Nonchondritic $^{142}$Nd in suboceanic mantle peridotites

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[1] The discovery that several solid Earth reservoirs have a superchondritic $^{142}$Nd/$^{144}$Nd ratio led to the hypothesis that either the bulk silicate Earth is not chondritic or that a subchondritic reservoir lies hidden somewhere within the Earth’s interior. One important reservoir, i.e., mid-ocean ridge peridotites representing the main component of the upper oceanic mantle and the source of mid-ocean ridge basalts, has never been tested for $^{142}$Nd/$^{144}$Nd. We determined the $^{142}$Nd/$^{144}$Nd ratio in clinopyroxene separated from two peridotites and a pyroxenite from the SW Indian Ridge and one peridotite from the northern Mid-Atlantic Ridge. All samples analyzed have superchondritic $^{142}$Nd/$^{144}$Nd ratios in line with mantle-derived material measured to date, except for some ancient cratonic rocks.

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1. Introduction

[2] For many years, the bulk silicate Earth (BSE), that is the Earth’s interior excluding the metallic core, was assumed to have relative abundances of refractory lithophile elements similar to those of chondritic meteorites [e.g., *McDonough and Sun*, 1995; *Palme and O’Neill*, 2003], commonly regarded as representing the building blocks of our Planet. The main isotopic tracer of this concept was the Sm–Nd system, two neighboring REE that are both refractory lithophile elements [e.g., *DePaolo and Wasserburg*, 1976a, 1976b]. Based on the assumption of a chondritic
Earth, widely accepted models on the differentiation of the Earth’s mantle and on the generation of the continental and oceanic lithosphere have been proposed [e.g., Jacobsen and Wasserburg, 1980; Allegre et al., 1983; Hofmann, 1988]. However, the discovery that the $^{142}$Nd/$^{144}$Nd ratio of chondritic meteorites is systematically lower than in most terrestrial rocks [Boyet and Carlson, 2005] has stimulated a reexamination of this concept.

[3] The $^{142}$Nd is generated by decay of $^{146}$Sm, with a half-life of 103 Ma, much shorter than the half-life of the $^{147}$Sm to $^{143}$Nd decay system (106 Ga). The higher than chondritic $^{142}$Nd/$^{144}$Nd ratio of terrestrial rocks implies either an overall non-chondritic BSE, or the existence of a complementary reservoir with lower than chondritic Sm/Nd ratio that is hidden somewhere in the Earth’s interior [Boyet and Carlson, 2005, 2006; Bourdon et al., 2008; Carlson and Boyet, 2008; Caro et al., 2006; Caro and Bourdon, 2010; Murphy et al., 2010; Labrosse et al., 2007; O’Neill and Palme, 2008; Warren, 2008]. Due to the relatively short half-life of the $^{146}$Sm to $^{142}$Nd decay reaction, and given that Nd is more incompatible than Sm, the nonchondritic $^{142}$Nd/$^{144}$Nd of most terrestrial rocks may have resulted from a major differentiation event affecting the mantle of the very young Earth [Boyet et al., 2003; Boyet and Carlson, 2005; Caro et al., 2003, 2006; Harper and Jacobsen, 1992].

[5] Evidence for the creation and survival of compositionally heterogeneous reservoirs in the early Earth is provided by both positive [Boyet and Carlson, 2006; Caro et al., 2003, 2006; Bennett et al., 2007; Harper and Jacobsen, 1992] and negative [O’Neil et al., 2008] $^{142}$Nd anomalies in Hadean and Eoarchean crustal rocks compared to modern mantle-derived rocks. With the exception of some samples from the 1.48 Ga Khariar alkaline complex of India [Upadhyay et al., 2009], all samples of mantle-derived rocks younger than 3.5 Ga so far measured have analytically indistinguishable $^{142}$Nd/$^{144}$Nd ratios, roughly 18–20 ppm higher than measured in ordinary and enstatite chondrites [Andreasen et al., 2008; Boyet et al., 2005; Boyet and Carlson, 2006; Carlson et al., 2007; Caro et al., 2006; Murphy et al., 2010]. This suggests that post 3.5 Ga mixing of the mantle has almost entirely erased the compositionally distinct mantle reservoirs created by Hadean Earth differentiation [e.g., Bennett et al., 2007].

