A young Moon-forming giant impact at 70–110 million years accompanied by late-stage mixing, core formation and degassing of the Earth

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New W isotope data for lunar metals demonstrate that the Moon formed late in isotopic equilibrium with the bulk silicate Earth (BSE). On this basis, lunar Sr isotope data are used to define the former composition of the Earth and hence the Rb–Sr age of the Moon, which is $4.48 \pm 0.02$ Ga, or 70–110 Ma (million years) after the start of the Solar System. This age is significantly later than had been deduced from W isotopes based on model assumptions or isotopic effects now known to be cosmogenic. The Sr age is in excellent agreement with earlier estimates based on the time of lunar Pb loss and the age of the early lunar crust ($4.46 \pm 0.04$ Ga). Similar ages for the BSE are recorded by xenon and lead–lead, providing evidence of catastrophic terrestrial degassing, atmospheric blow-off and significant late core formation accompanying the ca 100 Ma giant impact. Agreement between the age of the Moon based on the Earth’s Rb/Sr and the lead–lead age of the Moon is consistent with no major losses of moderately volatile elements from the Earth during the giant impact. The W isotopic composition of the BSE can be explained by end member models of (i) gradual accretion with a mean life of roughly 35 Ma or (ii) rapid growth with a mean life of roughly 10 Ma, followed by a significant hiatus prior to the giant impact. The former assumes that approximately 60 per cent of the incoming metal from impactors is added directly to the core during accretion. The latter includes complete mixing of all the impactor material into the BSE during accretion. The identical W isotopic composition of the Moon and the BSE limits the amount of material that can be added as a late veneer to the Earth after the giant impact to less than $0.3^{+0.3}_{-0.2}$ per cent of ordinary chondrite or less than $0.5^{+0.6}_{-0.2}$ per cent CI carbonaceous chondrite based on their known W isotopic compositions. Neither of these on their own is sufficient to explain the inventories of both refractory siderophiles such as platinum group elements and rhenium, and volatiles such as sulphur, carbon and water.

Keywords: geochemistry; isotopes; Earth science

1. Introduction

For many years the origin of the Moon has been intertwined with issues surrounding how the Earth itself formed. The Moon is unusual in its large size relative to its host
planet. The most widely accepted model for its origin is that a Mars-sized impactor
struck the proto-Earth with a glancing blow, adding the final approximately 10 per
cent of the Earth’s mass and generating a hot, partly vaporized debris disc from
which the Moon accreted (Cameron & Benz 1991; Canup & Asphaug 2001). This
‘giant impact’ nicely explains the angular momentum of the Earth–Moon system
and has come to be viewed not so much as an oddity but rather as a normal example
of the stochastic and oligarchic accretion events that built the terrestrial planets
(Chambers 2004). Other prominent features of the planets are ascribed to such
catastrophic collisions. For example, giant impacts are viewed by some as
responsible for the high density of Mercury (Benz et al. 1987).

Giant impacts are thought to have had a marked effect on the Earth’s chemical
evolution. It has been argued that volatiles and early atmospheres were lost (Ahrens
1990; Pepin 1997; Pepin & Porcelli 2006), part of the crust and outer mantle of the
Earth were eroded (Palme 2000; Palme et al. 2003) and magma oceans were formed
that led to the main stages of core formation, mantle self-oxidation and eventually
the late segregation of chalcophile element-bearing sulphides (Wade & Wood 2005;
Wood & Halliday 2005). This ‘modern’ view of the Earth and the inner Solar System
as a dynamic environment with extensive planetesimal and planet migration (e.g.
Bottke et al. 2006) and concomitant fundamental changes in internal chemistry
driven by external processes contrasts with earlier views of the inner Solar System
as an environment in which the composition of planets as a function of location was
dictated by nebular conditions (e.g. Turekian & Clark 1969). Scott & Taylor (2000)
pointed out the apparent existence of a nebular control on the degree of oxidation of
terrestrial planetary mantles and argued for a relatively restrictive feeding zone
model. At the present time it is not clear to what extent such evidence of spatial
variations and nebular controls is to be reconciled with the evidence of considerable
migration of material in the terrestrial-planet-forming region (Bottke et al. 2006).

A key piece of evidence in support of the giant impact theory has been the age of
the Moon itself (Tera et al. 1973; Wasserburg et al. 1977; Hanan & Tilton 1987;
2000; Halliday & Porcelli 2001; Kleine et al. 2005; Touboul et al. 2007). All of these
studies, but in particular the lunar W and Sr isotopic compositions, provide
powerful evidence that the Moon had to have formed more than 10 million years
after the start of the Solar System, after comparable-sized bodies had been formed
by runaway growth (Lissauer 1987; Chambers & Halliday 2007).

