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Broad bounds on Earth's accretion and core formation constrained by geochemical models

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The Earth formed through the accretion of numerous planetary embryos that were already differentiated into a metallic core and silicate mantle. Prevailing models of Earth's formation, constrained by the observed abundances of metal-loving siderophile elements in Earth's mantle, assume full metal–silicate equilibrium, whereby all memory of the planetary embryos' earlier differentiation is lost[1,2]. Using the hafnium–tungsten (Hf–W) and uranium–lead (U–Pb) isotopic dating systems, these models suggest rapid accretion of Earth's main mass within about 10 million years[3–6] (Myr) of the formation of the Solar System. Accretion terminated about 30[3,7] or 100[4,5] Myr after formation of the Solar System, owing to a giant impact that formed the Moon. Here we present geochemical models of Earth's accretion that preserve some memory of the embryos' original differentiation. These disequilibrium models allow some fraction of the embryos' metallic cores to directly enter the Earth's core, without equilibrating with Earth's mantle. We show that disequilibrium models are as compatible with the geochemical observations as equilibrium models, yet still provide bounds on Earth's accretion and core formation. We find that the Hf–W data mainly constrain the degree of equilibration rather than the timing, whereas the U–Pb data confirm that the end of accretion is consistent with recent estimates of the age of the Moon[8,9]. Our results indicate that only 36% of the Earth's core must have formed in equilibrium with Earth's mantle. This low degree of equilibration is consistent with the siderophile element abundances in Earth's mantle.

Impacts of numerous Moon- to Mars-sized planetary embryos on the growing Earth released sufficient energy to induce melting and core formation within the Earth[10,11]. As metal segregation is thought to happen much faster than accretion, the timescale of core formation can be used to determine the rate of Earth's accretion. The Hf–W systematics of Earth's mantle yield model timescales for accretion that are faster than those estimated on the basis of U–Pb systematics. The equilibrium two-stage model ages are $t_{2,\text{eq}}^{\text{Hf–W}} = 31.0 \pm 4.4$ Myr (refs 6,12–14) and $t_{2,\text{eq}}^{\text{U–Pb}} = 55.9$–$130.5$ Myr. The model ages calculated in an exponential growth model are roughly a factor of three smaller, with $\tau_{a,\text{eq}}^{\text{Hf/W}} = 10.6 \pm 0.5$ Myr and $\tau_{a,\text{eq}}^{\text{U–Pb}} = 21.6$–$51.0$ Myr (τ_a corresponds to the time taken to achieve 63% growth; the time to achieve 95% growth is similar to the two-stage model ages; Supplementary Methods). Several models were proposed to account for this disparity in calculated accretion timescales, including disequilibrium during core formation[15–17], a late segregation of Pb-bearing sulphides to the Earth's core[18,19] and the addition of Pb by a late veneer subsequent to core formation[7]. The main source of uncertainty in using Hf–W systematics to determine the core formation timescale is the strong dependence of the system on the degree of metal–silicate equilibration[12,15–17]. Some authors have argued that U–Pb systematics place no constraint on core formation because neither the bulk Earth Pb isotopic composition nor the bulk Earth U/Pb ratio is sufficiently well known[20,21]. Further uncertainty arises because some recent experiments seem to indicate that Pb was not partitioned into the Earth's core[22], although this result has been questioned by others[23] owing to the high C contents of the metal phase in those experiments. In any case, the U–Pb age of the Earth seems to have some significance, because it is similar to the age of the Moon[8,9].

