

Refertilization of lithospheric mantle beneath the Yangtze craton in south-east China: evidence from noble gases geochemistry

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Abstract

The Yangtze craton (YC), in eastern China, is one of the oldest cratons in the world and is characterized by a complex tectonic and geodynamic evolution. This evolution regards most of the eastern China craton, which since Mesozoic time has undergone significant thinning (>200 km) of Archean lithosphere. This thinning favored the refertilization of the old refractory subcontinental lithospheric mantle (SCLM) by the upwelling of younger fertile asthenosphere. Whether this feature is localized only beneath certain areas of eastern China or is a more widespread characteristic of the mantle, including the YC, is a matter of debate.

In order to constrain the history of the YC SCLM, we have measured the He- and Ar-isotopic compositions of fluid inclusions hosted in mantle xenoliths in the Lianshan area, which is part of the poorly investigated YC in south-east China. We also report new mineral chemistry and trace element compositions of clinopyroxenes from the same suite of samples, for comparison with noble gases. Two distinct types of xenoliths can be identified: Type 1, characterized by mantle-like He-isotopic ($^3\text{He}/^4\text{He}$) ratios (up to 9.1 Ra), represents fragments of a fertile lithospheric mantle; Type 2, showing $^3\text{He}/^4\text{He}$ values in the SCLM range ($^3\text{He}/^4\text{He} < 7$ Ra), represents shallow relicts of a refractory mantle. The patterns of rare-earth elements as well as the Y and Yb concentrations in the clinopyroxenes normalized to primitive mantle (Y_N and Yb_N , respectively) indicate that fractional partial melting might have affected the local mantle by <3% in Type 1 and up to 20% in Type 2 xenoliths from Lianshan, respectively. The range of $^4\text{He}/^{40}\text{Ar}^*$ ($^{40}\text{Ar}^*$ is corrected for atmospheric contamination) ranges from 4.9×10^{-4} to 3.6×10^{-1} , which is below the typical production ratio of the mantle ($^4\text{He}/^{40}\text{Ar}^* = 1-5$); this range is however compatible with this fractional partial melting. The variable $^3\text{He}/^4\text{He}$ and $^4\text{He}/^{40}\text{Ar}^*$ values in Lianshan xenoliths suggest that the local mantle source

was also influenced by kinetic fractionation, possibly triggered by metasomatic melts. Metasomatism associated with carbonatitic melts, together with fluxing by CO₂-rich fluids, have permeated the mantle beneath Lianshan, generating the observed decoupling between noble gases and trace elements. The interpretative framework is also applicable for other mantle xenoliths from eastern China, indicating that the refertilization of the SCLM by ascending mantle-like melts is common also to YC, which can be identified using noble gases.

Keywords: Yangtze craton, Peridotite xenoliths, Noble gases, Fluid inclusions, Mantle refertilization, MORB, SCLM

1. Introduction

Eastern China represents a major cratonic area of the Eurasia continent and is one of the oldest on Earth (3.6 Ga; Liu et al., 1992). It has a complex geological history, since it experienced a series of subduction/collision events that induced lithosphere thinning and rejuvenation in the late Mesozoic and Cenozoic (Li et al., 1993; Robinson et al., 1999; Zhang et al., 2003). An old, cold, thick (>180 km) and refractory lithosphere was replaced by a young, hot, thin (70–80 km), and fertile mantle (Menzies et al., 1993, 2007; Griffin et al., 1998; Fan et al., 2000). The widespread occurrence of intraplate basaltic volcanism (Figure 1a) in eastern China of Mesozoic-Cenozoic, which host mantle-derived xenoliths, provides an excellent opportunity for studying the continental lithosphere and any interaction with underlying mantle (Li et al., 2002; Xu & Liu, 2002; Ma et al., 2006; Wei et al., 2012; Lu et al., 2013; Zheng et al., 2007, 2015).

The isotopic composition of helium (³He/⁴He, reported in units of R/Ra, where Ra is the ³He/⁴He of atmosphere = 1.39×10⁻⁶) is a powerful tracer for revealing mantle heterogeneities and determining crust–mantle interactions (e.g., Sano et al., 1986; Staudacher et al., 1986; Moreira & Allegre, 2002; Hilton & Porcelli, 2014). Radiogenic ⁴He is accumulated from the radioactive decay of U- and Th-series radionuclides and is concentrated in the continental crust, whereas ³He is mostly primordial in origin and has been stored in the Earth's interior since its early accretion (e.g., Clarke et al., 1969). Previous studies have established that the ³He/⁴He of the sub continental lithospheric mantle (SCLM) (6.1±0.9 Ra; e.g., Dunai & Porcelli, 2002; Gautheron & Moreira, 2002) is lower than mid ocean ridge basalt (MORB) mantle (8±1 Ra; Graham, 2002). Recently, it has been proposed that there is probable bias in the estimate of the helium isotope composition of SCLM, and the accepted range of values has been expanded to 6.1±2.1 Ra (Day et al., 2015). In contrast, plume-related materials show significantly higher ³He/⁴He values (≥50 Ra; e.g. Stuart et al., 2003) relative to the MORB mantle, confirming the sensibility of this tracer in distinguishing between different

reservoirs of earth's interior. The simultaneous presence of MORB- and SCLM-type helium could be diagnostic of a rejuvenation event superimposed over lithosphere mantle values, however the considerable overlap between MORB- and SCLM-like helium makes differentiating between these two sources difficult. However, further constraints on these modifying processes can be gained by use of $^4\text{He}/^{40}\text{Ar}^*$, which is particularly powerful when coupled with $^3\text{He}/^4\text{He}$. Indeed, previous studies demonstrated that $^4\text{He}/^{40}\text{Ar}^*$ is a diagnostic tracer of magmatic degassing, and it is useful to evaluate the extent and type of mantle partial melting, and/or the presence of other processes affecting the source (e.g., Yamamoto et al., 2009; Burnard et al., 2010; Correale et al., 2012, 2014). Therefore, the study of noble gases in mantle-derived xenoliths hosted in Mesozoic-Cenozoic basalts from eastern China can yield useful information about this complex segment of the mantle. To date, few studies have focused on noble gases geochemistry (Xu et al., 1998, 2003; Li et al., 2002; Wu et al., 2003, 2004; Ma et al., 2006; Chen et al., 2007; He et al., 2011; Tang et al., 2014) in Chinese xenoliths, and all of them investigated only the northern and central part of eastern China. These studies revealed the presence of both a MORB-like and a radiogenic component in the mantle beneath NCC (North China Craton), corroborating the hypothesis of rejuvenation of lithosphere in this sector of China, however it remains unknown as to if this phenomena has also affected the mantle beneath south-east China. With the aim of constraining the noble gas characteristics of the SCLM beneath south-east China and identifying geological processes acting to modify its pristine mantle signature, we investigate the He- and Ar-isotopic compositions of fluid inclusions trapped in minerals separated from mantle xenoliths found in Cenozoic basalts outcropping in the Lianshan area (Subei basin) (Figure 1b,c). The noble gas systematics are combined with the mineral chemistry and geochemistry of trace elements in clinopyroxenes from the same suite of samples. Finally, the results from this study are discussed in the regional context of eastern China, so as to better elucidate the role and effects of lithospheric thinning and asthenosphere mantle upwelling beneath YC.

2. Geological setting

Eastern China is subdivided into five main zones: the Xing-Meng orogenic belt to the north, the NCC and the Qinling-Dabie-Sulu ultrahigh pressure metamorphic belt in the centre, and the YC and Cathaysia blocks to the south (Figure 1a,b). The last two zones amalgamated at ~880 Ma to form the South China block (SCB; Figure 1b) (Li et al., 2009; Zhao & Cawood, 2012).

