Isotopes as clues to the origin and earliest differentiation history of the Earth

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Measurable variations in 182W/183W, 142Nd/144Nd, 129Xe/130Xe and 136XePu/130Xe in the Earth and meteorites provide a record of accretion and formation of the core, early crust and atmosphere. These variations are due to the decay of the now extinct nuclides 182Hf, 146Sm, 129I and 244Pu. The 182Hf–182W system is the best accretion and core-formation chronometer, which yields a mean time of Earth’s formation of 10 Myr, and a total time scale of 30 Myr. New laser shock data at conditions comparable with those in the Earth’s deep mantle subsequent to the giant Moon-forming impact suggest that metal–silicate equilibration was rapid enough for the Hf–W chronometer to reliably record this time scale. The coupled 146Sm–147Sm chronometer is the best system for determining the initial silicate differentiation (magma ocean crystallization and proto-crust formation), which took place at ca 4.47 Ga or perhaps even earlier. The presence of a large 129Xe excess in the deep Earth is consistent with a very early atmosphere formation (as early as 30 Myr); however, the interpretation is complicated by the fact that most of the atmospheric Xe may be from a volatile-rich late veneer.

Keywords: Earth; origin; early differentiation; isotopes

1. Introduction

There are a few big questions that have always occupied people’s minds—how our planet Earth formed and evolved into a habitable (for us) planet is one of them. Planetary exploration is now going beyond the bounds of our own Solar System. However, there is yet much we can learn from the study of our own planet to obtain a general understanding of the origin of the Earth-like habitable planets in our Solar System and beyond. The big picture of planet formation remains poorly understood; for example, the issues such as the orbits and the timing of formation of giant planets versus small rocky planets, etc., are still actively debated. Knowing precisely the timing of the Earth’s formation and the detailed conditions in the solar nebula near its orbit can be crucial for understanding the global process of planet formation in general. While the earliest history of the Earth remains poorly constrained, isotopic studies offer a valuable window into this period of time.

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Earth (the Hadean period) is essentially non-existent in the rock record, except for rare zircons 4.0–4.35 Ga old found in sediments ca 3 Ga old in Western Australia, this is probably the time when liquid water appeared on our planet and may also have been the time when life began on the Earth.

The long-lived isotopic chronometers ($^{87}$Rb–$^{87}$Sr, $^{147}$Sm–$^{143}$Nd, $^{176}$Lu–$^{176}$Hf and $^{238,235}$U–$^{232}$Th–$^{206,207,208}$Pb) provide some broad constraints on the evolution of the Hadean Earth. Their variations point to a prolonged differentiation of the Earth’s crust and mantle, with a mean age of crust extraction of ca 1.8 Ga (Jacobsen & Wasserburg 1979). Also, $^{143}$Nd/$^{144}$Nd and $^{176}$Hf/$^{177}$Hf isotopic variations in the oldest terrestrial samples point to significant early silicate differentiation within the first 100 Myr of the Earth’s formation (Jacobsen & Dynek 1988; Bizzarro et al. 2003).

Because the extinct radionuclides were live only during the early Solar System (ESS) history, they are powerful tracers of early differentiation processes (Harper & Jacobsen 1992; Jacobsen & Harper 1996; Jacobsen 2005a). Recently, substantial efforts have been made to use extinct nuclide systems for investigation of this time period. Jacobsen & Harper (1996) showed for the first time how to apply such systems for modelling the rate of the Earth’s accretion, the rate of core formation and the evolution of the mantle and crust at very early times. In principle, isotopic variations of the decay products of the longer-lived extinct radionuclides $^{146}$Sm, $^{244}$Pu, $^{129}$I and $^{182}$Hf, as well as the nearly extinct isotope $^{235}$U, can shed some light on these processes. Despite the significant contributions of these systems to knowledge of the timing and processes of early planetary differentiation, their potential for understanding different aspects of the early histories of terrestrial planets is still under development. Two of these chronometers ($^{146}$Sm and $^{235}$U) are particularly useful when coupled with the long-lived chronometers $^{147}$Sm and $^{238}$U.

The principles of using both long-lived and extinct systems for the modelling of planetary mantle and crust evolution have been discussed in detail before (Jacobsen & Wasserburg 1979; Jacobsen & Harper 1996; Jacobsen 2005a). For long-lived systems (such as $^{147}$Sm–$^{143}$Nd), the radiogenic isotope effect, $\epsilon_{143\text{Nd}}$, yields approximately the mean age of the mass of a reservoir. This result is independent of the functional form of the reservoir growth curve and is close to a two-stage model age. For short-lived systems (such as $^{146}$Sm–$^{142}$Nd), the radiogenic isotope effect, $\epsilon_{142\text{Nd}}$, also depends on the mean age of the mass of a reservoir, but in a more complex way than for long-lived systems. In particular, it is highly dependent on the functional form of the reservoir growth curve, so the mean age is usually not equal to a two-stage model age.

The goal of this paper is to review the current state of knowledge of the formation of the Earth, its core and the conditions on the earliest Earth. Radiogenic isotope data are discussed and explored with simple models that are useful in deciphering the Earth’s early history.

2. Isotopic systems and processes

The principle that parent–daughter isotopes date or track chemical fractionations in radiogenic systems is often used to determine a chronology of nebular processes, accretion of the Earth, its core formation and early silicate differentiation. Ideally,
an isotope system should ‘see’ only one of these processes—if several processes fractionate the parent–daughter element ratio at different time scales, then an unambiguous interpretation of a reservoir isotopic composition may not be possible. Both long-lived decay systems (238,235U–206,207Pb and 147Sm–143Nd) and extinct nuclide systems (182Hf–182W, 146,147Sm–142,143Nd and 129I–129Xe, 244Pu–242Xe) are used here in an effort to understand the variety of major types of differentiation events that cause elemental fractionations in the ESS (figure 1).

Previous research on initial Solar System abundances of extinct radionuclides has contributed greatly to our understanding of the processes and time scale involved in the formation of the Solar System (cf. Jacobsen 2005b; Kita et al. 2005). Nebular processes are likely to operate on a time scale of 10 Myr or less. There is now increasing evidence that the time scale of the formation of calcium–aluminium-rich inclusions (CAIs) and chondrules in the nebula is only 1–2 Ma, and that achondrite parent bodies may have formed and differentiated within 2–4 Ma of the origin of the Solar System. In fact, some achondrite parent bodies may have differentiated within the first 1 Myr after CAI formation (Jacobsen 2005a; Kleine et al. 2005a).

Large-scale gas–dust fractionations during the stages of disc formation and planetesimal accretion in the solar nebula may lead to very large elemental fractionations between volatile and refractory elements (cf. Wai & Wasson 1977; Cassen 1996). At this stage the U–Pb, I–Xe and Pu–Xe systems are strongly fractionated, making them potentially useful chronometers for constraining the timing of volatile depletion in meteorite parent bodies. Other systems (Sm–Nd, Hf–W and Lu–Hf) are not significantly fractionated at this stage. Differentiation...
of planetesimals and planets leads to core formation by the separation of metal–sulphide melt from silicates, which results in a major fractionation of lithophile relative to siderophile and chalcophile elements (U–Pb and Hf–W). The Hf–W system is uniquely fractionated at this stage, making this system the most reliable core-formation chronometer (figure 1). Although all isotopic systems may be somewhat fractionated in magma oceans and subsequent processes such as crust formation, silicate mantle differentiation and mantle stratification, only the Sm–Nd and Lu–Hf systems are not fractionated in earlier stages. This makes them ideal chronometers for tracing early silicate mantle differentiation.

The coupled $^{146,147}$Sm–$^{142,143}$Nd system is a particularly attractive chronometer because accretion and core formation are not likely to fractionate Sm and Nd. The Sm–Nd system is fractionated by silicate differentiation, so the coupled systematics should provide the best estimate of the timing of the earliest planetary silicate mantle and crust differentiation. A useful property of this system is that it is likely to have been completely homogenized in the silicate mantle at a time shortly after the last giant impact of the Earth’s accretion. Consequently, the earliest silicate differentiation event recorded by this chronometer must post-date the last major mass accretion event during the Earth’s formation.

