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Dear Editor,

Please find enclosed our manuscript (LITHOS6474R2- favourably received and recommended for publication with minor revision): **“Refertilized mantle keel below the Southern Alps domain (North-East Italy): Evidence from Marosticano refractory mantle peridotites”** by Valentina Brombin, Costanza Bonadiman, Massimo Coltorti, M. Florencia Fahnstock, Julia G. Bryce and Andrea Marzoli, revised with additional English corrections.

The final version of this text was reviewed and corrected by an English-native and an English-fluent co-author. We hope that you will find this version now suitable for publication in *Lithos*.

Regards,

for the authors,

Valentina Brombin

A handwritten signature in black ink that reads "Valentina Brombin". The signature is written in a cursive style with a large initial 'V'.

Refertilized mantle keel below the Southern Alps domain (North-East Italy): Evidence from Marosticano refractory mantle peridotites

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ABSTRACT

The Veneto Volcanic Province (VVP), a Cenozoic magmatic province in northeastern Italy, is one of the widest volcanic areas of the Adria plate. It consists of five main volcanic districts, and its most primitive products **common** most mantle xenoliths. In this study, we present a newly discovered xenolith suite from the Marosticano district that contains peridotites with compositional characteristics of mineral assemblages that provide insight into an unexpected nature **for** the sub-continental lithospheric mantle (SCLM) of the Adria plate. In contrast to xenoliths from other VVP sites previously studied (i.e.: Val d'Adige and Lessini Mts.), Marosticano xenoliths exhibit highly refractory compositions typical of on-craton peridotites. In particular, high olivine forsteritic contents (Fo: 91-93) indicate high degrees of partial melting (>25%) that should lead to the complete consumption of clinopyroxene. Major and trace element compositions further link these peridotite fragments to early Proterozoic cratonic mantle, and the juxtaposition of clinopyroxene within these rocks suggests like **most on-craton clinopyroxene**, Marosticano clinopyroxene have a metasomatic legacy. The i) LREE-enrichments of Marosticano clinopyroxene and ii) the dissolved CO₂ mole fractions (up to 1.0) for the inferred clinopyroxene-forming melt are consistent with

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HIGHLIGHTS

Petrology and geochemistry of newly discovered Adria plate mantle xenoliths present unexpected cratonic features.

Xenolith clinopyroxene record metasomatic overprinting of restitic peridotite from carbonatite/CO₂-rich silicate melts.

Cratonic keel is preserved only in the Marosticano district, while the rest of VVP mantle domains are interpreted as circumcratonic portions subject to rejuvenation from asthenospheric-derived melts.

1 **Refertilized mantle keel below the Southern Alps domain (North-East Italy): Evidence from**
2 **Marosticano refractory mantle peridotites**

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18 continental lithospheric mantle (SCLM) of the Adria plate. In contrast to xenoliths from other VVP
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38 HIGHLIGHTS

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41

42 Xenolith clinopyroxene record metasomatic overprinting of restitic peridotite from carbonatite/CO₂-
43 rich silicate melts.

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48

49 KEYWORDS

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51

52 **1. Introduction**

53

54 The stability of continents is intimately linked to the underlying sub-continental lithospheric mantle
55 (SCLM). Peridotite xenoliths hosted in intraplate basaltic rocks provide a useful way to evaluate the
56 petrological features and evolution of the SCLM in terms of mineral compositions, modal
57 abundance and to fluid modification (Liu et al., 2015).

58 The mantle xenoliths occurring in Veneto Volcanic Province (VVP; SE Alps, NE Italy, Fig. 1)
59 depict the “big” picture of the SCLM beneath the Adria plate, the African promontory of the
60 central-western Mediterranean area. In the Cretaceous the VVP region was involved in a
61 convergence between Africa and Eurasia plates, inducing subduction processes of the latter
62 southeastward (Schmid et al., 1997; von Blanckenburg and Davies, 1995). In spite of the immense
63 quantity of seismic, structural, petrologic, and geochemical data compiled over at least five decades,
64 the Adria microplate (Fig. 1, inset) remains an enigmatic aspect in the geodynamic evolution of the
65 Africa-Eurasia collision system (Carminati and Doglioni, 2012; Lustrino, et al., 2011). It has been
66 considered either to be in crustal continuity with the African mainland or separated from the latter
67 by an oceanic plate (Catalano et al., 2000; Lustrino et al., 2011; Muttoni et al., 2001; Schmid et al.,
68 2008).

69 Mantle xenoliths from a few VVP localities previously investigated (Lessini Mts. and Val d’Adige
70 localities; Fig. 1) reveal variably depleted mantle domains, which were subsequently enriched by
71 one or more episodes of metasomatism as recorded by widespread interstitial recrystallized glassy
72 patches (Beccaluva et al., 2001; Gasperini et al., 2006; Morten et al., 1989; Siena and Coltorti,
73 1989). In this paper, we describe results from a petrological and geochemical study of a newly
74 discovered occurrence of mantle xenoliths from the Marostica Hills, in the Marosticano district of
75 the VVP. We then interpret our findings to constrain the mantle domain underlying the northern
76 (continental) sector of the Adria plate, with the ultimate goal of shedding insight dynamic processes
77 at work during plate boundary interaction (Carminati and Doglioni, 2012).

78

79 2. Geological setting

80

81 The Central-Western Mediterranean area is a geologically young area, mostly developed during the
82 last 30 Ma. Geological structures and the igneous activity within this region are intimately linked
83 with the relative movements of two large plates (Africa and Europe) plus a number of smaller
84 continental and oceanic plates (e.g., Lustrino et al., 2011). A key smaller plate, likely an African
85 promontory, is the Adria (or Apulia) plate in which the VVP (Fig. 1) constitutes one of the largest
86 and most important magmatic provinces. During the Cenozoic, the Veneto and Trentino regions
87 were affected by extensive volcanic activity, mainly basic-ultrabasic in composition that took place
88 intermittently from the late Paleocene to the late Oligocene (Barbieri et al., 1982, 1991; De Vecchi
89 et al., 1976; De Vecchi and Sedea, 1995; Piccoli, 1966). Most of the VVP products are spread over
90 a NNW to SSE elongated area of about 1,500 km². Five main volcanic districts can be defined from
91 west to east (Fig. 1): (1) the Val d'Adige district, between Arco and Rovereto; (2) the Lessini Mts.
92 district between Val d'Adige and the Schio-Vicenza tectonic line; (3) the Marosticano district, east
93 of the Schio-Vicenza line; (4) the Berici Hills district, which is separated from (5) the Euganean
94 Hills, the southernmost district, by the Riviera dei Berici line (Beccaluva et al., 2007). Most VVP
95 volcanic products are relatively undifferentiated lavas, and range in composition from nephelinites
96 to quartz (Qz)-normative tholeiitic basalts. They tend to be spatially and temporally distributed,
97 becoming gradually younger and less alkaline toward SE. Differentiated products only occur in the
98 Euganean district, where quartz-trachytes and rhyolites predominate (Milani et al., 1999, and
99 references therein). Nephelinites and basanites commonly carry spinel-peridotite mantle xenoliths
100 (Beccaluva et al., 2001; 2007).

101 The mafic volcanism in the VVP is thought to be related to extensional tectonics in the Southern
102 Alps foreland as response to Alpine orogenesis (De Vecchi and Sedea, 1995; Milani et al., 1999;
103 Zampieri, 1995). Geophysical data (Ansorge et al., 1992; Giese and Bunes, 1992) indicate a rather
104 normal thickness of the continental crust under the VVP, with a NW-SE elliptical mantle dome

105 culminating at about 28 km beneath the Lessini Mts., while the lithosphere-asthenosphere boundary
106 has been detected at a depth of ~100 km (Panza and Suhadolc, 1990).
107 Isotopic signatures, notably $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (18.8-19.8 and 0.703-0.704,
108 respectively) led Beccaluva et al. (2001, 2007) to argue that the SCLM beneath the Adria plate has
109 been enriched by metasomatizing agents, likely including FOZO or HIMU components. This
110 signature may be related to the European Asthenospheric Reservoir (EAR; Hoernle et al., 1995), a
111 large mantle upwelling extending from the eastern Atlantic to Europe and the Mediterranean area.
112 Alternatively, Wilson and Patterson (2001), and more recently Lustrino and Wilson (2007) argued
113 that this Tertiary-Quaternary volcanism is related to diapiric upwelling of small-scale, finger-like,
114 convective instabilities from the base of the upper mantle.

115

116 3. Petrography

117

118 The Marosticano xenoliths were sampled in the quarry of Monte Glosio (MG), a few kilometers east
119 of Marostica (Fig. 1). The basanitic host lavas show a porphyritic texture with phenocrysts of
120 olivine, clinopyroxene, and magnetite set in a fine-grained groundmass composed of clinopyroxene,
121 plagioclase, and oxides. The xenoliths are generally subrounded or (more rarely) angular, ranging in
122 size from a few centimeters up to 10 cm. Heavy fracturing and alteration are present throughout of
123 the suite. Only five samples were sufficiently fresh to permit a complete petrological
124 characterization. These samples also showed no evidence of host magma infiltration.

125 The Marosticano xenoliths are peridotites with complete spinel-facies equilibration. They display a
126 coarse-grained protogranular texture following the nomenclature of Mercier and Nicholas (1975).
127 Two of the five investigated xenoliths are harzburgites with 4% clinopyroxene (~~epx~~), one is low-
128 ~~epx~~ (6%) lherzolite and two are lherzolites with 9-13% ~~epx~~ (Table 1). In two out of three lherzolites,
129 orthopyroxene (~~opx~~) is modally scarce (12-14%) as compared to typical peridotites (e.g.,
130 Streckeisen, 1974). All Marosticano peridotites are characterized by large crystals of olivine (~~ol~~)

131 and ~~opx~~ (up to 2 mm across) with smaller grains of ~~cpx~~ (0.5-1 mm in size) and spinel (~~sp~~) (up to 1
132 mm across). These latter show a typical holly-leaf or lobate shape, while ~~ol~~ and pyroxene crystals
133 display curvilinear grain boundaries. Kinking is common in ~~ol~~, while ~~opx~~ display exsolution
134 lamellae and, rarely, show sieved rims. ~~Cpx~~ are always smaller in size with respect to ~~opx~~ and show
135 large cloudy portions (~~spongy cpx~~).

136 Several types of pyrometamorphic textures are superimposed on these features. They consist of (1)
137 cloudy, spongy ~~cpx~~ crystals: the recrystallized portion generally replaces the whole crystal, in rare
138 cases it covers only the rim zones (Fig. 2a, b); (2) reaction areas ~~involving primary opx, cpx and sp,~~
139 ~~with a secondary assemblage~~ made up of small crystals of ~~ol, cpx,~~ vermicular ~~sp~~ and rare glass (Fig.
140 2c, d); (3) brown to pale yellow glassy patches containing secondary crystals of ~~ol, cpx and sp.~~ The
141 secondary paragenesis is generally too small to be analyzed by Electron MicroProbe (EMP) and
142 therefore was not considered for *in-situ* analysis.

143

144 4. Analytical methods

145

146 The modal composition of Marosticano samples was estimated by point counting with more than
147 1000 points for each thin section. Major element compositions of minerals from xenoliths and host
148 lavas were determined by ~~Electron Microprobe~~ (EMP), using a Cameca SX50 instrument at the
149 Istituto di Geoscienze e Georisorse, CNR, Padova (Italy). Trace element concentrations in ~~cpx and~~
150 ~~opx~~ were obtained by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-
151 MS) at the Department of Earth Sciences, University of New Hampshire (USA) using an Analyte
152 Excite 193 nm excimer laser plumbed into a Nu instruments AttoM high-resolution inductively
153 coupled plasma mass spectrometer. Two out of five samples were sufficiently unaltered so as to
154 be suitable for bulk rock analysis, which was performed on powder pellets using an ARL Advant-
155 XP spectrometer at the Dipartimento di Fisica e di Scienze della Terra, Università di Ferrara (Italy).

156 More extensive descriptions of the analytical procedures, together with the standards supporting the
157 analyses, are reported in the on-line Supplementary material.

158

159 **5. Mineral Chemistry**

160

161 Within each xenolith, minerals are generally homogeneous in composition with no significant
162 chemical variation between core and rims of the same crystal. The latter is observed only for
163 spongy crystals and grains close to reaction areas (Fig. 2). When these areas are near the contact
164 with host basanites, ~~ol and cpx~~ core and rim analyses were performed and compared with ~~ol and~~
165 ~~cpx~~ phenocrysts in order to check if they could be the result of the host magma infiltration.
166 Representative analyses of ~~ol, opx, cpx, and sp~~ are reported in Tables A-D of the ~~Supplementary~~
167 ~~online~~ material.

168

169 *5.1 Major element composition*

170

171 Olivine is chemically unzoned in Monte Glosso (MG) lherzolites and harzburgites. It shows a
172 narrow compositional range with Fo content $[=100 \times \text{Mg}/(\text{Mg}+\text{Fe})_{\text{mol}}]$ varying from 91.3 to 92.2 for
173 lherzolites and from 90.5 to 92.5 for harzburgites (Fig. 3a), with high Ni contents (2600-3620 ppm
174 and 2670-3540 ppm in lherzolites and harzburgites, respectively). Though conspicuous variability
175 of Ni in ~~ol~~ within individual samples may suggest a potential interaction between MG xenoliths and
176 the host magma, the invariant Fo contents for each sample are inconsistent with melt-xenolith
177 reaction ~~explaining the variable Ni contents~~. Specifically, it is noteworthy, that ~~ol~~ phenocrysts from
178 the host lavas have Fo ~~content~~ ranging from 86.1 to 87.2 and Ni contents from 2240 to 2251 ppm,
179 suggesting that melt-xenolith reaction may explain only a small ~~component~~ of the variable Ni
180 contents found in the MG xenolith suite (Fig. 3b).


