Early Silicate Earth Differentiation

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Abstract

The discovery of small ^{142}Nd anomalies in early Archean rocks has brought about a revolution in our understanding of early planetary differentiation processes. ^{142}Nd is a radiogenic isotope produced by the decay of now-extinct ^{146}Sm in crustal and mantle reservoirs. Given that ^{142}Nd heterogeneities can be produced only prior to 4.2 Gya, this short-lived chronometer provides selective information on the very early evolution of primordial silicate reservoirs. This information is particularly crucial for Earth, where the fingerprints of the earliest crustal formation processes have been almost entirely erased from the geological record. This article reviews the history of the field, from the pioneering applications of the ^{147}Sm-^{143}Nd and ^{146}Sm-^{142}Nd systems to ancient crustal rocks, to the more recent insights gained from application of ^{146}Sm-^{142}Nd to meteorites and lunar samples.

1. INTRODUCTION

REE: rare earth element

The first hundred million years of planetary evolution were punctuated by highly energetic collisions between Moon-to-Mars-sized embryos (Chambers 2001, Chambers 2004). These giant impacts likely created global magma oceans on the accreting planets (Benz & Cameron 1990, Melosh 1990) and thus provided the energy required for differentiating planetary mantles. In small bodies such as the Moon and Mars, these early events were recorded by radiogenic isotope systems, which point to very early (4.4–4.5 Gya) formation of mantle and crustal reservoirs (e.g., Blichert-Toft et al. 2002, Borg & Draper 2003, Debaille et al. 2008, Elkins-Tanton et al. 2003, Snyder et al. 2000, Taylor et al. 2009). On Earth, however, continuous exchanges between the mantle and crust have led to apparently complete rejuvenation of the surface over the past 4.5 Ga (Condie 2000). As a result, the isotopic and chemical heterogeneities observed in modern mantle-derived rocks reflect later production and recycling of continental and oceanic crust through geological time (Allegre et al. 1980, Armstrong 1968, Hofmann 1988) and bear no relation to primordial mantle differentiation processes.

Despite the homogenizing effect of crustal recycling and mantle convection, isotopic heterogeneities resulting from primordial differentiation of Earth's mantle were not completely erased from the geological record. Small isotopic anomalies, created by radioactive decay in Hadean (4–4.5 Gya) silicate reservoirs, have been sampled by Archean magmatism and preserved in these ancient rocks long after the early terrestrial crust had disappeared. These isotopic signatures can be used to date the formation of these now vanished reservoirs and to quantify their interactions through geological time. This chronological information provides key constraints on early crustal formation processes that would otherwise remain inaccessible owing to the lack of a preserved Hadean rock record.

The most commonly employed isotope systems for studying early silicate Earth differentiation are the ^{147}Sm-^{143}Nd and ^{146}Sm-^{142}Nd chronometers. These systems regularly exhibit sufficient parent-daughter fractionation during partial melting so as to allow isotopic differences to develop in planetary reservoirs. In addition, they have quite different half-lives, which make them sensitive to processes that took place at different periods of Earth's history. The ^{147}Sm-^{143}Nd chronometer, with a half-life of 103 Ga, provides an integrated record of mantle-crust evolution over the past 4.5 Ga, whereas the short-lived ^{146}Sm-^{142}Nd chronometer provides selective information on very early events (>4.2 Gya). Applied together, the ^{147}Sm-^{143}Nd and ^{146}Sm-^{142}Nd systems represent a powerful tool for unraveling the chronology and nature of early mantle-crust differentiation processes.

This review begins with an examination of commonly accepted ^{147}Sm-^{143}Nd constraints on the evolution of the mantle-crust system over the past 4.5 Ga. The fundamental aspects of ^{147}Sm-^{143}Nd geochemistry are reviewed, with emphasis on unresolved issues raised by the Archean ^{143}Nd record. These questions are addressed in light of recent advances in the application of the ^{146}Sm-^{142}Nd system, which provide a new way of estimating the age of differentiation of primordial silicate reservoirs and shed light on the dynamics of the mantle-crust system during the first billion years of Earth history. The last part of this review covers the ^{142}Nd record of meteorites and lunar samples, and discusses the implications of very early differentiation processes with regard to the structure and bulk composition of the silicate Earth.

2. Nd ISOTOPE ESSENTIALS

2.1. Chronometric Equations

Sm is an intermediate rare earth element (REE) with seven isotopes, four of which are radioactive: The long-lived ^{147}Sm α-decays to ^{143}Nd with a half-life of 103 Ga, and now-extinct ^{146}Sm, with a shorter half-life of 106 Ma, decayed into ^{142}Nd (Audi et al. 1997). ^{148}Sm and ^{149}Sm are also radioactive, decaying to ^{144}Nd and ^{145}Nd, respectively, but their half-lives are too long to generate detectable radiogenic effects in planetary materials. The chronometric equation describing the closed-system evolution of the ^{143}Nd/^{144}Nd ratio in reservoir i can be obtained from the following mass balance relationship:

$$^{147}\mathrm{Sm}_{t_p} + {}^{143}\mathrm{Nd}_{t_p} = {}^{147}\mathrm{Sm}_t + {}^{143}\mathrm{Nd}_t, \tag{1}$$

where t is time running forward from the origin of the solar system ($t_0 = 0$) to the present day [$t_p = 4.567$ Ga (Bouvier et al. 2007)]. Substituting $^{147}\mathrm{Sm}_t = {}^{147}\mathrm{Sm}_{t_p} e^{\lambda_{147}(t_p - t)}$ into Equation 1 yields the following expression:

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)^i_t = \left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)^i_{t_p} + \left(\frac{^{147}\mathrm{Sm}}{^{144}\mathrm{Nd}}\right)^i_{t_p} (1 - e^{-\lambda_{147}(t_p - t)}), \tag{2}$$

where $\lambda_{147} = 6.53 \times 10^{-3}$ Ga^{-1} is the decay constant of ^{147}Sm. This standard chronometric equation can be used for any radiogenic system in which the parent nuclide is extant (e.g., ^{87}Rb-^{87}Sr, ^{176}Lu-^{176}Hf). For a short-lived radioactivity such as ^{146}Sm ($\lambda_{146} = 6.74$ Ga^{-1}), the present-day parent/daughter isotopic ratio (i.e., ^{146}Sm/^{144}Nd) is almost zero, and thus isotope evolution needs to be expressed relative to initial solar system parameters,

$$\left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)^i_t = \left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)^i_{t_0} + \left(\frac{^{146}\mathrm{Sm}}{^{144}\mathrm{Nd}}\right)^i_{t_0} (1 - e^{-\lambda_{146} t}). \tag{3}$$

The general chronological equation for the ^{146}Sm-^{142}Nd system is then obtained by decomposing $(^{146}\mathrm{Sm}/^{144}\mathrm{Nd})^i_{t_0}$ into readily measurable parameters,

$$\left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)^i_t = \left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{t_0} + \left(\frac{^{146}\mathrm{Sm}}{^{144}\mathrm{Sm}}\right)_{t_0} \left(\frac{^{144}\mathrm{Sm}}{^{147}\mathrm{Sm}}\right)_{t_p} \left(\frac{^{147}\mathrm{Sm}}{^{144}\mathrm{Nd}}\right)^i_{t_p} (1 - e^{-\lambda_{146} t}), \tag{4}$$

where $(^{146}\mathrm{Sm}/^{144}\mathrm{Sm})_{t_0} = 0.0085 \pm 0.0007$ is the initial abundance of ^{146}Sm in the early solar system (Boyet et al. 2010), and $(^{144}\mathrm{Sm}/^{147}\mathrm{Sm})_{t_p} = 0.20454$. The present-day parent/daughter ratio in reservoir i is usually expressed as ^{147}Sm/^{144}Nd (instead of ^{144}Sm/^{144}Nd) to maintain consistency with the ^{147}Sm-^{143}Nd chronometric equation (Equation 2).

2.2. Geochemical Properties

The Sm-Nd isotopic schemes present ideal properties for tracing the evolution of differentiated silicate reservoirs (e.g., DePaolo & Wasserburg 1976, Jacobsen & Wasserburg 1979). Both elements are refractory and lithophilic; as a result, the Sm/Nd ratio is not affected by metal-silicate segregation, and volatility-controlled fractionation is limited to high-temperature processes (Boynton 1975, Davis & Grossman 1979). On planetary scales, Sm/Nd fractionation occurs during partial melting and fractional crystallization related to crustal formation and differentiation. As Sm and Nd are both incompatible, they are enriched in partial melts and depleted in solid residues, so planetary crusts concentrate a large budget of these elements (Hofmann 1988, Taylor & McLennan 1985). Nd has a larger ionic radius and is therefore more incompatible than Sm. Consequently, crustal reservoirs have lower Sm/Nd ratios than their complementary depleted mantles (DMs). Closed-system evolution of differentiated silicate reservoirs will, therefore, result in the development of distinct radiogenic ^{143}Nd/^{144}Nd signatures. If differentiation took place prior to extinction of ^{146}Sm (that is, >4.2 Gya), ^{143}Nd/^{144}Nd heterogeneities will be associated with variations in the ^{142}Nd/^{144}Nd ratio, which are often referred to as ^{142}Nd anomalies.

By convention, variations in $^{142}Nd/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios in planetary reservoirs are expressed in parts per 10,000 relative to a reference isotopic ratio, using the epsilon notation,

CHUR: chondritic uniform reservoir

BSE: bulk silicate Earth

$$\varepsilon^{142,143}\mathrm{Nd} = \left[\frac{(^{142,143}\mathrm{Nd}/^{144}\mathrm{Nd})_i}{(^{142,143}\mathrm{Nd}/^{144}\mathrm{Nd})_{Ref}} - 1\right] \times 10^4. \quad (5)$$

For the ^{147}Sm-^{143}Nd system, the reference ratio for normalization is the chondritic composition [labeled CHUR for chondritic uniform reservoir (DePaolo & Wasserburg 1976)]. For the ^{146}Sm-^{142}Nd system, the convention is to use a terrestrial standard for normalization so that the present-day mantle and crust have, by definition, $\varepsilon^{142}Nd = 0$.

3. THE ^{147}Sm-^{143}Nd SYSTEM AS A TRACER OF MANTLE-CRUST EVOLUTION

3.1. Early Developments

The ^{147}Sm-^{143}Nd isotope system was first developed as a chronometer for dating basaltic achondrites (Lugmair & Scheinin 1975). In comparison with the Rb-Sr system, which was already successfully applied as a dating technique, application of the Sm-Nd scheme was viewed as more challenging, owing to the limited range of Sm/Nd fractionation in planetary material. Two important properties of the Sm-Nd chronometer, however, motivated its application to problems linked to mantle-crust differentiation. First, in contrast to more volatile elements such as Rb, Sm and Nd were not significantly affected by cosmochemical fractionation in the solar nebula (Larimers & Anders 1967, Wasson & Chou 1974). Their relative abundance in chondrites is constant, averaging $^{147}Sm/^{144}Nd = 0.1966 \pm 0.004$ (Bouvier et al. 2008, Jacobsen & Wasserburg 1984, Patchett et al. 2004), and this chondritic value is indistinguishable from the solar composition within the $\pm 7\%$ uncertainty of photosphere estimates (Asplund et al. 2006). It was thus conservatively assumed that the bulk silicate Earth (BSE) and other terrestrial planets had perfectly chondritic Sm/Nd and $^{143}Nd/^{144}Nd$ ratios. As discussed in Section 5, this assumption is now being reconsidered in light of recent evidence from the ^{146}Sm-^{142}Nd system. However, for the past 30 years, the CHUR parameters have provided an important reference for the interpretation of isotopic signatures in planetary reservoirs, in terms of enrichment or depletion relative to a primitive mantle (PM) (e.g., DePaolo 1980; DePaolo & Wasserburg 1976, 1979; Jacobsen 1988; Jacobsen & Wasserburg 1979; Richard et al. 1976).