In this paper, the age of the Moon is re-examined in the light of new data from
which it is argued that the Moon most likely formed as late as 70–110 Ma
(million years) after the formation of the first nebular solids. Such a protracted
accretion history explains several issues concerning the isotope geochemistry of
the Earth and the Moon. However, it also raises the question of the degree to
which such a late, large-scale impact can any longer be viewed as part of the
main stages of the Earth’s growth.

2. Previous attempts to date the Moon

The early extensive geochronological studies of lunar samples that followed the
Apollo sample returns did not provide an unequivocal exact age of the Moon
itself, only that it had formed by 4.45 Ga. The review by Wasserburg and
colleagues (Wasserburg et al. 1977) concluded that ‘The actual time of aggregation of the Moon is not precisely known, but the Moon existed as a planetary body at 4.45 Ga, based on mutually consistent Rb–Sr and U–Pb data. This is remarkably close to the $^{207}$Pb–$^{206}$Pb age of the Earth and suggests that the Moon and the Earth were formed or differentiated at the same time.’ This indication of a close agreement between isotopic ages for early events in the history of the Earth and the Moon appeared broadly consistent with the first results reported using the $^{182}$Hf–$^{182}$W (half-life $Z$ 8.9 Ma) chronometer. Small tungsten isotopic effects were found in a wide range of lunar rock samples, and the high Hf/W of the lunar interior implied that the Moon formed sufficiently early that $^{182}$Hf was still extant, but sufficiently late that the effects were not large (Lee et al. 1997; Halliday 2000). The best estimate based on these early results was ca 50–60 Ma after the start of the Solar System. Direct cosmogenic effects on W were shown to be negligible (Masarik 1997). Subsequently, it was demonstrated that lunar samples with high Ta/W and prolonged exposure are affected by cosmogenic $^{182}$Ta, which decays to $^{182}$W (Leya et al. 2000; Lee et al. 2002; Kleine et al. 2005). It was also demonstrated that the W isotopic composition of carbonaceous chondrites and initial $^{182}$Hf/$^{180}$Hf of the Solar System were incorrect (Kleine et al. 2002; Schoenberg et al. 2002; Yin et al. 2002). In fact, on the basis of a simple growth history for the Earth it was suggested that the Moon may have formed as early as 30 Ma (Kleine et al. 2002; Jacobsen 2005). However, most recent estimates have been in the range 30–55 Ma (Halliday 2003, 2004; Kleine et al. 2005). The reason why all of these age estimates are late is that the Moon has a very high Hf/W ratio (Lee et al. 1997; Kleine et al. 2005, 2008), and as such the most important observation with every study is that the W isotopic composition is not very radiogenic, indicating that the Moon formed after most $^{182}$Hf had decayed.

Most recently, Touboul et al. (2007) showed that all W isotope variation on the Moon is the result of cosmogenic production. Eliminating this effect, the Moon has the same W isotopic composition as the bulk silicate Earth (BSE) ($\delta^{182}$W = 0). Even the previously reported W isotopic effects in lunar metals appear to be cosmogenic. Assuming this represents the composition of the entire Moon, as seems likely, the Moon clearly formed in isotopic equilibrium with the BSE at a time when $^{182}$Hf was extinct. Therefore, the age is constrained to be more than 45 Ma after the start of the Solar System but less than the age of the oldest lunar rock. Strictly speaking, this is dating the time of W depletion in the lunar mantle, which presumably developed in the early lunar magma ocean.

The ages of the oldest rocks on the Moon and the bracketing constraints they place on its age have been studied quite extensively (e.g. Tera et al. 1973; Papanastassiou & Wasserburg 1976; Wasserburg et al. 1977; Hanan & Tilton 1987; Carlson & Lugmair 1988; Shih et al. 1993; Alibert et al. 1994; Norman et al. 2003). The most pristine lunar anorthosite, 60025, has been the subject of particularly intense study using Sr, Nd, and Pb isotopes. The oldest precise ages obtained were those of Hanan & Tilton (1987), who showed that the Pb isotopic compositions of different fractions yielded a range of model ages. Their best estimate for the age of the Moon based on these data was 4.50 ± 0.01 Ga (or 70 ± 10 Ma after the start of the Solar System). However, Carlson & Lugmair (1988) published Nd isotopic data for 60025 and obtained a $^{147}$Sm–$^{143}$Nd isochron defining a younger age of