### 3. Evidence from isotopic studies of meteorite parent bodies

Most material in the Solar System has an isotopic composition that represents an average of the different stars that contributed matter to our proto-stellar cloud. To a very good first-order generalization, these materials from diverse nucleosynthetic sources have been rather well mixed isotopically, either in the process of Solar System formation or in the interstellar medium beforehand. Therefore, the primordial solar nebula is often considered a chemically and isotopically ‘uniform reservoir’ (usually approximated by chondrites and called chondritic uniform reservoir (CHUR) by isotope geochemists). However, some exceptions from this generalization exist. For example, some primitive meteorites have preserved up to a few ppm of refractory presolar grains, probably hundreds of ppm of presolar silicates and up to 1000 ppm of diamonds. These grains retain the isotopic signatures of their individual stellar sources, providing valuable insight into stellar and galactic evolution, nucleosynthesis and solar nebular processes (cf. Meyer & Zinner 2006). But more importantly, the presolar grains provide unequivocal evidence that the Solar System was neither completely homogenized, nor processed at temperatures sufficiently high to erase the signatures of diverse presolar stellar sources.

(a) The problem of isotopic heterogeneity

The heavy isotopes in the ESS may not have been as well mixed as previously thought. The nucleosynthetic processes that produced the heavy elements ($r$-, $s$- and $p$-processes) were not necessarily homogenized to the extent that various planetary bodies have identical initial isotopic compositions of elements such as Ba (Ranen & Jacobsen 2006). It has been shown that Ba, Mo and Zr in bulk carbonaceous chondrites are enriched in the $r$- and $p$-processes compared with
the s-process (Yin et al. 2001, 2002a; Ranen & Jacobsen 2006; Andreasen & Sharma 2007; Carlson et al. 2007) while Nd isotopes are deficient in $^{142}\text{Nd}$, an s-only isotope (Boyet & Carlson 2005; Andreasen & Sharma 2007; Carlson et al. 2007; Ranen & Jacobsen 2008a). Although this complicates our ability to define reference values, these isotopic heterogeneities do provide insight into the processes in the early solar nebula and demonstrate that isotopic signatures of infalling interstellar materials are preserved in the various components of carbonaceous chondrites. For example, the study of the Ba isotopic composition of carbonaceous and ordinary chondrites (Ranen & Jacobsen 2006; Andreasen & Sharma 2007; Carlson et al. 2007) found excesses of up to 50 ppm in some Ba isotope ratios. Note that there was an apparent difference between the results reported by Ranen & Jacobsen (2006) and those of Andreasen & Sharma (2007) and Carlson et al. (2007). This is due to the different mass spectrometric normalization procedures (Andreasen & Sharma 2007; Ranen & Jacobsen 2008a, b), which may always leave some ambiguity in what ratio actually has the anomaly. The data from all three studies are, however, consistent with r-process excesses in Ba isotopes of carbonaceous chondrites. The best explanation of these Ba isotope differences between bulk planetary bodies is an incomplete mixing of nucleosynthetic components, not a fractionation within a planet. Furthermore, the Ba isotope data suggest a $^{142}\text{Nd}$ (an s-only nuclide) deficit in chondrites, which is consistent with the differences in $^{142}\text{Nd}/^{144}\text{Nd}$ between carbonaceous chondrites and the Earth reported by Carlson et al. (2007). Thus, we believe that the observed difference in $^{142}\text{Nd}/^{144}\text{Nd}$ between chondrites and the Earth are not due to Sm–Nd fractionation and/or $^{146}\text{Sm}$ decay in the early Earth, but rather are due to an imperfect mixing in the ESS of the products of different nucleosynthetic processes. This example illustrates the need for a better understanding of how to account for such isotopic heterogeneities when inferring the correct initial isotopic compositions of various Solar System objects. A very accurate estimate of the bulk Earth evolution of the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio is crucial for using the $^{146}\text{Sm}/^{142}\text{Nd}$ system. This requires a clear identification of all nucleosynthetic components (e.g. ($^{142}\text{Nd}/^{144}\text{Nd}_i$, Sm/Nd and ($^{146}\text{Sm}/^{144}\text{Sm}_i$)) and understanding how they are mixed together to set the observed range of values in the Solar System.

(b) Mixing and transport in the nebula

There is still intense discussion whether the shortest-lived now extinct radionuclides (SLRs), such as $^{26}\text{Al}$ and $^{60}\text{Fe}$, are homogeneously or heterogeneously distributed in the ESS. Their relatively high abundance in the ESS means that they were injected (by a supernova) either into the presolar cloud (Vanhala & Boss 2002) or onto the surface of the solar nebula (Ouellette et al. 2005). Such injection is thought to occur via narrow Rayleigh–Taylor (RT) fingers (Vanhala & Boss 2002), which could lead to highly variable initial abundances of SLRs. The scatter in initial $^{26}\text{Al}/^{27}\text{Al}$ ratios observed in meteoritic components, ranging from values of approximately 0 to typical (‘canonical’) CAI values of approximately $4.5 \times 10^{-5}$ or even higher (approx. $7 \times 10^{-5}$) (cf. Young et al. 2005), can be attributed to either spatial or temporal heterogeneity due to decay of the SLRs, or both. If the injection was into the proto-solar cloud then it may have caused efficient mixing of the SLRs prior to
disc formation. If the shortest-lived SLRs were injected into the solar nebula, then shortly after the arrival of each RT finger their distribution in the nebula must have been spatially heterogeneous, possibly explaining some of the observed range of $^{26}$Al/$^{27}$Al ratios.

To address the latter issue, Boss (2006, 2007) investigated a marginally gravitationally unstable disc that is able to transport injected SLRs over distances of approximately 10 AU in approximately 1000 years, implying a similar time scale for mixing and attaining spatial homogeneity. The expected level of spatial heterogeneity in $^{26}$Al/$^{27}$Al was calculated as a function of time in the solar nebula, following a single injection event. The injection transient dies away on a time scale of approximately 1000 years, as expected, and seems to reach a steady-state dispersion level of approximately 10 per cent. This low degree of spatial heterogeneity, if correct, implies that variations in $^{26}$Al/$^{27}$Al ratios must be primarily due to radioactive decay but not initial heterogeneity.

Thus, if the assumptions in the models of Boss (2006, 2007) are valid, it supports the use of SLRs as relatively accurate chronometers for the solar nebula. The approach of Boss (2006, 2007) may be valid during the early history of the solar nebula disc (high mass and high accretion heating), before planetesimals can agglomerate. As the disc thins out and cools and planetesimals start forming, the existing heterogeneities will be easier to preserve by the fact that they accrete into planetesimals and that nebular mixing at later times in the nebula is not very efficient.

\[(c)\] Accretion and magmatism of the first planetesimals

Magmatic iron meteorites have $\varepsilon_W$-values similar to those of CAIs that define the initial solar value (Yin et al. 2002b; Yin & Jacobsen 2003; Markowski et al. 2006; Schersten et al. 2006). The $^{182}W/^{183}W$ ratios in many iron meteorites have been lowered by neutron capture reactions resulting from an exposure to cosmic rays (Masarik 1997; Leya et al. 2003). The iron meteorites with the oldest exposure ages have in general yielded the lowest $\varepsilon_W$-values, but those with minor or no cosmogenic effects have $\varepsilon_W$-values identical to CAIs (Markowski et al. 2006; Qin et al. 2007). This strongly suggests that core formation in their parent bodies occurred within the first ca 0.5 Myr of the Solar System (Jacobsen 2005a; Kleine et al. 2005a; Schersten et al. 2006; Markowski et al. 2007).

The eucrite meteorites define a rough Hf–W isochron corresponding to an age of 3–4 Myr (Quitté et al. 2000; Yin et al. 2002b; Kleine et al. 2004a). One eucrite (Asuka 881394) appears to date to within 1–2 Myr of Solar System formation while the eucrite Ibitira yields a time of ca 10 Myr later. Internal isochrons for one group of angrites (Sahara 99555 and D’Orbigny) yield crystallization ages of ca 3–5 Myr while another group (NWA2999, LEW86010 and Angra dos Reis) has a Hf–W age of ca 10 Myr (Markowski et al. 2007). The time scales based on the Hf–W system in the eucrite and angrite parent bodies are consistent with the results of U–Pb, Mn–Cr and Al–Mg chronometry (figure 2), suggesting that $^{26}$Al was an important heat source for the differentiation of these asteroids. Most importantly, the rough consistency of these chronometers for multiple samples from differentiated parent bodies demonstrates their validity for studying early planetary differentiation processes.

