



Lead isotope evidence for a young formation age of the Earth–Moon system



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ABSTRACT

A model of a giant impact between two planetary bodies is widely accepted to account for the Earth–Moon system. Despite the importance of this event for understanding early Earth evolution and the inventory of Earth's volatiles critical to life, the timing of the impact is poorly constrained. We explore a data-based, two-stage Pb isotope evolution model in which the timing of the loss of volatile Pb relative to refractory U in the aftermath of the giant impact is faithfully recorded in the Pb isotopes of bulk silicate Earth. Constraining the first stage Pb isotopic evolution permits calculating an age range of 4.426–4.417 Ga for the inflection in the U/Pb ratio related to the giant impact. This model is supported by Pb isotope data for angrite meteorites that we use to demonstrate volatility-driven, planetary-scale Pb loss was an efficient process during the early Solar System. The revised age is ~ 100 Myr younger than most current estimates for the age of the Moon but fully consistent with recent ages for lunar ferroan anorthosite and the timing of Earth's first crust inferred from the terrestrial zircon record. The estimated loss of $\sim 98\%$ of terrestrial Pb relative to the Solar System bulk composition by the end of the Moon-forming process implies that the current inventory of Earth's most volatile elements, including water, arrived during post-impact veneering by volatile-rich bodies.

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The formation of planetary bodies is thought to occur in stages where rapidly-formed 10–100 km diameter planetesimals accumulate to form differentiated planetary embryos and, finally, planets. The efficiency of this process, as demonstrated by the widespread occurrence of meteorites from ancient differentiated planetesimals, is consistent with the proto-Earth having mainly accreted within 30 Myr (Kleine et al., 2009) of the formation of the Sun at 4567.3 ± 0.16 Ma (Connelly et al., 2012). Energetic collisions between planetary embryos and planets occur during the late evolution of a nascent planetary system, due to orbital destabilisation after dissipation of the gaseous disk (Morbidelli et al., 2012). Such cataclysmic events have sufficient energy to vaporize at least part of a growing planet, thus influencing the final volatile inventory of planetary bodies. In the Solar System, this process is best exemplified by the giant impact that formed the Earth–Moon system, which may have caused significant loss of the proto-Earth's pre-existing volatile elements (Tucker and Mukhopadhyay, 2014). Despite the importance of this event for our understanding of the dynamics of terrestrial planet formation, early Earth evolution and the inventory of Earth's volatiles

critical to life, the timing of the impact is poorly constrained (Gaffney and Borg, 2014; Borg et al., 2011; Nemchin et al., 2009; Halliday, 2008; Bottke et al., 2015). This reflects the lack of terrestrial and lunar rocks old enough to date this event but a tangible record may be preserved in the global loss of volatile elements, including Pb, associated with the Moon-forming impact (Paniello et al., 2012).

The double decay of refractory ^{235}U and ^{238}U to ^{207}Pb and ^{206}Pb , respectively, with different decay rates results in radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, or $(^{207}\text{Pb}/^{206}\text{Pb})_r$, that are uniquely related to the time since the last closure of the system. With the slopes of lines in $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{207}\text{Pb}/^{204}\text{Pb}$ space corresponding $(^{207}\text{Pb}/^{206}\text{Pb})_r$ of that system, any line defined in this space by analyses of genetically-related materials derives a so-called Pb–Pb age that represents the time passed since last closure. A line connecting the average value of Earth's modern mantle and the isotopic composition of the early Solar System derives a $(^{207}\text{Pb}/^{206}\text{Pb})_r$ “age” of ~ 4.44 Ga (Fig. 1). With the main accretion phase of Earth thought to have been complete within ~ 30 Myr of the formation of the Solar System at 4.567 Ga (Kleine et al., 2009; Connelly et al., 2012), this age cannot reflect the age of the Earth, an observation known as the “Pb Paradox” (Allègre, 1969). A common attribute of most solutions to the Pb paradox involves Pb in Earth's mantle having evolved in at least two stages to account

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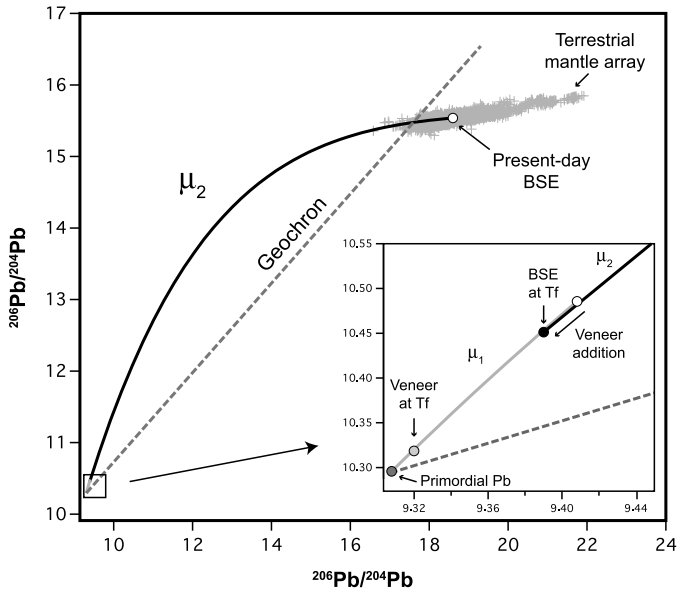


Fig. 1. A Pb–Pb diagram showing the two stage evolution from the Solar System initial composition (Tatsumoto et al., 1973) to that of the modern mantle (Table 1) as defined by the average of mantle Pb isotopic values (grey crosses) available in the Geochemistry of Rocks of the Oceans and Continents (GEOROC) database (Table 1). Inset shows the transition from μ_1 to μ_2 , with the offset in the end of the first stage and the beginning of the second stage growth lines reflecting an instantaneous addition at T_f of CI chondrite-like material with a μ -value of 0.19 to Earth's mantle (Palme and Jones, 2004, Table 2).