181 Opx from unreacted core to reacted rims is chemically unzoned and frequently contains elongate
182 oriented rods of exsolved cpx. Opx mg# [=100 x Mg/(Mg+Fe)_{mol}] values vary from 91.2 to 92.8 for
183 both lherzolites and harzburgites, like the coexisting ol grains. Contents of Al₂O₃ in opx are highly
184 variable in lherzolite (1.68-4.18 wt.%) whereas a more restricted range is shown by harzburgites
185 (1.78-2.60 wt.%), reflecting a common “harzburgitic” melting degree, or limited temperature-
186 dependent subsolidus exchange with sp (Brey et al., 1999) (Fig. 3c). Contents of TiO₂ in lherzolites
187 are more variable (0-0.07 wt.%) than those of harzburgites (0-0.03 wt.%).

188 By texture the most reactive phase, cpx bears evident compositional heterogeneity within each
189 individual sample for most compositional features but mg#. Along with the coexisting ol and opx,
190 mg#_{cpx} ranges from 91.0 to 93.3 across all lithologies. By contrast, the Al₂O₃, Cr₂O₃ and to lesser
191 extent Na₂O are highly variable in both lherzolite and harzburgite cpx. Lherzolites generally show a
192 larger range in Al₂O₃ (1.73-4.53 wt.%), Cr₂O₃ (0.72-1.64 wt.%) and Na₂O (0.49-1.89 wt.%)
193 compared to harzburgites (Al₂O₃= 0.63 to 3.79 wt.%; Cr₂O₃= 0.89-1.52 wt.%; Na₂O= 0.35-1.18
194 wt.%; Fig. 3). The high chromium contents classify these crystals as chromiferous cpx (Morimoto,
195 1988) with TiO₂ being always less than 0.60 wt.% (Fig. 3f). Mg# values in cpx for both lherzolite
196 and harzburgite are not correlated with Al₂O₃, Na₂O, and TiO₂ distribution as would be expected for
197 a mantle residual trend or, in turn, for alkaline basic-ultrabasic magma fractionation lines (Fig. 3d-f).
198 Accordingly, we interpret negligible, if any interactions between peridotites and basanitic host lavas.
199 Large compositional variations are exhibited in sp cr# [=100 x Cr / (Cr+Al)_{mol}] and mg#, with
200 overlapping values for both lherzolite and harzburgite. However, cr# and mg# are homogenous
201 within each individual sample with the exception of harzburgite MG13 (Fig. 3g). Across the
202 samples, cr# and mg# vary from Cr-rich in harzburgite (cr#: 38.3-67.2; mg#: 56.2-69.6) to Al-rich
203 types in lherzolite (cr#: 30.4-52.7; mg#: 62.2-75.9).

204

205 5.2 Pyroxene trace elements

206

207 Representative *in situ* (LA-ICP-MS) trace element analyses of pyroxenes are reported in Tables E-F
208 of the on-line Supplementary material. The values are shown in chondrite-normalized incompatible
209 trace elements (Fig. 4a, b; 5a, b) and rare earth element (REE) diagrams (Fig. 5c, d). In order to
210 characterize the "original" features of the MG lithospheric domain prior to the metasomatic event,
211 trace element contents of ~~the cores~~ of both ~~opx~~ and unreacted ~~cpx~~ core were considered. One
212 sample (harzburgite MG13) **has only opx with rare cpx crystals occurring in reaction areas.**  Here
213 their small size (<30 μm) prevent high resolved quantitative analysis.

214 Both lherzolite and harzburgite bear ~~opx~~ with heavy REE (HREE) contents in a narrow range
215 ($(\text{Tb/Lu})_N$ in lherzolites= 0.05-0.44; in harzburgites= 0.13-0.47) but large light (L)- middle (M)REE
216 variability between ~~grains and samples~~ (e.g., Eu_N). MG16 lherzolite shows distinctive ~~opx~~ REE
217 contents with nearly flat M-HREE ($(\text{Dy/Lu})_N=0.39-0.49$) and LREE downward convex enrichments
218 ($(\text{La/Nd})_N=0.27-0.79$) (Fig. 4a). MG1, MG6 lherzolite and MG14 harzburgite preserve residual M-
219 HREE signatures ($(\text{Dy/Lu})_N=0.18-0.37$; Fig. 4a, b) typical of the ~~sp~~ stability field after melt
220 extraction co-existing with an apparent LREE enrichment ($(\text{La/Nd})_N=1.05-13.1$). In turn, ~~opx~~ of
221 MG13 harzburgite shows an overall M-HREE enrichment ($(\text{Dy/Lu})_N=0.41-0.42$; Fig. 4b). Finally,
222 Ti shows both positive and negative anomalies in both xenolith rock types.

223 Across all lithologies MG ~~cpx~~ have an overall high REE content ($\Sigma\text{REE}=185-621$ ppm) and
224 distinctive LREE enrichment relative to HREE (La_N up to 100 times chondritic; $(\text{La/Yb})_N$ in
225 lherzolites = 9.58-26.68; $(\text{La/Yb})_N$ in harzburgites = 13.88-19.24).

226 The geochemical data, taken together, allow for two groups of ~~cpx~~ compositions to be defined.
227 Group-1 includes ~~cpx~~ of ~~lherzolites~~ MG1, MG6 and ~~harzburgites~~ MG13, MG14, which shows an
228 almost flat M-HREE pattern ($(\text{Sm/Lu})_N= 1.31-4.76$) with abrupt (more than one order of
229 magnitude) LREE-enrichment ($(\text{La/Nd})_N= 1.53-6.18$). Almost all these ~~cpx~~ display a positive Eu
230 anomaly ($\{\text{Eu}_N/[(\text{Sm}+\text{Gd})_N/2]\}= 1.07-1.68$) (Fig. 5c). In turn, group-2 is constituted by ~~cpx~~ of
231 MG16 lherzolite only, which show distinctive convex upward REE pattern with a steep negative
232 slope from Nd to Lu ($(\text{Nd/Lu})_N=14.0-18.0$) and a maximum at Pr_N (114-143) (Fig. 5d).

233 The entire MG ~~cpx~~ population has variable high Th and U content (Th and U up to 3.03 and 0.63
234 ppm, respectively) with negative ~~anomalies in~~ Ti and HFSE (e.g. Nb, Ta, Zr, and Hf), the most
235 evident being the Zr anomaly in harzburgite with $Zr^* = (Zr_N / [(Nd+Hf)_N / 2]) = 0.09-0.24$ (Fig. 5a, b). It
236 should be noted that MG unreacted ~~cpx~~ have trace elements contents similar or even higher than
237 those of primary and secondary ~~cpx~~ from mantle xenoliths of the Lessini Mts. (Beccaluva et al.,
238 2001; Fig. 6).

239

240 6. Geothermobarometry

241

242 To estimate the temperature conditions under which the MG ~~sp~~ lherzolites and harzburgites were
243 equilibrated, we used the two-pyroxene geothermometer based on Fe/Mg exchange of Brey and
244 Köhler (1990) which we will denote as T_{BK} . ~~Ol-sp~~ geothermometers of Wells (1977) and Taylor
245 (1998) were also applied for comparative purposes and are denoted as T_W and T_T , respectively. For
246 the thermo-barometric calculations, we considered only cores of unreacted ~~opx and cpx~~ grains that
247 were in close contact.

248 Though some studies provide barometry, mainly based on the Ca distribution of ~~ol and cpx~~ (e.g.,
249 Köhler and Brey, 1990), determining appropriate barometry in ~~sp~~-bearing peridotites (Medaris,
250 1999; O'Reilly et al., 1997) is challenging. Therefore, we assume the equilibrium pressure from
251 experimental stability phase relationships (Caldeira and Munhá, 2002). Taking into account the
252 absence of amphiboles (which could modify the peridotite mineral stability fields) and the presence
253 of ~~sp~~ as the sole aluminum-bearing phase, an upper limit of 2.1 GPa and a lower limit of 0.9 GPa
254 are set (Caldeira and Munhá, 2002; Green and Hibberson, 1970; Green and Ringwood, 1970;
255 O'Neill and Wall, 1987; Siena and Coltorti, 1989). This pressure approximation agrees with the
256 maximum depth of the local SCLM, constrained by seismic profiles (Carminati and Doglioni, 2012)
257 to fall within the 1.5-2.0 GPa range. The pyroxene Fe/Mg exchange is largely dependent on
258 temperature (Brey and Köhler, 1990; Wells, 1977; Wood and Banno, 1973) and is relatively

259 insensitive to pressure; temperatures calculated at 1.0 GPa and 2.0 GPa show only minor variations
260 (<10°C). Accordingly, primarily for comparative purposes, temperature calculations were made at a
261 fixed pressure of 1.5 GPa.

262

263 *6.1 Equilibration temperatures*

264

265 MG spinelherzolites record residual temperatures in the range of 923-1058°C. The highest value
266 (MG16) is comparable with those recorded by the two MG harzburgites (MG13: 1117 ± 20°;
267 MG14: 1033 ± 30°C; Table 2). This is in agreement with its low cpx content (6%), which could
268 reflect a residual character analogous to harzburgites. We compared MG peridotites equilibration
269 temperatures with those from the nearby districts of Lessini Mts. and Val d'Adige calculated with
270 the Wells (1977) and Taylor (1998) geothermometers (Gasperini et al., 2006).

271 For comparison, equilibration temperature of a few Lessini Mts. and Val d'Adige peridotites were
272 recalculated together with MG samples of this work applying the three thermobarometric models
273 (Table 2). We observed that: i) as seen in other geothermobarometric studies (e.g., Greenfield et al.,
274 2013), T_T values are always lower than T_{BK} and T_W ; ii) with the exception of one sample from
275 Lessini Mts., differences between T_{BK} and T_W within each sample are negligible (<20°C); iii) T_T
276 diverges from T_{BK} by 2 to 78°C and diverges from T_W from by 19 to 78°C.

277 Taking this into account, the temperature range of 923-1117°C recorded by MG peridotites is
278 higher than most of Val d'Adige (T_{BK} : 896-902°C) and of Lessini Mts. (T_{BK} : 885-975°C) xenoliths.
279 Looking at the entire VVP mantle domain, the high equilibration temperatures recorded for
280 mantle xenoliths are only comparable to the highly metasomatized Lessini Mts. peridotites (1130 ±
281 60°C) studied by Siena and Coltorti (1989) (Fig. 7).

282

283 *6.2 Oxygen fugacity*

284

285 Oxygen fugacities for Marosticano peridotites were estimated using the method of Ballhaus et al.
286 (1991) using temperatures provided by the Brey-Köhler thermometer (T_{BK}). Calculated fO_2 values
287 are plotted in Fig. 7 in logarithmic units with respect to the fayalite-magnetite-quartz (FMQ) buffer
288 ($\Delta\log fO_2$). Estimates for the two spinel-harzburgites range from +0.6 to +0.9, while for the spinel-
289 lherzolites the range is wider (-0.6 to +1.1), with MG6 lherzolite being the most reduced sample.
290 With the exception of the latter xenolith, MG peridotites are more oxidized than Val d'Adige
291 lherzolites (Table 2 and Fig. 7, $\Delta\log fO_2$ (FMQ) from +0.2 to +0.3 as calculated for compositions
292 from Gasperini et al., 2006 and T_{BK} from Table 2). The Lessini Mts. peridotites also yield more
293 variability in the recorded redox conditions ($\Delta\log fO_2$ (FMQ) from -1 to +1, calculated from data of
294 Gasperini et al., 2006 and Siena and Coltorti, 1993; Table 2) encompassing the entire range of
295 Marosticano and Val d'Adige samples (Fig. 7).

296

297 7. Discussion

298

299 7.1. A cratonic origin?

300

301 The highly refractory bulk composition of lherzolites ($Al_2O_3 < 1.03$ wt.%, mg# 90.3-91.6; Table 3),
302 associated with low Al_2O_3 contents, high mg# values in both pyroxenes and spinel of MG peridotites
303 (Fig. 3c-d and Tables B-D in the on-line Supplementary material) testify for a large extraction of
304 basaltic melts from the Marosticano mantle domain which appears the most residual of the entire
305 VVP (e.g., Lessini Mts. lherzolites: $Al_2O_3 > 2.52$ wt.% and mg# 85.8-89.9).

306 Peridotites with refractory composition are expected in Phanerozoic and Proterozoic off-craton
307 mantle and ophiolites. They generally follow the so-called “residual or oceanic trend”, explained as
308 an extraction of basaltic components, resulting in an increase of Fo content in spinel accompanied by
309 increased spinel modal content (Boyd, 1989). Refractory peridotites characterize also the cratonic
310 mantle, but they rarely follow the oceanic trend (Bernstein et al, 2007; Boyd, 1989; Boyd et al.,

1997; Ionov et al., 2010). They are characterized by ol with a range of high Fo content (~91-94) at extremely variable modal ol content (~40-75%). In particular, the high Fo of ol in sp-bearing (shallow) cratonic peridotites with relatively low opx modal content (<20%) (e.g., Tanzanian, Greenland, and Slave Cratons) are indicative of high degrees (~30 to 50%) of partial melting in thermal regime active only till Archean/early Proterozoic time (Ionov et al., 2010; Walter, 2003).

MG ol plotted (Fig. 3a) in the Boyd diagram (Boyd, 1989; Boyd et al., 1997) plot off the oceanic trend, and follow the general behavior of cratonic ol (i.e. Kapvaal, Tanzanian, Greenland and Slave Cratons). While most of the Val d'Adige and Lessini Mts. exhibit lower ol modal contents at lower Fo following the oceanic trend (Fig. 3a). In addition Marosticano ol have also Ni values higher than those of Lessini Mts. but similar to those of Val d'Adige (Fig. 3b).

