Composition of the Earth’s interior: the importance of early events

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The detection of excess $^{142}$Nd caused by the decay of 103 Ma half-life $^{146}$Sm in all terrestrial rocks compared with chondrites shows that the chondrite analogue compositional model cannot be strictly correct, at least for the accessible portion of the Earth. Both the continental crust (CC) and the mantle source of mid-ocean ridge basalts (MORB) originate from the material characterized by superchondritic $^{142}$Nd/$^{144}$Nd. Thus, the mass balance of CC plus mantle depleted by crust extraction (the MORB-source mantle) does not sum back to chondritic compositions, but instead to a composition with Sm/Nd ratio sufficiently high to explain the superchondritic $^{142}$Nd/$^{144}$Nd. This requires that the mass of mantle depleted by CC extraction expand to 75–100 per cent of the mantle depending on the composition assumed for average CC. If the bulk silicate Earth has chondritic relative abundances of the refractory lithophile elements, then there must exist within the Earth’s interior an incompatible-element-enriched reservoir that contains roughly 40 per cent of the Earth’s $^{40}$Ar and heat-producing radioactive elements. The existence of this enriched reservoir is demonstrated by time-varying $^{142}$Nd/$^{144}$Nd in Archaean crustal rocks. Calculations of the mass of the enriched reservoir along with seismically determined properties of the D” layer at the base of the mantle allow the speculation that this enriched reservoir formed by the sinking of dense melts deep in a terrestrial magma ocean. The enriched reservoir may now be confined to the base of the mantle owing to a combination of compositionally induced high density and low viscosity, both of which allow only minimal entrainment into the overlying convecting mantle.

Keywords: Earth’s interior; terrestrial magnetism; Nd isotopes; early differentiation

1. Introduction

Models of the compositional variability of the solid Earth are inexorably linked to the mechanism and energy budget of the Earth’s formation. When planetary accretion was viewed as a gentle process, involving the accumulation of relatively small (less than 100 km diameter) planetesimals, predicted temperatures of planet formation ranged from ‘below the melting point of lavas’ for the Earth’s

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surface to less than 300°C for the Moon (Urey 1951). Cold accretion models predict that the composition of planetary interiors primarily should reflect the heterogeneity of the accreted objects, modified by metal–silicate separation, but only little affected by igneous processing of the silicate portion of the planet.

This view vanished soon after the first lunar landing when it was found that the Moon is a highly chemically differentiated object with a highlands crust dominated by a single mineral, plagioclase, and an interior whose composition reflects the consequences of extracting the large amounts of plagioclase that make up the lunar highlands crust (Wood et al. 1970). The chemical complementarity between lunar crust and mantle rapidly gave rise to the concept that the Moon had at one time been largely molten (Taylor & Jakes 1974). In this model, chemical differentiation of the lunar crust and mantle was accomplished through gravitational separation of crystals and liquids as the magma ocean cooled and solidified. Chronological studies of lunar rocks show that this major step in lunar differentiation occurred within a couple of hundred million years of Solar System formation (e.g. Tera & Wasserburg 1974; Carlson & Lugmair 1988; Nyquist et al. 1995). Following recognition that the Shergottite, Nakhlite and Chassignite (SNC) meteorites probably derive from Mars, chemical and isotopic study of these planetary fragments showed that Mars too is a highly differentiated object, with the separation of mantle from crust occurring within tens of millions of years of Solar System formation (Harper et al. 1995; Borg & Draper 2003; Foley et al. 2005; Caro et al. 2008; Debaille et al. 2008). A demonstration of even quicker igneous processing of smaller planetary objects is provided by the ca 4563 Ma ages obtained for parent body differentiation of the angrite and eucrite meteorites (Lugmair & Shukolyukov 1998; Amelin 2008; Markowski et al. 2008). The rapid and global early igneous processing of planetary objects is no longer a surprise given the recognition that (i) the latter stages of planetary accretion involve energetic collisions between very large objects (Wetherill 1990), (ii) planet formation occurred fast enough to allow 26Al and 60Fe to serve as important early heat sources (Lee et al. 1977) and (iii) core formation was rapid with the resultant release of large amounts of gravitational potential energy in the planetary interior.

Given the obvious examples of planetary-scale early igneous differentiation of Mars, the Moon and at least two asteroidal-sized planetesimals, one can question why a renowned scientist such as Harold Urey suggested that planets formed cold. An answer is that Urey had only the Earth for an example, and the evidence for early differentiation of the Earth is not obvious. Comparison of the composition of some mantle rocks with the compositional trends seen in meteorites led Jagoutz et al. (1979) to suggest that the Earth’s mantle still contains material that is little differentiated when compared with the chondritic building blocks of the planet. While postulating the cause of the compositional distinction between continental crust (CC) and oceanic crust, many models suggest that continent extraction from a ‘primitive’ mantle left only a portion of the mantle depleted in the elements that are strongly enriched in the CC (Jacobsen & Wasserburg 1979; DePaolo 1980; Allègre 1982). In these models, half or more of the mantle remains undifferentiated with chondritic relative abundances of at least the refractory lithophile elements. Though there is considerable debate over the rate of CC production over time (e.g. Rudnick 1995), chronological data for the rocks that now make up the continents show that CC production has
occurred throughout the Earth’s history (e.g. Patchett & Samson 2003) through low-degree melting of the mantle, probably aided by the melting-point depression caused by the injection of water into the mantle at subduction zones (e.g. Rudnick & Gao 2003). Continent formation, at least of the continents that now exist on the Earth, is not the result of magma ocean differentiation on the Earth.

While it is true that some important groups of Earth rocks do not deviate greatly in their content of refractory lithophile elements compared with chondritic meteorites, the silicate Earth clearly is depleted in those elements that probably partitioned into iron metal during core formation (the siderophile elements; e.g. Jagoutz et al. 1979; McDonough & Sun 1995). Results from the study of the $^{182}$Hf/$^{182}$W radiometric system show that core formation occurred during the first 30 Ma of the Earth’s history (Kleine et al. 2002; Yin et al. 2002a). Core formation is a good example of an early differentiation event that created a ‘missing’ reservoir, the core, whose composition must be inferred from the comparison of chondritic compositions and the deficiency of siderophile elements in the mantle. Luckily, the core also is large enough, and sufficiently compositionally distinct, to be seen seismically (Guttenberg 1914; Brush 1980) because the chemical consequences of core formation on the mantle are not particularly clear-cut. For example, the Ni/Co ratio (Wanke 1981) and the relative abundances of the highly siderophile elements (Chou et al. 1983), such as the platinum-group elements, are surprisingly close to chondritic, though the abundances of all of these elements are much reduced when compared with chondrites. Models of metal–silicate equilibrium, at least at low pressure, suggest that these elements should be strongly fractionated from one another by core formation (e.g. Righter & Drake 2003). All of these indicators led to Urey’s, and many others’, conclusion that the Earth did not experience a major early differentiation event similar to that seen on Mars and the Moon. Instead, the prevailing model, with the exception of core formation, is that whatever chemical variation is present in the Earth’s interior results primarily from the gradual extraction of CC over the Earth’s history.

