

# Meter-scale Nd isotopic heterogeneity in pyroxenite-bearing Ligurian peridotites encompasses global-scale upper mantle variability

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## ABSTRACT

**Pyroxenites embedded in peridotite are often invoked as a major cause of short-length scale isotopic heterogeneities in the upper mantle, but there has been little direct evidence. We report spatially controlled chemical and Sr-Nd isotopic compositions of pyroxenites and their host peridotites from an ophiolitic mantle sequence in the Northern Apennines, Italy, with depleted mantle compositions, representing a surface exposure of veined upper mantle, a potential source for mid-oceanic-ridge basalts (MORB). Interaction between pyroxenites and adjacent mantle rocks results in centimeter-scale chemical modifications in the host peridotites, systematically lowering their Sm/Nd ratios. Over time, this interaction causes the host peridotite at >0.1 m scale to acquire an isotopic heterogeneity larger than the range defined by the peridotite and pyroxenite end-members. Moreover, the <sup>143</sup>Nd/<sup>144</sup>Nd variation of a single outcrop covers most of the global Nd isotopic variability documented in abyssal peridotites. Such pyroxenite-peridotite veined mantle domains may represent the enriched component rarely found in abyssal peridotites, but often invoked to account for the low end of <sup>143</sup>Nd/<sup>144</sup>Nd variations in MORB.**

## INTRODUCTION

Many lines of evidence indicate that the upper mantle is chemically and isotopically heterogeneous on many length scales (e.g., Hofmann, 2003, and references therein). The concept of a mantle containing incompatible element enriched pyroxenite layers in a peridotite matrix (a “marble cake mantle”) has become a paradigm of mantle geochemistry and the origin of basalt (e.g., Zindler et al., 1984; Allègre and Turcotte, 1986). Preferential melting of pyroxenitic components has been invoked to explain the chemical and isotopic variability of basalts (e.g., Hirschmann and Stolper, 1996; Stracke et al., 1999; Salters and Dick, 2002), and their role in basalt generation is supported by experimental studies (Lambart et al., 2013, and references therein) and geochemical models (e.g., Kogiso et al., 2004; Sobolev et al., 2005; Stracke and Bourdon, 2009). Previous studies have documented large isotopic (Nd, Sr, Hf, Pb) variations at small-length scales in the mantle, and ascribed them to different processes, such as mafic components, melt-rock reaction, and variable degrees of melt refertilization (e.g., Brueckner et al., 1988; Reisberg et al., 1989; Pearson et al., 1993; Bodinier et al., 2004; Le Roux et al., 2009). However, direct observations of the scale and amplitude of isotopic heterogeneity induced by pyroxenite emplacement into host peridotite are still limited. Recent studies have reported on pyroxenites within abyssal peridotites (e.g.,

Dantas et al., 2007; Warren et al., 2009). The first detailed isotopic study of veined peridotites in an oceanic setting (Warren et al., 2009) demonstrated that large-amplitude mantle heterogeneity occurs on length scales of <1 km at the Southwest Indian Ridge; however, the limited spatial resolution of dredged peridotites in their study did not allow the observation of the extent of interaction between pyroxenite-forming melt and peridotite. Studies of ultramafic massifs have revealed that pyroxenitic components show large compositional variability reflecting multiple origins, including crystallization of asthenospheric melts, melt-peridotite reaction products, or recycling of subducted oceanic crust into the asthenosphere (e.g., Bodinier and Godard, 2003; Downes 2007). Whereas several works have shown that pyroxenite intrusions lead to local chemical changes in surrounding peridotites (e.g., Loubet and Allègre, 1982; Bodinier et al., 1990; Rivalenti et al., 1995; Mukasa and Shervais, 1999), only a few studies have focused on isotopic investigation of pyroxenites and spatially associated peridotite (Reisberg et al., 1989; Bodinier et al., 1990, 2004; Pearson et al., 1993; Becker, 1996). The role of pyroxenite intrusions in modifying the isotopic compositions of the host peridotite remains poorly constrained because, in most of cases, the primary relationship between pyroxenite and host peridotite is partially obscured by subsequent processes such as deformation-driven