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4.44 ± 0.02 Ga or 130 ± 20 Ma after the start of the Solar System. Carlson and Lugmair suggested that the age of the Moon lay in the range 4.44–4.51 Ga. The interpretation of the difference between the Nd and the Pb results was not clear. However, if all of the data of Hanan and Tilton are replotted on a conventional Pb–Pb isochron and regressed using standard procedures, the different fractions define a scattered isochron, the best-fit slope of which is 4.45 ± 0.10 Ga, within error of the 147Sm–143Nd isochron age of Carlson and Lugmair. Although the apparent scatter is large, there is no reason why these two isotopic systems should be concordant unless they are dating the same event. Therefore, it appears likely that the apparently old single-stage Pb–Pb ages for some individual fractions reported by Hanan and Tilton actually reflect the common Pb correction that was applied and/or later disturbance of the systematics. The anorthosite itself formed a little over 100 Ma after the start of the Solar System. This would be consistent with the more recent evidence for the age of the anorthositic crust (Norman et al. 2003.) The anorthositic crust has long been associated with the magma ocean that formed after the giant impact, but it is possible that tidal heating played an important role in melting the lunar interior and the Earth’s deep mantle (Zahnle et al. 2007). Under these circumstances, large-scale magmatism may have persisted for a significant period of time after cooling from the magma ocean. Therefore, it is not clear how strong a constraint the age of the earliest anorthositic crust is on the age of the Moon except to provide a latest possible time of formation of 4.46 ± 0.04 Ga (Norman et al. 2003). On this basis, the Moon formed between 45 and 150 Ma after the start of the Solar System.

3. Evidence that the Moon formed at 70–110 Ma

To date an entire object such as the Moon, as opposed to some of the oldest rocks, one needs to use a chemical fractionation that is associated with planet formation. Currently, the most promising system for the Moon would appear to be Sr isotopes owing to the extreme depletion in Rb that appears to have accompanied its formation. In order to determine an age for the Moon from Sr isotopes one needs to know the parent/daughter (Rb/Sr) ratio over the time leading up to the Moon’s formation. Carlson & Lugmair (1988) used the Rb/Sr of the Earth (0.03) to derive an age for the Moon. However, although it was originally argued quite strongly by some that the similarity of isotopic and chemical characteristics of the Earth and the Moon must mean that the latter was derived from the former (Wänke & Dreibus 1986; Ringwood 1989), almost every dynamic simulation of the giant impact provides evidence that the Moon is largely derived from the impactor ‘Theia’ (e.g. Cameron & Benz 1991; Canup & Asphaug 2001). Therefore, without knowing the Rb/Sr of Theia one cannot deduce the Moon’s age from its Sr isotopic composition. Halliday & Porcelli (2001) assumed an upper bound on Theia’s Rb/Sr using the solar value (0.3). On this basis, the Moon formed more than 11 ± 1 Ma after the start of the Solar System, but nothing further can be deduced. From the point of view of confirming a late origin, this still is a crucial constraint; there are no known dynamic models of planet formation that can explain such a late origin, unless the Moon was formed from a pre-existing planetary object via fission or impact.

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However, recent views of the Moon’s origin open up the possibility that its age can in fact be determined quite accurately using Rb–Sr chronology. The Moon shares exactly the same oxygen (O) isotopic composition as the Earth \( \text{(Wiechert et al. 2001).} \) It has been argued that this is because the Earth isotopically equilibrated with the lunar accretion disc via a vapour atmosphere \( \text{(Pahleven & Stevenson 2007).} \) The idea of lunar condensation from a very hot vapour is consistent with extreme enrichment in refractory elements \( \text{(Taylor et al. 2006).} \) This new model resolves the difficulty of the fact that every isotopic signature carried by the Earth is identical in the Moon, despite large-scale variability elsewhere in the Solar System. It has not been clear whether the model can be applied to include all of the more refractory elements such as Sr. The identical W isotopic compositions of the BSE and the Moon \( \text{(Touboul et al. 2007) provide new evidence that such equilibration must have included highly refractory elements.} \) The only other giant impact explanation for the similarity in oxygen isotopes is that the impacting planet Theia formed in the same vicinity as the proto-Earth, thereby sharing isotopic characteristics. This scenario has the difficulty of requiring that Theia was at a similar heliocentric distance as the Earth but did not collide for more than 45 Ma. More importantly, it does not explain the similarity in W isotopic composition. There is no reason why Theia’s silicate portion should have the exact same W isotopic composition as that of the Earth, since it requires an identical level of oxidation and history of accretion and core formation for both bodies, despite their different sizes; several studies show that this is highly unlikely \( \text{(Lee & Halliday 1997; Kleine et al. 2004; Foley et al. 2005; Markowski et al. 2007).} \) Therefore, this new W isotopic constraint is immensely important because it provides evidence that equilibration of refractory elements has to have occurred if the giant impact theory is correct. There is a caveat to this argument, namely that the volatility of W during planetary accretion may bear little resemblance to that associated with nebular condensation. In particular, it is dependent on oxygen fugacity and whether a metal phase is present. It is usually assumed that the impactor, Theia, was differentiated with a metallic core, leading to the Fe-depleted lunar composition. Similarly, it is commonly assumed that conditions were not sufficiently oxidizing for W to be volatile. These assumptions may need to be re-examined.

