# Mixing, volatile loss and compositional change during impact-driven accretion of the Earth

**Alex N. Halliday**

*Department of Earth Sciences, ETH Zentrum, NO, Sonneggstrasse 5, Zürich, CH8092, Switzerland*

**The degree to which efficient mixing of new material or losses of earlier accreted material to space characterize the growth of Earth-like planets is poorly constrained and probably changed with time. These processes can be studied by parallel modelling of data from different radiogenic isotope systems. The tungsten isotope composition of the silicate Earth yields a model timescale for accretion that is faster than current estimates based on terrestrial lead and xenon isotope data and strontium, tungsten and lead data for lunar samples. A probable explanation for this is that impacting core material did not always mix efficiently with the silicate portions of the Earth before being added to the Earth's core. Furthermore, tungsten and strontium isotope compositions of lunar samples provide evidence that the Moon-forming impacting protoplanet Theia was probably more like Mars, with a volatile-rich, oxidized mantle. Impact-driven erosion was probably a significant contributor to the variations in moderately volatile element abundance and oxidation found among the terrestrial planets.**

It has been proposed on the basis of new W isotopic measurements for chondrites[1–3] that the Earth formed slightly faster than was previously thought because the original W isotopic data for carbonaceous chondrites are now known to be inaccurate by 150–200 p.p.m.. The mean life for accretion, $\tau$, is the inverse of the time constant for exponentially decreasing growth and corresponds to the time taken for 63% of the planet to accrete[4,5]. A $\tau$ value of $\sim$11 Myr is obtained with continuous core formation modelling using the revised Solar System parameters[1]. This new 'fast' result contrasts with the various values of 15 to 40 Myr defined by Pb isotopic data using the same models[5]. These calculations of $\tau$ assume total equilibration of incoming metal and silicate with the bulk silicate Earth (BSE) and no change in parent/daughter ratio in the total and silicate Earth during accretion. Here these assumptions are examined. It is proposed that the faster rates deduced from decay of $^{182}$Hf to $^{182}$W probably reflect contrasting behaviour of refractory, as opposed to volatile, elements. By modelling the data in a parallel fashion, insight into the conditions, timescales and processes of Earth accretion can be gained.

Of particular interest is whether accreting material really equilibrated isotopically with the silicate portion of the Earth—an essential tenet of accretion rate models. Some accretion and core formation simulations provide evidence against this[6–10]. If the incoming metallic core totally fragments into very small droplets upon impact[9] because of Rayleigh–Taylor instabilities, say, then equilibration could be relatively efficient. If, however, some of the incoming core material forms large dense masses[10], then equilibration with silicate before core coagulation seems unlikely. A second issue is whether moderately volatile elements were lost during accretion[11]. Much of the depletion in volatile elements in the terrestrial planets is thought to have occurred in the early solar nebula[12]. Whether the additional dramatic differences between the Earth, Moon and Mars are the product of later losses during accretion has been less clear[11,12]. Because Pb is moderately volatile, late changes in budgets will affect U–Pb but not Hf–W chronology. Lastly, changes in oxidation state in protoplanetary mantles can be deduced from time-integrated Hf/W ratios because of the change in core–mantle W partitioning. Therefore, W isotopes offer a fingerprint of protoplanetary environments, analogously to the recent modelling of Sr isotopes[11].

## Realistic accretion models

Large-scale impact-driven accretion is thought to be responsible for 99% of the Earth's growth[13]. Much of the impacting material is thought to have been differentiated planets and planetesimals[14], although undifferentiated volatile-rich objects probably also played a part. This complex accretion history is not well simulated by existing isotopic models. Two-stage U–Pb and Hf–W model ages have long been used to define an artificial time at which the Earth's core instantaneously formed or last equilibrated with the silicate Earth[15–17]. Although once considered useful, such calculations, especially when based on short-lived nuclides, are of little meaning for open systems like the Earth that grew over a significant time interval[5,13]. Dynamic simulations indicate that accretion of the Earth took about $5 \times 10^6$ years in the presence of a minimum-mass solar nebula[18] or $10^7$–$10^8$ years with no nebular gas[13], rendering two-stage model ages meaningless in terms of precise rates or absolute time. This is particularly true of $^{182}$Hf, with a half-life of 9 Myr, because late core formation would have no effect on the W isotopic composition of the Earth. The two-stage Hf–W model age for the Earth's core is 30 Myr (refs 1–3). This defines the last time, if ever, that the Earth could have globally re-equilibrated. However, there is no basis for believing that such an event occurred and, as far as W isotopes are concerned, roughly half the Earth's core could have formed much later.

A more practical and realistic approach is to assume what seems likely, that the core grew in approximately constant proportion to the Earth's mass. The isotopic data then define an accretion rate[1,5]. There exists a strong basis for this in theory and observation. The energy from accretion and radioactive decay should result in a rapid build-up of heat, leading to widespread early melting and core formation[8–10,19]. This is confirmed by $^{107}$Pd–$^{107}$Ag and $^{182}$Hf–$^{182}$W data for iron meteorites, many of which formed at pressures expected for small planetesimal cores[20]. Most significantly, continuous core formation is consistent with the approximately constant mantle–core proportions inferred from iron depletion in silicates from Asteroid 4 Vesta, Mars and the Earth[21]. These objects are (roughly) 1, 10 and 100% of the mass of the Earth.