In this paper, we explore new evidence that the Earth, like Mars and the Moon, experienced a global differentiation event within tens of millions of years of its formation that left the silicate earth with a subtly, but importantly, modified composition. This early differentiation can reconcile a number of observations concerning chemical characteristics of mantle-derived rocks that have become increasingly difficult to explain with the conventional model. The primary evidence for this conclusion comes from the decay of $^{146}$Sm to $^{142}$Nd, which occurs with a half-life of 103 Ma (Lugmair & Marti 1977). In the case of Mars and the Moon, the early planetary-scale differentiation events are clearly shown in most radiometric systems (Tera & Wasserburg 1974; Carlson & Lugmair 1988; Jagoutz 1991; Harper et al. 1995; Nyquist et al. 1995; Borg & Draper 2003; Foley et al. 2005; Rankenburg et al. 2006; Boyet & Carlson 2007; Caro et al. 2008; Debaille et al. 2008). On the Earth, with the exception of U–Pb (Patterson 1956) and Hf–W (Kleine et al. 2002; Yin et al. 2002a), which are affected by core formation, the effect of early differentiation of the silicate earth on conventional radiometric systems (Rb–Sr, Sm–Nd, Lu–Hf and U–Th–Pb) is sufficiently subtle that it has been masked by the continuing differentiation of the Earth’s interior caused by the growth of the CC. Because the variations in

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$^{142}$Nd/$^{144}$Nd were generated long before the present CC existed, the $^{146}$Sm–$^{142}$Nd system provides a nearly unique avenue to distinguish early, from continuing, differentiation of the Earth.

2. $^{146}$Sm–$^{142}$Nd basics

Both samarium and neodymium are members of the rare-earth elements (REE) and as such belong to the group of elements known as refractory lithophile elements, which reflects their high condensation temperatures (higher than 1400°C) and insolubility in iron metal. Though the suggestion has been made (Andreasen et al. 2008), there is not yet any convincing evidence that the REE will gain siderophile or chalcophile tendencies at the high pressures and temperatures expected for terrestrial core formation. Thus, the abundance of REE in the core is expected to be very low with the implication that fractionation of Sm from Nd by core formation is unlikely. Similarly, the very high condensation temperatures of Sm and Nd make it unlikely that they are fractionated by volatile loss in the solar nebula; a conclusion that is supported by Sm–Nd data from a variety of meteorites that will be discussed below. Sm and Nd can be fractionated by partial melting of silicate rocks or fractional crystallization of silicate melts. During melting in the shallow mantle, the REE strongly prefer the melt over the residual solid, with the ‘incompatibility’ in the solid decreasing from light to heavy REE. The primary phases controlling REE abundance and fractionation during melting in the shallow mantle are clinopyroxene and garnet (e.g. Irving 1978). Clinopyroxene slightly prefers Sm over Nd and hence will lead to melts that have somewhat lower Sm/Nd ratios than the starting solid. Garnet, and its higher-pressure analogue majorite, exerts increasing influence on REE partitioning at higher pressure. Garnet strongly concentrates the heavy over light REE and will cause substantial fractionation of Sm from Nd if it is present during melting. The REE are compatible in Ca-perovskite, but not in Mg-perovskite, and both prefer Sm over Nd (Kato et al. 1988; Drake et al. 1993; Taura et al. 2001; Corgne et al. 2005); so again, melts in equilibrium with perovskite in the lower mantle are likely to have lower Sm/Nd ratios than the solids.

Two isotopes of Sm decay by alpha-emission to two isotopes of Nd. In use since the early 1970s (Lugmair 1974), the decay of $^{147}$Sm to $^{143}$Nd (106 Gyr half-life) has been applied to a wide range of terrestrial and planetary chronological and geochemical tracing studies. The much shorter half-life and low initial abundance of $^{146}$Sm, on the other hand, have limited the use of the $^{146}$Sm–$^{142}$Nd system primarily to examining events that occurred within the first couple of hundred million years of Solar System history. Estimates of the initial abundance of $^{146}$Sm in the Solar System cluster around $^{146}$Sm/$^{144}$Sm = 0.008 ± 0.001 (Lugmair & Marti 1977; Lugmair & Galer 1992; Prinzhofer et al. 1992). A Solar System initial $^{146}$Sm/$^{144}$Nd = 0.008 is used for all calculations reported here.

In terms of detecting early differentiation events, the key difference between these two decay systems is the time intervals over which the record changes in Sm/Nd ratio. Over the first 200 Ma of Solar System history, $^{142}$Nd/$^{144}$Nd increased by 208 ppm and $^{143}$Nd/$^{144}$Nd by 522 ppm at a chondritic $^{147}$Sm/$^{144}$Nd = 0.1960. By contrast, over the next 200 Ma, $^{143}$Nd/$^{144}$Nd increased by another 522 ppm, but $^{142}$Nd/$^{144}$Nd increased by only 54 ppm. Since 4.0 Ga, $^{142}$Nd/$^{144}$Nd
has increased by only 6 ppm while $^{143}\text{Nd}/^{144}\text{Nd}$ has increased by over 10 000 ppm. With the current measurement precisions limited to approximately $\pm 5$ ppm on $^{142}\text{Nd}/^{144}\text{Nd}$, significant variations in $^{142}\text{Nd}/^{144}\text{Nd}$ thus were generated only prior to ca 4 Ga. Chemical differentiation events that change the Sm/Nd ratio of a rock after 4 Ga will result in changes to the trajectory of $^{143}\text{Nd}$ ingrowth, but will have essentially no significant effect on $^{142}\text{Nd}/^{144}\text{Nd}$. Mixing between materials with low and high $^{142}\text{Nd}/^{144}\text{Nd}$ can reduce the spread in $^{142}\text{Nd}/^{144}\text{Nd}$ at any time in the Earth’s history, but increases in the spread of $^{142}\text{Nd}/^{144}\text{Nd}$ can only be created in the first ca 500 Ma of the Earth’s history, when $^{146}\text{Sm}$ was still alive.

3. Non-chondritic $^{142}\text{Nd}/^{144}\text{Nd}$ in terrestrial rocks and its implications

During the development of the $^{147}\text{Sm}$–$^{143}\text{Nd}$ system in the late 1970s and early 1980s, measurements of Nd in a variety of ‘whole-rock’ chondritic meteorites showed no distinction from terrestrial $^{142}\text{Nd}/^{144}\text{Nd}$ at measurement precisions of $\pm 30$ ppm (Jacobsen & Wasserburg 1980, 1984; Prinzhofer et al. 1992). Not until measurement precisions dropped below approximately 15 ppm was it possible to distinguish the systematic difference between chondritic and terrestrial $^{142}\text{Nd}/^{144}\text{Nd}$ (Nyquist et al. 1995; Boyet & Carlson 2005; Andreasen & Sharma 2006; Carlson et al. 2007). Figure 1 shows the offset in $^{142}\text{Nd}/^{144}\text{Nd}$ between chondrites and terrestrial rocks. Also plotted in figure 1 are data for basaltic eucrites because these planetesimal melts have near-chondritic Sm/Nd ratios and were formed within a few million years of Solar System formation (Lugmair & Shukolyukov 1998). They thus offer an opportunity to examine the initial Nd isotopic characteristics at a ‘planetesimal’ scale for a non-Earth object, rather than the less than a few gram sample sizes used for the chondrite analyses. As seen in figure 1, all chondrites and basaltic eucrites analysed so far have a $^{142}\text{Nd}/^{144}\text{Nd}$ ratio lower than measured for any terrestrial rock. Using all the published high-precision data for chondrites (Nyquist et al. 1995; Boyet & Carlson 2005; Andreasen & Sharma 2006; Rankenburg et al. 2006; Carlson et al. 2007), the average $^{142}\text{Nd}/^{144}\text{Nd}$ ratios for the meteorites, weighted according to the measurement error on individual analyses, are: carbonaceous chondrites $=-32\pm3$ (excluding the data for the CV3 chondrite Grosnaja, which has an unusually high Sm/Nd ratio (Carlson et al. 2007)); ordinary chondrites $=-18\pm3$; enstatite chondrites $=-17\pm10$; and basaltic eucrites $=-23\pm6$. All values are expressed in parts per million difference from the average value obtained for a terrestrial Nd standard with errors expressed at the $2\sigma$ level. Correcting each measured value to an average chondrite $^{147}\text{Sm}/^{144}\text{Nd}=0.1960$ (average for the chondrite Sm–Nd data reported by Jacobsen & Wasserburg (1980, 1984), Prinzhofer et al. (1992), Patchett et al. (2004), Boyet & Carlson (2005), Andreasen & Sharma (2006), Rankenburg et al. (2006) and Carlson et al. (2007)) provides the following average values for $^{142}\text{Nd}/^{144}\text{Nd}$ in the samples where Sm/Nd ratio data were reported: C-chondrite $=-31\pm3$ ($n=14$); O-chondrite $=-16\pm3$ ($n=11$); E-chondrite $=-13\pm10$ ($n=2$); and basaltic eucrite $=-21\pm6$ ($n=4$). The distinction between chondrite and terrestrial $^{142}\text{Nd}/^{144}\text{Nd}$ has now been confirmed by four different laboratories. There seems little question that chondrites have lower $^{142}\text{Nd}/^{144}\text{Nd}$ than terrestrial rocks, but there remain several possible interpretations of this distinction.