Assuming Sr, similar to W, to be isotopically equilibrated between the BSE and the proto-lunar disc, the initial Sr isotopic composition of the Moon would have been generated by isotopic evolution within the Earth itself. Therefore, the Rb/Sr of the Earth of 0.03 provides a reasonable best estimate of the parent/daughter ratio. There are two independent lines of evidence to support this ratio: (i) the correlation between Nd and Sr isotopes in the mantle and (ii) the Ba/Rb ratio of the BSE \( \text{(McDonough et al. 1992).} \) The latter provides support for the former value. In the following calculations, a 10 per cent uncertainty on the Rb/Sr is assumed. However, both of these calculations depend on chondritic refractory element ratios for the Earth. If the Earth has non-chondritic refractory element ratios or high Sm/Nd \( \text{(Caro et al. 2008),} \) the calculated Rb/Sr of the Earth would be significantly lower, assuming this fractionation to be a feature of melting. This would mean that the Rb–Sr age of the Moon is later than calculated here.

The data for the initial Sr isotopic composition of the Moon have not changed greatly over the past 20 years. However, the initial Sr isotopic composition of the Solar System upon which any model age constraints need to be based has been

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the subject of new evidence. All of the previous constraints have been based on data for Allende CAIs. The initial study undertaken by Gray et al. (1973) yielded data, the more unradiogenic of which were not well reproduced by the subsequent study of Podosek et al. (1991). Nyquist et al. (2004) have reported data for CAIs from Efremovka, a more pristine carbonaceous chondrite than Allende, which preserves the oldest well-defined Pb–Pb ages (Amelin et al. 2002). The Sr isotopic compositions are again more radiogenic than that reported by Gray et al. (1973). A possible explanation for this discrepancy is that some of the Allende CAIs are isotopically fractionated or anomalous as demonstrated by Patchett (1980). The degree to which the Sr isotopic composition is adequately corrected for natural as opposed to instrumental fractionation is unknown and could be important for strongly fractionated systems such as the Allende CAIs. However, more recent data for relatively unaltered Efremovka CAIs and for a pristine quickly chilled early basaltic angrite, SAH 99555, appear to provide self-consistent and probably stronger constraints.

Using the Earth’s Rb/Sr of 0.03 and a $^{87}\text{Sr}/^{86}\text{Sr}$ lunar initial of 0.69906±2 (Halliday & Porcelli 2001) yields an age of 76±26 Ma or 99±25 Ma for the giant impact, depending on whether one uses the angrite SAH99555 initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.69896±2 at 5 Ma (Nyquist et al. 2004; Markowski et al. 2007) or the Efremovka CAIs initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.69893±2 at 0 Ma (Nyquist et al. 2004) to define the initial composition of the Solar System. Assuming these two approaches to be self-consistent one is left with an age of 87±13 Ma or 4.48±0.02 Ga relative to the present day.

These calculations do not depend on the assumption that the Rb/Sr ratio of the Earth was constant over the first 100 Ma of the Earth’s history. During the Earth’s oligarchic growth, Sr would have been added along with its associated Rb. The mixed $^{87}\text{Sr}/^{86}\text{Sr}$ ratio would then be coupled with the mixed Rb/Sr regardless of the history of how that mixture was derived, provided the variations in Rb/Sr were established early, i.e. in the solar nebula, and there were no late selective losses or gains of Rb during accretion. Only if Rb was lost or gained without Sr during the later stage evolution would the age be affected. There is no obvious mechanism for merely adding Rb without Sr. Therefore, if the Earth started accreting material that was more volatile depleted and accreted material that was, on average, less volatile depleted over time as is sometimes considered likely (e.g. Newsom 1990), the age would be unaffected, provided there were no late-stage losses of Rb. This latter effect would make the apparent age of the Moon younger than it really was. Such late-stage losses of Rb are difficult for a body of the size of the Earth unless the alkalis were partitioned into a hot vapour rock atmosphere and this was partially lost during impact events (Halliday 2004).