*Phil. Trans. R. Soc. A* (2008)
Figure 2. (a–c) Relatively consistent chronologies of differentiated meteorite parent bodies and CAIs by comparison of U–Pb (Lugmair & Galer 1992; Amelin et al. 2002, 2006; Zartman et al. 2006; Amelin 2007), Mn–Cr (Lugmair & Shukolyukov 1998; Glavin et al. 2004; Sugiura et al. 2005; Wadhwa et al. 2005), Al–Mg (Lee et al. 1977; Baker et al. 2005; Spivak-Birndorf et al. 2005; Wadhwa et al. 2005) and Hf–W ages (Yin et al. 2002a; Kleine et al. 2005a; Markowski et al. 2007) for both old (D’Orbigny and Sahara 99555) and young angrites (LEW 86010, NWA 2999 and Angra dos Reis (ADOR)), two eucrites (Ibitira and Asuka 881394) and CAIs. To be fully consistent, all the samples should fit perfectly on lines with slopes identical to those in the diagrams (but not necessarily precisely in the position shown).

Phil. Trans. R. Soc. A (2008)
4. Formation of the Earth and the Moon

The process of terrestrial planet building probably began when a large population of small bodies (planetesimals) of roughly similar sizes coagulated into a smaller population of larger bodies. At early times, the size distribution of objects became skewed by runaway accretion towards a few large planetary embryos. These then accreted the smaller leftover bodies, and at some time one of the embryos probably became dominant and could be identified as the proto-Earth. At the later stages of such a hierarchical accretion series, sweep-up of the smaller embryos by the proto-Earth in its neighbourhood led to giant collisions. The last major Earth-forming collision could have been between two bodies of approximately half the Earth’s mass to form the Earth, but it is more commonly thought to have been between the Earth and a 1–2× Mars-sized body. At the end of this process, only the Earth remained, at approximately 1 AU. This is now considered the standard astrophysical scenario for the Earth’s accretion (cf. Canup & Agnor 2000; Kortenkamp et al. 2000) and was introduced in cosmochemistry by Jacobsen & Harper (1996); see also Jacobsen (2003a) where this scenario was specifically used for the Hf–W chronometer.

(a) The Hf–W chronometer

The $^{182}$Hf–$^{182}$W system (8.9 Myr half-life) is clearly the most favourable chronometer of core formation during planet-building processes as it directly tracks metal–silicate segregation. This chronometer has successfully been applied to provide time constraints for a variety of processes and events associated with the formation and earliest evolution of planetary bodies. The primary interest in the Hf–W system for the Earth in all initial studies was its potential for dating core formation (Harper & Jacobsen 1994, 1996a; Lee & Halliday 1995; Halliday et al. 1996; Jacobsen & Harper 1996).

It is now well established that the silicate Earth exhibits a W-isotopic composition that is more radiogenic than that of chondritic meteorites (Kleine et al. 2002; Schoenberg et al. 2002; Yin et al. 2002a, b), demonstrating that the differentiation of the Earth into a mantle and core occurred within the lifetime (30–50 Myr) of $^{182}$Hf in the early Earth. This is clearly seen from the fact that the bulk silicate Earth (BSE) with its high Hf/W ratio has a radiogenic $^{182}$W/$^{183}$W signature approximately 2 ε-units higher than the chondritic value.

(b) Modelling of metal–silicate separation in the terrestrial planets

Metal segregation to form the core is now widely believed to have happened in an early terrestrial magma ocean, with final metal–silicate equilibration at very high $P$ and $T$ (Rubie et al. 2003). Figure 3 shows schematically three different types of continuous models that have been used for tracing core formation based on the isotope and trace element composition of the silicate Earth. All models assume that the Earth accretes from material (dust and planetesimals) with a chondritic Hf/W ratio and a chondritic W-isotopic composition, including the possibility that the planetesimals were internally differentiated into silicate mantles and metal cores.
The first model in figure 3a proposed by Jacobsen & Harper (1996) assumes only local equilibrium. In this model, new additions to the Earth are immediately differentiated into metal and silicate (locally equilibrated), with the metal sinking to the core without equilibrating with the remaining silicate mantle. Thus, newly segregated core material in this case reflects only the average isotopic composition of the material added to the Earth.

The second model in figure 3b was developed for the Hf–W isotopic system by Harper & Jacobsen (1996a). Jacobsen (2005a) presented a new and detailed description of this magma ocean (MO) differentiation model. Newly segregated core material is assumed to reflect the average isotopic composition of the silicate mantle due to equilibration in a magma ocean. This model is currently the most widely used model for interpreting Hf–W chronometry of the Earth (cf. Yin et al. 2002b; Halliday 2004; Jacobsen 2005a; Kleine et al. 2005b).

The third model in figure 3c was proposed by Li & Agee (1996); it was inspired by an earlier cartoon of Stevenson (1990, fig. 6). In this model, newly segregated core material is assumed to have equilibrated at the bottom of a magma ocean whose depth of approximately 700–1200 km was estimated based on Ni and Co partitioning.

Figure 3. Three different models of core formation: (a) local equilibrium model, (b) magma ocean (MO) equilibrium model, and (c) metal pond model. The Earth is assumed to accrete from material of the solar nebula (dust and planetesimals) with a chondritic Hf/W ratio and W-isotopic composition.
The time scale of core formation in the Earth

As mentioned above, the $^{182}$W/$^{183}$W of the Earth's mantle is $1.9 \pm 0.2$ W-units higher than the chondritic value. This means that the formation of the Earth's core, at least in part, occurred when $^{182}$Hf was still live in the Earth, i.e. within the first 50 Myr of the Solar System. The difference between the $\varepsilon_{W}$-value in BSE and CHUR ($\varepsilon_{W(CHUR)}$) together with the BSE Hf/W ratio approximately 13 times higher than the chondritic value provide the basis for such a calculation. A plot of $\varepsilon_{W(CHUR)}$ versus the mean time of core formation in different models is shown in figure 4.

A two-stage model age of 29 Myr for the time of core formation is shown as the intersection of the two-stage model line in figure 4 with $\varepsilon_{W(CHUR)}$. This age is valid only if core formation occurred as a single event at a well-defined moment in time. It would require for the core and the silicate mantle to equilibrate completely at a single moment in time with no later additions to the Earth. Since this is not very likely, the two-stage age is unlikely to have strict

Figure 4. Models for the timing of core formation in the Earth. The figure shows the expected $\varepsilon_{W(CHUR)}$ for a range of mean times of core formation in the Earth for three different models of core segregation: a two-stage model, a magma ocean model and a local equilibrium model. For the observed $\varepsilon_{W(CHUR)}$-value of +2, we obtain as shown 29, 10.6 and 108 Myr for the mean time of core formation. We believe that the magma ocean segregation model yields the most realistic estimate (10.6 Myr) for the mean time of core formation.

(c) The time scale of core formation in the Earth

As mentioned above, the $^{182}$W/$^{183}$W of the Earth's mantle is $+1.9 \pm 0.2$ W-units higher than the chondritic value. This means that the formation of the Earth's core, at least in part, occurred when $^{182}$Hf was still live in the Earth, i.e. within the first 50 Myr of the Solar System. The difference between the $\varepsilon_{W}$-value in BSE and CHUR ($\varepsilon_{W(CHUR)}$) together with the BSE Hf/W ratio approximately 13 times higher than the chondritic value provide the basis for such a calculation. A plot of $\varepsilon_{W(CHUR)}$ versus the mean time of core formation in different models is shown in figure 4.

A two-stage model age of 29 Myr for the time of core formation is shown as the intersection of the two-stage model line in figure 4 with $\varepsilon_{W(CHUR)} = +1.9$. This age is valid only if core formation occurred as a single event at a well-defined moment in time. It would require for the core and the silicate mantle to equilibrate completely at a single moment in time with no later additions to the Earth. Since this is not very likely, the two-stage age is unlikely to have strict
time significance. One possibility is that, if the interior of the fully grown Earth was so hot that it allowed complete equilibration of the mantle and the core, then the age for complete formation of the Earth’s core would be ca 30 Myr.