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Isotopic variation at the whole-rock scale has now been identified in a number of elements in primitive meteorites (Black & Pepin 1969; Clayton et al. 1973; Rotaru et al. 1992; Podosek et al. 1997; Dauphas et al. 2002; Yin et al. 2002; Becker & Walker 2003; Brandon et al. 2005; Andreasen & Sharma 2006, 2007; Shukolyukov & Lugmair 2006; Carlson et al. 2007; Trinquier et al. 2007; Yokoyama et al. 2007). For the larger of the anomalies, particularly those found in preserved

(a) Nucleogenic heterogeneity in the solar nebula

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presolar grains (e.g. Meyer & Zinner 2006) and in the very small number of highly isotopically anomalous calcium–aluminium-rich inclusions in carbonaceous chondrites (e.g. McCulloch & Wasserburg 1978), there is no question that the anomalies reflect different nucleosynthetic contributions by stars outside the Solar System.

Nucleosynthetic heterogeneities are a concern for interpreting Nd isotopic variations because the different isotopes of Nd and Sm are made by different nucleosynthetic processes in stars (Burbidge et al. 1957). Imperfect mixing of the nucleosynthetic contributions from various stars thus could result in variations in $^{142}\text{Nd}/^{144}\text{Nd}$ that are not related to $^{146}\text{Sm}$ decay. Specifically, $^{142}\text{Nd}$ is made primarily by s-process nucleosynthesis (Arlandini et al. 1999) while $^{144}\text{Nd}$ and $^{146}\text{Nd}$ are made by a combination of s- and r-process nucleosyntheses (Qian et al. 1998). In addition, $^{146}\text{Sm}$ is made by the p-process (Woosley & Howard 1978). As seen in figure 2, the $^{142}\text{Nd}/^{144}\text{Nd}$ data for chondrites show only limited correlation with Sm/Nd ratio, particularly when comparing the data for ordinary chondrites with that for carbonaceous chondrites. In part, this reflects the limited spread in Sm/Nd ratio and $^{142}\text{Nd}/^{144}\text{Nd}$, but the distinction between carbonaceous chondrites, ordinary chondrites and eucrites in figure 2 clearly cannot be explained solely by $^{146}\text{Sm}$ decay with variable bulk-rock Sm/Nd ratios.

Ranen & Jacobsen (2006) suggested that the difference in $^{142}\text{Nd}/^{144}\text{Nd}$ between chondrites and terrestrial rocks reflects nucleosynthetic heterogeneity on the basis of anomalies they measured in the abundance of $^{137}\text{Ba}$ and $^{138}\text{Ba}$ in a variety of chondrites. These anomalies have not been confirmed in either

Figure 2. Sm/Nd versus $^{142}\text{Nd}/^{144}\text{Nd}$ isochron diagram for the meteorite data reported by Boyet & Carlson (2005) and Carlson et al. (2007). The lines show the expected slope for an object 4.568 Ga in age that formed with a Solar System initial $^{146}\text{Sm}/^{144}\text{Sm} = 0.008$ (Lugmair & Galer 1992). The lower line passes through the average Sm/Nd and $^{142}\text{Nd}/^{144}\text{Nd}$ measured for O-chondrites, while the upper line is displaced by 18 ppm in $^{142}\text{Nd}/^{144}\text{Nd}$ to show the offset of the meteorite data from terrestrial $^{142}\text{Nd}/^{144}\text{Nd}$. Circles, C-chondrite; triangles, O-chondrite; diamonds, E-chondrite; squares, basaltic eucrite.
previous (Hidaka et al. 2003) or more recent studies (Andreasen & Sharma 2007; Carlson et al. 2007; Wombacher & Becker 2007). Although excesses in $^{135}\text{Ba}$ and $^{137}\text{Ba}$, which are related to variations in the ratio of r- to s-process components, have been observed in carbonaceous chondrites, they have not been observed in ordinary chondrites or eucrites (Hidaka et al. 2003; Andreasen & Sharma 2007; Carlson et al. 2007). Furthermore, when Ba isotopic anomalies are measured in carbonaceous chondrites, they show little or no correlation with the magnitude of $^{142}\text{Nd}$ deficit measured in the same sample (Carlson et al. 2007). Consequently,
Ba isotopic anomalies in carbonaceous chondrites appear to have little or no significance for the interpretation of the $^{142}\text{Nd}/^{144}\text{Nd}$ difference between chondrites and terrestrial rocks.

Of greater concern is the discovery that carbonaceous chondrites contain approximately 100 ppm deficits in $^{144}\text{Sm}$ (Andreasen & Sharma 2006; Carlson et al. 2007), which, like $^{146}\text{Sm}$, is produced by the p-process. This offset in $^{144}\text{Sm}$ is shown in figure 3. According to the calculations presented by Andreasen & Sharma (2006), a 100 ppm deficit in $^{144}\text{Sm}/^{152}\text{Sm}$ would translate into an $11^{+9}_{-21}$ ppm deficit in $^{142}\text{Nd}/^{144}\text{Nd}$ due to the reduced abundance of $^{146}\text{Sm}$. This difference accounts well for the lower $^{142}\text{Nd}/^{144}\text{Nd}$ measured in carbonaceous chondrites compared with ordinary chondrites. The effect does not appear to be significant for ordinary and enstatite chondrites, basaltic eucrites or lunar samples, as all these materials have the same $^{144}\text{Sm}/^{152}\text{Sm}$ as measured for terrestrial rocks (figure 3).

The Sm and Nd results thus do indicate the presence of nucleosynthetic variability in carbonaceous chondrites. While this provides further proof that carbonaceous chondrites are not a good reference for the bulk composition of the terrestrial planets, raising the average $^{142}\text{Nd}/^{144}\text{Nd}$ data of the carbonaceous chondrites by $11$ ppm to account for the p-process heterogeneity brings the average carbonaceous chondrite $^{142}\text{Nd}/^{144}\text{Nd}$ value to $-21$ ppm below terrestrial, a value that is similar to that obtained for other meteorite groups. This strengthens the suggestion that the observed difference between chondritic and terrestrial $^{142}\text{Nd}/^{144}\text{Nd}$ does not reflect nucleogenic heterogeneity in the solar nebula, but instead is best explained by the decay of $^{146}\text{Sm}$.

(b) A non-chondritic Earth?