In association with high-Fo ol, MG peridotites show high Mg-opx in the range of 30-12% modal contents (Table 1), out of any "ideal" Phanerozoic (abyssal, oceanic and continental) off-craton melting trend (Niu, 2004; Pelorosso et al., 2016). Instead, they recall a general ol-opx behavior recorded in "shallow" (garnet-free) cratonic mantle and interpreted as physical segregation of ol and opx in high-pressure melting residuum and polybaric re-equilibration (Bernstein et al., 2007; Ionov et al., 2010). In addition, trace element distributions in opx from MG16 lherzolite and MG13 harzburgite show almost flat M-HREE profiles (i.e. $(Dy/Yb)_N$), consistent with an original subsolidus equilibrium with garnet (Bonadiman et al., 2005). In garnet-bearing lherzolites at progressively decreasing sub-solidus T (1300-900°C), opx decreases the total REE contents with equal M-HREE solid-solid partition coefficient (Sun and Liang, 2014). In turn opx of MG1, MG6 and MG14 seem to be originally equilibrated in the sp stability field showing the typical steep slope for M-HREE at comparable subsolidus temperature (1000-900°C) (Sun and Liang, 2014) (Fig. 4a, b).

Spinel, the distinctive phase of the great majority of off-craton mantle xenoliths, has cr# (30-67) which suggests a residual component neither coherent with the oceanic residual trend (i.e. "OSMA"; Arai, 1994a, 1994b) nor with the more fertile VVP-mantle fragment (cr# 9-12). On the

337 other hand, Marosticano ~~sp~~ mimic the tendency observed for ~~sp~~ coexisting with ~~ol~~ in shallow on-
338 craton (garnet-free) xenoliths (Bernstein et al., 2007).

339 In this refractory P-T system, ~~ol~~ Fo of 91.5 and ~~sp~~ cr# of 60.0 would suggest strong (or complete)
340 ~~cpx~~ consumption by high degrees of partial melting (>25%; Bernstein et al., 2007; Bonadiman et al.,
341 2005; Hellebrand et al., 2001; Scott et al., 2016; Walter, 2003) that are typical of the Archean or
342 early Proterozoic mantle (Walter, 2003). Therefore, we suggest that the partial melting occurred at
343 high melting T and thus more likely in an old mantle thermal regime. Subsequently, the
344 Marosticano mantle was enriched, forming the observed ~~cpx~~ (~~cpx~~ modal contents 4-13%) in MG
345 xenolith. These are thus secondary in nature in accordance with several studies demonstrating that
346 most ~~cpx~~ in on-craton mantle may have a metasomatic legacy (Grégoire et al., 2003; Pearson et al.,
347 2003; Simon et al., 2003; 2007).

348 To sum up, Marosticano xenoliths are characterized by cratonic fingerprints (~~Fig. 3a~~), according to
349 major and trace element compositions of the peridotite phases, and Re-Os geochronological
350 modeling (T model age: 2.1-2.9; Brombin et al., in prep.). These geochemical characteristics are
351 evident only for the Marosticano mantle fragments, whereas the rest of the VVP mantle is, as
352 expected, off-craton SCLM. The sole, intriguing link between on-craton and off-craton VVP mantle
353 is the similarity of the Re-Os ages, ranging between 1.9 to 2.1 Ga, with a unique value at 3.1 Ga for
354 the entire VVP domain. These results speak in favor for a continuum geodynamic set which
355 includes on-craton and off-craton mantle portions, as more frequently reported.


356 Cratonic signatures in off-craton ~~sp~~ bearing mantle xenoliths derived from ~~intra-plate~~
357 are recognized in a few mantle xenolith populations, e.g. in the Massif Central (France; Lenoir et al.,
358 2000), West Otago (New Zealand; Liu et al., 2015; Scott et al., 2014, 2016) and Cape Verde
359 (Bonadiman et al., 2005; Coltorti et al., 2010).


360 In the Massif Central, two contrasting shallow lithospheric domains are faced. Relatively refractory
361 (i.e., $\text{Al}_2\text{O}_3 < 2.0$ wt.%) and highly fertile (i.e., $\text{Al}_2\text{O}_3 > 4.0$ wt.%) ~~herzolites and harzburgites~~
362 interpreted as reminiscent of cratonic and circumcratonic SCLM domains, respectively (Lenoir,


363 2000). West Otago ~~sp~~-peridotites with high variable Re depletion Os model ages (0.5-2.7 Ga)
364 would represent relicts of Archean depleted mantle residues recycled through the asthenosphere
365 over Ga timescales along with more fertile convecting mantle (~~Liu et al., 2015; McCoy-West et al.,~~
366 ~~2013~~). Therefore, different remnants of shallow lithospheric domains are incorporated within the
367 young (<300 Ma) Zealandia microplate.

368 It is important to note that “shallow” (garnet-free) cratonic mantle is not exclusive of continental
369 setting. Cape Verde Islands lie in the Atlantic Ocean, in a clearly oceanic setting. Here Archean ~~sp~~-
370 bearing mantle xenoliths, ~~record~~ garnet precursor and K-rich metasomatism (Bonadiman et al.,
371 2005), suggesting the involvement of ancient geochemical reservoir also for the genesis of oceanic
372 basalts (Coltorti et al., 2010).

373 Although Archean cratons are considered ancient continental nuclei characterized by tectonic
374 inactivity for at least the past 2 Ga and low heat flow, recent studies show that their highly
375 refractory mantle roots are intensively modified over time by mechanical destructions (lithospheric
376 thinning and incipient rifting) and by episodic rejuvenation events (Foley, 2008; Tang et al., 2013;
377 Zhang et al., 2009a; Zhang et al., 2012).


378  The Wyoming Craton and North China Craton are well-known examples of complete chemical
379 rejuvenation by varying degrees of refertilization (Eggler and Furlong, 1991; Fan and Menzies,
380 1992; Tang et al., 2008, 2012, 2013). In turn, other cratons might have not yet suffered large-scale
381 removal of their ancient keels but they are in the early stages of disruption due to the efficiency of
382 extensive regime (Foley, 2008). We recall that Lessini Mts. and Val d’Adige xenoliths are generally
383 fertile lherzolites with ~~cpx and opx~~ coherently showing the typical LREE-depleted, M-REE flat and
384 steep H-LREE fractionated patterns respectively (Beccaluva et al., 2001; Lenoir et al., 2000). These
385 features are chemically contrasting with the refractory nature and the LREE enrichments of
386 Marosticano xenolith population.

387  These differences could be interpreted in terms of compositional rejuvenation of the circumcratonic
388 domains. Lessini Mts. and Val d’Adige xenoliths may be ~~the~~ fragments of the ancient SCLM,

389 strongly refertilized by infiltration of asthenosphere-derived melts, rather than newly accreted “off-
390 craton” SCLM. By contrast, Marosticano domain could be interpreted as the vestige of an old
391 (Archean?) SCLM block that underwent depletion via melt extraction and was afterward
392 pervasively metasomatized by ~~CO₂-rich silicate melts~~, a process, however,  was not able to erase
393 fully the original cratonic nature.

395 *7.2 Metasomatic origin of clinopyroxene in Marosticano xenoliths*

396
397 Despite the general refractory features of MG peridotites, a superimposed metasomatic process is
398 manifested by major and trace element geochemistry of both pyroxenes. Trace-element
399 compositions of Marosticano cpx show variable enrichment characteristics, inconsistent with a
400 residual origin after melt extraction (e.g. Sun et al., 2012). They exhibit a notable LREE-enrichment
401 (Fig. 5c, d), a fractionated REE pattern and a general HFSE depletion (Fig. 5a, b) with respect to CI
402 model trace element abundances (Sun and McDonough, 1989). Taken together, these signatures
403 confirm that cpx is a phase either formed by a reaction of a residual peridotite with metasomatic
404 melts or it is a new phase directly crystallized from the metasomatic agents.

405 As nearby VVP districts (Lessini and Val d’Adige) are thought to have been affected by silicatic
406 metasomatism (Beccaluva et al., 2001), we first evaluated whether the MG mantle segment **could**
407 **have been also explained**  by the same type of metasomatism. Taking into account only those
408 Lessini and Val d’Adige samples that show cpx modal contents and cpx-opx-mg# values
409 comparable to those of MG xenoliths, trace element compositions of MG cpx are significantly
410 enriched compared to the primary, spongy and secondary VVP cpx (Fig. 6). This suggests that MG
411 were pervaded by a metasomatic agent that was different from that which affected the rest of the
412 VVP region. However, both group-1 and group-2 cpx are more enriched in LREE (Fig. 5c, d) and
413 depleted in Ti and ~~in~~ HFSE (e.g., Zr, Fig. 5a, b) arguing against a “pure” alkali silicate melt
414 metasomatism and favouring instead the contribution of a carbonatic component. In fact,

415 experimentally produced silica-bearing carbonatite melts crystallize cpx_1 with major element
416 composition similar to both MG group-1 and group-2 cpx_1 (Fig. 3d-f).

417 Enrichment in LREE accompanied by strong HFSE depletion (Fig. 5a, b) of group-1 and group-2
418 cpx_1 is notably assigned to an effect of the cpx_1 -carbonatite partitioning as shown by experimental
419 and empirical data by Dasgupta et al. (2009), Dixon et al. (2008), Gudfinnsson and Presnall (2005)
420 and Pokhilenko et al. (2015). This geochemical effect has been observed in various carbonatite
421 metasomatized mantle xenoliths from both oceanic and continental settings (i.e: Spitsbergen, Ionov,
422 1998; North China Craton; Sun et al., 2012; New Zealand, Scott et al., 2016; Comores Archipelago;
423 Coltorti et al, 1999).

424 Cpx group-2 mimics the steep M-HREE fractionated pattern, but they have remarkably higher
425 LREE content with respect to cpx_1 formed by a carbonatitic/ CO_2 -rich silicate melt experimentally
426 obtained at pressure of 6.6 GPa in equilibrium with garnet (Dasgupta et al., 2009) (Fig. 8). The
427 calculated $^{cpx/carb}D_{La}$ at this pressure is 0.006 but systematically increases with decreasing pressure
428 and with the sp appearance (Dasgupta et al., 2009). Therefore, if we consider REE cpx_1 /carbonatite
429 partition coefficients calculated for 2 GPa and 1100-1150°C (e.g., $^{cpx/carb}D_{La}$ of 0.09; Klemme et al.,
430 1995) we can reproduce the general shape of the L- to M-HREE pattern of both MG cpx_1 groups
431 (Fig. 8).

432 The only remarkable difference between group-1 and group-2 cpx_1 is that the former shows a less
433 steep, or flat, HREE pattern indicating ~~that carbonatitic melts migrated and interacted with slightly~~
434 ~~different peridotitic wallrocks. This could be attributed to a~~ chromatographic fractionation of a
435 metasomatic agent interacting with different peridotitic wallrock (Ionov et al., 2002; Sen et al.,
436 1993). In this scenario, the concentration fronts of the migrating melts are controlled by the ion-
437 exchange with the peridotitic matrix. In general, the fronts of the more incompatible elements (e.g.,
438 LREE) travel faster than those of less incompatible ones (e.g., M-HREE) producing enrichments in
439 LREE and depletion or flatness in HREE of the whole rock depending on the original peridotitic
440 matrix (Ionov et al., 2002). In this frame, the cpx group-1 records a continuum feeding of REE from

441 the carbonatitic melt to a possible residual (primary?) ~~cpx~~₁ (Ionov et al., 2002; Pokhilenko et al.,
442 2015; Sen et al., 1993). On the contrary, the convex-upward REE patterns of ~~cpx~~ group-2₁ may
443 reflect nearly complete equilibration between the peridotite matrix (mainly ~~ol-opx~~₁) and the
444 metasomatic melt (Dasgupta et al., 2009; Dixon et al., 2008).

445 In anhydrous garnet-free peridotites, restitic ~~opx~~₁ is the counterpart of ~~cpx~~₁ to incorporate the
446 incoming geochemical budget. The only evidence of metasomatic effects in the MG orthopyroxenes
447 is their high Ti content (up to 281 ppm), not coherent with their low Al₂O₃ (~~Fig. 9~~; Scott et al.,
448 2016) and in antithesis with the carbonatitic enrichment described for the ~~cpx~~₁. This can be
449 explained by the action of CO₂-rich silicate melts which could primarily impart a carbonatite-like
450 trace element signature in ~~cpx~~₁ (i.e., L-REE) hiding the potential effects of silicate melts (i.e., Ti
451 enrichment), that in turn is magnified in the residual ~~opx~~₁ (Scott, et al., 2016). Spinel-facies ~~cpx~~₁
452 prefers most trace elements, including Ti, compared to ~~opx~~₁ however, relative to elements with
453 slightly larger and smaller atomic radii (Eu and Dy), Ti is slightly less favorably partitioned into
454 ~~cpx~~₁ (Eggins et al., 1998; Scott, et al., 2016). This nuance leads to the formation of small negative Ti
455 anomalies in ~~cpx~~₁ and a corresponding positive anomaly in ~~opx~~₁ (Scott et al., 2016). Consequently,
456 both negative and positive Ti anomalies observed in MG ~~opx~~₁ could be due to a chromatographic
457 fractionation effect during the interaction between carbonatite/CO₂-rich silicate melts and a
458 ~~different~~ peridotitic wallrock where ~~cpx~~₁ was present or not (Ionov et al., 2002; Scott et al., 2016;
459 Sen et al., 1993).