[6] Given the above, it is important that all major mantle reservoirs be well constrained as far as Nd isotopic composition. Although the main component of the suboceanic upper mantle is peridotite, no $^{142}$Nd data on suboceanic peridotite have been reported to date. The only direct mantle samples measured for $^{142}$Nd are garnet inclusions in diamonds from the Finsch (South Africa) kimberlite: they show normal mantle $^{142}$Nd/$^{144}$Nd values [Caro et al., 2008]. The $^{142}$Nd/$^{144}$Nd of the suboceanic mantle has been inferred from measurements on four mid-ocean ridge basalt (MORB) samples, one from the East Pacific Rise, one from the Indian Ridge [Boyet and Carlson, 2005, 2006], and two of unspecified location [Caro et al., 2006], and on a number of ocean island basalts [Boyet et al., 2005; Boyet and Carlson, 2006; Caro et al., 2006; Andreasen et al., 2008; Murphy et al., 2010]. But MORB and ocean island basalts are generated by partial melting of mantle sources consisting of peridotite plus probably other enriched components (pyroxenite, eclogite), possibly derived from subducted lithosphere [Zindler and Hart, 1986; Hart, 1988; Hofmann, 1997; Salters and Dick, 2002; Hofmann, 2003; Cipriani et al., 2004; Seyler et al., 2004]. These enriched components, if present in significant quantity in the mantle source of MORB, would dominate the Nd content of any partial melt of the mixed source. Therefore, we attempted to analyze $^{142}$Nd/$^{144}$Nd directly in mantle-derived mid-ocean ridge peridotites (MORP) that may
Table 1. Nd Isotopic Composition for Standards and Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{144}$Nd (V)</th>
<th>Ratios</th>
<th>$^{142}$Nd/$^{144}$Nd</th>
<th>$^{143}$Nd/$^{144}$Nd</th>
<th>$^{145}$Nd/$^{144}$Nd</th>
<th>$^{146}$Nd/$^{144}$Nd</th>
<th>$^{148}$Nd/$^{144}$Nd</th>
<th>$^{150}$Nd/$^{144}$Nd</th>
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</thead>
<tbody>
<tr>
<td>La Jolla Nd</td>
<td>4.22</td>
<td>540</td>
<td>0.0000324</td>
<td>0.0000084</td>
<td>1.1418402</td>
<td>0.5118455</td>
<td>0.3483982</td>
<td>0.7223257</td>
</tr>
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<td>La Jolla Nd</td>
<td>3.94</td>
<td>540</td>
<td>0.00002157</td>
<td>0.0000065</td>
<td>1.1418373</td>
<td>0.5118465</td>
<td>0.3484006</td>
<td>0.7208362</td>
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<tr>
<td>La Jolla Nd</td>
<td>5.13</td>
<td>540</td>
<td>0.0000884</td>
<td>0.000023</td>
<td>1.1418419</td>
<td>0.5118452</td>
<td>0.3483987</td>
<td>0.7213001</td>
</tr>
<tr>
<td>La Jolla Nd</td>
<td>2.53</td>
<td>540</td>
<td>0.0000545</td>
<td>0.000036</td>
<td>1.1418362</td>
<td>0.5118424</td>
<td>0.3483976</td>
<td>0.7225038</td>
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<tr>
<td>La Jolla Nd</td>
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<td>0.0000357</td>
<td>0.000016</td>
<td>1.1418453</td>
<td>0.5118467</td>
<td>0.3483975</td>
<td>0.7226496</td>
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<tr>
<td>Mean, 6 La Jolla Nd standards</td>
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</tr>
<tr>
<td>SV84-D1-1 Cpx</td>
<td>2.72</td>
<td>540</td>
<td>0.0000150</td>
<td>0.0000480</td>
<td>1.1418358</td>
<td>0.5118451</td>
<td>0.3483983</td>
<td>0.722209</td>
</tr>
<tr>
<td>2σ mean</td>
<td>0.0000002</td>
<td>0.000017</td>
<td>0.0000023</td>
<td>0.000015</td>
<td>0.000003</td>
<td>0.0000017</td>
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<tr>
<td>SV84-D1-1 Cpx/La Jolla (ppm)</td>
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<td>EDUL21-1-1 Cpx</td>
<td>1.60</td>
<td>540</td>
<td>0.0000066</td>
<td>0.000011</td>
<td>1.1418348</td>
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<tr>
<td>2σ mean</td>
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<td>0.000017</td>
<td>0.0000023</td>
<td>0.000015</td>
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<td>0.0000017</td>
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<tr>
<td>EDUL21-1-1 Cpx/La Jolla (ppm)</td>
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<tr>
<td>EDUL23-2-4 Cpx</td>
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<td>0.00185</td>
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<td>0.0000034</td>
<td>0.0000021</td>
<td>0.000009</td>
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<tr>
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<td>1.72</td>
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<td>0.0000206</td>
<td>0.0000523</td>
<td>1.1418270</td>
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<td>0.724233</td>
</tr>
<tr>
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<td>0.0000005</td>
<td>0.000012</td>
<td>0.0000037</td>
<td>0.0000020</td>
<td>0.000069</td>
<td>0.000026</td>
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<td></td>
</tr>
<tr>
<td>Average of the 2 runs</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2σ mean</td>
<td>0.0000128</td>
<td>0.0000046</td>
<td>0.0000044</td>
<td>0.0000004</td>
<td></td>
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<tr>
<td>EDUL69-8-3 Cpx</td>
<td>0.64</td>
<td>270</td>
<td>0.0000330</td>
<td>0.00267</td>
<td>1.1418406</td>
<td>0.5137145</td>
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<td>0.72389</td>
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<tr>
<td>2σ mean</td>
<td>0.0000020</td>
<td>0.000011</td>
<td>0.0000069</td>
<td>0.0000041</td>
<td>0.000011</td>
<td>0.0000056</td>
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<tr>
<td>EDUL69-8-3 Cpx/La Jolla (ppm)</td>
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<tr>
<td>2σ mean</td>
<td>0.0000150</td>
<td>0.000012</td>
<td>0.0000069</td>
<td>0.0000041</td>
<td>0.000011</td>
<td>0.0000056</td>
<td></td>
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</tr>
</tbody>
</table>