Continuous models of core formation should yield a more realistic time constraint. Here we consider the continuous models of figure 3 with exponentially decreasing rates of accretion and with the core-formation rate limited by (and equal to) the accretion rate, as first discussed by Jacobsen & Harper (1996).

First, the local equilibrium model yields a very long mean time of core formation of 108 Myr (and a 90% core-formation time of 249 Myr). We do not believe that this mechanism is viable for the Earth, because the evidence for an early hot magma ocean would almost certainly lead to extensive, if not complete, equilibration of metal and silicates (Rubie et al. 2003).

The magma ocean differentiation model yields a mean time of core formation of 10.6 Myr (and a 90% core-formation time of 24 Myr), even shorter than the two-stage model age (Yin et al. 2002b; Jacobsen 2005a). If this model is correct, the Hf–W results strongly suggest that the Earth’s core formation took place earlier than stated in many recent publications on the Hf–W system (Halliday 2004; Kleine et al. 2004b; Wood & Halliday 2005).

A few recent studies have considered this second model, with only partial equilibration, to argue for longer times of accretion and core formation (Halliday 2004; Kleine et al. 2004b). Then the calculated age of core formation strongly depends on how much of the core material of newly accreted objects equilibrated with the Earth’s mantle before joining its core (Harper & Jacobsen 1996a; Halliday 2004; Kleine et al. 2004b; Jacobsen 2005a; Nimmo & Agnor 2006). As the degree of re-equilibration decreases, the calculated mean core-formation age becomes increasingly younger, with its limit of 108 Myr (for the mean time of core formation) being set by the local equilibrium model (90% at 249 Myr). Since accretion of the Earth probably occurred by a number of distinct large impacts delivering large masses of core material, the question is what is the limiting size (if any) of an impactor that is still capable of complete core disruption and W equilibration of its material with the Earth’s mantle before joining the Earth’s core (cf. Harper & Jacobsen 1996a). If such equilibration does not occur, the W evolution of the Earth’s mantle would be a complicated function of the internal differentiation of individual impactors, the degree of re-equilibration during and after impacts, their timing as well as the W-isotopic composition and Hf/W ratios of the mantles of the proto-Earth and impactors. The issue of equilibration in the magma ocean model will be discussed in more detail below.

The metal pond model can in principle yield a similar time scale for core formation as the magma ocean model. However, this type of model can be ruled out because it would leave a lower mantle with $e_{W(CHUR)}$ in the range from +9 to +18 (figure 5) since it would have to be isolated prior to ca 10 Myr. The W-isotopic compositions of rocks that are likely to sample the deep Earth show no evidence for such a component (Schersten et al. 2004).

While some models can be eliminated from further consideration, there is still uncertainty in determining an age for the Earth’s core owing to the question of metal–silicate equilibration. What is needed is to understand both the physical and chemical behaviours of metal–silicate mixtures at the high $P$ and $T$ that existed in the Earth subsequent to the last giant impact. An alternative is to date
the formation of the Moon, which was most probably the last major event during the Earth’s accretion (Canup & Asphaug 2001). We discuss the aspects of both of these approaches below.

\[ (d) \] \textit{Hf–W equilibration in a magma ocean at very high pressures and temperatures}

The most recent simulations of the Moon-forming giant impact (Canup 2004) assumed a collision between a proto-Earth and a Mars-sized planetesimal resulting in nearly complete disruption of the projectile and a significant destruction and re-accretion of the Earth. The peak shock pressures and temperatures in the Earth reached approximately 10–20 min after this impact were 300–500 GPa and 20 000–30 000 K, respectively (figure 6). In about a day, the bound planet–disc system is formed, with the Moon to be accreted later from

\[ S. B. Jacobsen et al. \]

\[ Phil. Trans. R. Soc. A (2008) \]
the debris disc. The central planet of approximately 99.4 per cent of Earth’s mass is enveloped into a hot (7000–8000 K) silicate atmosphere. The hottest (higher than 12 000 K) material in the central planet is the projectile’s metal, most of which is located around the original proto-Earth’s core. The silicate temperatures range from approximately 2000 to 10 000 K, with the hottest (higher than 6000 K) material being both near the core–mantle boundary (CMB) and on the surface. Such a temperature distribution in the post-giant-impact Earth implies that the projectile’s core and most of the Earth’s mantle must be molten to form a deep, hot magma ocean extending from the Earth’s surface down to the CMB ($P > 100$ GPa). This primary magma ocean is expected to evolve rapidly to a shallower (approx. 700 km) one lasting for centuries (Solomatov 2000). Such high pressures and temperatures are beyond the reach of modern experimental techniques employed by Earth scientists.

Our recent experiments on high-energy-density laser-induced shock melting of powdered Fe metal–dunite targets (Petaev et al. 2007, 2008; Remo et al. 2007, 2008) at pressures and temperatures comparable with those of the putative Moon-forming giant impact (figure 6) have shed light on the behaviour of the metal–silicate system during and immediately after the giant impact. It was found that the homogenization of target materials was very rapid: it takes less than 10 ns to homogenize an approximately 1 mm target. This is too fast for a diffusion-driven process, and is due to turbulent mixing (by Richtmyer–Meshkov instabilities) in the ablation melt layer driven by the shock waves. Scaling of the experimental results to the predicted giant impact conditions suggests complete turbulent mixing of the metal and silicate of the impactor material in just a few hours. The experiments also suggest that the post-giant-impact
terrestrial magma ocean could have been much more ferrous (15–25 wt% FeO) than the current mantle (7.6 wt%). This implies that more than half of the FeO from the primary magma ocean must have been reduced to Fe to be transported into the Earth’s core as metal droplets. The high efficiency of this process in metal–silicate equilibration has already been demonstrated (Rubie et al. 2003; Melosh & Rubie 2007). Therefore, it seems safe to conclude that our experimental results validate the Hf–W system as the best tool for dating core formation in terrestrial planets.

(e) The age of the Moon and the lunar magma ocean

The first Hf–W measurements of lunar samples (Lee et al. 1997) suggested that the Moon had a substantially higher εW-value (+3 to +5) than the Earth. It is now clear that a significant portion of the observed 182W excess in lunar samples did not result from 182Hf decay, but was instead caused by the 181Ta (n, γ) 182Ta (β−) 182W reaction due to an exposure to cosmic rays on the surface of the Moon (Leya et al. 2000; Lee et al. 2002; Yin et al. 2003). This fact severely compromises the application of Hf–W chronometry to lunar samples. Lee et al. (2002) used the correlation of 182W/183W and Ta/W measured in mineral separates from several mare basalts to infer 182W/183W values unaffected by cosmic rays (by extrapolating to Ta/W = 0). This yielded an εW-value for the Moon approximately 1.5 ε-units higher than for the Earth (Lee et al. 2002). Kleine et al. (2005b) measured the W-isotopic composition of lunar metals because they contain no Ta and would be free of cosmogenic 182W. Their reported Hf–W fossil isochron, with a slope corresponding to ca 30 Myr for the time of magma ocean crystallization on the Moon, is consistent with the Hf–W age of 30 Myr for the Earth. Kleine et al. (2005b) preferred an age of the Moon of 40 ± 10 Myr and showed an isochron corresponding roughly to this time as a line going through the middle point in their diagram. The follow-up work on lunar metals by Touboul et al. (2007) determined the W-isotopic composition of metals from a comprehensive set of lunar samples with short exposure times (and hence potentially small cosmogenic 183W components) that show no 182Hf-induced 182W/183W variations within the lunar mantle (and W-isotopic composition identical to the silicate Earth), implying a late (ca 60 Myr) formation time of lunar basalt magma sources. Owing to the lack of W-isotopic variations in the lunar basalt sources, it will be important to determine the age of the Moon by methods other than Hf–W.