Table 1
Pb isotopic composition of bulk silicate Earth upon formation and today.

	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$
Pb_i^a	9.307	10.294
$\text{Pb}_{\text{today}}^b$	18.665	15.524

Notes:

^a Primordial Pb isotopic composition of the Solar System from (12) represents Canyon Diablo troilite as our best estimate of the initial Pb isotopic composition of Earth.

^b The average Pb isotopic composition of the modern mantle as estimated from all available Pb isotopic analyses of mantle-derived rocks in the GEOROC database (<http://georoc.mpch-mainz.gwdg.de/georoc/>).

for its evolution from the initial Solar System primordial values defined by iron meteorites (Tatsumoto et al., 1973) to today (e.g. Allègre et al., 1982; Galer and Goldstein, 1996; Murphy et al., 2003; Albarède et al., 2013 and see review by Hofmann, 2014). Such models require a significant U/Pb fractionation event that changes the μ -value through Pb loss from or gain to the mantle sometime at or after 4.44 Ga. Previous models to account for the change in μ value include Pb loss to the core (Halliday, 2004; Wood and Halliday, 2005) or hidden reservoir (Murphy et al., 2003), and Pb addition to a high-U/Pb proto-Earth by veneering (Albarède, 2009). We explore an alternative model in which the event responsible for the dramatic global change in the U/Pb ratio is the cataclysmic impact associated with the formation of the Moon. Published ages of lunar samples older than 4.44 Ga have generally precluded models in which the Moon-forming impact drives the change in μ value of bulk silicate Earth. However, several recent studies casting doubt on the robustness of the older ages of lunar samples opens the possibility of a younger Moon-forming impact than has been generally accepted (Borg et al., 2011; Gaffney and Borg, 2014; Carlson et al., 2014).

Five independent parameters are required to fully model a two stage Pb isotopic evolution, namely the initial and final Pb isotopic compositions of the bulk silicate Earth, the effective first stage and second stage $^{238}\text{U}/^{204}\text{Pb}$ values (μ_1 and μ_2 , respectively) and, fi-

nally, the time of the U–Pb fractionation event (T_f) that changes μ_1 to μ_2 . Of these, the starting Pb isotopic compositions of the Solar System is best known from U-free troilite in the Canyon Diablo Type IAB iron meteorite (Tatsumoto et al., 1973; Table 1) whereas the Pb isotopic composition of bulk silicate Earth can be estimated from an average of all measured recent mantle-derived rocks (Fig. 1, Table 1). The μ_2 -value of the modern mantle is more debated but is generally thought to be between 8–10 (Stacey and Kramers, 1975; Galer and Goldstein, 1996). This leaves Earth's average pre-fractionation μ_1 -value and the timing of the fractionation event (T_f) as unknowns. Constraining the μ_1 -value for the first stage of Earth's history will allow the last variable, the age of T_f and, therefore, the Moon-forming impact, to be constrained. Since the age of T_f is determined from the slope of the line connecting the Pb isotopic composition at T_f and modern mantle Pb in $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{207}\text{Pb}/^{204}\text{Pb}$ space, μ_2 is not required to determine the age of T_f . Instead, μ_2 can be calculated once μ_1 has been determined.

Pb isotope compositions evolve systematically through the decay of U according to the general equation:

$$\left(\frac{^{20x}\text{Pb}}{^{204}\text{Pb}}\right)_{t_2} = \left(\frac{^{20x}\text{Pb}}{^{204}\text{Pb}}\right)_{t_1} + \left(\frac{^{23y}\text{U}}{^{204}\text{Pb}}\right)_{\text{today}} (e^{\lambda t_1} - e^{\lambda t_2}) \quad (1)$$

where t_1 and t_2 represent the time in the past of the start and end of a stage of Pb evolution, respectively, $(^{20x}\text{Pb}/^{204}\text{Pb})_{t_2}$ refers to the Pb isotopic composition at the respective times and λ refers to the decay constant of the respective parent radionuclides. For calculations here, we use the decay constants of Jaffey et al. (1971) and adapt a Solar $^{238}\text{U}/^{235}\text{U}$ ratio of 137.786 (Connelly et al., 2012). As expressed by Eq. (1), the Pb isotopic composition of any material today (where $t_2 = 0$ Ma) depends on its initial Pb isotopic composition (Pb_i), $^{23y}\text{U}/^{204}\text{Pb}$ ratio and time passed as a closed system. From the Solar System primordial Pb isotopic composition, a model of the Pb isotopic evolution of early Earth to determine the Pb isotopic composition at T_f requires understanding the processes that affected the U–Pb budget of the mantle throughout this first stage.

1. Constraining Earth's first stage U–Pb evolution

The first stage of Pb isotopic evolution, from the primordial values of the proto-Earth to just before the U/Pb fractionation event that we relate to the giant impact at T_f , is not predicted to reflect a single, inherited μ -value. Instead, the U/Pb ratio at T_f reflects the initial inherited abundances of U and Pb from Earth's precursor materials, Pb loss by devolatilization during impact-driven accretion of planetesimals and planetary embryos, possible Pb sequestration during core formation and the addition of a potentially Pb-rich veneering material to the proto-Earth prior to T_f . Whereas the degree of Pb loss or gain from bulk silicate Earth by impact-driven devolatilization during accretion, core formation and veneering cannot be definitively determined, the Pb isotopic evolution during the first stage may be evaluated and adequately constrained for the sake of determining the end point of the first stage Pb evolution and, by extension the age of T_f . This is accomplished by understanding the processes of terrestrial planet accretion and using proxy measurements of different Solar System materials.