In early Mesozoic time, the YC subducted below NCC along a suture by forming the Qinling-Dabie-Sulu belt (e.g. Zheng et al., 2015). The subduction of YC is responsible for a rapid refertilization of the old refractory lithospheric mantle through melt-peridotite interaction during

105 the Mesozoic, which started from the southern margin of the NCC (Zhang et al., 2002; Fan et al.,
106 2004; Xu et al., 2004; Zhang et al., 2012).
107 In mid and late Mesozoic, much of eastern China was intruded by granitic plutons, associated with a
108 continental arc resulted from the western Pacific subduction system (Chung et al., 1994; Ren et al.,
109 2002). This arc was active until the occurrence in Cenozoic of rollback of subduction zones that
110 also induced in southeastern China asthenospheric upwelling, lithospheric mantle erosion and
111 extension, as exemplified by the opening of the South China Sea and other early Tertiary basins
112 (Zhai et al., 2007; Zheng et al., 2007; Santosh, 2010; Yang et al., 2012; Li et al., 2012; Guo et al.,
113 2013; Tang et al., 2013). One of these is the Subei basin sited in the northern part of the lower
114 YC (Figure 1a,b), to the east of the TLFZ, and characterized by a basement of about 30 km of
115 continental crust (Zhang et al., 1988). During the Cenozoic, the Subei basin experienced intensive
116 basaltic volcanism that produced rare tholeiites and widespread mantle xenoliths-bore alkali basalts.
117 These alkali basalts were classified (in order of decreasing age) as the Shijingshan, Liuhe,
118 Huanggang, Fangshan and Guizhishan groups. The Lianshan basalts (Figure 1b,c) belong to the
119 Huanggang group that is entirely constituted by alkali olivine basalts erupted at 10–12 Ma (Shao et
120 al., 1989). The present study focused on mantle xenoliths included in these basalts.

121

122 **3. Samples and analytical methods**

123 The 16 mantle-derived xenoliths studied here were collected in a quarry of columnar joints from
124 Cenozoic Lianshan basalts (Figure 1c) and are classified in Table 1. Samples 09LS09 and 09LS20
125 are the same as those investigated by Lu et al. (2013)(i.e., reported as samples LS0909 and LS0920,
126 respectively, in their Table 1). All samples are fresh with no visible surface alteration and most
127 range in size from 5 to 10 cm, although some are larger than 20 cm (see Figure 1d).

128 The compositions of major and trace elements of minerals from the Lianshan xenoliths were
129 analyzed at the GEMOC National Key Centre at Macquarie University (Sydney, Australia). Major
130 elements were analyzed using an electron microprobe (CAMECA SX100) fitted with five crystal
131 spectrometers (EMP). The usual operating conditions were an accelerating voltage of 15 keV, a
132 sample current of 20 nA, and a counting time of 10 s for peaks and 5 s for the background on either
133 side of a peak. The standards were natural minerals, and corrections were performed using the
134 method of Pouchou and Pichoir (1984). Trace elements compositions of clinopyroxene were
135 determined by laser ablation using a 213-nm Nd-YAG laser attached to an inductively coupled
136 plasma mass spectrometry system (Agilent 7700). Operating conditions included a beam diameter
137 of 55 μm with a pulse frequency of 5 Hz and a laser intensity of around 0.150 mJ. Each analysis
138 included data from a 60-s initial recording of the background and then a 120-s recording of sample

139 data, followed by 30 s of washout. ^{43}Ca and NIST 610 glass were used as the internal and external
140 standards, respectively; these were combined to calibrate the fractionation derived from ablation,
141 transportation and excitation processes, and the matrix effect in the data using the online GLITTER
142 4.4 software (Griffin et al., 2008).

143 In order to analyze the noble gases composition of fluid inclusions, the xenoliths were crushed and
144 mineral separated by hand-picking under a binocular microscope, following standard protocols
145 (e.g., Martelli et al., 2011; Correale et al., 2012). Between 0.72 and 1.87 g of crystals (olivines
146 and/or pyroxenes that were 0.5–2 mm in size) were selected, and each mineral phase was analyzed
147 separately. Due to the small amount of gas released from the fluid inclusions, each mineral phase
148 could only be analyzed for samples 11LS16, 11LS58, 11LS61 and 11LS66. For other samples, we
149 analyzed 2.1–8.9 g of olivine, orthopyroxene and clinopyroxene (1–2 mm in size) simultaneously.
150 Separated minerals were cleaned ultrasonically, and then gases were extracted by in-vacuo, single-
151 step crushing at about 200 bar, with the system connected to a preparation line and then to a mass
152 spectrometer (MS). As is widely known from literature (Samson et al., 2003), noble gases are
153 trapped in primary and secondary (when present) fluid inclusions inside crystals. We used single-
154 step crushing to minimize the contribution of noble gases from the crystal lattice to the fluid
155 inclusions trapped in crystals (e.g., Kurz, 1986; Hilton et al., 1993, 2002). We point out that this
156 technique is the most conservative in order to analyze a fluid composition that reflects that of the
157 magmatic/mantle source. Indeed, as subsequently discussed in Section 5.1.2 and 5.1.3, melting or
158 step-heating techniques release a bulk gaseous phase including noble gases trapped in fluid
159 inclusions and in crystal matrix and which could severely compromise the understanding of pristine
160 isotopic signatures. The elemental and isotopic compositions of noble gases were determined at the
161 laboratory of INGV-Palermo (Italy). ^3He , ^4He and ^{20}Ne were measured by a split-flight-tube MS
162 (GVI-Helix SFT), while ^{36}Ar , ^{38}Ar (not shown) and ^{40}Ar were analyzed by a multicollector MS
163 (GVI-Argus). Typical blanks for He, Ne and Ar were $<10^{-14}$, $<10^{-16}$ and $<10^{-14}$ mol, respectively.
164 Further details about the sample preparation and analytical procedures are available elsewhere
165 (Nuccio et al., 2008; Martelli et al., 2014; Rizzo et al., 2015).

166

167 **4. Results**

168 **4.1 Petrography and mineral chemistry**

169 All of the collected xenoliths are spinel lherzolites except for samples 11LS17 and 11LS39 (spinel
170 harzburgites) and sample 11LS61 (dunite). Modal compositions were estimated using the area
171 proportion, and are reported in Table 1 together with the other main petrographic features of the
172 sample suite.

173 The peridotites have dominantly porphyroclastic textures with minor coarse-grained, sheared and
 174 fine-grained textures. The most of xenoliths show porphyroclastic microtextures and ~10% olivines
 175 are larger than 4 mm. Spongy textures are extensively developed in the samples having these
 176 microtextures. Some large orthopyroxenes show fine exsolution lamellae of clinopyroxene. The
 177 other samples mainly show protogranular (coarse-grained) and fine-grained textures. Clinopyroxene
 178 in these xenoliths contain abundant CO₂ fluid inclusions identified by Raman analyses, which is not
 179 common in xenoliths with porphyroclastic microtextures (Lu et al., 2013).

180 The Mg# of the Lianshan olivines varies from 89.2 to 91.7 (Table 2). In detail, samples 11LS13,
 181 11LS43, 09LS09 and 09LS20 exhibit the lowest Mg# values (≤ 90), falling within the values typical
 182 for fertile lherzolite (Lu et al., 2013). These values are comparable with Mg# measured in xenoliths
 183 from the Cathaysia block, as shown by Lu et al. (2013). No obvious relationship exists between
 184 Mg# and the CaO concentrations of olivines in the Lianshan xenoliths. However, the Mg# and the
 185 NiO and MnO concentrations of olivines are weakly correlated. The NiO concentrations are high
 186 (3600–4800 ppm), similar to those of the refractory Hebi xenoliths (Zheng et al., 2001).

187 The orthopyroxenes exhibit Mg# values between 89.6 and 92.2. Samples 11LS43, 09LS09 and
 188 09LS20 show the lowest Mg# values (≤ 90.0) and the highest Al₂O₃ concentrations (> 3.15 wt%).
 189 The orthopyroxenes mostly exhibit NiO concentrations between 700 and 1200 ppm.