physical mixing of isotopically enriched pyroxenites and host peridotite (Reisberg et al., 1989; Becker, 1996), or late-stage pyroxenite partial melting (Pearson et al., 1993). In the Lherz orogenic peridotite, a detailed bulk-rock investigation on an amphibole-garnet pyroxenite dike by Bodinier et al. (2004) documented that Nd isotopic contamination by melt infiltrating from the pyroxenite dike is restricted to the first 20 cm of the wall rock peridotite, mostly as a result of melt-rock reaction. In all these studies, the Nd isotope ratios of the host peridotites remained within the range defined by the pyroxenite and country peridotite end members (Reisberg et al., 1989; Bodinier et al., 2004).

We report detailed and spatially controlled trace-element and Nd-Sr isotope data on pyroxenite-peridotite traverses from a well-preserved Northern Apennine (Italy) ophiolitic mantle sequence with a depleted upper mantle composition, to assess the effect of melt-host peridotite reactions caused by pyroxenite emplacement. The results demonstrate that deep pyroxenite intrusions in peridotite can induce, over time, large isotopic variability in the host mantle, which is even larger than the variability defined by the lherzolite and pyroxenite themselves, and nearly encompasses the global Nd isotopic heterogeneity documented in oceanic peridotites.

## FIELD BACKGROUND AND SAMPLES

The Northern Apennine ophiolites are remnants of the Jurassic Ligurian Tethys oceanic lithosphere and are considered a fossil analogue of passive continental margins and slow to ultra-slow spreading ridges (Rampone and Hofmann, 2012, and references therein). Peridotite-pyroxenite associations investigated in this study are from three 100-m-long peridotite slivers from the eastern sector of the External Liguride (EL) Unit (Fig. DR1 in the GSA Data Repository<sup>1</sup>). Although the EL peridotites have been inferred

<sup>1</sup>GSA Data Repository item 2013293, isotopic methods, Figure DR1, and data tables (Tables DR1–DR5), is available online at [www.geosociety.org/pubs/ft2013.htm](http://www.geosociety.org/pubs/ft2013.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

to be exposed subcontinental lithospheric mantle (Rampone et al., 1995; Marroni et al., 1998), their mid-oceanic-ridge basalt (MORB)-like isotopic composition and their chemical characteristics suggest that they were formed by lithospheric accretion of ordinary asthenospheric mantle (Rampone et al., 1995). The EL peridotites thus offer an excellent opportunity to investigate the chemical and isotopic modifications induced by pyroxenite emplacement and related melt-rock reaction in a MORB-type mantle source before it undergoes partial melting and basaltic melt extraction, as reflected in isotopic studies of orogenic peridotites (e.g., Pearson and Nowell, 2004).

Pyroxenites occur within peridotites as centimeter-scale layers (<1 to ~15 cm) subparallel to the tectonite mantle foliation (Fig. 1A). They are irregularly distributed, and may

locally constitute as much as 50% of an outcrop (Fig. DR1). They originated by crystal accumulation from enriched tholeiitic melts at pressures (1.3–1.8 GPa) compatible with the presence of garnet in the primary mineral assemblage (Borghini et al., 2012). Subsequently, this mantle sector experienced a subsolidus, low-temperature tectonic exhumation, not perturbed by partial melting or melt-rock interaction processes (Borghini et al., 2011), thus preserving the chemical and isotopic variability acquired at mantle depths.

Pyroxenites range from spinel-bearing clinopyroxene to websterite. Thin (>2 cm) irregular orthopyroxene-rich borders along the pyroxenite-peridotite contact and large blebs of orthopyroxene in the adjacent (~4 cm) peridotites indicate interaction between pyroxenite-derived melts and the host peridotite. We examined

centimeter-scale profiles across the pyroxenite-peridotite boundary and distinguished (1) pyroxenite layers, (2) wall-rock peridotite as much as 4 cm from the pyroxenite, (3) host peridotite from 4 to 12 cm from the pyroxenite (Fig. 1B), and (4) country-rock peridotites, sampled in pyroxenite-free outcrops at least 2 m from pyroxenite layers.