Models attempting to explain the formation of the terrestrial planets have long recognized the problem of building larger bodies from dust in that metre-sized objects have insufficient gravity or sticking properties to efficiently accrete to one another (Weidenschilling, 1977). This perceived impediment to planet formation, known as the “metre size barrier”, has been avoided in recent models where nuclei formed in high density regions of the turbulent disk via streaming instabilities leading to the effective formation of ~ 50 km diameter asteroids (Johansen et al., 2007).

These planetesimals seeds undergo runaway gas-drag assisted accretion of mm- to cm-sized volatile-depleted chondrules to form planetary embryos up to Mars's size along with smaller asteroids within 3 Myr (Johansen et al., 2015). In addition to continued growth by chondrule accretion, smaller planetesimals may collide and accrete to form embryos. In this model, Mars represents a stranded embryo whereas Earth's larger mass was likely predominantly achieved through the subsequent collision and accretion of embryo-sized bodies. This model predicts that the precursor material for Earth and Mars was a mixture dominated by chondrules complemented with a minor amount of finer-grained matrix. It is now well established that the chondrule forming process results in a significant increase of the μ -value above that for the bulk Solar System, with compositions ranging from at least 30 to 250 (Connelly et al., 2012; Bollard, 2016). Therefore, a mixture dominated by chondrules over matrix like that observed in inner Solar System ordinary and enstatite chondrites (Lodders, 2000; but also Fitoussi and Bourdon, 2012) effectively ensures that the precursor material for Earth would have been volatile depleted relative to the bulk Solar System composition based on volatile-rich meteorites such as CI chondrites. Consistent with this interpretation, Earth's volatile depletion is predicted by the accretion of Earth within the dry, volatile depleted inner region of the protoplanetary disk where temperatures were too high for large amounts of volatile elements, including water, to be incorporated into the solids that would accrete to form the terrestrial planets. With Pb being a volatile element and U being a highly-refractory element, the accretion of volatile-depleted material would result in a significant increase on Earth's inherited μ -value relative to the bulk Solar System value of ~ 0.19 inferred from primitive chondrites as defined by carbonaceous chondrites (Palme and Jones, 2004).

In addition to using inner and outer Solar System volatility arguments to predict the U/Pb ratio of Earth's precursor materials, a proxy for the source material that accreted to form Earth may be inferred from the abundances of nuclides that track genetic relationships between solids, asteroids and planets. The abundances of ^{48}Ca , ^{50}Ti and ^{54}Cr establish a genetic link between achondrites, ordinary and enstatite chondrites, Mars and Earth that formed within the volatile-depleted inner protoplanetary disk (Schiller et al., 2015; Trinquier et al., 2007, 2009). In contrast, carbonaceous chondrites have distinct isotopic signatures that are attributed to the volatile-rich outer Solar System (Trinquier et al., 2009; Larsen et al., 2016). Using these isotopic signatures, we have identified the unequilibrated (L3) ordinary chondrite NWA 5697 as a suitable material to test the hypothesis that volatile-depleted inner Solar System material akin to Earth's building blocks had an elevated μ -value relative to bulk Solar System. We subjected NWA 5697 to a stepwise dissolution procedure (see Supplementary Information for methods) that parses Pb into separate aliquots to evaluate the relative proportions of Pb_i , radiogenic Pb (Pb_r) and terrestrial contaminant Pb (Pb_c). This permits the identification and subtraction of terrestrial Pb contamination that would erroneously lower the μ -value estimate of these meteorites if determined by bulk U and Pb elemental analyses.

2. Determining the bulk μ -value for NWA 5697

The μ -value of L3 ordinary chondrule NWA5697 was determined by assuming all constituents of this meteorite formed in the first 5 Myr of the Solar System, allowing sufficient Pb_c with a composition of Stacey and Kramers (1975) to be subtracted so that all corrected points lie along a 4.567 Ga isochron that passes through primordial Pb on a $^{204}\text{Pb}/^{206}\text{Pb}$ vs $^{207}\text{Pb}/^{206}\text{Pb}$ diagram (Fig. 2a and Table S1). The bulk $^{204}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ values were calculated by dividing the total number of moles of the appropriate isotopes, ^{206}Pb , ^{207}Pb and ^{204}Pb , measured in all steps. Since the

