



## Asteroidal impacts and the origin of terrestrial and lunar volatiles

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### ARTICLE INFO

#### Article history:

Received 22 May 2012

Revised 20 October 2012

Accepted 22 October 2012

Available online 2 November 2012

#### Keywords:

Earth

Moon

Asteroids

Composition

Impact processes

### ABSTRACT

Asteroids impacting the Earth partly volatilize, partly melt (O'Keefe, J.D., Ahrens, T.J. [1977]. *Proc. Lunar Sci. Conf.* 8, 3357–3374). While metal rapidly segregates out of the melt and sinks into the core, the vaporized material orbits the Earth and eventually rains back onto its surface. The content of the mantle in siderophile elements and their chondritic relative abundances hence is accounted for, not by the impactors themselves, as in the original late-veener model (Chou, C.L. [1978]. *Proc. Lunar Sci. Conf.* 9, 219–230; Morgan, J.W. et al. [1981]. *Tectonophysics* 75, 47–67), but by the vapor resulting from impacts. The impactor's non-siderophile volatiles, notably hydrogen, are added to the mantle and hydrosphere. The addition of late veneer may have lasted for 130 Ma after isolation of the Solar System and probably longer, i.e., well beyond the giant lunar impact. Constraints from the stable isotopes of oxygen and other elements suggest that, contrary to evidence from highly siderophile elements, ~4% of CI chondrites accreted to the Earth. The amount of water added in this way during the waning stages of accretion, and now dissolved in the deep mantle or used to oxidize Fe in the mantle and the core, may correspond to 10–25 times the mass of the present-day ocean. The Moon is at least 100 times more depleted than the Earth in volatile elements with the exception of some isolated domains, such as the mantle source of 74220 pyroclastic glasses, which appear to contain significantly higher concentrations of water and other volatiles.

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### 1. Introduction

It is widely accepted that the Earth is severely depleted in volatile elements with respect to the Sun and carbonaceous chondrites (Anders and Owen, 1977; Palme and O'Neill, 2005). The trend between volatility and depletion is particularly robust for the most typical lithophile elements such as K, Rb, Cl, and Zn. Depletion of volatile elements in the Moon is even stronger (Ganapathy and Anders, 1974), as attested to by the deficit of K and Pb with respect to refractory U, which poses a problem when taking into account recent observations that the lunar mantle contains higher-than-expected amounts of other volatile components, such as water (Hauri et al., 2011; Saal et al., 2008).

There is growing consensus that the Earth accreted in the inner Solar System where temperatures were too high for volatile elements to condense, implying that any volatiles now present in

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the Earth were delivered subsequently during later stages of terrestrial accretion (Owen and Bar-Nun, 1995). Addition of volatiles from the outer Solar System carried by debris of undifferentiated planetesimals, the so-called late veneer, during the clearing stages of the debris disk, is consistent with current understanding of accretion dynamics (Albarède, 2009; Morbidelli et al., 2000; Robert, 2001). There is, however, no consensus on whether late veneer addition is sufficient to account for the terrestrial abundances of volatile elements (Albarède, 2009; Chou, 1978; Halliday, 2008; Hirschmann and Dasgupta, 2009; Marty and Yokochi, 2006).

How the fraction of a percent of carbonaceous CI chondrites originally deemed to account not only for highly siderophile elements (Chou, 1978) but also possibly for the amount of volatiles in the Earth (Javoy, 1998; Marty and Yokochi, 2006) can be reconciled with evidence from other isotopic systems, which push this proportion to several percent (Lodders, 2000) and even higher (Fitoussi and Bourdon, 2012; Warren, 2011), is unclear. The high end of these estimates corresponds to an amount of volatile-rich material intermediate between the masses of the Moon and Mars. The present work focuses on the process by which water and volatiles

may have been added to the Earth and the Moon, on how much water and volatiles are still present and in which form, and on the timing and duration of the late veneer stage of accretion.

## 2. The role of vaporization in establishing planetary inventories

Historically, the concept of late veneer was introduced to resolve conflicting evidence between experiments predicting that highly siderophile elements (HSEs) and, among them, the platinum-group elements (PGEs), should be taken up entirely by the metal phase upon core segregation from the mantle, and the detectable abundances of PGEs and their chondritic relative distribution in the modern mantle (Chou, 1978; Jagoutz, 1979; Morgan et al., 1981). More recently it has become increasingly apparent from the high values of experimental metal/silicate partition coefficients of HSE that their concentrations in the terrestrial mantle cannot have been established by metal/silicate equilibrium, whether metal was emulsified or not (Murthy, 1991, see also Mann et al. (2012) and Walker (2009) and references therein). The excess HSE correspond to 0.4–0.7% of chondritic material, which must have been added sufficiently late in Earth's accretionary history to prevent it from equilibrating with the core.

This estimate of the late veneer proportion, however, neglects both vaporization and metal segregation during impact and therefore underestimates the amount of material added (Fig. 1). The minimum kinetic energy of material impacting the Earth is scaled by the escape velocity ( $11.2 \text{ km s}^{-1} = 62.7 \text{ MJ kg}^{-1}$ ) (Melosh, 1989). For a radial component of impact velocity of  $15 \text{ km s}^{-1}$  (Chyba, 1991), the liberated energy largely surpasses the vaporization enthalpy of olivine ( $\sim 3 \text{ MJ kg}^{-1}$ ) (Ahrens and O'Keefe, 1972). The energy of the impact is dissipated by shock waves in both the target and the projectile but the distribution of the energy released conditions the fate of the material (O'Keefe and Ahrens, 1977; Tonks and Melosh, 1993). For a random distribution of asteroid velocities, collision is expected to be oblique with a most probable angle of impact of  $45^\circ$  (Pierazzo and Melosh, 2000b). Oblique impacts generate a jet of high-speed, dense, hot vapor (Melosh and Sonett,

