LETTERS

Cooling of the Earth and core formation after the giant impact

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Kelvin calculated the age of the Earth to be about 24 million years by assuming conductive cooling from being fully molten to its current state[1]. Although simplistic[2], his result is interesting in the context of the dramatic cooling that took place after the putative Moon-forming giant impact, which contributed the final ~10 per cent of the Earth's mass[3,4]. The rate of accretion and core segregation on Earth as deduced from the U–Pb system[5] is much slower than that obtained from Hf–W systematics[6–8], and implies substantial accretion after the Moon-forming impact, which occurred 45 ± 5 Myr after the beginning of the Solar System. Here we propose an explanation for the two timescales[5,9]. We suggest that the Hf–W timescale reflects the principal phase of core-formation before the giant impact. Crystallization of silicate perovskite in the lower mantle during this phase produced Fe^{3+}, which was released during the giant impact[10], and this oxidation resulted in late segregation of sulphur-rich metal into which Pb dissolved readily, setting the younger U–Pb age of the Earth. Separation of the latter metal then occurred 30 ± 10 Myr after the Moon-forming impact. Over this time span, in surprising agreement with Kelvin's result, the Earth cooled by about 4,000 K in returning from a fully molten to a partially crystalline state.

The rates and timing of the processes by which the Earth accreted and differentiated are generally studied using chronometers such as ^{129}I–^{129}Xe, ^{182}Hf–^{182}W, $^{235/238}U$–$^{207/206}Pb$ and ^{244}Pu–^{136}Xe. In each case, relatively simple assumptions are made about how parent and daughter isotopes distribute themselves between the developing geochemical reservoirs, and a model age or timescale for the process of interest is calculated. The Hf–W and U–Pb chronometers, for example, yield, in principle, the time of formation of the core[11]. In these cases, the parent elements (Hf and U) exhibit lithophile behaviour and are retained in silicate reservoirs during accretion, whereas the daughters (W and Pb) are considered to be strongly partitioned into the growing core. This partitioning enables us to calculate an apparent time of core formation assuming separation in a single step. A more realistic approach is to take account of growth of the Earth over millions of years with progressive segregation of the core as more material was added[12] (Fig. 1). In such models the growth of the Earth can be viewed as taking place at an exponentially decreasing rate, as follows (Fig. 1):

$$F_t = 1 - e^{-\lambda \Delta t} \qquad (1)$$

where F_t is the cumulative fractional mass of the Earth relative to the present day at time t, λ is the time constant for accretion ($= 1/\tau$, where τ is the mean life) and $\Delta t = t_o - t$ (where t_o is the age of the Solar System).

If it is assumed that all accreting material mixed isotopically with the silicate Earth, that the accretion rate decreased exponentially with time and that the parent/daughter element ratios were fractionated in a constant fashion during core formation, a time constant for

accretion and core formation can be derived[13]. On this basis, both Hf–W and U–Pb should yield the same time constant (or its inverse, the mean life). Instead, the U–Pb timescales are more protracted than those of Hf–W (ref. 11) (Fig. 1).

One possible explanation for the disparity is that the U–Pb timescale is closer to the true Earth accretion rate, and that the short Hf–W timescale is due to incomplete equilibration of impactor metal with the silicate Earth[5]. This idea can be tested using independent estimates of the accretion rate of the Earth. The only precise estimate is provided by the time of the Moon-forming giant impact. The most widely accepted model for the origin of the Moon is that a Mars-sized object collided with the Earth at the end of its accretion, and generated the angular momentum and an Fe-depleted Moon from the resulting debris disk[14]. This is considered to have added the last ~10% of the Earth's mass. Therefore, the age of the Moon defines the last major growth stage for the Earth. The Hf–W age of the Moon appears to lie between 40 and 50 Myr (refs 5, 9, 11). With the Moon forming at 45 ± 5 Myr after the beginning of the Solar System, it can be shown that on average, 70–90% of the metal in the core was added under conditions of W isotopic equilibrium with the growing silicate Earth[15]. The small amount of disequilibrium explains why the Hf–W age appears older than is expected from the age of the Moon, but does not eliminate the discrepancy with U–Pb.
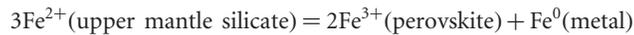
The simplest explanation for the difference in age is, of course, that Pb actually entered the Earth's core at a later stage than W. This would have required the conditions of core formation to change during the later stages of accretion. As shown below, such a change almost certainly occurred.