460 Though we cannot resolve if this metasomatism initially occurred in the garnet stability field and
461 continued in shallower portions of the MG mantle we can assume that the product of such
462 metasomatism may be stabilized at P conditions of the ~~sp~~-stability field. Accordingly, we interpret
463 the geochemical characteristics (major and trace elements) acquired by MG pyroxenes as consistent
464 with "new" ~~cpx~~₁ formed by the interaction of a carbonatitic melt with a cratonic flavored ambient
465 peridotite (Griffin et al., 1999; Spengler et al., 2006). Notably, experimental studies (e.g., Dasgupta
466 et al., 2006, 2007; Green, 2015; Hammouda and Keshav, 2015; Hirose, 1997) suggest that a carbon-

467 rich peridotite is necessary to form alkaline and in particular ultra-alkaline mantle melts. Similarly,
468 carbonatitic components have been hypothesized as important contributors to VVP alkaline- to
469 ultra-alkaline magmas, the hosting lavas that ferry VVP mantle xenoliths to the surface (Beccaluva
470 et al., 2007).

471

472 *7.3 Relationship between carbonatite/CO₂-rich silicate metasomatism and fO_2 conditions*

473

474 As carbonatitic/CO₂-rich silicate melts contain large amounts of dissolved fluids, they are able to
475 mobilize volatile elements (C-OH-, but also Na and K as lithophile elements); accordingly, their
476 interaction with the peridotite matrix may affect the redox conditions (Dasgupta et al., 2013). MG
477 peridotites represent a cratonic "enclave" of continental mantle of the Adria plate that was later
478 pervaded by carbonatite metasomatism. The high fO_2 (Fig. 7), comparable with the other VVP
479 mantle occurrences and within the range of ~~the subcontinental lithospheric mantle~~ (Foley, 2011), is
480 not compatible with a cratonic origin but requires a late oxidation event, preserved until the xenolith
481 exhumation by Cenozoic host lavas. Volatile mass transport occurs mostly by fluid and silicate
482 (with prevailing H₂O) or carbonate ~~melts~~ (with prevailing CO₂) as function of the redox state of the
483 mantle (Foley, 2008, 2011; Frost and McCammon et al., 2008; Pokhilenko et al., 2015). Assuming
484 the relatively high oxidizing conditions of Marosticano peridotites were affected by CO₂-bearing
485 melts, we calculated CO₂ mole fractions of such melt(s) using the equation of Stagno and Frost
486 (2010). We obtained CO₂ mole fractions close to or slightly higher than 1.0, taking into account the
487 T- fO_2 values independently calculated from the silicate parageneses (Table 2). This is also evident
488 in the diagram of fO_2 as a function of potential T (Goncharov et al., 2012), where almost all the
489 Marosticano peridotites straddle the field for carbonatite and CO₂ fluid (Fig. 10). This may suggest
490 that the Marosticano geothermobarometric conditions record this matrix/carbonatitic melt
491 interaction, rather than the T- fO_2 values of the initial cratonic lithospheric mantle.

492 The variable redox states ~~of the MG xenolith population~~ may also influence the Eu oxidation state

493 (Eu³⁺ or Eu²⁺; Henderson, 1984) and may explain why this element is enriched in group-1 cpx. In
494 oxidized magma, Eu is an incompatible element in the trivalent form (Eu³⁺), while in reduced
495 magma, it is preferentially incorporated into plagioclase in its divalent form (Eu²⁺). This ion-
496 exchange process explains the negative Eu anomaly in many terrestrial basalts showing plagioclase
497 as liquid phase. However, Eu speciation is highly sensitive to small redox variations. Thus the
498 different accommodation of Eu in minerals may change rapidly (McLennan, 2001).

499 Almost all group-1 cpx have M-HREE flat profiles with evident positive Eu anomaly (Fig. 5a, c).
500 ~~These anomalies~~ are not accompanied by a positive K (not reported) or Sr anomaly, that could be
501 assigned to the melting of pre-existing phlogopite and plagioclase ~~respectively~~, in the protolith
502 (Marchesi et al., 2013; Tang et al., 2017), neither of which were observed in any Marosticano
503 xenolith. In other xenolith suites, examination of the Eu content in garnet and cpx in eclogites led to
504 the suggestion that the positive Eu anomaly results from the interplay between crystal chemistry
505 and redox conditions during metasomatism (Griffin and O'Reilly, 2007). Karner et al. (2010)
506 determined the Eu partition coefficient between augite and melt ($D_{Eu}^{cpx/melt}$) in samples crystallized
507 from a highly Eu spiked Martian basalt ~~composition~~ at different fO_2 conditions. These authors
508 observed that $D_{Eu}^{augite/melt}$ steadily increases with fO_2 since Eu³⁺ is more compatible than Eu²⁺ in
509 the pyroxene structure; thus increasing fO_2 leads to greater Eu³⁺/Eu²⁺ in the melt, allowing for more
510 Eu (total) to partition into the cpx. It is worth noting that positive Eu anomalies are occasionally
511 observed in cpx from metasomatized suboceanic mantle or subcontinental cratonic mantle in both
512 sp and garnet stability field, irrespective of the nature of the metasomatic melts (e.g., xenoliths from
513 Loch Roag, North Atlantic Craton, Northern Scotland, Hughes et al., 2015; from Siberian Craton,
514 Pearson et al., 1995; Slave Craton, Heaman et al., 2002; Kaapval craton, Jacob et al., 2003). On the
515 basis of these considerations, we suggest that a small variation of the redox state may induce Eu to
516 modify its solid/solid, solid/melt partitioning behavior, without any change of the large-scale
517 geochemical process.

518 The interaction between the Marosticano residual mantle with a carbonatite/CO₂ rich silicate melt is


519 explained by a possible chromatographic fractionation effect only in group-1 peridotite. This leads
520 to a “local” variation of fO_2 oxidizing conditions and by consequence to a “local” increase of the
521 Eu^{3+}/Eu^{2+} ratio in the melt and to higher Eu concentration in the newly formed ~~cpx~~ Group-2
522 clinopyroxene is suggested to crystallize from the carbonatitic/ CO_2 -rich silicate melts that control
523 the environmental redox condition.

524

525 8 Conclusions

526

- 527 • Petrological and geochemical features of the newly discovered Marosticano peridotite xenoliths
528 indicate that they represent a mantle segment geochemically distinctive from the other VVP
529 peridotites (i.e., Lessini Mts. and Val d’Adige), contributing to enlarge the knowledge of spatial
530 heterogeneity within the mantle of this region.
- 531 • ~~MG~~ lherzolites and ~~cpx~~-bearing harzburgites demonstrate complete ~~sp~~ facies equilibration.
532 Mineral major and trace elements features are comparable to those observed for on-craton
533 peridotites worldwide.
- 534 • Marosticano ~~cpx~~ are secondary in nature and they exhibit a substantive LREE-enrichment, a
535 fractionated REE pattern with positive Eu anomaly, almost flat (~~cpx~~ group 1) or steep (~~cpx~~
536 group 2) HREE patterns, and a remarkable HFSE depletion. These characteristics are attributed
537 to a chromatographic separation of a metasomatic agent with high carbonatitic/ CO_2 -rich silicatic
538 components.
- 539 • Marosticano samples record relatively high oxidation conditions similar to those of the VVP
540 off-craton xenoliths (e.g. Lessini Mts.) but anomalous for a proper cratonic environment. These
541 T- fO_2 relationships are probably due to the oxidizing nature of CO_2 -rich circulating fluids.
- 542 • The variable, but generally high, redox states of the ~~MG~~ xenolith could be responsible for the
543 positive Eu anomaly in ~~cpx~~ group-1. As higher fO_2 leads to higher Eu^{3+}/Eu^{2+} in the melt
544 increasing the element partitioning in ~~cpx~~ the positive Eu anomaly could result from the

545 relatively high redox condition₁ of the Marosticano mantle fragment during the formation of
546 group-1 cpx₂. On the contrary, group-2 cpx₁ that do not show positive Eu anomalies₁ may show
547 the fingerprint of a carbonatitic/CO₂-rich silicate melt metasomatism, **therefore still recording** 
548 the original redox condition₁.

- 549 • Within the SCLM sampled by VVP magmatism, only Marosticano xenoliths show evidence of
550 carbonatitic metasomatic overprinting of a likely cratonic mantle domain. All the other mantle
551 VVP mantle xenoliths exhibit characteristics of off-craton lithospheric mantle variably affected
552 by Na-alkaline silicatic metasomatism.
- 553 • The lithospheric mantle beneath the Adria plate₁ has been affected by complex ~~enrichment and~~
554 refertilization processes, related to a geodynamic scenario dominated by extension-related
555 magmatism in response to the near active collision between Eurasia and Africa plates (~~Fig. 11~~).
- 556 • The geochemical features of Marosticano mantle xenoliths introduce a cratonic component in
557 the geodynamic evolution of the Adria plate system in the general frame of the geodynamical
558 reconstruction of the Africa/Eurasia collision. From our current study, together with literature
559 data, we interpret that the cratonic keel is preserved only in the Marosticano district, while
560 Lessini Mts. and Val d'Adige mantle domains could be circumcratonic portions refertilized by
561 infiltration of asthenospheric-derived melts (Fig. 11).

562

563

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565

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572

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862

863 **Figure captions**

864

865 Fig. 1. Geological map of the Veneto Volcanic Province (De Vecchi and Seda, 1995), showing the
866 location of Monte Glosio, xenolith site in Marosticano volcanic district. Inset a) Locations of VVP
867 in the Italian peninsula, European, African and Adria Plates. The white arrows show the subduction
868 directions (modified after Carminati and Doglioni, 2012-modified).

869

870 Fig. 2. Photomicrographs of representative microstructures in the MG xenoliths. (a) clinopyroxene
871 with cloudy, spongy rims near a kinked olivine; (b) clinopyroxene with cloudy, spongy rims; (c)
872 reaction areas surrounding a spinel, constituted by small crystals of olivine, clinopyroxene, spinel
873 and rare glass; (d) orthopyroxene crystals showing a reaction rim composed of secondary
874 clinopyroxene and olivine.

875

876 Fig. 3. ~~Compositional variations vs mg# [$\text{MgO}/(\text{MgO}+\text{FeO})\text{mol}\%$] for MG xenoliths, Lessini Mts.~~
877 ~~peridotites (from Beccaluva et al., 2001; Gasperini et al., 2006; Morten et al., 1989; Siena and~~
878 ~~Coltorti, 1989), Val d'Adige xenoliths (from Gasperini et al., 2006): (a) modal olivine~~
879 ~~compositional variation (wt.%) vs Fo, the “oceanic trend” (from Boyd, 1989) is also shown.~~ (b)
880 ~~olivine compositional variation in terms of Ni (ppm) vs. Fo; fields of olivines from Archean craton~~
881 ~~peridotites, both garnet and spinel facies (Kelemen et al., 1998) and Phanerozoic mantle array~~
882 ~~(Takahashi, 1987) are also plotted; (c) orthopyroxene compositional variation in terms of Al_2O_3 vs.~~
883 ~~mg#; (d) clinopyroxene compositional variation in terms of Al_2O_3 vs. mg#; (e) clinopyroxene~~
884 ~~compositional variation in terms of Na_2O vs. mg#; (f) clinopyroxene compositional variation in~~
885 ~~terms of TiO_2 vs. mg#; (g) spinel compositional variation in terms of Cr_2O_3 vs. mg# . In b, d, e, f~~
886 ~~hypothetical trend of interaction with M. Glosso host lava is shown. In d, e, f black crosses represent~~
887 ~~average major element compositions of cpx crystallized from silica-bearing carbonatite melts (from~~
888 ~~Dasgupta et al., 2009), they are plotted for defining metasomatic agents of MG xenoliths. Filled and~~
889 ~~open symbols are for lherzolite (Lh) and harzburgite (Hz), respectively.~~

890

891 Fig. 4. Chondrite-normalized (Sun and McDonough, 1989) incompatible trace elements ~~diagrams~~
892 ~~for opx in MG lherzolites (a) and harzburgites (b).~~

893

894 Fig. 5. Chondrite-normalized (Sun and McDonough, 1989) incompatible trace elements ~~diagrams~~
895 ~~of cpx group-1 (a) and cpx group-2 (b).~~ Chondrite-normalized (Sun and McDonough, 1989) REE
896 ~~patterns of cpx group-1 (c) and cpx group-2 (d).~~

897

898 Fig. 6. ~~Comparison of chondrite-normalized (Sun and McDonough, 1989) trace element~~
899 ~~distributions of MG cpx (this study) and primary, spongy, secondary cpx from VVP xenoliths~~

900 ~~(Beccaluva et al., 2001) that exhibit comparable cpx modal contents and cpx-opx mg# values.~~
901 ~~Patterns of VVP cpx (Beccaluva et al., 2001) are represented with shadowed areas.~~

902

903 Fig. 7. Temperatures and $\Delta\log fO_2$ relative to the buffer reaction fayalite-quartz-magnetite ($\Delta\log fO_2$
904 FQM). Temperatures are calculated using the approach of Brey and Köhler (1990). $\Delta\log fO_2$
905 estimates are calculated with ~~the method of Ballhaus et al., 1991.~~ P is fixed at 1.5 GPa. ~~Filled and~~
906 ~~open symbols are for lherzolite (Lh) and harzburgite (Hz), respectively.~~ T- fO_2 conditions of Lessini
907 and Val d'Adige lherzolites are calculated using EMP data from Gasperini et al., 2006. Shadowed
908 area represents the T- fO_2 range of highly metasomatized Lessini xenoliths previously reported in
909 Siena and Coltorti (1989).

910

911 Fig. 8. ~~Comparison of chondrite-normalized~~ REE patterns of MG cpx (this study),
912 ~~carbonatitic/CO₂-rich silicate melt experimentally~~ obtained at pressure 6.6GPa in equilibrium with
913 garnet (Dasgupta et al., 2009) and modeled cpx formed by a carbonatitic/CO₂-rich silicate melt
914 applying $D^{cpx/carb}$ calculated at 2 GPa 1100-1150°C (Klemme et al., 1995) (shadowed area).
915 ~~Chondrite compositions for the normalisation of all compositions are~~ from Sun and McDonough
916 (1989).