A serious shortcoming of current geochemical models of Earth's accretion and core formation is that their entire parameter space has never been fully explored. For instance, all of the models use specific growth curves without investigating the entire range of possible curves. It thus remains unclear whether the particular accretion curve chosen provides the best approximation of Earth's accretion. Furthermore, existing models of disequilibrium[15–17,24] have not studied the combined constraints of both isotopic and siderophile element observations. To address these important questions, we developed a geochemical box model for metal–silicate differentiation in the growing Earth. In the model, material of the planetary embryos is assumed to differentiate into mantle and core at time 0 (the time of Solar System formation), with metal and silicate in equilibrium with one another. This assumption seems reasonable, given the evidence for very early differentiation of meteorite parent bodies[12,25]. Over the course of the accretion, the embryo material is added to the Earth at some rate described by a function $M(t)$ that determines the fraction of the Earth that has accreted at time t. Two forms for $M(t)$ are commonly chosen: a step function (two-stage model),

$$M(t) = \begin{cases} 0, & 0 < t < t_2, \\ 1, & t > t_2 \end{cases} \tag{1}$$

where all of the accretion occurs at a particular instant t_2; or an exponential

$$M(t) = 1 - e^{-t/\tau_a} \tag{2}$$

that has similarities with the accretion curves produced by some n-body simulations[26,27]. τ_a is the corresponding mean age. A useful two-parameter generalization of the exponential accretion model is the Weibull accretion model,

$$M(t) = 1 - e^{-(t/\alpha)^\beta} \tag{3}$$

where α is a timescale parameter (time taken to accrete 63% of the Earth) and β is a shape parameter. When $\beta < 1$ accretion

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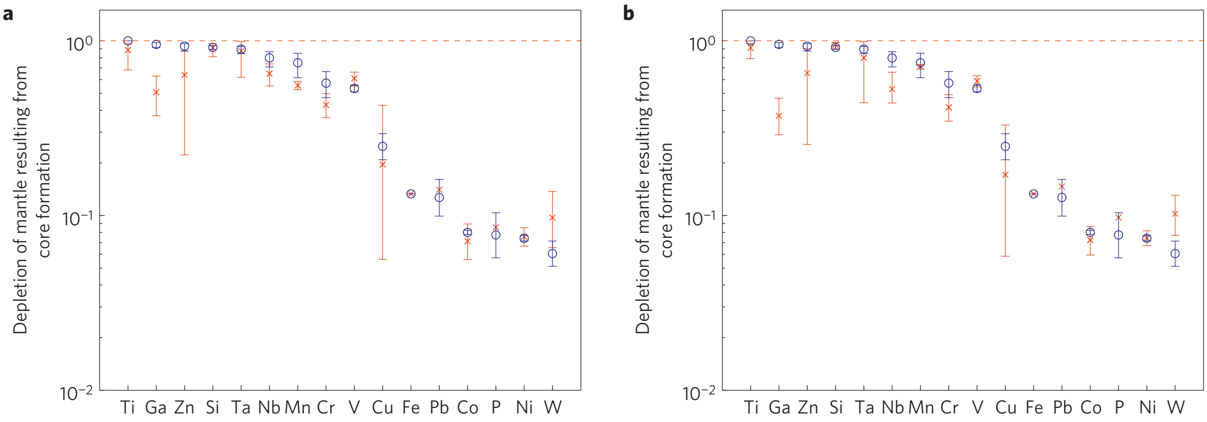

Figure 1 | Present-day mantle depletion for a variety of moderately siderophile elements. The blue dots give target values[1,2]; the red crosses give model results using experimental partition coefficients[1,2,29,30]. The error bars give 1σ uncertainties. **a**, An equilibrium scenario ($k = 1$), where oxygen fugacity increases from $\Delta IW = -4.26$ to -0.83. The pressure of equilibration is 31% of that at the core–mantle boundary. **b**, A disequilibrium scenario ($k = 0.42$), where oxygen fugacity increases from $\Delta IW = -2.62$ to -0.57, and the pressure of equilibration is 31% of that at the core–mantle boundary. Equilibration in the embryos is assumed to take place at 9 GPa, 2,700 K and $\Delta IW = -2.62$.

happens faster than exponential at early times, and slower than exponential at late times.