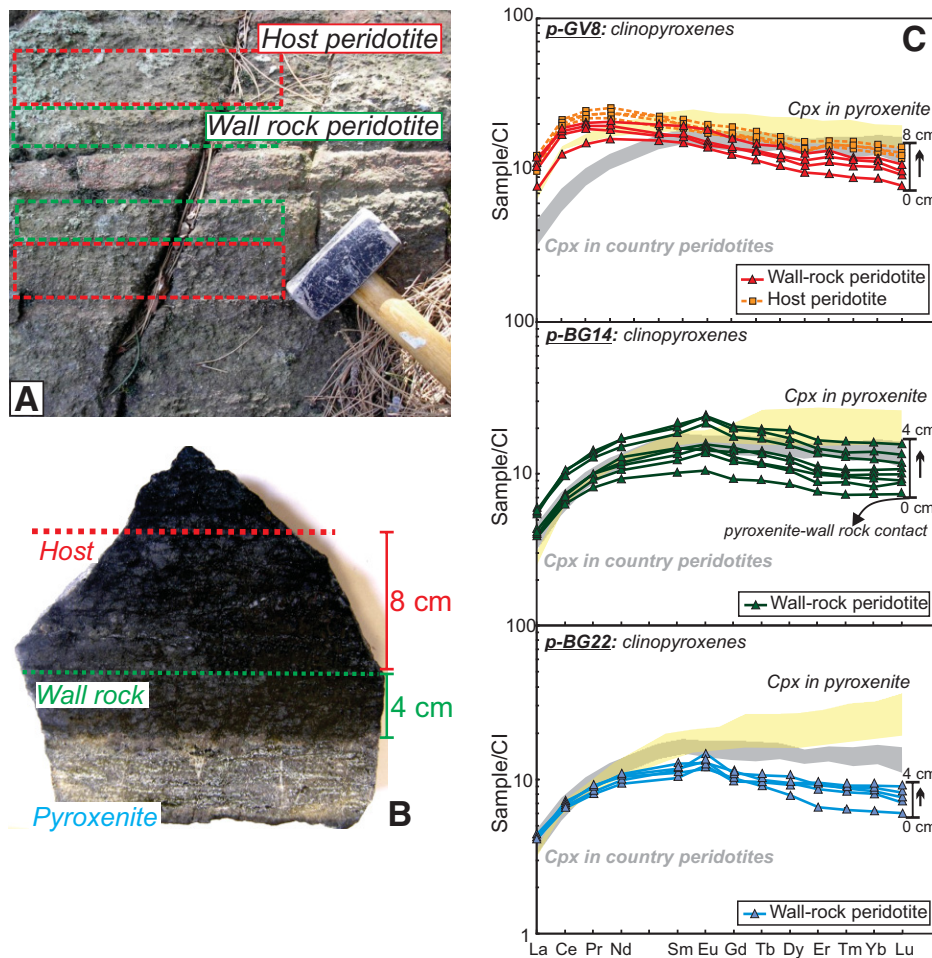
## RESULTS AND DISCUSSION

Wall-rock and host peridotites have higher Al, Ca, and Si abundances and slightly lower Mg numbers compared to country-rock peridotites (Tables DR1 and DR2 in the Data Repository). Chemical variations in wall-rock and host peridotites are consistent with systematic enrichment in modal orthopyroxene and depletion in modal olivine toward the pyroxenites, also indicated by the calculated modal abundances (Table DR3). These modal and chemical modifications call for the reaction  $\text{SiO}_2 + \text{olivine} \rightarrow \text{orthopyroxene}$  due to reactive percolation of a silica-saturated melt into the peridotites.