917

918 Fig. 9. Orthopyroxene Ti (ppm) and Al₂O₃ (wt.%) contents are consistent with depletion due to melt
919 extraction followed by Ti enrichment due to and CO₂-rich silicatic metasomatism (from Scott et al.,
920 2016).

921

922 Fig. 10. Oxygen fugacity ($\Delta\log fO_2$) vs. temperature for MG xenoliths. Stability fields of diamond,
923 graphite and carbonates are delineated by the graphite/diamond transition and the EMOD/G and
924 D/GCO oxygen buffers (Goncharov et al., 2012 and references therein). Almost all the Marosticano
925 peridotites straddle the fields for carbonatite and CO₂ fluid suggesting that the Marosticano

926 geothermobarometric conditions record the interaction between matrix and carbonatite/CO₂-rich
927 silicate metasomatic melts.

928

929 Fig. 11. Summary sketch of the model presented of the processes significant in the VVP mantle
930 during the European/Adria collision. Purple denotes the cratonic keel preserved beneath the
931 Marosticano district, and blue represents the refertilized cratonic portions due to the infiltration of
932 asthenospheric-derived melts beneath the Lessini Mts. and Val d'Adige districts.

933 **Supplementary material**

934

935 **1. Analytical methods**

936

937 Major element compositions of minerals from xenoliths and host lavas were analyzed at the Istituto
938 di Geoscienze e Georisorse, CNR, Padua (Italy) on Electron MicroProbe (EMP), using ZAF on-line
939 data reduction and matrix correction procedure. An acceleration voltage of 20 keV and sample
940 currents of 20 nA with 10-20 s counting time on peak position was used. Synthetic oxide standards
941 (MgO, FeO, MnO, ZnO, NiO, Al₂O₃, Cr₂O₃, TiO₂ and SiO₂) were used. Analytical precision is
942 better than $\pm 2\%$ for elements in the range of >10 wt.%, better than 5% for elements in the range 2-
943 10 wt.%, and better than 10% for elements in the range 0.5-2 wt.%.

944

945 Trace element concentrations in cpx and opx were obtained by Laser Ablation Inductively Coupled
946 Plasma Mass Spectrometry (LA-ICP-MS) at the Department of Earth Sciences, University of New
947 Hampshire (USA) using an Analyte Excite 193 nm excimer laser plumbed into a Nu instruments
948 AttoM high resolution inductively coupled plasma mass spectrometer. Typical spot size was 65 μm ,
949 and laser operating conditions were 6.0 mJ at 80% output, fluence of 8.1 J/cm² and repetition rate of
950 5 Hz. Silicate glass MPI-Ding standard, ML3B-G (Jochum et al., 2006), was used as the calibration
951 standard every four sample spots to correct for within-run instrumental drift. Resulting data were
952 then processed with the Iolite software package, using calcium data from EMPA as an internal
953 standard. Precision and accuracy were assessed to be within 10% for ppm-level concentrations by
954 repeated measurements of KH-1 and KL2-G as independent standards. Results of the repeated
955 “blind” standard results are present in Supplementary material Table G.

956

957 Two out of five samples only were suitable for bulk rock analyses. Major elements were determined
958 by Wavelength Dispersive X-Ray Fluorescence Spectrometry (WDXRF) on pressed powder pellets

959 at the Dipartimento di Fisica e di Scienze della Terra, Università di Ferrara (Italy), using an ARL
960 Advant-XP spectrometer, following the full matrix correction method proposed by Traill and
961 Lachance (1966). Accuracy is generally lower than 2% for major oxides.

962

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970

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972

973 **On-line Supplementary material (Excel file)**

974 Major (wt.%) abundances of representative olivine (Table A), orthopyroxenes (Table B),
975 clinopyroxenes (Table C) and spinel (Table D) in MG spinel peridotite xenoliths. Trace element
976 (ppm) abundances of representative orthopyroxenes (Table E), clinopyroxenes (Table F) in MG
977 spinel peridotite xenoliths. Table G: Standard used for LA-ICP-MS analyses. The values are in ppm.

1 Refertilized mantle keel below the Southern Alps domain (North-East Italy): ~~evidence~~

2 Evidence from Marosticano refractory mantle peridotites

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11
12 ABSTRACT

13 The Veneto Volcanic Province (VVP), a ~~Tertiary-Cenozoic~~ magmatic province in northeastern Italy,
14 is one of the widest volcanic areas of the Adria ~~p~~Plate. It consists of five main volcanic districts,
15 ~~with the and its~~ most primitive products commonly hosting mantle xenoliths. In this study, we
16 present a newly ~~discovered found~~ xenolith suite from the Marosticano district that ~~consists~~
17 ~~of contains~~ peridotites ~~revealing with~~ compositional characteristics of mineral assemblages that
18 ~~allow to depict provide insight into~~ an unexpected nature for the sub-continental lithospheric mantle
19 (SCLM) of the Adria plate. In contrast to ~~xenoliths from other VVP sites previously studied the~~
20 ~~majority of MVP xenolith population~~ (i.e.: Val d'Adige and Lessini Mts.), Marosticano xenoliths
21 exhibit highly refractory compositions typical of on-craton peridotites. In particular, high olivine
22 forsteritic contents (Fo: 91-93) indicate high degrees of partial melting (>25%) that should lead to
23 the complete consumption of clinopyroxene. Major and trace element compositions further link
24 these peridotite fragments to ~~Early-early~~ Proterozoic cratonic mantle, and the juxtaposition of
25 clinopyroxene within these rocks suggests like most on-craton clinopyroxene, Marosticano
26 clinopyroxene have a metasomatic legacy. The i) LREE-enrichments of ~~these Marosticano~~

27 | clinopyroxenes and ii) the dissolved CO₂ mole fractions (up to 1.0) for the inferred clinopyroxene-
28 | forming melt ~~speaks in favor of~~ are consistent with carbonatite/CO₂-rich silicatic melts as ~~the~~
29 | metasomatic agents. The latter could be responsible for the equilibrium temperatures (1033-
30 | 1117 °C) and oxidizing conditions ($\Delta\log/O_2$ (FMQ)=-0.6 - +1.1), anomalously high for a ~~proper~~
31 | cratonic environment but similar to the off-craton VVP xenoliths.

32 | The cratonic signature and carbonatite/CO₂-rich silicate ~~metasomatic-metasomatism evidences~~
33 | found together in the Marosticano mantle xenoliths reveal ~~how SCLM can preserve~~ that ancient
34 | features can be preserved even in SCLM, even if drawn-in a young, active geodynamic ~~scenario~~
35 | setting as the Adria plate boundary. In this framework Lessini Mts. and Val d'Adige xenoliths could
36 | be interpreted as the typical features of circumcratonic reminiscent domains affected by
37 | refertilization due to infiltration of asthenosphere-derived melts, rather than newly accreted "off-
38 | craton" SCLM. These new interpretations could be useful for completing the reconstruction of the
39 | Africa/Eurasia interplay during the Alpine collision.

40 |

41 | HIGHLIGHTS

42 | Petrology and geochemistry of newly discovered Adria ~~Plate-plate~~ mantle xenoliths presents
43 | unexpected cratonic features.

44 |

45 | ~~Xenolith-c~~clinopyroxenes record metasomatic overprinting of restitic peridotite from
46 | carbonatite/CO₂-rich silicate melts.

47 |

48 | Cratonic keel is preserved only in the Marosticano district, while the rest of VVP mantle domains
49 | are interpreted as circumcratonic portions ~~inable subject~~ to rejuvenation ~~due to~~ from asthenospheric-
50 | derived melts.

51 |

52 | KEYWORDS

53 Veneto Volcanic Province, cratonic mantle xenoliths, carbonatite metasomatism, rejuvenation.

54

55 1. Introduction

56

57 The stability of continents is intimately linked to the underlying sub-continental lithospheric mantle
58 (SCLM). Peridotite xenoliths hosted in intraplate basaltic rocks provide a useful way to evaluate the
59 petrological features and evolution of the SCLM in terms of mineral compositions, modal
60 abundance and to ~~evidence-fluid~~ modification ~~o-by fluids~~ (Liu et al., 2015).

61 ~~The mantle xenoliths occurring in Veneto Volcanic Province Together with mantle xenoliths of~~
62 ~~Sardinia and Iblei Mts. (Sicily) (Beccaluva et al., 2009), the relevant number of xenolith sites~~
63 ~~occurring in Veneto Volcanic Province~~ (VVP; SE Alps, NE Italy, Fig. 1) depicts the "big" picture
64 of the SCLM beneath the Adria plate, the African promontory of the central-western Mediterranean
65 area. ~~During In the~~ Cretaceous ~~this region~~ the VVP region was involved in a convergence between
66 Africa and Eurasia plates, inducing subduction processes of the latter southeastward (Schmid et al.,
67 1997; von Blanckenburg and Davies, 1995). ~~Despite In spite of~~ the immense quantity of seismic,
68 structural, petrologic, and geochemical data compiled over at least five decades, the Adria
69 microplate (Fig. 1, inset) remains an enigmatic aspect in the geodynamic evolution of the Africa-
70 Eurasia collision system (Carminati and Doglioni, 2012; Lustrino, et al., 2011). It has been
71 considered either to be in crustal continuity with the African mainland or separated from the latter
72 by an oceanic plate (Catalano et al., 2000; Lustrino et al., 2011; ~~Muttoni et al., 2001; Schmid et al.,~~
73 ~~2008~~).

74 Mantle xenoliths from a few VVP localities ~~were already previously~~ investigated (Lessini Mts. and
75 Val d'Adige localities; Fig. 1) revealing variably depleted mantle domains, which were
76 subsequently enriched by one or more episodes of metasomatism as recorded by widespread
77 interstitial recrystallized glassy patches (Beccaluva et al., 2001; Gasperini et al., 2006; Morten et al.,
78 1989; Siena and Coltorti, 1989). In this paper, we describe results from a

79 ~~The~~ petrological and geochemical study of ~~the newa newly discovered~~ occurrence of mantle
80 xenoliths from the Marostica Hills, ~~that constituted in~~ the Marosticano district of the VVP, ~~may~~
81 ~~help to better~~ We then interpret our findings to constrain the mantle domain underlying the northern
82 (continental) sector of the Adria ~~Plate~~plate, with the ultimate goal of shedding insight into dynamic
83 processes at work during plate boundary interaction and ultimately to understand its relative plate
84 motion (Carminati and Doglioni, 2012).

86 2. Geological setting

88 The Central-Western Mediterranean area is a geologically young area, mostly developed during the
89 last 30 Ma. ~~Of the~~geological structures and the igneous activity ~~developed~~ within this ~~area~~region
90 are intimately linked with the relative movements of two large plates (Africa and Europe) plus a
91 number of smaller continental and oceanic plates (e.g., Lustrino et al., 2011). ~~A key smaller plate,~~
92 ~~likely~~ Between them, of particular relevance is the existence of an African promontory, ~~is the~~ called
93 Adria (or Apulia) ~~plate in which~~ where the VVP (Fig. 1) constitutes one of the largest and most
94 important magmatic provinces. ~~In fact, d~~During the TertiaryCenozoic, the Veneto and Trentino
95 regions were affected by extensive volcanic activity, mainly basic-ultrabasic in composition that
96 took place intermittently from the ~~l~~ate Paleocene to the ~~l~~ate Oligocene (Barbieri et al., 1982,
97 1991; De Vecchi et al., 1976; De Vecchi and Sedea, 1995; Piccoli, 1966). Most of the VVP
98 products are spread over a NNW to SSE elongated area of about 1,500 km². Five main volcanic
99 districts can be defined from west to east (Fig. 1): (1) the Val d'Adige district, between Arco and
100 Rovereto; (2) the Lessini Mts. district between Val d'Adige and the Schio-Vicenza tectonic line; (3)
101 the Marosticano district, east of the Schio-Vicenza line; (4) the Berici Hills district, which is
102 separated from (5) the Euganean Hills, the southernmost district, by the Riviera dei Berici line
103 (Beccaluva et al., 2007). Most VVP volcanic products are relatively undifferentiated lavas, and
104 range in composition from nephelinites to quartz (Qz)-normative tholeiitic basalts. They tend to be

105 spatially and temporally distributed, becoming gradually younger and less alkaline toward SE.
106 Differentiated products only occur in the Euganean district, where quartz-trachytes and rhyolites
107 predominate (Milani et al., 1999, and references therein). Nephelinites and basanites commonly
108 carry spinel-peridotite mantle xenoliths (Beccaluva et al., 2001; 2007).
109 The mafic volcanism in the VVP is thought to be related to extensional tectonics in the Southern
110 Alps foreland as response to Alpine orogenesis (De Vecchi and Sedea, 1995; Milani et al., 1999;
111 Zampieri, 1995). Geophysical data (Ansorge et al., 1992; Giese and Bunes, 1992) indicate a rather
112 normal thickness of the continental crust under the VVP, with a NW-SE elliptical mantle dome
113 culminating at about 28 ~~km-4m~~ beneath the Lessini Mts., while the lithosphere-asthenosphere
114 boundary has been detected at a depth of ~100 ~~km-4m~~ (Panza and Suhadolc, 1990).
115 Isotopic signatures, notably $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (18.8-19.8 and 0.703-0.704,
116 respectively) led Beccaluva et al. (2001, 2007) to argue that the SCLM beneath the Adria plate has
117 been enriched by metasomatizing agents, likely including FOZO or HIMU components. This
118 signature may be related to the European Asthenospheric Reservoir (EAR; Hoernle et al., 1995), a
119 large mantle upwelling extending from the eastern Atlantic to Europe and the Mediterranean area.
120 Alternatively, Wilson and Patterson (2001), and more recently Lustrino and Wilson (2007) argued
121 that this Tertiary-Quaternary volcanism is related to diapiric upwelling of small-scale, finger-like,
122 convective instabilities from the base of the upper mantle.