The partitioning of W and Pb between metals and silicates depends strongly on the oxygen fugacity of equilibrium and the sulphur content of the metal. The FeO content of the upper mantle (8 wt%), combined with the estimated Fe content of the core (80%; refs 16, 17), indicates that equilibrium core segregation would occur at 1.5–2 $\log f_{O_2}$ units below the iron–wüstite (Fe–FeO) buffer[18]. Under these conditions, W would be a siderophile element while Pb partitioning into the metal phase would be very weak[19]. Currently, the upper mantle is much more oxidized, however, exhibiting oxygen fugacities about 4 $\log f_{O_2}$ units higher than those needed for Fe saturation[20]. Under these more oxidizing conditions, the only 'metallic' phase stable in the mantle is an Fe-Ni sulphide such as that found commonly in mid-ocean-ridge basalt[21]. Importantly, Pb is chalcophile, exhibiting partition coefficients of the order of 2,000 between iron sulphide liquid and iron metal[22], whereas W is the opposite with partitioning values of the order of 0.01 (ref. 23). Segregation of a small amount of late sulphide liquid, the 'Hadean matte'[24], could therefore have been a process that fractionated U/Pb, re-setting the U–Pb age with almost no effect on W. This leads to questions of when the Earth's mantle became oxidized and whether or not such a
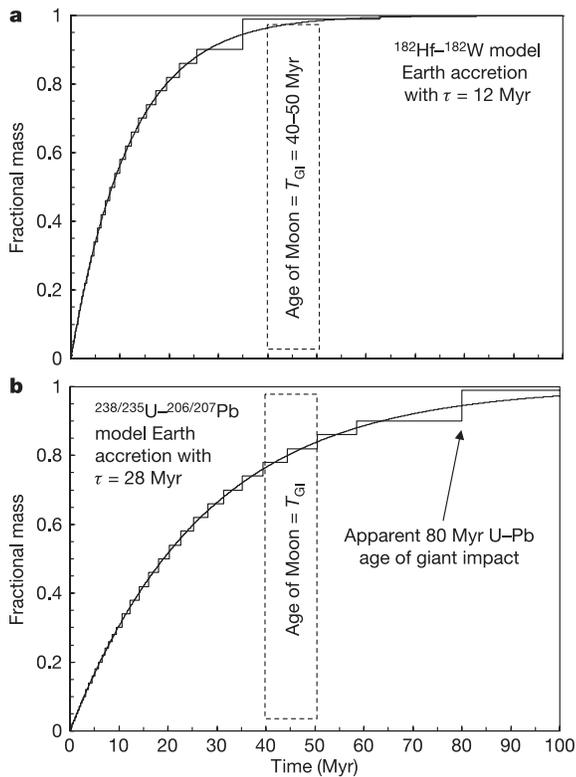
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sulphur-rich liquid can have been extracted from it at the end of core formation.

Oxidation of the Earth's mantle is normally ascribed to dissociation of H_2O at the end of accretion, with loss of hydrogen to space[25]. The amount of H_2O that would be required to oxidize FeO in order to reach the current Fe_2O_3 content of the mantle ($\sim$0.3 wt%) is extremely large, however, close to the current volume of the hydrosphere. Ascribing oxidation to this mechanism also begs the question of why Mars, a more volatile-rich planet than Earth, has a more reduced mantle than does the Earth. Recent experimental results[10] demonstrate, however, that a large planet such as the Earth undergoes 'self-oxidation' at pressures and depths beyond those required to stabilize the magnesium silicate perovskite phase, $(Mg,Fe)SiO_3$. The latter phase, dominant in the lower mantle (below 660 km depth) has such a strong affinity for Fe^{3+} that it forces disproportionation of Fe^{2+} as follows[10]:

$$3Fe^{2+}(\text{upper mantle silicate}) = 2Fe^{3+}(\text{perovskite}) + Fe^0(\text{metal})$$

Fe^{3+} replaces Mg^{2+} in the perovskite structure, charge-balanced by substitution of Al^{3+} for Si^{4+}. Thus, when the Earth had grown large

enough (about the size of Mars) to stabilize perovskite in the lower mantle, then, with core segregation removing metal produced by the above reaction, the Fe^{3+}/Fe^{2+} ratio of the lower mantle started to increase. The vigour of accretion and core segregation would certainly have caused continuous dissolution and re-precipitation of the perovskite with release of Fe^{3+} to the overlying mantle. Given an episodically very deep ($>$1,000 km) magma ocean[26,27], this process would have oxidized the molten upper mantle and as recently shown[27], generated the observed mantle abundances of moderately siderophile elements.