aData for $^{144}$Nd is expressed in volts (10^{-11}amps). The $^{146}$Nd/$^{144}$Nd is as measured, not fractionation corrected.
better reflect the composition of the end-member incompatible-element-depleted mantle reservoir.

2. Samples, Methods and Results

2.1. Samples

One challenge with determining precise Nd isotopic compositions in oceanic peridotites is that generally they are residual after partial melting and extraction of MORB; thus, their Nd content, mostly concentrated in cpx, is exceedingly low (range in cpx from 0.02 to 2–3 ppm). Given that $^{142}$Nd/$^{144}$Nd determinations of sufficient precision with state of the art mass spectrometry require a minimum of 200 ng Nd, >500 mg of pure cpx need to be separated. We chose relatively unserpentinized, cpx-rich peridotites, two from the Southwest Indian Ridge, one from the Knipovich Ridge in the northern Mid-Atlantic Ridge and two from the Mid-Atlantic Ridge at 11°N; one pyroxenite sample from the SWIR was also analyzed (Table 1 and Figure 1).

All five peridotite samples contain the primary mineral assemblage typical of MORP, i.e., olivine-opx-cpx-spinel. The two SWIR samples were collected from a portion of the global ridge system with low spreading rate (~8 mm/yr). They contain ~5–8% modal cpx [Seyler et al., 2003]. Their spinel and opx Cr# (~100 Cr/(Cr + Al)) suggest they are residual after ~15% partial melting. The Knipovich ridge sample is relatively undepleted (Cr# in spinel is 12.7, in opx 7.6). The two samples from the MAR are from an exposed lithospheric section at 11°N [Bonatti et al., 2003]; they contain ~2% modal cpx and have undergone a moderate extent of melting (~10% F). The SWIR pyroxenite consists of granular cpx (~70%; Mg# = 88.7) and olivine (~30%; Fo = 84.7); its mineral chemistry is similar to that of other pyroxenites and cumulates from the mid-ocean ridge system.