190 Clinopyroxenes are Cr-Diopside, with Cr₂O₃ concentrations varying between 0.79 and 1.45 wt%,
 191 and have Mg# values ranging between 90.6 and 94.2. Samples 11LS13, 11LS33, 09LS09 and
 192 09LS20 show the lowest Mg# values (≤ 91.2).

193 Spinel has highly variable concentrations of Cr₂O₃ (8.6–39.3%, Table 2) and thus also Cr# values
 194 (8.8–46.5), which is usually correlated with the extent of partial melting (Hellebrand et al., 2001).
 195 The xenoliths with the lowest Cr# of spinels (< 13.9) are samples 11LS13, 11LS16, 11LS17,
 196 11LS66, 09LS09 and 09LS20. These samples partially coincide with the samples having the lowest
 197 Mg# values of clinopyroxenes (i.e. 11LS13, 11LS33, 09LS09 and 09LS20) because these probably
 198 reflect the lowest degrees of melt extraction.

199 The xenoliths, having low Mg# in olivines, orthopyroxenes and clinopyroxenes, and low Cr# in
 200 spinels, are typically derived from a fertile mantle. Conversely, the composition of the other
 201 xenoliths is opposite, and they are considered to represent a portion of the refractory mantle. Based
 202 on the petrochemical classification of Lu et al. (2013), who studied a separate suite of xenoliths
 203 from the Lianshan area, xenoliths with porphyroclastic textures and low Mg# in olivines,
 204 orthopyroxenes and clinopyroxenes were classified as Type 1. The other xenoliths showing
 205 protogranular (coarse-grained) and an opposite behavior of Mg# in olivines, orthopyroxenes and
 206 clinopyroxenes were classified as Type 2. Lu et al. (2013) established this classification by using a

limited number of samples in their suite only, and so we must consider the possibility of slight differences in some of the limits they established leading to incorrect classification of part of our samples. We therefore classified our xenoliths based on trace elements patterns (Section 4.2), which more closely reflect source characteristics and processes that eventually modify the mantle. Equilibration temperatures calculated from Ca-in-orthopyroxene thermometer, orthopyroxene-clinopyroxene thermometer (Brey and Kohler, 1990), and clinopyroxene–orthopyroxene–olivine–spinel thermometers (Sachtleben and Seck, 1981) are given in Table 3. Estimates based on the Ca-in-orthopyroxene thermometer (Brey and Kohler, 1990) for the xenoliths studied here yield a homogeneous temperature of $905\pm41^{\circ}\text{C}$. This range is comparable to that found by Lu et al. (2013) in another suite of samples collected from the same area ($T=928\pm36^{\circ}\text{C}$). There is not a clear distinction between xenoliths showing porphyroclastic textures and low Mg# in olivines, orthopyroxenes and clinopyroxenes (typically derived from a fertile mantle), and the other xenoliths. This indicates that the refractory and fertile lithospheric mantles are not compositionally stratified but coexist over a range of depths. Due to the fact that no garnet-bearing xenoliths are found in Lianshan area, we cannot construct a geotherm for this area. However, xenoliths from other places in SCB define a common geotherm corresponding to a surface heat flux of $\sim 60\text{--}70\text{ mW/m}^2$ (Xu et al., 1996; Zheng et al., 2015), which is significantly hotter and thinner than those of typical cratons ($\sim 40\text{ mW/m}^2$ and $>200\text{ km}$). Therefore, we argue that YC has also been delaminated and significantly thinned.

4.2 Trace elements composition

Trace elements data for clinopyroxene crystals separated from peridotite samples are listed in Table 4 and are plotted as patterns of rare-earth elements (REE) in Figure 2. We focus only on clinopyroxene crystals (i.e. not for the whole rocks) since clinopyroxene in the anhydrous spinel peridotites host the most amount of trace elements and can thus be used as tracers of mantle processes (Salters & Shimizu, 1988; Meen et al., 1989; Yaxley et al., 1998; Lu et al., 2013). The patterns of REE of clinopyroxenes are quite variable, and can be divided in two main groups: the first group (samples 11LS06, 11LS17, 11LS33, 11LS39, 11LS57, 11LS58, 11LS61, 11LS66, 09LS09 and 09LS20) is characterized by an LREE-depleted pattern [$(\text{La}/\text{Yb})_{\text{N}}=0.20\text{--}0.68$] and flat HREE [$(\text{Gd}/\text{Yb})_{\text{N}}=0.75\text{--}1.62$] (Figure 2 plot top), with samples 11LS06 and 11LS39 (grey symbols in Figure 2) showing a slightly different pattern with concave-upward LREE. Samples in this group exhibit a variable enrichment degree with respect to chondrite [$\text{clinopyroxene}/\text{Chondrite}=5\text{--}10$ and <5 (red and black/grey symbols in Figure 2, respectively)], with negative anomalies in Ba, Nb and Ti, and positive anomalies in U and Th (Table 4). The second group (samples 11LS16, 11LS25,

11LS43 and 11LS59) is characterized by an LREE-enriched pattern $[(La/Yb)_N=2.57-7.20]$, with samples 11LS43 and 11LS59 showing a concave-upward pattern (Figure 2 mid plot). Samples in the second group also show negative anomalies in Ba, Nb, Ta, Zr, Hf and Ti, and positive anomalies in U and Th (Table 4). Sample 11LS32 shows transitional features between these two groups, since it is characterized by a flat pattern of REE $[(La/Yb)_N=1.65]$ (Figure 2 bottom plot) and negative anomalies in Ba, Nb, Zr, Hf and Ti (Table 4).

Taking into account the evidence from the trace element patterns described above, and considering the classification made by Lu et al. (2013), we establish that: the Type 1 samples are 11LS06, 11LS17, 11LS33, 11LS39, 11LS57, 11LS58, 11LS61, 11LS66, 09LS09 and 09LS20; the Type 2 samples are 11LS16, 11LS25, 11LS43 and 11LS59; and sample 11LS32 shows transitional features. The classification in Type 1 and Type 2 mantle from Lu et al. (2013) is consistent with others study from NCC including the presence of a fertile and refractory mantle (Zheng et al. 1998, 2001, 2006, 2007). The patterns of REE from Lu et al. (2013) and from other studies of NCC are reported in figure 2 for comparison with our samples.

4.3 Light noble gases in fluid inclusions

The elemental and isotopic compositions of He, Ne and Ar in Lianshan peridotite xenoliths are reported in Table 5. The ranges of He (Figure 3), Ne and Ar concentration were 1.89×10^{-15} – 4.86×10^{-13} mol/g, 1.89×10^{-18} – 3.88×10^{-16} mol/g, and 2.63×10^{-12} – 3.08×10^{-11} mol/g, respectively. The concentrations of Ar and Ne were partially affected by addition of atmospheric component, as is evident from the observed variability in $^4He/^{20}Ne$ (10–3000) and $^{40}Ar/^{36}Ar$ (370–4585). Indeed, these data plot along a binary mixing trend between an atmosphere-derived component and a mantle source (Figure 4). Thus, ^{40}Ar was corrected by assuming that all ^{36}Ar measured in the sample is of atmospheric origin, and it is reported as $^{40}Ar^*$ as calculated using the following formula:

$$^{40}Ar^* = ^{40}Ar_{measured} - ((^{40}Ar/^{36}Ar)_{air} \times ^{36}Ar_{measured})$$

$^4He/^{40}Ar^*$ in Lianshan xenoliths varies between 4.9×10^{-4} and 3.6×10^{-1} (Figure 5), with all the measured values being significantly below the mantle production ratio ($^4He/^{40}Ar^*=1-5$; e.g., Ozima & Podosek, 1983; Marty, 2012) based on typical $^{232}Th/^{238}U$ and K/U values.

