Lithospheric mantle evolution in the Afro-Arabian domain: insights from Bir Ali mantle xenoliths (Yemen)

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ABSTRACT

Detailed petrological and geochemical investigations of an extensive sampling of mantle xenoliths from the Neogene-Quaternary Bir Ali diatreme (southern Yemen) indicate that the underlying lithospheric mantle consists predominantly of medium- to fine-grained (often spinel-peridotites (85-90%) and spinel-pyroxenites (10-15%) foliated) thermobarometric estimates in the P-T range of 0.9-2.0 GPa and 900-1150 °C. Peridotites, including lherzolites, harzburgites and dunites delineate continuous chemical, modal and mineralogical variations compatible with large extractions of basic melts occurring since the late Proterozoic (~2 Ga, according to Lu-Hf model ages). Pyroxenites may represent intrusions of subalkaline basic melts interacting and equilibrated with the host peridotite. Subsequent metasomatism has led to modal changes, with evidence of reaction patches and clinopyroxene and spinel destabilization, as well as formation of new phases (glass, amphibole and feldspar). These changes are accompanied by enrichment of the most incompatible elements and isotopic compositions. 143Nd/144Nd ranges from 0.51419 to 0.51209 (ϵ_{Nd} from +30.3 to -10.5), $^{176}Hf/^{177}Hf$ from 0.28459 to 0.28239 (ϵ_{Hf} from +64.4 to -13.6), and ²⁰⁸Pb/²⁰⁴Pb from 36.85 to 41.56, thus extending from the depleted mantle (DM)

towards the enriched OIB mantle (EM and HIMU) components. ³He/⁴He (R/R_A) ratios vary from 7.2 to 7.9 with He concentrations co-varying with the most incompatible element enrichment, in parallel with metasomatic effects. These metasomatic events, particularly effective in harzburgites and dunites, are attributable to the variable interaction with alkaline basic melts related to the general extensional and rifting regime affecting the East Africa-Arabian domain during the Cenozoic. In this respect, Bir Ali mantle xenoliths resemble those occurring along the Arabian margins and the East Africa Rift system, similarly affected by alkaline metasomatism, whereas they are distinctly different from xenoliths located within the Ethiopian-Yemen continental flood basalt province that are pervasively refertilized by plume-related subalkaline melts.

1. Introduction

Mantle xenoliths exhumed from the Neogene-Quaternary alkaline volcanism in the Afro-Arabian domain provide a powerful tool to unravel the complex mantle dynamics of a region that after Oligocene continental flood basalt (CFB) magmatism (Hofmann et al., 1997; Pik et al., 1998; Beccaluva et al., 2009) and rifting processes (Natali et al., 2011; 2013a) progressed from continental break-up to the development of oceanic basins. Though a mantle plume is generally called upon to explain the voluminous, chemically distinct CFB magmatism in the region, the plume contributions have diminished over time, as suggested by seismic images of the Afar region, where transition from continental rifting to incipient seafloor spreading has been studied in detail (Bastow et al., 2011; Hammond et al., 2013).

In the Afro-Arabian region, mantle xenoliths entrained in Neogene-Quaternary alkaline volcanics are found in two main occurrences (Fig. 1): i) within the northern Ethiopian-Yemen plateau area (Beccaluva et al., 2011) and ii) in the neighbouring rift structures radiating from the Afar triple junction along the Red Sea-Gulf of Aden Arabian margins (Henjes-Kunst et al., 1990; Blusztajn et al., 1995; Chazot et al., 1996; Baker et al., 1998) as well as along the Main Ethiopian and Kenya-Tanzania rifts to the south (Kaeser et al., 2006; Aulbach et al., 2011; Beccaluva et al., 2011; Bianchini et al., 2014).

Although mantle xenoliths related to the CFB area show evidence of pervasive refertilization by Afar plume melts (Beccaluva et al., 2011), other mantle xenoliths collected

outside this area, along the Arabian margin and the East Africa Rifts, display more complex histories of depletion and enrichment events (Baker et al., 1998; Reisberg et al., 2004; Aulbach et al., 2011; Bianchini et al., 2014). In this paper we present new bulk rock and mineral major and trace element data, as well as Nd-Hf-Pb-He isotope systematics, for an extensive sample suite from Bir Ali (Yemen), located on the southern Arabian margin, ca. 500 km eastward of the CFB from the Ethiopian-Yemeni plateau. These data help to define: i) the predominant composition of the lithospheric mantle section underlying the southernmost Arabian margin; ii) secular variation in terms of depletion and enrichment events; and iii) the geochemical and isotopic signature of the metasomatic events that are both related and unrelated to the Afar plume.

2. Methods

The mantle xenoliths studied in this work were collected from pyroclastic material of the Bir Ali diatreme, which is part of the Pliocene-Quaternary Balhaf Bir Ali alkaline volcanic province (Mallick et al., 1990), located in the central southern part of Yemen (Fig. 1). Sixty-two ultramafic xenoliths (up to 20 cm in size) were selected for detailed investigations after preliminary petrographic analysis. The freshest portions (weighting between 15 and 30 g) were crushed and subsequently powdered in an agate mill.