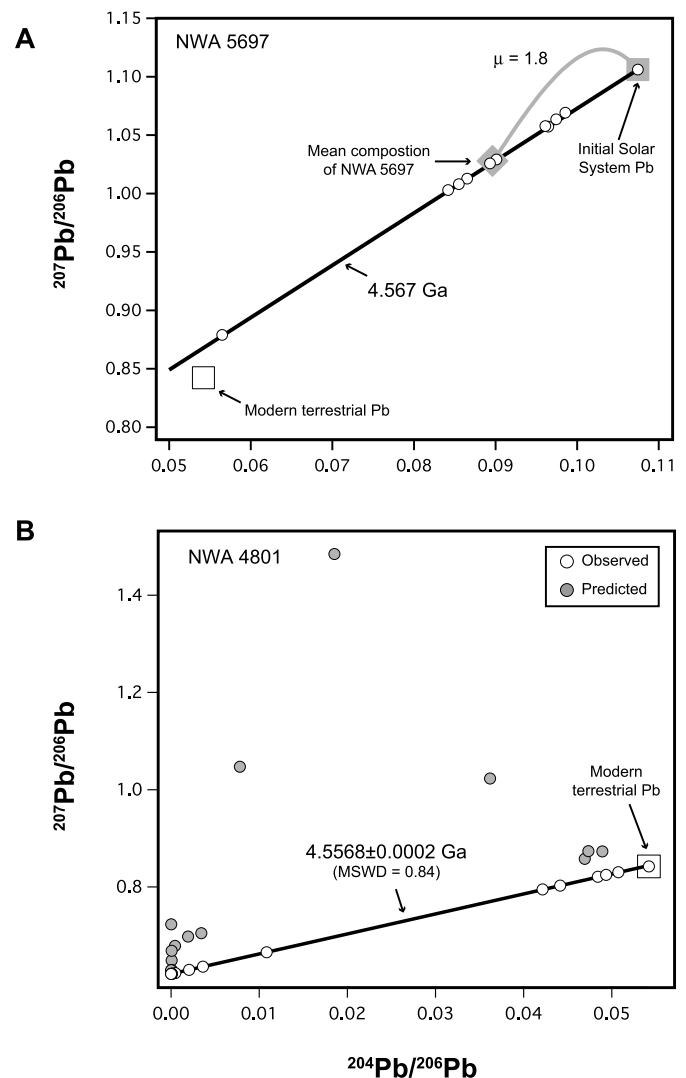


Fig. 2. (a) An inverse Pb–Pb isochron diagram showing the results (Table S1) of stepwise dissolution of the ordinary chondrite NWA 5697 with each point corrected for an appropriate amount of contaminant terrestrial Pb to define an array corresponding to radiogenic Pb growth from Solar System initial composition for 4.5673 Gyr (see Supporting Information). The bulk $^{204}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ compositions are based on the corrected total molar abundances of ^{206}Pb , ^{207}Pb and ^{204}Pb in all dissolution steps. A μ -value of 1.8 accounts for this bulk Pb isotopic composition to have evolved from the primordial Solar System composition (Tatsumoto et al., 1973). (b) An inverse Pb–Pb diagram showing the results (Table S2) of a stepwise dissolution of angrite NWA 4801 with each point (open symbols) corrected for laboratory blank of 0.2 pg. The filled symbols represent the Pb isotopic composition of each point mixed with modelled radiogenic Pb ingrowth between 4.5645 Ga and 4.5568 Ga as explained in the text and Supporting Information. MSWD = Mean Square Weighted Deviation, a measure of the goodness of fit of the line where a value above 2 indicates excess scatter outside of the errors on individual measurements.

samples were spiked immediately upon dissolution, any loss of Pb in the subsequent purification process will not affect this calculation. This provides a bulk Pb isotopic composition such that the relative proportion of Pb_r and Pb_i in this sample and the appropriate amount of U to generate the Pb_r can be determined.

We show in Fig. 2a that the μ -value for NWA 5697 is approximately 1.8, a value that is substantially elevated relative to CI chondrites and consistent with the abundance of chondrules in this group. A μ -value around 1.8 is consistent with a 90/10 mixture of chondrules/matrix with a conservative average chondrule μ -value of 30 (Connelly et al., 2012) and matrix μ -value of 0.19. If drag-assisted chondrule accretion is the dominant process of form-

ing planetary embryos in <3 Myr (Johansen et al., 2015), then we expect Earth’s precursor material to have had an average μ -value comparable to this estimate. That chondrules control the volatile element inventory of planetary bodies at the time of accretion accounts for the lack of stable isotope fractionation of moderately volatile elements such as K in planetary bodies (Humayun and Clayton, 1995). This is a predictable outcome of devolatilization related to chondrule formation in high ambient gas pressures (Alexander et al., 2008) rather than by post-accretion planetary volatile loss.

With the terrestrial planets precursor material constrained by ordinary chondrites with a μ -value of ~ 1.8 , we now use Mars to evaluate the degree to which this value might vary in embryos as a result of different chondrules/matrix ratios relative to NWA 5697 and/or by Pb loss by devolatilization associated with impact-driven planetesimal accretion. The average μ -value for Mars’ mantle of 2–4 has been calculated as that necessary for Pb to have evolved from the primordial Solar System composition to the initial Pb isotopic composition at ~ 0.20 Ga shergottites (Gaffney et al., 2007). Assuming that Mars accreted from a mixture of material comparable to Earth as suggested by similar ^{50}Ti and ^{54}Cr signatures (Trinquier et al., 2009, 2007), the elevated Martian mantle μ -value implies that some Pb was lost during or after accretion or that embryos inherited a greater chondrules/matrix ratio than the ordinary chondrite NWA 5697. If the former is correct, the offset of 1.8 to 4.0 requires loss of 55% of the Pb relative to the precursor material. This moderate amount of Pb loss indicates that Pb sequestration to the core was not a highly efficient process in the formation of planetary embryos. This is consistent with the low Pb contents of iron meteorites (e.g. Tatsumoto et al., 1973) and suggests that Pb loss to core formation is a minor contributor to the evolution of the U/Pb ratios of planetary bodies. As such, we use Mars as an analogue for the early Earth and infer that the Earth’s μ -value never rose significantly above the value of ~ 4 at this stage.

Stochastic late accretion processes may contribute significantly to the final volatile element inventory of a growing planet. In the case of Earth, numerical simulations suggest that up to 11% of its mass may have been acquired as late-accreted material over the first 150 Myr of Earth’s evolution (Jacobson et al., 2014). In our model, we assume a late accretion history for Earth that includes 11% of its mass that is represented by a veneer of outer Solar System material, including the last 0.5% inferred to have delivered the highly-siderophile elements currently residing in Earth’s mantle (Walker, 2009). If Earth’s composition prior to the late accretion phase was comparable to Mars, the addition of 11% of ^{54}Cr -rich outer Solar System, volatile-rich material is consistent with the elevated terrestrial ^{54}Cr signature relative to Mars (Trinquier et al., 2007). The effect of this veneer accretion on the isotopic composition and U–Pb ratio of Earth’s mantle at T_f is dependent on the time of the main accretion phase. We model a smooth, approximately log-normal decrease in the amount of veneer accreting to the Earth with time (Jacobson et al., 2014) to evaluate the range of final conditions with: i) the main accretion phase ending between 10 and 60 Myr after t_0 and ii) with 0–60% of Pb progressively lost from the system during impact driven accretion (Fig. 3 and Supporting Information). Assuming precursor materials with a μ -value of 1.8 and with impact-driven Pb loss and pre- T_f veneering as defined, this model returns effective μ -values that range from 0.88 to 1.41 at T_f for the main accretion phase ending between 10 and 60 Myr after t_0 (Figs. 3 and 4) and for 0 to 60% Pb loss. Despite the significant effect veneering has on Earth’s μ -value, Mars remains a good proxy for proto-Earth’s μ -value without any early veneer, given that Mars would have accreted only $\sim 6\%$ of the veneer received by Earth (Schlichting et al., 2012).