Although the low concentration of He in the atmosphere means that such contamination has an almost negligible effect on the He-isotopic composition, the $^3He/^4He$ ratios were corrected using the measured $^4He/^{20}Ne$ as a metric for atmosphere-derived contamination in the following equation (from Giggenbach et al., 1993):

$$R/Ra = ((R_M/Ra)(He/Ne)_M - (He/Ne)_A)/((He/Ne)_M - (He/Ne)_A)$$

where subscripts M and A refer to measured and atmosphere theoretical values, respectively [(He/Ne)_A=0.318]. The results are reported in Table 5 and are hereafter expressed as Rc/Ra values. The correction is small or negligible for most of the samples, with the maximum bias of ~0.1 Ra appearing in the sample showing the lowest ⁴He/²⁰Ne and ⁴⁰Ar/³⁶Ar. The ³He/⁴He ratio varies from 3.01 to 9.16 Ra (Figures 3 and 5), showing no clear relation between ³He/⁴He and the He concentration (Figure 3). We argue that among Type 1 xenoliths, samples 11LS39, 11LS61 and 11LS66 have a ³He/⁴He in the typical MORB range or slightly higher (³He/⁴He=7.08–9.43 Ra). All of the other Type 1 samples fall within the SCLM range (<8.2 Ra, Gautheron & Moreira, 2002), but we infer that they reflect the secondary mantle processes discussed below. Sample 11LS32 shows transitional features (based on the criteria discussed in Section 4.2), and displays a MORB-like ³He/⁴He value (7.35 Ra), similar to samples 11LS39, 11LS61 and 11LS66. Among Type 2 xenoliths, samples 11LS16, 11LS43, 11LS25 and 11LS59 show typical SCLM-like features (3.33<³He/⁴He<6.64 Ra, Gautheron & Moreira, 2002). None of the Type 2 xenoliths have ³He/⁴He falling within the MORB range.

5. Discussion

5.1 Post-magmatic processes affecting noble gases in fluid inclusions

5.1.1 Atmospheric contamination

We used two sensitive isotopic ratios to detect the presence of atmosphere-derived component in fluid inclusions: ⁴He/²⁰Ne and ⁴⁰Ar/³⁶Ar (Table 5, Figure 4). All samples fall along a computed curve of binary mixing between MORB and an atmosphere-derived endmember. Evidence of atmosphere-derived component in the Ar-isotopic composition has already been reported for mantle xenoliths from eastern NCC (Tao et al., 2001; Wu et al., 2003, 2004; Lai et al., 2005; Ma, 2006; He et al., 2011; Tang et al., 2014), for fluid inclusions from other geodynamic contexts (e.g., Etna: Nuccio et al., 2008; Correale et al., 2014; Stromboli: Martelli et al., 2014; Santorini: Rizzo et al., 2015; Turrialba: Di Piazza et al., 2015), and for several xenoliths sampled from different segments of the SCLM (Nagao & Takahashi, 1993; Patterson et al., 1994; Dunai & Baur, 1995; Matsumoto et al., 1998, 2000, 2001, 2002, 2005; Yamamoto et al., 2004; Gautheron et al., 2005; Hopp et al., 2007; Czuppon et al., 2009, 2010; Hopp & Ionov, 2011; Martelli et al., 2011, 2014; Correale et al., 2012).

308 Tang et al. (2014) identified the presence of atmosphere-derived heavy noble gases (i.e. Ar, Kr and
309 Xe) in eastern NCC and suggested that these were efficiently recycled by subduction processes into
310 the SCLM beneath eastern China, and probably reflect metasomatism induced by melts/fluids
311 derived from the subducted Paleo-Pacific oceanic crust. Late Mesozoic-Cenozoic subduction of the
312 Pacific plate also occurred in the South China. Thus, the presence of an atmosphere-derived
313 component is probably an intrinsic characteristic of the mantle below the whole eastern China, and
314 thus also below the Lianshan area, that was preserved during subduction and subsequently isolated
315 from the denser, underlying, convective mantle (Matsumoto et al., 2000, 2002; Yamamoto et al.,
316 2004; Hou et al., 2011; Tang et al., 2014).

317 Alternatively, this could represent a near-surface feature that is acquired from crystal fractures that
318 are exposed to the atmosphere and liberated when the minerals are crushed (Nuccio et al., 2008;
319 Correale et al., 2012, 2014). However, this seems less likely in the case of Lianshan xenoliths
320 considering the recycling of atmosphere-derived heavy noble gases observed across a broad area of
321 eastern China.

322

323 **5.1.2 Cosmogenic and nucleogenic ^3He production in the crystals**

324 The wide range of $^3\text{He}/^4\text{He}$ for the Lianshan xenoliths suggests that they could be subjected to one
325 or more post-eruptive processes, such as (1) the addition of cosmogenic ^3He (Kurz, 1986; Ballentine
326 & Burnard, 2002), and/or (2) the radiogenic ingrowth of ^4He into the crystal matrix (e.g., Graham et
327 al., 1987).

328 The production of cosmogenic ^3He varies strongly with geographic location (e.g., elevation and
329 latitude) and the exposure history of the rock to the cosmic rays. Since the Lianshan xenoliths were
330 collected from a quarry, such exposure is unlikely. In addition, all of the studied xenoliths erupted
331 during the same period (i.e., Lianshan basalts at 10–12 Ma; Shao et al., 1989; Lu et al., 2013). This
332 means that the eventual modification of $^3\text{He}/^4\text{He}$ ratio would be strictly dependent from the ^4He
333 concentration of each sample. If the production of cosmogenic ^3He had acted to modify the
334 Lianshan samples, the increase in $^3\text{He}/^4\text{He}$ would be more evident in samples with the lowest ^4He
335 concentration, but this is not observed. For example, sample 11LS13 has the lowest ^4He
336 concentration in the sample suite (0.19×10^{-14} mol/g) and its $^3\text{He}/^4\text{He}$ is 4.35 Ra, which is among the
337 lowest measured in Lianshan xenoliths (Figure 3). Conversely, sample 11LS61 has the highest
338 $^3\text{He}/^4\text{He}$ (8.6–9.1 Ra) but a ^4He concentration of 19.92×10^{-14} mol/g, which is among the highest ^4He
339 concentrations of the data set. This confirms that the difference in $^3\text{He}/^4\text{He}$ observed in our data set
340 cannot be attributed to different inputs of cosmogenic ^3He .

341 Nucleogenic ^3He is produced in the $^6\text{Li}(n, \alpha) \rightarrow ^3\text{H}(\beta) + ^3\text{He}$ reaction, which is triggered by
 342 thermalized neutrons from (α, n) reactions within the rocks (Andrews & Kay, 1982; Lal, 1987).
 343 Nucleogenic production is a function of the Li concentration of the sample and is typically less
 344 significant than the generation of cosmogenic ^3He by spallation-induced reactions in rocks that are
 345 moderately rich in Li (Lal, 1987). However, starting from a nucleogenic ^3He production rate of
 346 $6.13 \times 10^{-6} \text{ atoms g}^{-1} \text{ yr}^{-1} \text{ ppm}^{-1} \text{ Li}$ per neutron $\text{cm}^{-2} \text{ yr}^{-1}$, a neutron absorption mean free path of
 347 76.5 cm for ultramafic rocks (Lal, 1987), a neutron production rate of approximately 2 neutrons g^{-1}
 348 $\text{ppm}^{-1} \text{ U yr}^{-1}$ per gram of rock and 0.7 neutrons $\text{g}^{-1} \text{ ppm}^{-1} \text{ Th yr}^{-1}$ per gram of rock (Dunai et al.,
 349 2007), we calculated the amount of nucleogenic ^3He produced in our samples over the past 12 Ma
 350 (Table 5). Assuming that 100% of the produced ^3He diffused into the fluid inclusions, only some of
 351 the samples with the lowest ^3He concentrations would have been significantly affected by the
 352 production of nucleogenic ^3He . In reality, the calculated nucleogenic ^3He produced in samples
 353 11LS25, 11LS33 and 11LS43 exceeds the measured amount, which is impossible. This means that
 354 the assumption of 100% diffusion of ^3He into the fluid inclusions is unrealistic. Based on the studies
 355 in mantle xenoliths from other cratonic areas worldwide of Barry et al. (2015) and Day et al. (2015),
 356 who assumed the diffusion up to 10% of radiogenic ^4He into the fluid inclusions, we calculated the
 357 corrected $^3\text{He}/^4\text{He}$ values for our samples based on 1% and 10% nucleogenic ^3He transfer by
 358 diffusion or α recoil (Table 5). Due to most of the corrected $^3\text{He}/^4\text{He}$ values being similar to those
 359 measured, we conclude that the $^3\text{He}/^4\text{He}$ variability of Lianshan xenoliths cannot be attributed to the
 360 post-eruptive addition of nucleogenic ^3He . This conclusion is also supported by the findings of
 361 Matsumoto et al. (2000), who argued that ^3He is unlikely to diffuse from the crystal lattice into fluid
 362 inclusions at typical surface temperatures.

