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Earth and Planetary Science Letters 250 (2006) 254–268

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A new geochemical model for the Earth's mantle inferred from ^{146}Sm–^{142}Nd systematics

Maud Boyet *, Richard W. Carlson

Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd. NW. Washington DC, 20015, USA

Received 28 February 2006; received in revised form 14 July 2006; accepted 18 July 2006
Available online 7 September 2006
Editor: C.P. Jaupart

Abstract

New measurements of ^{142}Nd/^{144}Nd in kimberlites, carbonatites, komatiites, ocean island basalts from Pitcairn, and mid-ocean ridge basalts from the Pacific and Indian Oceans show no deviation from the terrestrial Nd standard within an external reproducibility of 8 ppm. Measurements of mafic rocks from Isua Greenland confirm previous discoveries of an excess of between 0 and 17 ppm in the ^{142}Nd/^{144}Nd of these rocks. Since the terrestrial Nd standard has a ^{142}Nd/^{144}Nd approximately 20 ppm higher than measured in chondrites and eucrites, all terrestrial rocks so far analyzed have superchondritic ^{142}Nd/^{144}Nd. This requires either that the bulk silicate earth has a superchondritic Sm/Nd ratio or that the Earth experienced a global differentiation event within a couple of hundred million years of planet formation that created complementary incompatible element enriched and depleted mantle reservoirs. If that portion of the mantle involved in the production of continental crust was originally characterized by incompatible element depletion (i.e. high Sm/Nd) rather than chondritic relative abundances of refractory lithophile elements, as is commonly assumed, the mass of mantle affected by continent formation may constitute as much as 80% or more of the mantle. The abundances of K, U and Th in this early-formed depleted mantle are 60–70% of those calculated for a "chondritic" mantle, which removes the inference that half of the ^{40}Ar produced over Earth history must still reside in the mantle and explains why the mantle component characterized by high ^{3}He/^{4}He has superchondritic Nd and Hf isotopic composition. If these concentrations characterize the whole mantle, this implies a bulk-earth Urey ratio of ~0.3 and hence that much of the heat escaping the Earth's interior is primordial and not the result of radioactive decay over Earth history. If the bulk silicate earth is presumed to have chondritic abundances of refractory lithophile elements, there must be an incompatible element enriched reservoir buried deep enough in to mantle to preclude its involvement in mantle convection and its contribution to surface volcanism because no terrestrial rock with ^{142}Nd/^{144}Nd less than chondritic has been identified.

Keywords: TIMS; ^{142}Nd anomaly; radiogenic isotope tracers; early Earth differentiation; mantle composition

1. Introduction

A variety of lines of evidence support the idea that at least some features of mantle composition can be attributed to differentiation events that occurred during, or shortly following, Earth formation. Until recently, most of these indicators of early Earth differentiation were

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* Corresponding author. Present address: Transferts Lithosphériques, UMR 6524 "Magmas et Volcans" CNRS-UJM-UBP-IRD, UFR Sciences et Techniques, 23 rue du Docteur Paul Michelon F42023 Saint-Etienne cedex 02, France.

E-mail address: Maud.Boyet@univ-st-etienne.fr (M. Boyet).

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doi:10.1016/j.epsl.2006.07.046

restricted to elements affected by core segregation (Hf–W, siderophile elements) [1–4] and formation of the atmosphere [5]. Moreover, geochemical data highlight the lack of a "primitive mantle" signature in any lava erupted at Earth's surface [6], yet the isotopic variability in surface lavas indicates that chemical heterogeneities have been preserved for billions of years in the convecting mantle (see review of [7,8]). Our recent work using the short-lived ^{146}Sm–^{142}Nd ($T_{1/2}$ = 103 Myr) system allowed the measurement of a small, but significant, difference of ~20 ppm (part per million) in the ^{142}Nd/^{144}Nd ratio between various types of meteorites and terrestrial samples [9]. Compared to chondritic meteorites, the elevated ^{142}Nd/^{144}Nd of all terrestrial samples measured so far requires these rocks to have come from a high Sm/Nd ratio reservoir formed during the lifetime of ^{146}Sm, i.e. during the first few hundred Myr of solar system history. Sm and Nd are both refractory and lithophile elements and were probably not fractionated during processes such as accretion and core formation. Moreover, these elements are present in nearly constant proportions in different groups of chondrites [9–12] and thus do not seem easily fractionated by "nebular" processes. These characteristics led the long-lived ^{147}Sm–^{143}Nd ($T_{1/2}$ = 106 Ga) chronometer to be one of the most powerful radiometric systems used to trace the long-term chemical evolution of the silicate portion of the Earth. Because of the long half-life of ^{147}Sm, however, this system cannot easily discriminate whether the high ^{143}Nd/^{144}Nd of the mantle that produces mid-ocean ridge basalts (MORB) reflects the increase in Sm/Nd in the mantle caused by the extraction of continental crust over earth history or instead was caused by early global differentiation of Earth's mantle such as may have occurred during a magma ocean formed early in Earth history.

Today we have the new consideration that the elevated ^{142}Nd/^{144}Nd of terrestrial rocks compared to chondrites requires that the Earth either (i) did not accrete from material with refractory elements present in precisely chondritic abundances, or (ii) has undergone a global scale silicate differentiation following accretion. The latter option requires the presence of terrestrial materials with ^{142}Nd/^{144}Nd both higher and lower than chondritic. The former option could be reconciled with terrestrial variation in ^{142}Nd/^{144}Nd, but also would be consistent with no variation in terrestrial ^{142}Nd/^{144}Nd if homogenization of the silicate earth occurred after ^{146}Sm had decayed away. So far, significant excesses (between 6 and 30 ppm) relative to the terrestrial Nd standard have been measured only in a small number of 3.8 Ga samples collected in the southwestern part of Greenland (Isua Supracrustal Belt, Amitsoq gneiss) [13–16].

In this paper, we present ^{142}Nd measurements using the new-generation of thermal-ionization mass spectrometer that allows the measurement of Nd isotope ratios with high precision (~6 ppm). In the quest to identify the magnitude of terrestrial variation in ^{142}Nd/^{144}Nd, we have remeasured the mafic samples collected in the Isua Supracrustal Belt previously analyzed by Boyet et al. [13] in order to document the ^{142}Nd excess in these samples using the new TIMS-based technique. Secondly, we focused on rocks that might sample the missing, low ^{142}Nd/^{144}Nd reservoir, if it indeed exists. These rocks include kimberlites and carbonatites because they represent the most incompatible element rich melts on Earth, and at least some workers believe them to be of deep mantle origin [17]. We also have analyzed ocean island basalts from Pitcairn Island, which represents the EM1 end member of the oceanic isotopic components [18], and Archean komatiites that again may have been derived from deep-seated sources. In the second part of this paper, we investigate the long-term chemical evolution of a non-chondritic mantle and its consequences for different chemical and isotopic tracers and the heat budget of the Earth in order to reconcile geochemical data with geophysical observations and models of mantle convection.

2. Materials and methods

2.1. Sample description

Group I kimberlites were selected from Brazil, S.W. Greenland, Montana, Colorado, Siberia, and South Africa. The oldest kimberlites are 600 Ma and were collected from the Safartoq formation (S.W. Greenland). Most group 1 kimberlites have positive initial $\varepsilon_{143\text{Nd}}$ [19] and $\varepsilon_{176\text{Hf}}$ [20] reflecting a source depleted in incompatible elements. In contrast, the isotopic composition of samples from Brazil, Montana and Colorado suggest significant long-term incompatible element enrichment of their sources [21,22]. An initial report of a deficiency in ^{182}W in the Monastery kimberlite from South Africa [23] suggested core–mantle interaction in the source of this kimberlite and hence a very deep origin. This signature has not been confirmed in more recent studies [24].