(f) Summary

The 182Hf–182W extinct isotopic system is the most favourable chronometer for examining metal–silicate fractionation and dating core formation in the Earth. The BSE has a radiogenic 182W/183W signature that is approximately 2 εW-units higher than the chondritic value. The time scale of metal–silicate separation calculated for the Earth is model dependent. The most logical model is a magma ocean equilibration model in which newly segregated core material reflects the average isotopic composition of the silicate mantle. New shock melting experiments at pressures and temperatures comparable with those in the Earth after the Moon-forming impact suggest very efficient homogenization.
Continuous models of core formation will lead to the most realistic time constraint on metal–silicate separation. The favoured magma ocean differentiation model gives a mean time of core formation of 10.6 Myr, implying that core formation in the Earth took place rather quickly. Thus, the Earth started with a very hot and deep magma ocean that allowed core formation to proceed quickly. It is vital to use consistent models of isotopes and trace elements to fully explore the effects of metal–silicate fractionation as well as late giant impacts such as the formation of the Moon.

5. The earliest crust and mantle evolution

The very small volume of early (more than 3.5 Ga) Archaean crust preserved today (less than 1% of the present continental volume) has been interpreted as indicating that crustal growth did not begin until ca 4.0 Gyr ago, before which the silicate Earth remained well mixed and essentially undifferentiated. However, the inferred initial 143Nd/144Nd ratios of many early Archaean rocks are higher than that of the bulk Earth, implying that by 3.8 Ga ago the volume of the crust must have been as large as approximately 40 per cent of the present value (Jacobsen 1988; Jacobsen & Dymek 1988). When combined with measurements of 142Nd/144Nd ratios in Isua samples from west Greenland as well as other 143Nd/144Nd and 176Hf/177Hf isotopic variations in the oldest terrestrial samples (Jacobsen & Dymek 1988; Bizzarro et al. 2003), this evidence points to a significant early silicate differentiation within the first 100 Myr of the Earth’s formation (Harper & Jacobsen 1992).

The first terrestrial 142Nd anomaly of +33 ppm (relative to the BSE), or $\varepsilon_{142\text{Nd}} = 0.33$, was reported by Harper & Jacobsen (1992) in the ca 3.8 Ga old supracrustal rock IE715-28 from Isua, west Greenland. This sample and a number of other Isua samples had previously been measured for 143Nd/144Nd variations by Jacobsen & Dymek (1988). The IE715-28 sample was selected for the initial study owing to its very high initial $\varepsilon_{143\text{Nd}}$ value of approximately +3–4. This sample was expected to be a likely place for finding a 142Nd excess. Additional measurements of 142Nd/144Nd for other Isua samples (including one that had a significant $\varepsilon_{142\text{Nd}}$ of 0.12 and initial $\varepsilon_{143\text{Nd}} = 1.5$) as well as in the ca 4.0 Ga Acasta rocks were reported by Jacobsen & Harper (1996).

Strong evidence for an early silicate differentiation comes from the measurements of 143Nd/144Nd and 142Nd/144Nd ratios in the ca 3.8 Ga old supracrustal rocks of Isua, west Greenland (Harper & Jacobsen 1992; Jacobsen & Harper 1996). They interpreted the coupled 146,147Sm–142,143Nd systematics as evidence that the fractionation of Sm/Nd took place ca 4.47 Ga ago, due to the extraction of a light rare-earth element-enriched primordial crust. These findings were initially controversial because measuring 142Nd/144Nd with sufficient precision is difficult. However, in the past five years these results have been confirmed by a number of groups (Boyet et al. 2003; Caro et al. 2003; Bennett et al. 2007) who carried out much more detailed studies of a variety of samples from the Isua supracrustals. This work has led to a general consensus that the initial silicate differentiation in the Earth began within ca 100 Myr after Solar System formation.
(a) The significance of the difference between $^{142}\text{Nd}/^{144}\text{Nd}$ in the Earth and chondrites

A problem with the $^{146}\text{Sm}-^{142}\text{Nd}$ chronometer that was recognized by Harper & Jacobsen (1992) was the difficulty of establishing the BSE value for this system with sufficient accuracy. They wrote ‘...$^{142}\text{Nd}/^{144}\text{Nd}$ in the Nd$\beta$ standard may not be equal to the bulk Earth value. New high-precision measurements of $\epsilon_{142}\text{Nd}$ in meteorites and young terrestrial basalts are required if we are to resolve this issue’. Harper & Jacobsen (1993) discussed this issue further and commented on the fact that chondrites appear to have an approximately 30 ppm lower $^{142}\text{Nd}/^{144}\text{Nd}$ value than the BSE. More recently, Boyet & Carlson (2005) have also reported values for chondrites that were substantially lower (20–40 ppm) than the terrestrial value. Harper & Jacobsen (1993) outlined the four principal ways to produce such differences: (i) nuclear variation of initial $^{146}\text{Sm}/^{144}\text{Sm}$; (ii) nuclear variation of initial $^{142}\text{Nd}/^{144}\text{Nd}$; (iii) variation in Sm/Nd; and (iv) radiogenic evolution of $^{142}\text{Nd}/^{144}\text{Nd}$ in a Sm/Nd-fractionated ‘parental’ reservoir before $^{146}\text{Sm}$ is extinct. Boyet & Carlson (2005) preferred the fourth option. They attributed the observed differences in the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio between the Earth and chondrites to the formation of an early enriched crust (formed within 30 Myr of Solar System formation) that subsequently sunk to the CMB, cut off from other mantle processes, so it could not be sampled again. This scenario is called into question by Ba isotopes (Ranen & Jacobsen 2006), which suggested that the Earth may have a different $^{142}\text{Nd}/^{144}\text{Nd}$ composition compared with chondrites due to incomplete mixing of the solar nebula (option (ii)).

(b) The $^{146}\text{Sm}/^{144}\text{Sm}$ ratio in the Earth and other Solar System objects

$^{146}\text{Sm}$ was clearly live during the formation of the Solar System. This is seen in figure 7, which plots the literature $^{146}\text{Sm}/^{144}\text{Sm}$ ratios versus ages inferred from coupled $^{146,147}\text{Sm}-^{142,143}\text{Nd}$ data (Ranen & Jacobsen 2007) for a variety of different meteorites, including several classes of differentiated meteorites such as eucrites, mesosiderites and angrites. Although these data display substantial scatter, the average trend in $^{146}\text{Sm}/^{144}\text{Sm}$ corresponds to a value of $0.009 \pm 0.002$ at 4.567 Ga. This is slightly higher than the value of 0.008 that has been used in the past (e.g. Harper & Jacobsen 1992; Boyet & Carlson 2005). The range of 0.007–0.011 in the initial Solar System $^{146}\text{Sm}/^{144}\text{Sm}$ values implies $\pm 70$ ppm variation in the present $^{142}\text{Nd}/^{144}\text{Nd}$ between planetary objects if it reflects real variations rather than uncertainties in the measurements. Thus, the $^{142}\text{Nd}/^{144}\text{Nd}$ difference between the Earth and chondrites can be explained either by the variability in the initial $^{146}\text{Sm}/^{144}\text{Sm}$ ratio or by the incomplete mixing of $^{142}\text{Nd}$ in the solar nebula. For a precise chronometry to be valid at the 5 ppm level in $^{142}\text{Nd}/^{144}\text{Nd}$, it is necessary to show that $^{146}\text{Sm}/^{144}\text{Sm}$ was uniform to within 1.4 per cent. Currently, there is a 20 per cent spread in this ratio, so we clearly need new and better data to help constrain what the precise initial $^{146}\text{Sm}/^{144}\text{Sm}$ ratio of the Solar System was, and whether or not these p-process nuclides were heterogeneously distributed. In spite of its large possible variations of 20 per cent, $^{146}\text{Sm}$ still appears to be as well mixed as other extinct nuclides ($^{26}\text{Al}$, $^{53}\text{Mn}$ and $^{182}\text{Hf}$; see figure 2).
Radiogenic isotope effects in igneous rocks that sample convectively stirred mantle reservoirs