As accretion proceeds, material from the mantle of the embryos is added directly to the Earth's mantle. However, a mass fraction k of material from the core of the embryos chemically equilibrates with the Earth's mantle before joining the Earth's core, with the remaining fraction $1-k$ added directly to the Earth's core. When $k = 1$, the model is an equilibrium model, and all memory of differentiation in the embryos is lost. For $k < 1$ there will be some memory of the embryos' differentiation. k represents a simple parametrization of the complex interactions that take place between metal and silicate during accretion. The degree of metal–silicate equilibration depends crucially on the physical conditions under which metal–silicate segregation takes place[10]. For example, in a turbulently convecting magma ocean the metal may fall through the liquid silicate as small droplets, equilibrating in the process. However, it is unclear whether the metal cores of newly accreted objects always emulsify in this way, and some cores may have directly merged with Earth's core without substantial metal–silicate equilibration.

The chemical equilibration processes that take place both in the embryos and during Earth's accretion are described by metal/silicate partition coefficients D, which are functions of the temperature, pressure and oxygen fugacity conditions under which chemical equilibration takes place. Thus, the partitioning is likely to have changed markedly over the course of Earth's accretion. We model this with the approach used by Wade and Wood[1]. The point of last metal–silicate equilibration is assumed to be at the base of a magma ocean, which is at some fixed fraction of the depth to the core–mantle boundary. Thus, as the planet grows, the pressure at the base of the magma ocean increases. The temperature at the base of the magma ocean is simply a function of this pressure, set by the constraint that it lies on the peridotite liquidus, and also increases as the Earth grows. The oxygen fugacity is also assumed to evolve over the course of the accretion, linearly increasing with $M(t)$ after the first 10% of the accretion[2]. Using parametrizations of experimental data on metal–silicate partitioning[1,28–30], the expected siderophile element depletion of the mantle resulting from core formation can be calculated.

In agreement with earlier work, models with full equilibration ($k = 1$) can produce good fits to the observed siderophile element abundances (Fig. 1a), and require an increase in oxygen fugacity of around three log units over the course of accretion[1,2]. However, equally good fits can be found in scenarios with partial equilibration, as shown in Fig. 1b. Thus, the siderophile element

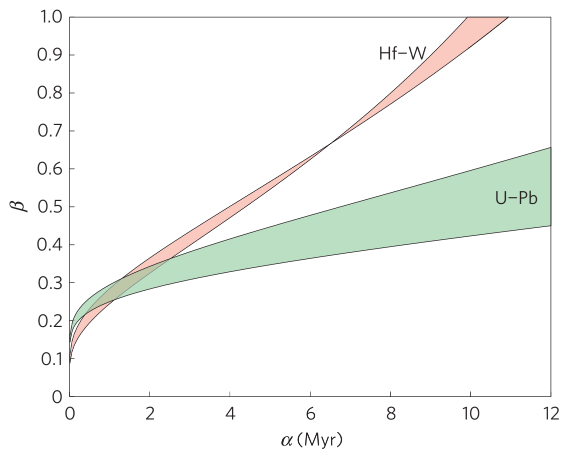

Figure 2 | Values of the Weibull timescale parameter α and shape parameter β compatible with the observed isotope systematics. Constant partitioning and full equilibration ($k = 1$) is assumed. For Hf-W, the uncertainty resulting from uncertainty in D_W is shown ($D_W = 21$–44). For U-Pb, D_{Pb} is assumed constant, $D_{Pb} = 13$, but the uncertainty resulting from unknown bulk lead isotopic composition is shown. When $\beta = 1$, the exponential accretion model is recovered, with scale parameters $\alpha^{Hf-W} = 9.9$–10.9 Myr and $\alpha^{U-Pb} = 21.5$–50.1 Myr. There is a region of overlap between Hf-W and U-Pb around $\alpha = 0.4$–2.5 Myr, $\beta = 0.22$–0.36.

depletions in Earth's mantle are not evidence for equilibrium core formation and consequently cannot be used to argue for complete metal–silicate equilibration when interpreting the isotopic observations. In partial equilibration scenarios, the conditions of differentiation in the embryos are important, and these are very poorly constrained. There is a trade-off between conditions in the embryos and conditions on Earth, and good fits can be found for a wide range of different embryo conditions (Supplementary Methods). Thus, the siderophile element abundances may reflect not only the conditions of core formation in the growing Earth but also the conditions of core formation in the embryos.