All carbonatites analyzed come from southwestern part of Greenland. The Tupertalik carbonatite, dated at 3 Ga, is the oldest sampled carbonatite on Earth [25]. Negative $\varepsilon_{176\text{Hf}}$ measured in separated baddeleyites and zircons from the Qaqarssuk and Tupertalik carbonatites have been interpreted as reflecting the participation of an early-formed enriched source, now hidden in the deep terrestrial mantle [25].

Samples from the Isua Supracrustal Belt are 3.8 Gyr old basalts and gabbros with mineral assemblage corresponding to the amphibolite facies. Analyzed samples were collected in the western part of the belt. Details on the geological setting and information on sample locations can be found in [13].

Five samples from Pitcairn Island have been measured. These lavas represent the EM1 mantle end member defined by Hart and Zindler [18]. Although the Sr, Nd, and Pb isotopic composition of EM1 could be explained by the mixing of subduction-recycled sediments into the mantle source, Pitcairn basalts have oxygen isotope composition similar to normal mantle values, which lessens the likelihood that sediments were involved in creating this end member [26]. Moreover, Pitcairn basalts recently were shown to have Ne isotopic compositions bearing a strong signature of solar Ne relative to other oceanic island basalts like Hawaiin lavas [27]. We have selected samples with the lowest ^{206}Pb/^{204}Pb and ^{143}Nd/^{144}Nd among those analyzed by Eiler et al. [26] as these characteristics would be predicted for an early-formed (e.g. pre-4.53a) enriched mantle reservoir [9].

Komatiites analyzed in this study include 2.8 Ga samples from the Kostomuksha greenstone belt (Baltic Shield, Russia) and 2.7 Ga komatiites from the Belingwe Greenstone Belt (Zimbabwe) [28,29]. These komatiites were selected because they share a particularly radiogenic initial Os isotopic composition interpreted to reflect a contribution of recycled mafic crust older than 4.2 Ga in their mantle sources [29]. This signature also could be the result of chemical exchange at the core–mantle boundary, but this interpretation is the subject of some debate [24,30].

Finally, two mid-ocean ridge basalts from the Indian and Pacific Oceans have been selected. With very high ^{143}Nd/^{144}Nd ratios ($\varepsilon_{143\text{Nd}} = 10.5$; [31]), these samples reflect a mantle source with long-term light rare earth element (REE) depletion and provide a test of whether this depleted source, and the distinction between Pacific and Indian MORB, relate to early differentiation events.

2.2. Methods

The samples were dissolved using a mixture of HF–HNO_3 (3:1) ultra-pure acids. All details on the analytical work have been described in [9]. For the samples reported here, ^{140}Ce/^{146}Nd and ^{147}Sm/^{146}Nd never exceeded 0.00006 and 0.00001 respectively, which is below that commonly measured in the La Jolla Nd standard (^{140}Ce/^{146}Nd between 0.00002 and 0.0001). Nd isotopic composition was measured using the new generation of thermal-ionization mass spectrometer (Thermo-Finnigan Triton) in DTM as Nd^+ using outgassed zone-refined double Re filaments. Each measurement corresponds to 27 blocks of 20 ratios (8 s integration) using amplifier rotation in static mode. Nd isotope ratios were corrected for mass fractionation using an exponential law and the ratio ^{146}Nd/^{144}Nd = 0.7219. Two different Nd standards have been frequently measured (La Jolla and JNdi-1) and the current reproducibility on the ^{142}Nd/^{144}Nd ratio is lower than 6 ppm (2σ). Isotope ratios are expressed in ε units and calculated relative to the average value for the La Jolla standard set measured in the same barrel as the samples ($\varepsilon_{142\text{Nd}} = (^{142}\text{Nd}/^{144}\text{Nd})_{\text{sample}}/(^{142}\text{Nd}/^{144}\text{Nd})_{\text{La Jolla}} - 1) \times 10000$). More than five La Jolla measurements were performed with each sample barrel and these measurements were averaged to provide the standard values used to calculate $\varepsilon_{142\text{Nd}}$ for samples measured in the same barrel.

3. Results

Nd isotope ratios measured for the samples studied here are presented in Table 1. Samples have been measured between one and seven times but only the mean value of multiple measurements is reported in Table 1. All kimberlites, carbonatites, mid-ocean ridge basalts, Pitcairn basalts, and komatiites measured here have similar ^{142}Nd/^{144}Nd ratios within error (2σ) and all these samples have ^{142}Nd/^{144}Nd that overlaps the value measured for La Jolla Nd (Fig. 1). Most samples were analyzed several times and the external reproducibility obtained on the ^{142}Nd/^{144}Nd ratio is lower than 8 ppm. The high error obtained for the Brazilian kimberlite 3-Facao (±14 ppm, 2σ), reflects two measurements with relatively different $\varepsilon_{142\text{Nd}}$: -0.09 ± 0.07 and 0.11 ± 0.06, but the average of these two measurements is indistinguishable within uncertainty from La Jolla Nd.

Samples collected in the Isua Supracrustal Belt show a relatively wide range of ^{142}Nd/^{144}Nd values, from 0 to +0.17 ε unit. Three of these samples were previously measured using a multiple-collector inductively coupled plasma mass spectrometer (MC-ICPMS) [13]. Although precisions obtained in the new TIMS measurements are significantly better, both measurements are in agreement within error. These three samples, with sample 460257 ($\varepsilon_{142\text{Nd}}$ of 0.32 ± 0.20 previously measured with MC-ICPMS) define a ^{147}Sm–^{143}Nd isochron (MSWD = 7.0) giving an age of 3760 ± 36 Ma and an intercept of