In fact, the model Rb–Sr age of the Moon is in perfect agreement with the estimate of 4.47±0.02 Ga by Tera et al. (1973) based on $^{235/238}\text{U–}^{207/206}\text{Pb}$ chronology and dominated by the time of major Pb loss from the Moon. An age of 4.48±0.02 Ga for the Moon is also similar to the $^{147}\text{Sm–}^{143}\text{Nd}$ age of 4.44±0.02 Ga for 60025, the best preserved early lunar rock (Carlson & Lugmair 1988). Whereas there was an apparent hiatus between the Moon formation and the oldest lunar rocks, this has now been closed within error and the latest age of the lunar anorthositic crust of 4.46±0.04 Ga (Norman et al. 2003) provides compelling evidence that this is a tangible remnant of an early-formed and quickly crystallized magma ocean generated by the giant impact.
The argument is somewhat circular but the good agreement between the time of Pb depletion on the Moon and the model Rb–Sr age of the Earth-lunar disc equilibration provides evidence of Pb loss from the lunar accretion disc associated with the giant impact or events shortly thereafter. Furthermore, there is no expectation of this apparent age agreement if the Earth lost significant Rb during the giant impact. Therefore, it would appear that the Earth did not lose significant moderately volatile elements such as K, Rb, Tl or Pb during the giant impact. This is particularly important because there is strong evidence for late loss of the heavy elements Pb and Xe from the BSE, as discussed below.

4. The lead and xenon ages of the Earth may reflect the 70–110 Ma giant impact

A giant impact at \textit{ca} 100 Ma changes a number of paradigms and paradoxes regarding the earliest development of the Earth. Perhaps most strikingly, a giant impact this late extends the accretion history of the Earth to a point that there is now excellent agreement with the lead and xenon isotopic composition of the BSE. A number of scientists have attempted to deduce the Earth’s age from lead isotope systematics since the classic studies of Holmes (1946), Houtermans (1946) and Patterson (1956). More recent treatments by Allègre et al. (1995) and Galer & Goldstein (1996) showed that the Pb isotopic composition of the BSE yields an ‘age’ of roughly 100 Ma after the start of the Solar System. These are relatively simple two-stage model ages equivalent to assuming that U/Pb fractionation by core formation took place instantaneously. The difference between the model Hf–W age of \textit{ca} 30 Ma (Kleine et al. 2002; Yin et al. 2002) and the \textit{ca} 50–150 Ma 235/238U–207/206Pb (or ‘Pb–Pb’) ages (Allègre et al. 1995; Galer & Goldstein 1996) was highlighted by Halliday (2003, 2004) and Wood & Halliday (2005). They argued that, whereas the former related to the main stages of growth and core formation, the latter reflected either segregation of sulphide to the core following cooling after the giant impact, or an unexplained late volatile loss. It is now clear that this lead isotopic age in the Earth defines the Moon-forming giant impact that irrevocably left its mark on the U–Pb systematics of the Earth as well as the Moon.

As with Rb, an element as heavy as Pb is gravitationally bound for an object of the size of the Earth. However, if it was atmophile (Halliday 2004) it could be carried by hydrodynamic escape (Hunten et al. 1987) and this would be consistent with the timing of xenon loss. The extreme fractionation of Xe (depletion in light isotopes) is thought by some to be the result of hydrodynamic escape of a very large atmosphere (Hunten et al. 1987). The giant impact may well have resulted in major loss of atmospheric volatiles from the Earth (Ahrens 1990; Pepin 1997). As previously noted (e.g. Allègre et al. 1995), the Pb–Pb age is similar to the 129I–129Xe age of the Earth’s degassing and atmospheric loss, commonly given as \textit{ca} 100 Ma after the start of the Solar System (Allègre et al. 1995; Pepin 1997; Zhang 1998). At one stage it was hard to explain why the timing of the volatile loss was younger than the giant impact determined from the Hf–W data. Most recently, Pepin & Porcelli (2006) proposed two events in Xe systematics, one at 20–50 Ma related to the Moon-forming giant impact and
the second at 95–100 Ma related to some other major loss event. These two events are based on the difference between the Xe isotope produced by the decay of $^{129}$I and Pu. At the present time, this apparent ancient heterogeneity is puzzling given the very evident history of extensive mantle mixing recorded in all other isotopic systems. If the Moon-forming giant impact did not occur until ca 100 Ma the question arises as to what the earlier Xe event refers to.

Now the Earth’s episode of Xe loss at 100 Ma (Pepin 1997; Pepin & Porcelli 2006) can be related to the timing of loss of atmophile and moderately volatile elements such as Rb and Pb from the accretion disc from which the Moon formed (Tera et al. 1973). Given the above evidence that Rb was not lost from the Earth itself during the giant impact, it is highly unlikely that Pb was lost at this time. The giant impact involved the addition of Fe, Ni and other siderophile elements that were added to the core at ca 100 Ma and constitute approximately 10 per cent of its current mass. As such, it is more likely that Pb was lost from the BSE by addition to the core. Therefore, the Pb–Pb age of the Earth defines the last time a significant fraction of Pb was added to the Earth and then partitioned into the core.