The average $^{147}\text{Sm}/^{144}\text{Nd}$ ratio for 60 measurements of chondritic meteorites is $0.1960\pm 0.0033$ for a total range in Sm/Nd ratio of only slightly greater than 3 per cent (Jacobsen & Wasserburg 1980, 1984; Prinzhofer et al. 1992; Patchett et al. 2004; Boyet & Carlson 2005; Andreasen & Sharma 2006; Rankenburg et al. 2006; Carlson et al. 2007). There is no systematic difference between the Sm/Nd ratio of different chondrite classes. For an average chondritic $^{147}\text{Sm}/^{144}\text{Nd}=0.1960$, to evolve an 18 ppm excess in $^{142}\text{Nd}/^{144}\text{Nd}$ requires a $^{147}\text{Sm}/^{144}\text{Nd}=0.2085$ if this Sm/Nd ratio was established at Solar System formation at 4.568 Ga (Amelin et al. 2002; Bouvier et al. 2007). Delaying formation of the high Sm/Nd ratio material would require this ratio to increase. For example, if the high Sm/Nd ratio reservoir formed at 4.50 Ga, and had a chondritic Sm/Nd ratio between 4.568 and 4.50 Ga, it would need a $^{147}\text{Sm}/^{144}\text{Nd}=0.216$ to evolve the same excess of 18 ppm in $^{142}\text{Nd}/^{144}\text{Nd}$.

The limited variation in Sm/Nd ratio observed in all chondrites is consistent with the refractory lithophile nature of these two elements and the expectation that they should not be fractionated by the volatility and metal–silicate separation that dominates the compositional variation of chondrites. Basaltic eucrites and angrites, both of which are very volatile depleted compared with chondrites, have Sm/Nd ratios within the range exhibited by chondrites, so the expectation of limited accretionary fractionation of Sm from Nd continues up to at least the size scale of large asteroids. While it is certainly possible that the
available collection of chondrites does not represent the full compositional spectrum of planetary building blocks, the process that would lead to the formation of planetary embryos with Sm/Nd ratio well above the range displayed by chondrites is not obvious. The individual components of chondrites (e.g. chondrules and minerals) do show significant ranges in Sm/Nd ratio (Amelin & Rotenburg 2004), but the significance of this for planetary modelling is not yet clear as chondrite parent body metamorphism can increase the Sm/Nd ratio of chondrules that equilibrate with the strongly REE-rich phosphate minerals that grow during metamorphism. Thus, while this internal redistribution of REE between components in chondrites can create variation in Sm/Nd ratio within a chondrite, if the whole chondrite is accreted to a growing planet, the internal variation in Sm/Nd ratio is inconsequential for the bulk Sm/Nd ratio of the growing planet. One could hypothesize selective collisional removal of incompatible-element-rich, low Sm/Nd crusts from planetesimals, with the Earth preferentially accreting the high Sm/Nd mantles of these objects (e.g. a presentation at this meeting; O’Neill & Palme 2008). An alternative means of removing a low Sm/Nd component is explosive eruption of small-volume melts from small planetesimals that have minimal gravity to prevent the escape of the erupted material into space (Warren 2008). Examples of the complementary low Sm/Nd ‘crusts’ or erupted material, however, are not present in the existing meteorite collection. The Moon is a possible candidate for a light-REE-enriched, low Sm/Nd ratio, complement to the Earth (Nyquist et al. 1979; Carlson & Lugmair 1988), but recent studies have shown that the Moon formed with either chondritic (Rankenburg et al. 2006) or terrestrial-like 142Nd/144Nd (Nyquist et al. 1995; Boyet & Carlson 2007), not the subchondritic 142Nd/144Nd necessary to balance out the Earth–chondrite difference in 142Nd/144Nd. As mentioned previously, eucrites show their derivation from a parent object with Sm/Nd ratio approximately the same as chondritic (e.g. Righter & Drake 1997). Whether or not samples from Mars imply a planet with near-chondritic (Debaille et al. 2008) or superchondritic (Caro et al. 2008) Sm/Nd is currently a subject of some debate, as the interpretation of the available data depends strongly on the details of the petrogenetic history of the SNC meteorites.

There is thus no strong reason to suggest that the bulk Earth has a suitably superchondritic Sm/Nd ratio to explain its approximately 18 ppm excess in 142Nd/144Nd compared with chondrites. Regardless of the bulk composition of the Earth, the discussion presented in the following sections regarding the compositional characteristics of an early formed high Sm/Nd ratio reservoir in the Earth’s mantle are not dependent on the bulk Earth having a chondritic Sm/Nd ratio. By contrast, the arguments for a ‘hidden’ incompatible-element-rich, low Sm/Nd reservoir are very sensitive to the true composition of the bulk Earth. If the 18 ppm excess in 142Nd/144Nd measured for all terrestrial rocks indeed represents the value of the bulk Earth, then there is no strong argument, at least from Sm–Nd, that the Earth contains a missing enriched reservoir. A decidedly non-chondritic Earth, however, would have rather drastic consequences for most compositional models for the solid Earth, as these are almost universally based on the assumption that the bulk Earth has chondritic relative abundances of the refractory lithophile elements (e.g. McDonough & Sun 1995; Palme & O’Neill 2003).
Eliminating nucleogenic heterogeneity and a bulk Earth with strongly non-chondritic relative abundances of the refractory lithophile elements leaves an early igneous differentiation of the planet as the likely cause of the observed difference in $^{142}\text{Nd}/^{144}\text{Nd}$ between terrestrial rocks and chondrites. At this point, it is important to mention that an early global differentiation event does not deny the ‘traditional’ view that formation of the CC has resulted in depletion of some portion of the mantle in incompatible elements. This model is almost certainly correct, but the superchondritic $^{142}\text{Nd}/^{144}\text{Nd}$ of both the CC and the mantle source of mid-ocean ridge basalts (MORB) show that these two chemically complementary reservoirs cannot be combined in any mass proportion in order to return to a chondritic starting composition. The derivation of both the CC and the MORB-source mantle from an already incompatible-element-depleted reservoir formed early in the Earth’s history, while $^{146}\text{Sm}$ was still alive, presents a number of interesting alternative explanations for fundamental aspects of mantle geochemistry and the compositional and dynamic evolution of the Earth.

As mentioned previously, in order to evolve the approximately 18 ppm excess $^{142}\text{Nd}/^{144}\text{Nd}$ in terrestrial rocks compared with the chondrites requires a minimum $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.2085 if the early differentiation event occurred exactly at the start of Solar System formation, 4.568 Ga ago. There is, however, a trade-off between the time of formation of the high Sm/Nd ratio reservoir and its Sm/Nd ratio, as illustrated in figure 4. Delaying formation of the reservoir with superchondritic Sm/Nd ratio by 100 or 200 Ma after Solar System formation would require it to have much higher $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of 0.222 and 0.244,
respectively. These ratios are not outside the realm of possibility, and, in fact, span the range suggested for the early Moon (Boyet & Carlson 2007). Because changes in Sm/Nd ratio also will affect the evolution of $^{145}$Nd/$^{144}$Nd, the combination of $^{142}$Nd–$^{143}$Nd systematics can offer somewhat tighter constraints on the timing of an early terrestrial differentiation event. For example, a reservoir formed at 4.468 Ga with $^{147}$Sm/$^{144}$Nd = 0.222 will evolve the appropriate 18 ppm excess in $^{142}$Nd/$^{144}$Nd, but will today have a present-day $\epsilon^{143}$Nd = +15, where $\epsilon^{143}$Nd is defined as

$$\epsilon^{143}\text{Nd} = \left[ \frac{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample}}}{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{chondrite}}} - 1 \right] \times 10000. \quad (3.1)$$