Table 1
Nd isotope composition measured for terrestrial samples

Location	Sample	Name	N^a	D^b	ε_{142Nd}	2σ	$^{143}Nd/^{144}Nd$	2σ	ε_{145Nd}	2σ	ε_{148Nd}	2σ	ε_{150Nd}	2σ
Brazil	Kimberlite	11-Lim 1-2	2	1	0.01	0.03	0.512327	0.000001	0.03	0.02	−0.07	0.09	−0.28	0.16
	Kimberlite	8.3 Ranchos	2	1	−0.07	0.03	0.512353	0.000001	0.03	0.00	0.05	0.01	−0.09	0.10
	Kimberlite	3-Facao	2	1	0.03	0.14	0.512352	0.000003	−0.01	0.03	0.03	0.02	0.00	0.12
Safartoq	Kimberlite	Kim1	3	1	0.07	0.03	0.512382	0.000001	0.00	0.02	0.06	0.05	0.16	0.10
	Kimberlite	Kim4	3	1	0.07	0.04	0.512265	0.000002	0.01	0.03	0.06	0.05	0.03	0.07
	Kimberlite	Kim5	3	1	0.00	0.03	0.512375	0.000001	−0.03	0.06	−0.03	0.08	−0.05	0.03
	Kimberlite	Kim15	3	1	0.03	0.02	0.512400	0.000002	0.04	0.05	0.01	0.09	−0.10	0.02
	Kimberlite	Kim16	3	1	0.07	0.03	0.512414	0.000003	0.00	0.02	0.05	0.10	0.04	0.14
	Kimberlite	Kim18	3	1	0.05	0.05	0.512347	0.000002	0.03	0.03	0.10	0.12	0.14	0.16
Siberia	Kimberlite	Me-5211	4	1	0.03	0.05	0.512786	0.000003	0.00	0.03	−0.01	0.05	−0.04	0.12
	Kimberlite	Nrb-440	2	1	0.02	0.02	0.512494	0.000002	−0.02	0.01	−0.09	0.00	−0.23	0.05
	Kimberlite	Nv414	3	1	0.04	0.02	0.512580	0.000001	0.01	0.03	0.00	0.08	0.11	0.21
	Kimberlite	P-14088	3	1	0.05	0.04	0.512713	0.000003	0.09	0.04	−0.02	0.04	−0.03	0.20
	Kimberlite	Pd 2/25	2	1	−0.06	0.03	0.512578	0.000001	0.01	0.00	−0.02	0.04	−0.09	0.00
	Kimberlite	Zk-18	2	1	0.00	0.06	0.512563	0.000001	0.04	0.01	0.01	0.03	−0.12	0.08
Montana	Kimberlite	HK-3a	3	1	0.06	0.03	0.512336	0.000002	0.03	0.05	0.04	0.01	0.17	0.19
Colorado	Kimberlite	13-19K	4	1	0.04	0.08	0.512451	0.000002	0.02	0.02	−0.01	0.05	0.00	0.21
South Africa	Kimberlite	Pipe 200	3	1	−0.04	0.06	0.512717	0.000002	0.00	0.04	−0.08	0.03	−0.19	0.07
	Kimberlite	Monastery	3	1	−0.01	0.03	0.512725	0.000001	0.04	0.02	−0.04	0.10	−0.09	0.17
Qaqarssuk	Carbonatite	Qi	6	2	−0.01	0.04	0.512655	0.000002	−0.04	0.09	0.04	0.10	0.00	0.24
Safartoq	Carbonatite	S10	4	2	0.08	0.06	0.512404	0.000002	0.01	0.03	−0.02	0.06	−0.06	0.11
Tupertalik	Carbonatite	T	7	2	0.05	0.08	0.510701	0.000010	0.00	0.05	−0.02	0.12	0.01	0.30
Pacific Ocean	MORB	SD8-3	2	1	−0.03	0.02	0.513161	0.000001	0.02	0.07	−0.05	0.00	−0.18	0.06
Indian Ocean	MORB	O113T	1	1	−0.06	0.05	0.513116	0.000002	0.05	0.04	0.08	0.07	0.02	0.10
Isua Supracrustal Belt	Metabasalt	00-004	3	1	0.03	0.02	0.511845	0.000001	0.02	0.03	−0.07	0.03	−0.22	0.07
	Metagabbro	00-009	2	2	0.14	0.06	0.512871	0.000005	0.00	0.11	−0.09	0.18	−0.01	0.59
	Metagabbro	00-013a	2	2	0.17	0.05	0.513110	0.000004	0.01	0.07	0.04	0.10	0.09	0.20
	Metagabbro	00-013b	1	1	0.13	0.05	0.513342	0.000002	0.03	0.04	0.03	0.07	0.03	0.09
	Metabasalt	00-014	3	1	−0.03	0.06	0.512914	0.000003	0.01	0.02	−0.09	0.01	−0.16	0.11
	Metabsalt	00-021	2	1	0.03	0.05	0.512251	0.000003	0.01	0.03	−0.09	0.04	−0.25	0.06
	Pillow lava	00-022	1	1	0.15	0.06	0.513091	0.000003	0.06	0.05	−0.14	0.09	−0.10	0.12
	Pillow lava	00-023	1	1	0.16	0.05	0.512211	0.000002	0.08	0.04	−0.18	0.07	−0.35	0.09
	Metabasalt	00-036	1	1	0.03	0.05	0.514130	0.000002	−0.01	0.03	−0.06	0.06	0.02	0.08
	Metabasalt	00-047	1	1	−0.05	0.05	0.510691	0.000003	−0.03	0.04	−0.19	0.07	−0.42	0.10
Pitcairn (EMI)	Basalt	Pit 1	2	1	0.00	0.06	0.512383	0.000001	−0.06	0.01	−0.10	0.03	−0.22	0.03
	Basalt	Pit 3	2	1	0.05	0.08	0.512395	0.000001	0.07	0.01	−0.01	0.05	−0.10	0.03
	Basalt	Pit 4a	2	1	0.03	0.03	0.512539	0.000001	−0.03	0.02	−0.06	0.07	−0.09	0.04
	Basalt	Pit 12	2	1	0.08	0.08	0.512478	0.000001	0.01	0.03	−0.05	0.07	−0.13	0.03
	Basalt	Pit 13	2	1	−0.01	0.04	0.512460	0.000001	0.04	0.00	0.02	0.03	−0.08	0.04
Belingwe greenstone belt	Komatiites	TN4	1	2	0.00	0.07	0.513215	0.000004	0.00	0.01	−0.01	0.12	−0.04	0.20
	Komatiites	TN5	1	1	0.04	0.05	0.513223	0.000002	0.12	0.04	0.02	0.06	0.00	0.08
	Komatiites	TN6	1	1	0.07	0.04	0.513223	0.000002	0.14	0.03	0.07	0.06	−0.13	0.08
Kostomuksha greenstone belt	Komatiites	9493	1	1	0.00	0.06	0.513622	0.000003	0.07	0.05	−0.08	0.08	−0.17	0.12
	Komatiites	9496	1	1	0.01	0.05	0.513489	0.000002	0.06	0.04	−0.02	0.06	−0.16	0.09

$^{142}Nd/^{144}Nd$ measurements are expressed in ε_{142Nd} notation $[=((^{142}Nd/^{144}Nd)_{sample}/(^{142}Nd/^{144}Nd)_{standard}-1)\times 10^4]$ relative to the La Jolla standard. $^{143}Nd/^{144}Nd$ ratios are reported relative to a value of 0.511860 for La Jolla standard. Uncertainties are 2 standard deviation (2σ) for terrestrial samples. External reproducibility obtained on repeated standard measurements for $^{142}Nd/^{144}Nd$ is 6 ppm, i.e. 1.141848 ± 0.000007. (a) N is the number of measurements, and (b) D signifies the number of dissolution procedures.

0.507813 ± 0.000047 ($\varepsilon_{142Nd}=1.9\pm0.9$). This chronology is consistent with the age of the Isua Supracrustal Belt formation determined by U–Pb [32] or Sm–Nd [33] systematics. The significant excesses in ^{142}Nd measured in mafic samples (ε_{142Nd} between 0.13 and 0.17) are similar to those measured in metasediments from Isua by Caro et al. [14].

Therefore, in all the samples studied here, significant ^{142}Nd excesses relative to La Jolla Nd were measured only for five samples from Isua. La Jolla Nd, however, has a $^{142}Nd/^{144}Nd$ between 15 and 30 ppm higher than measured in a variety of chondritic and eucritic meteorites [9], which indicates that all terrestrial rocks analyzed so far have elevated $^{142}Nd/^{144}Nd$ compared to