The fact that the loss of Xe from the Earth at 100 Ma was not accompanied by large losses of moderately volatile elements and Pb, despite the extreme depletion in the Moon, could mean that these elements were not atmophile which in turn could indicate that the Earth’s surface was not at a very high temperature prior to the giant impact. This contrasts with a common view that the Earth was blanketed by a nebular or steam atmosphere that kept it hot in between accretionary atmospheric blow-off events (Ahrens 1990).

5. The history and mechanisms of core formation with a late giant impact

A possible accretion model that satisfies the W isotopic composition of the silicate Earth with a giant impact at 100 Ma is shown in figure 1a. These accretion models are not unique but are usually based on an idealized accretion scenario in which the Earth accretes at exponentially decreasing rates with an overall increase in the size of less frequent impactors (Halliday et al. 1996; Jacobsen & Harper 1996; Halliday 2004). In previous W isotope modelling there has been difficulty reconciling the age of the Moon with the W isotopic composition of the BSE, which should be less radiogenic unless there was disequilibrium between the incoming metal of the impactor and the BSE (Halliday 2004). Therefore, in some previous models a fraction of the metal in the impactor does not equilibrate with the BSE but is instead added directly to the core. This has the effect of not completely ‘resetting’ the W isotopic composition of the BSE towards chondritic values when an impact occurs. The more protracted the accretion history, the less opportunity there is for the BSE to generate its W isotopic composition, which is slightly radiogenic relative to chondrites (Kleine et al. 2002; Schoenberg et al. 2002; Yin et al. 2002) via radiogenic ingrowth. Therefore, slower accretion should mean more disequilibrium during accretion (Halliday 2004).

The W isotope models shown in figure 1b,c illustrate this effect and involve a simple model of stepped accretion and concomitant core formation with the exception of a 0.9 per cent late veneer and 0.1 per cent late heavy bombardment
The Pb isotopic effects of a simple model of this nature have already been calculated (model A in Halliday 2004) and define a composition that is, within significant uncertainty, identical to the average of the various estimates for the Pb isotopic composition of the BSE. Two W isotope scenarios are shown in figure 1. The first (figure 1b) involves total equilibration of incoming metal with the BSE during the entire accretion history. This yields a present day $\varepsilon^{182}\text{W}$ of the BSE of $-1.8$, which is within error of chondritic values ($-1.9 \pm 0.1$) and clearly does not represent the accretion history of the Earth, which has a present day $\varepsilon^{182}\text{W}_{\text{BSE}}=0$. The second (figure 1c) includes 60 per cent disequilibrium during all of the accretion history apart from the late veneer. That is, 60 per cent of the incoming metal mixes directly with the Earth’s core and does not mix with the BSE. This second model satisfies the condition that the $\varepsilon^{182}\text{W}$ of the BSE equals zero. The more protracted the accretion history, the more disequilibrium that is needed to generate the difference in $\varepsilon^{182}\text{W}$ between the BSE and chondritic compositions. This is a highly protracted accretion scenario compared with all previous models and corresponds to a mean life of continuous accretion at exponentially decreasing rates of ca 35 Ma. This is just a model of what may be possible from the data. It assumes, for example, that the bulk silicate fraction of Theia has a Hf/W similar to that of the BSE and that its accretion history was equivalent to that of the Earth when it was this size. It also assumes a 1 per cent late veneer that never equilibrates with the core. All of these assumptions could be wrong, as discussed in Halliday (2003, 2004).

Figure 1. (a) A schematic involving exponentially decreasing accretion growth model for the Earth culminating in a Moon-forming giant impact at 100 Ma. (b) The W isotopic evolution of the model shown in (a) if no disequilibrium during accretion is included. (c) The W isotopic evolution of the model shown in (a) if 60% core mixing is allowed during accretion.

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assumption is that the Earth has chondritic refractory element ratios such as Hf/W. This should now be questioned given the evidence presented by Caro et al. (2008) that the $\varepsilon^{142}$Nd values of the Earth, the Moon and Mars are best explained by a planetary Sm/Nd ratio that is higher than chondritic. If this is caused by melting in the solar nebular the Hf/W ratio would also be elevated leading to more protracted time scales for accretion.