Though values of $^{143}$Nd/$^{144}$Nd this high are found in some terrestrial rocks, the major light-REE-depleted reservoir on the Earth, the mantle source of MORB, has an average $\epsilon^{143}$Nd closer to approximately +10. Furthermore, given models for the depletion of the MORB-source mantle by continental extraction over the Earth’s history, the early formed light-REE-depleted reservoir should have a lower $^{143}$Nd/$^{144}$Nd than the MORB source, because the additional depletion of the MORB source will raise its Sm/Nd ratio, and hence, with time, its $^{143}$Nd/$^{144}$Nd. A reservoir formed at 4.518 Ga (50 Ma after Solar System formation) with $^{147}$Sm/$^{144}$Nd = 0.2134 will evolve to present-day $^{142}$Nd/$^{144}$Nd = +18 ppm and $^{143}$Nd/$^{144}$Nd = +10.2, which provides a reasonable upper limit of 50 Ma for the timing of early terrestrial depletion in this almost certainly overly simplistic two-stage evolution model (figure 4). If formed at 4.568 Ga, a reservoir with $^{147}$Sm/$^{144}$Nd = 0.2085 would today have an $\epsilon^{143}$Nd of +7.4 (figure 4). These models assume that the two early formed chemically complementary reservoirs evolved separately, with no mixing, through the Earth’s history. We will discuss in §6 of this paper that terrestrial $^{142}$Nd/$^{144}$Nd variation measured in the Archaean samples suggests that mantle dynamics included mixing between these reservoirs in the first 500 Ma of the Earth’s history.

4. Consequences of early differentiation for compositional models of the Earth’s interior

With only a few exceptions, to be discussed in §5, both the CC and the mantle source of MORB have the same superchondritic $^{142}$Nd/$^{144}$Nd. Besides the obvious implications for an early differentiation event on the Earth, this result subtly, but importantly, modifies a number of conclusions regarding the mass proportion of the incompatible-element-depleted MORB mantle compared with the whole mantle. Traditional calculations relating the formation of the incompatible-element depletion characterizing the MORB-source mantle to continent extraction perform the following mass balance to calculate the volume of the depleted mantle:

$$[X]_{\text{BSE}} \times (M_{\text{CC}} + M_{\text{DMM}}) = [X]_{\text{CC}} \times M_{\text{CC}} + [X]_{\text{DMM}} \times M_{\text{DMM}}, \quad (4.1)$$

where $[X]$ is the concentration of an element $X$ in the bulk silicate Earth (BSE), depleted MORB-source mantle (DMM) or CC, and $M$ gives the mass of the reservoir. With the estimates of the composition of the BSE derived from

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chondrite analogues (McDonough & Sun 1995), CC (Taylor & McLennan 1985; Rudnick & Gao 2003) and MORB mantle (Salters & Stracke 2004; Workman & Hart 2005), and the mass of the CC, one can solve this equation for the mass of the MORB-source mantle,

$$M_{DMM} = M_{CC} \times \frac{[X]_{CC} - [X]_{BSE}}{[X]_{BSE} - [X]_{DMM}}.$$  \hfill (4.2)

With the recognition that both the MORB-source mantle and CC have superchondritic $^{142}$Nd/$^{144}$Nd, this equation must be replaced with

$$M_{DMM} = M_{CC} \times \frac{[X]_{CC} - [X]_{EDR}}{[X]_{EDR} - [X]_{DMM}},$$  \hfill (4.3)

where EDR stands for the early formed depleted reservoir characterized by a Sm/Nd ratio sufficiently high to evolve the 18 ppm excess $^{142}$Nd/$^{144}$Nd seen in most terrestrial rocks compared with chondrites. Because the Nd isotopic data offer more constraints on Sm/Nd ratio than the concentrations of either element, this equation can be rewritten as

$$M_{DMM} = M_{CC} \times \frac{(Sm/Nd)_{EDR} - (Sm/Nd)_{CC}}{(Sm/Nd)_{DMM} - (Sm/Nd)_{EDR}} \times \frac{[Nd]_{CC}}{[Nd]_{DMM}}.$$  \hfill (4.4)

The mere fact that the early depleted reservoir is, by definition, poorer in incompatible elements than BSE estimates based on chondritic analogues requires the MORB-source mantle to occupy a greater volume of the mantle than estimated when starting from a ‘primitive’ mantle with chondritic relative abundances of the refractory lithophile elements.

An additional factor leading to an increase in the estimated size of the depleted reservoir comes from the fact that most estimates of the incompatible-element composition of the MORB-source mantle start with an average of MORB composition (Salters & Stracke 2004; Workman & Hart 2005). Moving from the composition of a basaltic melt to the composition of its mantle source requires knowledge of element partitioning during melting, and particularly the degree of partial melting that produced the ‘average’ basalt. At the moderately low degrees of melting involved in MORB genesis, small variations (± 1 or 2%) in the assumed degree of partial melting can have significant consequences for the calculated abundances of highly incompatible elements in the MORB-source mantle.

One approach to reconstructing the incompatible-element abundances in the MORB source starts with the abundances of only moderately incompatible elements (e.g. Yb, Lu) because these elements are not as strongly fractionated between melt and residual solid (Salters & Stracke 2004). Consequently, the extrapolation from melt to source abundance for these elements is not as sensitive to the degree of partial melting compared with more highly incompatible elements. Once these moderately incompatible-element abundances are determined in the source, the abundances of more incompatible elements are calculated through the use of element ratios that appear to be insensitive to degree of partial melting (Salters & Stracke 2004). This approach, however, requires several steps along the list of incompatible elements that cannot be made by comparing element ratios alone. These steps are made by using the radiogenic isotopic composition of MORB to calculate parent/daughter ratios.
assuming some model for the time evolution of parent/daughter ratio in the MORB source. For example, using an estimate of the abundance of Lu in the MORB source, one can estimate the abundance of the much more incompatible Hf through the use of the Hf isotopic composition of MORB. Once the Hf abundance is obtained, the Sm abundance can be calculated from the constant Sm/Hf ratio observed in MORB, and then the Nd abundance in the MORB source can be calculated with reference to the Sm/Nd ratio needed to explain the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio in MORB.

The steps in estimating the composition of the MORB-source mantle, which use radiogenic isotopic compositions, however, are sensitive to the model used to explain the evolution of the isotopic composition in the MORB source. For example, assuming that the MORB-source mantle started with chondritic Sm/Nd and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and then became incompatible-element depleted by continent extraction, using a mean age of the continents of 1.8 Ga results in a calculated MORB source $^{147}\text{Sm}/^{144}\text{Nd}=0.235$ (Salters & Stracke 2004). By contrast, if the mean age of continent extraction is pushed back to 3.4 Ga, the calculated MORB source $^{147}\text{Sm}/^{144}\text{Nd}$ is 0.217 (Salters & Stracke 2004). The cause of this is clear. The shorter the time allowed to grow $^{143}\text{Nd}$ in the depleted mantle, the higher the Sm/Nd ratio must be. The superchondritic $^{142}\text{Nd}/^{144}\text{Nd}$ of the MORB source requires a source with $^{147}\text{Sm}/^{144}\text{Nd}$ of at least 0.2085 to have been present shortly after the Earth’s formation, which would lead to a present-day $\varepsilon^{143}\text{Nd}=+7.4$. In this case, most of the superchondritic $^{143}\text{Nd}/^{144}\text{Nd}$ observed in the MORB source is the result of its derivation from the early depleted reservoir. Continent extraction has resulted in additional depletion (e.g. increase in Sm/Nd), which has contributed no more than an additional approximately 3 epsilon unit increase in $^{143}\text{Nd}/^{144}\text{Nd}$ in the MORB-source mantle. As a result, calculations of the composition of the MORB-source mantle, which assume that it derives not from a primitive mantle with chondritic relative abundances of refractory lithophile elements, but from a mildly incompatible-element-depleted source formed within 50 Ma of the Earth’s formation, result in a MORB-source composition that is less incompatible-element depleted than previous calculations (Boyet & Carlson 2006).