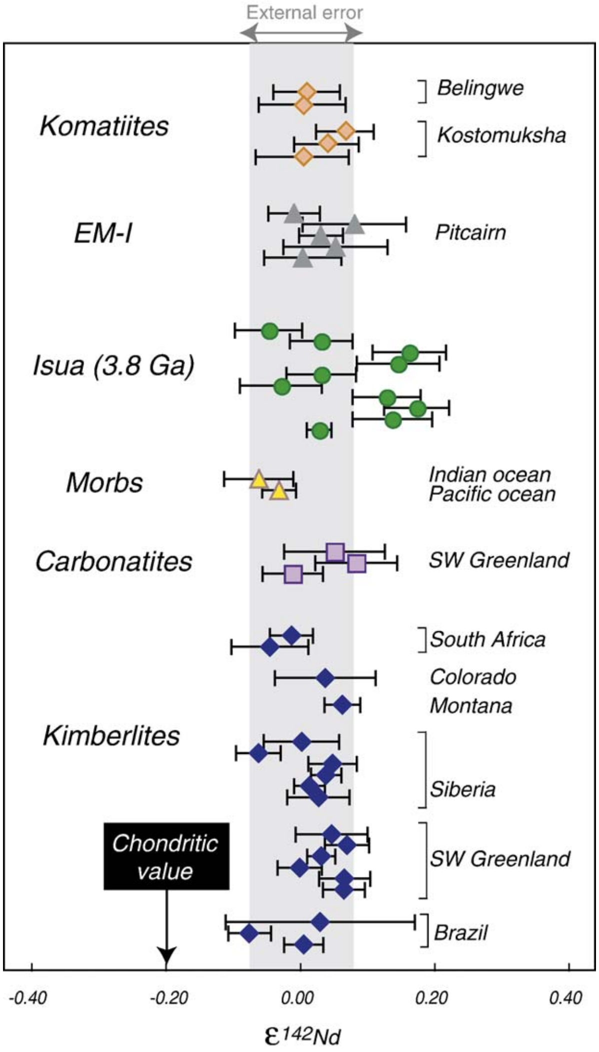


Fig. 1. ^{142}Nd/^{144}Nd in the samples analyzed here, expressed ($\varepsilon_{142\mathrm{Nd}}$) as parts in 10,000 deviation from the average measured for the La Jolla Nd standard, which is approximately 0.2 $\varepsilon_{142\mathrm{Nd}}$ higher than the average measured for chondrites and eucrites [9]. The grey bar shows the average external precision obtained on repeat analyses of the same sample. Error bars on the individual points show the 2σ deviation obtained for multiple measurements of each sample. Only 5 samples from Isua show deviation outside of analytical uncertainty from the ^{142}Nd/^{144}Nd measured for La Jolla Nd.

the presumed building-blocks of our planet, the chondritic meteorites.

4. Implications of the non-chondritic ^{142}Nd/^{144}Nd in terrestrial rocks

The ^{142}Nd excess in terrestrial rocks compared to chondrites potentially can be explained in one of three ways. 1) The difference reflects imperfect mixing of r- and s-process nuclides in the solar nebula. In this case, the variation in ^{142}Nd is not due to ^{146}Sm decay but instead reflects nucleosynthetic anomalies in meteorites compared to Earth. 2) The Earth has a Sm/Nd ratio higher than chondritic. 3) The Earth experienced a global differentiation while ^{146}Sm was still present that led to the formation of chemically complimentary reservoirs within the Earth, one with Sm/Nd higher, and one with Sm/Nd lower, than chondritic.

4.1. Nucleosynthetic anomalies

This suggestion was made in light of the discovery of isotopic variation in Ba in chondrites [34], and follows on recent discoveries of isotope anomalies in Mo, Ru [35] and Os [30] at the whole meteorite scale. For the meteorite analyses reported in Boyet and Carlson [9], Sm isotopic composition also was determined primarily as a measure of the neutron capture effects on ^{149}Sm due to cosmic ray exposure, which also can affect ^{142}Nd. Sm has two pure s-process isotopes, ^{148}Sm and ^{150}Sm, and ^{142}Nd also is produced purely by the s-process. ^{150}Sm also is produced by neutron addition to ^{149}Sm and hence cannot be used to check for nuclear anomalies in samples, such as meteorites, that have experienced exposure to cosmic rays (Fig. 2). Based on the few calcium–aluminum-rich inclusions in the carbonaceous chondrite Allende where incomplete mixing of s- and r-process nuclides has been clearly demonstrated, a 20 ppm deficit in ^{142}Nd should be accompanied by a roughly 70 ppm deficit in ^{148}Sm [36].

As shown in Fig. 2, measurements of ^{148}Sm/^{152}Sm in the meteorites analyzed by Boyet and Carlson [9] overlap within uncertainty with the terrestrial standard. The average ^{148}Sm/^{152}Sm measured for Allende shows a 27 ± 13 ppm excess compared to the terrestrial Sm standard, but ordinary chondrites (2 ± 15 ppm), eucrites (−17 ± 18 ppm), and Isua samples (−12 ± 12 ppm) show no resolvable difference in ^{148}Sm/^{152}Sm. These results thus do not support the suggestion that the difference in ^{142}Nd/^{144}Nd between meteorites and terrestrial rocks reflects nucleogenic isotope anomalies in meteoritic Nd. Instead, they support the suggestion that this difference is the result of the decay of now extinct ^{146}Sm.

4.2. A non-chondritic Earth

The Earth's mantle does not have chondritic abundances of many elements, for example siderophile and volatile elements (e.g. [37]). The former group of elements presumably is sequestered away in Earth's core, while the volatile elements may never have been present in chondritic abundances in the terrestrial

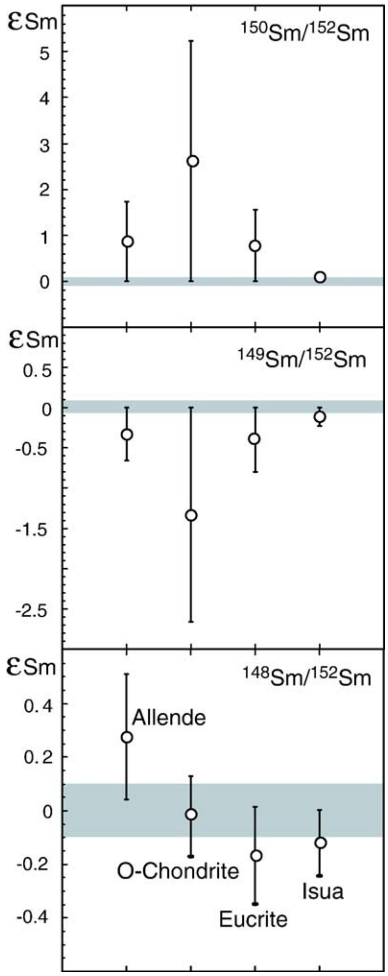


Fig. 2. Average Sm isotopic composition measured for 4 Isua samples in comparison to the results obtained for chondrites and eucrites [9]. All data are expressed ($\varepsilon_{\mathrm{Sm}}$) as parts in 10,000 deviation from the value obtained for the laboratory terrestrial Sm standard. The grey bars in each panel show the external precision obtained on the laboratory Sm standard. Bars on each sample subset show the range (2σ) obtained on the samples included in the average. For chondrites, and somewhat for eucrites, the large range obtained for ^{149}Sm/^{152}Sm and ^{150}Sm/^{152}Sm reflects neutron capture on ^{149}Sm due to the variable cosmic-ray exposure ages of the samples included in the average. Note the scale change on the panel showing ^{148}Sm/^{152}Sm variation, which is not significantly affected by cosmic ray exposure and hence shows more limited variation than ^{149}Sm and ^{150}Sm.

planets. Sm and Nd, however, are both refractory and lithophile and hence should not be fractionated by either core formation or various volatile loss processes. Indeed, within the various classes of chondritic meteorites, ^{147}Sm/^{144}Nd varies only between 0.193 and 0.200 [9,10,12,38]. In order to evolve a 20 ppm excess in ^{142}Nd/^{144}Nd compared to chondrites, assuming an average chondrite ^{147}Sm/^{144}Nd = 0.1948 [9], would require the Earth to have a ^{147}Sm/^{144}Nd of at least 0.209, higher than any value measured for a bulk chondrite.