Figure 2 shows the effects when ferric iron is recycled back into a melt of peridotitic composition under upper mantle conditions. Oxygen fugacity increases by about 3 log units as the Fe^{3+} content increases to the current upper mantle value. This is accompanied by destabilization of coexisting metal so that sulphur-rich liquids are the only metallic phases that can coexist with the putative magma ocean. Thus, crystallization and re-crystallization of perovskite would have raised the Fe^{3+} content of the upper mantle and terminated metal segregation from the latter. Sulphur, which had partitioned between metal and silicate, would then have begun to build in concentration in the silicate. Oxidation of later infalling metal by the ferric iron present in the magma ocean would have raised the FeO content of the mantle and left sulphur dissolved in the molten silicate.

The giant impact is believed to have added $\sim$10% to the mass of the Earth and caused complete melting[14], thereby releasing more Fe^{3+} through complete perovskite dissolution. At this stage, temperatures in the silicate Earth ranged from about 4,600 to 10,000 K (ref. 14), and the sulphur present before impact, together with any added to Earth from the impactor, would have been highly soluble in the liquid mantle. Note that lunar basalts are relatively rich in chalcophile elements[28], implying that the impactor added significant amounts of sulphide to the Earth. Sulphur solubility in silicate melt decreases strongly on cooling, leading to exsolution, in Fe-bearing systems, of an FeS-rich liquid[29]. Thus, during cooling, an FeS-rich
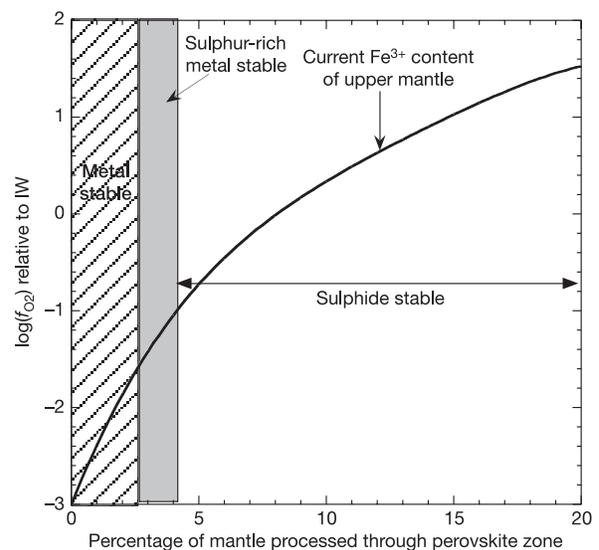

Figure 1 | Application of the growth model to the determination of the time of the Moon-forming impact. a, Using Hf–W chronometry; **b**, using U–Pb chronometry; the growth model is given in Methods. The tungsten isotopic composition of the silicate Earth implies a mean life of accretion (τ) of about 12 Myr and growth from 90% to 99% (due to the giant impact) about 35 Myr after the start of the Solar System. Pb data, in contrast, are consistent with a mean life of accretion of 28 Myr, implying growth from 90% to 99% at about 80 Myr (ref. 5). A possible explanation to consider for this is that accretion was protracted, as indicated by Pb isotope data, but that isotopic equilibration between impactors and the silicate Earth was incomplete[5]. However, the Hf–W age of the Moon (T_{GI}) provides an independent test of this and is now reasonably well-defined, lying in the range 40–50 Myr (refs 5, 9, 15). Although incomplete equilibration explains the W isotopic composition of the BSE, it is inadequate as an explanation for the later apparent ages determined from Pb isotopes. A viable alternative explanation is that Pb was lost from the BSE at a relatively late stage, following formation and segregation of iron sulphide, thereby increasing the $^{238}U/^{204}Pb$ ratio of the BSE.

Figure 2 | Calculated effect of perovskite crystallization on the Fe^{3+} content and hence oxygen fugacity (f_{O_2}) of a magma ocean of peridotite composition. The calculation began by assuming peridotitic mantle of current composition containing 8% FeO. Perovskite crystallized from a melt of this composition contains about 3.5% 'FeO', but rather than being entirely ferrous, half of the iron is actually ferric[10,32]. The Fe^{3+} content of the molten mantle increases as perovskite crystallizes, dissolves releasing Fe^{3+} and recrystallizes at the base of the magma ocean. This 'processing' of the mantle was converted from Fe^{3+} content to oxygen fugacity using experimental data on silicate melts[33]. Oxygen fugacities are expressed relative to the iron–wüstite (IW; Fe–FeO) buffer.

liquid would have 'rained-out' of the liquid mantle, extracting chalcophile elements such as Pb and Te from the mantle. Segregation of an extremely small volume (<1%) of this sulphide matte to the core would have resulted in a young apparent U-Pb age of core formation but would have had no effect on the Hf–W age because the [182]Hf parent was already effectively extinct. The matte would have removed about 1,500 p.p.m. of sulphur (as FeS) from the mantle, an amount which, given the strong temperature dependence of FeS solubility in silicate melts[29] and the chalcophile nature of the impactor[28], seems reasonable.