Even continuous core-formation models have not addressed in detail the isotopic effects that arise with large-scale impacts such as built the Earth. Here it is assumed that accretion starts with runaway growth of objects up to 1% of the size of the Earth[22]. Further accretion proceeds via collisions between such differentiated objects[13,14]. It is widely believed that the Moon formed as a result of such a collision between the proto-Earth and an impacting Mars-sized differentiated planet Theia[6,7], after which very little further growth occurred. Therefore, the model culminates in a '9% giant impact' (that is, an impact contributing 9% of the current mass of the Earth) which was followed by a late veneer of 0.9% of the current mass of the Earth[23]. (See Fig. 1 for details.) The smooth curves in Fig. 1 show the exponentially decreasing rates of growth. The step function curves define the growth used in the isotopic calculations. The approximated $\tau$ and timing of each increment are calculated from the timing of the giant impact, $t_{GI}$, to achieve an overall exponentially decreasing rate of growth. The use of a step function means that the isotopic results that derive from a particular $\tau$ only approximate to that deduced from a truly continuous exponential function. Furthermore, the actual growth history is largely unknown. Neither matters for this study because it is the difference between the chronometers that is of interest.

It is assumed that the impactors and their cores grow at the same absolute rate as the Earth did when of equivalent size. The isotopic evolution of metal and silicate reservoirs in the proto-Earth, and of impacting planetesimals and planets, are tracked in detail with increasing mass. The metal–silicate partitioning, the degree to which W and Pb in the cores of the impactors equilibrate with the silicate Earth, and the $^{238}U/^{204}Pb$ of the total Earth, $\mu_{TOTE}$, which may change if fractions of volatile Pb are blown-off, can all be varied at any stage. The proportion of the Moon that forms from core and silicate material from Theia, and silicate from the Earth, can also be adjusted.

## Timescales for accretion from Pb isotope data for the Earth

The age of the Earth is primarily determined using Pb isotopes[15,17,24]. The slope of the line connecting the composition of the present-day BSE with the Solar System's primordial Pb in $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ space defines a model time of fractionation of U/Pb. However, in an open system like the accreting Earth, the composition relates to the accretion flux[5]. Eleven estimates[25–35] of the Pb isotopic composition of the BSE are shown in Table 1. From these the model $t_{GI}$ and $\tau$ necessary to achieve a growth profile like those shown in Fig. 1 have been calculated (model A, Table 1). The values of $t_{GI}$ range between 52 and 167 Myr with $\tau$ of 18 to 57 Myr. It is hard to find a realistic mechanism for shortening these timescales to achieve agreement with Hf–W. The calculated Pb isotopic composition depends on the fractionation of $^{238}U/^{204}Pb$ for the BSE ($\mu_{BSE}$)

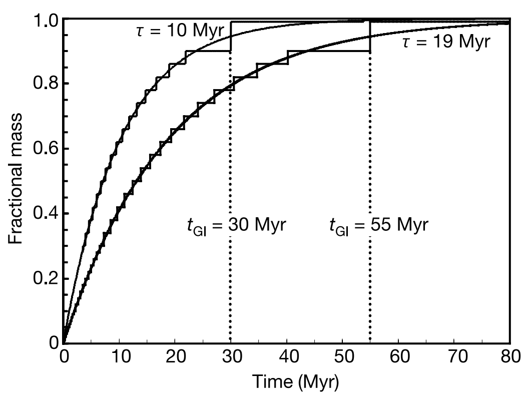


**Figure 1** The change in mass fraction of the Earth as a function of time. For the model used, two accretion scenarios are shown, calculated from a giant impact at 30 and 55 Myr after the start of the Solar System. The approximated $\tau$ is the time taken to achieve 63% growth. Both this and the timing of each increment are calculated from $t_{GI}$ to achieve an overall exponentially decreasing rate of growth for the Earth broadly consistent with dynamic simulations. The smooth curves show the corresponding exponentially decreasing rates of growth. The step function curves define the growth used in the isotopic calculations. It is assumed that the earliest stage of growth is a runaway process that builds the Earth to 1% of its current mass over $\sim 10^5$ years, as suggested by simulations[22]. Further growth of the Earth was dominated by stochastic collisions between these objects[13]. The overall rate of accretionary growth of the Earth may have decreased in some predictable fashion with time, but the growth events would have become more widely interspersed and larger. Therefore, the model simulates further growth by successive additions of objects of 1% of the current mass of the Earth, until it reached 10% of its current mass, then by 2% objects, up to 30% and then by 4% objects up to 90%. The Moon-forming giant impact is thought to be the last of these major collisions that affected the Earth[6,7]. The most widely accepted scenario is that this took place when the Earth was ~90% of its current mass and involved an impactor planet, Theia, that was ~10% of the (then) mass of the Earth[6,7]. Therefore, in the model the giant impact contributes a further 9% of the current Earth mass. There is evidence against large amounts of accretion after the giant impact. For example, significant further accretion would probably have disrupted the identical oxygen isotopic compositions of the Earth and Moon[49]. In the model, a late veneer, for which some evidence exists[23], contributes an additional 0.9%. There is a final 0.1% added after this. The exact sizes of growth increments are somewhat arbitrary in this model but this is of little consequence.

