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Maud Boyet, Michael O. Garcia, Raphaël Pik, Francis Albarède. A search for 142 Nd evidence of primordial mantle heterogeneities in plume basalts. Geophysical Research Letters, 2005, 32, pp.L04306. 10.1029/2004GL021873. hal-00098369

HAL Id: hal-00098369

https://hal.science/hal-00098369

Submitted on 2 Feb 2021

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# A search for <sup>142</sup>Nd evidence of primordial mantle heterogeneities in plume basalts

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Received 29 October 2004; revised 6 December 2004; accepted 5 January 2005; published 19 February 2005.

[1] In order to assess whether material differentiated shortly after terrestrial accretion is still present in the deep mantle, we investigated hot spot basalts for 142Nd/144Nd anomalies that could attest for the presence of live 146Sm  $(T_{1/2} = 103 \text{ My})$  at the time the mantle source of these basalts formed. We analyzed high  ${}^{3}\text{He}/{}^{4}\text{He}$  basalts from Loihi and Ethiopia and normal  ${}^{3}\text{He}/{}^{4}\text{He}$  basalts from Iceland. Although the  ${}^{143}\text{Nd}/{}^{144}\text{Nd}$  ratios of these basalts reflect a source with long-term LREE (light rare earth elements) depletion, no resolvable 142Nd anomalies were detected. Taking the analytical uncertainties (10-20 ppm) into account, however, the present results do not rule out the possibility that a large proportion of material fractionated very early in the Earth's history may still be hidden in the deep mantle. Citation: Boyet, M., M. O. Garcia, R. Pik, and F. Albarède (2005), A search for <sup>142</sup>Nd evidence of primordial mantle heterogeneities in plume basalts, Geophys. Res. Lett., 32, L04306, doi:10.1029/2004GL021873.

#### 1. Introduction

[2] The patterns of noble gas isotope compositions in basalts are widely considered as requiring that the deep mantle is essentially undegassed [Allègre et al., 1983]. A mantle source with high <sup>3</sup>He/<sup>4</sup>He (unradiogenic) ratios [Kurz et al., 1982] and solar Ne [Honda et al., 1991] is commonly associated with hot spots such as Hawaii or Iceland. The mantle component hosting this unradiogenic He and solar Ne is characterized by moderately depleted Sr and Nd isotopic signatures and received several more or less equivalent denominations: FOZO (for FOcal ZOne) [Hart et al., 1992], PHEM (for Primitive HElium Mantle) [Farley et al., 1992] or C (for Common) [Hanan and Graham, 1996]. In contrast, the concept that the mantle source of hot spots contains recycled oceanic crust [Hofmann and White, 1982], however, is also well entrenched. The positive correlation between  $\delta^{18}$ O and  $\delta^{187}$ Os/ $\delta^{188}$ Os suggests the presence of altered basalt [Lassiter and Hauri, 1998], while Sr excesses have been interpreted as revealing a low-pressure gabbroic component [Sobolev et al., 2000] and the Hf-Nd-Pb isotopic correlations in Hawaiian basalts attest to a contribution from pelagic sediments [Blichert-Toft et al., 1999]. These geochemical characteristics are consistent with tomographic evidence that some subducted plates reach the core-mantle boundary [Grand et al., 1997; van der Hilst et al., 1997].

[3] The 146Sm-142Nd system with its half-life of 103 My also has the potential of identifying primordial heterogeneities in the Earth's mantle. Both the parent and daughter nuclides are refractory and lithophile rare earth elements (REE). They did not fractionate during accretion and core segregation. We contend that high <sup>3</sup>He/<sup>4</sup>He ratios does not necessarily signal material with chondritic abundances and therefore that the \$^{146}Sm-^{142}Nd\$ system complements <sup>3</sup>He/<sup>4</sup>He evidence. The liberation of the gravitational energy from the accretion and core formation and from the heat of the extinct radioactive nuclides <sup>26</sup>Al and <sup>60</sup>Fe on a time scale of a few My triggered the wholesale melting of the Earth's mantle, at least down to a certain depth in the upper mantle. On top of the molten mantle, a buoyant conductive lithosphere of hydrous minerals, notably serpentine, strongly reduced heat escape from the magma [Boyet et al., 2003]. At the high pressures of the melt/cumulate interface, CO<sub>2</sub> and H<sub>2</sub>O solubility is so high that no gas phase can evolve which would strip He from the melt. Gases in general and <sup>3</sup>He in particular distribute themselves among the coexisting solid and liquid phases just as any other incompatible elements such as Th or Nd. Although the persistence of <sup>142</sup>Nd anomalies needs very early Sm/Nd magmatic fractionation, <sup>3</sup>He should still be ubiquitous in the undegassed material. For example, a silicate/melt fractionation event taking place at the time of core formation 30 My after the isolation of the Solar Nebula [Kleine et al., 2002; Yin et al., 2002] capable of creating a typical anomaly of +1000 ppm (+10  $\epsilon$ ) on the <sup>143</sup>Nd/<sup>144</sup>Nd ratio in the modern mantle would also create a 20 ppm anomaly on its <sup>142</sup>Nd/<sup>144</sup>Nd ratio. Such <sup>142</sup>Nd anomalies are resolvable by modern mass spectrometry techniques.