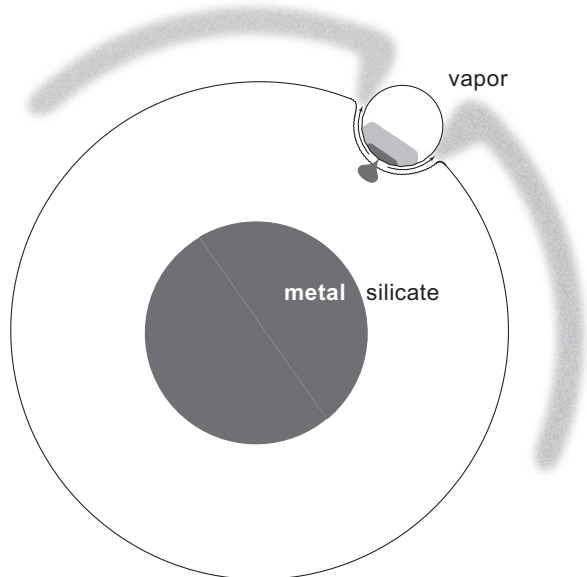
1986). Schultz (1996) demonstrated that, because of the friction from high shear stresses developing upon oblique impact, the amount of material vaporized increases when the angle of impact decreases with a maximum at  $30^\circ$ . In an oblique impact, the projectile itself is partly vaporized, partly molten (Pierazzo and Melosh, 2000a). Overall, it may be expected that about 10% of the impactor, even for small objects down to 5 km in size, is volatilized during the original impact (Canup, 2004; Pierazzo and Melosh, 2000a). Part of the vapor produced immediately condenses upon decompression and rains back onto the Earth, while the rest escapes into orbit under the combined effects of pressure gradient and exchange of angular momentum within the different layers of the jet (Stevenson, 1987). To draw an analogy with lunar impact models, the time scale for radiative cooling of the proto-lunar disk is  $10^2$ – $10^3$  years (Pahlevan and Stevenson, 2007). Meanwhile, the trajectories of the orbiting condensates evolve by momentum exchange, with some material migrating beyond the Roche limit (2.9 times the Earth radius) where it accretes to the Moon, whereas most of the remaining material falls back onto Earth (Canup and Esposito, 1995; Takeda and Ida, 2001).

A consequence of a high-velocity impact therefore is that the impactor is partly vaporized, with most of the vapor raining back down onto the Earth's surface and further into the terrestrial mantle. Vaporization of the terrestrial mantle itself at the contact with the impactor does not affect terrestrial inventories. If the incoming asteroid is undifferentiated, the impact indiscriminately adds siderophile, lithophile, and volatile elements from the impactor. It has been argued, however, that the heat released by the decay of  $^{26}\text{Al}$  and by repeated collisions will lead quickly to the differentiation of most impactors larger than  $\sim 30 \text{ km}$  (Ricard et al., 2009; Yoshino et al., 2003). Canup's (2004) simulations addressed such a case for the Moon-forming event. It was found that the impactor's core, present as an arm sheared past the target, re-coalesces and re-impacts the planet. To a large extent this new impact is equivalent to downrange ricocheting, which Schultz et al. (2006) demonstrated significantly contributes to the overall vaporization of the impactor.

Meanwhile, the non-vaporized part of the impactor undergoes extensive melting and, if the core is not already differentiated, iron segregates from the silicate. In order to explain the  $^{182}\text{Hf}$ – $^{182}\text{W}$  observations of the Earth–Moon system, it has been argued that equilibration of the terrestrial mantle with metal from the impactor is incomplete (Dahl and Stevenson, 2010; Kleine et al., 2009; Rudge et al., 2010; Schönbächler et al., 2010). Dahl and Stevenson (2010) ascribed limited exchange to multiple causes: (1) a 'hidden reservoir' effect, which accounts for the lack of contact of the metal with the far side and the solid deep mantle; (2) channeling of coalescing metal diapirs (Golabek et al., 2008); and (3) a 'core crash' effect which reflects the impactor's metal plunging directly through the Earth's mantle into the core as seen in simulations (Canup and Asphaug, 2001).

Whether the impacting asteroids are differentiated or not, decoupling between sinking metal and vapor rain on the planetary surface is expected. Any non-vaporized HSE sink into the terrestrial core and do not show up in the modern mantle inventory. Consequently, since the temperatures reached after impact are high enough to achieve the volatilization of large amounts of material (Canup, 2004; Pahlevan and Stevenson, 2007), HSE abundances in the BSE do not reflect the true proportion of late veneer but mostly its vaporized fraction as condensed in the wake of the impact.

The escape velocity being much smaller on the Moon ( $2.4 \text{ km s}^{-1} = 2.9 \text{ MJ kg}^{-1}$ ) than on Earth ( $11 \text{ km s}^{-1}$ ), a much smaller fraction of impactors should hit the Moon at velocities significantly less than that of elastic waves ( $9 \text{ km s}^{-1}$ ). A substantial part of the energy released by the impact therefore is allowed to



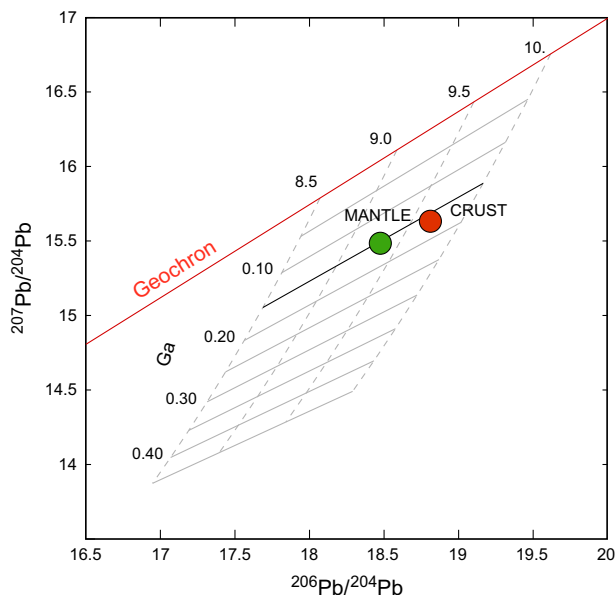
**Fig. 1.** Impact between a late-veener asteroid and Earth. The high impact velocity, which must exceed Earth's escape velocity ( $11 \text{ km s}^{-1}$ ), liberates enough energy for the impactor and part of the terrestrial mantle to melt and for a fraction of the material to vaporize. Metal (black) separates from the silicate (dark gray) and sinks into the core, while the vapor orbits the Earth until it cools and falls out, thereby modifying the composition of the terrestrial mantle and crust.

break free from the shock front. Impactors become fragmented, eventually molten, and, as shown by the chemistry of the lunar regolith (McKay et al., 1991), largely incorporated into the uppermost planetary layers as fragments of rocks and melts.