Major and trace elements (Ni, Co, Cr, V and Sr) were analysed by X-ray fluorescence (XRF) on powder pellets, using a wavelength-dispersive automated ARL Advant'X spectrometer at the Department of Physics and Earth Sciences, University of Ferrara. Accuracy and precision are better than 3% for Si, Ti, Fe, Ca, and K, 7% for Mg, Al, Mn and Na and 10% for trace element compositions (above 10 ppm). Rare earth elements (REE), Sc, Y, Zr, Hf, Nb, Ta, Th, and U were analysed (after HF-HNO3 dissolution of rock powders in teflon beakers) by inductively coupled plasma mass spectrometry (ICP-MS) at the Department of Physics and Earth Sciences, University of Ferrara, using an X Series Thermo-Scientific spectrometer according to a procedure involving both external calibration and the use of "internal standards" (known amounts of Rh, In, Re and Bi added to the sample solutions). Accuracy and precision, based on the replicated analyses of samples and standards (JGb1, JGb2, UBN) are better than 10% for all elements at the ppm level.

Major element mineral compositions were obtained at the CNR-IGG Institute of Padova with a Cameca SX-50 electron microprobe (fitted with four wavelength dispersive spectrometers) at an accelerating voltage of 15 kV, specimen current of 15 nA and 2 μm beam size, using natural silicates and oxides as standards. The analysis of glasses utilized a different setup, including defocussing and reducing the beam current to 2 nA in order to mitigate the loss of alkalies. Trace element analyses on minerals and glass were carried out at the CNR-IGG of Pavia by LAM ICP-MS, using an Elan DRC-e mass spectrometer coupled with a Q-switched Nd:YAG laser source (Quantel Brilliant). The operating conditions were similar to those described by Melluso et al. (2014), with ~ 50 μm laser spot diameter and implementation of CaO content (independetly determined by microprobe analysis) as an internal standard. Data reduction was carried out using the GLITTER software package (van Achterbergh et al., 2001). Precision and accuracy, better than 10% for concentrations at the ppm level, were assessed by repeated analyses of NIST SRM 612 and BCR-2 standards (Miller et al., 2012 for additional procedural details).

For the Nd-Hf-Pb isotopic analyses, aliquots of hand-picked clinopyroxene separates (100-300 mg) and bulk rock powders (300-600 mg) were digested in the clean laboratory of the Department of Earth Sciences at the University of New Hampshire. Samples were first leached in hot (~120°C) 6N HCl to remove any surface contaminants (cf. Wittig et al., 2006) following techniques outlined in Blichert-Toft and Albarède (2009). Resulting residues were subsequently digested in a mixture of concentrated HF-HNO₃. Hafnium was separated as described by Blichert-Toft et al. (1997) and Blichert-Toft (2001). The REE fractions recovered from the first cation-exchange column used in the Lu-Hf separation protocol were loaded on Ln-Spec columns to separate Nd. Isotopic measurements were carried out on the Nu Plasma 500 HR multiple-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the Ecole Normale Supérieure in Lyon. Instrumental mass fractionation was corrected relative to 179 Hf/ 177 Hf = 0.7325 and 146 Nd/ 144 Nd = 0.7219 using an exponential law, and instrument performance was assessed by analysis of the JMC-475 Hf and Rennes inhouse Nd standards for Hf and Nd, respectively. The JMC-475 Hf standard, run throughout the analytical session (n=16), yielded 176 Hf/ 177 Hf = 0.282166 \pm 0.000012 (2 σ); since this value is identical within error to the accepted value of 0.282163 ± 0.000009 (Blichert-Toft et al., 1997), no corrections were applied to the data. Total procedural Hf blanks were less than 30 pg. BCR-1 processed with the same chemical procedure gave 0.512646 ± 0.000011 (2σ), similar to the recommended value from the GEOREM database (Jochum et al., 2005). The Rennes in-house Nd standard run throughout the analytical session (n=16) gave 143 Nd/ 144 Nd = 0.511968 ± 0.000013 (2σ), well within analytical uncertainty of previously reported means of 0.511961 ± 0.000013 (Chauvel and Blichert-Toft, 2001). Accordingly no corrections were made to the data. Total procedural Nd blanks were less than 30 pg.

Lead was separated using the techniques described in Bryce and DePaolo (2004), and Pb isotopic measurements also were carried out on the Nu Plasma 500 HR MC-ICP-MS at the Ecole Normale Supérieure in Lyon. For Pb, instrumental mass fractionation was corrected via Tl normalization as described in White et al. (2000), and ratios were additionally adjusted for instrumental drift and accuracy using the sample-standard bracketing technique described in Albarède et al. (2004) and the NIST SRM values reported in Eisele et al. (2003). Eight NIST SRM 981 run as "blind" samples amongst the ten bracketing standards analyzed yielded averages (with 2σ external precision) of 208 Pb/ 204 Pb = 36.728 (0.024), 207 Pb/ 204 Pb = 15.498 (0.011) and 206 Pb/ 204 Pb = 16.941 (0.012). Total procedural Pb blanks were less than 100 pg.