A second advantage of the Sm-Nd system lies in its relative resistance to element redistribution during metamorphism, which allows the precise determination of the initial isotopic composition of ancient rocks at the time of their formation (e.g., Basu et al. 1984, Blichert-Toft et al. 1999, Moorbath et al. 1997, Shirey & Hanson 1986, Wilson & Carlson 1989). The initial $^{143}Nd/^{144}Nd$ composition (henceforth noted $\varepsilon^{143}Nd_{initial}$) can be obtained from the *y*-intercept of a whole-rock isochron or from back-calculating in situ ^{147}Sm decay at the supposed age of crystallization. This initial isotopic signature reflects both the Sm/Nd ratio and the Nd residence time in the mantle or crustal reservoir from which the parental magmas are derived. Juvenile rocks derived from a DM will have positive $\varepsilon^{143}Nd_{initial}$, whereas a negative $\varepsilon^{143}Nd_{initial}$ reflects melting or assimilation of a preexisting crustal component.

The pioneering results obtained by DePaolo & Wasserburg (1976) suggested that $\varepsilon^{143}Nd_{initial}$ values in Archean and Proterozoic rocks were close to that expected for a PM with chondritic Sm/Nd and $^{143}Nd/^{144}Nd$ ratios. These authors concluded that either Earth's mantle had not experienced very early differentiation, or ancient crustal and mantle reservoirs were remixed prior to

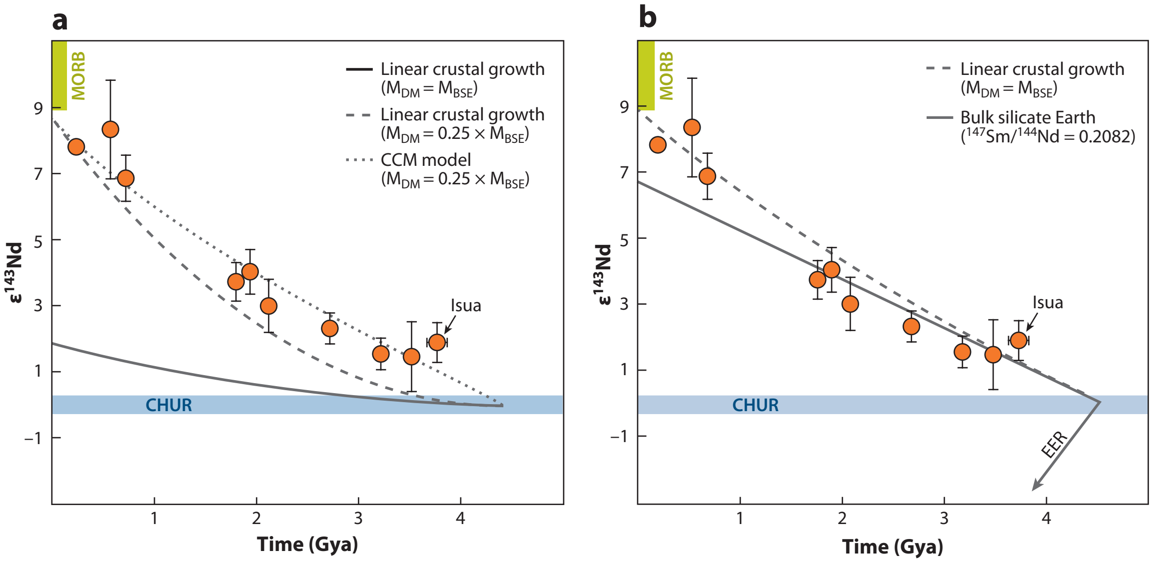

Figure 1

$\varepsilon^{143}Nd_{initial}$ in juvenile mafics and ultramafic rocks (*orange circles*), from 3.8 Gya to present [data from Basu et al. (1984), Lahaye et al. (1995), Polat & Munker (2004), Shirey & Hanson (1986), Vervoort & Blichert-Toft (1999), Vervoort et al. (1994), Wilson & Carlson (1989)]. The trend toward increasingly radiogenic signatures indicates derivation from a mantle reservoir with a Sm/Nd ratio 5–10% higher than the chondritic uniform reservoir (CHUR). (*a*) The standard interpretation is that the observed trend reflects continuous crustal formation from a chondritic primitive mantle. This model, however, provides a good fit to ^{143}Nd data only if the depleted mantle (DM) represents less than 25% of the bulk silicate Earth (BSE). Extraction of the present-day continental mass from the entire mantle would generate much smaller radiogenic effects in the depleted reservoir. This model also fails to account for the radiogenic $\varepsilon^{143}Nd_{initial}$ in the oldest rocks (Caro & Bourdon 2010). Armstrong (1991) interpreted this as reflecting rapid growth of the continental crust prior to 4 Gya and subsequent evolution in steady state until the present day. Similar to the standard growth model, Armstrong's Constant Crustal Mass (CCM) model can generate the observed isotopic evolution only if the upper mantle has remained separated from the lower mantle for >4 Ga. (*b*) ε^{143}Nd evolution of the primitive mantle and DM assuming a superchondritic composition for the BSE ($^{147}Sm/^{144}Nd = 0.2082$; $\varepsilon^{143}Nd = +6.9$) resulting from the loss of an early enriched reservoir (EER) at an early stage of Earth's formation (see discussion in Section 5). The predicted evolution matches that defined by juvenile rocks until 2 Gya, after which the DM deviates toward increasingly radiogenic ε^{143}Nd. In this nonchondritic Earth model, continuous extraction of the continental mass from the whole mantle can account for this deviation, without the need to call upon massive early crustal growth (Caro & Bourdon 2010). Abbreviation: MORB, mid-ocean ridge basalt.

the formation of the oldest cratons. In retrospect, the alignment of $\varepsilon^{143}Nd_{initial}$ along the CHUR evolution line was fortuitous, as it is now well established that mafic rocks as old as 3.8 Ga have positive $\varepsilon^{143}Nd_{initial}$ values (e.g., Blichert-Toft et al. 1999, Moorbath et al. 1997). As shown in **Figure 1*a***, juvenile rocks display increasingly radiogenic $\varepsilon^{143}Nd_{initial}$ values through time, indicating their extraction from a depleted reservoir with an Sm/Nd ratio 5–10% higher than chondritic. The roughly chondritic $\varepsilon^{143}Nd_{initial}$ reported in early studies reflected mixtures between mantle-derived magmas and the unradiogenic crustal material, and had no significance in terms of bulk terrestrial composition.

Despite the early recognition that no terrestrial reservoir had evolved along the isotopic evolution line predicted for CHUR, the chondritic BSE hypothesis remained a cornerstone of models of crustal evolution and chemical geodynamics (e.g., Albarede & Rouxel 1987, Allegre 1982, Jacobsen 1988, Zindler & Hart 1986). An important result of early Sm-Nd investigations was

MORB: mid-ocean ridge basalt

CMB: core-mantle boundary

that mid-ocean ridge basalts (MORBs) have positive ε^{143}Nd values between +7 and +12, indicating extraction from a mantle reservoir with a time-integrated depletion history (DePaolo & Wasserburg 1976, Richard et al. 1976, Salters & Stracke 2004). This, in turn, requires that a significant budget of trace elements was extracted from the mantle and isolated in a long-lived reservoir with low Sm/Nd and subchondritic ε^{143}Nd. The continental crust, with a mean age of 2 Ga and ε^{143}Nd of −15, satisfies all these constraints (Jacobsen & Wasserburg 1979, McCulloch & Wasserburg 1978, Taylor et al. 1983). Thus, for the past 30 years, continuous crustal growth has been widely considered to be the major cause of the chemical and isotopic evolution of the mantle (Hofmann 1988, Jacobsen 1988, Jacobsen & Wasserburg 1979).

3.2. Unresolved Issues

Two observations sharply contradict the standard mantle-crust evolution model. First, the ubiquity of positive $\varepsilon^{143}Nd_{initial}$ in the most ancient crustal rocks indicates that the sampled upper mantle had experienced depletion in incompatible elements several hundred million years prior to the stabilization of the oldest cratons (e.g., Bennett et al. 1993, Moorbath et al. 1997). Because the present-day continental mass contains only a negligible amount of pre-3-Ga-old terranes (Condie 2000), the formation of the continents as we observe them today cannot account for large-scale mantle depletion in the early Archean. This implies either that the volume of the early Archean crust was much larger in the past or that an early (>4 Gya) event depleted Earth's mantle prior to the onset of continental growth.

The second challenge to the standard model is that the present-day crust does not contain a large enough budget of REEs to balance the radiogenic ε^{143}Nd measured in MORBs, unless the MORB source represents less than 25% of the total mass of the mantle (Caro & Bourdon 2010, DePaolo 1980, Jacobsen & Wasserburg 1979). Extraction of the continental crust from the whole mantle would generate only a small radiogenic effect of +2 in the DM (**Figure 1*a***), far below the observed MORB value of +9 (Salters & Stracke 2004). This observation was first interpreted as evidence for layered mantle convection with strict separation at the 660-km discontinuity (Allegre 1982). The requirement for a less degassed reservoir to account for the low flux of ^{4}He from the mantle (O'Nions & Oxburgh 1983) and to satisfy argon mass balance constraints (Allegre 1982, Allegre et al. 1996) also supported the idea of a primitive lower mantle. However, this model fell into disfavor as tomographic imaging of the deep mantle showed evidence for vertical exchanges through the 660-km discontinuity (e.g., Grand 2002, Montelli et al. 2004), lending support to whole-mantle convection models. Although these observations do not preclude the existence of a deep primitive reservoir, they demonstrate that the lower mantle is not completely isolated from the upper mantle. The striking absence of primitive trace element or isotopic ratios in oceanic island basalts (Hofmann et al. 1986, Zindler & Hart 1986), including those originating from deep mantle plumes (Montelli et al. 2004), precludes a simple model of layered convection with a chondritic lower mantle.

The requirement for a DM reservoir in the early Archean quickly became a cornerstone of the Big Bang model of crustal growth (Armstrong 1981), also known as the Constant Crustal Mass model. Armstrong (1991) showed that positive ε^{143}Nd values in the Archean mantle can be explained by this end-member scenario, whereby a continental mass similar to that of the present day already was formed by 4 Gya and has since remained in a steady state under balanced production and recycling fluxes (see Harrison 2009 for a review). Alternative models involving permanent or transient storage of a Hadean mafic crust at the core-mantle boundary (CMB) were also shown to provide a satisfying fit to ^{143}Nd data (Chase & Patchett 1988, Galer & Goldstein 1991, Tolstikhin et al. 2006). Although these models involve very different processes, they have one important feature in common: They call for the creation of long-lived enriched reservoirs at a very early stage of Earth's evolution. This leads to a paradoxical observation: Although the isotopic and chemical heterogeneities in oceanic basalts reflect mantle-crust exchanges in relatively recent times (Allegre et al. 1980, Christensen & Hofmann 1994, Sun 1980, Tatsumoto 1978), the main features of ^{147}Sm-^{143}Nd systematics in the silicate Earth appear to result from a much earlier event (>4 Gya). This apparent paradox is most evident when considering hidden reservoir models. For example, Tolstikhin et al. (2006) suggested that the D″ layer formed through recycling of a dense basaltic proto-crust immediately following Earth's accretion. These authors estimated that the recycling of 25×10^{27} g of komatiitic crust (the approximate mass of D″) would satisfy Nd mass balance constraints and account for the isotopic evolution of the DM, without the need to call upon layered mantle convection. This reservoir, therefore, would represent 10 times the mass of the continental crust and concentrate 25% of the total REE budget of the silicate Earth. An outstanding question thus arises as to why heterogeneities found in oceanic island basalts are dominated by the recycling of continental and oceanic crust, whereas the geochemical signature of the much larger hidden reservoir is so strikingly absent from mantle plumes thought to originate at the CMB.