### 3. A chronological framework for volatile addition

Although the late veneer scenario shares many features with the late oxidative stage of the familiar two-stage accretion model (Wänke and Dreibus, 1988; Wood et al., 2006) (or to use a dated expression ‘heterogeneous accretion’), the chronology of the events that defined the modern composition of the Earth nevertheless remains contentious. The isotopic observations used to assign an age to the early accretion of the planet, the segregation of its metallic core, the giant lunar impact, and the late addition of material from the outer Solar System, have received different interpretations. A two-stage evolution model applied to the  $^{182}\text{Hf}$ – $^{182}\text{W}$  data for terrestrial samples and chondrites indicates an age of 30 Ma after accretion (Kleine et al., 2002; Schoenberg et al., 2002; Yin et al., 2002) originally interpreted as the time of last equilibration between the Earth’s mantle and core. Consequently, the similar W isotope composition of the Earth and the Moon could mean that the giant lunar impact took place at the end of terrestrial core formation at 30 Ma. Alternatively, the W isotopic composition of the Earth–Moon system and silicate-metal disequilibrium have been taken to signify that the collision post-dates the decay of  $^{182}\text{Hf}$  and hence that the age of the giant lunar impact is older than 60 Ma (Halliday, 2008; Touboul et al., 2007).

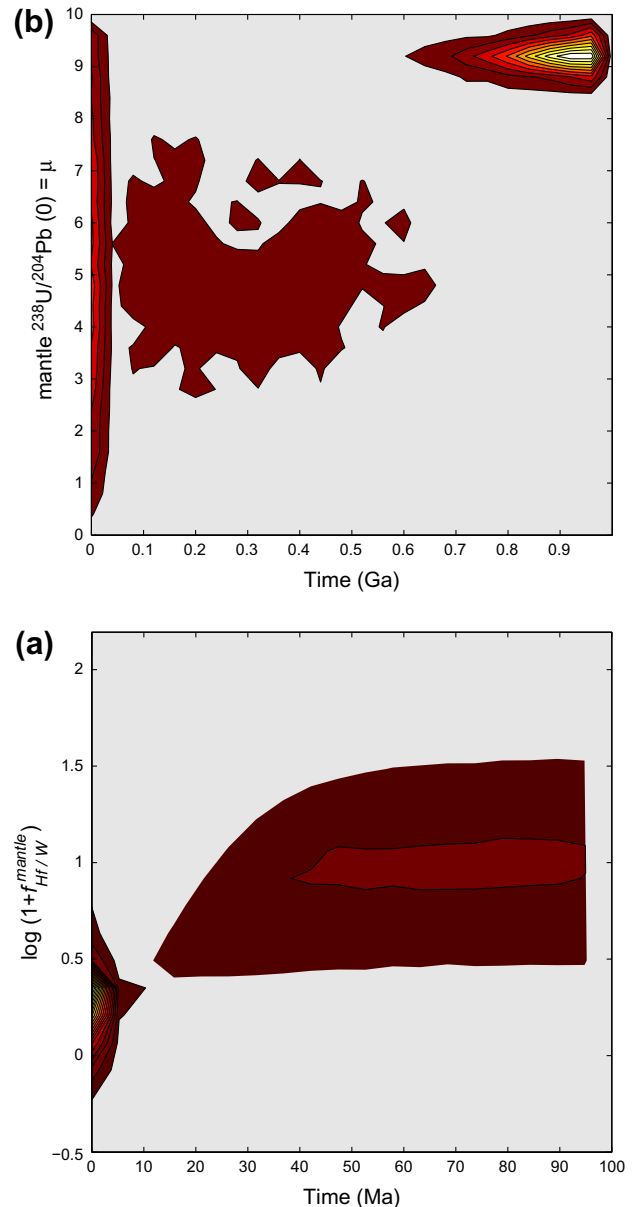
A two-stage evolution model of Pb isotopes for both the upper mantle and the crust of the Earth also is consistent with a late event of U/Pb fractionation, more specifically at  $\sim 150$  Ma after Solar System formation (Allegre et al., 1995) (Fig. 2). As discussed



**Fig. 2.** Conventional two-stage evolution of Pb in the terrestrial mantle and crust. The average Pb isotope composition of the mantle ( $^{206}\text{Pb}/^{204}\text{Pb} = 18.38$  and  $^{207}\text{Pb}/^{204}\text{Pb} = 15.48$ ) is the most probable values of thousands of literature data. The average crust is from Stacey and Kramers (1975). The initial Pb isotope composition of the Solar System is from Blichert-Toft et al. (2010). Ages shown as labels of solid lines (secondary isochrons) are those of the U/Pb fractionation. Labels along the geochron (single-stage isochron of the Solar System) are the  $^{238}\text{U}/^{204}\text{Pb}$  ( $\mu$ ) values of the Bulk Silicate Earth after this event. Whether considering the crust or the mantle Pb isotope compositions, these results attest to protracted U/Pb fractionation well beyond the  $\times 10$  Ma ages revealed by the  $^{182}\text{Hf}$ – $^{182}\text{W}$  system ( $T_{1/2} = \text{Ma}$ ).

further below, the direction of fractionation is that of U/Pb increase in the BSE during this event.

Any two-stage model of isotopic evolution clearly is an oversimplification that requires further testing. Some of the W isotope evolution models, such as those of Kleine et al. (2009) and Rudge et al. (2010), assume a priori explicit functions of mass accretion rates with time, which may be seen as rather arbitrary, and evaluate the extent of core–mantle equilibration as a function of the time of impact. This extent is still open for debate (Dahl and Stevenson, 2010; Ichikawa et al., 2010; Kendall and Melosh, 2012; Rubie et al., 2003). We were nevertheless able to corroborate



**Fig. 3.** The domain of acceptable trajectories for parent–daughter fractionation in the Earth for the Hf–W (a) and U–Pb (b) systems (two-dimensional histograms). Each model consists of 5–10 intervals randomly located over the first 100 Ma (Hf–W) and 1.5 Ga (U–Pb) of Earth history. The parent/daughter ratios remain constant within each interval, but increase from one interval to the next from the chondritic value.  $10^7$  models have been run for each figure. See Jacobsen and Harper (1996) and Kleine et al. (2009) for the constitutive equations. A model is rejected when its present-day  $\epsilon_W$  with respect to the Bulk Silicate Earth falls outside the  $-0.5$  to  $0.5$  epsilon range, and, for U–Pb models, when the mantle Pb isotope composition falls outside the ellipse defined by  $^{206}\text{Pb}/^{204}\text{Pb} = 18.38 \pm 0.03$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.480 \pm 0.005$ , with  $r = 0.8$ .