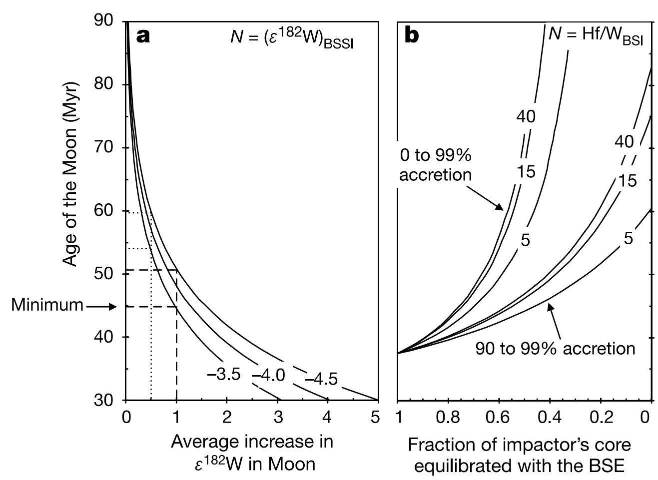


**Figure 2** The age information that can be derived from W isotope data for the Earth and Moon at the present time is strongly model dependent. All calculations assume $(Hf/W)_{BSS} = 1.136$, $(Hf/W)_{BSE} = 15$, $(Hf/W)_{MOON} = 22$, $\epsilon\,^{182}W_{BSSI} = -1.9$ and a half-life of hafnium-182, $\lambda\,^{182}Hf$, of $0.077 \times 10^{-6}\,yr^{-1}$. (BSS, bulk Solar System.) In **a**, the effects on the calculated age of the Moon of not knowing the average amount of radiogenic, as opposed to inherited or cosmogenic, $^{182}W$ are shown. The increase in $\epsilon W$ within the Moon as a function of decay of primordial $^{182}Hf$, as can be deduced from currently available data, is almost certainly less than 1 unit and may be less than 0.5. The data are therefore fully consistent with independent estimates for an age of the Moon (hence giant impact) >45 Myr after the start of the Solar System. The different curves are based on differing values[3] of the $\epsilon\,^{182}W_{BSSI}$, which directly affects the calculated $(^{182}Hf/^{180}Hf)_{BSSI}$. In **b**, the effect on calculated Hf–W timescales for the Earth's formation of incomplete mixing and equilibration of impacting core material is illustrated. This plot shows the true time of the giant impact that generates $\epsilon\,^{182}W_{BSE}$ of zero as a function of various levels of incomplete mixing of the impacting core material with the BSE. The lower curves are for disequilibrium during the giant impact alone. The upper curves correspond to disequilibrium during the entire accretion process up to and including the Giant Impact. The different curves for different $Hf/W_{BSI}$ (the Hf/W in the silicate portion of the impactor) also are shown. All curves are calculated with $\epsilon\,^{182}W_{BSSI} = -3.5$. The effect of using more negative values[3] is to yield more protracted calculated timescales for the giant impact.

relative to $\mu_{TOTE}$ during growth. The $\mu_{TOTE}$ of 0.7 used here is based on Earth's K/U ratio (ref. 15). Even if the K/U ratio of the Earth has been overestimated[36], a reduction only serves to increase $\mu_{TOTE}$, extending the timescales. A 10% increase in $\mu_{TOTE}$ changes $t_{GI}$ from >52 to >54 Myr. It has been proposed that the $\mu_{TOTE}$ is much higher and that core formation only increased $\mu_{BSE}$ by a factor of 2.5 (ref. 37). This increases the calculated timescales greatly (Table 1, model B). Incomplete mixing and lack of equilibration between the Pb of the core of Theia and the BSE during the giant impact would also increase timescales.

It is conceivable that a fraction of the Earth's Pb was lost during accretion. This effect should be small because of Earth's gravity. A comparison between the $(Rb/Sr)_{BSE}$ and the time-integrated Rb/Sr of the material that made the Moon, assuming a similar starting composition, indicates a <50% loss of Rb from the Earth[11]. Assuming ~90% of Earth's Pb is partitioned into the core, such loss is less likely (probably <5%). In the unlikely scenario that $\mu_{TOTE}$ did change from ~0.35 to ~0.7 during the giant impact, the calculated $t_{GI}$ would still be in the range 40 to 135 Myr (Table 1, model C).

Therefore, no likely scenarios that might have affected U–Pb preferentially eliminate the discrepancy with the Hf–W $\tau$ of 11 Myr and $t_{GI}$ of 30 Myr. It is possible that all of the Pb estimates are incorrect, but even the three most recently published[25–27] yield $t_{GI} > 50$ Myr and $\tau > 20$ Myr (Table 1). These timescales are similar to those deduced from I–Xe and Pu–Xe chronometry[38], which indicate that the last major Xe loss from the Earth's atmosphere took place 50 to 80 Myr after the start of the Solar System[39]. It has been proposed that this was caused by atmospheric blow-off during the giant impact[39,40].

## The age of the Moon

The age of the Moon itself provides an important test of whether such model Pb age calculations are correct. However, this is not yet well defined. Most of the precise estimates for the earliest age of the Moon are based on U–Pb and Sm–Nd and are 70 to 120 Myr (ref. 41), 50 to 70 Myr (ref. 42) and 50 to 100 Myr (ref. 43). The initial Sr isotopic composition of the Moon[11,43] also makes sense in terms of an origin at ≥50 Myr because this yields a realistic time-integrated Rb/Sr for the mix of Earth and Theia of ≤0.07—similar to or less than the present-day Rb/Sr of Mars, as expected[11].