363

364 **5.1.3 Radiogenic ^4He ingrowth from U and Th decay**

365 The radiogenic production of ^4He in the crystal lattice of mafic minerals from the decay of U and
 366 Th retained therein could induce a decrease in $^3\text{He}/^4\text{He}$ of fluid inclusions, and thus could explain
 367 the $^3\text{He}/^4\text{He}$ variability in this data set. Such a decrease could only occur if sufficient radiogenic ^4He
 368 is produced (i.e., depending on the concentrations of U and Th in the minerals) and if ^4He diffuses
 369 or is transferred by α recoil into the fluid inclusions. The production of radiogenic ^4He is a function
 370 of time and the U and Th concentrations in the minerals. Based on this and that Lianshan xenoliths
 371 have been brought to the surface by the same lavas that erupted 10–12 Ma, the different $^3\text{He}/^4\text{He}$
 372 values of our samples could be the consequence of their variable U and Th concentrations. This
 373 would lead to the production of different amounts of radiogenic ^4He in the crystals during the same
 374 time frame. Alternatively, if individual samples have variable ^3He compositions and ^4He is

375 produced (and transferred) in a consistent manner, this would result in variable $^3\text{He}/^4\text{He}$ values. In
 376 order to check for these possibilities, we calculated the amounts of radiogenic ^4He produced in the
 377 investigated xenoliths, and we quantitatively assessed their influence on the original He-isotopic
 378 signature. Following Ballantine and Burnard (2002), the amount of ^4He produced from each
 379 radioisotope [R], expressed as a function of present day concentration in the rock, is

$$381 \quad ^4\text{He atoms g}^{-1} \text{ yr}^{-1} = X_r [\text{R}] (N_A/A_r) \times 10^{-6} (e^{\lambda t} - 1) \times \text{yield}_r$$

382
 383 where X_r is the fractional natural abundance of isotope R, N_A is Avogadro's number, A_r is the molar
 384 mass of R (g), λ_r is the decay constant of R (yr^{-1}), yield_r is number of α particles emitted in the
 385 complete decay chain, [R] is the concentration of R (ppm) and t is the age (yr).

386
 387 The results are reported in Table 5. Assuming the U and Th concentrations measured in Lianshan
 388 xenoliths, we calculated that the radiogenic ^4He produced during the past 12 Ma would be always
 389 from one to four orders of magnitude higher than the ^4He content measured in fluid inclusions.
 390 Matsumoto et al. (2002) compared the He released from the crushing and melting of Archaean
 391 komatiites, and concluded that ~1% of ^4He ingrowth could diffuse into the fluid inclusions. Barry et
 392 al. (2015) adopted the same assumption in order to correct the $^3\text{He}/^4\text{He}$ measured in Siberian
 393 xenoliths of 160–360 Ma. However, based on the assumption of 1% transfer from the matrix to
 394 fluid inclusions, the calculated radiogenic ^4He is higher than the measured ^4He in most of the
 395 samples, leading to unrealistic ratios. This means that the amount of radiogenic ^4He that diffused
 396 into the fluid inclusions of our samples is very small or negligible, which is probably due to the
 397 young age of the host basalts (10–12 Myr). Also, radiogenic ^4He (as well as
 398 cosmogenic/nucleogenic ^3He) normally remains in the crystal lattice and cannot be released by
 399 single-step crushing (i.e., the technique employed in this study), which preferentially releases the
 400 gas retained in fluid inclusions (e.g., Kurz, 1986).

401 We therefore conclude that post-magmatic radiogenic ingrowth cannot explain the He-isotopic
 402 variations observed in this study and we can consider our measurements of $^3\text{He}/^4\text{He}$ representative
 403 of the local mantle source.

405 **5.2 Secondary processes occurring in the mantle**

406 **5.2.1 Partial melting**

407 Figure 6 plots the Y_N (0.29–4.32) versus the Y_{bN} (0.59–4.40) normalized to the primitive-mantle
 408 compositions of McDonough and Sun (1995). To facilitate comparisons with our data we also plot

409 the Lianshan xenoliths investigated by Lu et al. (2013) and other mantle xenoliths from Hebi, Fuxin
 410 and the TLFZ forming part of the NCC [TLFZ, Zheng et al. (1998, 2006) and Xu et al. (1998);
 411 Hebi, Zheng et al. (2001); Fuxin, Zheng et al. (2007)]. An overall positive correlation is observed,
 412 which is reasonably related to partial melting (Norman, 1998). The plotted trend of fractional partial
 413 melting suggests that most of the Type 1 xenoliths from Lianshan reflect melting percentages lower
 414 than 3% (Figure 6). These samples are also characterized by the lowest Cr# of spinels and Mg# of
 415 clinopyroxenes typical of low degrees of melt extraction (Hellebrand et al., 2001). The other Type 1
 416 xenoliths and most of the Type 2 xenoliths are compatible with ~10% of melting. Only samples
 417 11LS32 (transitional) and 11LS59 (Type 2) plot along the same trend, but at a slightly higher
 418 fractional partial melting (15–20%) (Figure 6). We point out that the assumption of a batch partial
 419 melting trend (curve not shown) would have lead the samples with the lowest Y_N and Yb_N to be
 420 resulted from 40–50% of fractional partial melting. However, such high degrees of batch melting
 421 are considered unrealistic for the Phanerozoic mantle (Zimbelman & Gregg, 2000; Lu et al., 2013).
 422 Our inferences are broadly consistent with the findings of Lu et al. (2013) on Lianshan xenoliths
 423 and comparable with evidence obtained from the other mantle xenoliths from the NCC [TLFZ,
 424 Zheng et al. (1998, 2006) and Xu et al. (1998); Hebi, Zheng et al. (2001); Fuxin, Zheng et al.
 425 (2007)]. All these authors highlighted that the lowest and highest degrees of partial melting
 426 correspond to a fertile mantle and a refractory lithosphere, based on the modeling of Y and Yb
 427 contents in the clinopyroxene.