The data summarized above suggest that Pb was lithophile during most of Earth's accretion. At a late stage, owing to oxidation of the mantle, Pb became chalcophile such that most of it was lost to the core in a sulphide liquid. The results of modelling 11 estimates of the Pb isotopic composition of the bulk silicate Earth (BSE) in such a fashion[5], assuming the giant impact at 45 Myr, are shown in Fig. 3. The $^{238}U/^{204}Pb$ of the BSE (μ_{BSE}) is assumed to be 0.7—identical to the total Earth, until the point at which it increases owing to sulphide segregation, generating the $^{238}U/^{204}Pb$ determined from its Pb isotopic composition. The timing of this event is shown in Fig. 3 and ranges from approximately 50 to 160 Myr after the start of the Solar System. Use of the three most recent estimates defines a more restricted range from 65 to 85 Myr, 30 ± 15 Myr after a 45 ± 5 Myr
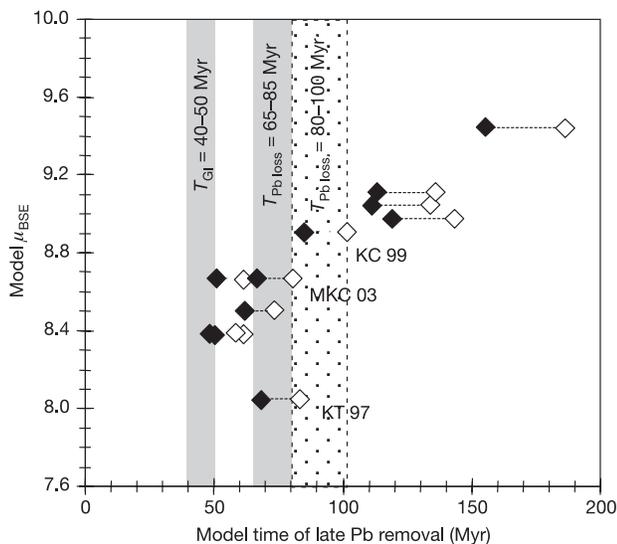
Figure 3 | Results of modelling 11 estimates of the Pb isotopic composition of the BSE with late stage loss of Pb[5]. It is assumed that Pb remained lithophile until a point in time when the majority was instantaneously partitioned into the core to achieve the $^{238}U/^{204}Pb$ or μ of the BSE plotted on the y axis. This is the μ defined by the single-stage Pb isotopic age of the Earth given by the present Pb isotopic composition. The exact μ value is not very sensitive to the accretion and partitioning history because it is provided by $^{206}Pb/^{204}Pb$, reflecting decay of long-lived ^{238}U. The accretion history and exact time of Pb segregation is more sensitive to $^{207}Pb/^{204}Pb$ dominated by early and rapid decay of relatively short-lived ^{235}U. It is assumed the giant impact occurred at 45 Myr after the beginning of the Solar System, defining the timing of growth of the Earth from 90% to 99% of its present mass. It can be seen that the model age for the timing of the increase in μ of the BSE postdates the 45 Myr age of the giant impact. The overall range in ages is broad but much narrower (65–85 Myr) for the three most recent estimates of the Pb isotopic composition of the BSE (KT97, KC99 and MKC03 as referenced in ref. 5). This approximates the time when, we suggest, sulphide was extracted from the silicate Earth. If lead were in fact partly siderophile during early Earth accretion, the timing of sulphide formation would be even later. The open symbols show the results for the same calculation assuming that before sulphide segregation lead was partly siderophile, leading to a μ for the BSE of 2.0 instead of 0.7. The timescales are increased somewhat, the three most recent estimates of the Pb isotopic composition of the BSE yielding values of 80–100 Myr.