At one time it was thought that there were well-defined W isotope variations produced by $^{182}$Hf decay within the Moon, yielding model ages of ~55 Myr (ref. 44). A major portion of this was produced from cosmogenic $^{182}$Ta (refs 45, 46). The revised average Solar System composition has been used to yield a Hf–W model age of ~30 Myr for the Moon[1,2]. This does not define the actual age of the Moon, however, because it assumes that the Moon formed from undifferentiated (with respect to Hf–W) chondritic material. There exists a great deal of evidence against this, and using the chondritic value as a reference merely provides a likely minimum time-span.

Most values of $\epsilon$W (the fractional deviation in parts per $10^4$ from the $^{182}W/^{184}W$ for the BSE) values for lunar rocks that are reasonably precise ($\leq \pm 1$) after crude cosmogenic corrections are in the range zero to one[5,45,46]. One sample has a well-defined excess of $\epsilon W \approx 1.5$ based on internal systematics[46]. Some of the remaining data needed to be treated with caution until more accurate cosmogenic corrections can be applied. Nevertheless, there is a prevalence of $\epsilon$W values close to zero that has been taken as evidence that this was the initial composition still preserved in lunar reservoirs that underwent little subsequent radiogenic increase[5]. The average radiogenic increase of $\epsilon$W of the lunar mantle is probably <1.0 and may well be <0.5. Therefore, the Hf–W age of the Moon is probably >44 and may be >54 Myr (Fig. 2a). The $\epsilon W_{BSSI}$ (where BSSI is bulk Solar System initial) is also not yet well defined and may have been lower than recently assumed[3]. If so, the Moon formed even later (Fig. 2a).

## Tungsten isotopic disequilibrium and mixing during accretion

Given the above tentative but self-consistent evidence that the giant impact probably occurred >45 Myr after the start of the Solar System, the $\epsilon W_{BSE}$ of zero can now be used to constrain conditions during accretion. Using $(Hf/W)_{BSE} = 15$, a $\tau$ of ~13 Myr and a $t_{GI}$ at 38 Myr are obtained with the model presented here. This small difference from $\tau \approx 11$ Myr (ref. 1) mainly reflects the different style of model that is smooth versus punctuated. If the $\epsilon W_{BSSI}$ was lower[3], say −4.0, the best estimate for $t_{GI}$ would increase from 38 to 43 Myr. If $(Hf/W)_{BSE}$ started much lower but then with the loss of volatiles during the giant impact W became more siderophile, the calculated $t_{GI}$ would increase slightly from 38 to 41 Myr. All these modifications to conditions during accretion or the fundamental Hf–W parameters still result in calculated $t_{GI} < 45$ Myr.

In contrast, incomplete mixing and equilibration of impacting core material is a very effective way of producing Hf–W timescales that seem too short (Fig. 2b). The $t_{GI}$ extends to >70 Myr with incomplete equilibration of Theia's core with the BSE. The timescale is even longer if partial equilibration includes earlier episodes (Fig. 2b). Therefore, the simplest explanation for faster W isotopic accretion rates is incomplete equilibration of W.

It is normally assumed that accreted W must approach equilibrium with the silicate Earth, otherwise the BSE would not be almost chondritic[5]. The small (0.2‰) excess $^{182}$W that now has

Table 1 **Calculated values for the Earth's accretion timescale based on lead isotopes**

| Estimate | Reference | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $\mu_{BSE}$ | Model A | | Model B | | Model C | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $t_{GI}$ | $\tau$ | $t_{GI}$ | $\tau$ | $t_{GI}$ | $\tau$ |
| MKC-03 | 25 | 18.07 | 15.54 | 8.66 | 72 | 25 | 196 | 68 | 59 | 20 |
| KC-99 | 26 | 18.27 | 15.60 | 8.91 | 90 | 31 | 253 | 87 | 73 | 25 |
| KT-97 | 27 | 17.44 | 15.16 | 8.04 | 74 | 25 | 199 | 69 | 60 | 21 |
| GG-91 | 28 | 18.11 | 15.617 | 8.67 | 54 | 19 | 147 | 51 | 44 | 15 |
| L-91 | 29 | 17.92 | 15.47 | 8.50 | 65 | 23 | 177 | 61 | 53 | 18 |
| K-89 | 30 | 17.822 | 15.445 | 8.38 | 54 | 19 | 145 | 50 | 44 | 15 |
| AL-89 | 31 | 18.34 | 15.551 | 9.05 | 119 | 41 | 343 | 118 | 97 | 33 |
| A-88 | 32 | 18.40 | 15.58 | 9.11 | 120 | 41 | 349 | 120 | 98 | 34 |
| ZH-88 | 33 | 18.619 | 15.565 | 9.44 | 165 | 57 | 503 | 173 | 134 | 46 |
| D-84 | 34 | 17.83 | 15.457 | 8.38 | 52 | 18 | 139 | 48 | 42 | 14 |
| DZ-79 | 35 | 18.252 | 15.476 | 8.98 | 127 | 44 | 368 | 127 | 103 | 36 |