It is well established that all radiogenic isotope ratios of long-lived systems (such as $^{143}\text{Nd}/^{144}\text{Nd}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{204}\text{Pb}$, etc.) exhibit a substantial range of values in mantle-derived magmas, reflecting long-term chemical heterogeneities in the mantle. This is expected because, subsequent to the magma ocean phase of a planet, the low solid-state chemical diffusion rates imply that subreservoirs created by mass transport into and out of the mantle effectively exist as distinct geochemical entities for all time, except when they are affected by melting. By tracking these subreservoirs, the full range of isotopic values in the mantle can be used to understand the significance of the dispersion in the data. Kellogg et al. (2002) showed how this could be done by applying simple statistics combined with conventional box models. They showed that the distribution of isotope ratios can then be parametrized primarily as a function of the stirring time ($\tau_{\text{stir}}$), effective melt fraction, sampling volume and mass transport history in addition to chemical differentiation parameters. The net effect of mechanical stirring in the mantle is to change the length scales of the heterogeneity (figure 8a). Because in general the long axis of the heterogeneity is much greater than any reasonable length scale of concern, the relevant length scale of the heterogeneity is the one that has been progressively shortened by mantle convection. In the case of exponential stretching, which is most likely for mantle convection, this short axis

![Figure 7. Estimate of initial $^{146}\text{Sm}/^{144}\text{Sm}$ in meteorites (compilation from Ranen & Jacobsen 2007). From these data, it can be inferred that the initial $^{146}\text{Sm}/^{144}\text{Sm}$ of the Solar System is approximately $0.009 \pm 0.002$. Divnoe and Acapulco are primitive achondrites, Ibitira, Caldera and Moama are eucrites; Angra dos Reis and LEW 86010 are angrites; Vaca Muerta, Mt Padbury and Morristown are mesosiderites; and Caddo County is an IAB iron meteorite.](http://rsta.royalsocietypublishing.org/)

(c) Radiogenic isotope effects in igneous rocks that sample convectively stirred mantle reservoirs

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is $l_h(t) = l_h(t_0)\exp[(t - t_0)/\tau_{\text{stir}}]$, where $t_0$ is the time at which the heterogeneity was created and $l_h(t_0)$ is the initial characteristic length scale of the heterogeneity. The length of the short axis, $l_h$, decreases exponentially with the stirring time constant, $\tau_{\text{stir}}$ (ca 0.5 Ga for the Earth). The mantle is sampled by basaltic volcanism with a sampling length scale $l_s$, which will typically be much larger than $l_h$ (figure 8b). Therefore, mantle-derived igneous rocks always represent mixtures of multiple layers of diverse origin in any planet with solid-state convection (Kellogg et al. 2002).

The range of likely $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic heterogeneity in depleted mantle could be as high as $\varepsilon_{143\text{Nd}} = 25$ in old depleted reservoirs, while recent depletions would be close to $\varepsilon_{143\text{Nd}} = 0$ (Kellogg et al. 2002). The reason that probability distributions for real mid-ocean ridge basalts (MORB) data show an average value of +10, with most samples in the range of 8–12, is well understood and
modelled based on the work of Kellogg et al. (2002). Model MORB in this model yielded a very similar, close to Gaussian, distribution and peak in the model MORB histogram, and yielded directly the average depleted mantle value.

(d) Proposed scenarios

Proposed scenarios for interpreting $^{142}\text{Nd}/^{144}\text{Nd}$ in the early Earth are shown in figure 9. The box model in figure 9a explains the difference between chondrites and the Earth by radiogenic evolution of Nd within the Earth as a result of formation and burial of an early Nd-rich crust reservoir, which is now isolated in the D'' layer of the mantle (Boyet & Carlson 2005). In figure 9b are three possible explanations that invoke either initial isotopic differences (nucleosynthetic) or chemical (Sm/Nd) differences between chondrites and the Earth. The first two differences (in Sm/Nd or $^{146}\text{Sm}/^{144}\text{Nd}$ between the Earth and chondrites) result in a different radiogenic evolution of the Earth and chondrites. The final possibility is that the Earth and chondrites always had slightly different $^{142}\text{Nd}/^{144}\text{Nd}$ ratios.

In the D'' model, the difference in $^{142}\text{Nd}$ between the Earth and chondrites was attributed to the decay of now extinct $^{146}\text{Sm}$ (Boyet & Carlson 2005) in an early formed depleted mantle reservoir that became the only one sampled later in the Earth's history. This model calls for the formation of a liquid enriched in incompatible elements (having a low Sm/Nd ratio) at the end of magma ocean crystallization. This liquid becomes denser than the overlying mantle and sinks to the CMB and never interacts thereafter with the rest of the silicate Earth. In such a scenario, the material that has become known as the BSE does not have the Sm/Nd ratio of the bulk Earth and chondrites. If this happened within the first 30 Myr of the Earth's formation, such a process could account for the difference in $^{142}\text{Nd}/^{144}\text{Nd}$ between the Earth and chondrites.
A further evaluation of the deep hidden enriched layer scenario can be done based on a fossil isochron diagram (Figure 10). The present observable silicate Earth has $\varepsilon_{142\text{Nd}} = 0$. The Sm/Nd chemical fractionation factor (defined as usual: $f_{\text{Sm/Nd}} = (\text{Sm/Nd})_{\text{sample}}/(\text{Sm/Nd})_{\text{CHUR}} - 1$) needed to explain an $\varepsilon_{142\text{Nd}} = 0$ in the observable Earth as a depleted reservoir evolving from a chondritic value of $\varepsilon_{142\text{Nd}} = -0.2$ (the complement to the early enriched crust) depends, as shown, strongly on its time of formation. For typical enriched crustal values of $f_{\text{Sm/Nd}} \sim -0.4$ (cf. Jacobsen 1988), the early enriched reservoir would today have a $\varepsilon_{142\text{Nd}}$ value in the range of $-0.4$ to $-1.4$. No terrestrial samples have ever been confirmed to have $\varepsilon_{142\text{Nd}}$ less than 0, so this reservoir could not have contributed to any later volcanism. Figure 10 shows the position of fossil isochrons for times of formation of 30, 100 and 200 Myr. The corresponding required $f_{\text{Sm/Nd}}$-values for the depleted reservoir are 0.077, 0.12 and 0.24. The present-day depleted mantle has an $f_{\text{Sm/Nd}}$ of approximately 0.2–0.25 based on MORB studies (cf. Jacobsen 1988). Thus, a relatively late formation of 200 Myr implies a chemical depletion similar to the modern MORB source. The inferred average $\varepsilon_{143\text{Nd}}$-values in the early formed depleted mantle at 3.8 Ga and today for
reservoir formation times of 30, 100 and 200 Myr after Solar System formation are also shown in figure 10. The inferred present $\varepsilon_{143\text{Nd}}$-value of 8.7 for a formation time of 30 Myr is roughly consistent with the mean value of present MORB (+10) but requires an $f^{\text{Sm}/\text{Nd}}$-value of 0.077, inconsistent with the typical MORB values cited above. Differentiation times of 100 and 200 Myr yield $\varepsilon_{143\text{Nd}}$-values that are substantially higher (13.8 and 26.4, respectively) than observed for the depleted mantle. Today’s MORB source with an $\varepsilon_{143\text{Nd}}$ value of approximately +10 yields a mean time of continent extraction of 1.8 Ga (Jacobsen & Wasserburg 1979), which is also inconsistent with massive early enriched reservoir extraction at 30 Myr after Solar System formation. It is clear from the mean age of the mantle and crust of ca 1.8 Ga that the depletion in the mantle cannot primarily be due to proto-crust extraction. Also, the inferred average $\varepsilon_{143\text{Nd}}$-values in the depleted mantle at 3.8 Ga are in the range 1.4–2.1. This is similar to the typical initial $\varepsilon_{143\text{Nd}}$-values of Isua supracrustals (Jacobsen & Dymek 1988), but samples from this area typically exhibit $\varepsilon_{143\text{Nd}}$ of approximately 0.15 (solid squares in figure 10; Bennett et al. 2007) rather than 0 as predicted by the Boyet & Carlson (2005) model. Also the dashed line (ca 200 Myr reference isochron through $\varepsilon_{142\text{Nd}} = 0$) through the Itsaq data points is consistent with $\varepsilon_{142\text{Nd}} = 0$ for the bulk Earth rather than $-0.2$ as observed in chondrites. Thus the D" model is inconsistent with much of the evidence for the coupled Sm–Nd chronometer.