EDM: early depleted mantle

4. THE TERRESTRIAL ^{146}Sm-^{142}Nd RECORD: ZOOMING IN ON EARLY EVENTS

4.1. The Coupled ^{146,147}Sm-^{142,143}Nd Chronometer

The main difficulty in testing models of early mantle-crust evolution lies in the poor chronological resolution of the ^{147}Sm-^{143}Nd system. This limitation can be illustrated in the context of a two-stage model of mantle-crust evolution (**Figure 2*a***). In this simple model, a PM experiences instantaneous differentiation at $t = t_{\mathrm{d}}$, leading to the formation of an enriched crust and one or several depleted reservoirs. During the second stage ($t > t_{\mathrm{d}}$), differentiated reservoirs evolve as closed systems (i.e., there is no further recycling or crustal growth after t_{d}). The ^{143}Nd/^{144}Nd evolution of an early depleted mantle (EDM) can then be derived from Equation 2:

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_t^{\mathrm{EDM}} = \left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{t_{\mathrm{p}}}^{\mathrm{PM}} + \left(\frac{^{147}\mathrm{Sm}}{^{144}\mathrm{Nd}}\right)_{t_{\mathrm{p}}}^{\mathrm{PM}} [1 - e^{\lambda_{147}(t_{\mathrm{p}}-t_{\mathrm{d}})}] + \left(\frac{^{147}\mathrm{Sm}}{^{144}\mathrm{Nd}}\right)_{t_{\mathrm{p}}}^{\mathrm{EDM}} [e^{\lambda_{147}(t_{\mathrm{p}}-t_{\mathrm{d}})} - e^{\lambda_{147}(t_{\mathrm{p}}-t)}]. \quad (6)$$

From Equation 6, it is apparent that the isotopic composition of the EDM at a given time is not only dependent on the age of differentiation of the mantle (t_{d}) but also on the extent of Sm/Nd fractionation during differentiation [i.e., $(^{147}\mathrm{Sm}/^{144}\mathrm{Nd})^{\mathrm{EDM}}$]. The latter cannot be measured directly because mantle-crust exchanges for the past 4.5 Ga have long erased the geochemical fingerprint of the earliest crust. Therefore, the ^{147}Sm-^{143}Nd chronometric equation of the EDM is underconstrained, preventing an accurate determination of t_{d}.

This limitation prompted the development, in the mid-1990s, of the short-lived ^{146}Sm-^{142}Nd chronometer (Harper & Jacobsen 1992). With a half-life of 106 Ma, ^{146}Sm can be considered extinct after only 500 Ma. This isotope system thus provides a selective record of mantle-crust differentiation processes that took place prior to 4.2 Gya. Lugmair et al. (1983) demonstrated the presence of ^{146}Sm in the early solar system, reporting large ^{142}Nd excesses from α-recoil in carbon-chromite fractions of the Allende meteorite. The initial ^{146}Sm/^{144}Sm ratio was then estimated more precisely using mineral isochrons in chondrites and achondrites, yielding a value of 0.0085 ± 0.0007 (Boyet et al. 2010, Lugmair & Galer 1992, Prinzhofer et al. 1992).

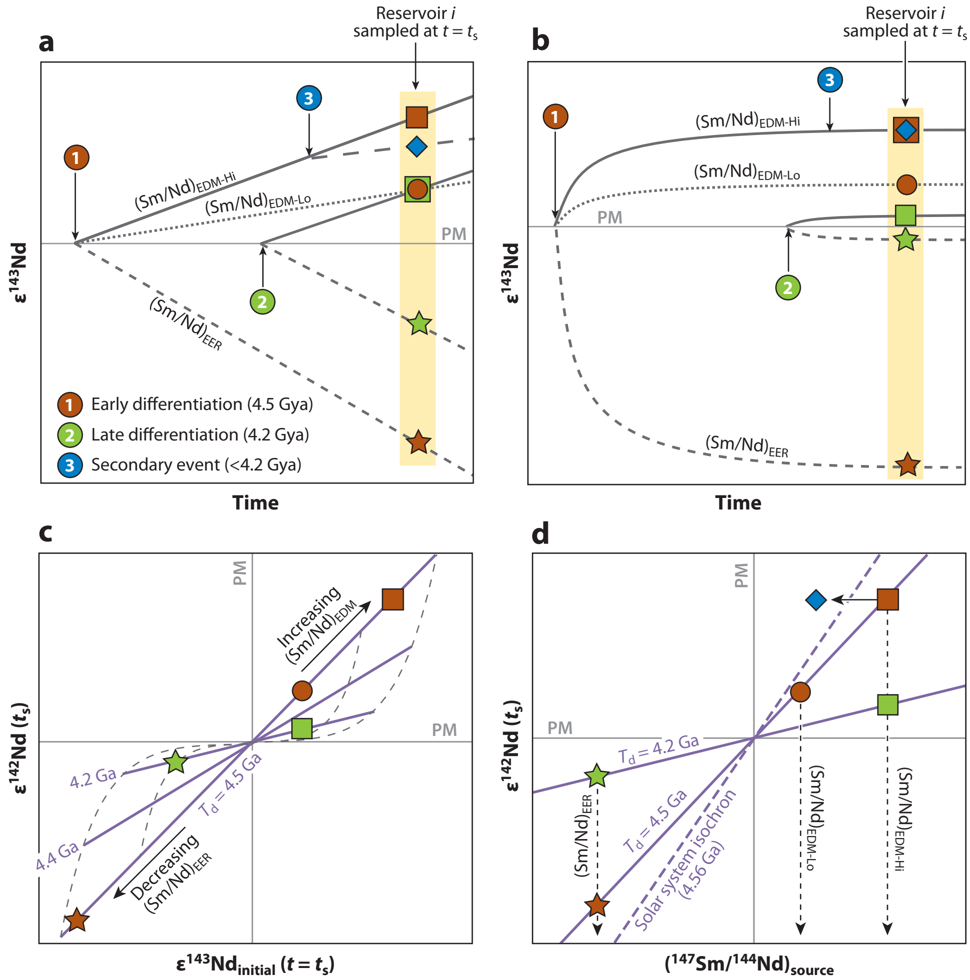

Figure 2

Illustration of the two-stage model of isotopic evolution for the coupled ^{146,147}Sm-^{142,143}Nd chronometer. The model assumes instantaneous differentiation 4.5 Gya and 4.2 Gya, corresponding to $t_d = 0.06$ Ga and 0.36 Ga after solar system formation, respectively, for two early depleted mantle (EDM) reservoirs (labeled EDM-Hi and EDM-Lo) and a complementary early enriched reservoir (EER). A case illustrating the effect of late (<4.2 Gya) disturbance of the Sm-Nd systems is also shown. (*a*) Because of its long half-life, the ^{147}Sm-^{143}Nd system does not provide precise chronological information. Positive $\varepsilon^{143}\text{Nd}_{\text{initial}}$ in the early Archean mantle could reflect formation of a highly depleted mantle during a late (4.2 Gya) event or more moderate mantle depletion at an earlier (4.5 Gya) stage. (*b*) The ^{146}Sm-^{142}Nd chronometer, with a shorter half-life, is more sensitive to small time differences, which allows the two aforementioned scenarios to be distinguished. In addition, the ^{142}Nd composition of crustal rocks should be less sensitive to late (<4.2 Gya) metamorphic disturbance compared with their ^{143}Nd signature. (*c*) By coupling both isotope systems, a model age of differentiation T_d can be estimated (T is time running backward from the present day to the origin of the solar system, so that $T_d = 4.567 - t_d$). This also provides an estimate of the Sm/Nd ratio in the parent reservoir. (*d*) ^{142}Nd data are often represented in planetary isochron diagrams. Here the ε^{142}Nd values of the rocks are plotted against the ^{147}Sm/^{144}Nd ratio of their mantle (or crustal) source reservoir, which is estimated directly using the initial ^{143}Nd/^{144}Nd composition of the rock. Planetary isochrons resulting from crystallization of global magma oceans should intersect the solar system isochron at a composition corresponding to that of the primitive mantle (PM). This method can be used to test compositional models for the terrestrial planets.

Because the ^{146}Sm-^{142}Nd system shares the same properties as the ^{147}Sm–^{143}Nd couple (**Figure 2*b***), a chronometric equation similar to that derived above can be obtained for the ^{142}Nd/^{144}Nd evolution of the EDM:

$$\left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_t^{\mathrm{EDM}} = \left(\frac{^{142}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{t_\mathrm{p}}^{\mathrm{PM}} + \frac{(^{146}\mathrm{Sm}{}^{144}\mathrm{Sm})_{t_0}}{(^{147}\mathrm{Sm}/^{144}\mathrm{Sm})_{t_\mathrm{p}}} \left[\begin{array}{l} \left(\frac{^{147}\mathrm{Sm}}{^{144}\mathrm{Nd}}\right)_{t_\mathrm{p}}^{\mathrm{PM}} \times e^{-\lambda_{146} t_\mathrm{d}} \\ + \left(\frac{^{147}\mathrm{Sm}}{^{144}\mathrm{Nd}}\right)_{t_\mathrm{p}}^{\mathrm{EDM}} \times [e^{-\lambda_{146} t_\mathrm{d}} - e^{-\lambda_{146} t}] \end{array}\right]. \quad (7)$$

By combining both chronometers, one obtains a system of two equations (Equations 6 and 7) from which both the age of differentiation (t_d) and the ^{147}Sm/^{144}Nd ratio of the EDM can be estimated without assumptions regarding the composition of the early crust (**Figure 2*c*,*d***). It was therefore anticipated that this coupled ^{146,147}Sm-^{142,143}Nd chronometer would provide a means of distinguishing differentiation resulting from magma ocean crystallization from that produced by later crustal growth.

4.2. The Archean ^{146}Sm-^{142}Nd Record

Harper & Jacobsen (1992) presented the first attempt to measure the ^{142}Nd composition of terrestrial rocks. These authors reported a positive anomaly of 33 ppm in a volcaniclastic metasediment from the Isua Greenstone Belt (3.8 Gya, West Greenland). Using the coupled ^{146,147}Sm-^{142,143}Nd chronometer, Harper & Jacobsen concluded that Earth's mantle had experienced global differentiation immediately following accretion. However, these results were met with skepticism after several groups reported normal ^{142}Nd compositions for early Archean rocks at a ± 20 ppm level of precision (Goldstein & Galer 1992, McCulloch & Bennett 1993, Regelous & Collerson 1996). Subsequently, Sharma et al. (1996) showed that a ^{142}Nd excess in Harper & Jacobsen's sample could not be ruled out but that the uncertainty quoted by the authors was probably underestimated.