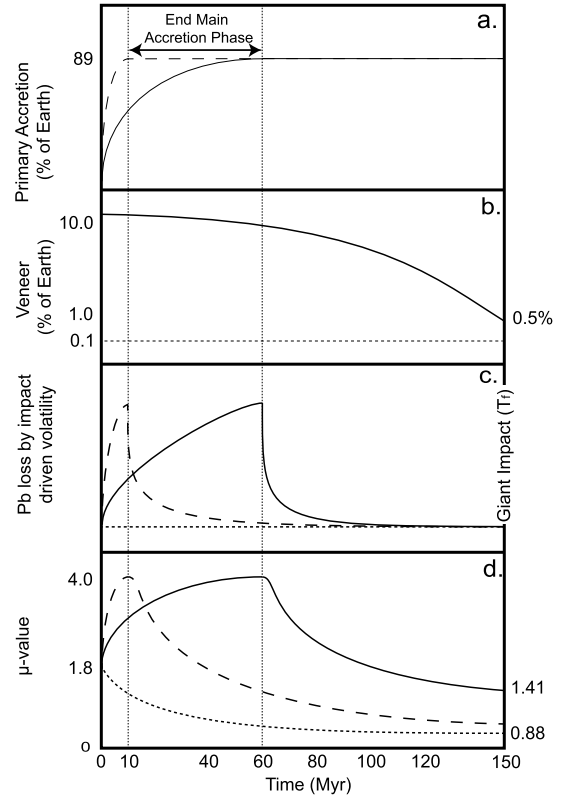


Fig. 3. Sketches of different model parameters (see Supporting Information) as a function of time after T_0 including: a) primary accretion of the proto-Earth through embryo impacts in the end-member scenarios of the main accretion phase ending at 10 Myr (dashed) and 60 Myr (solid) after t_0 , b) cumulative amount of outer Solar System veneer that was added to Earth after the indicated time relative to t_0 (after Jacobson et al., 2014), c) amount of Pb lost by impact driven volatility related to the main accretion phase in end-member scenarios of the main accretion ending by 10 Myr (dashed) and 60 Myr (solid) after t_0 and d) the effective μ -value through time with starting materials with a μ -value of 1.8, total amount of outer Solar System veneer added according to (b) and impact-driven devolatilization according to (c) ending at 10 Myr (long-dashed) and 60 Myr (solid) after t_0 and without impact-driven devolatilization (short-dotted).

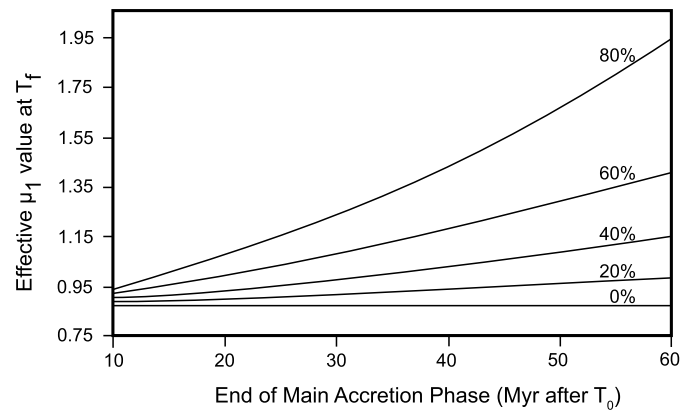


Fig. 4. The calculated effective μ_1 -value at T_f as a function of the timing of the end of the main accretion phase for different degrees of Pb loss (0–80% where Mars represents a value of $\sim 60\%$). We use the calculated end member values of 0.88 and 1.41 as lower and upper estimates for the effective μ_1 -value at T_f after first-stage Pb devolatilization between 0–60% combined with the end of the main accretion phase at 10–60 Myr to evaluate the effects on the timing of the U/Pb fractionation event at T_f . The effective μ_1 -value is calculated as the μ -value necessary for Pb to have evolved from primordial Pb to the Pb isotopic composition defined in the model just before T_f (see Supporting Information). This is distinct from the actual μ_1 -value at T_f , which reflects the relative isotopic abundance of ^{238}U and ^{204}Pb at that time.

3. The age of the Moon-forming event

With the first stage evolution (from t_0 to T_f) modelled to end with an effective μ_1 -value between 0.88 and 1.41, we now explore the second stage evolution from T_f to today's mantle. The starting point for the second stage evolution corresponds to the range of Pb isotopic compositions at T_f described above plus primitive chondrite material represented by CI carbonaceous chondrites as a "late veneer" in the amount of 0.5% of the mass of Earth (Walker, 2009). This addition has the effect of slightly lowering the Pb isotopic ratios given the high concentration of Pb and relatively low μ -value (0.19) of CI chondrites. The veneer is added instantaneously in the model at the time of the U/Pb fractionation event rather than in diminishing amounts over several 100 million years as might be the case in reality. However, the timing and rate of CI chondrite addition does not impact the final Pb isotopic composition, provided the veneer material is eventually well mixed into the mantle. Ages between 4.426 and 4.417 Ga for T_f are calculated using Eq. (1) and the slopes of lines connecting the average modern Pb isotopic compositions of the mantle with the range of predicted Pb isotopic composition at T_f . The range of ages reflects the varying starting Pb isotopic composition at T_f due to the uncertainty in the timing of the end of the main accretionary phase and the amounts of Pb lost to volatility during impact accretion. The μ_2 -values necessary to derive today's Pb isotopic composition of the mantle are calculated to only vary between 9.235 and 9.241 but they are not required for the age calculation. The increase in the effective μ -value from 0.88–1.41 at T_f to the μ -value of 9.24 for today's mantle represents the loss of between 85–95% of the Pb present in the mantle at T_f , an amount consistent with that predicted for Pb loss by Albarède et al. (2015). As we conclude that the only mechanism capable of driving such a dramatic loss of Pb from the mantle this late in Earth's history is the cataclysmic impact associated with the formation of the Moon, we infer that the age range of 4.426 and 4.417 Ga for T_f represents the permissible age range for the formation of the Earth–Moon system. This age is consistent with the Hf–W age estimates that indicate the Earth–Moon system formed at least 50–60 Myr after T_0 (Touboul et al., 2007; Kleine et al., 2009) but inconsistent with the age estimate based on the I–Pu–Xe system that returns a model-dependent age of 40 ± 20 Myr after T_0 (Avice and Marty, 2014).