Although the marked changes in partitioning behaviour over the course of accretion are key to understanding the siderophile element abundances, the main constraints that the isotopic observations place can be understood within the context of simpler constant partitioning models. Such a model can be seen in Fig. 2, which shows an equilibrium Weibull accretion model of the Earth

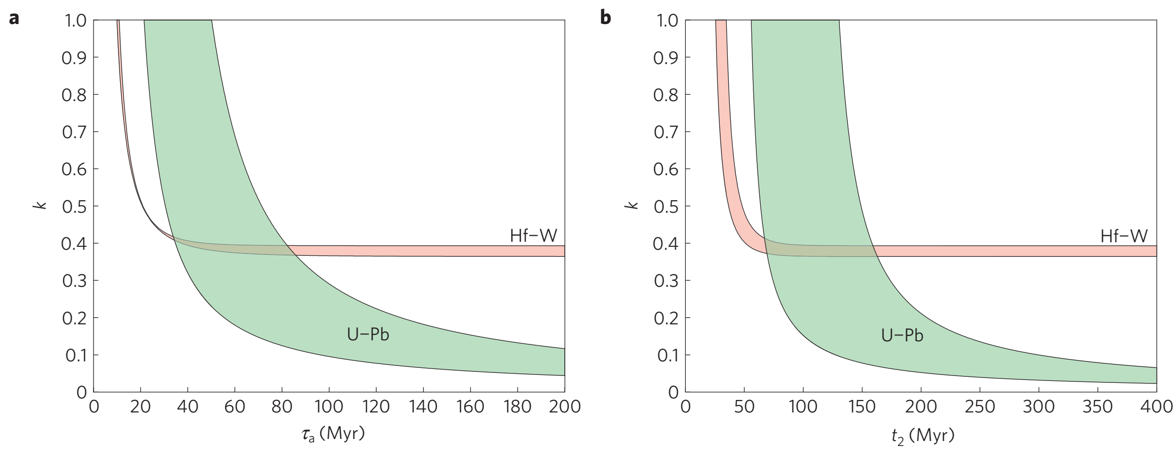

Figure 3 | Disequilibrium models with exponential accretion and step-function (two-stage) accretion. a, Exponential mean accretion age τ_a as a function of equilibration fraction k. Uncertainties are as in Fig. 2. For full equilibration ($k = 1$) the model age ranges are non-overlapping $\tau_{a,\mathrm{eq}}^{\mathrm{Hf-W}} = 9.9$-$10.9$ Myr and $\tau_{a,\mathrm{eq}}^{\mathrm{U-Pb}} = 21.5$-$50.1$ Myr. **b**, Two-stage age t_2 as a function of equilibration fraction k. For full equilibration ($k = 1$) the model age ranges are non-overlapping $t_{2,\mathrm{eq}}^{\mathrm{Hf-W}} = 25.7$-$34.8$ Myr and $t_{2,\mathrm{eq}}^{\mathrm{U-Pb}} = 55.9$-$130.5$ Myr. In both **a** and **b** the region of overlap has k near to the asymptotic values for Hf–W (for very slow accretion $k^{\mathrm{Hf-W}} = 0.36$-0.39).