When a more precise thermal ionization mass spectrometer was developed in the early 2000s, it became possible to break the 20 ppm precision barrier of the previous generation of instruments and resolve effects of >5 ppm on the ^{142}Nd/^{144}Nd ratio (Caro et al. 2003). The first high-precision ^{142}Nd study was conducted on early Archean metasediments from the Isua Greenstone Belt characterized by a positive $\varepsilon^{143}\mathrm{Nd}_{\mathrm{initial}}$ of $+1.9 \pm 0.6$ (Caro et al. 2003, 2006). The results showed a ubiquitous ^{142}Nd anomaly of 15 ± 6 ppm compared with modern oceanic basalts. Further analyses revealed that the lithologies from the Isua Greenstone Belt and West Greenland craton exhibit slightly different ^{142}Nd signatures ranging from +7 ppm for 3.65-Ga-old tonalites to +20 ppm for >3.85-Ga-old amphibolites (Bennett et al. 2007, Boyet & Carlson 2006, Boyet et al. 2004, Caro et al. 2006). Larger effects (>20 ppm) were not confirmed, as high-precision analyses of Harper & Jacobsen's (1992) sample showed no detectable excess at the ± 10 ppm level of precision (Papanastassiou et al. 2003).

Two recent studies also reported negative ^{142}Nd anomalies, indicating the preservation of Hadean crustal components in early Archean terranes. O'Neil et al. (2008) first measured ε^{142}Nd values down to −15 ppm in mafic amphibolites and felsic gneisses from the Nuvvuagittuq Greenstone Belt (NGB, Quebec). In contrast to West Greenland rocks, ^{142}Nd effects in NGB rocks display a well-defined correlation with their Sm/Nd ratio (**Figure 3**). The debate has centered on the significance of this correlation. If interpreted as an isochron, a crystallization age of $4{,}280^{+53}_{-81}$ Ma can be estimated for the protolith of the faux amphibolite, making the NGB the oldest (oceanic) crustal sequence preserved on Earth. This age, however, is significantly older than the ^{147}Sm-^{143}Nd age of $3{,}819 \pm 270$ Ma defined by the amphibolite (O'Neil et al. 2008). Similarly,

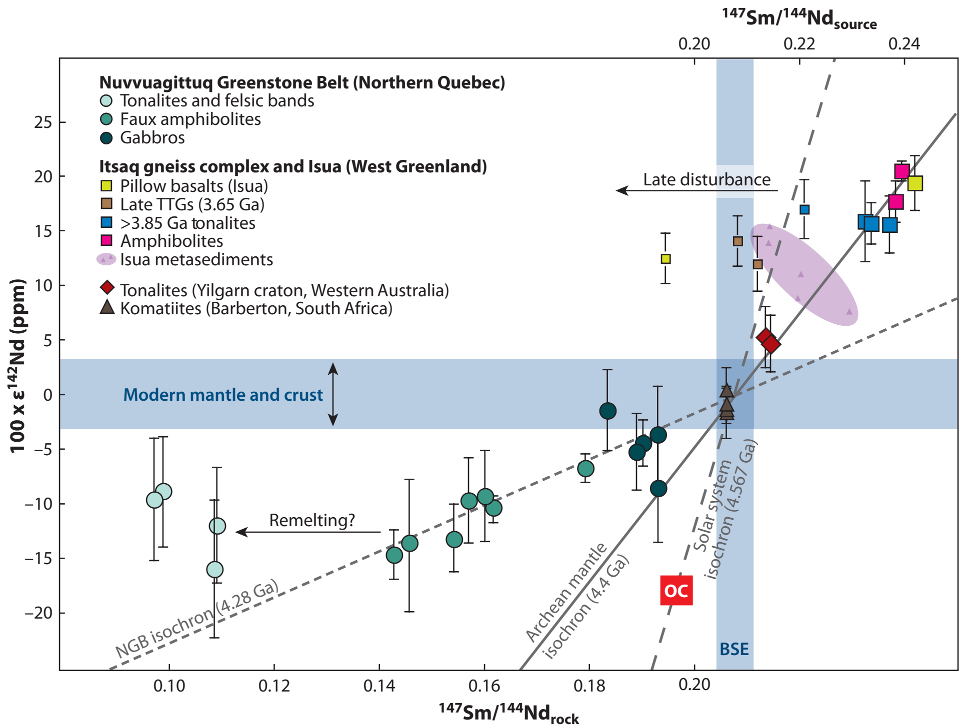

Figure 3

Coupled ^{146,147}Sm-^{142,143}Nd systematics in early Archean rocks from the West Greenland and Yilgarn cratons (Bennett et al. 2007, Caro et al. 2006), Barberton komatiites (Caro et al. 2006), and the Nuvvuagittuq Greenstone Belt (NGB; O'Neil et al. 2008). ε^{142}Nd values in NGB samples are plotted against their respective ^{147}Sm/^{144}Nd ratios. If interpreted as an isochron, the trend defined by the faux amphibolites and gabbros defines an age of 4.28 Ga. For early Archean rocks from West Greenland and the Yilgarn Craton, positive anomalies are inherited from a depleted mantle source. Therefore, data for individual rock samples are plotted against the ^{147}Sm/^{144}Nd ratio of their source reservoir, which was estimated from their $\varepsilon^{143}Nd_{initial}$ values using the two-stage model equations presented in Section 4.1. The depleted ε^{142}Nd signatures of the West Greenland and Yilgarn TTGs (tonalites, trondhjemites, granodiorites) define a mixing relationship between an early depleted mantle (ε^{142}Nd = 15–20 ppm, ^{147}Sm/^{144}Nd = 0.23–0.24) and an undifferentiated reservoir with ε^{142}Nd = 0 and ^{147}Sm/^{144}Nd = 0.208. The NGB isochron and the early Archean mantle array converge toward this common end member, which likely defines the composition of Earth's primitive mantle. The Barberton komatiite appears to be derived from this primitive reservoir, whereas intermediate ε^{142}Nd values found in tonalites of the Yilgarn craton reflect a mixed source. Late disturbance of the ^{147}Sm-^{143}Nd system is evident in several samples of the Isua Greenstone Belt and the Itsaq gneiss complex, as previously documented (Polat et al. 2003). Samples represented by smaller squares are likely to have experienced such disturbance as these samples yield model ages in excess of the age of the solar system. The depleted and enriched components represented here cannot be cogenetic. Formation of the NGB postdates by several hundred million years the event that led to differentiation of the Isua mantle source. The solar system isochron, which passes through the composition of ordinary chondrites (OCs), is shown for comparison. Abbreviation: BSE, bulk silicate Earth.

U-Pb zircon dates from orthogneisses crosscutting supracrustal units provide only a minimum age of >3,750 Ma for the NGB (Cates & Mojzsis 2007). O'Neil et al. (2008) speculated that the observed ε^{142}Nd versus Sm/Nd array might be a mixing line, rather than a true isochron, reflecting the assimilation of a >4.28-Ga-old, light REE–rich component in the 3.8-Ga-old parental melt of the amphibolite.

Upadhyay et al. (2009) recently reported a second case. These authors found negative ε^{142}Nd in a 1.48-Ga-old syenite intruding the early Archean Kharyar craton (India). Four samples have distinctly lower ^{142}Nd signatures of −8 to −13 ppm compared with a terrestrial standard, whereas three others yield normal ^{142}Nd composition within errors. As the rocks are too young to have developed in situ ^{142}Nd effects, the authors interpreted these results as reflecting a variable degree of assimilation of a >4.2-Ga-old mafic component at lower crustal levels during emplacement of the syenitic magma. A puzzling aspect of the results is that both the anomalous and the normal group include samples with identical $\varepsilon^{143}Nd_{initial}$ values. This observation is seemingly inconsistent with mixing models, as such processes would necessarily generate coupled variations in $\varepsilon^{143}Nd_{initial}$ and ε^{142}Nd. If these results are confirmed, however, they would suggest that Hadean mafic or ultramafic components were incorporated and preserved within the roots of much younger Archean cratons (Upadhyay et al. 2009).

OC: ordinary chondrite

4.3. The Age of the Early Terrestrial Crust

Although ^{142}Nd investigations of Archean terranes are still in their infancy, a new picture of early mantle-crust evolution is starting to emerge from the data presented above. As shown in **Figure 1*a***, juvenile rocks older than 2.5 Ga have fairly homogeneous $\varepsilon^{143}Nd_{initial}$ signatures. Thus, from the perspective of this long-lived isotope system, the Archean mantle appears to be uniformly depleted. However, when the coupled ^{142,143}Nd systematics is considered, it is apparent that at least two distinct reservoirs are needed to account for mantle heterogeneity in the early Archean (**Figure 3**). On the one hand, rocks from the West Greenland craton and Isua Greenstone Belt are derived from a depleted mantle, with $^{147}Sm/^{144}Nd = 0.23–0.24$ and $\varepsilon^{142}Nd = +15–20$ ppm. On the other hand, the Barberton komatiite and gabbros from the Nuvvuagittuq Greenstone Belt were extracted from a primitive reservoir, with $\varepsilon^{142}Nd = 0$ and $^{147}Sm/^{144}Nd = 0.208$. (This primitive end-member has a superchondritic Sm/Nd composition; this aspect will be discussed further in Section 5.) The intermediate values measured in Yilgarn tonalites appear to reflect mixing between these two end-members.

By combining ^{142,143}Nd data for all Archean rocks, a well-defined mantle isochron is obtained that is similar to that defined by martian shergottites and lunar basalts (Brandon et al. 2009, Caro et al. 2008b, Debaille et al. 2007) (**Figure 3**). This isochron establishes the age of differentiation of Earth's mantle at 150–180 Ma after formation of the solar system (i.e., 4.39–4.42 Gya). This age is significantly younger than the 30–70 Ma age range calculated by Bennett et al. (2007) because these authors estimated a model age based on the assumption of a chondritic BSE (CHUR). Indeed, forcing the Archean mantle isochron to pass through the chondritic composition [ordinary chondrite (OC) in **Figure 3**] would result in a much steeper slope and thus an older age. However, as shown in Section 5, the assumption of a perfectly chondritic bulk Earth is no longer justified, calling into question the validity of CHUR model ages.

4.4. Differentiation and Composition of Hadean Silicate Reservoirs

A plausible but speculative interpretation of ^{146,147}Sm-^{142,143}Nd chronological constraints is that early mantle differentiation resulted from crystallization of a deep magma ocean following the Moon-forming giant impact (Bennett et al. 2007; Caro et al. 2003, 2005). According to ^{182}Hf-^{182}W chronometry, this event probably took place >50 Ma after formation of the solar system (Touboul et al. 2007) and led to global melting of Earth's interior (Canup 2004). During the initial stage of solidification, crystallization of Mg-perovskite in the lower mantle, followed by majorite and olivine in the upper mantle, would have concentrated incompatible elements in an enriched residual liquid (Abe 1997, Agee 1990, Solomatov & Stevenson 1993a). Although this initial stage was probably rapid (10^3–10^6 years; Abe 1997), fractionation of the REE and other incompatible species likely would have taken place at a later stage, when this residual liquid segregated according to its density contrast with crystal cumulates (Solomatov & Stevenson 1993a,b). Depending on the blanketing effect of the early atmosphere, model calculations suggest that final solidification of the terrestrial magma ocean would have taken place 10^7–10^8 years after the giant impact (Abe 1997, Matsui & Abe 1986).