The mechanism by which the Earth would acquire a non-chondritic Sm/Nd is not clear. The Sm/Nd ratio, unlike Lu/Hf [12] and Re/Os [39], shows no consistent difference between different classes of chondritic meteorites. Sm and Nd, however, can be fractionated by magmatic processes. Evidence for superchondritic Sm/Nd in Earth's mantle has been available since the first high precision measurements of Nd isotopic composition in terrestrial rocks [40] showed that MORB have roughly 10 ε-unit excess in ^{143}Nd/^{144}Nd compared to chondrites. This excess usually is interpreted as reflecting the extraction of the incompatible element rich, and low Sm/Nd, continental crust from the mantle to leave a residue, the MORB source mantle, with high Sm/Nd [41,42]. When this process of mantle depletion started, however, has seen considerable debate [43]. Positive $\varepsilon_{143\mathrm{Nd}}$ is a common characteristic of mantle-derived rocks throughout Earth history and few would debate that the positive $\varepsilon_{143\mathrm{Nd}}$ of late-Archean rocks reflects their derivation from a mantle source with superchondritic Sm/Nd. Similar evidence of high Sm/Nd sources for early Archean rocks has been more contentious, in part because of the debate over whether the measured Sm/Nd ratio of these old rocks has been disturbed by metamorphism, resulting in erroneous estimations of the initial ^{143}Nd/^{144}Nd [44,45]. The fact that all terrestrial rocks have ^{142}Nd/^{144}Nd higher than chondritic should resolve at least the question of whether or not there were superchondritic Sm/Nd sources in the Archean mantle.

Using a simple two-stage model, Boyet and Carlson [9] calculated that a Sm/Nd ratio high enough to generate an excess of 20 ppm in ^{142}Nd/^{144}Nd would be high enough to exceed a present day $\varepsilon_{143\mathrm{Nd}} = 10$ if the high Sm/Nd reservoir formed at any time after 30 Myr after solar system origin, or after about 4,540 Ma. Chronological constraints on this event are weak in that mixing between early formed high and low Sm/Nd reservoirs could modify this timescale. The demonstration of up to 17 ppm excesses in ^{142}Nd/^{144}Nd in the Isua samples shows that heterogeneity in ^{142}Nd/^{144}Nd in the early Archean mantle did exist, but the homogeneity of ^{142}Nd/^{144}Nd in all other terrestrial rocks so far analyzed indicates that this initial heterogeneity was mixed away rather rapidly.

4.2.1. Consequences for estimates of mantle composition

Most previous estimates of the composition of the mantle source of MORB, the so-called Depleted MORB Mantle or DMM, combine approaches that use trace

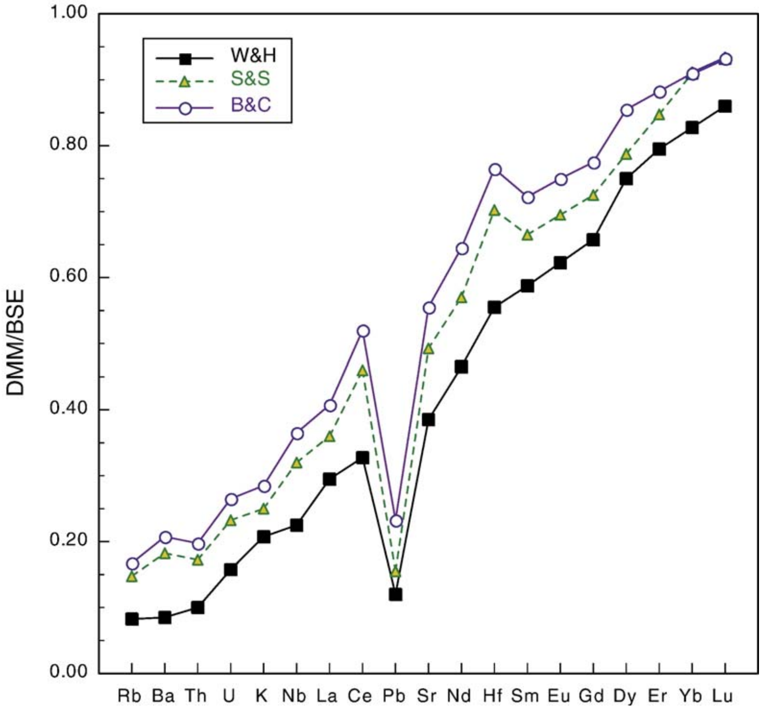


Fig. 3. Bulk silicate earth (BSE) [64] normalized trace element concentrations calculated for the mantle source of mid-ocean ridge basalts using the Sm/Nd and Lu/Hf ratios calculated as described in the text (named B & C). Lu and Yb concentration are fixed as described in [46], Eu, Gd, Dy and Er abundances are set by a linear (on a BSE normalized basis) extrapolation between Yb and Sm, and all other element abundances (except for Sm, Nd, and Hf) are calculated using the set of "constant" ratios in MORB from the "D-MORB" column of Table 3 in [46]. We obtained the following contents (in ppm): Rb = 0.1, Ba = 1.37, Th = 0.016, U = 0.0054, K = 68.4, Nb = 0.24, La = 0.26, Ce = 0.87, Pb = 0.035, Sr = 11.1, Nd = 0.81, Hf = 0.22, Sm = 0.29, Eu = 0.12, Gd = 0.42, Dy = 0.58, Er = 0.39, Yb = 0.40, Lu = 0.063. Note that the new DMM composition is more enriched in highly-incompatible elements compared to previous estimates (W&H = [47] and S&S = [46]).

element compositions of mid-ocean ridge basalts and/or abyssal peridotites and their isotopic compositions that allow calculation of parent–daughter elemental ratios [46,47]. Since these models are based on the assumption that DMM is the result of continent extraction, and that prior to continent extraction the mantle had chondritic relative abundances of refractory lithophile elements, the degree of depletion calculated for DMM depends on the assumed age when continent extraction began. The sooner in Earth history continents formed, the less incompatible element depleted DMM needs to be in order to satisfy the current isotopic compositions measured for MORB. Similarly, if some portion of the superchondritic Sm/Nd of DMM results from continent extraction from an early-formed incompatible element depleted, i.e. high Sm/Nd, mantle, then DMM will be less depleted than estimated with the assumption that the starting source had chondritic relative abundances of the refractory lithophile elements.

We illustrate this point by following the same continuous continental extraction model beginning at 3 Ga as used by Workman and Hart [47] in their recent calculation of the DMM composition. Instead of assuming that the mantle prior to continent formation had chondritic refractory lithophile element abundances, however, we assume a mantle with the higher Sm/Nd needed to explain the terrestrial superchondritic ^{142}Nd/^{144}Nd. Although the rate of growth of continent through time is still a debatable issue, with end members ranging from continuous production [48], no growth [49], to episodic crust-formation [50,51], by using the same continental growth model as Workman and Hart, we can more readily recognize the differences in DMM composition imposed by the assumption of a non-chondritic starting mantle composition.