Helium isotope analyses were performed at Oregon State University (OSU) following methods described in Graham et al. (2014) and using a Nu Instruments® noble gas mass spectrometer. Briefly, \sim 450-600 mg of olivine were handpicked to be free of surface alteration, ultrasonically cleaned and dried. Samples were crushed online to extract gases trapped in association with melt and fluid inclusions. Reactive gases were removed with liquid nitrogen traps and SAES getters and noble gases were separated onto a cryogenically controlled charcoal trap at 10 K. The trap was warmed to 45 K and helium was admitted directly to the mass spectrometer for isotope ratio and peak height (concentration) determination. Line blanks were always performed before sample analysis and typically were $<5x10^{-11}$ cm 3 STP 4 He.

3. Results

Bulk rock major and trace element concentrations are reported in Table 1, and major and trace element data on constituent minerals and glasses are reported in Tables 2 and 3, respectively.

The modal abundance of main mineral constituents were obtained by least squares mass balance calculations between whole rock and mineral major elements compositions (Table 1). Classification based on the relative abundances of olivine (ol) - orthopyroxene (opx) - clinopyroxene (cpx) divides the samples into spinel (sp)-peridotites (32 lherzolites, 11 harzburgites and 10 dunites) and sp-pyroxenites *s.l.* (4 olivine-pyroxenites and 5 pyroxenites; Fig. 2).

3.1. Petrography and mineral chemistry

Figure 3 shows the main textural characteristics of the Bir Ali xenoliths. Following the nomenclature of Harte (1977) most of the peridotite samples show medium- to fine-grained (0.5-2 mm) granuloblastic textures, with curvilinear to straight grain boundaries and variable extent of recrystallyzation with 120° triple junctions. Many of these samples show tabular textures characterized by variable foliation defined by elongated olivines (aspect ratio up to 4:1) and trails of brown spinels (Fig. 3a and 3b).

Widespread annealing processes are indicated by the scarcity of porphyroclastic as well as by coarser-grained (up to 5 mm) textures in olivine-rich parageneses (Fig. 3c), particularly dunites, as obseserved in other xenolith suites (Tommasi et al., 2008; Baptiste et al., 2012; Zaffarana et al., 2014 and references therein). It is worth noting that textural characteriscs of Bir Ali xenoliths are remarkably different from those of many other occurrences in the Afro-Arabian system, where coarse-equant textures (or protogranular according to Mercier and Nicolas, 1975) are predominant and dunites are absent (Beccaluva et al., 2007; 2008; 2011; Natali et al., 2013b). Instead, Bir Ali xenoliths texturally resemble the predominantly refractory xenoliths from East Greenland (Bernstein et al., 1998).

Olivine is generally medium- to coarse-grained and moderately kink-banded, varying in composition from Fo 88.0 to Fo 90.2 in lherzolites, Fo 89.3-90.6 in harzburgites, and Fo 89.2-92.9 in dunites. It is worth noting the widespread occurrence in olivine of secondary fluid inclusions (up to 10 µm in size) in healed fractures, mainly in dunites. Orthopyroxene is medium- to fine-grained and commonly shows cpx exsolution *lamellae*; the whole compositional range in peridotites is from En 88.9 to En 93.3. Clinopyroxene is generally fine-grained and often interstitial, displaying opx exsolution *lamellae* in the largest crystals;

its composition is in the range En 49.4-54.0 Fs 0.9-2.4 Wo 44.5-48.3, with Mg# varying between 91.5 and 92.6 (with the exception of lherzolite BA48 having Mg# 86.8) and Cr# between 7.1 and 14.3. A peculiar clinopyroxene composition is recorded in dunite BA33 (En 44.7 Fs 0.5 Wo 54.8), which exhibits distinctive high CaO (23.2 wt%), Al₂O₃ (9.54 wt%) and TiO₂ (3.27 wt%) contents, suggesting interaction with magmatic melts. Dark brown spinel is scarce, small-sized, often aligned in trails and shows the following compositional ranges: Mg# 79.8-80.3 and Cr# 11.8-14.1 in lherzolites, Mg# 75.1-77.9 and Cr# 20.4-24.3 in harzburgites, and Mg# 73.0-76.3 and Cr# 19.7-31.9 in dunites. Reaction textures are particularly widespread in harzburgites and dunites and mainly consist of "spongy" borders in clinopyroxene, opacized rims around spinel, fine-grained aggregates of olivine and clinopyroxene, glassy patches, rare plagioclase (An 52-70), and sporadic pargasitic amphibole (Fig. 3d and 3e).

Spinel-pyroxenites are represented either as individual xenoliths or as discrete domains texturally equilibrated within peridotites. They are characterized by variously re-crystallized igneous textures - with medium-grained pyroxenes and interstitial spinel - which locally fade to granuloblastic domains (Fig. 3f). Clinopyroxene is always dominant over orthopyroxene and both pyroxenes show mutual exsolution *lamellae*. Clinopyroxene varies in the range En 47.2-51.5 Fs 3.1-7 Wo 46.5-47.6, whereas orthopyroxene varies from En 83.8 to 88.5. Olivine is weakly deformed with Fo 82.2-88.2. Spinel is brown to dark green in color with Mg# 56.5-67.0 and Cr# 13.5-22.8 (Table 2). These compositions are similar to those reported for analogous Bir Ali xenoliths by Ali and Arai (2007). Reaction textures similar to those observed in peridotites are also present.