Another way to look at this follows the $^{143}\text{Nd}$ evolution of the MORB source. In the case where the portion of the mantle parental to the MORB source starts with $^{147}\text{Sm}/^{144}\text{Nd}=0.2085$ at 4.568 Ga, the mildly depleted MORB source of Boyet & Carlson (2006) with $^{147}\text{Sm}/^{144}\text{Nd}=0.220$ would require that the MORB source had this Sm/Nd ratio for 2.0 Ga in order to reach the $\varepsilon^{143}\text{Nd}$ approximately +10 characterizing the present-day MORB source. By contrast, very depleted models for the MORB source, such as that of Workman & Hart (2005) with a very high $^{147}\text{Sm}/^{144}\text{Nd}=0.249$, would require only 0.5 Ga to reach $\varepsilon^{143}\text{Nd}=+10$ starting from an ancient reservoir with $^{147}\text{Sm}/^{144}\text{Nd}=0.2085$. The average age of the CC as inferred from Sm/Nd systematics of continental sediments is ca 2 Ga (Goldstein et al. 1984), which supports the idea that the composition of the MORB source lies closer to the mildly depleted composition implied by the derivation of the MORB source by continent extraction from a reservoir initially depleted very early in the Earth’s history.

Using this slightly less depleted MORB-source composition (table 1) in the mass balance described by equation (4.4) leads to the conclusion that the
Table 1. Composition of major terrestrial reservoirs. (CC, continental crust; BSE, bulk silicate Earth; DMM, depleted MORB mantle; EDR, early depleted reservoir; EER, early enriched reservoir; T&M, Taylor & McLennan (1985); R&G, Rudnick & Gao (2003); M&S, McDonough & Sun (1995); B&C, Boyet & Carlson (2006). Numbers under EDR and EER give the percentage of mantle occupied by these reservoirs. Present-day isotopic compositions of CC and DMM are calculated assuming growth with EDR parent/daughter ratios from 4.568 to 2.0 Ga followed by ingrowth using the parent/daughter ratios of each CC estimate. The DMM isotopic composition is calculated using the EDR estimate derived from the T&M crust composition.)

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<th>EDR (96%)</th>
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<td>0.71517</td>
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</table>

MORB-source mantle must occupy the major portion of the mantle. For example, using an incompatible-element-enriched estimate for the average CC (Rudnick & Gao 2003), the combination CC plus MORB-source mantle will not end up with a Sm/Nd ratio high enough to evolve the superchondritic...
$^{142}$Nd/$^{144}$Nd of terrestrial rocks even if the whole mantle is currently as depleted as estimated for the MORB source. If the average CC is less incompatible-element enriched (Taylor & McLennan 1985), then the MORB-source mantle must occupy proportionately less of the mantle, but even with this continental composition estimate it must occupy approximately 74 per cent of the mantle.

Replacing the traditional concept of a ‘primitive’ mantle that has chondritic relative abundances of refractory lithophile elements with an incompatible-element-depleted mantle also offers some important new interpretations of the range in mantle isotopic compositions detected through studies of ocean island basalts (White 1985; Zindler & Hart 1986). Chief among these is that the primitive mantle, i.e. the mantle before CC was extracted, no longer should be expected to have chondritic Nd and Hf isotopic compositions. Instead, given a simple two-stage model for mantle differentiation that involves an initial incompatible-element depletion shortly after the Earth’s formation followed by gradual additional depletion as a result of the growth of CC, the primitive mantle should have $\varepsilon^{143}$Nd approximately +7 and a corresponding $\varepsilon$Hf approximately +15 (table 1). These isotopic compositions calculated for the early depleted reservoir are close to a mantle component that was once called PREMA for ‘prevalent mantle’ (Zindler & Hart 1986) because it represents the most abundant composition in ocean island (and continental) basalts worldwide. This component later took on the acronym FOZO, for ‘focus zone’ of isotopic variation in oceanic basalts (Hart et al. 1992). An important aspect of FOZO is that it is the mantle component with the lowest $^4$He/$^3$He. Because low $^4$He/$^3$He is associated with ‘primitive undegassed’ sources in the Earth’s interior (Craig & Lupton 1976), the association of the lowest $^4$He/$^3$He with decidedly super-chondritic Nd isotopic compositions (Class & Goldstein 2005) is much more easily explained if this component is not chondritic mantle, but is instead the early depleted reservoir.

Because so much of the Earth’s Rb is in the CC, the calculated Sr isotopic composition of this early depleted reservoir is very sensitive to the assumed Rb content of the bulk CC. For example, using Taylor & McLennan’s (1985) estimate of bulk CC composition, the calculated present-day $^{87}$Sr/$^{86}$Sr of the early depleted reservoir is 0.7046 (table 1), which, in combination with an $\varepsilon^{143}$Nd = +7, would place this component to the right (high $^{87}$Sr/$^{86}$Sr) of the mantle Nd–Sr isotope array. To put the early depleted reservoir on the mantle Nd–Sr isotope array at $\varepsilon^{143}$Nd = +7 and $^{87}$Sr/$^{86}$Sr = 0.7038 would require the bulk CC to have an Rb concentration closer to 30 ppm than the 37 ppm suggested by the crust model of Taylor & McLennan’s (1985).

Replacing ‘chondritic’ mantle with an incompatible-element-depleted early formed mantle reservoir also means that ocean island basalts that deviate to less radiogenic Nd and Hf, and more radiogenic Sr and Pb, than predicted for the early depleted mantle reservoir carry isotopic signatures of incompatible-element enrichment rather than depletion. The most obvious explanation for this is that at least small volumes of recycled crust or metasomatically enriched mantle are an almost ubiquitous presence in the sources of ocean island basalts (Hofmann & White 1982). Small amounts of recycled crust, presumably in the form of sediments, could also explain why even the FOZO component has Pb isotopic compositions lying to the right (high $^{206}$Pb/$^{204}$Pb) side of the terrestrial
geochron. Given that average CC (Rudnick & Gao 2003) has a Pb concentration more than 100 times that of the early depleted mantle (Boyet & Carlson 2005), even a fraction of a per cent by mass of sediment mixed into the early depleted mantle will result in displacement of the Pb isotopic composition of the mixture to the right of the geochron.

5. A missing enriched reservoir?

The compositional characteristics of the early formed incompatible-element-depleted reservoir described above remain true whether or not a complementary reservoir enriched in incompatible elements exists within the Earth’s interior. If the bulk Earth has chondritic relative abundances of refractory lithophile elements, then mass balance with the early formed depleted reservoir requires the presence of an incompatible-element-enriched reservoir within the Earth. The compositional characteristics of such a reservoir can be calculated through a mass-balance approach similar to the continent–depleted mantle mass balance described above using the equation

$$\frac{[X]_{\text{BSE}}}{M_{\text{BSE}}} \times M_{\text{BSE}} = \frac{[X]_{\text{EER}}}{M_{\text{EER}}} \times M_{\text{EER}} + \frac{[X]_{\text{EDR}}}{M_{\text{EDR}}} \times M_{\text{EDR}},$$

(5.1)

where EER stands for the early formed enriched reservoir. In this equation, the mass of the BSE is the only reasonably well-known parameter, with the concentration of element $X$ in the BSE being derived by assuming a chondritic relative abundance for refractory lithophile elements (McDonough & Sun 1995). The composition of the early depleted reservoir (table 1) is calculated by the MORB source–CC mass balance described by equation (4.3), which also offers some constraint on the mass of this reservoir by using equation (4.4), although this constraint is dependent on the concentration assumed for average CC. As seen in figure 5, the composition of the early depleted reservoir is not strongly dependent on the assumed composition of the MORB source and CC owing to the requirement that this reservoir has a Sm/Nd ratio high enough to evolve the 18 ppm superchondritic $^{142}\text{Nd}/^{144}\text{Nd}$ of terrestrial rocks.