[4] The existence of <sup>142</sup>Nd anomalies and therefore of live 146Sm at the time of wholesale differentiation of the planetary mantle is well documented in eucrites (up to 300 ppm) [Prinzhofer et al., 1992; Wadhwa and Lugmair, 1996], Martian meteorites (100 ppm) [Harper et al., 1995], and even lunar samples (30 ppm) [Nyquist et al., 1995]. The <sup>142</sup>Nd anomalies reported in Archean samples also attest to the fact that the terrestrial mantle went through a major Sm/ Nd fractionation event within a few tens of My after planetary accretion [Boyet et al., 2003; Caro et al., 2003; Harper and Jacobsen, 1992]. All the 142Nd terrestrial anomalies detected are positive and so far have been exclusively observed in 3.8 Gyr samples from the Isua Supracrustal Belt (West Greenland). Therefore, 600 My after the beginning of the Earth's accretion, this primordial reservoir had not been completely remixed with the rest of the mantle in spite of the Archean mantle being hotter and mantle convection stronger than today. Here we present new

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**Table 1.** <sup>142</sup>Nd and <sup>143</sup>Nd isotopic data for Iceland, Ethiopia and Loihi (Hawaiian Volcano) samples<sup>a</sup>

Sample	Туре	Mg#	<sup>3</sup> He/ <sup>4</sup> He	N	$\epsilon_{142Nd} \pm 2\sigma_m$	$\epsilon_{143Nd} \pm 2\sigma_{r}$
			Icelana	!		
9323	aph. bas.	55.70		3	$0.24 \pm 0.17$	$8.06 \pm 0.15$
9244	aph. bas.	53.40		5	$0.18 \pm 0.14$	$7.79 \pm 0.13$
9356	picrite	71.60		3	$-0.05 \pm 0.17$	$9.04 \pm 0.13$
9376	picrite	61.60	8 - 10	4	$0.06 \pm 0.12$	$9.08 \pm 0.12$
9377	picrite	65.30		5	$0.07 \pm 0.11$	$9.64 \pm 0.09$
9381	picrite	76.30		5	$-0.07 \pm 0.14$	$9.56 \pm 0.11$
9390	picrite	78.90		4	$-0.03 \pm 0.12$	$10.12 \pm 0.10$
9394	picrite	68.80		1	$-0.18\pm0.20$	$10.00 \pm 0.17$
			Ethiopia	a		
E38	HT2	68.74	16.4	2	$0.03 \pm 0.18$	$6.01 \pm 0.14$
E39	HT2	-	19.6	6	$-0.07 \pm 0.13$	$5.91 \pm 0.12$
395	LT	39.23	-	6	$0.02 \pm 0.14$	$4.78 \pm 0.11$
E156	alk. bas.	-	9.9	3	$0.12 \pm 0.15$	$5.85 \pm 0.12$
E181	LT	-	-	3	$-0.08 \pm 0.19$	$4.60 \pm 0.16$
E202	LT	50.99	-	5	$-0.05 \pm 0.11$	$2.10 \pm 0.10$
E216	LT	60.19	-	5	$-0.07 \pm 0.14$	$8.25 \pm 0.11$
E266	alk. bas.	-	13.2	4	$-0.07 \pm 0.17$	$3.85 \pm 0.13$
E268	alk. bas.	-	16.9	4	$-0.03 \pm 0.19$	$3.32 \pm 0.16$
3271	alk. bas.	-	15.7	2	$-0.07\pm0.16$	$2.69 \pm 0.14$
		i	Loihi (Haw	vaii)		
158-4	basanitoid	-	(220)	4	$0.01 \pm 0.12$	$6.74 \pm 0.11$
1801-5	tholeiite	56.251		6	$0.06 \pm 0.13$	$5.87 \pm 0.11$
1801-19	tholeiite	55.77	22 - 35	6	$-0.08 \pm 0.12$	$6.16 \pm 0.10$
1802-4b	alk. bas.	46.25		3	$-0.08 \pm 0.10$	$6.15 \pm 0.08$
804-1	tholeiite	58.51		6	$0.09 \pm 0.09$	$6.04 \pm 0.08$
1804-21	trans. bas.	57.17		9	$0.00 \pm 0.08$	$6.03 \pm 0.07$

