carbonaceous chondrites, specifically of the CI-CM types (Gaffey *et al.* 1993). The extraterrestrial flux to Earth is dominated by carbonaceous micrometeorites (Engrand & Maurette 1998). They lack a strict equivalent among macroscopic samples but their closest analogues are CM carbonaceous chondrites (Kurat *et al.* 1994). Most xenoliths in meteorite regolithic breccias share affinities with carbonaceous chondrites, which implies that asteroids were embedded in a swarm of carbonaceous material (Anders 1978). The lunar regolith is enriched in trace elements relative to indigenous lunar rocks. The trace element pattern of this enriched compound best matches that of carbonaceous chondrites, implying in turn that the lunar regolith contains 1-2% of carbonaceous debris (Keays *et al.* 1970).

When an asteroid or a comet strikes the Earth, part of it and of Earth's atmosphere might be ejected back into space. Recent analytical and computational modelling of impact induced erosion led Newman *et al.* (1999) to conclude that impact events would not remove significant atmospheric gases. As discussed above, the isotopic ratio of hydrogen supports the contribution of carbonaceous chondrites for the origin of water on Earth. Recent observations indicate that comets are enriched in deuterium relative to the oceans by a factor of two, which prevents the possibility that comets contributed a significant fraction of Earth's hydrosphere (<10%) unless one calls on hypothetical comets. It is noteworthy that all the three comets so far measured originate in the Oort cloud, and the scientific community is in need of the determination of the D/H ratio in Kuiper belt objects to ascertain the idea that comets did not significantly contribute to Earth's oceans. Delsemme (1988) calculated the composition of comets and we give an updated version of this compilation where uncertainties were propagated rigorously and the dust composition was modified according to Jessberger *et al.* (1988). The D/H ratio of the deep mantle is much lower than that of Earth's surface (Deloule *et al.* 1991). An appealing possibility is that the D/H ratio of the deep mantle is a remnant of the hydrogen isotopic composition of

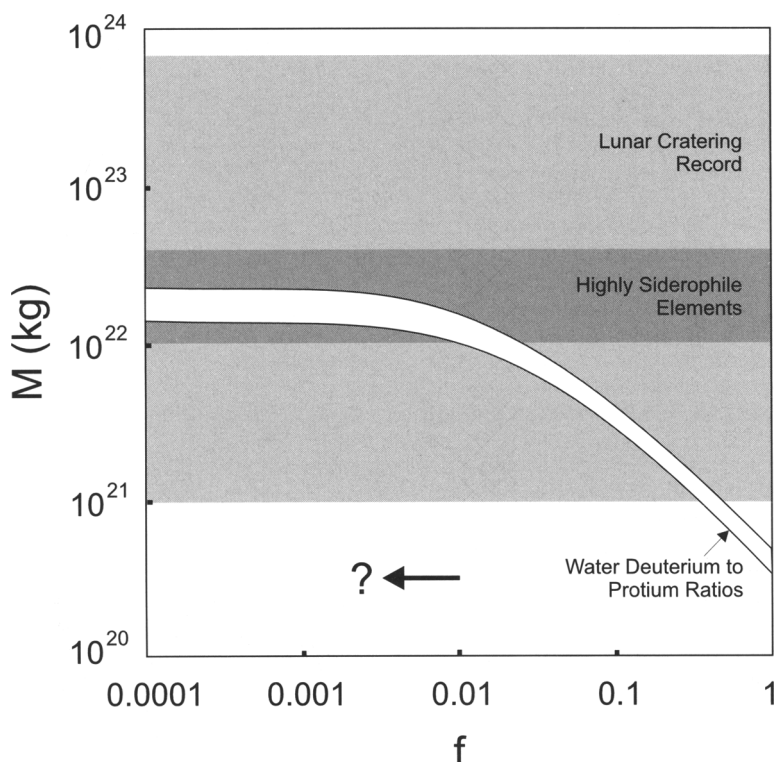


Fig. 5. The mass (M) of asteroids and comets that fell on Earth is reported as a function of the mass fraction (f) of comets among impacting bodies. Lunar cratering record (Chyba 1990), highly siderophile elements (Chyba 1991) and water deuterium to protium ratios (Dauphas *et al.* 2000) are shown. If these three approaches record the late bombardment over the same period of time, then M is $c. 2 \times 10^{22}$ kg and $f \leq 0.01$. Actually, the mass of asteroids and comets evaluated by the lunar cratering record and highly siderophile elements depends on the mass fraction of comets. Given the level of uncertainty on all these estimates (M and f are reported in a log–log plot), taking this effect into account would not affect our conclusions.