Rudge et al.'s (2010) chronology by running  $10^7$  Monte-Carlo approximations of a history broken down into 8 arbitrary stages with constant Hf/W ratios. Fig. 3a shows in the form of a two-dimensional histogram the evolution of the Hf/W ratio for the models which reproduce the modern W isotopic composition of the Earth. The core–mantle separation is essentially completed in about 30 Ma, which is consistent with the findings of Yin et al. (2002) and Rudge et al. (2010).

Likewise, the Pb isotope compositions of both the terrestrial mantle and crust invariably plot to the right of the geochron as defined by meteorites, which is the essence of the so-called Pb paradox (Allègre et al., 1980) and calls for U/Pb (or rather the value  $\mu$  of the  $^{238}\text{U}/^{204}\text{Pb}$  ratio extrapolated to today) of the BSE to have been increasing with time. Again, we ran  $10^7$  Monte-Carlo approximations of a history of  $n$  stages ( $i = 1, \dots, n$ ) with  $n = 5\text{--}10$ , in which the only constraint used was a stepwise increase of  $\mu_{\text{BSE}}$  in the Earth's mantle through a sequence of closed-system intervals. The isotopic ratios are calculated by the standard equation:

$$(^{206}\text{Pb}/^{204}\text{Pb})_{T_{i+1}} = (^{206}\text{Pb}/^{204}\text{Pb})_{T_i} + \mu_{\text{BSE}}(e^{\lambda^{238}\text{U}T_i} - e^{\lambda^{238}\text{U}T_{i+1}})$$

in which  $\lambda$  represents the decay constant of  $^{238}\text{U}$  and  $T$  is the geological age. Increasing  $\mu_{\text{BSE}}$  is by far the most important factor, as it affects the modern Pb isotope composition of silicates over 4.5 Ga of terrestrial evolution. By allowing a range of contribution of chondritic material, we checked that any instantaneous change of Pb isotope composition associated with the accretion of asteroidal material is essentially negligible. The range of  $\mu$  values prevalent prior to 30 Ma deduced from the Monte-Carlo runs is fairly broad ( $5 \pm 2$  at the 2-sigma level), but well above the  $\mu$  value of chondrites ( $\sim 0.3$ ), which indicates that the proto-Earth was born missing Pb with respect to the ambient nebular gas (Albarède, 2009) (see also Ballhaus et al. (submitted for publication)). The time at which the  $\mu$  of BSE reached its modern value of about  $\sim 9.5$  is not precisely constrained, but clearly corresponds to late events and can be accounted for by a single U/Pb fractionation event at  $\sim 130$  Ma (Albarède, 2009; Nebel et al., 2011; Wood and Halliday, 2010) (Fig. 2). Alternatively, the U/Pb fractionation process can be more continuous, which is the case for the exponential accretion investigated by Rudge et al. (2010), or for models similar to the one we just described in which  $\mu$  increases with time. Again, characteristic times for the  $\mu$  rate of change are of the order of 100–150 Ma. The fully unconstrained model of Fig. 3b lacks a precise time line for late accretion and U/Pb fractionation can occur as late as 700 Ma as in some early models (Albarède and Juteau, 1984; Stacey and Kramers, 1975), or as early as  $\sim 100$  Ma after time zero, as in models with a prescribed accretion history. However, when other chronologies are taken into account, such as I–Pu–Xe (unless Xe was lost over most of Earth's history (Marty, 2012; Pujol et al., 2011)) and Rb–Sr (Albarède, 2009; Halliday, 2008; Nebel et al., 2011; Wood and Halliday, 2010), it seems inescapable that the volatile content of the BSE went through a major change well after 100 Ma after time zero.

The difference in time scales recorded by the  $^{182}\text{Hf}$ – $^{182}\text{W}$  and U–Pb systems is so large that these chronometers ought to record events of different nature: because of the short  $^{182}\text{Hf}$  half-life, W isotopes record early fractionation events, while Pb isotopes record a late history of U/Pb fractionation. The major difficulty with the assumption of a young Moon is to explain how the memory of the  $\sim 30$  Ma Hf/W fractionation was preserved through the lunar impact (Dahl and Stevenson, 2010; Kleine et al., 2009; Rudge et al., 2010). In addition, the oldest age of the first lunar samples crystallized,  $110 \pm 40$  after time zero (Norman et al., 2003), makes the agreement with the U–Pb and I–Pu–Xe terrestrial record extremely tight, but Borg et al. (2011) argued that the lunar anorthosite 60025 is 150–200 Ma, which would permit the lunar and terres-

trial isotopic records to be mutually consistent. The lunar literature data accordingly have been interpreted as indicating that the Moon formed well after the major event of terrestrial core segregation (Borg et al., 2011; Halliday, 2008; Touboul et al., 2007). It is not clear, however, how the time line and the processes involved with the young Moon and the late veneer models relate to each other. Given the complexity of the issues, there is little hope to constrain the degree of equilibration between silicate and metal by independent observations. We consider that the major virtue of the standard chronology with a giant lunar impact and the associated major event of terrestrial core formation at 30 Ma followed by late veneer delivery has the merit of satisfying both chronological and geochemical evidence. About 150 Ma after formation of the Solar System is also a point in time that has been argued on the basis of dynamic models to correspond to occasional scattering of Moon-sized objects from the asteroid belt into the inner terrestrial zone (Raymond et al., 2006).

#### 4. The status of water as a volatile

Water-bound hydrogen in the Solar System behaves coherently with respect to other volatile elements. For example, once normalized to refractory calcium, Zn and water in chondrites are remarkably well correlated (Fig. 4). Nitrogen, which forms the gaseous molecules  $\text{N}_2$  and  $\text{NH}_3$ , and carbon, which forms  $\text{CO}_2$  and  $\text{CH}_4$ , show similar trends. The choice of the refractory element used for normalization does not affect the strength of the correlations, and we interpret these arrays as reflecting mixing between distinctive planetary components, one nearly volatile-free and the other remarkably rich in H, C, N, and Zn. We will see that the volatile-free component is itself a binary mixture. This correlation is reminiscent of those observed between the mass-independent oxygen isotope fractionation parameter with the stable isotopes of Cu (Luck et al., 2003), Zn (Luck et al., 2005), and Cr (Moynier et al., 2011b), and with the nucleosynthetic anomalies of  $^{54}\text{Ti}$  (Trinquier et al., 2007),  $^{50}\text{Ti}$  (Trinquier et al., 2009), and  $^{84}\text{Sr}$  (Moynier et al., 2012) in chondrites.