Perhaps the most important assumption that should be questioned is that accretion takes place at an exponentially decreasing rate as predicted by Wetherill (1986). If instead the main stage accretion of the Earth was completed relatively quickly, generating radiogenic W in the BSE, and the Moon-forming event was an isolated incident that re-formed the Earth relatively late, then disequilibrium is not needed to explain the W isotopic composition of the BSE. This is shown in figure 2 in which the present-day W isotopic composition of the BSE and the Moon reflects a very late admixing of the entire W from Theia into the silicate Earth with no direct mixing between the two cores. This is accomplished with quite rapid growth in the first stage with an accretionary mean life of $ca$ 10 Ma not unlike that in many dynamic simulations (Wetherill 1986; Jacobsen & Harper 1996). With the addition of a 1 per cent late veneer, the W isotopic composition of the BSE is replicated. This means that it is no longer necessary to call upon disequilibrium during accretion to explain the W isotopic composition of the BSE (Halliday 2004). Note that the inclusion of a veneer is an assumption based on current thinking that is not required by these kinds of models. In fact, it is possible from W isotopes to address the mass and composition of this late veneer, as discussed below.

6. The lack of a late veneer

The late veneer is widely considered to have added the refractory highly siderophile elements to the silicate Earth (Chou 1978; Wänke & Dreibus 1988; Newsom 1990) and has been invoked as a possible source for the Earth’s water (e.g. Dauphas et al. 2000; Morbidelli et al. 2000). It could also be the main source of carbon and sulphur in the silicate Earth (Yi et al. 2000). The composition of
the BSE relative to CI carbonaceous chondrites is shown in figure 3. An important facet of the study of Touboul et al. (2007) is that, within a very high level of precision, the W isotopic composition of the silicate Earth is the same as that of the Moon. Although this might make sense in terms of equilibration it is not expected in terms of our understanding of the subsequent history of the two bodies. The fact that the BSE and the Moon are identical in W isotopic composition precludes significant additions to the Earth or the Moon after the giant impact. Even if the Moon formed by fission rather than a giant impact, the same argument would still apply. Note that the late veneer has to be added to the Earth after the giant impact because it has to post-date the latest stage of core formation, which has to be no earlier than the removal of the large budget of siderophile elements contributed by the impacting planet Theia.

The precise measurement of the W isotopic composition of the Moon therefore provides an important new constraint that should be refined further with additional measurements because it effectively limits the size of any late veneer of material that was added to the Earth after the giant impact. Similar arguments have previously been made on the basis of oxygen isotopes (Halliday et al. 2001; Wiechert et al. 2001). The rationale is roughly as follows. Objects that are accreted to the Earth and the Moon will not be affected greatly by the difference in gravity if they are delivered from the far reaches of the asteroid belt as has been proposed for watery carbonaceous chondritic material (Morbidelli et al. 2000). They are travelling so fast that by the time they reach the Earth the dominant difference in delivery flux is going to be a function of the exposed cross-sectional area of the two objects rather than their mass. On this basis, the Moon should accrete approximately 5 per cent of the mass of material that is added to the Earth. Therefore, given the difference in mass between the Earth and the Moon, a 1 per cent late veneer added to the Earth should be accompanied by approximately a 5 per cent veneer on the Moon. In fact the Moon’s late veneer is 0.02 per cent
Therefore, if there is a late veneer on the Earth, it is likely to have been generated by a single large (e.g. 0.01 Earth mass) impactor. Of course, a way around this argument is to propose that the Moon’s late veneer was never incorporated into the lunar interior but was added after the crust formed (Walker et al. 2004). However, this would mean an enriched lunar surface equivalent to a chondrite layer of a few per cent of lunar mass, which is not observed.

The mass of the Earth’s late veneer is based on the degree of depletion of highly siderophile elements such as the platinum group elements (figure 3). These should have been partitioned into the core in proportion to their partition coefficients. Instead they are present in roughly chondritic relative abundances (Chou 1978; Newsom 1990; Palme & O’Neill 2003). Some have viewed the late veneer as responsible for the budgets of more volatile elements. For example, approximately 1 per cent of water-rich (20% H2O) carbonaceous chondrites would easily provide sufficient water to yield the Earth’s hydrosphere and estimated mantle water budget (Morbidelli et al. 2000). The difference between the W isotopic composition of the BSE and the Moon is currently irresolvable at $\varepsilon^{182}W = 0.09 \pm 0.10$ (Touboul et al. 2007). The composition of sample 74275 ($-0.24 \pm 0.25$) would appear to offer an even tighter constraint but the degree to which an individual datum such as this can be relied upon without similar values from other samples needs to be verified with more data. The results of a series of calculations of the isotopic effect of adding CI material to the BSE are shown in figure 4. To do this in a comprehensive fashion requires that the calculations all generate $\varepsilon^{182}W_{BSE} = 0$ and $\text{Hf/W}_{BSE} = 15$. Therefore, the mass and composition of the late veneer has to be factored into the calculation of the development of the Hf/W of the BSE and that has to be factored into the W isotopic evolution of the BSE with a fixed age of the Moon of between 80 and 110 Ma after the start of the Solar System. It is assumed that accretion prior to the late veneer always included equilibration between incoming metal and the BSE. The rate of accretion prior to the giant impact is adjusted to achieve $\varepsilon^{182}W_{BSE} = 0$. The results (figure 4) show that a significant late veneer of CI material (i.e. 0.5%) could be added to the BSE without compromising the similarity with the isotopic