Thermo-barometric estimates, based on the thermodynamic models of Brey and Kohler, (1990) and Kohler and Brey, (1990), indicate that Bir Ali mantle xenoliths equilibrated in the temperature (T) and pressure (P) ranges 900-1150°C and 9-20 kbar, with most samples clustering in the T-P conditions 900-1000 °C and 12-17 kbar. The lack of garnet in the pyroxenite parageneses indicates that most Bir Ali mantle xenoliths equilibrated in the "Seiland subfacies" of spinel-peridotite facies (Bodinier and Godard, 2014), thus suggesting pressure not exceeding 18 kbar (Porreca et al., 2006). These estimates are consistent with

those reported by Ali and Arai (2007) for Bir Ali, by Stern and Johnson (2010) for the Arabian Peninsula, and by Conticelli et al. (1999) for Southern Ethiopia.

3.2. Bulk rock chemistry

The variation diagrams shown in Fig. 4 indicate that Bir Ali mantle xenoliths fall into two distinct groups, both of which are characterized by a remarkable compositional continuity.

Peridotite xenoliths plot along compositional trends characterized by a continous decrease in SiO₂, CaO, Al₂O₃, TiO₂ and V concentrations in fertile lherzolites, approaching the primitive mantle (PM), to extremely depleted dunites. By contrast, compatible elements, such as Ni, are positively correlated with MgO from lherzolites to dunites. These variations could be attributed to either magma extraction (Niu, 1997) or melt redistribution and interaction in the mantle region (Kelemen et al., 1995a, 1995b; Le Roux et al., 2007; Bodinier and Godard, 2014). In the same diagrams, pyroxenites are distinctly different from peridotites and are comparatively more enriched in SiO₂, Al₂O₃, CaO, TiO₂ and V, and depleted in MgO, Ni and Cr. Their bulk chemistry (Table 1), approaching basaltic compositions, is comparable to that of pyroxenite mantle xenoliths from other locations within the Arabian peninsula (Stern and Johnson, 2010, and references therein). By contrast, Bir Ali pyroxenites show remarkable differences with respect to those from the northern Ethiopian plateau (Injibara and Dedessa), which are comparatively enriched in orthopyroxene (Beccaluva et al., 2011).

Bulk rock chondrite (Ch)-normalized REE of Bir Ali xenoliths are reported in Fig. 5. With respect to the peridotite compositions, the middle (M) and heavy (H) REE distribution is positively correlated with the modal clinopyroxene content, as usually observed in mantle rocks (Bedini and Bodinier, 1999; Coltorti et al., 1999; Beccaluva et al., 2001, 2007; 2008; 2011). Accordingly, the MREE and HREE contents range from 0.4 to 1.9 times chondrite in the lherzolites, from 0.3 to 0.6 in the harzburgites and from 0.2 to 0.6 in most of the dunites. A notable exception is that of three dunites (characterized by abundant reaction textures and presence of glass and amphibole), which show MREE and HREE contents ranging from 0.7 to 1.4 times chondrite. Enrichment in the most incompatible elements (e.g., light (L) REE) is indicated by the La_N/Yb_N ratio ranging from 0.3 to 1.9 in lherzolites, 0.4-2.6 in harzburgites and 0.7-4.1 in dunites, with the highest ratios corresponding to samples showing the most

widespread reaction textures. Pyroxenites show HREE abundances ranging between 4.6 and 12.2 times chondrite, where the absolute REE concentrations increase from ol-pyroxenites to pyroxenites. They display slightly positively fractionated REE patterns with La_N/Yb_N increasing from 1.9 to 3.0, in broad agreement with the abundance of modal clinopyroxene.

3.3. Trace element systematics of clinopyroxene, amphibole and glass

Incompatible element data for clinopyroxene, amphibole and glass from Bir Ali xenoliths are reported in Table 3. Chondrite-normalized REE distributions in clinopyroxene from Bir Ali mantle peridotites are shown in Fig. 6a. Flat M-HREE patterns are observed for all clinopyroxenes ranging from 5.3 to 14.9 times chondrite, whereas LREE distribution is highly variable with La_N/Yb_N ranging from 0.2 in lherzolites unaffected by metasomatism to 3.4 in harzburgites affected by metasomatic enrichment. Sample BA8, a dunite, records the strongest LREE metasomatic enrichment in clinopyroxene, with La_N/Yb_N as high as 3.9.

Chondrite-normalized REE distributions in pargasitic amphibole and glass in reaction textures observed in Bir Ali dunite xenoliths are reported in Fig. 6b. The amphibole M-HREE patterns (in dunite BA8) is around 24 times chondrite with $La_N/Yb_N = 4.3$. It resembles those of the coexisting clinopyroxene, suggesting that the two phases were in equilibrium with the same metasomatic agent. The REE distribution in glass (in dunite BA33) is characterized by average HREE around 20.3 times chondrite and La_N/Yb_N of 7.0. The above data suggest that these new phases and their geochemical enrichments were induced by alkali-silicate metasomatic agents whose effects are attested to by modal and textural disequilibrium. To constrain the nature of these metasomatising agents, incompatible element modelling was done based on the compositions of the most enriched clinopyroxene and pargasitic amphibole using partition coefficients (Kd) for mineral/alkaline basic melt from Zack and Brunn (1998) and Dalpe and Baker (1994), respectively. The calculated metasomatising agents are in reasonable agreement with the incompatible element distribution of basic alkaline lavas from Cenozoic volcanic districts of the African plate (also considering the possible melt-peridotite interactions), but are inconsistent with carbonatitic magmas (Fig. 7a). Comparison on a regional scale (Fig. 7b) indicates that metasomatic agents inferred for Bir Ali are consistent with those deduced for other mantle xenoliths from the Afro-Arabian domain, which are