Considering all the contradictions resulting from the D" model, we think it is more likely that the $^{142\text{Nd}}/^{144\text{Nd}}$ value measured in most silicate rocks represents the BSE. Most measurements of terrestrial rocks are within 5 ppm of $\varepsilon_{142\text{Nd}} = 0.0$ (cf. Boyet & Carlson 2006). As for the $\varepsilon_{143\text{Nd}}$ in MORB, this most frequently observed value is also most probably the average value in the Earth’s mantle today. Materials with significant negative or positive $\varepsilon_{142\text{Nd}}$-values do not exist as separate large reservoirs in the mantle today, but are likely to occur as small-scale heterogeneities within all mantle reservoirs. The evidence for such early differentiation has largely been destroyed by a combination of mantle convection and crust–mantle recycling.

The task now is to choose between three possible inherited differences between the Earth and chondrites: the Sm/Nd ratio, $^{146\text{Sm}}/^{144\text{Sm}}$ or $^{142\text{Nd}}/^{144\text{Nd}}$ (or all of them together?). Ranen & Jacobsen (2006) made a case for this being due to an initial difference in $^{142\text{Nd}}/^{144\text{Nd}}$. In this paper we have discussed the possibility of $^{146\text{Sm}}/^{144\text{Sm}}$. It is clear that more work is needed to understand whether the apparent differences in $^{146\text{Sm}}/^{144\text{Sm}}$ are real or due to analytical uncertainties. Harper & Jacobsen (1993) argued that it is unlikely that such a difference is due to the Earth having an unusually high Sm/Nd ratio; however, Caro et al. (2008) recently supported such a scenario.

(e) Pb isotopes in the early Earth

It was once thought that the concentration of Pb in the silicate portion of the Earth was depleted primarily by its partitioning into a metal–sulphide core, leaving the lithophile U behind. Consequently, the apparently young U/Pb age of the silicate Earth has been widely assigned to core formation. However, it is now known that the U/Pb ratio was also strongly fractionated in the Earth’s precursor materials by incomplete condensation and/or volatilization in the

Phil. Trans. R. Soc. A (2008)
The earliest Pb-isotopic evolution in the Earth, therefore, corresponds to a chronological model with at least two stages of fractionation: (i) nebular partitioning followed by (ii) partitioning of Pb into the core. These stages are a consequence of Pb being both volatile and chalcophile. The Pb abundance in the BSE plots very close to a volatility-related depletion trend defined by the elements that are believed not to partition into the core (McDonough & Sun 1995). It seems clear that the nebular fractionation is dominant and that the core-related fractionation would have to be very accurately determined compared with the volatility-related fractionation in order to obtain a credible result for the timing of core formation based on the U–Pb system.

The fact that the Pb-isotopic composition in the depleted mantle plots to the right of the 4.567 Ga ‘geochron’ in a $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plot (figure 11) can also be explained by the dominance of its Pb budget by recycled subducted Pb derived from both hydrothermally altered MORB crust and sediments formed by weathering of the upper continental crust (Asmerom & Jacobsen 1993). Therefore, Pb-isotopic systematics of mantle-derived basalts does not imply ‘late’ formation of the Earth by up to 100 Myr, as was once widely believed.

The ultimate causes of the observed shift in mantle Pb to the right of the geochron are: (i) the vertical differentiation of the continental crust into upper and lower crusts and (ii) partitioning of continentally derived U into MORB.
Both altered MORB and upper crust have U/Pb ratios higher than the BSE value and develop a radiogenic bulk composition over time. For $\mu_{\text{BSE}} \sim 7.7$, $\mu_{\text{LC}} \sim 3.5$ and a mean age of accretion and core formation of 10 Myr, Kellogg et al. (2007) obtained model MORB compositions that are within the field of real MORB (figure 11). Clearly, there is no need to infer a late core formation to explain Pb isotopes.

Crustal recycling of Pb provides a much more likely explanation of the Pb isotope shift in the modern mantle than delayed core formation. Also, if Hf–W was affected by disequilibrium, so was U–Pb. There is no reason to believe that the U–Pb system gives a better estimate for core formation than Hf–W because the disequilibrium will affect both systems. Owing to all these possibilities, the interpretation of Pb isotopes remains controversial (Halliday 2004; Wood & Halliday 2005, 2006; Kamber & Kramers 2006; Yin & Jacobsen 2006). Also, owing to these problems, we do not believe that Pb isotopes place strong constraints on the chronology of core formation and accretion.

(f) Summary

In conclusion, a combination of isotopic systems can be used to constrain some aspects of the earliest silicate differentiation in the Earth. The long-lived $^{147}\text{Sm}^{143}\text{Nd}$ system provided the first evidence that the earliest mantle-derived rocks came from a source that had previously gone through a differentiation process. However, the long-lived $^{147}\text{Sm}^{143}\text{Nd}$ system alone cannot give an exact time of depletion. The extinct $^{146}\text{Sm}^{142}\text{Nd}$ system provided the first clear evidence of very early mantle depletion (Harper & Jacobsen 1992; Jacobsen & Harper 1996) and has now been extended to many new samples of the Isua supracrustal belt (Boyet et al. 2003; Caro et al. 2003, 2006; Bennett et al. 2007). Most samples show a $^{142}\text{Nd}$ anomaly ranging from approximately 10 to 15 ppm. A two-stage evolution model can be used to constrain the age of this depletion event to within ca 100 Myr after the birth of the Solar System. The Lu–Hf system can potentially be another powerful tracer of early differentiation in the Earth, complementary to the $^{147}\text{Sm}^{143}\text{Nd}$ system. However, while the bulk Earth and Solar System concentrations and decay constant are well known for the $^{147}\text{Sm}^{143}\text{Nd}$ system (though not necessarily for the $^{146}\text{Sm}^{142}\text{Nd}$), there is a controversy over what these values are for the Lu–Hf system. Using the two different published $^{176}\text{Lu}$ decay constants yields very different interpretations of the early Earth’s differentiation (cf. Bizzarro et al. 2003; Jacobsen 2003b). Thus, the coupled $^{147,146}\text{Sm}^{143,142}\text{Nd}$ chronometer remains the most powerful tool to study how the silicate Earth evolved.

6. Early atmospheres, sources of water and organics for the Earth

Both observations and models of proto-planetary discs provide some clues to the delivery of highly volatile elements, in particular water and organics, to the early Earth. Figure 12 illustrates radial temperature distributions in accreting circumstellar discs calculated using the model of Sasselov & Lecar (2000) with observational input from Hartmann et al. (1998). The three lines represent three different times of disc evolution: (i) the hottest disc at high accretion rates
Figure 12. Calculated thermal evolution of the solar nebula in a plot of temperature ($T$) versus radial distance ($r$) from the Sun (based on Sasslov & Lecar 2000). The three lines represent three different stages in the development of a disc: from the hottest at high accretion rates ($10^{-6}M_\odot$ per year) and age of $10^5$ years, to the oldest, passive proto-planetary disc at $5 \times 10^6$ years (solid line, 0.1 Myr; long dashed line, 0.5 Myr; dashed line, 5 Myr). The upper dotted horizontal line (at 1350 K) shows the radial location of the dust coagulation/evaporation front for each disc.

($10^{-6}M_\odot$ per year) and age of $10^5$ years, (ii) an intermediate disc at $5 \times 10^5$ years, and (iii) the oldest, passive proto-planetary disc at $5 \times 10^6$ years. The upper dotted horizontal line at 1350 K shows the radial location of the dust (silicate and FeNi metal) coagulation/evaporation front and the lower dotted line is the snow line in the solar nebula. This suggests that the gas in the inner Solar System must be gone by 5 Myr when the snow line reaches 1 AU, otherwise the Earth would have accreted large quantities of volatiles. This is broadly consistent with astronomical observations that also suggest that the gas in the discs is gone by 5–10 Myr (Hartmann 2005; Russell et al. 2006). In general, the detailed relationship between the (radially dependent) time scales of nebular gas dissipation and planetary accretion throughout the Solar System (and even the physical mechanism of dissipation itself) remains unclear. The record carried by noble gas isotopes may provide useful constraints on this problem. The accretion of a massive solar-composition atmosphere onto a growing planetary nucleus is an unavoidable consequence of accretion in the presence of gas once a proto-planet attains a mass that is roughly 10 per cent of the mass of the Earth (Hayashi et al. 1979). Accretion models suggest that the Earth reached this point as rapidly as 100 000 years after the completion of the main phase of solar accretion (Aarseth et al. 1993; Wetherill & Stewart 1993).