428 There is no clear distinction between the $^4\text{He}/^{40}\text{Ar}^*$ values for Type 1, Type 2 and transitional
 429 xenoliths (Figure 5). Most samples overlap within a range ($4.9 \times 10^{-4} < ^4\text{He}/^{40}\text{Ar}^* < 3.6 \times 10^{-1}$) that is
 430 sensibly lower than the typical production ratio of the mantle ($^4\text{He}/^{40}\text{Ar}^* = 1-5$; e.g. Ozima &
 431 Podosek, 1983; Marty, 2012). This suggests that the pristine $^4\text{He}/^{40}\text{Ar}^*$ of the mantle source has
 432 been modified. The inference from trace elements geochemistry is that partial melting can
 433 potentially lower this ratio. In fact, the partition coefficient of He ($D_{\text{He}^{\text{olivine/melt}}} = 1 \times 10^{-4}$; Heber et
 434 al., 2007) is one order of magnitude lower than that of Ar ($D_{\text{Ar}^{\text{olivine/melt}}} = 1 \times 10^{-3}$; Heber et al., 2007).
 435 In order to evaluate this process, we assumed an initial $^4\text{He}/^{40}\text{Ar}^*$ of 2.5 (average production ratio of
 436 the mantle, e.g. Ozima & Podosek, 1983; Marty, 2012), and calculate that batch melting cannot
 437 reproduce the lowest $^4\text{He}/^{40}\text{Ar}^*$ measured in the Lianshan data set. Even an unrealistically high
 438 percentage (i.e. 100%) of melting would generate a maximum $^4\text{He}/^{40}\text{Ar}^*$ of only 2.6×10^{-1} .
 439 Alternatively, an increase in the fractional partial melting of the mantle (Wilson et al., 1989) of up
 440 to 0.1% (red dotted arrow in Figure 5) would be able to decrease the ratio to 4.8×10^{-4} . Assuming
 441 the same starting composition of the mantle for both Type 1 and Type 2 xenoliths, variable degrees
 442 of fractional partial melting (up to 0.1%) can be considered realistic, since this would imply small

local geothermal anomalies. Based on the results from a simulation of isobaric melting of a mantle peridotite from the Hyblean plateau (Sicily, Italy) performed by Correale et al. (2014), we suggest that fractional partial melting up to 0.1% corresponds to a temperature increase of only a few degrees. We therefore infer that fractional partial melting could explain the extremely low $^4\text{He}/^{40}\text{Ar}^*$ measured in Lianshan xenoliths and thus the variability of this ratio in the data set.

As a consequence of melting processes, the decrease in $^4\text{He}/^{40}\text{Ar}^*$ in the mantle should be associated with a decrease in the content of Y and Yb in the clinopyroxene. However, we do not observe this, instead we note a discrepancy between the percentages of fractional partial melting estimated from trace elements data (~3–20%) and $^4\text{He}/^{40}\text{Ar}^*$ values (~0.1%); the latter produce only tiny extents of melting and no significant differences irrespective of the type of xenoliths considered. Burnard et al. (2010) identified the low solubility of noble gases in metasomatic carbonatitic melts as the main cause of decoupling between noble gases and trace elements. The carbonatitic melts expressly do not transport noble gases, but are enriched in trace elements. Alternatively, decoupling could be triggered by a fluxing of CO_2 -dominated fluids with a mantle-like $^4\text{He}/^{40}\text{Ar}^*$ signature (Porcelli et al., 1986; Matsumoto et al., 2000; Dunai & Porcelli, 2002; Martelli et al., 2011; see Section 5.2.3). This could explain the similarity in the $^4\text{He}/^{40}\text{Ar}^*$ values measured in Type 1 and Type 2 xenoliths in the present study, leading to the estimation of different percentages of fractional partial melting with respect to what is observed based on the data for trace elements. Therefore, superimposing multiple events of metasomatism with contrasting fluid compositions (i.e., carbonatitic versus silicate melts and fluxing of CO_2 -rich fluids; see Section 5.2.3) could variably modify the geochemistry of trace elements and noble gases, leading to partial decoupling between these two indicators.

Finally, it is necessary to account for the possibility of $^4\text{He}/^{40}\text{Ar}^*$ being strongly modified by kinetic fractionation among noble gases in the mantle, as a consequence of the variable diffusivities of ^3He , ^4He and ^{40}Ar (see Section 5.2.2). The possible simultaneous occurrence of all of these processes could explain the different degrees of partial melting estimated from the $^4\text{He}/^{40}\text{Ar}^*$ values, but we recall that the process of fractional partial melting still remains a valid explanation for the low $^4\text{He}/^{40}\text{Ar}^*$ values measured in Lianshan xenoliths.

5.2.2 Kinetic fractionation of $^3\text{He}/^4\text{He}$ and $^4\text{He}/^{40}\text{Ar}^*$

While fractional partial melting can adequately explain the observed range of $^4\text{He}/^{40}\text{Ar}^*$ values, this process cannot explain the variability of $^3\text{He}/^4\text{He}$. Alternatively, this variability could be due to kinetic fractionation of noble gases atomic species occurs in the mantle (Yamamoto et al., 2009). That study investigated worldwide mantle xenoliths having SCLM features, and hypothesized that

the magma channels crossing the mantle can generate kinetic fractionation of $^3\text{He}/^4\text{He}$ and $^4\text{He}/^{40}\text{Ar}^*$ as a consequence of their variable diffusivities. Specifically, the preferential partitioning in the melt of ^3He with respect to ^4He and of ^4He with respect to ^{40}Ar produces decreases in $^4\text{He}/^{40}\text{Ar}^*$ and $^3\text{He}/^4\text{He}$ values in the mantle. Following this approach and assuming the same boundary conditions as Yamamoto et al. (2009), we calculated how kinetic fractionation could modify the isotopic ratios of noble gases. We assumed that there were two possible mantle sources with the following characteristics: (1) $^3\text{He}/^4\text{He}=9\text{ Ra}$, which corresponds to the upper limit of MORB as well as to the highest He-isotopic ratio of Type 1 xenoliths; and (2) $^3\text{He}/^4\text{He}=7\text{ Ra}$, which corresponds to the upper limit for the SCLM as well as to the highest He-isotopic ratio of Type 2 xenoliths. For both assumptions we used $^4\text{He}/^{40}\text{Ar}^*=2.5$, which is consistent with the assumption made for fractional partial melting (continuous black lines in Figure 5). The two curves reported in Figure 5 depict the trends of how $^3\text{He}/^4\text{He}$ and $^4\text{He}/^{40}\text{Ar}^*$ are modified as a consequence of this process; however, they do not accurately fit our data set. We argue that the poor fit of our data set could be due to the superimposition of partial melting processes (Section 5.2.1), which strongly decrease the $^4\text{He}/^{40}\text{Ar}^*$ values. Indeed, with this assumption, the same simulation of the kinetic fractionation process as described above performed at a lower $^4\text{He}/^{40}\text{Ar}^*$ (up to 0.0025) as a consequence of partial melting process (black dotted curves in Figure 5) would yield a good fit to our entire data set.

We point out that kinetic fractionation was also invoked by He et al. (2011) to explain the low $^3\text{He}/^4\text{He}$ and $^4\text{He}/^{40}\text{Ar}^*$ values measured in mantle xenoliths from the Changle volcanic area (eastern NCC). There is also evidence of the same process in the mantle for some xenoliths from a surrounding region of eastern China (i.e., the Korean peninsula) by Yamamoto et al. (2009), who developed this model.