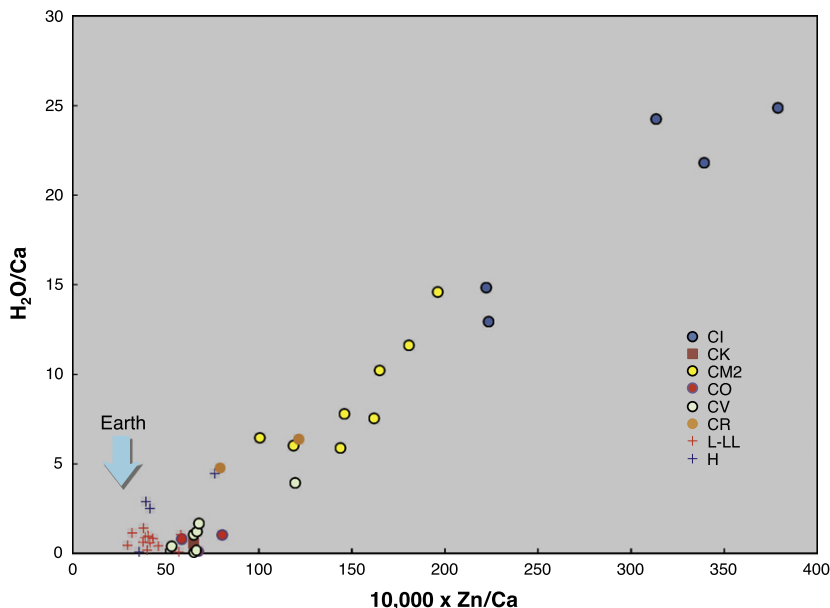
It is clear from Fig. 4 that the addition of small proportions of CI chondrites (15–20% water and 310 ppm Zn) to anhydrous chondrites is the only efficient way for a terrestrial planet to acquire significant amounts of water. Such a mixture should be detectable with oxygen isotopes. In order to explain the heterogeneities of oxygen isotope abundances across the Solar System, it has been suggested that water ice scattered beyond the frost line was endowed with dynamics of its own (Lyons and Young, 2005; Young et al., 2008; Yurimoto and Kuramoto, 2004), hence making its distribution with heliocentric distance a critical parameter of planetary water contents. The consistency between water-bound hydrogen and other volatile elements demonstrated in Fig. 4 shows, however, that decoupling of ice from other solids must have been limited. Fig. 4 will instead be shown to fit the coexistence in different parts of the Solar Nebula of unrelated nucleosynthetic components.

#### 5. Volatiles in the mantles of Earth and the Moon

##### 5.1. Earth

##### 5.1.1. The proportion of late veneer

In order to address the issue of how much wet late veneer was added to Earth and the Moon, we use a simple breakdown of oxygen isotope compositions of planetary material borrowed from Lodders (2000). Oxygen, which is a major constituent of common silicates, is both lithophile and moderately refractory. Because oxygen isotopes keep a record of nebular heterogeneities, they have



**Fig. 4.** The Zn–H<sub>2</sub>O correlation in chondritic materials. In order to account for the closure during volatile gain and loss, concentrations are normalized to a conservative refractory concentration (Ca). Values have been compiled from MetBase. The good correlation shows that the two volatiles, H<sub>2</sub>O and Zn, behave in a coherent way. If planets plot on this trend, Zn/Ca in both the Bulk Silicate Earth (Zn/Ca =  $20 \times 10^{-4}$  (Palme and O'Neill, 2005)) and the Moon ( $1 \times 10^{-4}$  (Morgan et al., 1978) or even less if Zn concentrations in lunar basalts are considered) places strong constraints on the water content of the mantles of both planets. Enstatite chondrites are not represented as their Zn contents have been perturbed by late-stage processes such as sulfide migration (Moynier et al., 2011a). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

been used to constrain the proportion of carbonaceous chondrites, the main carrier of water and volatile elements, added to the Earth. Lodders (2000) broke down the two-dimensional oxygen isotope compositions of planets into chondritic components according to the system of mass-balance equations:

$$\sum_i \phi_i \delta^{18}O_i = \delta^{18}O_{pl}$$

$$\sum_i \phi_i \delta^{17}O_i = \delta^{17}O_{pl}$$

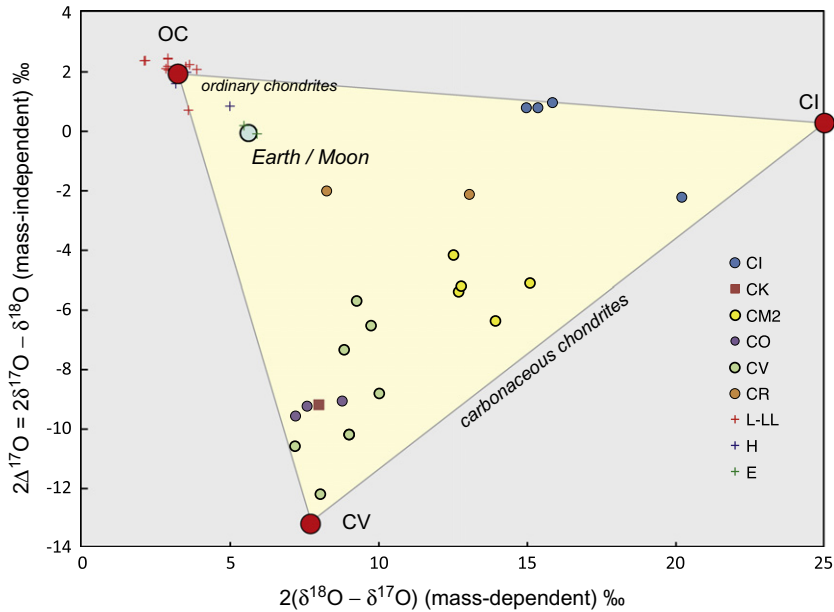
$$\sum_i \phi_i = 1$$

where  $\phi_i$  stands for the molecular proportion of oxygen contributed by the  $i$ th planetary component and  $\delta^{18}O$  stands for the relative deviation of  $^{18}O/^{16}O$  from that in Standard Mean Ocean Water. The subscript 'pl' refers to the planetary mix of components. The system therefore limits the number of independent planetary components to three. Lodders (2000) inferred that the volatile-rich component of the Earth can be accounted for by the accretion of 4% wet CI and 5% dry CV chondrites with a complement of dry ordinary H and enstatite EH chondrites.