123

124 3. Petrography

125

126 The Marosticano xenoliths were sampled in the quarry of Monte Glosio (MG), a few kilometers east
127 of Marostica (Fig. 1). The basanitic host lavas show a porphyritic texture with phenocrysts of
128 olivine, clinopyroxene, and magnetite set in a fine-grained groundmass composed of clinopyroxene,
129 plagioclase, and oxides. The xenoliths are generally subrounded or (more rarely) angular, ranging in
130 size from a few centimeters up to 10 cm. Heavy fracturing and alteration are present throughout of

131 the suite. Only five samples were sufficiently fresh to permit a complete petrological
132 characterization. These samples also showed no evidence of host magma infiltration.

133 The Marosticano xenoliths are peridotites with complete spinel-facies equilibration. They display a
134 coarse-grained protogranular texture following the nomenclature of Mercier and Nicholas (1975).

135 Two of the five investigated xenoliths are harzburgites with 4% clinopyroxene (cpx), one is low-
136 cpx (6%) lherzolite and two are lherzolites with 9-13% cpx (Table 1). In two out of three lherzolites,
137 orthopyroxene (opx) is modally scarce (12-14%) as compared to typical peridotites (e.g.,

138 Streckeisen, 1974). All Marosticano peridotites are ~~characterised~~-characterized by large crystals of
139 olivine (ol) and opx (up to 2 mm across) with smaller grains of cpx (0.5-1 mm in size) and spinel
140 (sp) (up to 1 mm across). These latter show a typical holly-leaf or lobate shape, while ol and
141 pyroxene crystals display curvilinear grain boundaries. Kinking is common in ol, while opx display
142 exsolution lamellae and, rarely, show sieved rims. Cpx are always smaller in size with respect to
143 opx and show large cloudy portions (spongy cpx).

144 Several types of pyrometamorphic textures are superimposed on these features. They consist of (1)
145 cloudy, spongy cpx crystals: the recrystallized portion generally replaces the whole crystal, in rare
146 cases it covers only the rim zones (Fig. 2a, b); (2) reaction areas involving primary opx, cpx and sp,
147 with a secondary assemblage made up of small crystals of ol, cpx, vermicular sp and rare glass (Fig.
148 2c, d); (3) brown to pale yellow glassy patches containing secondary crystals of ol, cpx and sp. The
149 secondary paragenesis is generally too small to be ~~analysed~~-analyzed by Electron MicroProbe
150 (EMP) and therefore was not considered for *in-situ* analysis.

151

152 4. Analytical methods

153

154 The modal composition of Marosticano samples was estimated by point counting with more than
155 1000 points for each thin section. Major element compositions of minerals from xenoliths and host
156 lavas were determined by Electron Microprobe (EMP), using a Cameca SX50 instrument at the

157 Istituto di Geoscienze e Georisorse, CNR, Padova (Italy). Trace element concentrations in cpx and
158 opx were obtained by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-
159 MS) at the Department of Earth Sciences, University of New Hampshire (USA) using an Analyte
160 Excite 193 nm excimer laser plumbed into a Nu instruments AttoM high-resolution inductively
161 coupled plasma mass spectrometer. Two out of five samples ~~only~~ were sufficiently unaltered so as
162 to be suitable for bulk rock analysis, ~~that-which~~ was performed on powder pellets using an ARL
163 Advant-XP spectrometer at the Dipartimento di Fisica e di Scienze della Terra, Università di
164 Ferrara (Italy). More extensive descriptions of the analytical procedures, together with the standards
165 supporting the analyses, are reported in the on-line Supplementary material.

166

167 5. Mineral Chemistry

168

169 Within each xenolith, minerals are generally homogeneous in composition with no significant
170 chemical variation between core and rims of the same crystal. The latter is observed only for
171 spongy crystals and grains close to reaction areas (Fig. 2). When these areas are near the contact
172 with host basanites, ol and cpx core and rim analyses were performed and compared with ol and
173 cpx phenocrysts in order to check if they could be the result of the host magma infiltration.
174 Representative analyses of ol, opx, cpx, and sp are reported in Tables A-D of the Supplementary
175 online material.

176

177 5.1 Major element composition

178

179 Olivine is chemically unzoned in Monte Glosio (MG) lherzolites and harzburgites. It shows a
180 narrow compositional range with Fo content $[=100 \times \text{Mg}/(\text{Mg}+\text{Fe})_{\text{mol}}]$ varying from 91.3 to 92.2 for
181 lherzolites and from 90.5 to 92.5 for harzburgites (Fig. 3a), with high Ni contents (2600-3620 ppm
182 and 2670-3540 ppm in lherzolites and harzburgites, respectively). Though conspicuous variability

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183 of Ni in ol within individual samples may suggest a potential interaction between MG xenoliths and
184 the host magma, the invariant Fo contents for each sample are inconsistent with melt-xenolith
185 reaction explaining the variable Ni contents. Specifically, it is noteworthy, that ol phenocrysts from
186 the host lavas have Fo content ranging from 86.1 to 87.2 and Ni contents from 2240 to 2251 ppm,
187 suggesting that melt-xenolith reaction may explain only a small component of the variable Ni
188 contents found in the MG xenolith suite (Fig. 3b).

189 Opx from unreacted core to reacted rims is chemically unzoned and frequently contains elongate
190 oriented rods of exsolved cpx. Opx $mg\# = 100 \times Mg / (Mg + Fe)_{\text{mol}}$ values vary from 91.2 to 92.8 for
191 both lherzolites and harzburgites, like the coexisting ol grains. Contents of Al_2O_3 in opx are highly
192 variable in lherzolite (1.68–4.18 wt.%) whereas a more restricted range is shown by harzburgites
193 (1.78–2.60 wt.%), reflecting a common "harzburgitic" melting degree, or limited temperature-
194 dependent subsolidus exchange with sp (Brey et al., 1999) (Fig. 3c). Contents of TiO_2 in lherzolites
195 are more variable (0–0.07 wt.%) than those of harzburgites (0–0.03 wt.%).

196 By texture the most reactive phase, cpx bears evident compositional heterogeneity within each
197 individual sample for most compositional features but $mg\#$. Along with the coexisting ol and opx,
198 $mg\#_{\text{cpx}}$ ranges from 91.0 to 93.3 across all lithologies. By contrast, the Al_2O_3 , Cr_2O_3 and to lesser
199 extent Na_2O are highly variable in both lherzolite and harzburgite cpx. Lherzolites generally show a
200 larger range in Al_2O_3 (1.73–4.53 wt.%), Cr_2O_3 (0.72–1.64 wt.%) and Na_2O (0.49–1.89 wt.%)
201 compared to harzburgites ($Al_2O_3 = 0.63$ to 3.79 wt.%; $Cr_2O_3 = 0.89$ – 1.52 wt.%; $Na_2O = 0.35$ – 1.18
202 wt.%; Fig. 3). The high chromium contents classify these crystals as chromiferous cpx (Morimoto,
203 1988) with TiO_2 being always less than 0.60 wt.% (Fig. 3f). $Mg\#$ values in cpx for both lherzolite
204 and harzburgite are not correlated with Al_2O_3 , Na_2O , and TiO_2 distribution as would be expected for
205 a mantle residual trend or, in turn, for alkaline basic-ultrabasic magma fractionation lines (Fig. 3d-f).
206 Accordingly, we interpret negligible, if any interactions between peridotites and basanitic host lavas.

207 Large compositional variations are exhibited in sp $cr\# = 100 \times Cr / (Cr + Al)_{\text{mol}}$ and $mg\#$, with
208 overlapping values for both lherzolite and harzburgite. However, $cr\#$ and $mg\#$ are homogenous

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209 within each individual sample with the exception of harzburgite MG13 (Fig. 3g). Across the
210 samples, cr# and mg# vary from Cr-rich in harzburgite (cr#: 38.3-67.2; mg#: 56.2-69.6) to Al-rich
211 types in lherzolite (cr#: 30.4-52.7; mg#: 62.2-75.9).

212

213 5.2 Pyroxene trace elements

214

215 Representative *in situ* (LA-ICP-MS) trace element analyses of pyroxenes are reported in Tables E-F
216 of the on-line Supplementary material. The values are shown in chondrite-normalized incompatible
217 trace elements (Fig. 4a, b; 5a, b) and rare earth element (REE) diagrams (Fig. 5c, d). In order to
218 ~~characterise~~ characterize the "original" features of the MG lithospheric domain prior to the
219 metasomatic event trace element contents of the cores of both opx and unreacted cpx core were
220 considered. One sample (harzburgite MG13) has only opx with rare cpx crystals occurring in
221 reaction areas, where their small size (<30 μm) prevent high resolved quantitative analysis.

222 Both lherzolite and harzburgite bear opx with heavy REE (HREE) contents in a narrow range
223 ((Tb/Lu)_N in lherzolites= 0.05-0.44; in harzburgites= 0.13-0.47) but large light (L)- middle (M)REE
224 variability between grains and samples (e.g., Eu_N). MG16 lherzolite shows distinctive opx REE
225 contents with nearly flat M-HREE ((Dy/Lu)_N=0.39-0.49) and LREE downward convex enrichments
226 ((La/Nd)_N=0.27-0.79) (Fig. 4a). MG1, MG6 lherzolite and MG14 harzburgite preserve residual M-
227 HREE signatures ((Dy/Lu)_N=0.18-0.37; Fig. 4a, b) typical of the sp-stability field after melt
228 extraction co-existing with an apparent LREE enrichment ((La/Nd)_N=1.05-13.1). In turn, opx of
229 MG13 harzburgite shows an overall M-HREE enrichment ((Dy/Lu)_N=0.41-0.42; Fig. 4b). Finally,
230 Ti shows both positive and negative anomalies in both xenolith rock types.

231 Across all lithologies MG cpx have an overall high REE content (ΣREE =185-621 ppm) and
232 distinctive LREE enrichment relative to HREE (La_N up to 100 times chondritic; (La/Yb)_N in
233 lherzolites = 9.58-26.68; (La/Yb)_N in harzburgites = 13.88-19.24).

234 The geochemical data, taken together, allow for two groups of cpx compositions to be defined.
235 Group-1 includes cpx of lherzolites MG1, MG6 and harzburgites MG13, MG14, which shows an
236 almost flat M-HREE pattern ($(\text{Sm}/\text{Lu})_{\text{N}} = 1.31\text{-}4.76$) with abrupt (more than one order of
237 magnitude) LREE-enrichment ($(\text{La}/\text{Nd})_{\text{N}} = 1.53\text{-}6.18$). Almost all these cpx display a positive Eu
238 anomaly ($([\text{Eu}_{\text{N}}/(\text{Sm}+\text{Gd})_{\text{N}}/2]) = 1.07\text{-}1.68$) (Fig. 5c). In turn, group-2 is constituted by cpx of
239 MG16 lherzolite only, which show distinctive convex upward REE pattern with a steep negative
240 slope from Nd to Lu ($(\text{Nd}/\text{Lu})_{\text{N}} = 14.0\text{-}18.0$) and a maximum at Pr_{N} (114-143) (Fig. 5d).
241 The entire MG cpx population has variable high Th and U content (Th and U up to 3.03 and 0.63
242 ppm, respectively) with negative anomalies in Ti and HFSE (e.g. Nb, Ta, Zr, and Hf), the most
243 evident being the Zr anomaly in harzburgite with Zr^* ($\text{Zr}_{\text{N}}/[(\text{Nd}+\text{Hf})_{\text{N}}/2]) = 0.09\text{-}0.24$ (Fig. 5a, b). It
244 should be noted that MG unreacted cpx have trace elements contents similar or even higher than
245 those of primary and secondary cpx from mantle xenoliths of the Lessini Mts. (Beccaluva et al.,
246 2001; Fig. 6).

247

248 6. Geothermobarometry

249

250 To estimate the temperature conditions under which the MG sp lherzolites and harzburgites were
251 equilibrated, we used the two-pyroxene geothermometer based on Fe/Mg exchange of Brey and
252 Köhler (1990) which we will denote as T_{BK} . Ol-sp geothermometers of Wells (1977) and Taylor
253 (1998) were also applied for comparative purposes and are denoted as T_{W} and T_{T} , respectively. For
254 the thermo-barometric calculations, we considered only cores of unreacted opx and cpx grains that
255 were in close contact.

256 Though some studies provide barometry, mainly based on the Ca distribution of ol and cpx (e.g.,
257 Köhler and Brey, 1990), determining appropriate barometry in sp-bearing peridotites (Medaris,
258 1999; O'Reilly et al., 1997) is challenging. Therefore, we assume the equilibrium pressure from
259 experimental stability phase relationships (Caldeira and Munhá, 2002). Taking into account the

260 absence of amphiboles (which could modify the peridotite mineral stability fields) and the presence
261 of sp as the sole aluminum-bearing phase, an upper limit of 2.1 GPa and a lower limit of 0.9 GPa
262 are set (Caldeira and Munhá, 2002; Green and Hibberson, 1970; Green and Ringwood, 1970;
263 O'Neill and Wall, 1987; Siena and Coltorti, 1989). This pressure approximation agrees with the
264 maximum depth of the local SCLM, constrained by seismic profiles (Carminati and Doglioni, 2012)
265 to fall within the 1.5-2.0 GPa range. The pyroxene Fe/Mg exchange is largely dependent on
266 temperature (Brey and Köhler, 1990; Wells, 1977; Wood and Banno, 1973) and is relatively
267 insensitive to pressure; temperatures calculated at 1.0 GPa and 2.0 GPa show only minor variations
268 ($<10^{\circ}\text{C}$). Accordingly, primarily for comparative purposes, temperature calculations were made at a
269 fixed pressure of 1.5 GPa.