5.2.3 Carbonatitic versus silicate metasomatism and CO_2 fluxing

The variable pattern of REE and the behaviour of some incompatible elements including LREE and large-ion lithophile elements (LILE) (i.e., U, Th and Sr) in mantle xenoliths may be indicative of the extent of melt extraction (see section 5.2.1), but also of the occurrence of mantle metasomatism. Enrichment in LREE and LILE is considered to be due to the presence of metasomatic melts (e.g., Coltorti et al., 1999; Zangana et al., 1999). In detail, high $(\text{La}/\text{Yb})_{\text{N}}$ and low Ti/Eu values observed in mantle clinopyroxenes have been widely considered to be key signatures of carbonatitic metasomatism (e.g., Meen, 1989; Coltorti et al., 1999; Rudnick et al., 1993; Klemme et al., 1995; Zheng et al., 2006; Howarth et al., 2014). These features of the trace elements have been observed in most of the Lianshan Type 2 xenoliths (see Table 4) according to Lu et al. (2013), who found

511 similar characteristics in another suite of Lianshan xenoliths. This finding suggests that Type 2
512 samples are compatible with a refractory mantle that has undergone carbonatitic metasomatism.
513 This is also consistent with $^3\text{He}/^4\text{He}$ values (Figures 3 and 5; 3.33-6.64 Ra) that fall within or below
514 the typical SCLM range. $^3\text{He}/^4\text{He}$ values lower than the SCLM range could result from kinetic
515 fractionation between ^3He and ^4He (see Section 5.2.2). Alternatively, the low $^3\text{He}/^4\text{He}$ values of
516 Type 2 xenoliths from the Lianshan area could also reflect mantle metasomatism by fluids and/or
517 melts derived from ancient subduction events experienced by eastern China (e.g., Robinson et al.,
518 1999; Zhang et al., 2003; Zheng et al., 2005, 2006; Tang et al., 2014).

519 Conversely, low $(\text{La}/\text{Yb})_{\text{N}}$ and variable Ti/Eu values are indicative of metasomatism related to
520 silicate melts (e.g., Zheng et al., 2006 and references therein). Type 1 samples, which are mostly
521 characterized by these features of the trace elements, are thus compatible with a mantle that has
522 undergone metasomatism related to silicate melts. Accordingly, the highest $^3\text{He}/^4\text{He}$ values (up to
523 9.16 Ra) measured in Type 1 xenoliths (Figures 3 and 5), falling within the typical MORB range,
524 could be the result of silicate metasomatism. We point out that this type of process is common in
525 cratonic areas that have undergone crustal thinning, as demonstrated for instance by Barry et al.
526 (2015), who identified basaltic metasomatism in the SCLM below the Siberian craton. We thus
527 infer that metasomatic processes affected the mantle beneath Lianshan area, and thus beneath YC.
528 Flat LREE patterns and intermediate $(\text{La}/\text{Yb})_{\text{N}}$ and Ti/Eu values reflect portions of the SCLM with
529 transitional features, which have probably undergone multiple episodes of metasomatism by both
530 carbonatitic and silicate melts.

531 532 **5.3 $^3\text{He}/^4\text{He}$ signature of Lianshan mantle and of eastern China**

533 With the aim of providing a regional overview on eastern China, we compared our $^3\text{He}/^4\text{He}$ and
534 $^4\text{He}/^{40}\text{Ar}^*$ measurements of Lianshan xenoliths with those made in other mantle xenoliths from
535 NCC (Figure 5). This sector of the craton, together with the SCB, is one the least-investigated areas
536 in the world regarding the He, Ne and Ar systematics in fluid inclusions from ultramafic xenoliths.
537 Only a few studies have characterized the features of the mantle beneath the NCC based on analyses
538 of noble gases (Xu et al., 1998, 2003; Li et al., 2002; Wu et al., 2003, 2004; Ma et al., 2006; Chen
539 et al., 2007; He et al., 2011; Tang et al., 2014), and most of them have used melting or step-heating
540 techniques (instead of in-vacuo crushing). As stated in Section 3, these techniques release
541 cosmogenic ^3He and radiogenic ^4He from the crystal matrix in addition to fluid inclusions (e.g.,
542 Matsumoto et al., 2002; Yamamoto et al., 2004; Zhang et al., 2013), thereby often compromising
543 the understanding of pristine isotopic signatures. Figure 5 plots the available data for $^3\text{He}/^4\text{He}$ and
544 $^4\text{He}/^{40}\text{Ar}^*$ in comparison with those from this study, and we distinguished those obtained using

crushing techniques (Xu et al., 2003; He et al., 2011; light-pink area in Figure 5) from those
 obtained using melting or step-heating techniques (Xu et al., 1998; Wu et al., 2003, 2004; Ma et al.,
 2006; Tang et al., 2014; light-green area in Figure 5). Notably, the data reported by Xu et al. (2003)
 and He et al. (2011), obtained from the volcanic fields in Nushan (Anhui Province, south-east of the
 NCC) and Changle (in the middle part of the TLFZ), respectively, mostly overlap with our samples.
 They show $^3\text{He}/^4\text{He}$ and $^4\text{He}/^{40}\text{Ar}^*$ values in the ranges of 3.2–8.6 Ra and 0.002–19.3, respectively.
 This means that the secondary processes occurring in the mantle – hypothesized to explain the
 variability of our data set – have potentially also affected the mantle portions beneath NCC. The
 highest He-isotopic ratio (i.e. 8.58 Ra) falls within the typical MORB range, also displaying a
 $^4\text{He}/^{40}\text{Ar}^*$ value consistent with the typical production ratio ($^4\text{He}/^{40}\text{Ar}^*=1\text{--}5$) of the mantle (Figure
 5). A few samples exceed this range, reaching $^4\text{He}/^{40}\text{Ar}^*$ values of 19.3. These high ratios could
 reflect magma degassing in this portion of the mantle, as suggested by He et al. (2011). Similar
 evidence was found in pyroxenitic xenoliths from the Hyblean plateau by Correale et al. (2012),
 who attributed the wide variability of $^4\text{He}/^{40}\text{Ar}^*$ (0.6–15) to degassing of pyroxenitic melts residing
 at depth and then ascending and intruding into the overlying peridotitic SCLM.

Previous melting and/or step-heating studies (e.g., Xu et al., 1998; Wu et al., 2003, 2004; Ma et al.,
 2006; Tang et al., 2014) show both the highest and lowest $^3\text{He}/^4\text{He}$ values ever reported for eastern
 China SCLM (Figures 3 and 5). The lowest $^3\text{He}/^4\text{He}$ samples also have the highest He
 concentrations (Figure 3), which probably reflects the addition of radiogenic ^4He to the pristine
 signature of the fluid inclusions. In contrast, high $^3\text{He}/^4\text{He}$ samples are associated with low He
 concentrations, suggesting addition of cosmogenic ^3He to modify the pristine signature (Figure 3).
 Therefore, these noble gases data obtained via melting or step-heating technique are likely not
 representative of the mantle source and cannot be directly compared with our samples, which are
 representative of actual helium isotope variation in the eastern China SCLM.

In summary, our study of He and Ar systematics in Lianshan xenoliths has identified the presence
 of mantle heterogeneity beneath this area, which is consistent with the conclusions reached by Lu et
 al. (2013) based on the mineral chemistry, trace elements and radiogenic-isotopic compositions (e.g.
 of Sr and Nd). The old (Archaean) and refractory SCLM beneath YC has been widely rejuvenated
 by the upwelling of a more fertile MORB-like mantle. This interpretation is consistent with local
 geodynamics (e.g., Zheng et al., 2015 and references therein), whereby westward subduction of the
 Pacific plate occurred during the late Mesozoic-Cenozoic and caused heat perturbation and
 upwelling of MORB-like asthenospheric melt/fluids in the SCLM of eastern China (Zheng et al.,
 2007; Zhang et al., 2012). This evidence is also consistent with mineralogical and petrological
 studies performed in mantle xenoliths of eastern China, mostly in the NCC.

579 These various lines of evidence lend credence to the hypothesis that the lithospheric mantle beneath
580 YC underwent a rejuvenation process by a fertile mantle, similar to that widely observed in NCC.
581 More investigations are necessary to better constrain whether these mantle characteristics can be
582 extended to all of eastern NCC and SCB. However, this study has revealed that noble gases in fluid
583 inclusions are powerful tracers for differentiating between pristine mantle and metasomatic fluids,
584 particularly when considered in conjunction with petrological features.