Earth-forming planetesimals, which later evolved as a result of the late accretion of asteroids and comets. Thus, the mass of asteroids and comets incident on Earth since the time of its accretion required to balance the low D/H ratio of the deep mantle is estimated to be 4×10^{20} to 2×10^{22} kg (Dauphas *et al.* 2000). It is worth while to note that fractionation of D/H within the Earth might explain the isotopic heterogeneity of Earth, but we wish to emphasize that the few elements for which there exists an isotopic heterogeneity are those that are not efficiently recycled, those that are prone to record the heterogeneous accretion of the Earth.

It is worth while to note that the estimates based on the lunar cratering record, highly siderophile elements and water deuterium to protium (D/H) ratios integrate the late bombardment of Earth over time scales that are not necessarily

identical. In the case of the lunar cratering record, time zero corresponds to the moment when the Moon formed. In the case of highly siderophile elements, time zero corresponds to the moment when the Earth's core formed. In the case of water deuterium to protium ratios, time zero corresponds to the moment when the bulk Earth had a D/H ratio lower than that of the present deep mantle. One might see the remarkably good agreement between the various approaches as merely coincidental. Alternatively, it means that the Moon, highly siderophile elements and water D/H ratios recorded the late heavy bombardment over the same period of time. If so, the mass of extraterrestrial matter that fell on Earth throughout its history must be the same from all point of views. The only locus where the mass of extraterrestrial matter incident on Earth is the same from all point of views is for low mass fractions of

comets among impacting bodies (<1%). This inference is highly speculative because it relies on the assumption that all three approaches integrated the late bombardment of Earth over the same period of time, but if it was proven to be right it would have strong implications for cometary dynamics and delivery of organic compounds to Earth.

It was suggested, based on water D/H ratios, that the late veneer consisted predominantly of carbonaceous asteroids and that the mass of extraterrestrial bodies incident on Earth since the time of its accretion was $c. 2 \times 10^{22}$ kg. The carbon and nitrogen concentrations of carbonaceous chondrites are 1.5×10^{-3} and 4.2×10^{-5} mol g⁻¹, respectively. If a late veneer supplied Earth with the water required to balance the low D/H of the deep mantle, then it should have contributed to Earth $c. 3 \times 10^{22}$ and 8×10^{20} mol of carbon and nitrogen, respectively. The Earth's surface (atmosphere + sediments + igneous crust) has 9×10^{21} and 3.5×10^{20} moles of carbon and nitrogen, respectively. These estimates are in surprisingly good agreement with the inferred contributions of late bombardment for carbon and nitrogen (3×10^{22} mol and 8×10^{20} mol, respectively) if one considers that a significant fraction of carbon and possibly nitrogen has been recycled into the mantle through time. It implies that carbonaceous asteroids might have contributed a significant fraction of hydrogen, carbon and nitrogen on Earth, presumably in the form of prebiotic molecules such as amino acids and heterocycles.

Conclusions

The major conclusion of this work is that there exists a chondritic-like component for volatile elements in the terrestrial mantle, not only for elements presenting a chemical affinity for silicates or metal such as C and N but also for chemically inert gases. A chondritic, rather than solar, origin for volatile elements is consistent with the stable isotope composition of H, C and N and eliminates in the case of H a major contribution from comets. However, a major fraction of He and Ne may be derived from the protosolar nebula and this contribution can only be seen for these two elements because of their high abundance in the PSN. Despite their chondritic characteristics, the absolute abundances of volatiles in the mantles are three orders of magnitude lower than those of chondrites, as are also strongly siderophile elements. It may well be possible that the growing Earth did not fully equilibrate with the forming proto-atmosphere and the core, and preserved minor (10^{-3}) frac-

tions undifferentiated and later incorporated in the convection of the mantle.

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