alkali-silicate in nature (Baker et al., 1998; Beccaluva et al., 2007; Beccaluva et al., 2008; Beccaluva et al., 2011; Natali et al., 2013b). By contrast, mantle xenoliths within the northern Ethiopian plateau exhibit interactions with subalkaline metasomatic agents, similar to the CFB related to the Afar Plume activity (Beccaluva et al., 2011).

3.4. Hf-Nd-Pb-He isotope systematics

Hf-Nd-Pb isotopic analyses were carried out largely on handpicked clinopyroxene separates and, for some samples, on bulk rock powders (Table 4). Helium isotopic ratios were measured on handpicked olivine crystals for peridotites and on bulk rocks for pyroxenites (Table 5). Results are reported in Figs. 8-10 and discussed on the basis of the notional depleted (DM), high-U/Pb (HIMU) and enriched (EM1, EM2) mantle components that refer to the different end-member compositions of ocean island basalts (OIB) and mid ocean ridge basalts (MORB) (Zindler and Hart, 1986; Carlson, 1995; Hofmann, 1997; Stracke et al., 2005).

The general distribution of Bir Ali peridotite xenoliths in terms of 143 Nd/ 144 Nd and 176 Hf/ 177 Hf span the DM signature or even more depleted compositions (ϵ_{Nd} up to +30.3 and ϵ_{Hf} up to +64.4) to less radiogenic values (ϵ_{Nd} as low as -4.0 and ϵ_{Hf} as low as +10.7; Fig. 8a). The lherzolites are characterized by the most depleted supra-chondritic compositions, whereas harzburgites and dunites show enriched compositions consistent with the observed incompatible element distribution. This isotopic distribution confirms that lherzolites and harzburgites/dunites represent the least and most metasomatized peridotite mantle domains, respectively. Pyroxenites overlap the peridotite field, with the exception of sample BA55 that exhibits an extremely enriched (sub-chondritic) composition (ϵ_{Nd} = -10.5; ϵ_{Hf} = -13.6).

Hafnium and Nd model ages were calculated with respect to both CHUR and DM for the most LREE-depleted clinopyroxene of lherzolites BA37 and BA43. Hafnium model ages are in the range of 2040-1800 Ma with respect to CHUR and 1670-1115 Ma with respect to DM. Nd model ages are comparatively younger, approaching 1300 (CHUR) and 1050 (DM) Ma. Notably, based on Nd model ages, Blusztajn et al. (1995) reported mantle depletion events > 1.6 Ga for spinel peridotite xenoliths from Saudi Arabia. The age discrepancy between Hf and Nd model ages can in part be attributed to the different susceptibility of the Lu-Hf and Sm-Nd isotopic systems to the metasomatic agents, which are characterized by a strong LREE (e.g.,

Nd) enrichement (cf. Bedini et al., 2004; Bianchini et al., 2014). From these estimates we conclude that significant partial melting events took place during the Proterozoic, and were followed by metasomatic interactions that variably perturbed the different isotopic systems.

Lead isotope systematics also are consistent with the aforementioned scenario with many lherzolites plotting close to DM, and harzburgites, dunites and pyroxenites generally clustering near the EM components (Fig. 87, b and c). Notably, the same depleted lherzolites used to derive the Lu-Hf and Sm-Nd model ages are those exhibiting unradiogenic Pb isotopic compositions, thus confirming that they escaped significant metasomatic effects. More radiogenic Pb compositions are displaced toward the EM2 isotopic end-member, whereas extreme radiogenic isotopic values, exceeding those of EM2, are recorded by the pyroxenite sample BA55 (206 Pb/ 204 Pb =19.73, 207 Pb/ 204 Pb =15.72, 208 Pb/ 204 Pb = 41.56). As mentioned above, these Pb isotopic signals are associated with the most enriched values for ε_{Nd} and ε_{Hf} , -10.5 and -13.6, respectively.

Figure 8 further shows the isotopic compositions of mantle xenoliths from other localities of the Arabian and African plates: Ataq, Yemen (Baker et al., 1998); Harrat Ash Shaam, Jordan (Shaw et al., 2007); East Africa - Mega in Southern Ethiopia (Beccaluva et al., 2011; Bianchini et al., 2014); Assab, Eritrea (Teklay et al., 2010) and from the Saharan Belt - Hoggar, Algeria (Beccaluva et al., 2007); Gharyan, Lybia (Beccaluva et al., 2008). From this comparison, it can be noted that the extreme Nd-Hf-Pb isotopic variability characterizing the Bir Ali xenoliths is similar to other xenolith populations from North Africa and East African-Arabian domains. A relevant exception is represented by mantle xenoliths from Assab and those located within the northern Ethiopian plateau (Injibara and Dedessa) which exhibit lesser (though significant) isotopic variability (143 Nd/144 Nd = 0.51284-0.51329, Beccaluva et al., 2011). This more restricted range in isotope composition my be inherited from pervasive interaction of these mantle sections with Afar plume-related CFB that display similar isotopic compositions (176 Hf/177 Hf = 0.28290-0.28319, 143 Nd/144 Nd = 0.51284-0.51307, Meshesha and Shinjo, 2007 and 2010; 208 Pb/204 Pb = 37.6-39.1, 207 Pb/204 Pb = 15.4-15.7, 206 Pb/204 Pb = 18.0-19.3; Pik et al., 2006).