4. The volatility of Pb

A significant increase in the U/Pb ratio of bulk silicate Earth related to the Moon-forming giant impact requires a process that would efficiently add U or remove Pb to/from at least the upper mantle on a planetary scale. Given the refractory nature of U and the lack of any identifiable source of additional U, we conclude that an increase in the U/Pb ratio could only have been achieved by reducing the abundance of Pb in bulk silicate Earth via: i) sequestering Pb to the core, ii) sequestering Pb to a hidden reservoir in mantle, or iii) loss of Pb to space in the aftermath of the Moon-forming impact by some de-volatilization process. Although Pb behaves as a siderophile element at high temperatures and across a wide range of pressures (Ballhaus et al., 2013), three lines of evidence indicate that Pb was not efficiently transferred to Earth's core at T_f . First, the abundances of volatile-siderophile and purely volatile elements in bulk silicate Earth are strongly correlated with their respective bond energies, suggesting that volatility mainly controls their distributions (Albarède et al., 2015). Secondly, despite the lack of pressure dependence on $K_d^{\text{metal-silicate}}$ values for Pb, the low concentrations of Pb in iron meteorites can only account for 5% of the missing Pb from silicate Earth (e.g. Tatsumoto et al., 1973). Thirdly, the average μ -value for Mars of 3 (Gaffney et al., 2007) indicates that Pb sequestration to the core on even

Table 2

Concentrations and relative abundances of U and Pb in CI chondrites from Palme and Jones (2004).

Pb in CI chondrites today	2500 ppb
U in CI chondrites today	8 ppb
Present-day μ -value for CI chondrites	0.19

Martian-sized bodies was not an efficient process. A hidden reservoir containing the missing Pb seems unlikely due to the lack of any conclusive evidence for its existence from other isotopic and geochemical systems and the strong correlation between elemental abundances and their volatility rather than their expected compatibility during planetary differentiation. Consequently, we conclude that Pb was lost from Earth by some process(es) involving devolatilization related to the giant Moon-forming impact.

To assess the volatility of Pb in a planetary setting, we turn to the basaltic angrites that are pristine, volatile-depleted volcanic and subvolcanic samples that originated on a 4-Vesta-sized parent body characterized by an early magma ocean and a small convecting Fe–Ni core that formed within the first 4 Myr of the Solar System (Weiss et al., 2008). The lack of shock features in angrites (Keil, 2012) suggests that impacting played a minor role in the formation of these magmas such that the magma ocean was initially established from heating by short-lived radionuclides. The absolute Pb–Pb ages of many of the angrite meteorites are already known and published (Amelin, 2008a, 2008b; Connelly et al., 2008; Bouvier et al., 2011; Keil, 2012; Schiller et al., 2015). A common feature of all U–Pb and Pb–Pb studies of angrites to date is their extremely high μ -values due to the low amounts or absence of Pb_i . No igneous process related to partial melting or fractional crystallization can account for the very high μ -values of the individual samples without the source region having an already elevated μ -value. Since one of the oldest angrites, D'Orbigny, possesses remnant magnetism indicative of a core dynamo, the absence of Pb_i in the oldest angrites (Connelly et al., 2008) could be related to dry accretion and/or core formation. However, the volatile (but not siderophile) elements Na, K and Rb are depleted by factors of 205–300 relative to Sm, La and Sr (Keil, 2012). Gallium, which is both siderophile and volatile, does not show a large depletion when corrected for volatile loss using the elements above, suggesting that sequestration of siderophile elements to the core is of minor importance for the volatile elements. As such, the high initial μ -value of the APB is best explained by the primary accretion of volatile depleted material, including Pb. Moreover, the angrites are enriched in heavy Si isotopes relative to Earth that have been interpreted to reflect fractionation related to impact-induced loss of volatiles rather than by core formation (Pringle et al., 2014; but see also Dauphas et al., 2015 who infer that the angrite's heavy Si isotope signature may be due to nebular processes and accretion of the angrite parent body).

The highly-elevated initial μ -value persistent in all the old angrites convincingly demonstrates that dry accretion in the inner Solar System results in a very elevated initial μ -value. However, the rapid growth of Pb_r in the U-rich angrites, especially ^{207}Pb in the first few million years when there is a high initial abundance of ^{235}U , makes the re-appearance of Pb with a very distinct, high $^{207}Pb/^{206}Pb$ (>2) ratio unavoidable unless there is an efficient process of Pb removal that continues to operate after accretion and core formation. To assess the retention of radiogenically-accumulated Pb on the parent body such that would have been incorporated into the younger angrites, we have analyzed the young, coarse-grained angrite NWA 4801 (Irving and Kuehner, 2007) to define its age and characterize its initial Pb inventory (see Supplementary Information for methods).