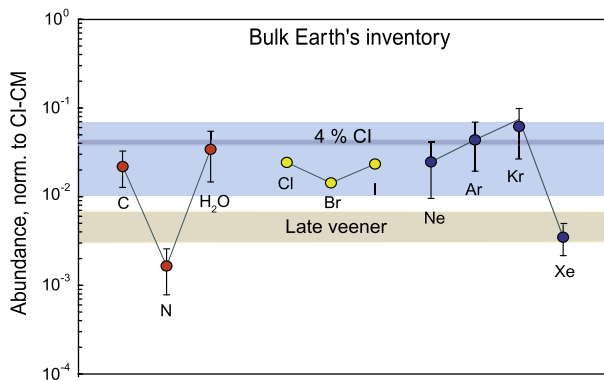
So far, the HSE and water contents of the BSE have been accounted for by a fraction of a percent of chondritic late veneer (Chou, 1978; Marty and Yokochi, 2006). If vapor from impacts is what brings the concentration level of HSE in the terrestrial mantle to the observed content, 5–10% vaporization of a late veneer made of 4% CI and 5% CV chondrites (Lodders, 2000) is also acceptable. Such a large addition is a significant phase of late accretion, since, for comparison, the masses of the Moon and Mars represent 1.2% and 11%, respectively, of the mass of the Earth. Regardless of the nature of the processes leading to oxygen heterogeneities, the wealth of stable isotope anomalies now makes it clear that the Solar Nebula was made of at least three genetically unrelated components (Burkhardt et al., 2011; Trinquier et al., 2007, 2009; Warren, 2011). In detail, the overall picture may be slightly more complicated and ordinary chondrites may themselves represent a mixture

of genetically unrelated components (Zanda et al., 2006), but a three-component representation of planetary objects is sufficient at this stage. For the sake of illustration, we went back to Lodders' equations described above and replaced  $\delta^{17}O$  and  $\delta^{18}O$  by two coordinates describing mass-dependent,  $x = 2(\delta^{18}O - \delta^{17}O)$ , and mass-independent,  $y = 2\delta^{17}O - \delta^{18}O = 2\Delta^{17}O$ , fractionation (Fig. 5). These coordinates are the projections of the data on the terrestrial fraction line and the 1:1 line, respectively, and parameterize independent nebular and planetary processes. We assessed a simple model of the Earth in which ordinary chondrites (H + L) are mixed with CI and CV and, after correction for O abundances in each component and the Earth (or, to follow Lodders, after taking the mass of the terrestrial core into account), we obtained a proportion of 6% CI and 8% CV. The proportion of the CI component is 50% higher than found by Lodders because enstatite chondrites were not allowed. It may also be lower for high values of the mass-dependent variable  $x$  value, i.e., if high-temperature material of CI-like late veneer reacted with water at low temperatures, as expected for comets (Aléon et al., 2009; McKeegan et al., 2006). In contrast, this proportion is not significantly affected by the presence of a solar-wind component with oxygen isotope compositions similar to those described by McKeegan et al. (2011). To sum up, Lodders' (2000) estimate of 4% CI in the Earth and the Moon therefore seems reasonably robust, which led us to keep this number for the rest of the discussion. It is also clear from Fig. 5 that the mix of CI + CV adopted by Lodders can be replaced by about 10% CM with little consequence. The *total* proportion of late veneer obtained by adding either a mix of CI and CV or unmixed CM (~10–14%) corresponds to the addition of a mass equivalent to that of Mars and is consistent with Rudge et al.'s (2010) and our own simulations discussed above.

These numbers are also consistent with other isotopic evidence. Although the HSE of the BSE is dominated by the fraction of late veneer vaporized during impact, the contribution of asteroidal material to non-siderophile, and in particular volatile terrestrial inventories consists of the bulk of the added material. Four percent



**Fig. 5.** Oxygen isotope compositions of the Earth and different groups of chondrites. Values have been compiled from MetBase. Following Lodders (2000), the Earth’s oxygen isotope composition is broken down into three chondritic components (red circles), but in a system of coordinates designed to separate mass-dependent,  $x = 2(\delta^{18}\text{O} - \delta^{17}\text{O})$ , from mass-independent,  $y = 2\delta^{17}\text{O} - \delta^{18}\text{O} \approx 2\Delta^{17}\text{O}$ , fractionation. Note that  $x + y = \delta^{18}\text{O}$ . The triangle represents all the data as mixtures of three end-members (ordinary chondrites L + C = OC, CI, and CO) contributing to the composition of all silicates including the mantles of the Earth and the Moon. The  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values are, respectively, +5.5 and 2.75 for the Earth, +5.0 and +3.5 for the OC component, -5.5 and -9.25 for CV, and +25 and +12.5 for CI. Once the oxygen content of each component is accounted for, this particular choice of components predicts that the Earth contains 6% CI, but this number can be arbitrarily reduced by increasing  $y$ , i.e., by allowing for more low-temperature weathering of the CI component. It can also be lowered by allowing enstatite chondrites as an end-member: Lodders’ (2000) breakdown uses E and H chondrites instead of a mixture of L and H, and the resulting CI contribution (4%) is considered the best estimate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 6.** Volatiles in the Earth and chondrites. Comparison of the Cl-normalized concentrations of terrestrial volatile elements with the amounts predicted by the conventional late veneer assumption (pale brown) and by the addition of 4% CI chondrites (blue). The shaded areas represent probable uncertainties. See Marty (2012) for a discussion of N and Xe anomalies. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

CI, the main volatile carrier, in the Earth agree with the consistent D/H ratios of carbonaceous chondrites and the terrestrial hydrosphere (Robert, 2001), with Marty’s (2012) inventories of most terrestrial volatiles (Fig. 6), and with Si isotopes in planetary materials (Fitoussi and Bourdon, 2012). Given the small deficit ( $1.9 \pm 0.1 \times 10^{-4}$ ) of radiogenic  $^{182}\text{W}$  abundances in carbonaceous chondrites with respect to the BSE (Kleine et al., 2004; Yin et al., 2002), addition of a few percent late-veener from a vapor of chondritic composition will not render W in the Moon and the Earth measurably different.