Calculated values for the $\tau$ and $t_{GI}$ given in Myr as deduced from different estimates of the Pb isotopic composition of the BSE using the type of accretion model shown in Fig. 1. All calculations assume continuous core formation and total equilibration between accreted material and the BSE. All $^{238}U/^{204}Pb$ ($\mu$) values are present-day equivalent values. The present-day $(^{206}Pb/^{204}Pb)_{BSE}$ can be used to place accurate limits on the current $\mu_{BSE}$ because the age of the Earth introduces a trivial uncertainty and early changes in $\mu$ are insignificant for present-day $(^{206}Pb/^{204}Pb)_{BSE}$. The single-stage Pb–Pb model age was used. Model A uses this $\mu_{BSE}$ to define the Pb depletion caused by core formation and to calculate the accretion timescales. Model A assumes no Pb loss from the Earth and $\mu_{TOTE} = 0.7$ (ref. 15). Model B assumes that Pb is depleted by a factor of only 2.5 by core formation as proposed in ref. 37. The $\mu_{TOTE}$ is then adjusted to yield the $\mu_{BSE}$ shown and is in the range 3 to 4. Model C is the same except that a $\mu_{TOTE} = 0.35$ is assumed until the giant impact when half the Earth's Pb is instantaneously lost. Such a model is dynamically difficult (see text). The $\mu$ of 0.35 merely represents the composition of all accreting material in this model. In every model $(^{206}Pb/^{204}Pb)_{BSSI} = 9.307$, $(^{207}Pb/^{204}Pb)_{BSSI} = 10.294$, $^{238}U/^{235}U = 137.88$, $\lambda^{235}U = 9.85 \times 10^{-10}\,yr^{-1}$, $\lambda^{238}U = 1.55 \times 10^{-10}\,yr^{-1}$.

been convincingly resolved[1–3] may record some extreme event in the range of conditions, such as the giant impact. This is consistent with simulations of accretion and core formation[6–10]. For illustrative purposes, if $t_{GI}$ were 55 Myr the amount of equilibration of Theia's core with the BSE during the giant impact would have been 26%, assuming 100% before and after equilibration and constant $(Hf/W)_{BSE}$ and $(Hf/W)_{BSI}$ of 15, where BSI is the bulk silicate impactor (Fig. 3a). Note that the giant impact would increase $\epsilon W_{BSE}$. However, the initial W isotopic composition of the Moon indicates that Hf/W in planetary mantles was anything but constant, as explained next.

## Mars-like protoplanets to the Earth–Moon system

The majority of giant impact simulations generate most of the Moon's mass from the silicate portion of Theia[6,7]. Tungsten isotopes provide a powerful constraint on the Moon's precursor materials. If the Moon was produced from the BSI with $(Hf/W)_{BSI} = (Hf/W)_{BSE} = 15$, the initial $\epsilon W$ of the lunar mantle would be >15. This is because Mars-sized planets like Theia are thought to have completed their growth early, like Mars[47].

Instead, the W isotopic composition of the Moon is very similar to the silicate Earth—slightly more radiogenic than the average Solar System as determined from carbonaceous chondrites[2]. Even admixing 5% of metal from Theia's core and 45% of BSE does not reproduce the W isotopic composition of the Moon. This is already beyond the limit of the proportions demonstrated in dynamic simulations. It is unlikely that accretion of Theia was much longer than implied by theory and observations of Mars-sized objects. It is of course possible that a massive reduction in the $\epsilon W_{BSI}$ was produced by a major impact on Theia just before the giant impact. However, such an *ad hoc* low-probability explanation is unnecessary.

The simplest explanation is that $(Hf/W)_{BSI}$ and possibly $(Hf/W)_{BSE}$ too, were substantially less than in the Moon or silicate Earth today. If $(Hf/W)_{BSI}$ and $(Hf/W)_{BSE}$ were <3 times the chondritic value, an initial $\epsilon W$ of zero to + 1 for the early Moon could be generated. This time-integrated Hf/W is almost identical to the Hf/W in the silicate Mars[21,47]. The explanation usually given is that the martian mantle was more oxidizing, leading to more lithophile behaviour of W. Independent evidence for greater oxidation of the mantle of Theia has been found in the higher Fe content of the lunar mantle[48], which again is like that inferred for Mars[21].

The time-integrated Rb/Sr for Theia deduced from lunar samples is also identical to Mars and is significantly more volatile-rich than the Earth and Moon[11]. Therefore, Rb losses and changes in oxidation state were both late (>10 Myr), well within the time realm of planetary growth via collisions. A simple explanation for the lunar data then is that volatile loss occurred from the material forming the Moon during the giant impact.

However, the similarity in oxygen isotopes provides evidence that the proto-Earth and Theia were made from a similar mix of materials[49]. If this is the case, impact-driven losses of volatiles also contributed to the Rb-depletion and oxidation-state of the terrestrial mantle. There is indeed a relationship between the Hf/W and Rb/Sr of inner Solar System primitive mantles, as deduced so far (Fig. 4). Hafnium and W are both refractory elements and there is no obvious explanation for this correlation unless the oxidation of planetary mantles is somehow related to loss of moderately volatile elements. This could be late, as in the case of the Moon, or very early, as in the case of Vesta.