We use the term "early depleted reservoir", or EDR to refer to the composition of the mantle before any crust had been formed. Our EDR composition starts with a ^{147}Sm/^{144}Nd equal to 0.209 as is needed to develop a ^{142}Nd/^{144}Nd excess of 20 ppm relative to chondrites, assuming that this high Sm/Nd has existed since solar system formation at 4567 Ma. Delaying formation of the EDR after this time increases the requisite Sm/Nd in the EDR due to the rapidly declining

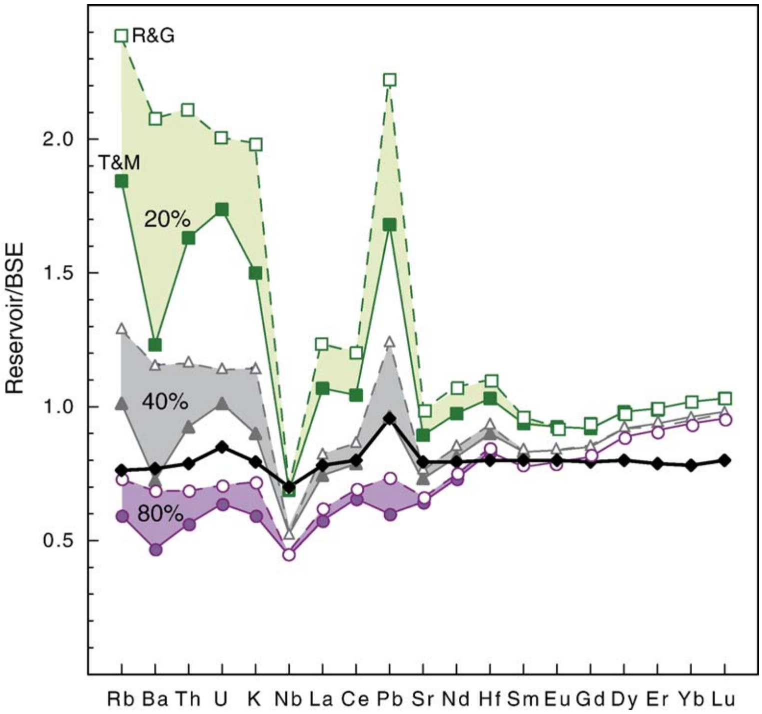
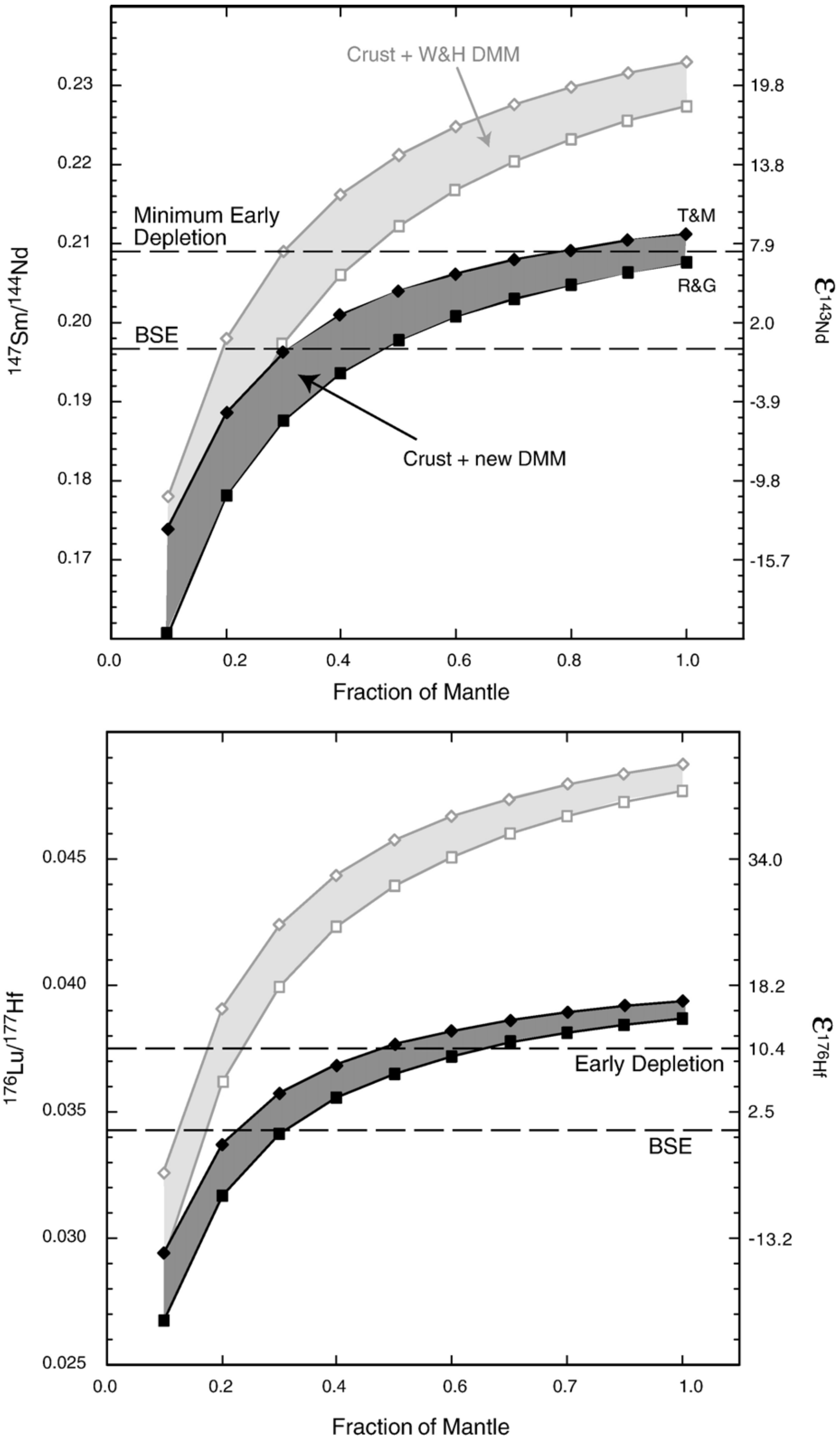


Fig. 4. BSE [64] normalized trace element abundances calculated for various mixtures of the depleted MORB mantle composition shown in Fig. 3 with two different estimates of the average composition of the continental crust (R&G = [63] and T&L = [62]). Each pair of calculated “primitive” mantle compositions is labeled with the mass percentage of the total mantle mass used to mix with the present day mass of continental crust. The black line denoted by diamonds is the recent revised estimate of the composition of the BSE from [68].

abundance of ^{146}Sm. A further critical piece of information for this modeling is the Lu/Hf ratio of the EDR because Lu/Hf provides an important element ratio that can be used to extrapolate these two parent–daughter ratios to the DMM abundance of a wide variety of incompatible trace elements by stepping through the list of “constant” trace element ratios observed in MORB (e.g. [46]). At the 3 Ga start time of continent formation in this model, $\varepsilon_{143\mathrm{Nd}}$ in the EDR is +2.7 relative to the standard chondritic Sm–Nd parameters [10,38]. Given recent issues concerning the value of the Lu decay constant [52–54], variable Lu–Hf systematics in chondritic meteorites [12,55,56], and a wide range in initial Hf isotopic compositions of early Archean to Hadean rocks and minerals [57,58], choosing appropriate Lu–Hf parameters to match the Sm–Nd modeling is not straightforward. We choose to use the Hf–Nd isotope correlation in Archean rocks [59], recalculating the $\varepsilon_{\mathrm{Hf}}$ values using the 1.867×10^{-11} yr^{-1} Lu decay constant [52,60] and the average carbonaceous chondrite Lu–Hf parameters [12] to arrive at a 3 Ga mantle Hf isotopic composition of $\varepsilon_{\mathrm{Hf}} = +4$. This then imposes a ^{176}Lu/^{177}Hf = 0.0375 on the EDR. We note that a value of $\varepsilon_{143\mathrm{Nd}} = +2.7$ at 3 Ga would correspond to +1.5 at 3.8 Ga, which is slightly lower than, but within uncertainty of, the initial ^{143}Nd/^{144}Nd ($\varepsilon_{143\mathrm{Nd}} = 1.9 \pm 0.9$) determined from the Sm–Nd isochron of the Isua samples that display excess ^{142}Nd/^{144}Nd and thus is consistent with the ^{147}Sm–^{143}Nd evolution displayed by early Archean rocks (e.g. [43]).