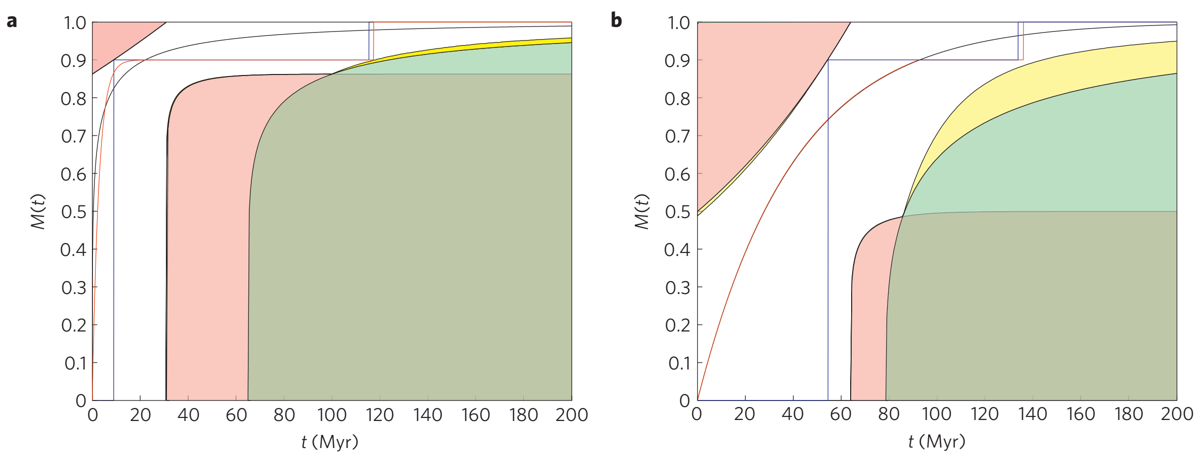

Figure 4 | Example accretion curves compatible with both Hf–W and U–Pb isotopic constraints. a, Full equilibration ($k = 1$). **b**, Partial equilibration ($k = 0.4$). Equilibrium two-stage ages $t_{2,\mathrm{eq}}^{\mathrm{Hf-W}} = 31.0$ Myr and $t_{2,\mathrm{eq}}^{\mathrm{U-Pb}} = 65$ Myr are assumed, with $D_{\mathrm{W}} = 32$ and $D_{\mathrm{Pb}} = 13$. These assumed values are demonstrative, not definitive. The shaded regions are forbidden given the Hf–W (pink), U–Pb (green) and combined (yellow) constraints. In **a**, three example curves are shown: Weibull (black) and two scenarios culminating in a giant impact at around 120 Myr (red/blue; refs 4,5). In **b**, an exponential model is shown (black) and two scenarios having a giant impact at around 130 Myr (red/blue).

with the values of α and β compatible with the Hf–W and U–Pb observations, assuming constant partitioning. There is a region of overlap around $\alpha = 0.4$–2.5 Myr, $\beta = 0.22$–0.36 where the two isotopic systems are consistent. Thus, having a rapid accretion at early times (63% of the Earth accreted in less than 2.5 Myr) and a slower accretion at late times is one way to match the isotopic observations with an equilibrium model. Thus, the apparent disparity between the previously calculated Hf–W and U–Pb timescales for Earth's accretion may simply reflect the choice of an improper accretion curve (that is, the exponential or two-stage models) rather than being a case for partial equilibration[15,17], late sulphide segregation[19] or late veneer Pb addition[7].

A key unknown in interpreting the isotopic observations is the degree of metal–silicate equilibration during core formation. This is demonstrated in Fig. 3b, where the two-stage age t_2 is given as a function of k for both Hf–W and U–Pb. Importantly, there is a region of overlap $k = 0.36$–0.41 and $t_2 = 67.1$–162.9 Myr where both systems are consistent. The exponential model ages (shown in Fig. 3a) also overlap, with $k = 0.37$–0.42 and $\tau_a = 33.9$–85.8 Myr. As can be seen by the flattening of the curves in Fig. 3 for large τ_a and t_2 for Hf–W, there is a minimum amount of equilibration required to be compatible with the observations. This minimum value is the same for any accretion curve, and is determined by the Hf–W observations to be in the range $k = 0.36$–0.39. For both two-stage and exponential models, the amount of equilibration required to get a match between Hf–W and U–Pb is very close to this lower bound. Hf–W thus provides very little information about the timing of accretion in such models, and essentially determines the degree of equilibration. U–Pb is less sensitive to the degree of equilibration and mostly determines the timing[17].