*Figure 4. The effect on the difference between the W isotopic composition of the Moon and the BSE of adding a late veneer of CI composition material based on the data in Kleine et al. (2004).*
composition of the Moon within the uncertainty of the W isotope measurements. The effects of such a veneer on the inventory of siderophile elements and water are shown in figure 5. It can be seen that this would easily be sufficient to generate the estimated water content of the silicate Earth (440 ppm) assuming that the CI material carries 20 wt% H₂O. It would also generate plenty of C and S.

However, the more refractory highly siderophile elements Re and Au are not well explained with this model. In fact, it has been argued that these elements are derived from a source more akin to ordinary chondrites (Walker et al. 2002; Drake 2005). The reason for this is twofold. First, the Os isotopic composition of the BSE matches that expected from a veneer with a Re/Os ratio like that of ordinary chondrites (Walker et al. 2002). Second, the Ru and Mo isotopic compositions of meteorites are correlated (Dauphas et al. 2004), and the BSE appears to be different from the composition of CI chondrites and more similar to ordinary chondrites (Drake 2005). Partly on this basis, Drake (2005) dismissed the late veneer as an explanation of the Earth’s water.

To explore the degree to which ordinary chondrites might have delivered the highly siderophile elements to the BSE, the same calculations have been repeated using the information that is available for their W isotopic compositions (Kleine et al. 2008). The results (figure 6) show that only a smaller (0.3 ± 0.3%) ordinary chondrite veneer can be tolerated. However, this alone could generate the budgets of the more refractory highly siderophile elements Re and Au (figure 7). It would, however, not provide anything like the required amounts of water and carbon.

To address this problem further, it is tempting to call upon a range of impactors as the explanation for the composition of the veneer. However, this runs into the above difficulty of delivering the veneer to the Earth without impacting the Moon and changing its composition. An alternative is that the water content of the Earth is a primary feature that predates and survived the
giant impact (Righter & Drake 1999; Drake 2005). Support for this theory is found in the surprisingly high water content of lunar volcanic glasses (Saal et al. 2008). Similarly, it has been argued that the highly siderophile refractory elements in the BSE may not reflect the late veneer so much as a change in partitioning as the silicate Earth became more oxidizing towards the end of accretion and core formation as a consequence of perovskite pumping (Wade & Wood 2005; Wood & Halliday 2005). With the young age for the Moon, such a self-oxidation model is no longer necessary to explain the Pb isotope systematics of the BSE.

Figure 6. The effect on the difference between the W isotopic composition of the Moon and the BSE of adding a late veneer of the H ordinary chondrite composition material based on the data in Kleine et al. (2008).

Figure 7. The effect on the budgets of Re, Au, S, C and water in the BSE of adding a late veneer of the H ordinary chondrite composition material assuming that this is the sole source of these elements. Based on the BSE concentrations of Re, 0.32 ppb; Au, 0.88 ppb; S, 200 ppm; C, 100 ppm; H₂O, 440 ppm; and the H ordinary chondrite concentrations of Re, 70 ppb; Au, 215 ppb; S, 2.0 wt%; C, 1100 ppm; H₂O, 1000 ppm %. 

giant impact (Righter & Drake 1999; Drake 2005). Support for this theory is found in the surprisingly high water content of lunar volcanic glasses (Saal et al. 2008). Similarly, it has been argued that the highly siderophile refractory elements in the BSE may not reflect the late veneer so much as a change in partitioning as the silicate Earth became more oxidizing towards the end of accretion and core formation as a consequence of perovskite pumping (Wade & Wood 2005; Wood & Halliday 2005). With the young age for the Moon, such a self-oxidation model is no longer necessary to explain the Pb isotope systematics of the BSE.

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Irrespective of these matters for further investigation, the constraint remains that the depletion of the silicate Earth in certain elements is hard to explain without an earlier more reduced stage of evolution (Wade & Wood 2005). Furthermore, as explained above, the general principle that some of the BSE highly siderophile element abundances are better explained by changes in partitioning with pressure (Righter et al. 1997; Righter & Drake 1999; Wade & Wood 2005), rather than by a late veneer, is supported by the W isotope data for the Moon. Further refinements to these challenging W isotope measurements should provide even more powerful constraints.

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A young Moon-forming giant impact