270

271 *6.1 Equilibration temperatures*

272

273 MG sp-lherzolites record residual temperatures in the range of 923-1058°C. The highest value
274 (MG16) is comparable with those recorded by the two MG harzburgites (MG13: $1117 \pm 20^{\circ}$;
275 MG14: $1033 \pm 30^{\circ}\text{C}$; Table 2). This is in agreement with its low cpx content (6%), which could
276 reflect a residual character analogous to harzburgites. We compared MG peridotites equilibration
277 temperatures with those from the nearby districts of Lessini Mts. and Val d'Adige calculated with
278 the Wells (1977) and Taylor (1998) geothermometers (Gasperini et al., 2006).
279 For comparison, equilibration temperature of a few Lessini Mts. and Val d'Adige peridotites were
280 recalculated together with MG samples of this work applying the three thermobarometric models
281 (Table 2). We observed that: i) as seen in other geothermobarometric studies (e.g., Greenfield et al.,
282 2013), T_{r} values are always lower than T_{BK} and T_{w} ; ii) with the exception of one sample from
283 Lessini Mts., differences between T_{BK} and T_{w} within each sample are negligible ($<20^{\circ}\text{C}$); iii) T_{r}
284 diverges from T_{BK} by 2 to 78°C and diverges from T_{w} from by 19 to 78°C.
285 Taking this into account, the temperature range of 923-1117°C recorded by MG peridotites is

286 higher than most of Val d'Adige (T_{BK} : 896-902°C) and of Lessini Mts. (T_{BK} : 885-975°C) xenoliths.
287 Looking at the entire VVP mantle domain, the high equilibration temperatures recorded for MG
288 mantle xenoliths are only comparable to the highly metasomatized Lessini Mts. peridotites (1130 ±
289 60°C) studied by Siena and Coltorti (1989) (Fig. 7).

290

291 6.2 Oxygen fugacity

292

293 Oxygen fugacities for Marosticano peridotites were estimated using the method of Ballhaus et al.
294 (1991) using temperatures provided by the Brey-Köhler thermometer (T_{BK}). Calculated fO_2 values
295 are plotted in Fig. 7 in logarithmic units with respect to the fayalite-magnetite-quartz (FMQ) buffer
296 ($\Delta\log fO_2$). Estimates for the two sp-harzburgites range from +0.6 to +0.9, while for the sp-
297 lherzolites the range is wider (-0.6 to +1.1), with MG6 lherzolite being the most reduced sample.
298 With the exception of the latter xenolith, MG peridotites are more oxidized than Val d'Adige
299 lherzolites (Table 2 and Fig. 7, $\Delta\log fO_2$ (FMQ) from +0.2 to +0.3 as calculated for compositions
300 from Gasperini et al., 2006 and T_{BK} from Table 2). The Lessini Mts. peridotites also yield more
301 variability in the recorded redox conditions ($\Delta\log fO_2$ (FMQ) from -1 to +1, calculated from data of
302 Gasperini et al., 2006 and Siena and Coltorti, 1993; Table 2) encompassing the entire range of
303 Marosticano and Val d'Adige samples (Fig. 7).

304

305 7. Discussion

306

307 7.1. A cratonic origin?

308

309 The highly refractory bulk composition of lherzolites ($Al_2O_3 < 1.03$ wt.%, mg# 90.3-91.6; Table 3),
310 associated with low Al_2O_3 contents, high mg# values in both pyroxenes and sp of MG peridotites
311 (Fig. 3c-d and Tables B-D in the on-line Supplementary material) testify for a large extraction of

312 basaltic melts from the Marosticano mantle domain which appears the most residual of the entire
313 VVP (e.g., Lessini Mts. lherzolites: $Al_2O_3 > 2.52$ wt.% and mg# 85.8-89.9).

314 Peridotites with refractory composition are expected in Phanerozoic and Proterozoic off-craton
315 mantle and ophiolites. They generally follow the so-called "residual or oceanic trend", explained as
316 an extraction of basaltic components, resulting in an increase of Fo content in ol accompanied by
317 increased ol modal content (Boyd, 1989). Refractory peridotites characterize also the cratonic
318 mantle, but they rarely follow the oceanic trend (Bernstein et al., 2007; Boyd, 1989; Boyd et al.,
319 1997; Ionov et al., 2010). They are characterized by ol with a range of high Fo content (~91-94) at
320 extremely variable modal ol content (~40-75%). In particular, the high Fo of ol in sp-bearing
321 (shallow) cratonic peridotites with relatively low opx modal content (<20%) (e.g., Tanzanian,
322 Greenland, and Slave Cratons) are indicative of high degrees (~30 to 50%) of partial melting in
323 thermal regime active only till Archean/~~early-early~~ Proterozoic time (Ionov et al., 2010; Walter,
324 2003).

325 MG ol plotted (Fig. 3a) in the Boyd diagram (Boyd, 1989; Boyd et al., 1997) plot off the oceanic
326 trend, and follow the general behavior of cratonic ol (i.e. Kapvaal, Tanzanian, Greenland and Slave
327 Cratons). While most of the Val d'Adige and Lessini Mts. exhibit lower ol modal contents at lower
328 Fo following the oceanic trend (Fig. 3a). In addition Marosticano ol have also Ni values higher than
329 those of Lessini Mts. but similar to those of Val d'Adige (Fig. 3b).

330 In association with high-Fo ol, MG peridotites show high Mg-opx in the range of 30-12% modal
331 contents (Table 1), out of any "ideal" Phanerozoic (abyssal, oceanic and continental) off-craton
332 melting trend (Niu, 2004; Pelorosso et al., 2016). Instead, they recall a general ol-opx behavior
333 recorded in "shallow" (garnet-free) cratonic mantle and interpreted as physical segregation of ol and
334 opx in high-pressure melting residuum and polybaric re-equilibration (Bernstein et al., 2007; Ionov
335 et al., 2010). In addition, trace element distributions in opx from MG16 lherzolite and MG13
336 harzburgite show almost flat M-HREE profiles (i.e. $(Dy/Yb)_N$), consistent with an original
337 subsolidus equilibrium with garnet (Bonadiman et al., 2005). In garnet-bearing lherzolites at

338 progressively decreasing sub-solidus T (1300-900°C), opx decreases the total REE contents with
339 equal M-HREE solid-solid partition coefficient (Sun and Liang, 2014). In turn opx of MG1, MG6
340 and MG14 seem to be originally equilibrated in the sp stability field showing the typical steep slope
341 for M-HREE at comparable subsolidus temperature (1000-900°C) (Sun and Liang, 2014) (Fig. 4a,
342 b).

343 Spinel, the distinctive phase of the great majority of off-craton mantle xenoliths, has cr# (30-67)
344 which suggests a residual component neither coherent with the oceanic residual trend (i.e.
345 “OSMA”; Arai, 1994a, 1994b) nor with the more fertile VVP-mantle fragment (cr# 9-12). On the
346 other hand, Marosticano sp mimic the tendency observed for sp coexisting with ol in shallow on-
347 craton (garnet-free) xenoliths (Bernstein et al., 2007).

348 In this refractory P-T system, ol Fo of 91.5 and sp cr# of 60.0 would suggest strong (or complete)
349 cpx consumption by high degrees of partial melting (>25%; Bernstein et al., 2007; Bonadiman et al.,
350 2005; Hellebrand et al., 2001; Scott et al., 2016; Walter, 2003) that are typical of the Archean or
351 ~~Early~~-early Proterozoic mantle (Walter, 2003). Therefore, we suggest that the partial melting
352 occurred at high melting T and thus more likely in an old mantle thermal regime. Subsequently, the
353 Marosticano mantle was enriched, forming the observed cpx (cpx modal contents 4-13%) in MG
354 xenolith. These are thus secondary in nature in accordance with several studies demonstrating that
355 most cpx in on-craton mantle may have a metasomatic legacy (Grégoire et al., 2003; Pearson et al.,
356 2003; Simon et al., 2003; 2007).

357 To sum up, Marosticano xenoliths are characterized by cratonic fingerprints (Fig. 3a), according to
358 major and trace element compositions of the peridotite phases, and Re-Os geochronological
359 modeling (T model age: 2.1-2.9; Brombin et al., in prep.). These geochemical characteristics are
360 evident only for the Marosticano mantle fragments, whereas the rest of the VVP mantle is, as
361 expected, off-craton SCLM. The sole, intriguing link between on-craton and off-craton VVP mantle
362 is the similarity of the Re-Os ages, ranging between 1.9 to 2.1 Ga, with a unique value at 3.1 Ga for

363 the entire VVP domain. These results speak in favor for a continuum geodynamic set which
364 includes on-craton and off-craton mantle portions, as more frequently reported.

365 Cratonic signatures in off-craton sp-bearing mantle xenoliths derived from intra-plate volcanic areas
366 are recognized in a few mantle xenolith populations, e.g. in the Massif Central (France; Lenoir et al.,
367 2000), West Otago (New Zealand; Liu et al., 2015; Scott et al., 2014, 2016) and Cape Verde
368 (Bonadiman et al., 2005; Coltorti et al., 2010).

369 In the Massif Central, two contrasting shallow lithospheric domains are faced. Relatively refractory
370 (i.e., $Al_2O_3 < 2.0$ wt.%) and highly fertile (i.e., $Al_2O_3 > 4.0$ wt.%) lherzolites and harzburgites are
371 interpreted as reminiscent of cratonic and circumcratonic SCLM domains, respectively (Lenoir,
372 2000). West Otago sp-peridotites with high variable Re depletion Os model ages (0.5-2.7 Ga)
373 would represent relicts of Archean depleted mantle residues recycled through the asthenosphere
374 over Ga timescales along with more fertile convecting mantle (Liu et al., 2015; McCoy-West et al.,
375 2013). Therefore, different remnants of shallow lithospheric domains are incorporated within the
376 young (<300 Ma) Zealandia microplate.

377 It is important to note that “shallow” (garnet-free) cratonic mantle is not exclusive of continental
378 setting. Cape Verde Islands lie in the Atlantic Ocean, in a clearly oceanic setting. Here Archean sp-
379 bearing mantle xenoliths, record garnet precursor and K-rich metasomatism (Bonadiman et al.,
380 2005), suggesting the involvement of ancient geochemical reservoir also for the genesis of oceanic
381 basalts (Coltorti et al., 2010).

382 Although Archean cratons are considered ancient continental nuclei characterized by tectonic
383 inactivity for at least the past 2 Ga and low heat flow, recent studies show that their highly
384 refractory mantle roots are intensively ~~modify-modified~~ over the-time by mechanical destructions
385 (lithospheric thinning and incipient rifting) and by episodic rejuvenation events (Foley, 2008; Tang
386 et al., 2013; Zhang et al., 2009a; Zhang et al., 2012).

387 ~~The~~ Wyoming Craton and North China Craton are well-known examples of complete chemical
388 rejuvenation by varying degrees of refertilization (Eggler and Furlong, 1991; Fan and Menzies,

389 1992; Tang et al., 2008, 2012, 2013). In turn, other cratons might have not yet suffered large-scale
390 removal of their ancient keels but they are in the early stages of disruption due to the efficiency of
391 extensive regime (Foley, 2008). We recall that Lessini Mts. and Val d'Adige xenoliths are generally
392 fertile lherzolites with cpx and opx coherently showing the typical LREE-depleted, M-REE flat and
393 steep H-LREE fractionated patterns respectively (Beccaluva et al., 2001; Lenoir et al., 2000). These
394 features are chemically contrasting with the refractory nature and the LREE enrichments of
395 Marosticano xenolith population.
396 These differences could be interpreted in terms of compositional rejuvenation of the circumcratonic
397 domains. Lessini Mts. and Val d'Adige xenoliths may be the fragments of the ancient SCLM,
398 strongly refertilized by infiltration of asthenosphere-derived melts, rather than newly accreted "off-
399 craton" SCLM. By contrast, Marosticano domain could be interpreted as the vestige of an old
400 (Archean?) SCLM block that underwent depletion via melt extraction and was afterward
401 pervasively metasomatized by CO₂-rich silicate melts, a process, ~~that~~ however, was not able to
402 erase fully the original cratonic nature.

403

404 7.2 Metasomatic origin of clinopyroxene in Marosticano xenoliths

405

406 Despite the general refractory features of MG peridotites, a superimposed metasomatic process is
407 manifested by major and trace element geochemistry of both pyroxenes. Trace-element
408 compositions of Marosticano cpx show variable enrichment characteristics, inconsistent with a
409 residual origin after melt extraction (e.g Sun et al., 2012). They exhibit a notable LREE-enrichment
410 (Fig. 5c, d), a fractionated REE pattern and a general HFSE depletion (Fig. 5a, b) with respect to C1
411 model trace element abundances (Sun and McDonough, 1989). Taken together, these signatures
412 confirm that cpx is a phase either formed by a reaction of a residual peridotite with metasomatic
413 melts or it is a new phase directly ~~crystallised~~ crystallized from the metasomatic agents.

414 As nearby VVP districts (Lessini and Val d'Adige) are thought to have been affected by silicatic
415 metasomatism (Beccaluva et al., 2001), we first evaluated whether the MG mantle segment could
416 have been also explained by the same type of metasomatism. Taking into account only those
417 Lessini and Val d'Adige samples that show cpx modal contents and cpx-opx mg# values
418 comparable to those of MG xenoliths, trace element compositions of MG cpx are significantly
419 enriched compared to the primary, spongy and secondary VVP cpx (Fig. 6). This suggests that MG
420 were pervaded by a metasomatic agent that was different from that which affected the rest of the
421 VVP region. However, both group-1 and group-2 cpx are more enriched in LREE (Fig. 5c, d) and
422 depleted in Ti and in HFSE (e.g., Zr, Fig. 5a, b) arguing against a "pure" alkali silicate melt
423 metasomatism and favouring instead the contribution of a carbonatic component. In fact,
424 experimentally produced silica-bearing carbonatite melts crystallize cpx with major element
425 composition similar to both MG group-1 and group-2 cpx (Fig. 3d-f).