The mass calculated for the early depleted reservoir is quite strongly dependent on the assumed composition of the average CC. Using the ‘basaltic-andesite’ average for CC (Taylor & McLennan 1985) reduces the mass of the early depleted reservoir to some 70–75 per cent of the mass of the mantle, with the enriched reservoir thus making up some 25–30 per cent of the mass of the mantle. This option approaches the mantle compositional structure model proposed by Kellogg et al. (1999) where the portion of the mantle above a radius of approximately 1600 km contains the early depleted reservoir. In this case, the EER would be enriched in incompatible elements only by about a factor of two compared with the previous estimates of a chondritic primitive mantle (table 1; figure 5). For example, this ‘large’ EER would have an Nd concentration of 2.2 ppm with present-day $^{142}\text{Nd}/^{144}\text{Nd}$ of $-38$ ppm compared with the terrestrial Nd standard (table 1). For a more evolved average CC (Rudnick & Gao 2003), however, the mass of the early depleted reservoir would expand to most of the mantle, with the EER becoming quite small. As a result, the incompatible-element concentrations of this reservoir would increase until they reach similar concentrations to that of the CC by the time the EER shrinks to,
for example, the mass of the D'' layer at the base of the mantle, which corresponds to approximately 4 per cent of the mass of the mantle (figure 5). A D''-sized EER would have Nd concentrations of 8.9 ppm with present-day $^{142}\text{Nd}/^{144}\text{Nd}$ of $-54$ ppm compared with the terrestrial Nd standard (table 1).

Regardless of the size and composition of the EER, to mass-balance the early depleted reservoir back to a chondritic BSE composition requires the EER to contain more than 40 per cent of the Earth’s K, U and Th (Boyet & Carlson 2005). This reservoir thus would also contain most of the radiogenic $^{40}\text{Ar}$ missing from the Earth’s atmosphere (Allègre et al. 1983; Albarède 1998) and would have quite substantial internal heat production, approximately 9 TW currently. The latter point exacerbates the question of why the enriched reservoir has remained a missing reservoir for most of the Earth’s history. We can only speculate on this question at this point.

Figure 5. Estimated incompatible-element concentrations for a variety of terrestrial reservoirs including the CC (grey squares, Taylor & McLennan 1985; boxed squares, Rudnick & Gao 2003) and depleted MORB mantle (triangles, Boyet & Carlson 2006) in comparison with calculations of the composition for early formed incompatible-element-depleted (EDR) and -enriched (EER) reservoirs. The EDR volumes (74 per cent, crosses (+), Taylor & McLennan 1985; 100 per cent, crosses (×), Rudnick & Gao 2003) are adjusted for each estimate of CC composition in order to give a Sm/Nd ratio high enough to evolve an 18 ppm excess in $^{142}\text{Nd}/^{144}\text{Nd}$. Using the Rudnick & Gao (2003) estimate, even adding back a volume of depleted MORB mantle equal to the mass of the mantle cannot produce a sufficiently high Sm/Nd ratio. The degree of enrichment of the EER depends strongly on its size. The two patterns for the EER show the composition of EERs equal to 26 per cent (diamonds, complementary to the EDR formed by extraction of the Taylor & McLennan (1985) composition continent) and to 4 per cent (circles) of the mass of the whole mantle calculated using the Rudnick & Gao (2003) average crustal composition. The latter is roughly equal to the mass of the D'' layer.
Two factors that would minimize remixing of the enriched reservoir into the rest of the mantle are an intrinsically dense chemical composition and a low viscosity. Seismic examination of ultra-low-velocity zones found within the D" layer shows them to have P- and S-wave velocity reductions suggestive of the presence of 2–15 per cent partial melt in the ultra-low-velocity zones and as much as 0.5 per cent partial melt throughout the D" layer (Lay et al. 2004). For liquid to persist in the D" layer rather than settle to the bottom or float out of the layer, the liquid needs to be either neutrally buoyant or slightly denser than surrounding solids (Lay et al. 2004). Though much remains to be understood about the properties of melts at D" pressures and temperatures, the possibility that melts in the deep mantle are denser than coexisting solids has been discussed for some time (Brown et al. 1987; Agee & Walker 1993; Ohtani & Maeda 2001). A dense melt in the deep mantle also provides an interesting explanation for the initial formation of the EER from deep melts of the magma ocean that sank, rather than floated (Elkins-Tanton 2008). Residual melts representing the remains of a basal magma ocean that evolved by fractional crystallization during the Earth's history also could produce a dense, incompatible-element-rich, layer at the base of the mantle (Labrosse et al. 2007). Zhong & Hager (2003) showed that only approximately 1 per cent density difference is needed to allow a dense lower layer to persist at the core–mantle boundary over the age of the Earth, a possibility that is further enhanced if the lower layer has a low viscosity as a result of the presence of melt (Namiki 2003). The combination of high-density and low-viscosity melt would thus serve to explain why a layer with considerable internal heat generation could persist deep in the mantle.

6. Terrestrial variation in $^{142}\text{Nd}/^{144}\text{Nd}$ and implications for early mantle dynamics

Although presented at the end of this paper, the story of $^{142}\text{Nd}/^{144}\text{Nd}$ variation in the Earth actually began with the detection of significant excesses in $^{142}\text{Nd}/^{144}\text{Nd}$ in a small set of ancient rocks from Greenland (Bennett & McCulloch 1992; Harper & Jacobsen 1992; Sharma et al. 1996; Boyet et al. 2003; Caro et al. 2003, 2006; Boyet & Carlson 2006; Bennett et al. 2007). A variety of crustal rocks from Greenland, ranging in age from 3.85 to 3.6 Ga, display $^{142}\text{Nd}/^{144}\text{Nd}$ that ranges from 10 to 20 ppm higher than terrestrial standard Nd, or 28 to 38 ppm higher than chondritic. The variation in $^{142}\text{Nd}/^{144}\text{Nd}$ in terrestrial rocks provides unequivocal proof that differentiation of the Earth occurred while $^{146}\text{Sm}$ was present. The data also provide the strongest evidence yet for the presence of early formed incompatible-element-enriched and -depleted reservoirs within the Earth. By 3.85 Ga, $^{146}\text{Sm}$ had essentially decayed away. Consequently, the only way to change $^{142}\text{Nd}/^{144}\text{Nd}$ in mantle-derived rocks from that point on is to allow mixing between earlier formed reservoirs that grew distinct $^{142}\text{Nd}/^{144}\text{Nd}$ owing to the variations in Sm/Nd ratio while $^{146}\text{Sm}$ was still live.