The direct loss of heavy lithophile elements against the gravita-

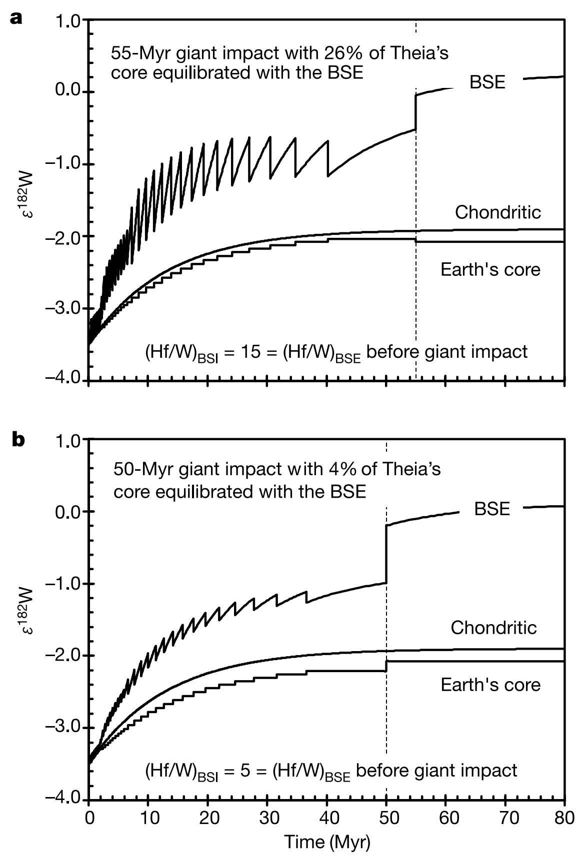


**Figure 3** The effects of disequilibrium on tungsten isotopic changes in the BSE can be large. In both **a** and **b** the evolution of the total Earth (chondritic), core and BSE are calculated, assuming $\epsilon\ ^{182}W_{BSSI} = -3.5$. $\epsilon\ ^{182}W$ are all expressed relative to the present day BSE. Note that in both cases the effect of the giant impact is to increase the $\epsilon\ ^{182}W_{BSE}$. **a**, A present-day $\epsilon\ ^{182}W_{BSE}$ of zero can be achieved if only 26% of Theia's core equilibrated with the BSE during a giant impact at 55 Myr. This model assumes that the Moon and Earth formed from protoplanets that had Hf/W in their silicate portions like that in the present Earth (15), which may be incorrect. **b**, In this model the Moon and Earth formed from protoplanets that had Hf/W in their silicate portions that was about a third of that in the present Earth, that is, more like Mars[21,47]. A present-day $\epsilon^{182}W_{BSE}$ of zero can be achieved if only 4% of the W in Theia's core equilibrated with the BSE during a giant impact at 50 Myr.

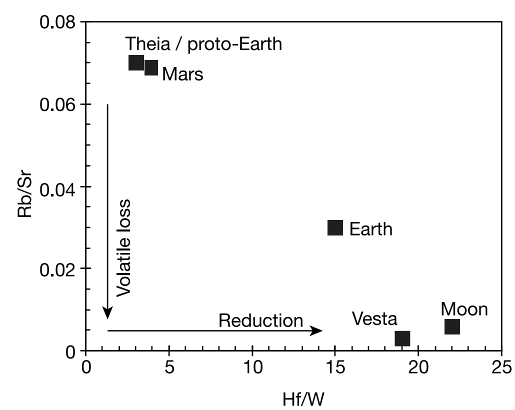


**Figure 4** Inner Solar System primitive mantles. The Hf/W appears to be negatively correlated with Rb/Sr in the primitive mantles of inner Solar System planetesimals and planets. A possible explanation for this is that the loss of moderately volatile elements was linked to loss of other volatiles during planetary collisions, such that the mantles changed from more oxidizing to more reducing. The Moon is an extreme example of this. That Theia is so like Mars in these respects provides evidence that such volatile-rich objects may have dominated the entire inner Solar System during the early stages of planetary accretion. The values for Theia are time-averaged (ref. 11 and this study).

tional force of the Earth is unlikely[11,48]. Losses from smaller accreting protoplanets are more readily accommodated. Therefore, the BSE composition shown in Fig. 4 may reflect admixing of planets and planetesimals that lost different amounts of volatiles at an earlier stage. However, it may also be that moderately volatile elements like Rb were partially atmophile because of high surface temperatures in hot early planetary environments[18,39]. Early proto-atmospheres were lost from the Earth, as indicated by Xe data[39], and very probably also from constituent protoplanets—possibly on more than one occasion. If moderately volatile incompatible elements were partially circulated through hot atmospheres[18] they may well have been lost during blow-off events[40]. A partially atmophile behaviour might also help to explain the greater isotopic equilibration of moderately volatile Pb versus refractory W during accretion.

The potential effects of changes in oxidation on the W isotopic evolution of the Earth could be significant, whether caused by changes in the composition of accreted material or blow-off (Fig. 3b). For example, growth from protoplanets with Hf/W = 5 until a giant impact at 50 Myr leading to volatile loss and a corresponding increase in $(\mathrm{Hf/W})_{\mathrm{BSE}}$ to the value of 15 found today achieves a $\epsilon\,^{182}\mathrm{W}_{\mathrm{BSE}}$ of zero with only 4% equilibration between silicate and newly accreted metal during the giant impact. The abundances of highly siderophile elements in the upper mantle[50] could then relate to this event, plus the superimposed effects of the late veneer[23,48]. Furthermore, much of the variability in moderately volatile elements and oxidation in the inner Solar System may be the cumulative effect of collisions between early-formed planetesimals that were, in general, more Mars-like. □

Received 29 August; accepted 9 December 2003; doi:10.1038/nature02275.