2.2. Methods

Clinopyroxenes were handpicked under a microscope and leached following a procedure by Snow et al. [1993]. Dissolution and preliminary Nd separation steps were performed at LDEO using standard techniques. Nd was separated in a two column procedure using Eichrom TRU spec resin to separate the rare earth elements, followed by a-hydroxy isobutyric acid (α-HIBA) (where 0.5 ml H$_2$O$_2$ was added to 100 ml of α-HIBA just prior to the column procedure to reduce any Ce4+ that was present in the sample after the dry down from the first column) [e.g., Boyet and Carlson, 2005] to separate Nd from all other REE. An additional pass through the Nd separation column was performed at DTM in order to improve on the separation of Sm from Nd. The α-HIBA procedure at DTM contributes a Nd blank of 2 pg. Combined with the dissolution and processing blank of 51 pg for the procedures performed at Lamont, given the large samples sizes used for these analyses, the chemical processing blanks were negligible.

Isotopic measurements were performed with the DTM Thermo-Fisher Triton thermal ionization mass spectrometer following procedures similar to those described by Boyet and Carlson [2005]. These measurements were performed shortly after the faraday cups were replaced in April of 2008. The samples were run as Nd+ on double Re filaments with ion currents of $^{144}$Nd ranging from 2 to $5 \times 10^{-11}$ amps for the standards. Signal sizes for the samples are given in Table 1. Because the samples were not spiked, we do not know exactly how much Nd was present, but given the signal sizes produced, we estimate that between 50 and 200 ng of Nd was loaded on each filament. Data were obtained statically monitoring all Nd isotopes, $^{140}$Ce and $^{147}$Sm in separate faraday cups. Full runs consisted of 540 ratios of 8 s signal integrations using amplifier rotation. Data are fractionation corrected to $^{144}$Nd/$^{144}$Nd = 1.385233 (equivalent to $^{146}$Nd/$^{144}$Nd = 0.7219) in order to simplify cor-

Figure 1. Map of the mid-ocean ridge system with the location of peridotites and pyroxenite samples of this study and of MORB samples analyzed to date for $^{142}$Nd. Map was generated using GeoMapApp (www.geomapapp.org/) and the Global Multi-Resolution Topography Synthesis [Ryan et al., 2009].
rection for Sm interference, assuming exponential mass dependency for the fractionation. Ce interferences -\(^{142}\text{Ce}/^{144}\text{Nd}\) in the samples ranged from 1 to 4 ppm and are thus negligible. Sm interferences -\(^{144}\text{Sm}/^{144}\text{Nd}\) for samples SV84-D1-1 and EDUL23-2-4 were approximately 10 ppm whereas the Sm interference was more significant for samples EDUL21-1-1 (690 ppm) and EDUL69-8-3 (547 ppm) most likely because these samples had very high Sm/Nd ratios as suggested by their high measured -\(^{143}\text{Nd}/^{144}\text{Nd}\). The magnitude of Sm interference on Nd is approximately 15 and 10 times higher on -\(^{148}\text{Nd}\) and -\(^{150}\text{Nd}\), respectively, compared to that on -\(^{144}\text{Nd}\). The effects of Sm interference on Nd are thus dramatically different than the “domain mixing” [Hart and Zindler, 1989; Upadhyay et al., 2008; O’Neil et al., 2008; Andreasen and Sharma, 2009] deviation from exponential mass fractionation that produces similar sign and magnitude offsets of -\(^{142}\text{Nd}/^{144}\text{Nd}\) and -\(^{148}\text{Nd}/^{144}\text{Nd}\), but 3 times this offset in -\(^{150}\text{Nd}/^{144}\text{Nd}\) compared to runs that follow the normal fractionated by -\(^{1}\%\) per AMU compared to standard Sm. The Sm correction is based on the La Jolla standard. For sample EDUL69-8-3, a similar revised Sm correction based on -\(^{148}\text{Nd}/^{144}\text{Nd}\) would raise the Sm-corrected -\(^{142}\text{Nd}/^{144}\text{Nd}\) to 14 ppm higher than the standard, which, given the large uncertainty associated with this analysis, is still within analytical uncertainty of the standard -\(^{142}\text{Nd}/^{144}\text{Nd}\). Using instead the -\(^{150}\text{Nd}/^{144}\text{Nd}\) as an indicator of inaccurate Sm correction in EDUL69-8-3 would result in a corrected -\(^{142}\text{Nd}/^{144}\text{Nd}\) lower than, but within error, of the standard.