The consequences of magma ocean crystallization for the structure and chemical composition of the mantle remain the most speculative aspect of early silicate Earth evolution (Caro et al. 2005, Labrosse et al. 2007). Because trace elements are highly concentrated in residual liquids, extensive crystal/melt separation is needed to achieve significant fractionation. Trapping of a minor amount of liquid in an olivine or perovskite cumulate would buffer any trace element fractionation created by crystallization of these mineral phases. Thus, REE fractionation in the magma ocean is controlled not only by the nature of the crystallizing mineral assemblage but also by the differential rates of melt migration and progression of the solidification front (Solomatov & Stevenson 1993a). At the pressures of the upper mantle, melt percolation is expected to be faster than the rate of solidification (Solomatov & Stevenson 1993a). This would have favored the migration of this residual liquid toward the surface and the formation of the first terrestrial proto-crust. However, in the rapidly cooling lower mantle, the magnitude of Sm/Nd fractionation would be limited by the lower efficiency of melt percolation and by the buffering effect of Ca-perovskite (Caro et al. 2005, Corgne et al. 2005). In this magma ocean scenario, the depleted signature of the Archean mantle would more likely reflect differentiation of the uppermost mantle. The Archean mantle array (**Figure 3**) may then be seen as reflecting rehomogenization of a deep PM with shallow reservoirs that had been depleted by extraction of a residual melt during the final stage of magma ocean solidification.

An alternative interpretation, which does not require global melting of Earth's interior, is that early mantle depletion was caused by massive extraction of continental crust starting 4.5 Gya (**Figure 4**). Initially proposed by Armstrong (1981), this highly speculative model has found support in studies of Hadean detrital zircons from the Jack Hills metaconglomerate (<4.4 Gya, Western Australia) (e.g., Amelin et al. 1999, Caro et al. 2008a, Harrison 2009). Jack Hills zircons are interpreted as having crystallized from hydrous meta- and peraluminous magmas in an environment characterized by a relatively low heat flow (Hopkins et al. 2008). ^{176}Lu-^{176}Hf studies of Jack Hills reported highly unradiogenic $\varepsilon^{176}Hf_{initial}$ as early as 4.3 Gya, and the evolution of $\varepsilon^{176}Hf_{initial}$ versus time requires sequestration of the zircons in a low Lu/Hf crustal reservoir extracted from the mantle ~4.4 to 4.5 Gya (**Figure 4**) (Harrison et al. 2005, 2008; Kemp et al. 2010). On the basis of these results, Harrison et al. (2005, 2008) suggested that sites of granite generation similar to modern subduction zones were in place and that they led to the development of continental masses similar to present-day continents as early as 4.5 Gya, whereas Kemp et al. (2010) favored a model involving a predominantly mafic crust formed 4.46 ± 0.12 Gya. Independently of these different interpretations, the general agreement between the model age of mantle depletion recorded by the ^{146}Sm-^{142}Nd system and the ages obtained from Hf isotope studies suggests that part or all of the proto-crust quickly evolved into a highly differentiated reservoir that contained both felsic and mafic components. Although they may have been present in different proportions, these Hadean lithologies appear compositionally similar to their Archean and Proterozoic counterparts (Harrison 2009, Kemp et al. 2010, O'Neil et al. 2008). This leaves open the possibility that early mantle differentiation resulted from the onset of continental growth rather than from magma ocean crystallization.

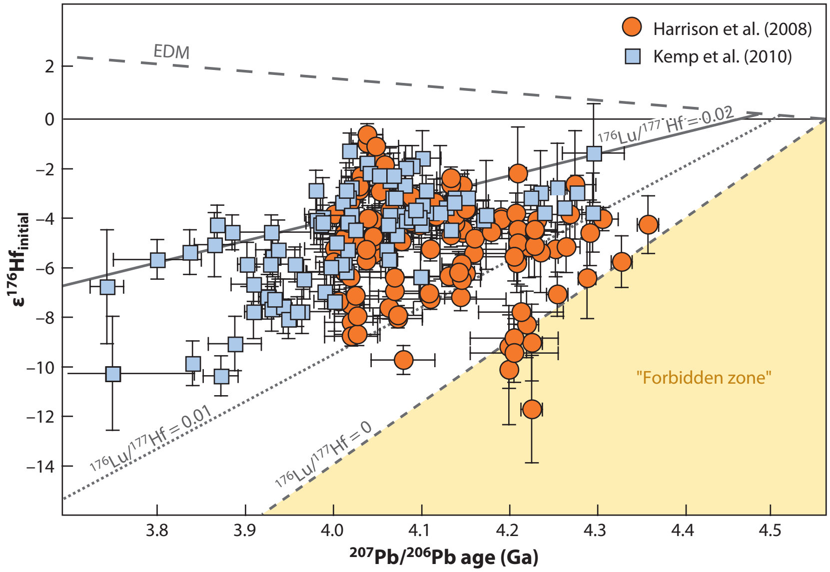

Figure 4

In situ Hf-Pb isotopic data for Hadean and early Archean zircons from the Jack Hills metaconglomerate (Harrison et al. 2008, Kemp et al. 2010). Most grains have $\varepsilon^{176}Hf_{initial}$ ranging between the predicted evolution of a mafic crust with $^{176}Lu/^{177}Hf = 0.02$ and that of a felsic reservoir with $^{176}Lu/^{177}Hf = 0.01$ (Harrison et al. 2008, Kemp et al. 2010). Although the geodynamic implications of these results have remained a matter of debate (Kemp et al. 2010), the results clearly indicate the presence of differentiated crustal terranes 4.4–4.5 Gya. This crustal reservoir formed immediately following terrestrial accretion and remained preserved from recycling in the mantle for 1–2 Ga, in agreement with ^{146}Sm-^{142}Nd constraints on early mantle-crust evolution (**Figure 5**). Abbreviation: EDM, early depleted mantle ($^{176}Lu/^{177}Hf = 0.0375$; Caro & Bourdon 2010).

4.5. Longevity of the Hadean Crust

The longevity of the Hadean crust is perhaps one of the most speculative aspects of early crustal evolution. Models range from very short-lived, unstable crusts (e.g., van Thienen et al. 2004) to long-lived reservoirs with a lifetime similar to that of present-day continents (Armstrong 1981, Galer & Goldstein 1991). As shown in **Figure 5**, the preservation of the anomalous ^{142}Nd signature in the Archean mantle provides a first-order constraint on the lifetime of the now-vanished proto-crust. In essence, a stable Hadean reservoir is needed to allow the preservation of ^{142}Nd heterogeneity in the mantle until 3.6 Gya and possibly later (Bennett et al. 2010), but this early crust must have been largely remixed in the mantle by the end of the Archean to account for the perfectly homogeneous ^{142}Nd signature of the present-day mantle and crust (Andreasen et al. 2007, Boyet & Carlson 2006, Caro et al. 2006, Murphy et al. 2010). As shown in **Figure 5**, these observations are consistent with a lifetime on the order of 1–2 Ga for the Hadean crust (Caro et al. 2006, Jacobsen & Harper 1996).

The requirement for a long-lived proto-crust could provide important, albeit indirect, information on the composition of Hadean silicate reservoirs. As shown in **Figure 5**, a felsic crust with a lifetime of 1–2 Ga would evolve toward negative ^{142}Nd anomalies of −20 to −30 ppm during the Archean. This is due to the low Sm/Nd ratios in felsic lithologies favoring the development of negative $\varepsilon^{142}Nd$ effects within relatively short periods of time. Reworking of Hadean crustal terranes within the growing Archean continental mass should have left a detectable fingerprint

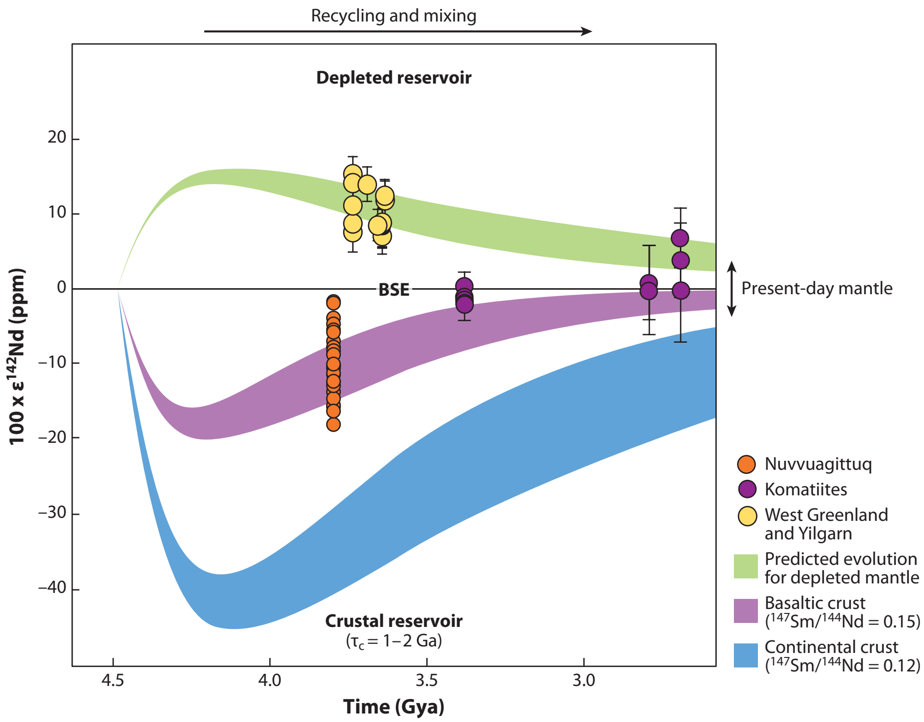

Figure 5

Isotopic evolution of differentiated crustal and mantle reservoirs calculated using a two-box model with recycling (Caro et al. 2006). In this model, crustal and mantle reservoirs differentiated 4.5 Gya and subsequently evolved at steady state. In contrast to the simple two-stage model described in Section 4.1, differentiated reservoirs do not evolve as perfectly closed systems but instead exchange material at a constant rate. In essence, recycled crustal material is balanced by new additions from the complementary depleted mantle. The average ε^{142}Nd evolution of the crust is then a function of its bulk composition and the residence time of Nd in this reservoir [i.e., the lifetime of the crust (τ_c)]. The preservation of ^{142}Nd anomalies in the early Archean mantle requires extraction of a primordial crust with a lifetime of approximately 1–2 Ga. The blue curve represents the isotopic evolution of a continental reservoir with a composition similar to modern crust (i.e., ^{147}Sm/^{144}Nd = 0.12). The predicted evolution for the complementary depleted mantle is shown in green. The purple curve illustrates the evolution of a basaltic crust, with ^{147}Sm/^{144}Nd = 0.15 and τ_c = 1–2 Ga. The preservation of negative ^{142}Nd anomalies in the Archean is dependent upon the chemical composition of the crustal reservoir. Nuvvuagittuq Greenstone Belt data come from O'Neil et al. (2008). West Greenland data come from Bennett et al. (2007) and Caro et al. (2006). Komatiite data come from Caro et al. (2006) and Boyet and Carlson (2006). Abbreviation: BSE, bulk silicate Earth.

in the form of negative ^{142}Nd anomalies in early Archean metasediments and granitoids. So far, most studies of Archean rocks yielded either depleted (ε^{142}Nd $>$ 0) or primitive (ε^{142}Nd $=$ 0) signatures (Bennett et al. 2007; Boyet & Carlson 2005, 2006; Caro et al. 2006, 2008a), and the only confirmed occurrence of negative ^{142}Nd anomalies in the terrestrial rock record is derived from mafic lithologies (O'Neil et al. 2008). If these results were confirmed on a broader scale, they would favor models involving a predominantly mafic or ultramafic crust over those calling for rapid continental growth in the Hadean (Armstrong 1981, 1991). Indeed, a basaltic crust with a lifetime of 1–2 Ga would probably develop a smaller negative ^{142}Nd anomaly of −5 to −10 ppm (**Figure 5**), so its involvement in Archean crustal formation processes would be far more difficult to detect than the contribution of a Hadean felsic component.