585

586 **6. Conclusions**

587 We carried out the first study of noble gases isotopes in mantle xenoliths hosted in Cenozoic basalts
588 outcropping in the Lianshan area (YC). The same suite of samples has been studied for the mineral
589 chemistry and the trace elements composition of clinopyroxenes, and petrological data has been
590 coupled with noble gas isotope data in order to constrain the mantle source features. We conclude
591 that:

592 - The lithospheric mantle below the Lianshan area is heterogeneous and can be subdivided into two
593 types of xenoliths: Type 1, characterized by $^3\text{He}/^4\text{He}$ up to 9.1 Ra, LREE-depleted patterns and
594 $(\text{Y}/\text{Yb})_{\text{N}} > 3$, interpreted as a portion of a fertile MORB-like mantle which underwent <3% of
595 fractional partial melting; Type 2, characterized by $^3\text{He}/^4\text{He} < 7$ Ra, LREE-enriched patterns and
596 $(\text{Y}/\text{Yb})_{\text{N}} < 3$, reflecting a refractory SCLM-like mantle which underwent up to 20% of fractional
597 partial melting.

598 - Several mantle processes concurred to modify the pristine signature of the lithospheric source
599 beneath Lianshan. Diffusive kinetic fractionation has probably modified the $^3\text{He}/^4\text{He}$ and $^4\text{He}/^{40}\text{Ar}^*$
600 values of the pristine source. In addition, metasomatism of carbonatitic versus silicate melts and
601 fluxing by CO_2 -rich fluids permeating the mantle have most likely occurred in the local mantle,
602 complicating the signature of trace elements and noble gases, with the consequent estimation of
603 different extents of melt extraction for the two types of mantle.

604 - The old and refractory lithospheric mantle beneath YC was rejuvenated by the upwelling of a
605 fertile asthenospheric mantle, likewise to what widely observed in NCC. This means that the
606 disruption of Archean lithosphere with the upwelling of younger fertile asthenosphere could be a
607 common feature for most of eastern China.

608

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615

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922 **Captions of tables and figures**

923 Table 1. Petrographic characteristics and modal compositions of Lianshan peridotites.

924

925 Table 2. Major-element chemistry of olivines, pyroxenes and spinels from Lianshan peridotites.

926

927 Table 3. Equilibration temperature estimates for the Lianshan peridotite xenoliths (°C).

928

929 Table 4. Trace elements composition of clinopyroxenes.

930

931 Table 5. Elemental and isotopic analyses of noble gases from fluid inclusions retained in the mantle
932 xenoliths. The calculated nucleogenic ^3He and radiogenic ^4He concentrations for the studied
933 samples are also listed (see text for further details), as is $^3\text{He}/^4\text{He}$ corrected for the atmospheric
934 contribution ($^3\text{He}/^4\text{He}_{\text{corr-air}}$) and for the additions of 1% [$(^3\text{He}/^4\text{He})^{\text{a}}_{\text{corr-nucl}}$, $(^3\text{He}/^4\text{He})^{\text{c}}_{\text{corr-rad}}$] and
935 10% [$(^3\text{He}/^4\text{He})^{\text{b}}_{\text{corr-nucl}}$] nucleogenic and radiogenic He in the fluid inclusions.

936

937 Figure 1. (a) Map of eastern China (modified from Zheng et al., 2015). K, J-K, J and T indicate the
938 magmatic activity that occurred in the Cretaceous, Jurassic-Cretaceous, Jurassic and Triassic,
939 respectively. The Tan-Lu translithospheric Fault Zone is also indicated. (b) Detail of the South
940 China block (modified from Zheng et al., 2015) showing where the Lianshan xenoliths were
941 sampled (red star). (c) Outcrop of columnar basalts from the Lianshan area and (d) example of a
942 peridotite xenolith hosted in volcanic rocks.

943

944 Figure 2. Chondrite-normalized rare-earth elements patterns of clinopyroxenes from Lianshan
945 peridotites (modified from Sun & McDonough, 1989). The plot at the top reports the pattern of all
946 the xenoliths classified as Type 1, while that in the middle those belonging to Type 2. The plot at
947 the bottom reports the sample with transitional features. Yellow and blue areas represent the same
948 normalized patterns of clinopyroxenes from a fertile and refractory mantle respectively of another
949 suite of xenoliths from Lianshan area (light yellow and blue, Lu et al., 2013) and of NCC (dark
950 yellow and blue, Zheng et al., 1998; Zheng et al., 2001; Zheng et al., 2006; Zheng et al., 2007).

951

952 Figure 3. He concentration versus $^3\text{He}/^4\text{He}$ (Rc/Ra) of fluid inclusions from Lianshan xenoliths.
953 Light-pink and light-green areas are literature data of mantle xenoliths from eastern China (Xu et
954 al., 1998, 2003; Wu et al., 2003, 2004; Ma et al., 2006; Chen et al., 2007; He et al., 2011; Tang et

955 al., 2014) obtained by crushing and melting or step-heating techniques, respectively. The dotted red
956 line separates the MORB-like $^3\text{He}/^4\text{He}$ ($R/R_a > 7$) from the SCLM-like $^3\text{He}/^4\text{He}$ ($R/R_a < 7$).

957

958 Figure 4. Ar-isotopic ratio ($^{40}\text{Ar}/^{36}\text{Ar}$) versus $^4\text{He}/^{20}\text{Ne}$ of fluid inclusions from Lianshan xenoliths.
959 The curve defines a binary mixing trend between a MORB mantle [$^4\text{He}/^{20}\text{Ne} \sim 10,000$ (Marty et al.,
960 1983) and $^{40}\text{Ar}/^{36}\text{Ar} \sim 40,000$ (Graham, 2002)] and an atmospheric endmember [$^4\text{He}/^{20}\text{Ne} = 0.318$
961 (Marty et al., 1983) and $^{40}\text{Ar}/^{36}\text{Ar} = 295.5$ (Graham, 2002)].

962

963 Figure 5. He-isotopic ratio ($^3\text{He}/^4\text{He}$; R_c/R_a) versus $^4\text{He}/^{40}\text{Ar}^*$ of fluid inclusions from Lianshan
964 xenoliths. Light-pink and light-green areas are as in Figure 3. The continuous black curves indicate
965 $^3\text{He}/^4\text{He}$ and $^4\text{He}/^{40}\text{Ar}^*$ variations due to diffusive kinetic fractionation in the mantle, starting from
966 the upper limit of either a MORB-like source ($^3\text{He}/^4\text{He} = 9 R_a$) or an SCLM-like source ($^3\text{He}/^4\text{He} = 7$
967 R_a), having an average $^4\text{He}/^{40}\text{Ar}^*$ production ratio of 2.5 (Ozima & Podosek, 1983; Marty, 2012).
968 The black dotted curves indicate $^3\text{He}/^4\text{He}$ and $^4\text{He}/^{40}\text{Ar}^*$ variations due to the same process, starting
969 from the same MORB- and SCLM-like $^3\text{He}/^4\text{He}$ values, and having decreasing $^4\text{He}/^{40}\text{Ar}^*$ values as
970 a consequence of partial melting. The red line separates the MORB- and SCLM-like $^3\text{He}/^4\text{He}$
971 values, considering a mantle production with $^4\text{He}/^{40}\text{Ar}^* = 1-5$ (continuous red line) and a higher or
972 lower $^4\text{He}/^{40}\text{Ar}^*$ (> 5 and < 1 ; dotted red line) as a consequence of mantle degassing and partial
973 melting, respectively. See text for further details.

974

975 Figure 6. Y_N versus Yb_N of clinopyroxenes from Lianshan xenoliths (black, grey and white squares)
976 normalized to PM (modified from Sun & McDonough, 1989). The triangle symbols indicate
977 another suite of xenoliths from Lianshan studied by Lu et al. (2013). The grey area represents
978 mantle xenoliths from eastern North China craton (Zheng et al., 2001, 2007 and references therein).
979 The curve is the partial fractional melting curve from Norman (1998). Numbers on the fractional
980 partial melting curve are melting percentages. See text for further details.