The helium isotopic compositions (${}^{3}\text{He}/{}^{4}\text{He}$) of samples from Bir Ali show a restricted range from 7.2 to 7.9 R_A (Table 5). The mean ${}^{3}\text{He}/{}^{4}\text{He}$ ratio, weighted inversely to the

analytical error, is very well defined to be 7.74 ± 0.03 R_A and within the range of values for asthenosphere-derived MORB (Graham et al., 2014). Helium concentrations in the olivines (for peridotites) and bulk rocks (for pyroxenites) range between 2.4 and 580 nano-ccSTP/g. As reported in Fig. 9, these He abundances covary positively with La/Yb (whole-rock value, Table 1) and inversely with ε_{Nd} (Table 4), supporting evidence that the He isotope signature is carried by addition of a melt/fluid enriched in LREE and characterized by very unradiogenic Nd isotopic compositions. The Bir Ali 3 He/ 4 He values also fall within the range recorded for other xenoliths in the East African-Arabian domain (e.g. Mega, Injibara and Dedessa in Ethiopia, Beccaluva et al., 2011; Assab in Eritrea, Marty et al., 1996). As shown in Fig. 10, Bir Ali 3 He/ 4 He values appear to be systematically higher than those measured in peridotite xenoliths from Saharan belts (Azrou, Morocco: Natali et al., 2013b; Hoggar: Beccaluva et al., 2007; Gharyan: Beccaluva et al., 2008).

4. Discussion and concluding remarks

Extensive sampling of mantle xenoliths from Bir Ali suggests that spinel-peridotites represent the largest constituency (85-90%) of the southernmost Arabian lithosphere, with a significant presence of spinel-pyroxenites. Bir Ali peridotites are characterized by medium- to finegrained variably recrystallized textures with marked foliation and are significantly different from most xenolith populations of the East African Rift (EAR) system. Bir Ali xenoliths also show a peculiar compositional range from lherzolites (up to 13% clinopyroxene) to harzburgites and dunites (cpx down to < 1-2%), that delineates a continuous compositional trend with an uncommon abundance of dunites with respect to other EAR peridotite xenolith suites. As discussed by Bodinier and Godard (2014), the observed trend could, in principle, be ascribed to either melt extraction events or refertilization via melt-mantle rock reactions. Although the latter process certainly occurred (testified by modal metasomatism and incompatible element/isotopic enrichments), in our view melting processes played a dominant role in the lherzolite-harzburgite-dunite variation trend. In fact, in Bir Ali peridotites there are no bimodal or distinct elemental distributions such as observed in peridotite suites affected by pervasive refertilization (e.g., Lherz massif, Le Roux et al., 2007); instead, there is remarkable continuity of chemical, modal and mineralogical variations within peridotites, and there are significant inverse correlations between Mg, Ni, Co and Al, Ca, Ti, V, and HREE (Figs. 4 and 5), as expected from melt extraction modelling of fertile mantle compositions (Niu, 1997; 2004). Moreover, there are no anomalous olivine/pyroxene ratios in Bir Ali peridotites as observed in mantle xenoliths recording extensive melt-rock interaction (Kelemen et al., 1998; Beccaluva et al., 2004; Bianchini et al., 2011). On the contrary, Bir Ali harzburgites and dunites conform to refractory residua after polybaric high-degree (30-50%) melt extractions as proposed for Greenland xenoliths (Bernstein et al., 1998) and supported by experimental petrology data (Falloon et al., 1988; Walter, 1998). Furthermore, time constraints provided by Lu-Hf model ages suggest that partial melting events have occurred since the Paleo-Proterozoic (2 Ga). This supports the hypothesis that refractory peridotites formed under extremely high geothermal regimes, long before the Cenozoic tectonomagmatic events subsequently affected the continental lithospheric mantle in this region. Accordingly, we interpret Bir Ali peridotite xenoliths as remnants of a tecton-ically reworked proton mantle section (Deen et al., 2006; Griffin et al., 2009) that itself was structured and depleted by melting processes in the 2.5-1 Ga time span and subsequently involved in crustal growth during Neoproterozoic tectono-magmatic events (< 1 Ga, e.g. Stern and Johnson, 2010).