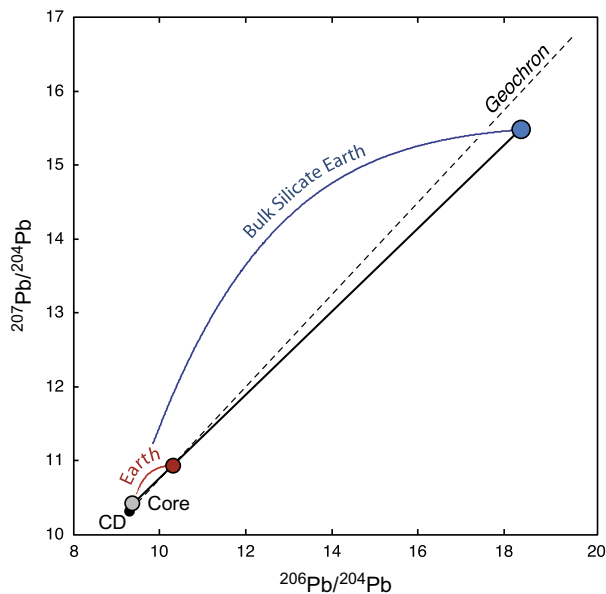
### 5.1.2. The terrestrial budget of Zn and Pb

Comparison between Pb and Zn offers its own perspective on terrestrial volatile and siderophile elements. Using abundances of 310 ppm Zn in CI and 110 ppm in CV and assuming that for the most part Zn does not fractionate into the core (Corgne et al., 2008) (see also Ballhaus et al., in preparation), Lodders’ (2000) proportions of volatile-rich components account for  $(0.04 \times 310 + 0.05 \times 110) \times (6/4) = 27$  ppm, or half of the 55 ppm Zn present in the BSE (Sun, 1982). In contrast to Zn, which is volatile and lithophile, Pb is volatile and siderophile at high temperatures (Wood and Halliday, 2010), actually nearly as siderophile as W (Ballhaus et al., in preparation). The fact that siderophile elements are massively entrained with metal into the core of the planet explains why the proportion of late veneer based on PGE abundances so far has been underestimated and this is also the main obstacle against closing the planetary mass balance for Pb and its isotopes. We can, however, use the comparable volatility of Pb and Zn to assess how much Pb segregated into the core. With  $f_c$  being the fraction of terrestrial  $^{204}\text{Pb}$  in the core, the evolution equations of  $^{206}\text{Pb}/^{204}\text{Pb}$  ( $x$ ) and  $^{207}\text{Pb}/^{204}\text{Pb}$  ( $y$ ) of the BSE in a two-stage closed system, read:

$$x_{\text{BSE}} = x_0 + (1 - f_c)\mu_{\text{BSE}}(e^{238\text{U}T_0} - e^{238\text{U}T_1}) + \mu_{\text{BSE}}(e^{238\text{U}T_1} - 1)$$

$$y_{\text{BSE}} = y_0 + (1 - f_c)\mu_{\text{BSE}}(e^{235\text{U}T_0} - e^{235\text{U}T_1})/137.88 + \mu_{\text{BSE}}(e^{235\text{U}T_1} - 1)/137.88$$

The system can be solved for  $\mu_{\text{BSE}}$  and  $f_c$  at different values of the age  $T_1$  of U/Pb fractionation. In these equations, the core is assumed to be U-free ( $\mu = 0$ ),  $T_0$  is the age of the Solar System (4.568 Ga), and  $x_0$  and  $y_0$  stand for the initial values of  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$ , respectively, in the Solar System (Blichert-Toft et al., 2010). The results indicate that 50% (if U/Pb fractionation



**Fig. 7.** Isotopic breakdown of terrestrial Pb among the core and the Bulk Silicate Earth. The curves represent radiogenic ingrowth. CD (Canyon Diablo) stands for the primordial Pb of the Solar System. The dashed line labeled 'Geochron' represents the position of all the planetary bodies formed within a few tens of Ma of Solar System isolation. Variations of the Bulk Silicate Earth value resulting from mixing different dominant Pb types from the mantle and the crust are nearly inconsequential. The last episode of Pb fractionation into the core cannot take place before  $\sim 150$  Ma. The fraction of Pb held by the core can be calculated by applying the lever rule to the whole Earth with the core and the BSE as end-members. Given other constraints, in particular the chronology (see text), the fraction of terrestrial Pb hosted by the core is in the range of 60–90%.

took place at 4.25 Ga) to 100% (if U/Pb fractionation took place at 4.43 Ga) of terrestrial Pb resides in the core (Fig. 7). These results reiterate the conclusion from the previous section that Pb isotopes in the BSE require a protracted history of U/Pb fractionation and we consider that a range of 60–90% of terrestrial Pb in the core is consistent with the chronological constraints. Galer and Goldstein (1996) pointed out that the current inventory of Pb in the BSE is accounted for by 1.5% CI chondrites. Bringing this figure to 4% requires that 60% of terrestrial Pb (neglecting the CV contribution), including much of the late veneer contribution, is now sequestered in the Earth's core. Because this simple first-order calculation is based on isotopic constraints, as opposed to assumptions on element abundances, it is robust (Nebel et al., 2011) and yet does not leave much room for large amounts of Pb predating the late veneer. Isotopes therefore do not record the fractionation of Pb inherited from the early stages of accretion, which is entrained into the core at an early stage as documented by the  $^{182}\text{Hf}$ – $^{182}\text{W}$  system, but rather shows that Pb from the late veneer has been dragged down with its metal fraction. The dual comparison of two volatile elements with different siderophile characters, Zn and Pb, and two siderophile elements with different volatilities, W and Pb, identifies the respective roles of volatility and core entrainment and provides the chronology of events.