The discussion up to this point illustrates that a variety of different accretion scenarios are compatible with the observations. Nevertheless, the observations still place important constraints. Isotopic observations fully determine the accretion curve $M(t)$ only when simple parametric forms are assumed, such as an exponential model or a two-stage model. In general, $M(t)$ will be underconstrained, but there are bounds that can be placed on $M(t)$, which are shown as pink (Hf–W) and green (U–Pb) shaded regions in Fig. 4. Slightly tighter bounds are obtained when both Hf–W and U–Pb constraints are considered together (yellow region).

Accretion curves compatible with the observations must lie wholly within the unshaded region.

The shaded regions shown in Fig. 4a provide a clear demonstration of the different constraints the Hf–W and U–Pb systems place on equilibrium accretion. Hf–W predominately constrains the early accretion; for example, it shows that at least 80% of the Earth must have accreted by 35 Myr; but it tells us very little about the late (>60 Myr) accretion other than that no more than 14% of the accretion can happen late: as far as the Hf–W observations are concerned the last 14% of the accretion could have happened yesterday. On the other hand, U–Pb tells us little about the early accretion, but strongly constrains the late accretion; for example, it shows that the final 10% of accretion must have begun by 120 Myr for the assumed parameters. The bounds on the accretion curve depend on the degree of equilibration, and Fig. 4b gives an example with partial equilibration.

We can simultaneously match both the siderophile element abundances and the isotopic constraints with a single model. However, there are a wide range of models, both equilibrium and disequilibrium, that are all equally compatible with the observations. On the basis of the Hf–W, U–Pb and siderophile element constraints, we cannot tell whether full core–mantle equilibration occurred or not, but we can constrain the degree of equilibration to be at least 36%. Thus, in spite of a wide range of geochemical observations, important details regarding Earth's accretion and core formation remain only poorly constrained. A better understanding of the physical and chemical conditions of metal–silicate fractionation as well as of the conditions prevailing in Earth's building blocks are needed before more tightly defined accretion curves for the Earth can be constructed.

Methods

The geochemical box model used throughout this work is governed by

$$\frac{\mathrm{d}}{\mathrm{d}t}((1-F)Mc_{\mathrm{m}}) = [(1-F)c_{\mathrm{me}} + kF(c_{\mathrm{ce}} - D_{\mathrm{c}}c_{\mathrm{m}})]\frac{\mathrm{d}M}{\mathrm{d}t} \quad (4)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}(FMc_{\mathrm{c}}) = [kFD_{\mathrm{c}}c_{\mathrm{m}} + (1-k)Fc_{\mathrm{ce}}]\frac{\mathrm{d}M}{\mathrm{d}t} \quad (5)$$

where $F = 0.323$ is the mass fraction of Earth that is core, k is the mass fraction of metal that equilibrates during accretion, D_{c} is the metal/silicate partition coefficient, c_{m} is the concentration of a chemical species in Earth's mantle, c_{c} is the concentration in Earth's core, c_{me} is the concentration in the mantle of the embryos, c_{ce} is the concentration in the core of the embryos and $M(t)$ is the fraction of the Earth that has accreted at time t.

The parameter k is a simple representation of the equilibration of the metal as it travels through the Earth's mantle to the core, and models the equilibration process as a simple mixture of fully equilibrated and unequilibrated material. The real situation may be more complicated, as different elements have different diffusivities and thus may equilibrate at different rates. Hence, the effective k could differ between different elements. For simplicity we treat k as a constant for all elements.