The linkage between the Bir Ali pyroxenites and the timing of these events is not straightforward because of the paucity of reliable age determinations. However, the ubiquitous presence in the Arabian Peninsula of pyroxenites (equilibrated within peridotites) indicates that they represent an important and extensive magmatic event in the lithospheric mantle at a regional scale. Major and trace element compositions of pyroxenites, particularly REE patterns, suggest a genetic link with subalkaline basaltic magmas. For that reason, we argue that Bir Ali pyroxenites formed by large intrusions of basic melts interacting with the host peridotite, in agreement with processes proposed for many pyroxenitic occurrences worldwide (Downes, 2007; Bodinier and Godard, 2014; and references therein). Pyroxenite formation could be either concomitant with the above-mentioned Paleo-Proterozoic partial melting processes or, more likely, related to Neo-Proterozoic magmatic events that extensively refertilized the Arabian lithospheric mantle, as suggested by Stern and Johnson (2010). An alternative hypothesis, which considers Bir Ali pyroxenites as remnants of oceanic crust recycled from ancient subductions events, appears unlikely owing to the absence of

deeply deformed textures and incompatible-element depleted (MORB type) patterns, as well as the lack of positive Eu (and Sr) anomalies inherited by former plagioclase-bearing parageneses (Bodinier and Godard 2014, and references therein).

The lithospheric mantle in the study region has clearly been affected by younger metasomatising agents as attested to by disequilibrium textures and formation of new phases (glass, amphibole and feldspar) together with incompatible element and isotope enrichments in both peridotites and pyroxenites. These metasomatic enrichments are, if at all, barely detectable in lherzolites, but are much more apparent in olivine-rich lithologies such as harzburgites and particularly dunites, in agreement with experimental results on compositional controls on peridotite permeability (Toramaru and Fuji, 1986). Moreover, metasomatic effects on refractory peridotites could be enhanced by their intrinsically low incompatible element content, whereas more intense metasomatic reactions are required to reset the trace element and isotopic signatures of lherzolites (Bianchini et al., 2014).

The resulting effects show that the depletion and enrichment processes affecting the Afro-Arabian lithospheric domain produced an extreme variability in the isotopic signatures, sometimes extending beyond the mantle array defined by the conventional mantle isotopic components (DM, EM and HIMU), indicating that the metasomatising agents were OIB-type alkaline basic melts. Therefore, the Bir Ali mantle section, compared with others from the Afro-Arabian domain, confirms that the general extensional regime radiating from the Afar triple junction and generating the Red Sea-Gulf of Aden-Main Ethiopian Rift system, was accompanied by shallow mantle upwelling events and metasomatic processes dominated by alkaline agents (Henjes-Kunst et al., 1990; Blusztajn et al., 1995; Bedini et al., 1997; Kaeser et al., 2006; Bedini et al., 2007; Shaw et al., 2007; Grégoire et al., 2009; Aulbach et al., 2011; Beccaluva et al., 2011). A notable exception is represented by mantle xenoliths included in Neogene-Quaternary alkaline volcanics located within the northern Ethiopian-Yemeni CFB province; in these xenoliths, petrological, geochemical and isotopic evidence indicates that the causative agents of mantle metasomatism were subalkaline melts closely resembling the tholeiitic magmas related to the Afar plume (Beccaluva et al., 2011; Bianchini et al., 2014). We conclude that the thermo-chemical effects of the Afar plume were confined to the lithospheric sections located within the northern Ethiopian-Yemeni CFB plateau, and were negligible in the adjacent regions.

Helium isotope ratios observed at Bir Ali correspond to values typical of the upper mantle, further evidence that Afar plume activity must have had only a limited influence on the surrounding lithosphere. The observation of slightly elevated ³He/⁴He in the East African-Arabian domain compared to other African occurrences such as those of the Saharan Belt (Fig. 10) suggests that the ³He/⁴He differences may relate to the age of the lithosphere or manifest infiltrating small-degree melts from the underlying asthenosphere. Additional spatial coverage in the Afro-Arabian region may help to elucidate the extent to which such migrating melts and fluids have overprinted the lithospheric mantle composition.

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Table captions:

Table 1 – Bulk rock major and trace element compositions of mantle xenoliths from Bir Ali.

Footnote: modal abundances have been obtained by mineral/bulk rock mass balance calculations. Rock abbreviations: Lh = lherzolite; Hz = harzburgite; Du = dunite; Ol-Px = olivine pyroxenite; Px = pyroxenite. Mineral abbreviations: Ol = olivine; Cpx = clinopyroxene; Opx = orthopyroxene. Mg# = mol [MgO/(MgO+FeO)]; LOI = loss on ignition.

Table 2 – Major element compositions of constituent mineral phases of mantle xenoliths from Bir Ali.

Footnote: Averaged analyses refer to relatively homogeneous compositions within each sample. Abbreviations as in Table 1. Other abbreviations: Sp = spinel; Pl = plagioclase; Amph = amphibole; $Mg\# = Mg/(Mg+Fe^{2+})$; Cr# = Cr/(Cr+Al). * = metasomatic reaction products.

Table 3 – Trace element compositions of constituent mineral phases of mantle xenoliths from Bir Ali.

Footnote: Averaged analyses refer to relatively homogeneous compositions within each sample. Abbreviations as in Table 2.

Table 4 – Nd-Hf-Pb isotopic compositions of mantle xenoliths from Bir Ali.

Footnote: Abbreviations as in Table 1. ε_{Nd} and ε_{Hf} are calculated with $^{143}Nd/^{144}Nd = 0.512638$ and $^{176}Hf/^{177}Hf = 0.282772$ (Blichert-Toft and Albarède, 1997) for present-day chondritic Earth.