5. THE CHONDRITIC ^{146}Sm-^{142}Nd RECORD AND THE CONUNDRUM OF THE MISSING RESERVOIR

EER: early enriched reservoir

CC: carbonaceous chondrite

In the previous section, the Archean mantle array was proposed to reflect ongoing homogenization of a deep primitive reservoir with shallow mantle domains depleted by melt extraction from the solidifying upper mantle. These heterogeneities have since been remixed by convection, yielding a homogeneous $\varepsilon^{142}Nd$ signature in the present-day mantle. A puzzling aspect of the Archean $^{142,143}Nd$ results, however, is that mantle-derived rocks with positive $\varepsilon^{143}Nd_{initial}$ are not always associated with positive $\varepsilon^{142}Nd$. For example, the 3.5-Ga-old Barberton komatiite, with an $\varepsilon^{143}Nd_{initial}$ of +1.4 [corresponding to $(^{147}Sm/^{144}Nd)_{source} = 0.208$], has a normal $\varepsilon^{142}Nd$ composition (Caro et al. 2006). A question thus arises as to which process is responsible for creating depleted $\varepsilon^{143}Nd$ signatures that are not associated with any ^{142}Nd effects.

The Barberton $^{142,143}Nd$ signature was initially interpreted as reflecting crustal extraction processes that depleted the upper mantle once ^{146}Sm was extinct (that is, <4.2 Gya) (Caro et al. 2006). However, when the Archean $^{142,143}Nd$ record is considered together with that of chondrites, a far less intuitive scenario emerges: The lack of a positive ^{142}Nd anomaly in the depleted Barberton mantle source is not related to late crustal extraction; rather, it is a consequence of the formation, prior to crystallization of the terrestrial magma ocean, of an early enriched reservoir (EER) that was never remixed into the mantle. In essence, the debate centers on one fundamental question: Is this missing reservoir hidden in the deep mantle, or was it lost during accretion of the proto-Earth?

5.1. The Chondritic ^{142}Nd Signature

Since the pioneering studies of the late 1970s, the interpretation of Nd isotopic data has relied on the fundamental assumption that the bulk Earth had a perfectly chondritic Sm/Nd ratio (Allegre et al. 1979, DePaolo & Wasserburg 1979, Jacobsen 1988, Jacobsen & Wasserburg 1979). Jacobsen & Wasserburg (1984) and subsequent studies (Bouvier et al. 2008, Patchett et al. 2004) showed that Sm/Nd does not vary by more than 4% among the different types of chondrite. A 4% heterogeneity in Sm/Nd should generate a dispersion of ±6 ppm in the $^{142}Nd/^{144}Nd$ ratio after 4.56 Ga. Therefore, if the silicate Earth had a chondritic Sm/Nd, its ^{142}Nd signature and that of chondrites should be indistinguishable at the level of precision achieved by modern mass spectrometers (±2–5 ppm).

High-precision studies of meteorites, however, yielded strikingly different results. Boyet & Carlson (2005) reported ^{142}Nd data from a set of meteorites including OCs and carbonaceous chondrites (CCs) as well as basaltic achondrites. Their results showed that all chondrites, regardless of their classification, are characterized by $\varepsilon^{142}Nd$ values shifted downward by approximately 20 ppm compared with terrestrial rocks (**Figure 6*a***). Basaltic eucrites, which have near-chondritic Sm/Nd ratios, also exhibited the same negative anomaly, suggesting that their parent asteroid (4-Vesta) accreted from chondritic material.

When examined in detail, it is apparent that the range of ^{142}Nd anomalies exhibited by CCs is much larger than that expected on the basis of their Sm/Nd heterogeneity. These meteorites have low $\varepsilon^{142}Nd$, ranging between −45 and −20 ppm, and this dispersion exceeds analytical uncertainty (**Figure 6*a***). Furthermore, $\varepsilon^{142}Nd$ values in CCs show no correlation with their Sm/Nd ratios, indicating that ^{142}Nd heterogeneities do not result from the decay of ^{146}Sm (Carlson et al. 2007). OCs, however, define a distinct population with a homogeneous and less negative $\varepsilon^{142}Nd$ signature of −18 ± 5 ppm (**Figure 6*a***).

The difference in composition between CCs and OCs has been interpreted as the result of incomplete mixing of isotopically diverse nucleosynthetic material in the early solar system

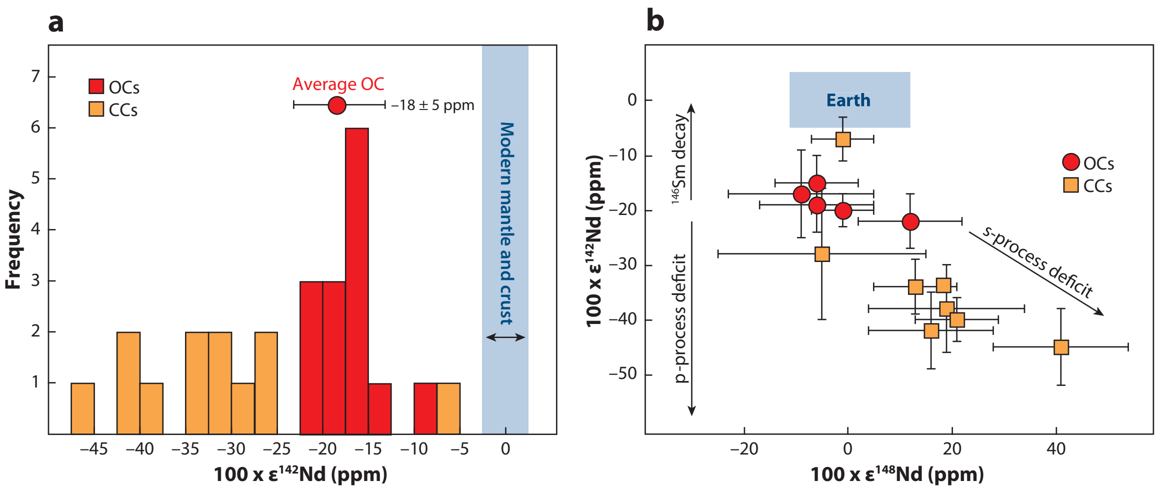

Figure 6

(*a*) Compilation of ^{142}Nd measurements in ordinary chondrites (OCs) and carbonaceous chondrites (CCs) compared with the modern terrestrial composition (Andreasen & Sharma 2006, Boyet & Carlson 2005, Carlson et al. 2007). OCs define a homogeneous population with an average ε^{142}Nd value of −18 ppm, whereas CCs exhibit more heterogeneous signatures. (*b*) The more negative ε^{142}Nd values observed in CCs display an inverse correlation with the abundance of the r-process nuclide ^{148}Nd (Carlson et al. 2007). This reflects a mixture between normal Nd and material carrying nucleosynthetic anomalies such as FUN (fractionation and unknown nuclear effects) inclusions or presolar grains (Carlson et al. 2007). OCs, however, have normal ^{148}Nd abundance within errors.

(Andreasen & Sharma 2006, 2007; Carlson et al. 2007). ^{142}Nd is produced mainly by s-process (slow neutron capture) in the interior of red giants, whereas heavier Nd isotopes are also produced by r-process (rapid neutron capture) in supernovae (Wallerstein et al. 1997). Accordingly, primordial heterogeneities arising from imperfect homogenization of nucleosynthetic products are expected to result in large ^{142}Nd anomalies. As shown in **Figure 6*b***, ^{142}Nd deficits in CCs are correlated with excesses of the r-only nuclide ^{148}Nd (Carlson et al. 2007). These effects appear to be inherited from material such as FUN (fractionation and unknown nuclear effects) inclusions or presolar grains, which long have been known to carry large nucleosynthetic anomalies (see Birck 2004 for a review). This interpretation is reinforced by the observation of similar deficits in s-process and p-process nuclides from other heavy elements such as barium (Andreasen & Sharma 2007, Carlson et al. 2007) and samarium (Andreasen & Sharma 2006). Overall, these observations demonstrate that the negative and heterogeneous ^{142}Nd signatures characterizing CCs partly reflect the incorporation of presolar material with a distinctively low abundance of s-process nuclides. In contrast, OCs, which exhibit normal isotopic composition for heavy elements, appear to be representative of planet-building material (Andreasen & Sharma 2006, 2007; Carlson et al. 2007). The ^{142}Nd excess of 18 ± 5 ppm in the accessible Earth compared with OCs has, therefore, been interpreted as resulting from ^{146}Sm decay, rather than from isotopic heterogeneity in the early solar system (Andreasen & Sharma 2006, Carlson et al. 2007).

5.2. Hidden Reservoir Models

The chondritic ^{142}Nd signature has potentially important consequences for our understanding of planetary formation. Yet, the interpretation of the ^{142}Nd excess observed in terrestrial rocks remains a contentious issue. If, as argued above, the negative anomaly in OCs is radiogenic, then it follows that the accessible mantle evolved for more than 4.5 Ga with a superchondritic Sm/Nd ratio. Boyet & Carlson (2005), following ^{142}Nd evidence for early mantle depletion, interpreted this observation in terms of internal differentiation processes. The rationale of their model is that if the BSE has a perfectly chondritic Sm/Nd ratio, then the more radiogenic ^{142}Nd/^{144}Nd composition of the accessible silicate reservoirs (i.e., the crust and the source reservoirs of oceanic basalts) must be balanced by a hidden reservoir with a low Sm/Nd ratio and subchondritic ε^{142}Nd (Boyet & Carlson 2005, 2006). Because no negative anomaly has been found in mantle-derived rocks, this hidden reservoir must have remained perfectly isolated from mantle convection throughout the entire Earth's history (Andreasen et al. 2007, Boyet & Carlson 2006, Caro et al. 2006, Murphy et al. 2010). Boyet & Carlson (2005) first suggested that a Hadean crust with a KREEP-like composition [i.e., having elevated potassium (K), rare earth elements (REEs), and phosphorus (P) contents] could have been recycled in the deep mantle and remained isolated near the CMB. As pointed out by Davaille et al. (2003), the density contrast between basaltic and peridotitic compositions may have been sufficient to prevent remixing of this early crust in the convective mantle, although it is doubtful that such a reservoir could have remained unsampled for the past 4.5 Ga. Alternatively, Labrosse et al. (2007) proposed that the superchondritic Sm/Nd ratio of the accessible mantle may reflect concentration of incompatible elements in a basal magma ocean. This reservoir would have formed owing to downward migration of intrinsically dense melts toward the CMB during crystallization of the lowermost mantle. Such a mechanism provides means to create a reservoir enriched in incompatible elements at the base of the mantle without the need to call upon crustal recycling. However, modeling of trace element partitioning at high pressure does not provide a satisfying fit to ^{142}Nd data, as separation and crystallization of the basal magma ocean would generate only negligible ^{142}Nd excesses (<2 ppm) in the DM. Furthermore, this model predicts continuous injection of isotopic heterogeneity in the convective mantle, as the less dense crystallized fraction is progressively reintrained in the mantle. This seems inconsistent with the lack of negative ε^{142}Nd signatures in oceanic basalts, which suggests that the hypothetical hidden reservoir does not contribute to the chemical and isotopic heterogeneity of the modern mantle (Andreasen et al. 2007, Boyet & Carlson 2006, Caro et al. 2006, Murphy et al. 2010).