giant impact. A more conservative assumption would be to assume, since perovskite started to crystallize when the Earth was quite small, that some sulphide extraction and Pb removal pre-dated the giant impact. This assumption, when used in conjunction with the Pb isotopic composition of the BSE, has the effect of delaying the calculated time of the most recent fractionation of U from Pb. The effect is shown in Fig. 3, in which the timing of sulphide segregation is shown (open symbols) calculated following early growth of the Earth and its core with a μ_{BSE} ($^{238}U/^{204}Pb$) of 2.0 instead of 0.7. The timing of the change to a higher μ ranges from 80 to 100 Myr (instead of 65–85 Myr) after the start of the Solar System for the three most recent estimates of the Pb isotopic composition of the BSE. Although we present its potential effects in Fig. 3, we consider it unlikely that significant amounts of 'early' sulphide were produced. This is because early accretion was accompanied by addition of substantial amounts of metal. Metal added to the molten upper mantle would have consumed ferric iron and held the oxygen fugacity below the point at which sulphide becomes stable (Fig. 2). Only after release of large amounts of Fe^{3+} from perovskite dissolution during the giant impact would the process depicted in Fig. 2 have led to a substantial increase in oxygen fugacity and sulphide precipitation. Thus the U–Pb age of the Earth (65–85 Myr after the beginning of the Solar System) most probably represents the very last stages of core segregation at the end of accretion.

The apparent time after giant impact for sulphide extraction (30 ± 15 Myr) is remarkably close to Lord Kelvin's final estimate (24 Myr)[1] for the time taken for the Earth to cool from fully molten to its current state. More recent models of convection and cooling of the Earth after a giant impact[30] indicate, however, that solidification of most of the mantle took only 3,000 yr. On the other hand, a shallow (50 km) slowly convecting, partially crystalline magma ocean might have existed for 10^8 yr (ref. 30). This indicates that the U–Pb age does not reflect the time taken for cooling to the point where sulphide 'rained-out' of the mantle. Rather, it must reflect the time taken to physically accumulate and extract the small volumes of sulphide involved. Thus, given the differences in physical processes involved, we conclude that the agreement of our results with Kelvin's age of the Earth is purely coincidental.

METHODS

Assumptions and model. To model the isotopic data usefully, one has to make assumptions about how accretion and core formation took place[13]. The simplest model is one in which the Earth accreted and then the core segregated. This provides a model age for the last total equilibration of the core and silicate Earth. Such ages are somewhat misleading, however, as such a single separation event almost certainly never occurred[5]. Dynamic simulations provide evidence that the Earth was in fact largely built by a stochastic series of collisions with other planetesimals and planets. The rate of accretion is expected to decrease with time, although the size of possible impacting planets would increase[31]. The model used here is identical to that of Halliday[5] (Fig. 1). The earliest stage of growth is a runaway process that builds the Earth to 1% of its current mass over $\sim10^5$ yr, as suggested by simulations. Further growth is dominated by collisions between these objects. The overall rate of accretionary growth of the Earth decreased with time, but the growth events would have become more widely interspersed and larger. Therefore, the model simulates further growth by successive additions of 1% Earth mass objects from 1% to 10% of the current mass, then by 2% objects to 30% and then by 4% objects to 90%. The Moon-forming giant impact is modelled as taking place when the Earth was $\sim$90% of its current mass, and involved an impactor planet Theia that was $\sim$10% of the (then) mass of the Earth (Fig. 1). Therefore, the giant impact contributes a further 9% of the current Earth mass. A late veneer contributes an additional 0.9%. There is a final 0.1% added after this. The same accretion timescale can therefore be expressed in two ways—as a model time of the giant impact (that is, the time at which the Earth grew from 90% to 99% of the current mass), and as a mean life of accretion for exponentially decreasing growth.

Calculations. All calculations in this Letter assume continuous core formation and total equilibration between accreted material and the BSE. The partition coefficients for U and Pb between the core and the silicate Earth were varied, as detailed in the text. All $^{238}U/^{204}Pb$ (or μ) values are present day equivalent values. The μ for the total Earth (μ_{TOTE}) = 0.7. The present day ($^{206}Pb/^{204}Pb)_{BSE}$ can be

used to place limits on the current μ_{BSE} because the age of the Earth introduces a trivial uncertainty and early changes in μ are insignificant for present day $(^{206}Pb/^{204}Pb)_{BSE}$. The single stage Pb–Pb model age was used to determine this. Note, however, that present day μ_{BSE} is somewhat uncertain because of the fractionation of U from Pb during geochemical processes, and that a variety of estimates are available in the literature. A range of model ages of sulphide segregation are obtained, as shown in Fig. 3. In every model, the Bulk Solar System Initial (BSSI) values are $(^{206}Pb/^{204}Pb)_{BSSI} = 9.307$ and $(^{207}Pb/^{204}Pb)_{BSSI} = 10.294$, with $^{238}U/^{235}U = 137.88$, and U decay constants $\lambda^{235} = 9.85 \times 10^{-10}\,yr^{-1}$, $\lambda^{238} = 1.55 \times 10^{-10}\,yr^{-1}$.

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