Figure 6a illustrates a model that can explain the variation in $^{142}\text{Nd}/^{144}\text{Nd}$ in terrestrial rocks through the Archaean. To reach a $^{142}\text{Nd}/^{144}\text{Nd}$ 40 ppm higher than chondritic by 3.9 Ga requires a $^{147}\text{Sm}/^{144}\text{Nd} = 0.225$ assuming that this high Sm/Nd ratio was established at 4.568 Ga. Delaying formation of this high Sm/Nd ratio reservoir until 30 Ma after Solar System formation would increase

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the required $^{147}\text{Sm}/^{144}\text{Nd}$ to 0.23. If mixing between depleted and enriched reservoirs was occurring between 4.56 and 3.9 Ga, then an even higher Sm/Nd ratio would be required in the early depleted reservoir. At this point, it may be worth noting that the calculated source of 4.44 Ga rocks from the lunar highlands crust had a $^{147}\text{Sm}/^{144}\text{Nd}$ ratio between 0.218 and 0.229 (Boyet & Carlson 2007). While other explanations are possible, this similarity in Sm/Nd ratio between the early Moon and Earth could indicate that the Moon formed from, or at least equilibrated with (Pahlevan & Stevenson 2007), the early depleted reservoir on the Earth. If so, the initial Nd isotopic composition of these ancient lunar crustal rocks may provide a better measure of the initial Sm/Nd ratio of the early depleted reservoir on the Earth, as it would have avoided the mixing between enriched and depleted reservoirs described below. In the model shown in figure 6, starting at 3.9 Ga, the enriched and depleted reservoirs are allowed to mix at a rate of 10 per cent of the mass of the enriched reservoir per 100 Ma. This mixing rate is arbitrary, chosen only to produce a $^{142}\text{Nd}/^{144}\text{Nd}$ evolution that passes through the upper border of the data from 3.9 to 3.6 Ga in figure 6a. The mixing is then stopped at 3.5 Ga after only 50 per cent of the enriched reservoir has been assimilated into the depleted reservoir. When mixing with the enriched reservoir stops, the remaining depleted reservoir has a $^{147}\text{Sm}/^{144}\text{Nd}$ = 0.21 and a $^{142}\text{Nd}/^{144}\text{Nd}$ 18 ppm higher than chondritic.

Figure 6b then applies this model to the evolution of $^{143}\text{Nd}/^{144}\text{Nd}$ throughout the Earth’s history in comparison with the initial $^{143}\text{Nd}/^{144}\text{Nd}$ measured in a variety of mantle-derived rocks (Bennett 2003). As seen in figure 6b, the evolution lines calculated for $^{143}\text{Nd}/^{144}\text{Nd}$ do a reasonable job of passing through the upper

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Figure 6. (a,b) Possible Nd isotope evolution scenarios for the Earth’s interior. Stage 1 involves growth with $^{147}\text{Sm}/^{144}\text{Nd}$=0.235 from 4.568 Ga to 4.0 Ga. Stage 2 involves mixing of the early formed depleted and complementary enriched reservoirs formed at the Earth’s formation at a rate of 10 per cent of the mass of the enriched reservoir per 100 Ma. The composition of the enriched reservoir is calculated by mass balance so that the enriched and depleted reservoirs sum to a reservoir with chondritic relative abundances of refractory lithophile elements (McDonough & Sun 1995). The mixing stops at 3.5 Ga after which stage 3 evolves the $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic composition with $^{147}\text{Sm}/^{144}\text{Nd}$=0.21. Open circles, SW Greenland; filled grey circles, Narryer (W Australia); filled black circles, Baberton (S Africa). Data from Boyet et al. (2003), Caro et al. (2003, 2006), Boyet & Carlson (2006) and Bennett et al. (2007).
$^{143}\text{Nd}/^{144}\text{Nd}$ limit of the data, at least until post 1.0 Ga. Deviation of points below the evolution lines could simply reflect the assimilation of some older, low $^{143}\text{Nd}$, crustal material into the samples plotted in the figure. The deviation of the points above the calculated evolution line in the Earth’s recent history probably reflects the additional depletion of the mantle caused by continent extraction.

A speculative, but nevertheless interesting, connection between the isotopic evolution shown in figure 6 and models for magma ocean evolution link the rapid initial differentiation to solidification of the magma ocean on a time scale of millions to tens of millions of years. Recent models have shown that one outcome of magma ocean crystallization is a buoyantly unstable layering where dense Fe-rich late-stage cumulates overlie low-density Mg-rich cumulates (Elkins-Tanton et al. 2005). Buoyancy forces cause this layering to overturn rapidly, which produces an ‘inverted’ geotherm, with colder materials underlying hot material recently excavated from the deep interior. The system is then buoyantly stable until a normal geotherm is returned through internal heat production, at which point mantle convection can begin (Elkins-Tanton et al. 2005). Linking the period of $^{142}\text{Nd}/^{144}\text{Nd}$ growth in the early depleted reservoir between 4.56 and 3.9 Ga with the relatively quiescent period following overturn of the magma ocean cumulates is an attractive possibility. The reduction of $^{142}\text{Nd}/^{144}\text{Nd}$ that occurred between 3.9 and 3.6 Ga could then reflect an initially vigorous period of renewed mantle convection that dredged up some of the deep early formed enriched reservoir and mixed it back into the overlying early depleted reservoir.

7. Summary and conclusions

Primitive carbonaceous chondrites display isotopic anomalies in Nd and Sm that are best explained by incomplete mixing of various nucleogenic contributions to the solar nebula, but these anomalies are found neither in ordinary or enstatite chondrites nor in basaltic eucrites. Carbonaceous chondrites thus are not good choices to represent the building blocks of the Earth. Correcting for these nucleogenic anomalies, however, still leaves all terrestrial rocks with $^{142}\text{Nd}/^{144}\text{Nd}$ higher than observed in any chondrite, most likely as a result of the decay of $^{146}\text{Sm}$ in a portion of the Earth that has superchondritic Sm/Nd ratio.

Modelling the consequences of the early terrestrial differentiation implied by the $^{142}\text{Nd}/^{144}\text{Nd}$ data provides a number of new views on the compositional structure of the Earth’s interior. These include the following.

— If a chondritic primitive reservoir exists within the Earth’s mantle, it has not contributed to the formation of any rock yet measured on the Earth.
— Both the continental and oceanic crusts were derived from the incompatible-element-depleted reservoir formed shortly after the Earth’s formation. The mass balance relating CC and the mantle source of MORB suggests that this early formed incompatible-element-depleted reservoir occupies between 75 and 100 per cent of the mantle.
— The association of low $^{4}\text{He}/^{3}\text{He}$ with superchondritic $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ in hot-spot-related ocean island basalts is consistent with them sampling the early depleted reservoir and suggests that some of this material, only slightly affected by continent extraction and recycling, still exists within the Earth’s interior.
— The mantle source of MORB is not as incompatible-element depleted as assumed in models that create the MORB source from extraction of the CC from a primitive mantle with chondritic relative abundances of the incompatible elements.

— If the bulk Earth has chondritic relative abundances of refractory lithophile elements, there must exist within the Earth’s interior an incompatible-element-enriched reservoir that contains roughly 40 per cent of the Earth’s $^{40}$Ar and radioactive heat-generation capacity. Variation in $^{142}$Nd/$^{144}$Nd in the early Archaean rocks shows that this enriched reservoir existed through at least the Archaean. If some of this reservoir remains, it must be trapped deep within the Earth in order to remain unsampled by surface volcanism for the last 3.5 Ga. Seismological characteristics of the D$^0$ layer at the base of the mantle along with the possibility that melt at this depth is of similar or higher density, and lower viscosity, than the surrounding solids offer the mechanisms of both the formation and the survival of a deep incompatible-element-rich reservoir.

The Nd evidence for early and global chemical differentiation of the Earth stresses the need for better understanding of the physical consequences of early extensive melting of the planet. Though detailed petrological and geodynamic models exist for the evolution of magma oceans on small planetary objects such as Mars (Elkins-Tanton et al. 2005) and the Moon (Ringwood & Kesson 1976; Longhi 1977; Elkins-Tanton et al. 2002), much work remains to understand the crystallization sequence, melt–solid relative densities and the consequences of vigorous convection (Tonks & Melosh 1990) on differentiation and mixing during evolution of a terrestrial magma ocean that extends to much higher pressures and temperatures than found on small planetary objects. The Nd results discussed here provide an example of the potential for early planetary differentiation to determine the compositional and dynamic history of the terrestrial planets.

**References**


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