5.3. The Age of the Missing Reservoir

An important constraint on the aforementioned models lies in the age of formation of the EER relative to the chronology of lunar and core formation. The minimum age of differentiation of this reservoir can be constrained by coupled ^{146,147}Sm-^{142,143}Nd chronometry using the two-stage model equations presented in Section 4.1 (Bourdon et al. 2008, Korenaga 2009). To apply this chronometer, we must first estimate the ε^{143}Nd and ε^{142}Nd values for the EDM complementary to the EER. Because the continental crust was extracted from the EDM, the present-day DM is chemically more depleted, and has a more radiogenic ε^{143}Nd, than the EDM. To estimate $\varepsilon^{143}\mathrm{Nd}_{\mathrm{EDM}}$, it is therefore necessary to "remix" the continental crust into the DM. In the most conservative scenario, whereby the continental crust was extracted from the entire mantle, mass balance constraints require that $R_{\mathrm{EDM}} = R_{\mathrm{CC}}\varphi_{\mathrm{CC}} + R_{\mathrm{DM}}\varphi_{\mathrm{DM}}$, where $R_i = (^{143}\mathrm{Nd}/^{144}\mathrm{Nd})_i$, $\varphi_i = (\mathrm{Nd})_i/(\mathrm{Nd})_{\mathrm{EDM}}$, and $(\mathrm{Nd})_i$ is the total number of moles of Nd in reservoir *i*. In addition, the Nd budget of the EDM is such that $(\mathrm{Nd})_{\mathrm{EDM}} = (\mathrm{Nd})_{\mathrm{BSE}} - (\mathrm{Nd})_{\mathrm{EER}}$ and that of the modern DM is $(\mathrm{Nd})_{\mathrm{DM}} < (\mathrm{Nd})_{\mathrm{EDM}} - (\mathrm{Nd})_{\mathrm{CC}}$. Using a BSE concentration of 1.25 ppm (McDonough & Sun 1995) and a crustal concentration of 20 ppm (Rudnick & Fountain 1995), one obtains an upper bound for $[\mathrm{Nd}]_{\mathrm{DM}}$ of <1.14 ppm, where $[\mathrm{Nd}]_i$ is the Nd concentration in reservoir *i*. As $\mathrm{R}_{\mathrm{CC}} = 0.5120$ and $\mathrm{R}_{\mathrm{DM}} = 0.5131$ (Salters & Stracke 2004), $\mathrm{R}_{\mathrm{EDM}}$ is constrained to be <0.5130, which corresponds to $\varepsilon^{143}\mathrm{Nd}_{\mathrm{EDM}} < +7$. This value represents a strict upper limit because it does not take into account the partitioning of Nd in the EER. If, for example, one considers that this reservoir contains 25% of the total Nd budget of the BSE, as suggested by Tolstikhin et al. (2006), then $[Nd]_{DM} < 0.83$ ppm, yielding $\varepsilon^{143}Nd_{EDM} < +6$.

The data compiled in **Figure 6*a*** suggest that the radiogenic ^{142}Nd excess in accessible terrestrial reservoirs is probably no less than 15 ppm. Application of the coupled $^{142,143}Nd$ chronometer using a chondrite-normalized $\varepsilon^{142}Nd_{EDM}$ value of >15 ppm and $\varepsilon^{143}Nd_{EDM} < +7$ shows that differentiation of the EER must have taken place less than 20 Ma after formation of the solar system (**Figure 7*a***, Model 1). If one considers a more realistic value of $\varepsilon^{143}Nd_{EDM} < +6$ (Model 2), then the age of the EER becomes identical within errors to that of the solar system (i.e., 4.567 Gya; Bouvier et al. 2007), which is seemingly incompatible with an internal differentiation process. This simple calculation also shows that the ^{142}Nd excess in the EDM cannot exceed 18 ppm, as this would yield model ages older than the age of the solar system (Model 3).

These chronological constraints outline a major challenge to all hidden reservoir models (Bourdon et al. 2008, Korenaga 2009). It has been estimated, on the basis of ^{182}Hf-^{182}W chronometry, that the earliest possible age of completion of core formation is likely >30 Ma (Kleine et al. 2004, Yin et al. 2002) and that the putative Moon-forming impact must have taken place >50 Ma

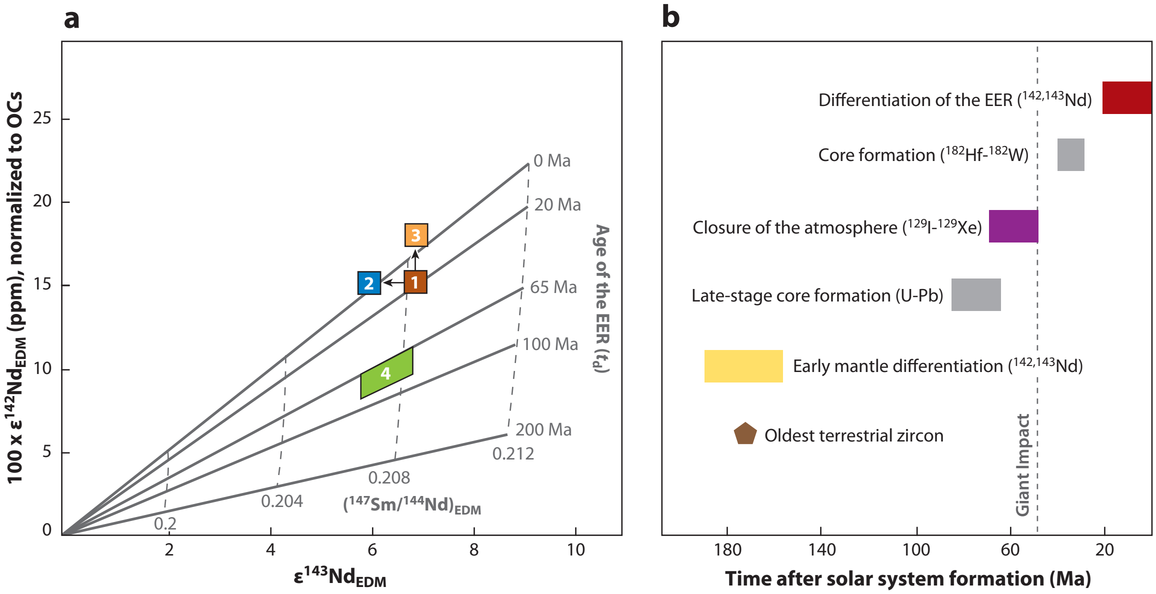

Figure 7

(*a*) Model age estimates for the hidden reservoir. Model 1 assumes that the early depleted mantle (EDM) has a ^{142}Nd excess of >15 ppm compared with ordinary chondrites (OCs) and a maximum $\varepsilon^{143}Nd_{EDM}$ of +7. This conservative model yields an age of 20 Ma after formation of the solar system (i.e., 4.546 Gya). As Model 1 does not take into account the budget of Nd stored in the early enriched reservoir (EER), this should be considered the youngest possible age. In Model 2, it is assumed that the hidden reservoir contains 25% of the Nd budget of the bulk silicate Earth (BSE) (Tolstikhin et al. 2006). The maximum $\varepsilon^{143}Nd_{EDM}$ is +6, and coupled $^{146,147}Sm$ chronometry yields a model age of 4.56 Ga ($t_d = 0$) for the hidden reservoir. A similar calculation assuming an $\varepsilon^{142}Nd_{EDM}$ excess of +18 ppm also yields a model age identical within errors to that of the solar system (Model 3). Conversely, if the Pb-Pb age of Earth (65–85 Ma) is considered as the earliest possible age for the hidden reservoir, then a maximum $\varepsilon^{142}Nd_{EDM}$ of +8 to +11 ppm is obtained (Model 4). $\varepsilon^{142}Nd$ values are normalized to OCs instead of a terrestrial standard. (*b*) Ages of differentiation of the major terrestrial reservoirs compared with that estimated for the EER. The minimum age of completion of core formation is based on ^{182}Hf-^{182}W chronometry (Kleine et al. 2004, Yin et al. 2002). The Pb-Pb age of Earth, which likely reflects late-stage core formation (Wood & Halliday 2010), is from Wood & Halliday (2005). The ^{129}I-^{129}Xe closure age of the atmosphere is from Kunz et al. (1998) and Ozima & Podosek (1999).

after solar system formation (Bourdon et al. 2008, Touboul et al. 2007). The Pb-Pb age of Earth, which is thought to reflect late-stage core formation (e.g., Gancarz & Wasserburg 1977, Pidgeon 1978), is estimated at 65–85 Ma (Wood & Halliday 2005, 2010), and the closure of the atmosphere recorded by xenon isotopes probably took place >50 Ma after formation of the solar system (Caffee et al. 1999, Kunz et al. 1998, Ozima & Podosek 1999, Pepin & Porcelli 2006). Thus, all four chronometers, although sensitive to different differentiation processes, consistently record ages younger than the age of the EER (**Figure 7*b***). It is difficult to envision how the separation of a long-lived silicate reservoir in the deep mantle could have taken place prior to completion of core formation. However, if one takes the Pb-Pb age of Earth as the earliest possible time for magma ocean crystallization, then the maximum ^{142}Nd excess in the EDM, for the two cases outlined above, is +8 to +11 ppm (Model 4), only half the value needed to account for the observations (**Figure 7*a***).

5.4. Hidden Reservoir Versus Lost Reservoir: A Lunar Perspective

A second test of hidden reservoir models comes from examination of ^{142}Nd systematics in lunar samples. It is well established that the Moon and the silicate Earth have identical oxygen and tungsten isotopic compositions (Touboul et al. 2007, Wiechert et al. 2001). This suggests that the Moon accreted from material ejected from Earth's mantle or from impactor material that had experienced extensive equilibration with the terrestrial magma ocean after the giant impact (Pahlevan & Stevenson 2007). In the aftermath of such an event, Earth's mantle would have been completely molten (Canup 2004) and partially vaporized, leading to the formation of a global magma ocean surrounded by a thick atmosphere of silicate dust and vapor (Pahlevan & Stevenson 2007). Average mantle temperatures after the giant impact were probably in excess of 10,000 K (Canup 2004), and turbulent convection in this hot magma ocean must have quickly rehomogenized any preexisting stratification. Therefore, it was reasoned that a Moon with chondritic ε^{142}Nd would imply that Earth was also chondritic at the time of the giant impact. Later internal differentiation would then be needed to account for the nonchondritic ^{142}Nd composition of the accessible silicate Earth.

Nyquist et al. (1995) were the first to apply the ^{146}Sm-^{142}Nd method to lunar rocks. These authors found that mare basalts and KREEPs plot along a linear array, which, if interpreted as an isochron, defines a late age of crystallization of 4.3 Ga. Rankenburg et al. (2006), using higher precision mass spectrometry, obtained results suggesting that ε^{142}Nd values reported by Nyquist et al. (1995) were overestimated. However, their measurements were affected by an analytical bias, and the subsequent revision by Brandon et al. (2009) yielded ε^{142}Nd compositions within errors of previous estimates (Boyet & Carlson 2007, Nyquist et al. 1995).