Following the approach of Workman and Hart [47], the two main evolution-stages are thus: (1) from 4.567 to 3.0 Ga, the silicate Earth evolves with a ^{147}Sm/^{144}Nd = 0.209 and ^{176}Lu/^{177}Hf = 0.0375 and (2) from 3.0 Ga, continuous continental crust extraction adds to the incompatible element depletion of the mantle to the degree needed to match the isotopic composition of present day MORB as listed in [47]. The present day parent/daughter ratios calculated for DMM following this method are ^{147}Sm/^{144}Nd = 0.220 and ^{176}Lu/^{177}Hf = 0.0413. These compare with ^{147}Sm/^{144}Nd = 0.248 and ^{176}Lu/^{177}Hf = 0.0521 from Workman and Hart [47]. Using these parent/daughter ratios and then the approach of Salters and Stracke [46], the trace element profile calculated here for DMM is shown in Fig. 3. The shape of the trace element profile is not surprising since the majority of the element abundances in DMM are determined from the same set of “constant ratios” used by Salters and Stracke [46], but the degree to which this curve is offset towards higher highly-incompatible-element abundances compared to previous estimates of the DMM composition shows the consequences of an early depletion event, or non-chondritic mantle, for these calculations.



One consequence of this elevation in the calculated incompatible element abundances of DMM is that a higher degree of melting is needed to produce an average MORB. Workman and Hart [47] show that the trace element pattern of primitive MORB magmas can be well matched by 6% melting of their highly-depleted DMM. In contrast, the less depleted DMM calculated here would have to melt to 8% to produce the same primary MORB basalt abundances. The 8% estimate is within the range of previous estimates (6–20%) [61] of the amount of melting needed to produce MORB and is less extreme than needed using the Workman and Hart DMM composition [47].

The important impact of a less depleted DMM, and a non-chondritic "primitive" Earth's mantle, e.g. the EDR, are their consequences for estimating the proportion of Earth's mantle affected by continent formation. Fig. 4 shows the simple mass balance of adding the new DMM composition to two estimates of average continental crust composition, the relatively mafic composition of Taylor and McLennan [62] and the more evolved composition of Rudnick and Gao [63]. In order to reach chondritic, or bulk-silicate-earth (BSE) abundances [64], between 30% and 60% of the mantle must have DMM composition in order to balance the incompatible element enrichment of the continental crust. At this mixing proportion, however, Fig. 4 shows that many of the "kinks" in the normalized incompatible element pattern calculated for the "primitive" mantle remain, for example the notable excess in Pb and low Nb and Ba contents. To eliminate these anomalies from the trace element pattern, one must add continental crust back to a volume of DMM equal to at least 80% of the total silicate Earth, though at this mixing proportion, the negative abundance anomaly at Nb still remains. The identical, and non-chondritic, Nb/U ratio of both MORB and OIB has been known for some time [65]. The persistence of the Nb deficit in the mantle throughout the mass balance modeling illustrated in Fig. 4 supports previous suggestions that at least some fraction of the Nb anomaly in the mantle predates continent formation and may reflect Nb partitioning into the core [66] or into a Nb-rich early formed crust that has been effectively isolated from the mantle over most of Earth history [67].

Involving greater than 60–80% of the mantle in continent formation, however, leaves the abundances of highly incompatible elements in the pre-continent-extraction mantle well below those estimated for the BSE [64] and even below, and more fractionated than, the new BSE composition proposed by Lyubetskaya and Korenaga [68]. This result conflicts with the previous paradigm that the mantle prior to continent formation must have had chondritic relative abundances of the refractory lithophile elements. Nevertheless, this is a requirement imposed by the superchondritic ^{142}Nd/^{144}Nd of terrestrial rocks.

Fig. 5 shows the crust-DMM mass balance for Sm/Nd and Lu/Hf ratios in the mantle. For a highly depleted DMM, like the Workman and Hart model, these parent daughter ratios increase rapidly as more DMM is added to the crust, reaching chondritic values at a mass of DMM roughly equal to 20–30% of the mantle, compared to 30–50% of the mantle using the DMM composition calculated here. Both these estimates are well within the range of numerous previous calculations that have considered continent-depleted mantle mass balance [41,42].

If the primitive mantle did not have chondritic relative refractory lithophile element abundances, but was more like the EDR assumed here, the highly depleted DMM [47] predicts only slightly higher proportional masses of DMM in the mantle (30–45%), but the more moderately depleted DMM requires much more of the mantle be affected by continent extraction, on the order of 80–100% based on Sm/Nd ratio (Fig. 5). A DMM that constitutes 80–100% of the mantle would have abundances of highly incompatible elements at roughly 50–70% (Fig. 4) of those estimated for the BSE [64]. Such low abundances of elements like K, U and Th would solve a number of puzzling issues in mantle geochemistry and geophysics. For a mantle K abundance of 250 ppm [64], roughly 50% of the ^{40}Ar produced over Earth history must still be resident in the mantle [69,70]. If instead, the bulk earth K abundance is 160 ppm, the amount of "missing" ^{40}Ar is much reduced if not eliminated completely [71,72]. Another important consequence of the more depleted mantle composition calculated here is that 60% lower abundance of K, U, and Th in the BSE would imply a bulk earth heat production due to radioactive decay of the heat

Fig. 5. Effect of different mantle fractions used to mass balance the continental crust on Sm/Nd and Lu/Hf ratio of the mantle prior to continent formation. Abscissa shows the mass fraction of the total mass of the BSE added to the present day mass of continental crust. Filled symbols show additions of depleted mantle of composition shown in Fig. 3 to two estimates of the average composition of the continental crust, diamonds indicating the Taylor and McLennan composition [62] and squares that of Rudnick and Gao [63]. Open symbols show the same mass balance using the more depleted MORB-source mantle composition proposed by [47]. Isotopic compositions listed on right axis of figures show the present day isotopic composition corresponding to the parent–daughter ratios on the left axis if this mantle reservoir formed at Earth formation 4.567 Ga. Horizontal lines show the parent–daughter ratios expected for a mantle of BSE [85] composition compared to the minimum Sm/Nd needed to explain the elevated $\varepsilon_{142\mathrm{Nd}}$ of terrestrial rocks compared to chondrites.

producing elements of only 12 TW, compared to the 20 TW with McDonough and Sun's BSE estimation [64]. This suggests that the Earth has a Urey ratio of ~0.3 and that a large fraction of the heat currently leaving Earth (44 TW; [73]) is the heat associated with Earth formation and is not the result of the radioactive decay of U, Th and K. The consequences and implications of such a low Urey ratio have been discussed in some detail by Lyubaetskaya and Korenaga [72].

If the Earth's mantle is as depleted in incompatible elements as suggested by this modeling, one might look for the signature of this non-chondritic primitive mantle in the radiogenic isotopic composition of mantle-derived rocks. The mantle sampled by ocean island basalts (OIB) provides our best evidence for the range of isotopic compositions available in the mantle. The relative deficiency of OIB with chondritic $^{143}Nd/^{144}Nd$, $^{176}Hf/^{177}Hf$ and Pb isotopic compositions near the Geochron (a requirement of any reservoir formed close in time to Earth formation), has for some time been a puzzle if more than half of the mantle retains chondritic Sm/Nd and Lu/Hf [6]. Following the mass balance used here, a DMM corresponding to 80% of the mantle would lead the model EDR to have $^{147}Sm/^{144}Nd$ of about 0.2049, which would produce a present day ε_{143Nd} of +4.9. The corresponding ε_{Hf} would be +12.2.