"Sample compositions giving rock types and Mg# values are from Stracke et al. [2003] for Iceland, Pik et al. [1998] for Ethiopia, and Garcia et al. [1995] for Loihi.  $^3$ He<sup>A</sup>He ratios are from Breddam et al. [2000] for Iceland, Marty et al. [1996] for Ethiopia, and Kurz et al. [1983] for Loihi. LT and HT2 refer to low-Ti and high-Ti basalts, respectively. The measurements were carried out on the Lyon VG Plasma 54 MC-ICPMS. N is the number of measurements. The Nd isotopic ratios were normalized for mass fractionation using  $^{146}$ Nd/ $^{144}$ Nd = 0.7219.  $\varepsilon_{142\text{Nd}} = \{(^{142}\text{Nd})^{144}\text{Nd})_{\text{standard}}$  refers to the JMC standard (batch 801149A) analyzed before the sample. Ce and Sm isobaric interferences were monitored at masses 140 and 147, respectively. The  $\varepsilon_{143\text{Nd}}$  values are calculated with respect to CHUR with a modern value of 0.512638. The final precision quoted for  $\varepsilon_{142\text{Nd}}$  and  $\varepsilon_{143\text{Nd}}$  for each sample corresponds to the weighted internal precisions (2σ<sub>m</sub>) of both the sample and standard runs.

<sup>142</sup>Nd isotopic data for samples collected from three well-characterized sites that each represents the expression of a mantle plume: (1) Loihi volcano, an extensively studied occurrence of oceanic hot spot volcanism, (2) Iceland, a hot spot located on the mid-Atlantic ridge, and (3) Ethiopian continental flood basalts (see auxiliary material¹). In order to minimize potential crustal contamination, a problem for more fractionated Icelandic lava [*Eiler et al.*, 2000], we selected samples with high MgO contents. *Caro et al.* [2003] found, as expected from the long-term geodynamic processing of the upper mantle, that mid-ocean ridge basalts show no <sup>142</sup>Nd anomaly. We will show that hot spot basalts, even those with the highest <sup>3</sup>He/<sup>4</sup>He ratios, also have chondritic <sup>142</sup>Nd isotopic abundances.

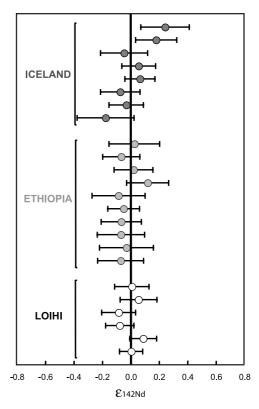
#### 2. Results

[5] All details of the chemical separation and mass spectrometry techniques are described elsewhere [Boyet et

al., 2003]. The Nd isotope compositions were measured by multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) in Lyon. Work on Isua mantlederived material demonstrated that by pooling data on the same samples, anomalies of <20 ppm (0.2  $\epsilon$ -units) can be clearly resolved by this technique [Boyet et al., 2003]. The <sup>142</sup>Nd isotopic data are reported in Table 1 and displayed in Figure 1. None of the samples analyzed here show a resolvable  $^{142}Nd$  anomaly: the values of  $\epsilon_{142Nd}$  fall between -0.18 and +0.24. The unweighted mean of  $\varepsilon_{142Nd}$  values for all the samples analyzed in the present study is  $0.00 \pm$ 0.20 (2-standard deviations). Sample 9323 from Iceland has the largest deviation (+0.24) but this analysis has not been replicated on separate dissolutions and the mean value is dominated by one of the three measurements, which has an  $\epsilon_{142Nd}$  of  $+0.51\pm0.34.$  Routine standard error  $(2\sigma_m)$  on  $\epsilon_{142Nd}$  is 10-20 ppm. Therefore, all the sample  $^{142}Nd/^{144}Nd$ ratios are chondritic within error bars. The Icelandic samples show the largest scatter, which can be explained by the particularly low Nd contents of picrites [Slater, 1996; Stracke et al., 2003]. The  $\varepsilon_{143\text{Nd}}$  values range between +8 and +10 for the Icelandic samples, between +5 and +6 for Loihi, and between +2 and +6 for Ethiopia.