A compilation of lunar ^{142}Nd data (Boyet & Carlson 2007, Brandon et al. 2009, Nyquist et al. 1995), excluding those requiring large corrections for neutron capture effects, is shown in **Figure 8**. As can be seen, the lunar array does not intersect the composition of OCs, as would be expected if the source reservoirs of lunar basalts had differentiated from a chondritic PM. In fact, the bulk ^{142}Nd composition of the Moon (corresponding to the intercept of the lunar array with the solar system isochron) is indistinguishable from that of the modern silicate Earth and lies within the errors of the primitive end-member defined by early Archean rocks (**Figure 3**). Caro et al. (2008b) interpreted this as reflecting differentiation of lunar and terrestrial primordial reservoirs from a primitive source with identical, but nonchondritic, Sm/Nd and ^{142}Nd/^{144}Nd ratios. This implies that the ^{142}Nd signature found in all modern terrestrial reservoirs is not restricted to the uppermost mantle and crust; instead, this radiogenic excess is a feature characterizing the entire Earth-Moon system. This precludes the possibility that the EER resulted from the crystallization

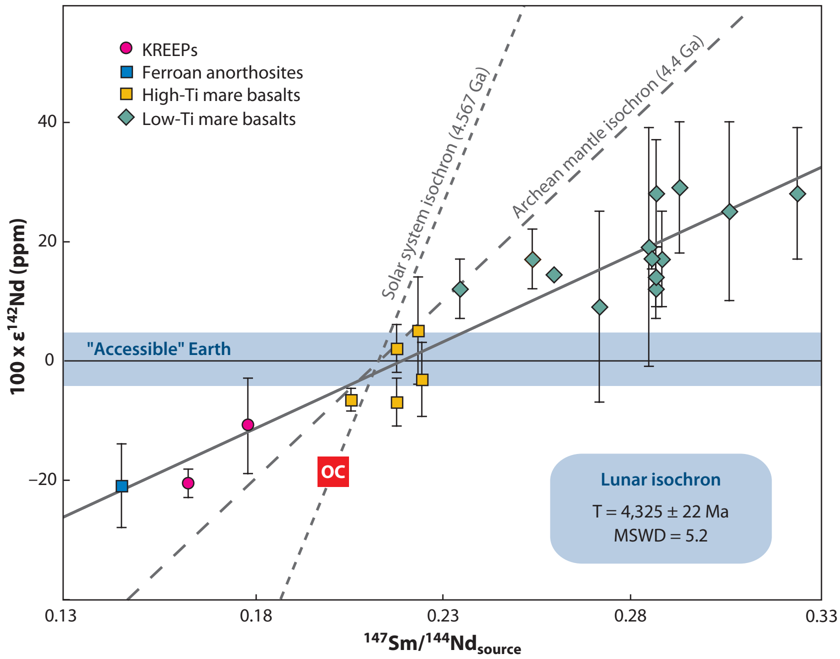

Figure 8

Coupled ^{146,147}Sm-^{142,143}Nd systematics of lunar rocks. The data are compiled from Nyquist et al. (1995), Boyet & Carlson (2007), and Brandon et al. (2009). A regression though all data yields an age of mantle differentiation of 4,325 × 22 Ma [mean standard weighted deviation (MSWD) = 5.2]. This late age may reflect either the final stage of solidification of the lunar mantle or subsequent overturn of magma ocean cumulates (Bourdon et al. 2008). The lunar array, the solar system isochron, and the Archean mantle isochron define a triple intersect at ε^{142}Nd ≈ 0, and ^{147}Sm/^{144}Nd ≈ 0.21, which likely defines the bulk composition of the Earth-Moon system (Caro et al. 2008b). Abbreviations: KREEPs, having potassium (K), rare earth elements (REEs), and phosphorus (P) contents; OC, ordinary chondrite.

of a magma ocean after the Moon-forming giant impact and eliminates the possibility that the Moon itself is the missing reservoir. Considered together with the chronological constraints on EER formation (see Section 5.3), the nonchondritic composition of the Moon makes it more difficult to explain the terrestrial ^{142}Nd signature in terms of an internal differentiation process (Boyet & Carlson 2007). Although a deep hidden reservoir might have formed prior to the giant impact and escaped rehomogenization in a largely molten mantle, this scenario seems unlikely. Rather, these constraints suggest that Earth accreted from material that had already experienced significant losses of enriched, low Sm/Nd material (Bourdon et al. 2008, Caro et al. 2008b). The Moon may have then inherited this nonchondritic signature from the proto-Earth.

5.5. Collisional Erosion Models

The idea that the bulk Earth and Moon may not have perfectly chondritic Sm/Nd ratios stands in contradiction with the standard paradigm that refractory elements did not experience fractionation during planetary formation. Such fractionation, however, may be an inevitable outcome of the accretion process. Simulations of planetary formation show that large impacts do not always result in the accretion of the impactor but also induce mass loss from the targets (Agnor & Asphaug

2004, Agnor et al. 1999). The net accretion of impactors occurs only in the case of low-velocity or head-on collisions, whereas high-velocity and tangential impacts tend to result in fragmentation of the impactor, ejection of mantle and crustal material from the target, and stripping of planetary cores from silicate mantles. In the simulations of Agnor & Asphaug (2004), hit and run collisions represent one-third to one-half of the large impacts on the proto-planets, suggesting that Earth and/or its precursors experienced significant loss of silicate components during one or several collisions.

O'Neill & Palme (2008) laid out the case for collisional erosion during Earth's accretion. These authors pointed out that the bulk Fe/Mg ratio of Earth (2.2) is significantly higher than the solar value of 1.9, suggesting 10% loss of silicate material relative to metal. O'Neill & Palme (2008) and Korenaga (2009) also suggested that erosional impacts on the proto-Earth induced preferential loss of crustal material, which depleted the mantle in incompatible elements and generated chemical fractionations similar to those commonly attributed to internal mantle-crust differentiation processes.

Empirically, this model is supported by numerous observations of planetary objects of the solar system, the most obvious example being the high density of Mercury, which likely results from collisional stripping of its silicate reservoirs (Benz et al. 1988). Differences in the density of smaller planetary bodies from the asteroid belt may have a similar cause (Asphaug 2009), which indicates that planets accreted from highly differentiated planetesimals that had lost variable amounts of silicate material. Lastly, the presence of a large impact crater on the southern side of Vesta provides evidence for erosional loss of planetary crusts. According to Thomas et al. (1997), Vesta's crater was caused by a collision with a 30 km-diameter impactor that resulted in the loss of 1% of the total mass of the planet. If the ejected material was predominantly crustal, with a composition similar to basaltic eucrites, then Vesta would have lost roughly a third of its REE budget in a single impact (Caro & Bourdon 2010). This shows that the trace element budgets of the terrestrial planets, which are highly concentrated in shallow crustal reservoirs, are likely to be severely affected by erosional impacts.

5.6. Mantle-Crust Evolution in a Nonchondritic Earth

A consequence of collisional erosion is that lithophilic elements are expected to be fractionated not only as a function of volatility but also according to their degree of compatibility in silicate melts. By removing crustal material from differentiated planetesimals, this process would have created in Earth and other terrestrial planets a REE signature resembling the pattern of mantle depletion produced by crustal growth (O'Neill & Palme 2008, Korenaga 2009). The associated Sm/Nd fractionation would be small (<10%) compared with cosmochemical fractionations experienced by more volatile elements in the solar nebula. However, even a slightly nonchondritic Sm/Nd for the BSE would contribute an entirely new perspective on the evolution of the mantle-crust system (Caro & Bourdon 2010, O'Neill & Palme 2008, Korenaga 2009). Specifically, if one assumes that the ^{142}Nd excess of 18 ppm characterizing the silicate Earth is due to the loss of a low Sm/Nd component 4.56 Gya (O'Neill & Palme 2008, Warren 2008), then the ^{147}Sm/^{144}Nd ratio and ε^{143}Nd composition of the BSE can be estimated to be 0.2082 and +6.9, respectively (Caro & Bourdon 2010). In this nonchondritic model, the DM (MORB source) would display a radiogenic excess of 2.1 ε-units compared with the BSE, instead of 9 ε-units in the CHUR model (**Figure 1*b***). This, in turn, modifies the mass balance relationships in the mantle-crust system. Assuming that this radiogenic excess is due to continental formation, the mass fraction of the DM can be estimated to be 90% of that of the silicate Earth, instead of the 25% estimated using CHUR parameters. It follows that separation of the upper and lower mantle would no longer be necessary to account for the radiogenic ε^{143}Nd signature characterizing the MORB source, a constraint more consistent with geophysical evidence for whole-mantle convection. These revised BSE parameters also provide an excellent fit to the observed ε^{143}Nd evolution of the Archean mantle. As illustrated in **Figure 1*b***, continuous extraction of the continental crust from the whole mantle can account for the isotopic evolution recorded in juvenile rocks from 3.8 Gya to present, obviating the need for early continental growth or a hidden reservoir at the CMB.

Collisional erosion of low Sm/Nd crustal components would thus provide a simple answer to the most puzzling questions raised by the ^{143}Nd systematics of the mantle (see Section 3.2). In particular, this process would explain why the EER does not appear to contribute isotopic or chemical heterogeneity to the modern mantle. It would also solve the apparent paradox of a seemingly depleted Archean mantle despite the scarcity of ancient (>4 Gya) continental crust. Lastly, a nonchondritic Earth model would make it easier to interpret isotope systematics in oceanic basalts, by eliminating Nd mass balance constraints for layered mantle convection and by associating primitive ^{3}He/^{4}He with primitive ε^{143}Nd signatures (Caro & Bourdon 2010). If correct, this interpretation would imply that early REE fractionation not only was produced by internal differentiation but also was generated by the accretion process at an earlier stage of planetary evolution. Distinguishing the effects of crustal differentiation and recycling from those arising from earlier collisional loss represents a major challenge in future studies of early mantle-crust differentiation.

SUMMARY POINTS

1. The presence of positive ^{142}Nd anomalies in rocks from the West Greenland and Yilgarn cratons is unambiguous evidence for early formation (4.39–4.42 Gya) of Earth's primordial crust. This Hadean reservoir was preserved from remixing in the mantle for at least 1 Ga after its formation. The modern mantle, however, has a homogeneous ^{142}Nd signature, indicating extensive rehomogenization of chemical and isotopic heterogeneities arising from early (>4.2 Gya) crustal formation processes.
2. Several lines of evidence suggest that this primordial differentiation was related to the crystallization of a global magma ocean following the giant impact. The lack of positive anomalies in several early Archean terranes—including the Barberton komatiite and gabbros from the Nuvvuagittuq Greenstone belt—requires that a substantial fraction of the mantle was not affected by this process. The preservation of pristine mantle domains until the early Archean may reflect nonfractional crystallization of the lower mantle due to rapid solidification rates compared with rates of melt percolation.
3. All classes of chondrites are characterized by negative ε^{142}Nd compositions compared with modern terrestrial samples. The heterogeneous ε^{142}Nd signatures observed in CCs reflect imperfect homogenization of presolar material carrying deficits in s-process nuclides (^{142}Nd) and p-process nuclides (^{146}Sm). However, the homogeneous anomaly found in OCs most likely results from ^{146}Sm decay in planetary reservoirs with fractionated REE abundances.
4. The superchondritic ^{142}Nd composition of the accessible Earth implies the formation of an EER that was never remixed into the mantle. Chronological constraints from coupled ^{146,147}Sm-^{142,143}Nd studies, as well as compositional estimates for the bulk Moon, indicate that this event took place prior to the giant impact and probably prior to completion of core formation, and thus predates the event that led to depletion of the Isua mantle source.

5. It has been speculated that collisional erosion, induced by hit-and-run collisions at an early stage of planetary accretion, preferentially removed crustal material from planetary embryos. This would have progressively depleted the accreting planets in incompatible elements and generated chemical fractionations similar to those associated with internal mantle-crust differentiation processes. Because of this similarity, the consequences of erosional impacts for the bulk composition of the terrestrial planets remain highly uncertain and represent a new, largely unexplored field of investigation.

DISCLOSURE STATEMENT

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