Clinopyroxene rare earth element (REE) abundances along pyroxenite-peridotite traverses also record the nature and scale of interaction between pyroxenite melt and the host rock. In each profile, clinopyroxene porphyroclasts in the wall rock have much lower Sm/Nd ratios compared to clinopyroxenes in the country-rock peridotite and the pyroxenite (Fig. 1C; Table DR4). The REE abundances in clinopyroxene from wall-rock peridotites progressively increase away from the pyroxenite-peridotite boundary (Fig. 1C). This chemical gradient appears to be generated by reactive percolation of melt, with decreasing melt mass from the pyroxenitic conduits, which preferentially enriched wall-rock and host peridotites in Nd over Sm. Here we discuss the effect of centimeter-scale Sm/Nd ratio modification on the Sm-Nd isotope system.

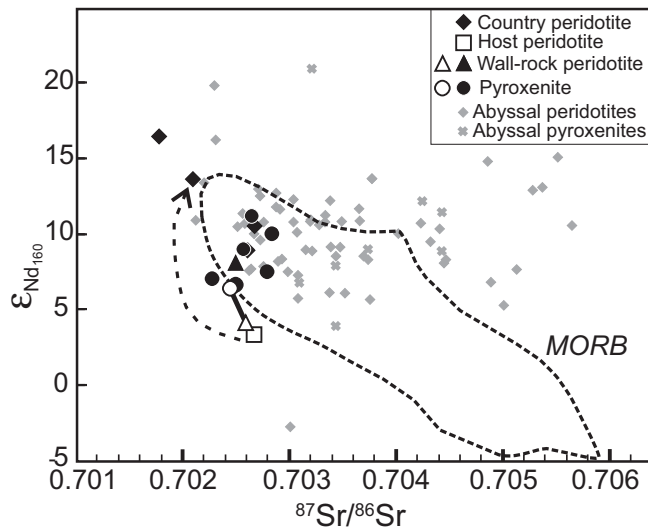
The Nd isotopes are present in terms of  $\epsilon_{\text{Nd}}$  values computed at 160 Ma (the inferred age of emplacement of this mantle sector beneath the ocean floor; Rampone and Hofmann, 2012), in order to make the data comparable with modern abyssal peridotites. No age correction is needed for the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, given negligible Rb contents in all the samples.  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon_{\text{Nd}}$  values plot within the “Depleted Mantle” end of the field of abyssal peridotites and MORB (Fig. 2; Table DR5). Except for two country-rock peridotites with extremely low Sr isotope ratios, the  $^{87}\text{Sr}/^{86}\text{Sr}$  range of the peridotites (wall rock, host, country rock) overlaps that of the pyroxenites and is confined to the interval 0.7023–0.7029 (Fig. 2). These depleted MORB  $^{87}\text{Sr}/^{86}\text{Sr}$  values are similar to those of the few published abyssal peridotite data sets not affected by seawater alteration (Cipriani et al., 2004; Warren et al., 2009).

Remarkably, our peridotite samples, over a 100 m scale, encompass nearly the entire Nd isotopic variability documented in abyssal



**Figure 1.** A: Representative spatially controlled pyroxenite-peridotite profile in a Ligurian (Italy) veined mantle outcrop. Dotted areas show the typical size of samples and where they were collected. B: A pyroxenite-peridotite sample; wall-rock peridotite has been distinguished by host peridotite on the basis of the occurrence of large orthopyroxene blebs (see text for details). C: Chondrite-normalized clinopyroxene rare earth element (REE) patterns for pyroxenite-peridotite profiles (GV8, BG14, BG22) and country-rock peridotites, normalized to chondrite of Anders and Grevesse (1989). The fields of clinopyroxene porphyroclasts from pyroxenites (yellow field) and country-rock peridotites (light gray field) are reported for comparison. Bar at right side of the REE patterns approximately indicates the distance of the in-situ laser analyses from the pyroxenite-wall-rock peridotite contact (Table DR4 [see footnote 1]).