Table 5 – Elemental and isotopic analyses of helium in mantle xenoliths from Bir Ali. ${}^{3}\text{He}/{}^{4}\text{He}$ is reported as (R/R_A) where R_A is the atmospheric ratio.

Figure captions:

Fig. 1 - Sketch map of the East African-Arabian domain with indication of Oligocene continental flood basalts (CFBs; Beccaluva et al., 2009) and the main mantle xenolith occurrences related to Neogene-Quaternary alkaline volcanism (Henjes-Kunst et al., 1990; Baker et al., 1998; Kaeser et al., 2006; Shaw et al., 2007; Teklay et al., 2010; Aulbach et al., 2011; Beccaluva et al., 2011). The main tectonic lineaments are after Bosworth et al. (2005) and Rogers (2006).

Fig. 2 - Composition of Bir Ali mantle xenoliths in terms of modal ol-opx-cpx from Table 1. Abbreviations as in Table 1.

Fig. 3 - Photomicrographs of Bir Ali mantle xenoliths showing: a) a typical fine- to medium-grained tabular texture in lherzolite (PPL); b) recrystallized granuloblastic texture in lherzolite (XPL); c) coarse-grained texture in dunite (PPL); d) reaction patch with metasomatic glass in dunite (PPL); e) metasomatic amphibole rimmed by microcrystals of spinel, olivine, clinopyroxene and plagioclase in dunite; note secondary fluid inclusions in olivine healed fractures close to the amphibole (PPL); f) weakly recrystallized medium-grained texture in pyroxenite (PPL). Abbreviations as in Table 2, PPL = plane-polarized light; XPL = cross-polarized light.

Fig. 4 - Variation diagrams of SiO₂, TiO₂, Al₂O₃, CaO, Ni and V versus MgO of mantle xenoliths from Bir Ali. Average pyroxenite composition (star, ± standard deviation) of mantle xenoliths from the Arabian Peninsula (Stern and Johnson, 2010) and pyroxenite fields from Dedessa and Injibara (shaded field - Northern Ethiopia; Beccaluva et al., 2011) are reported for comparison. Also reported are the average Greenland harzburgite xenoliths considered residual after 40% partial melting (Bernstein et al., 1998). Primitive mantle (PM) and extent of melting estimates (F), based on the mineral residual modes, are from Niu (1997).

Fig. 5 - Chondrite-normalized REE (+ Y) bulk rock distribution of Bir Ali mantle xenoliths. Normalizing values are from Sun and McDonough (1989).

Fig. 6 - Chondrite-normalized REE (+ Y) distribution of clinopyroxene (a), amphibole and glass (b) from Bir Ali mantle xenoliths. Normalizing are from Sun and McDonough (1989). Abbreviations as in Table 1 and 2.

Fig. 7 - a) Primordial Mantle (PM) — normalized incompatible element patterns of the calculated metasomatic agents that affected mantle xenoliths from Bir Ali compared with compositional ranges of alkaline basic melts and carbonatites (after Beccaluva et al., 2011, and references therein); b) PM-normalized incompatible element patterns of the calculated metasomatic agents of mantle xenoliths from Bir Ali compared with those of other Afro-Arabian mantle xenolith occurrences: Mega - Southern Main Ethiopian Rift and Dedessa and Injibara - Northern Ethiopia (Beccaluva et al., 2011); Azrou - Morocco (Natali et al., 2013b); Gharyan - Lybia (Beccaluva et al., 2008); Hoggar - Algeria (Beccaluva et al., 2007). Normalizing values are from Sun and McDonough (1989). See text for further explanations.

Fig. 8 - Hf-Nd (a) and Pb (b, c) isotopic compositions of bulk rock and clinopyroxene separates from Bir Ali mantle xenoliths. Composition of other mantle xenoliths included in Neogene-Quaternary volcanics from Afro-Arabian domains are reported for comparison: Ataq (Yemen, Baker et al., 1998), Harrat-Ash Shaam (Jordan, Shaw et al., 2007), Mega (Southern Main Ethiopian Rift, Bianchini et al., 2014), Hoggar (Algeria, Beccaluva et al., 2007), Gharyan (Lybia, Beccaluva et al., 2008), Assab (Eritrea, Teklay et al., 2010). The Afar plume signature is inferred from the composition of Oligocene CFB (Pik et al., 2006; Meshesha and Shinjo, 2007; 2010). This plume signature contrasts with the extreme isotopic variability (exceeding that of the classic mantle components) of the studied mantle xenoliths. Mantle end-members from Zindler and Hart (1986) and Stracke et al. (2005).

Fig. 9 - a) Bulk rock La/Yb ratio (whole rock, Table 1) versus He concentration (ccSTP/g); b) ε_{Nd} (Table 4) versus He concentration (ccSTP/g); c) He concentration (ccSTP/g) versus ³He/⁴He (R/R_A).

Fig. 10 – Histogram of ³He/⁴He (R/R_A) for Bir Ali mantle xenoliths compared with those from other Afro-Arabian occurences (Marty et al., 1996; Beccaluva et al., 2007, 2008, 2011; Natali et al., 2013b).