### 5.1.3. Water in the Earth

The content of water in the Earth derived from Lodders' (2000) proportions is significantly larger than most estimates. Neglecting other components and using 15% for the water content of CI would leave the Earth with 6000 ppm water and the BSE inclusive of the ocean with 9000 ppm water. The highest estimate by Marty (2012) for the BSE is 3000 ppm. Part of this water may have been used to oxidize iron at the surface of the Earth. Subduction of ferric iron held in the oceanic crust has long been suggested to account for

the rather high  $\text{Fe}^{3+}/\text{Fe}$  of the mantle (Albarede and Michard, 1986; Frost and McCammon, 2008; Turekian, 1968): oxidation of 12% (Bézos and Humler, 2005) of the  $\text{Fe}^{2+}$  contained in the mantle (6.3%) would consume 2400 ppm  $\text{H}_2\text{O}$ , the hydrogen liberated by water breakdown presumably being lost to space. Loss of electrons from the mantle and subsequent hydrogen escape may be enhanced upon reaction of subducted  $\text{Fe}^{3+}$  with the metallic core at the base of the mantle to produce  $\text{Fe}^{2+}$  silicates or oxides (Lécuyer and Ricard, 1999). Although Hirschmann and Dasgupta (2009) discussed a range of values well below that implied by addition of several percent CI chondrites (about 25 terrestrial oceans), they point out that the status of water in the deep mantle, provided the latter is not sampled by surface volcanism, is poorly understood. An appealing suggestion made by Panero et al. (2003) is that subduction of stishovite entrains substantial amounts of surface water into the deep mantle.

### 5.2. The Moon

Although geochemical differences between the Moon and Earth present some challenging questions, it is clear that the Moon is more depleted in volatile elements than the Earth's mantle. As a result of very different escape velocities ( $2.4$  vs  $11.2$   $\text{km s}^{-1}$ ), asteroids colliding with the Moon should be much less vaporized than those colliding with the Earth. Taking accretion escape velocities and gravitational focusing into account, Schlichting et al. (2012) estimated that the Earth/Moon mass accretion ratio is  $\sim 200$ . Once accretionary fluxes have been normalized to the ratio of their respective mantle masses (55), the lunar mantle is still depleted in late veneer by a factor of  $\sim 4$  with respect to BSE. Platinum group elements are depleted by a factor of approximately 20–40 in the lunar mantle with respect to BSE (Day et al., 2007, 2010; Morgan et al., 2001; Walker et al., 2004). Likewise, the  $\mu$  value of the lunar mantle typically is in excess of 500 (Premo et al., 1999), which contrasts with the value of  $\sim 9$  for the terrestrial mantle. Because Pb and PGEs are too heavy to escape the gravity field of the Moon, the 'missing component' of late-accreted siderophile elements invoked by Day et al. (2010) may have sunk as molten iron into the small lunar core.

Likewise, a late veneer contribution to the lunar mantle inventory of volatile elements of a factor of four smaller than the contribution to the terrestrial mantle is consistent with observations from some volatile elements but not all of them. The K/U ratio of the Moon (3000) is indeed about four times smaller than the terrestrial value (Taylor, 1987). In contrast, Zn in the lunar mantle ( $\sim 1$ – $3$  ppm, (Herzog et al., 2009)) is 18–55 times less concentrated than BSE. The Fe/Zn ratio does not fractionate significantly during mantle melting (Le Roux et al., 2010). This ratio is about 1000 in the terrestrial mantle against  $>100,000$  in the lunar mantle. Given the lithophile behavior of Zn, it is unlikely that the missing Zn is in the lunar core, assuming a core exists. Combining this observation with the heavier isotope composition of Zn in the Moon relative to the Earth, Paniello et al. (2012) concluded that lunar Zn was largely boiled off in the events associated with the giant lunar impact.

Until recently, the Moon was deemed exceedingly dry (Taylor et al., 2006) and it was therefore expected that other gaseous species, in addition to water, also were lost from the Moon. For this reason, the case of the so-called orange glass 74220 (Hauri et al., 2011) has elicited substantial interest. These unusual pyroclastic glasses brought back by the Apollo missions seem to be a product of volcanic fountaining (Heiken et al., 1974). Melt inclusions have been found to contain water in excess of 600 ppm (Hauri et al., 2011), which hints at mantle sources with tens of ppm of  $\text{H}_2\text{O}$ . Likewise, the  $^{238}\text{U}/^{204}\text{Pb}$  values reported for these samples are  $<35$  (Nunes et al., 1974) and their Zn concentrations are as high as 90–300 ppm, i.e., about two orders of magnitude larger than

for mare basalts. A substantial fraction of the Zn appears, however, to be hosted in surface coatings, possibly deposited by fumaroles (Herzog et al., 2009). Orange glass is clearly a local anomaly unrepresentative of the lunar interior as a whole and, overall, the lunar mantle should not contain large amounts of water.

The water inventory of the Moon most likely is limited by the extensive loss of the hydrogen delivered by the late veneer and by the lack of a lunar atmosphere. A conservative estimate is that all volatile elements in the Moon, i.e., water, Zn, and Pb, are depleted by at least a factor of 100 with respect to the Earth. A 'dry' BSE containing between 500 and 1500 ppm water would, therefore, be consistent with a lunar interior containing 5–15 ppm of water and even less if water was reduced to hydrogen under the highly reducing conditions of the Moon. For a 'wet' terrestrial mantle initially containing 3000–10,000 ppm water, the interior of the Moon could be endowed with as much as 30–100 ppm H<sub>2</sub>O. Such a range of values readily can be reconciled with the observations of water abundances in lunar glasses (Hauri et al., 2011; Saal et al., 2008).

## 6. Conclusions

Because vaporization during impact biases estimates of how much late veneer is added to a planet, it is inferred here, using constraints from PGE abundances in the terrestrial mantle, that the amount of volatile-rich material added to the Earth by late accretion is underestimated. We conclude that, in agreement with the oxygen isotope analysis of Lodders (2000) about 4% of CI chondrites were accreted to the Earth 130 Ma after the formation of the Solar Nebula and possibly later. The time scale of the late phases of accretion (>130 Ma) is provided by Pb isotopes, in contrast to the <sup>182</sup>Hf–<sup>182</sup>W system, which dates a much earlier event (30 Ma) of core–mantle fractionation. The Earth's mantle may have originally received as much as 9000 ppm of water, a large fraction of which has been used to oxidize iron in the mantle and the core, while the rest, possibly up to 3000 ppm, may still be hidden in the lower mantle, possibly subducted with stishovite. The Moon is overall highly depleted in water and volatile elements with respect to the Earth, though locally some parts of the lunar mantle may be enriched in volatiles.

## Acknowledgments

Discussions with Alexandro Morbidelli, Mark Rehkämper, and Bernie Wood are gratefully acknowledged. We also thank James Day and an anonymous reviewer for very useful suggestions, in particular for pointing out some critical misconceptions about impacts. The Agence Nationale de la Recherche through the T-Tauri Grant and the Programme National de Planétologie (CNRS–CNES) are thanked for support. The Wiess Foundation and the Chair of the Department of Earth Science made the stay of FA and JBT at Rice University possible.

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