**Figure 2. Present-day  $^{87}\text{Sr}/^{86}\text{Sr}$  versus initial  $\epsilon_{\text{Nd}}$  value (calculated to 160 Ma; see text for explanation) of the studied pyroxenites and peridotites (Table DR5 [see footnote 1]). Gray symbols are present-day  $\epsilon_{\text{Nd}}$  values of abyssal peridotites and pyroxenites (Snow et al., 1994; Salters and Dick, 2002; Cipriani et al., 2004, 2011; Warren et al., 2009; Kempton and Stephens, 1997). The mid-oceanic-ridge basalt (MORB) field (thin dashed line, from data set downloaded in May 2013 from www.petdb.org) is shown for comparison. Open symbols are from profile GV8 (Table DR5). Black line links samples from profile GV8 (pyroxenite, wall-rock, and host peridotites); black dotted arrow links the GV8 profile with its closest country-rock peridotite GV18 (at least 2 m from the pyroxenite layers).**



peridotites globally and, even more remarkably, this occurs over a few meters of outcrop (i.e., the spatially controlled pyroxenite-peridotite profile GV8 in Fig. 2). As a whole, our results mimic the Nd isotopic variability observed by Warren et al. (2009) in abyssal pyroxenite-peridotite associations, but provide the missing spatial resolution in previous studies, and thus constrain the origin of the heterogeneity.

The pyroxenite-free country-rock peridotites have systematically higher  $\epsilon_{\text{Nd}_{160}}$  than the reacted (wall-rock and/or host) peridotites (Fig. 2). This observation confirms that the Nd isotope range in the peridotite results from melt infiltration related to the pyroxenite emplacement. The three groups of spatially related pyroxenite-wall-rock peridotite samples define parallel  $^{147}\text{Sm}/^{144}\text{Nd}$  versus  $^{143}\text{Nd}/^{144}\text{Nd}$  linear correlations (Fig. 3). Importantly, these correlations do not reflect binary mixtures between pyroxenite components and country-rock peridotite, because in that case wall-rock and/or host peridotite compositions should be intermediate to the pyroxenites and peridotites, as seen in previous studies (e.g., Bodinier et al., 2004). Rather, the linear correlations require that reactive melt infiltration resulted in resetting of the Nd isotopes of the wall-rock and/or host peridotites to the values of the infiltrating pyroxenites, combined with variable lowering of the Sm/Nd ratios (Fig. 1C). Thus, the correlations in Figure 3 reflect the age of the pyroxenite melt intrusions. Sm-Nd isochrons defined by the pyroxenite-wall-rock pairs yield ages of 424–452 Ma (in good agreement with the errorchron defined by all Ligurian pyroxenites and wall-rock peridotites of  $433 \pm 51$  Ma), and initial  $\epsilon_{\text{Nd}_{430}}$  values range from  $+3$  to  $+8$ , which are reasonable values for enriched MORB. These ages and  $\epsilon_{\text{Nd}_i}$  indicate that

this mantle sector was significantly modified by pyroxenite melt infiltration during an event that occurred  $\sim 300$  m.y. before its exhumation at the seafloor at 160 Ma. Thus, the isotopic heterogeneity at 160 Ma (Fig. 2) resulted from the older pyroxenite emplacement (isotopic resetting and chemical modification of host peridotites, including decreases in the Sm/Nd ratio) followed by radioactive decay. The significantly higher  $\epsilon_{\text{Nd}_{430}}$  of country-rock peridotites ( $\epsilon_{\text{Nd}_{430}} = +7$  to  $+15$ ) compared to the pyroxenites ( $\epsilon_{\text{Nd}_{430}} = +3$  to  $+8$ ) indicates that the pristine mantle, prior to pyroxenite intrusion, had variable Nd isotope ratios due to even more ancient depletion event(s) (Rampone et al., 1995). Similar ancient melting