Because such a high percentage of Earth's Rb and Pb are stored in the continental crust, the Rb/Sr and U–Th/Pb of the mantle prior to continent formation calculated through the same mass balance approach depends strongly on the assumed abundances of Rb, Sr, U, and Pb in the continental crust. Using the DMM composition calculated here and assuming that it represents 80% of the mantle, adding the continental crust back to this DMM would suggest that the present day $^{87}Sr/^{86}Sr$ in the EDR lies between 0.7044 and 0.7055 with $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ in the range 17.9–18.8, 15.65–16.25, and 37.71–37.81, respectively using the Rudnick and Gao [63] or Taylor and McLennan [62] estimates for average continental composition. Excluding Pb isotopic characteristics for the moment, the isotopic composition calculated for the EDR lies within the range of the OIB isotopic component variably called FOZO [74], PHEM [75] or C [76] that represents the high $^{3}He/^{4}He$ component in OIB [77], commonly interpreted as the key signature of a "primitive" undegassed source. Following the model proposed here, variable extraction of continental crust from the mantle would produce a series of mantle compositions that lie between end member DMM (the mantle most affected by continent extraction) and FOZO/PHEM/C (EDR mantle unaffected by continent formation).

Even the lowest $^{206}Pb/^{204}Pb$ in this EDR, however has too high a $^{207}Pb/^{204}Pb$ to overlap the OIB data array. This problem could be overcome if the U/Pb estimated for the average continental crust were 5% lower. For example, mixing the Rudnick and Gao [63] average continental crust composition with a DMM equal to 80% of the mantle produces an EDR with a $^{238}U/^{204}Pb = 8.31$, which gives the present day $^{206}Pb/^{204}Pb = 17.9$ listed above. Increasing the crustal Pb abundance from 11 to 11.5 ppm in the Rudnick and Gao estimate would cause the $^{238}U/^{204}Pb$ of the EDR to decrease to 8.06, which in turn would lower its present day $^{206}Pb/^{204}Pb$ to 17.6 and $^{207}Pb/^{204}Pb$ to 15.48. These Pb isotopic compositions lie within, but at the low $^{206}Pb/^{204}Pb$ end, of the Pb isotope array seen for OIB.

4.2.2. Early silicate differentiation

The characteristics calculated for the EDR described above hold whether or not this reservoir simply represents a non-chondritic composition for the bulk silicate earth or was formed as the depleted component of an early terrestrial differentiation event. In this latter case, however, the Earth must contain an incompatible element enriched compliment to the EDR. The compositional characteristics of this enriched reservoir depend strongly on its size if the assumption is correct that the EDR and the enriched reservoir must sum back to chondritic relative abundances of refractory lithophile elements [9]. If this complementary enriched reservoir represents of order 20% of the mass of the mantle, and its composition is calculated on the assumption that the enriched reservoir and the EDR sum to the BSE composition given by McDonough and Sun [64], then the present day $^{87}Sr/^{86}Sr$, ε_{142Nd}, ε_{143Nd}, ε_{Hf}, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ of the enriched reservoir would be 0.7042, −0.18, −8, −29, 19.8, 16.8, and 40.3, respectively using the Rudnick and Gao estimate for continental composition [63]. These values are outside the range measured for any mantle-derived rock, although in Sr–Nd–Hf isotope space, they approach the composition of the low ε_{Hf} end-member that seems to be involved in the genesis of some kimberlites [20].

If an early formed enriched reservoir exists, the fact that all terrestrial rocks have the same superchondritic $^{142}Nd/^{144}Nd$ requires that the enriched reservoir has not significantly contributed to surface magmatism over Earth history and thus probably is isolated from mantle convection and preserved in the deep mantle [9]. The origin of the enriched component is speculative, but some evidence, including the isotopic composition of mantle noble gases [78,79], the depletion of Nb in Earth's mantle [67], and Sm–Nd isotope systematics [80] suggests that it may have formed as a primordial terrestrial crust that was unstable at Earth's surface. The observation of variable excesses of ^{142}Nd/^{144}Nd in rocks from Isua [13–15], but in no other terrestrial rock, suggests that the Hadean mantle was more depleted than calculated here for the EDR, but that some of the enriched primordial crust was mixed back into the mantle so that a homogeneous (at least as far as ^{142}Nd/^{144}Nd is concerned) EDR was formed in the mantle by shortly after 3.8 Ga.

Understanding this early era of Earth history is perhaps best done with the variety of short-lived radionuclides that were present on the early Earth. The Xe composition of the MORB source mantle has long been known to contain excesses in ^{129}Xe [81], which in this model may reflect degassing of the EDR during its formation. Another possible tracer for the EDR and its still-missing enriched compliment is the Nb–Zr radiometric system. ^{92}Nb decays into ^{92}Zr with a half-life 36 Myr and both elements are refractory and lithophile. However with an initial solar system ^{92}Nb/^{93}Nb ratio lower than 10^{-4} [82,83], the expected deviation in ^{92}Zr/^{90}Zr relative to the chondritic ratio due to an early silicate differentiation event is lower than the current external analytical reproducibility (±0.3 ε-unit, 2σ). So far, no ^{92}Zr anomaly has been measured in different terrestrial samples, including old zircons from Jack Hills (4.0 Byr, Australia) [83,84].

5. Conclusions

High-precision Nd isotope measurements have been performed on a wide variety of terrestrial samples selected to sample a variety of possible chemical reservoirs in the mantle. No variation in ^{142}Nd/^{144}Nd relative to the terrestrial standard value has been detected for kimberlites, carbonatites, komatiites, mid-ocean ridge basalts from different locations, or basalts from Pitcairn Island representing the EM1 mantle component. Only a few samples from the Isua Supracrustal Belt have ^{142}Nd/^{144}Nd excesses of up to 17 ppm, in agreement with previous results on samples coming from the same area [24–26]. These results indicate that all terrestrial samples come from a mantle reservoir characterized by a superchondritic Sm/Nd ratio.

The new constraint on mantle Sm/Nd ratio provided by the non-chondritic ^{142}Nd/^{144}Nd of terrestrial rocks allows a new estimation of the trace element content of the mantle source of mid-ocean ridge basalts (DMM), which is less depleted in incompatible elements than previous estimations. The combination of a less depleted DMM and a primitive mantle with superchondritic Sm/Nd requires the major portion (~80%) of the present-day mantle to be similar in composition to DMM. Adding the continental crust back to this large volume of depleted mantle leads to a primitive mantle composition that is depleted in highly incompatible elements by 30–50% compared to previous estimates of BSE compositions [64] with consequent implications for the heat budget and inventory of ^{40}Ar in the mantle. The Sr, Nd, Hf and Pb isotopic composition calculated for this early-depleted reservoir (EDR) are consistent with the FOZO/PHEM/C component identified in ocean island basalts. The fact that this component also is the high ^{3}He/^{4}He end member present in OIB suggests that a mantle reservoir with chondritic relative abundances of refractory lithophile elements does not contribute to ocean island or MORB volcanism, and thus may not exist. The incompatible element depletion characteristic of the mantle prior to continent formation may reflect either a bulk silicate earth composition that does not have chondritic relative abundances of refractory lithophile elements or an early differentiation event that produced complementary enriched and depleted reservoirs. Based on the isotopic characteristics expected for this enriched reservoir, mantle-derived rocks do not seem to show it as a mixing component, at least over the last 3.8 Byr of Earth history. This implies either that the enriched reservoir has been effectively "buried" in the deep mantle and has never contributed to surface magmatism, or that it simply does not exist.

Acknowledgments

We would like to thank M. Bizarro for providing us the samples of carbonatites, A. Gaffney for kimberlites from Greenland, V. Fedorenko for kimberlites from Siberia, I. Putchel for komatiites and E. Hauri for Pitcairn samples. Interesting conversations with M. Schönbächler, R. Walker and W. McDonough have contributed to enhance this manuscript, as well as comments of an anonymous reviewer. We are grateful to Rhea Workman for providing us her Matlab program for continental crust extraction calculation. Thanks to Mary Horan and Tim Mock for their help in the lab. This work was supported by the Carnegie Institution of Washington and the DTM Triton was purchased with the aid of a grant from the National Science Foundation.

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