5. Evaluating initial Pb in angrite NWA 4801

Angrite NWA 4801 has a medium-grained (0.1–1.2 mm) cumulate texture with no evidence of re-equilibration. It is composed of dark brown Al–Ti clinopyroxene, pure anorthite, calcic olivine, spinel, merrillite with minor metal and troilite (Irving and Kuehner, 2007). Ten of 11 partial dissolution steps of a whole rock chip and 3 residual dissolution steps of a pure clinopyroxene separate define a single line in $^{204}\text{Pb}/^{206}\text{Pb}$ vs $^{207}\text{Pb}/^{206}\text{Pb}$ space (Fig. 2b and Table S2) where the y-intercept represents pure radiogenic Pb and corresponds to an age of 4556.8 ± 0.2 Ma. The isochron projects back to an acceptable estimate of the modern terrestrial Pb (Pb_c) composition (Stacey and Kramers, 1975). Only the first dissolution step (L1) falls below the array. As such, NWA 4801 records a simple history of crystallization at 4556.8 ± 0.2 Ma followed by rapid cooling resulting in the observed well-behaved U–Pb systematics. The Pb–Pb data from this meteorite confirm that it is part of the young angrite suite, having crystallized ~ 10 Myr after formation of the first Solar System solids and 7.6 Myr after the oldest angrite formed (NWA 1670). Importantly, NWA 4801 contains a binary mixture of modern terrestrial Pb (Pb_c) and radiogenic Pb (Pb_r). The absence of any initial Pb (Pb_i) in this sample requires a very high μ -value that, for the sake of calculations here, we conservatively estimate at 1000. Given the similar degree of compatibility of U and Pb, we infer that this μ -value also applies to the source region for these angrites such that there was virtually no Pb present in the source region. The U concentration in the source region is less certain, but we note that the ratio of U concentrations between the Earth's primitive mantle and Mid Ocean Ridge Basalts is approximately 0.33. Using this value to estimate the U concentration in the source region of the angrites based on the U content of NWA 4801, we calculate that there should have been approximately 5.5 pg and 2.7 pg of radiogenic ^{207}Pb and ^{206}Pb , respectively, incorporated into our aliquot of NWA 4801 if the evolving Pb between T_0 and 4556.8 Ma was retained in the source region. Despite these amounts being easily resolved by our methods (see Fig. 2b), no points plot above the isochron precluding the presence of any initial Pb with a high $^{207}\text{Pb}/^{206}\text{Pb}$ ratio in this sample or in its source region at the time of its crystallization. As such, we conclude that Pb radiogenically produced in the first ~ 10 Myr of the angrite parent body must have been efficiently removed by a continuous or episodic mechanism from the mantle source region of these angrites before they crystallized.

While it is unavoidable that Pb was removed over this period, the question remains as to the mechanism responsible for such efficient removal of Pb. The presence of a magnetic field by 4563.4 ± 0.1 Ma (Weiss et al., 2008; Amelin, 2008a with age adjusted for U isotopic composition after Connelly et al., 2012) and the short-lived Hf–W system (Kleine et al., 2012) requires that core formation occurred early and was not responsible for the subsequent removal of Pb from the silicate mantle. As such, the only viable mechanism that operated long enough on the angrite parent body appears to have been evaporative loss of volatiles, including Pb, during the progressive solidification of a magma ocean, which may have been prolonged by impacting. Additional evidence for efficient planetesimal-scale Pb loss during energetic events comes from the high μ -value of the bulk Gujba chondrite that formed by re-accretion of impact-generated silicate and metal droplets ~ 5 Myr after Solar System formation (Bollard et al., 2015). Indeed, the lack of initial Pb_i in the silicate chondrules requires that any primordial and/or radiogenic Pb was lost at the time of the impact.

We conclude that up to 90% of Pb was lost from Earth's mantle at the time the Earth–Moon system was formed in some process related to the volatility of Pb. While the angrite NWA 4801 and Gujba meteorites demonstrate that volatile loss of Pb is an efficient

process in general, we review below the existing evidence for the mechanism(s) of Pb loss from the Earth–Moon system during the giant impact.

6. The volatile inventories of Earth and Moon

The Earth and, to an order of magnitude greater degree, the Moon are both depleted in volatile elements relative to CI chondrites that we take as a proxy for the Solar System (Albarède et al., 2015). This depletion of volatile elements in bulk silicate Earth (Albarède et al., 2015) has been attributed to primary accretion rather than the giant impact (Albarède, 2009). Early lunar formation models envisioning a Mars-sized impactor also predict that volatile loss from the proto-Earth related to the impact would be very localized and limited (e.g. Zahnle et al., 2007). However, more recent models to explain similarities in O, Cr, and W isotopic compositions of the Earth and Moon have invoked a more energetic collision and thorough mixing of sub-equal sized bodies resulting in a larger and hotter magma and vapour plume (Canup, 2012). This model presumes that Earth re-accreted a significant portion or all of its silicate portion from the magma–vapour plume.

Assuming that volatile elements were also homogeneously mixed immediately after the giant impact, the lower inventory of volatile elements in the Moon relative to Earth (Albarède et al., 2015) could be attributed to volatile loss in the Moon's precursor material during re-accretion (e.g. Ward, 2012; Canup et al., 2014; Albarède et al., 2015, pg. 572), volatile loss during the lunar magma ocean stage or by post-impact veneering of volatile-rich material on Earth. Numerical models of the dynamics of a post-impact two-phase (gas and magma) disk predict volatile loss from the Earth–Moon system leaving at least the Moon depleted in these elements during its accretion (Ward, 2012; Canup et al., 2014). But to our knowledge, no models specifically predict or address the dynamics of Earth's immediate re-accretion after collision or the fate of volatile elements in these more energetic events.