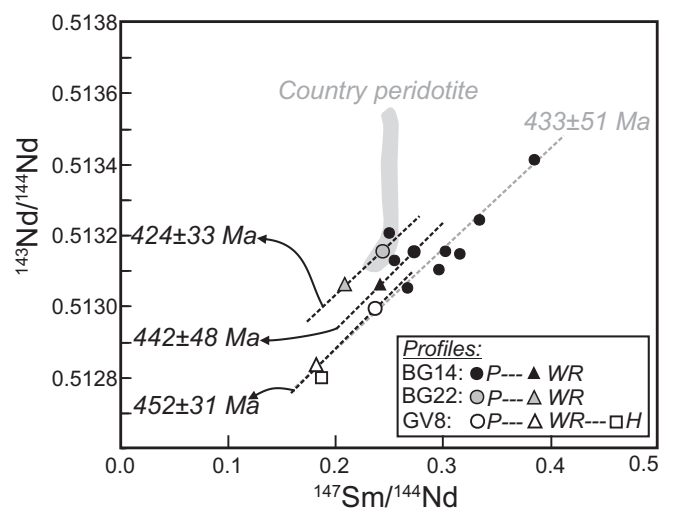
events have been documented in abyssal peridotites (Cipriani et al., 2004; Warren et al., 2009; Stracke et al., 2011).

Our results demonstrate that portions of the upper mantle are significantly modified by pyroxenite intrusions, leading to low  $\epsilon_{\text{Nd}}$  values over just a few hundred million years. We suggest that these may represent the low- $\epsilon_{\text{Nd}}$  component often invoked to explain the enriched end of the MORB isotopic variations (e.g., Zindler et al., 1984; Salters and Dick, 2002; Donnelly et al., 2004; Waters et al., 2011; Hornle et al., 2011), but rarely sampled in the abyssal peridotites (Fig. 2). The meter-scale mantle domains of the External Ligurian ophiolitic peridotites, which are composed of modified peridotite and high-Mg, low-alkali pyroxenites, are expected to produce melts chemically similar to those generated by peridotitic mantle sources (Lambart et al., 2013), but with an enriched (low)  $^{143}\text{Nd}/^{144}\text{Nd}$  isotopic imprint. In this manner, together with melts from the pristine (country rock) peridotite, the entire spectrum of  $^{143}\text{Nd}/^{144}\text{Nd}$  in MORB may be generated. Thus, the results of this work shed light on short-length-scale heterogeneity of potential MORB sources, providing a physical and geochemical portrayal of the veined or marble cake mantle.

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**Figure 3. Present-day  $^{143}\text{Nd}/^{144}\text{Nd}$  versus  $^{147}\text{Sm}/^{144}\text{Nd}$  in clinopyroxenes from the External Liguride (Italy) pyroxenites (black filled circles) (Table DR5 [see footnote 1]). Gray field is the composition of our country-rock peridotites. Different symbols refer to spatially controlled isotope profiles (P—pyroxenite; WR—wall-rock peridotite; H—host peridotite). Ages and initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios for the pyroxenite-wall-rock isochrons (black dashed lines) are:  $442 \pm 48$  Ma,  $0.51237 \pm 0.00008$ ,  $\epsilon_{\text{Nd}_i}$  (442) =  $5.9 \pm 1.5$  for BG14;  $424 \pm 33$  Ma,  $0.51248 \pm 0.00005$ ,  $\epsilon_{\text{Nd}_i}$  (424) =  $7.6 \pm 1$  for BG22;  $452 \pm 31$  Ma,  $0.51230 \pm 0.00004$ ,  $\epsilon_{\text{Nd}_i}$  (452) =  $4.8 \pm 0.8$  for GV8. Gray dashed line is the errorchron based on all the pyroxenites and wall-rock and/or host peridotites:  $433 \pm 51$  Ma, with an initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.51230 \pm 0.00009$ , and  $\epsilon_{\text{Nd}_i}$  (452) =  $4.3 \pm 1.8$ .**



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