1. Yin, Q. Z. *et al.* A short timescale for terrestrial planet formation from Hf–W chronometry of meteorites. *Nature* **418,** 949–952 (2002).
2. Kleine, T., Münker, C., Mezger, K. & Palme, H. Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf–W chronometry. *Nature* **418,** 952–955 (2002).
3. Schönberg, R., Kamber, B. S., Collerson, K. D. & Eugster, O. New W isotope evidence for rapid terrestrial accretion and very early core formation. *Geochim. Cosmochim. Acta* **66,** 3151–3160 (2002).
4. Jacobsen, S. B. & Harper, C. L. Jr in *Earth Processes: Reading the Isotope Code* (eds Basu, A. & Hart, S.) 47–74 (AGU, Washington DC, 1996).
5. Halliday, A. N. Terrestrial accretion rates and the origin of the Moon. *Earth Planet. Sci. Lett.* **176,** 17–30 (2000).
6. Cameron, A. G. W. & Benz, W. Origin of the Moon and the single impact hypothesis IV. *Icarus* **92,** 204–216 (1991).
7. Canup, R. M. & Asphaug, E. Origin of the moon in a giant impact near the end of the Earth's formation. *Nature* **412,** 708–712 (2001).
8. Yoshino, T., Walter, M. J. & Katsura, T. Core formation in planetesimals triggered by permeable flow. *Nature* **422,** 154–157 (2003).
9. Rubie, D. C., Melosh, H. J., Reid, J. E., Liebske, C. & Righter, K. Mechanisms of metal-silicate equilibration in the terrestrial magma ocean. *Earth Planet. Sci. Lett.* **205,** 239–255 (2003).
10. Stevenson, D. J. in *Origin of the Earth* (eds Newsom, H. E. & Jones, J. H.) 231–249 (Oxford Univ. Press, Oxford, 1990).
11. Halliday, A. N. & Porcelli, D. In search of lost planets – the paleocosmochemistry of the inner solar system. *Earth Planet. Sci. Lett.* **192,** 545–559 (2001).
12. Humayun, M. & Clayton, R. N. Potassium isotope cosmochemistry: Genetic implications of volatile element depletion. *Geochim. Cosmochim. Acta* **59,** 2131–2151 (1995).
13. Wetherill, G. W. in *Origin of the Moon* (eds Hartmann, W. K., Phillips, R. J. & Taylor, G. J.) 519–555 (Lunar Planetary Institute, Houston, 1986).
14. Taylor, S. R. & Norman, M. D. in *Origin of the Earth* (eds Newsom, H. E. & Jones, J. H.) 29–43 (Oxford Univ. Press, Oxford, 1990).
15. Allègre, C. J., Manhès, G. & Göpel, C. The age of the Earth. *Geochim. Cosmochim. Acta* **59,** 1445–1456 (1995).
16. Lee, D.-C. & Halliday, A. N. Hafnium–tungsten chronometry and the timing of terrestrial core formation. *Nature* **378,** 771–774 (1995).
17. Galer, S. J. G. & Goldstein, S. L. in *Earth Processes: Reading the Isotope Code* (eds Basu, A. & Hart, S.) 75–98 (AGU, Washington DC, 1996).
18. Hayashi, C., Nakazawa, K. & Nakagawa, Y. in *Protostars and Planets II* (eds Black, D. C. & Matthews, M. S.) 1100–1153 (Univ. Arizona Press, Tucson, 1985).
19. Sasaki, S. & Nakazawa, K. Metal-silicate fractionation in the growing Earth: energy source for the terrestrial magma ocean. *J. Geophys. Res.* **91,** B9231–B9238 (1986).
20. Carlson, R. W. & Lugmair, G. W. in *Origin of the Earth and Moon* (eds Canup, R. & Righter, K.) 25–44 (Univ. Arizona Press, Tucson, 2000).
21. Newsom, H. E. in *Global Earth Physics, A Handbook of Physical Constants* (ed. Ahrens, T. J.) 159–189 (AGU Reference Shelf 1, American Geophysical Union, Washington DC, 1995).
22. Lissauer, J. J. Time-scales for planetary accretion and the structure of the protoplanetry disk. *Icarus* **69,** 249–265 (1987).
23. Newsom, H. E. in *Origin of the Earth* (eds Newsom, H. E. & Jones, J. H.) 273–288 (Oxford Univ. Press, Oxford, 1990).
24. Patterson, C. C. Age of meteorites and the Earth. *Geochim. Cosmochim. Acta* **10,** 230–237 (1956).
25. Murphy, D. T., Kamber, B. S. & Collerson, K. D. A refined solution to the first terrestrial Pb-isotope paradox. *J. Petrol.* **44,** 39–53 (2003).
26. Kamber, B. S. & Collerson, K. D. Origin of ocean-island basalts: a new model based on lead and helium isotope systematics. *J. Geophys. Res.* **104,** 25479–25491 (1999).
27. Kramers, J. D. & Tolstikhin, I. N. Two terrestrial lead isotope paradoxes, forward transport modeling, core formation and the history of the continental crust. *Chem. Geol.* **139,** 75–110 (1997).
28. Galer, S. J. G. & Goldstein, S. L. Depleted mantle Pb isotopic evolution using conformable ore leads. *Terra Abstr.* **3,** 485–486 (1991).