#### 3. Discussion

[6] The present results show that, although the mantle sources of the studied basalts have positive  $\varepsilon_{143\mathrm{Nd}}$  values reflecting a source with long-term LREE depletion, no



**Figure 1.** Representation of  $^{142}$ Nd/ $^{144}$ Nd ratios expressed as  $\varepsilon_{142\text{Nd}}$  of hot spot samples listed in Table 1. This plot displays all the values used to derive the mean isotope compositions listed in Table 1 with samples organized by locality.

<sup>&</sup>lt;sup>1</sup>Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2004GL021873.

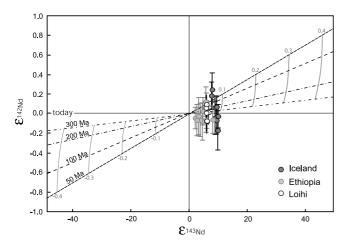


Figure 2. Different evolution trajectories of the Nd isotopic composition for a chondritic reservoir (equivalent to the BSE) fractionated very early in the history of the Solar System using a simple two-stage model evolution. The first stage starts at  $T_0$  with planetary accretion and undifferentiated chondritic material, the second stage at  $T_0$  +  $\Delta T$  with the wholesale differentiation of the mantle (equations (1) and (2)). The value of  $\varepsilon_{142Nd}$  in each reservoir strongly depends on the time interval  $\Delta T$  (black lines) and the corresponding parent-daughter fractionation factor  $f_{\text{Sm/Nd}}$  (grey curves). For closed-system evolution of the two parent-daughter pairs, the top right quadrant represents a depleted reservoir with a Sm/Nd ratio lower than the CHUR value. The bottom left quadrant defines the complementary enriched reservoir (Sm/Nd lower than to the CHUR value). The error bars correspond to the weighted internal precision (2-sigma errors) on each measurement and, for  $\varepsilon_{143Nd}$ , are smaller than the size of the symbols.

<sup>142</sup>Nd anomaly can be resolved. Although measurable <sup>142</sup>Nd anomalies have been observed in Isua metabasalts, mantle convection over the last 3.8 Gy seems to have obliterated all memory of the mantle primordial differentiation. Simple models may account for the present data:

- [7] 1. The terrestrial magma ocean never formed. Because of its strong gravity and abundant water, the Earth could not evolve a buoyant crust of anorthosite acting as an insulating boundary layer. Heat from accretion and radioactivity was radiated into space, the cold heavy crust foundered into molten magma, and melt quickly vanished [Davies, 1990]. This model neglects the presence of the hydrosphere, the ensuing hydration of the upper layer, and the formation of a buoyant hydrous lithosphere [Boyet et al., 2003]
- [8] 2. Contrary to the mantle of Mars and Moon, mineral segregation from the magma ocean produced too little Sm/Nd fractionation. This is unlikely since both majorite cumulates and the lithosphere should be prominently fractionated in the magma ocean.
- [9] 3. The <sup>142</sup>Nd anomalies observed in Isua metabasalts reveal local phenomena and not the wholesale differentiation of the mantle. The existing <sup>142</sup>Nd data are still too fragmentary for such a possibility to be assessed.
- [10] 4. Material differentiated in the first 10's of My of the Earth's history is remixed and interlayered with material reprocessed afterwards. Upon melting and extraction of hot

spot basalts into their volcanic system, mixing occurs. The mixture Nd is dominated by the recycled end-member whereas He and Ne are dominated by primitive undegassed end-member.