Based on noble gas evidence, a schematic three-stage evolution of the Earth’s mantle–atmosphere system during accretion has been proposed (Harper & Jacobsen 1996b). Stage I is when the proto-Earth grows large enough to accrete a massive H₂–He proto-atmosphere directly from the nebular gas (figure 13). The blanketing effect of the massive proto-atmosphere supports a global magma ocean into which solar gases dissolve. Stage II (not shown) is at the end of accretion when the solar proto-atmosphere has dissipated. Stage III is after the
main phase of the Earth’s accretion (figure 13) when the solar UV luminosity decreased to a level allowing an atmosphere to be retained and grown by mantle degassing and accretion of volatile-rich objects (‘late veneer’) scattered from the outer parts of the solar nebula. The late veneer adds only approximately 0.3–0.4 per cent to the total mass of the Earth.

Harper & Jacobsen (1996b) argued that accretion of a H₂–He proto-atmosphere on the Earth is consistent with the preserved noble gas isotope record of the Earth’s deep interior. The evidence comes from He and Ne. First, the inferred ³He abundance in the deep Earth is in a range similar to that observed in primitive carbonaceous chondrites. This similarity has been
attributed to the presence of a primitive undegassed reservoir preserved since the early stage of the Earth’s accretion when the planetary nucleus was not large enough to support impact energies over the threshold for degassing. The \(^3\)He accreted in this way to the deep Earth is likely to have been lost compared with the primitive meteorite values and is probably less than 1 per cent of the original value (as all other highly volatile elements). Thus, the inferred initial \(^3\)He

*Phil. Trans. R. Soc. A* (2008)
abundance of the deep Earth is at least two orders of magnitude higher than that expected from accretion of dust and planetesimals. Therefore, $^3$He in the deep Earth cannot be an accreted primitive component. The $^3$He in the mantle must instead be attributed to some additive mechanism, with the most likely one being magma ocean equilibration (ingassing) with a primitive H$_2$–He proto-atmosphere. The presence of a solar-like $^{20}$Ne/$^{22}$Ne ratio in the mantle (cf. Honda et al. 1991) provides further support for this scenario. It has been argued that because the highest $^{20}$Ne/$^{22}$Ne in mantle-derived basalts is only 12.5, similar to the implanted solar wind component, and substantially lower than the solar $^{20}$Ne/$^{22}$Ne value of 13.8, the solar-like Ne of the deep Earth results from a dust component enriched in implanted solar gas (neon-B with $^{20}$Ne/$^{22}$Ne $\sim$ 12.5) rather than from an ingassed component. However, an implanted component would probably be thoroughly degassed from early differentiated planetesimals due to $^{26}$Al heating. As discussed for Nd isotopes, basalts never sample the true endmembers in the mantle; they always represent mixtures of source materials formed and differentiated at different times in the Earth’s history. Therefore, the original deep mantle value of $^{20}$Ne/$^{22}$Ne is likely to have been very close to the solar value of 13.8. There is also a planetary heavy noble gas (Ar, Kr and Xe) component in the Earth’s mantle most probably accreted from dust and planetesimals. This is not surprising because these gases are strongly enriched relative to He and Ne in the planetary or meteoritic component.

Harper & Jacobsen (1996b) inferred that only approximately 80 per cent of the Earth grew in the presence of a solar-composition atmosphere acquired from the solar nebula. The dissipation of the solar nebula gas in the vicinity of 1 AU would require rapid accretion of the Earth, because the observations of protoplanetary discs imply a time scale for clearing out the inner nebula of the order of 5–10 Myr (see above). Thus, there may have been a stage with no atmosphere after the dissipation of the solar atmosphere. This would cause the magma ocean to freeze rapidly owing to the rapid heat loss during a phase with no atmosphere.

After the main phase of accretion, our present atmosphere started forming by mantle degassing and the addition of a late veneer of volatile-rich objects contributing another 0.3–0.4 per cent to the Earth’s mass. The $^{129}$I–$^{129}$Xe chronometer records fractionation caused principally by open-system Xe transport from the mantle to the early atmosphere (including losses from the atmosphere to space). Figure 14 shows a simple model with the interior of the Earth evolving from the initial solar value of $^{129}$Xe/$^{130}$Xe of 6.287 to the highest well-documented value of 7.5 measured in MORB samples (Kunz et al. 1998). The true endmember value is likely to be even higher; Jacobsen & Harper (1996) suggested a value of 13. The atmosphere has a $^{129}$Xe/$^{130}$Xe value of only 6.496; however, the atmosphere is mass fractionated by 3.5 per cent per mass unit (probably due to hydrodynamic escape fractionation of the early atmosphere; Pepin 1991), so by applying this correction we obtain 6.723, implying very early formation (less than 30 Myr). The likely late veneer addition complicates this. It is possible that the difference between the Earth’s atmosphere and mantle only reflects the difference between the $^{127}$I/$^{130}$Xe ratio of the late veneer and the mantle. Similar complications may also affect the $^{244}$Pu–$^{131}$–$^{136}$Xe chronometers.
7. Discussion and summary

The $^{182}$Hf–$^{182}$W systematics interpreted in terms of a magma ocean model of accretion and core segregation implies rapid accretion and core formation in the terrestrial planet region. Most of the Earth accumulated in ca 10 Myr; approximately 30 Myr after the origin of the Solar System, the Earth was almost completely grown. High-energy-density laser shock experiments (Remo et al. 2007, 2008) of melting of metal–silicate mixtures at ultrahigh $P$ and $T$ that simulate conditions thought to have occurred in the deep Earth subsequent to the Moon-forming giant impact point to very rapid metal–silicate equilibration under such conditions. These experimental results and subsequent elemental analysis (Petaev et al. 2007, 2008) appear to validate our Hf–W approach for constraining the time scale of the Earth’s formation. We have also shown that $^{238,235}$U–$^{206,207}$Pb chronometry is consistent with such rapid accretion and core formation.

The $^{146}$Sm–$^{142}$Nd chronometer points to proto-crust formation in the Earth ca 100 Myr after Solar System formation. This proto-crust and its complementary depleted reservoir have been intimately remixed by crust–mantle recycling and mantle convection. The hypothesis of Boyet & Carlson (2005) that the proto-crust formed at 30 Myr was subducted to become the D" layer leads to a number of inconsistencies with the coupled $^{146}$Sm–$^{147}$Sm chronometry. To resolve a number of issues related to this problem, much more work still remains to be done.

The solar He and Ne and a substantial planetary component of heavy noble gases (Ar and Xe) in the deep Earth are consistent with a rapid accretion of most of the Earth in the presence of a solar atmosphere. The source of noble gases in the present atmosphere may primarily be a late veneer (except for $^{40}$Ar, which is the product of $^{40}$K decay in the Earth). Therefore, it is difficult to get good chronological constraints on the formation of the atmosphere from the Pu–I–Xe chronometers.

The Earth was initially sufficiently hot that the magma ocean encompassed the entire mantle; otherwise there would be more isotopic W heterogeneities than are observed. There is a need to use consistent isotopic and trace element models to interpret such data in terms of a model where the magma ocean is the entire mantle.

With the recent discoveries of extrasolar planets with masses of less than 10 Earth masses (see Udry et al. (2007) and references therein), the discovery space for extrasolar planets already encompasses the mass range of small rocky planets. These planets appear to hold crucial key information for the formation process of both giant planets (where they act as cores; see Pollack et al. (1996) and Rafikov (2004)) and Earth-like planets. The details and timing of this formation process remain unclear. One major problem with the models is the inability to include refractory materials, small rocks and asteroids, together with the gas in the disc, and to account properly for their interactions (e.g. Cuzzi 2007; Johansen et al. 2007). Recovering the chronological timing and the details of the refractory material interactions in the proto-planetary disc near the Earth’s orbit is thus a unique opportunity to constrain the physical processes that matter at that stage of planet formation in general.
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Phil. Trans. R. Soc. A (2008)