If the partition coefficients vary with time, then the governing equations have to be solved numerically (Fig. 1). The partition coefficients are a function of temperature, pressure and oxygen fugacity and have been parametrized using regressions of experimental data[1,2,28–30]. There are uncertainties in the regression coefficients and these have been propagated through the model to generate the red error bars shown in Fig. 1. It should be noted that these red error bars may underestimate or overestimate the true uncertainty for two main reasons. First, errors have been included on only some of the regression coefficients used in the parametrization. If errors were included on all of the regression coefficients, then the error bars would be substantially larger[30], but not all authors report errors on all coefficients. Second, the errors on the regression coefficients have been assumed to be independent, so the true uncertainty could be larger or smaller depending on the degree of correlation between the regression coefficients, but this correlation is not reported. There are also uncertainties in the present-day mantle abundances, and these are shown in the blue error bars of Fig. 1.

A number of simple analytical results arise when the partitioning is constant, as assumed in Figs 2–4. Detailed derivations of the following results can be found in the Supplementary Methods. The two-stage ages with (t_2) and without ($t_{2,\mathrm{eq}}$) disequilibrium are related by

$$1 - \mathrm{e}^{-\lambda t_{2,\mathrm{eq}}} = \frac{k(1+R_{\mathrm{d}})}{1+kR_{\mathrm{d}}}(1-\mathrm{e}^{-\lambda t_2}) \quad (6)$$

where λ is the decay constant and $R_{\mathrm{d}} = FD_d/(1-F)$. D_d is the (assumed constant) metal/silicate partition coefficient of the daughter element (W or Pb). This is the relationship plotted in Fig. 3b.

The two-stage model ages t_2 and the exponential model ages τ_a are related by

$$\mathrm{e}^{-\lambda t_2} = \frac{\Gamma(2+kR_{\mathrm{d}})\Gamma(1+\lambda\tau_a)}{\Gamma(2+kR_{\mathrm{d}}+\lambda\tau_a)} \quad (7)$$

where $\Gamma(z)$ is the Gamma function, and this is used in plotting Fig. 3a.

A lower bound on k is given by

$$k \geq \frac{1-\mathrm{e}^{-\lambda t_{2,\mathrm{eq}}}}{1+R_d\mathrm{e}^{-\lambda t_{2,\mathrm{eq}}}} \quad (8)$$

and this describes the asymptotes for large t_2 and τ_a in Fig. 3.

The early accretion ($t \leq t_2$) is bounded by (pink and green regions, upper left of Fig. 4)

$$M(t) \leq \mathrm{e}^{\lambda(t-t_2)/(1+kR_{\mathrm{d}})} \quad (9)$$

and the late accretion ($t \geq t_2$) by (pink and green regions, lower right of Fig. 4)

$$M(t) \geq \left(\frac{\mathrm{e}^{-\lambda t_2} - \mathrm{e}^{-\lambda t}}{1-\mathrm{e}^{-\lambda t}}\right)^{1/(1+kR_{\mathrm{d}})} \quad (10)$$

The isotopic evolution of models with evolving partitioning behaviour, such as those in Fig. 1, does not differ substantially from the constant partition coefficient models of Figs 2–4. The only difference is that accretion needs to be slightly more protracted to match the same Hf–W and U–Pb observations. The requirement of more protracted accretion arises because both W and Pb are more siderophile during the early accretion than the late accretion, which causes a bias towards younger ages. For example, the disequilibrium model of Fig. 1b (evolving partitioning) requires an exponential accretion with $\tau_a = 49.7$ Myr and $k = 0.42$ as opposed to $\tau_a = 40.3$ Myr and $k = 0.40$ of Fig. 4b (constant partitioning).

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Author contributions

J.F.R. derived the model equations and carried out the calculations. J.F.R. and T.K. wrote the paper. B.B. conceptually designed the study. All authors discussed the results and implications and commented on the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at http://npg.nature.com/reprintsandpermissions. Correspondence and requests for materials should be addressed to J.F.R.