29. Liew, T. C., Milisenda, C. C. & Hofmann, A. W. Isotopic contrasts, chronology of element transfers and high-grade metamorphism: the Sri Lanka Highland granulites, and the Lewisian (Scotland) and Nuk (S.W. Greenland) gneisses. *Geol. Rundsch.* **80,** 279–288 (1991).
30. Kwon, S.-T., Tilton, G. R. & Grünenfelder, M. H. in *Carbonatites—Genesis and Evolution* (ed. Bell, K.) 360–387 (Unwin-Hyman, London, 1989).
31. Allègre, C. J. & Lewin, E. Chemical structure and history of the Earth: Evidence from global non-linear inversion of isotopic data in a three box model. *Earth Planet. Sci. Lett.* **96,** 61–88 (1989).
32. Allègre, C. J., Lewin, E. & Dupré, B. A coherent crust-mantle model for the uranium-thorium-lead isotopic system. *Chem. Geol.* **70,** 211–234 (1988).
33. Zartman, R. E. & Haines, S. M. The plumbotectonic model for Pb isotopic systematics among major terrestrial reservoirs—a case for bi-directional transport. *Geochim. Cosmochim. Acta* **52,** 1327–1339 (1988).
34. Davies, G. F. Geophysical and isotopic constraints on mantle convection: An interim synthesis. *J. Geophys. Res.* **89,** 6017–6040 (1984).
35. Doe, B. R. & Zartman, R. E. in *Geochemistry of Hydrothermal Ore Deposits* (ed. Barnes, H. L.) 22–70 (Wiley, New York, 1979).
36. Davies, G. F. Geophysically constrained mass flows and the $^{40}$Ar budget: a degassed lower mantle? *Earth Planet. Sci. Lett.* **166,** 149–162 (1999).
37. Azbel, I. Y., Tolstikhin, I. N., Kramers, J. D., Pechernikova, G. V. & Vityazev, A. V. Core growth and siderophile element depletion of the mantle during homogeneous Earth accretion. *Geochim. Cosmochim. Acta* **57,** 2889–2898 (1993).
38. Ozima, M. & Podosek, F. A. Formation age of Earth from $^{129}$I/$^{127}$I and $^{244}$Pu/$^{238}$U systematics and the missing Xe. *J. Geophys. Res.* **104,** 25493–25499 (1999).
39. Porcelli, D., Cassen, P. & Woolum, D. Deep Earth rare gases: Initial inventories, capture from the solar nebula and losses during Moon formation. *Earth Planet. Sci. Lett.* **193,** 237–251 (2001).
40. Benz, W. & Cameron, A. G. W. in *Origin of the Earth* (eds Newsom, H. E. & Jones, J. H.) 61–67 (Oxford Univ. Press, Oxford, 1990).
41. Tera, F., Papanastassiou, D. A. & Wasserburg, G. J. A lunar cataclysm at ~3.95 AE and the structure of the lunar crust. *Lunar Planet. Sci.* **IV,** 723–725 (1973).
42. Hanan, B. B. & Tilton, G. R. 60025: Relict of primitive lunar crust? *Earth Planet. Sci. Lett.* **84,** 15–21 (1987).
43. Carlson, R. W. & Lugmair, G. W. The age of ferroan anorthosite 60025: oldest crust on a young Moon? *Earth Planet. Sci. Lett.* **90,** 119–130 (1988).
44. Lee, D.-C., Halliday, A. N., Snyder, G. A. & Taylor, L. A. Age and origin of the Moon. *Science* **278,** 1098–1103 (1997).
45. Leya, I., Wieler, R. & Halliday, A. N. Cosmic-ray production of tungsten isotopes in lunar samples and meteorites and its implications for Hf-W cosmochemistry. *Earth Planet. Sci. Lett.* **175,** 1–12 (2000).
46. Lee, D.-C., Halliday, A. N., Leya, I., Wieler, R. & Wiechert, U. Cosmogenic tungsten and the origin and earliest differentiation of the Moon. *Earth Planet. Sci. Lett* **198,** 267–274 (2002).
47. Lee, D.-C. & Halliday, A. N. Core formation on Mars and differentiated asteroids. *Nature* **388,** 854–857 (1997).
48. Jones, J. H. & Palme, H. in *Origin of the Earth and Moon* (eds Canup, R. & Righter, K.) 197–216 (Univ. Arizona Press, 2000).
49. Wiechert, U. *et al.* Oxygen isotopes and the Moon-forming giant impact. *Science* **294,** 345–348 (2001).
50. Righter, K. & Drake, M. J. Effect of water on metal-silicate partitioning of siderophile elements: a high pressure and temperature terrestrial magma ocean and core formation. *Earth Planet. Sci. Lett.* **171,** 383–399 (1999).


**Acknowledgements** This paper benefited from discussions with, and comments from, T. Ahrens, W. Benz, R. Canup, R. Carlson, M. Drake, T. Grove, M. Humayun, T. Kleine, K. Mezger, C. Münker, H. Palme, D. Porcelli, M. Schönbächler, D. Stevenson, M. Walter, R. Wieler and H. Williams and was supported by ETH and Swiss National Science Foundation.

**Competing interests statement** The authors declare that they have no competing financial interests.

**Correspondence** and requests for materials should be addressed to A.N.H. (halliday@erdw.ethz.ch).