[11] We consider model 4 as the most likely but contend that the existence of primordial heterogeneities in the mantle source of hot spot basalts is not ruled out by the present observations. A faint hint at <sup>142</sup>Nd isotopic heterogeneities may be the broad dispersion of the raw  $\varepsilon_{142Nd}$  data ( $\pm 0.20$ ) with respect to the mean analytical error (±0.12) at the same 95 confidence level. The  $\varepsilon_{142Nd}$  -  $\varepsilon_{143Nd}$  diagram of Figure 2 shows the evolution trajectories of the Nd isotopic composition for a chondritic reservoir (equivalent to the Bulk Silicate Earth) fractionated very early in the history of the Solar System using a simple two-stage model evolution. The 142Nd-143Nd isotopic signature of this fractionated reservoir depends on two main parameters, the relative parent/daughter fractionation factor  $f_{\text{Sm/Nd}}$  with respect to chondrites and the age of this event. The two-stage model describes the evolution of a chondritic mantle undergoing Sm/Nd fractionation at time  $\Delta T$  after accretion. If  $T_0$  is the age of the Earth, the modern  $\varepsilon_{143Nd}$  and  $\varepsilon_{142Nd}$  values of the mantle are given by [Harper and Jacobsen, 1992]:

$$\varepsilon_{143\text{Nd}} \approx Q_{143} f_{\text{Sm/Nd}} T_0 \tag{1}$$

$$\varepsilon_{142\text{Nd}} \approx Q_{142} f_{\text{Sm/Nd}} \left( ^{146} \text{Sm} / ^{144} \text{Sm} \right) \times e^{-\lambda \Delta T}$$
(2)

where  $Q_{143} = 25.09 \text{ Gy}^{-1}$ ,  $Q_{142} = 353$ , ( $^{146}\text{Sm}/^{144}\text{Sm}$ ) $_{To}^{CHUR} = 0.008$  [*Prinzhofer et al.*, 1992] and  $\lambda$  stands for the decay constant of  $^{146}\text{Sm}$  (6.73 Ga $^{-1}$ ). Fractionation events younger than  $\sim$ 4.25 Ga or with Sm/Nd fractionation <10 percent produce  $\varepsilon_{142\text{Nd}}$  values indistinguishable from the BSE value within the typical analytical uncertainties of the techniques used in this work ( $\varepsilon_{142\text{Nd}} \approx 0.0 \pm 0.15$ ). In comparison, the highest anomaly reported so far on terrestrial samples is of +0.3  $\varepsilon$  [*Boyet et al.*, 2003; *Harper and Jacobsen*, 1992].

[12] Simulations tracking chemical tracers in convection models of the mantle suggest that primordial material formed during the initial mantle differentiation may have survived unmodified to the present day [Davies, 2002; Xie and Tackley, 2004]. Such a possibility has long been discounted on the basis that mantle convection would quickly homogenize the mantle and wipe out any primordial signal [O'Nions and Tolstikhin, 1996]. This is only true for the *mean* primordial signature of the primitive mantle and convective mixing will not obliterate all the remnants of primitive material in the lower mantle. If the mantle is a well-mixed reservoir, the probability that an atom is extracted at a given time is independent of its history in the reservoir (Poisson process). In this case, the residence times are distributed exponentially and the proportion of 4.56 Ga old Nd in a system with a 7 Gy mean residence time typical of Nd (F. Albarede, The survival of mantle geochemical heterogeneities, submitted to Structure, Composition, and Evolution of Earth's Mantle, Geophysisical Monograph Series, edited by R. van der Hilst et al., AGU, Washington, D. C.) is simply exp (-4.56/7) or about 50 percent. If the reservoir is not well mixed and old undegassed material lingers at the base of the mantle, the proportion of primordial material may be even larger [Gurnis and Davies, 1986]. Even in modest proportions, a

primordial component could therefore impart the high  ${}^{3}\text{He}/{}^{4}\text{He}$  value and the solar Ne signature to oceanic basalts which are otherwise characterized by the recycled character of their lithophile isotopic systems.

#### 4. Conclusion

- [13] We have shown that although the mantle sources of the basalts studied here have positive  $\epsilon_{143\mathrm{Nd}}$  values reflecting a source with long-term LREE depletion, no resolvable  $^{142}\mathrm{Nd}$  anomaly is detectable in these hot spot samples. The analytical precision does not however exclude the presence of material fractionated very early in the Earth's history in the mantle source of hot spots especially if this component is interspersed with material processed much later in the Earth's history.
- [14] Acknowledgments. We are grateful to Philippe Télouk for keeping the Plasma 54 in working conditions and to Janne Blichert-Toft for constant feedback in the lab. Dan McKenzie is thanked for providing the Theistareykir samples and for encouragement. Comments by two anonymous reviewers helped improve the readability of the manuscript. This work was supported by the Institut National des Sciences de l'Univers, in particular through the Program "Intérieur de la Terre" to FA, and by National Science Foundation grant 0336874 to MG.

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