Albarède et al. (2015, pg. 572) cite the depletion pattern of volatiles for the Moon as evidence for incomplete condensation of volatile elements in the aftermath of the giant impact, consistent with lunar Zn isotopic compositions (Paniello et al., 2012). For Earth, the comparable depletions of K, Rb and Cs with similar bond energies and $T_{50\%}$ temperatures but different masses have been cited as evidence for volatile depletion related to accretion rather than volatile loss from Earth or proto-Earth with a gravity field (Albarède, 2009). In the latter scenario, a correlation between elemental mass and abundances is predicted. In the case of the Moon, we concur with Albarède et al. (2015) who infer that comparable abundances of these same elements is consistent with a model of incomplete condensation from a volatile rich disk. To explain a similar but shallower trend for Earth's volatile elements (Albarède et al., 2015), we use the same argument in support of partial condensation of the magma–vapour plume resulting from the giant impact.

The consistently light Zn isotopic composition of Earth relative to CI chondrites is not expected in a simple model where Zn reflects mainly incomplete re-accretion of volatile elements from a magma–vapour plume in the aftermath of the giant impact (Albarède, 2009). However, the Zn isotopic composition may predominantly reflect Earth's precursor material akin to ordinary chondrites that are isotopically light due to the high abundance of chondrules (Luck et al., 2005). We infer that this bulk isotope signature was not heavily modified by either pre- or post-impact processes, despite re-accretion of as little as 10% of the Zn from the melt–vapour plume of the giant impact. The more variable, and in most cases heavier, Zn isotopic composition of the Moon (Paniello et al., 2012) may reflect the fact that it accreted an order of magnitude less Zn than Earth, resulting in measurable fractionation.

Alternatively, the Moon may have initially accreted from the debris disk with a comparably light Zn isotopic composition as the re-accreted Earth, but another 90% volatile loss during the lunar magma ocean stage may have driven variable degrees of Zn isotope fractionation as suggested by Paniello et al. (2012).

In summary, we agree with Albarède (2009) that Earth accreted relatively dry compared to CI chondrites and with a μ -value after primary embryo accretion between 2 and 4, corresponding to a 10–20 times increase in the U/Pb ratio relative to the Solar value. Our model begins to differ in the pre-impact veneering that is modelled to have contributed ~10% by mass to the proto-Earth and lowered the μ -value to 0.9 to 1.8. From this composition, the loss of ~85–95% of the Pb from a post-impact magma-vapour plume of the giant impact resulted in the final μ value of ~9.24 of bulk silicate Earth.

7. Early evolution of the Earth–Moon system

Based on the evolution of Pb isotopes in Earth's upper mantle, we infer that U and Pb were fractionated sometime between 4.426 and 4.417 Ga by devolatilization of Pb during the Moon-forming giant impact. As such, the first crystallization products of the lunar magma ocean that are widely inferred to have existed after the impact must have occurred after this time and, more realistically, up to 20 Myr later given the cooling time required from thermal modelling (Elkins-Tanton et al., 2011). Whereas this age range for the giant impact is inconsistent with several published ages for lunar rocks older than ~4.41 Ga, ages produced more recently with refined methods are systematically younger than 4.38 Ga. For example, the first concordant ages between multiple radiogenic systems (U–Pb, ^{147}Sm – ^{143}Nd and ^{146}Sm – ^{142}Nd) for a single sample of ferroan anorthosite, yields an age of 4359 ± 3 Ma (Borg et al., 2011). Accepting this young anorthosite as a floatation cumulate in a post-impact lunar magma ocean implies that the oldest lunar ages may not define true crystallization ages. Indeed, a recent re-evaluation of published Sm–Nd ages of anorthosites and Mg-suite rocks originally reported to be >4.4 Ga suggest that they may not be robust (Gaffney and Borg, 2014). A widely-cited older age of 4.417 Ga for 5 of 41 ion microprobe spot analyses of a single zircon crystal from lunar breccia 72215 (Nemchin et al., 2009) would appear to preclude a young formation age for the Moon. However, an average age of ~4.38 Ga for all 41 analyses may be a more reliable estimate given the potential for spurious old ages when Pb is redistributed within single crystals during dry, high-temperature metamorphism as documented in terrestrial zircons (McFarlane et al., 2005; Whitehouse et al., 2014). A younger age for this zircon is more consistent with the age range of ~4.35–4.00 Ga for 121 lunar zircons analyzed by the same technique.

Our revised timescale for the formation of the Earth–Moon system, which solves the long-standing Pb Paradox, also impacts our understanding of Earth's earliest evolution. It is commonly accepted that a deep magma ocean formed on Earth in the aftermath of the lunar-forming giant impact (Elkins-Tanton et al., 2011). If correct, such a catastrophic event is expected to have homogenized the mantle and, hence, erased any traces of pre-impact differentiation and stratification. The only direct evidence for the oldest rocks on Earth come from the Hadean zircon record, which currently places an upper limit of 4374 ± 6 Ma (Valley et al., 2014) for the existence of a primordial crustal reservoir. However, using chondritic meteorites as a proxy for bulk silicate Earth, the short-lived ^{146}Sm – ^{142}Nd and long-lived ^{176}Lu – ^{176}Hf systems have been used to record global silicate differentiation that may have occurred as early as 4.5–4.4 Ga (Kemp et al., 2010). A late Moon-forming event at 4.426–4.417 Ga can be reconciled with these data sets by a non-chondritic Earth, as suggested by Campbell and O'Neill (2012). Finally, our model requires that ~98% of Earth's original Pb inven-

tory was lost via devolatilization by the time of final crystallization of the terrestrial magma ocean, an amount consistent with that predicted by Albarède et al. (2015). Given the much higher volatility of water relative to Pb, Earth would have been essentially dry of water by this time. Thus, the current inventory of water on Earth must have been mainly accreted during a late veneering event after the late Moon-forming impact.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2016.07.010>.

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