[11] The results for sample EDUL21-1-1 present the additional problem that the very high -\(^{150}\text{Nd}/^{144}\text{Nd}\) determined for this sample suggests that it was contaminated with -\(^{150}\text{Nd}\) spike during dissolution or chemistry. If this is the correct interpretation of the high -\(^{150}\text{Nd}\) in this sample, correcting for the spike would lower the -\(^{142}\text{Nd}/^{144}\text{Nd}\) and -\(^{148}\text{Nd}/^{144}\text{Nd}\) in this sample by 0.3 and 5 ppm, respectively. As this adjustment would also affect the Sm correction described in the preceding paragraph, the -\(^{142}\text{Nd}/^{144}\text{Nd}\) of sample EDUL21-1-1 corrected for both spike and Sm interference would be 4 ppm higher than in the La Jolla standard.

[12] Of the six samples, four were successfully analyzed for -\(^{142}\text{Nd}\) (Table 1) although sample EDUL69-8-3 ran at both reduced signal size and number of ratios (270), resulting in a significantly increased uncertainty. Two of the samples (incidentally, the two with lowest cpx Nd concentrations) did not yield sufficient signals for analysis. The -\(^{142}\text{Nd}/^{144}\text{Nd}\) ratios in Table 1 are expressed in part per million differences from the mean value obtained for six measurements of the La Jolla Nd standard measured in the same barrel as the samples (Table 1 and Figure 2). External reproducibility on repeated measurements of the -\(^{142}\text{Nd}/^{144}\text{Nd}\) ratio of the La Jolla standard is 5 ppm, i.e., 1.141840 ± 0.000006 where the uncertainty is 2σ of the population. All the sample runs had internal run errors larger than this external reproducibility as a result of the smaller signal sizes (Table 1) used for the sample measurements. As a result, the internal errors for the sample data listed in Table 1 provide a more reliable estimate of the uncertainty of the sample data.

2.3. Results

[13] The -\(^{142}\text{Nd}/^{144}\text{Nd}\) ratios of the four samples (Table 1) are within error the same as in the La Jolla Nd standard (Figure 2). At least two of the samples have -\(^{143}\text{Nd}/^{144}\text{Nd}\) higher than typically observed in MORB and hence represent well the high Sm/Nd ratio, incompatible element depleted end-member of the oceanic mantle. Nevertheless, their -\(^{142}\text{Nd}/^{144}\text{Nd}\) ratios overlap within uncertainty with all measured modern mantle-derived rocks. The constancy of -\(^{142}\text{Nd}/^{144}\text{Nd}\) in modern mantle rocks in spite of the wide range in -\(^{143}\text{Nd}/^{144}\text{Nd}\) is consistent with continuing differentiation of the...
Because of the short half-life of $^{146}$Sm, the variability in terrestrial $^{142}$Nd/$^{144}$Nd must have been generated by events that fractionated Sm/Nd ratios within the first $\sim 300$–$400$ Ma of Earth history. The 18–20 ppm elevated $^{142}$Nd/$^{144}$Nd of the modern mantle compared to chondrites requires a minimum $^{147}$Sm/$^{144}$Nd ratio of 0.2085 [Carlson and Boyet, 2008] compared to the chondritic value of 0.1960 [Bouvier et al., 2008]. A source formed at 4.568 Ga with $^{147}$Sm/$^{144}$Nd = 0.2085 would today have an $\varepsilon^{143}$Nd = +7.4. Consequently, the higher $\varepsilon^{143}$Nd typical of MORB and particularly of the oceanic peridotite clinopyroxenes measured here suggests further increases of the Sm/Nd ratio of the mantle after $^{146}$Sm was extinct. The most likely process causing this increasing incompatible element depletion of the mantle is the extraction of the chemically complementary continental crust over the last 4 Ga of Earth history [e.g., Jacobsen and Wasserburg, 1980; Allegre et al., 1983; Hofmann, 1988].

3. Conclusions

Three ocean ridge peridotites and one pyroxenite have a superchondritic $^{142}$Nd/$^{144}$Nd, in line with what has been found to date in most other accessible Earth reservoirs. We conclude that a major Earth’s mantle reservoir, i.e., sub ocean ridge mantle peridotites, has nonchondritic $^{142}$Nd/$^{144}$Nd, supporting the concept that either the BSE is not chondritic, or that a subchondritic reservoir lies hidden somewhere deep enough in the mantle that it has not been sampled by surface volcanism.

Acknowledgments

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References