426 Enrichment in LREE accompanied by strong HFSE depletion (Fig. 5a, b) of group-1 and group-2
427 cpx is notably assigned to an effect of the cpx-carbonatite partitioning as shown by experimental
428 and empirical data by Dasgupta et al. (2009), Dixon et al. (2008), Gudfinnsson and Presnall (2005)
429 and Pokhilenko et al. (2015). This geochemical effect has been observed in various carbonatite
430 ~~metasomatized-metasomatized~~ mantle xenoliths from both oceanic and continental settings (i.e.
431 Spitsbergen, Ionov, 1998; North China Craton; Sun et al., 2012; New Zealand, Scott et al., 2016;
432 Comores Archipelago; Coltorti et al, 1999).

433 Cpx group-2 mimics the steep M-HREE fractionated pattern, but they have remarkably higher
434 LREE content with respect to cpx formed by a carbonatitic/CO₂-rich silicate melt experimentally
435 obtained at pressure of 6.6 GPa in equilibrium with garnet (Dasgupta et al., 2009) (Fig. 8). The
436 calculated ^{cpx-carb}D_{L3} at this pressure is 0.006 but systematically increases with decreasing pressure
437 and with the sp appearance (Dasgupta et al., 2009). Therefore, if we consider REE cpx/carbonatite
438 partition coefficients calculated for 2 GPa and 1100-1150°C (e.g., ^{cpx-carb}D_{L3} of 0.09; Klemme et al.,

439 1995) we can reproduce the general shape of the L- to M-HREE pattern of both MG cpx groups
440 (Fig. 8).

441 The only remarkable difference between group-1 and group-2 cpx is that the former shows a less
442 steep, or flat, HREE pattern indicating that carbonatitic melts migrated and interacted with slightly
443 different peridotitic wallrocks. This could be attributed to a chromatographic fractionation of a
444 metasomatic agent interacting with different peridotitic wallrocks (Ionov et al., 2002; Sen et al.,
445 1993). In this scenario, the concentration fronts of the migrating melts are controlled by the ion-
446 exchange with the peridotitic matrix. In general, the fronts of the more incompatible elements (e.g.,
447 LREE) travel faster than those of less incompatible ones (e.g., M-HREE) producing enrichments in
448 LREE and depletion or flatness in HREE of the whole rock depending on the original peridotitic
449 matrix (Ionov et al., 2002). In this frame, the cpx group-1 records a continuum feeding of REE from
450 the carbonatitic melt to a possible residual (primary?) cpx (Ionov et al., 2002; Pokhilenko et al.,
451 2015; Sen et al., 1993). On the contrary, the convex-upward REE patterns of cpx group-2 may
452 reflect nearly complete equilibration between the peridotite matrix (mainly ol-opx) and the
453 metasomatic melt (Dasgupta et al., 2009; Dixon et al., 2008).

454 In anhydrous garnet-free peridotites, restitic opx is the counterpart of cpx to incorporate the
455 incoming geochemical budget. The only evidence of metasomatic effects in the MG orthopyroxenes
456 is their high Ti content (up to 281 ppm), not coherent with their low Al_2O_3 (Fig. 9; Scott et al.,
457 2016) and in antithesis with the carbonatitic enrichment described for the cpx. This can be
458 explained by the action of CO_2 -rich silicate melts which could primarily impart a carbonatite-like
459 trace element signature in cpx (i.e., L-REE) hiding the potential effects of silicate melts (i.e., Ti
460 enrichment), that in turn is magnified in the residual opx (Scott, et al., 2016). Spinel-facies cpx
461 prefers most trace elements, including Ti, compared to opx; however, relative to elements with
462 slightly larger and smaller atomic radii (Eu and Dy), Ti is slightly less favorably partitioned into
463 cpx (Eggins et al., 1998; Scott, et al., 2016). This nuance leads to the formation of small negative Ti
464 anomalies in cpx and a corresponding positive anomaly in opx (Scott et al., 2016). Consequently,

465 both negative and positive Ti anomalies observed in MG opx could be due to a chromatographic
466 fractionation effect during the interaction between carbonatite/CO₂-rich silicate melts and a
467 different peridotitic wallrock where cpx was present or not (Scott et al., 2016; Ionov et al., 2002;
468 Scott et al., 2016; Sen et al., 1993).
469 Though we cannot resolve if this metasomatism initially occurred in the garnet stability field and
470 continued in shallower portions of the MG mantle we can assume that the product of such
471 metasomatism may be stabilized at P conditions of the sp stability field. Accordingly, we interpret
472 the geochemical characteristics (major and trace elements) acquired by MG pyroxenes as consistent
473 with "new" cpx formed by the interaction of a carbonatitic melt with a cratonic flavored ambient
474 peridotite (Griffin et al., 1999; Spengler et al., 2006). Notably, experimental studies (e.g., Dasgupta
475 et al., 2006, 2007; Green, 2015; Hammouda and Keshav, 2015; Hirose, 1997) suggest that a carbon-
476 rich peridotite is necessary to form alkaline and in particular ultra-alkaline mantle melts. Similarly,
477 carbonatitic components have been hypothesized as important contributors to VVP alkaline- to
478 ultra-alkaline magmas, the hosting lavas that ferry VVP mantle xenoliths to the surface (Beccaluva
479 et al., 2007).

480 *7.3 Relationship between carbonatite/CO₂-rich silicate metasomatism and fO₂ conditions*

483 As carbonatite/CO₂-rich silicate melts contain large amounts of dissolved fluids, they are able to
484 mobilize volatile elements (C-OH, but also Na and K as lithophile elements); accordingly, their
485 interaction with the peridotite matrix may affect the redox conditions (Dasgupta et al., 2013). MG
486 peridotites represent a cratonic "enclave" of continental mantle of the Adria ~~Plate-plate~~ that was
487 later pervaded by carbonatite metasomatism. The high fO₂ (Fig. 7), comparable with the other VVP
488 mantle occurrences and within the range of the subcontinental lithospheric mantle (Foley, 2011), is
489 not compatible with a cratonic origin but requires a late oxidation event, preserved until the xenolith
490 exhumation by Cenozoic host lavas. Volatile mass transport occurs mostly by fluid and silicate

491 (with prevailing H₂O) or carbonate melts (with prevailing CO₂) as function of the redox state of the
492 mantle (Foley, 2008, 2011; Frost and McCammon et al., 2008; Pokhilenko et al., 2015). Assuming
493 the relatively high ~~oxidising-oxidizing~~ conditions of Marosticano peridotites were affected by CO₂-
494 bearing melts, we calculated CO₂ mole fractions of such melt~~s~~₄ using the equation of Stagno and
495 Frost (2010). We obtained CO₂ mole fractions close to or slightly higher than 1.0, taking into
496 account the T_fO₂ values independently calculated from the silicate parageneses (Table 2). This is
497 also evident in the diagram of *f*O₂ as a function of potential T (Goncharov et al., 2012), where
498 almost all the Marosticano peridotites straddle the field for carbonatite and CO₂ fluid (Fig. 10). This
499 may suggest that the Marosticano geothermobarometric conditions record this matrix/carbonatitic
500 melt interaction, rather than the T_fO₂ values of the initial cratonic lithospheric mantle.

501 The variable redox states of the MG xenolith population may also influence the Eu oxidation state
502 (Eu³⁺ or Eu²⁺; Henderson, 1984) and may explain why this element is enriched in group-1 cpx. In
503 oxidized magma Eu is an incompatible element in the trivalent form (Eu³⁺), while in reduced
504 magma it is preferentially incorporated into plagioclase in its divalent form (Eu²⁺). This ion-
505 exchange process explains the negative Eu anomaly in many terrestrial basalts showing plagioclase
506 as liquid phase. However, Eu speciation is highly sensitive to small redox variations. Thus the
507 different accommodation of Eu in minerals may change rapidly (McLennan, 2001).

508 Almost all group-1 cpx have M-HREE flat profiles with evident positive Eu anomaly (Fig. 5a, c).
509 These anomalies are not accompanied by a positive K (not reported) or Sr anomaly, that could be
510 assigned to the melting of pre-existing phlogopite and plagioclase respectively, in the protolith
511 (Marchesi et al., 2013; Tang et al., 2017), neither of which were observed in any Marosticano
512 xenolith. In other xenolith suites, examination of the Eu content in garnet and cpx in eclogites led to
513 the suggestion that the positive Eu anomaly results from ~~the~~ interplay between crystal chemistry
514 and redox conditions during metasomatism (Griffin and O'Reilly, 2007). Karner et al. (2010)
515 determined the Eu partition coefficient between augite and melt (^{cpa/melt}D_{Eu}) in samples ~~crystallised~~
516 ~~crystallized~~ from a highly Eu spiked Martian basalt composition at different *f*O₂ conditions. These

517 authors observed that D_{Eu} augite/melt steadily increases with fO_2 since Eu^{3+} is more compatible
518 than Eu^{2+} in the pyroxene structure; thus increasing fO_2 leads to greater Eu^{3+}/Eu^{2+} in the melt,
519 allowing for more Eu (total) to partition into the cpx. It is worth noting that positive Eu anomalies
520 are occasionally observed in cpx from metasomatized suboceanic mantle or subcontinental cratonic
521 mantle in both sp and garnet stability field irrespective of the nature of the metasomatic melts (e.g.,
522 xenoliths from Loch Roag, North Atlantic Craton, Northern Scotland, Hughes et al., 2015; from
523 Siberian Craton, Pearson et al., 1995; Slave Craton, Heaman et al., 2002; Kaapval craton, Jacob et
524 al., 2003). On the basis of these considerations, we suggest that a small variation of the redox state
525 may induce Eu to modify its solid/solid, solid/melt partitioning behavior, without any change of the
526 large-scale geochemical process.

527 The interaction between the Marosticano residual mantle with a carbonatite/ CO_2 rich silicate melt is
528 explained by a possible chromatographic fractionation effect only in group-1 peridotite. This leads
529 to a “local” variation of fO_2 , ~~oxidising-oxidizing~~ conditions and by consequence to a “local” increase
530 of the Eu^{3+}/Eu^{2+} ratio in the melt and to higher Eu concentration in the newly formed cpx. Group-2
531 clinopyroxene is suggested to ~~crystallise-crystallize~~ from the carbonatitic/ CO_2 -rich silicate melts
532 that control the environmental redox condition.

533

534 8 Conclusions

535

- 536 • Petrological and geochemical features of the newly discovered Marosticano peridotite xenoliths
537 indicate that they represent a mantle segment geochemically distinctive from the other VVP
538 peridotites (i.e., Lessini Mts. and Val d’Adige), contributing to enlarge the knowledge of spatial
539 heterogeneity within the mantle of this region.
- 540 • MG lherzolites and cpx-bearing harzburgites demonstrate complete sp-facies equilibration.
541 Mineral major and trace elements features are comparable to those observed for on-craton
542 peridotites worldwide.

543 • Marosticano cpx are secondary in nature and they exhibit a substantive LREE-enrichment, a
544 fractionated REE pattern with positive Eu anomaly, almost flat (cpx group 1) or steep (cpx
545 group 2) HREE patterns, and a remarkable HFSE depletion. These characteristics are attributed
546 to a chromatographic separation of a metasomatic agent with high carbonatitic/CO₂-rich
547 silicatic components.

548 • Marosticano samples record relatively high oxidation conditions similar to those of the VVP
549 off-craton xenoliths (e.g. Lessini Mts.) but anomalous for a proper cratonic environment. These
550 T₂O₂ relationships are probably due to the ~~action-oxidizing nature~~ of CO₂-rich circulating fluids
551 ~~playing an oxidizing role~~.

552 • The variable, but generally high, redox states of the MG xenolith could be responsible for the
553 positive Eu anomaly in cpx group-1. As higher fO₂ leads to higher Eu³⁺/Eu²⁺ in the melt
554 increasing the element partitioning in cpx, the positive Eu anomaly could result from the
555 relatively high redox condition of the Marosticano mantle fragment during the formation of
556 group-1 cpx. On the contrary, group-2 cpx that do not show positive Eu anomalies may show
557 the fingerprint of a carbonatitic/CO₂-rich silicate melt metasomatism, therefore still recording
558 the original redox condition.

559 • Within the SCLM sampled by VVP magmatism, only Marosticano xenoliths show evidence of
560 carbonatitic metasomatic overprinting of a likely cratonic mantle domain. All the other mantle
561 VVP mantle xenoliths exhibit characteristics of off-craton lithospheric mantle variably affected
562 by Na-alkaline silicatic metasomatism.

563 • The lithospheric mantle beneath the Adria ~~Plate-plate~~ has been affected by complex enrichment
564 and refertilization processes, related to a geodynamic scenario dominated by extension-related
565 magmatism in response to the near active collision between Eurasia and Africa plates (Fig. 11).

566 • The geochemical features of Marosticano mantle xenoliths introduce a cratonic component in
567 the geodynamic evolution of the Adria ~~Plate-plate~~ system in the general frame of the
568 geodynamical reconstruction of the Africa/Eurasia collision. From our current study, together

569 with literature data, we interpret that the cratonic keel is preserved only in the Marosticano
570 district, while Lessini Mts. and Val d'Adige mantle domains could be circumcratonic portions
571 refertilized by infiltration of asthenospheric-derived melts (Fig. 11).

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573

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575

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582

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872

873 **Figure captions**

874

875 Fig. 1. Geological map of the Veneto Volcanic Province (De Vecchi and Sedea, 1995), showing the
876 location of Monte Glosio, xenolith site in Marosticano volcanic district. Inset a) Locations of VVP
877 in the Italian peninsula, European, African and Adria Plates. The white arrows show the subduction
878 directions (modified after Carminati and Doglioni, 2012-modified).

879

880 Fig. 2. Photomicrographs of representative microstructures in the MG xenoliths. (a) clinopyroxene
881 with cloudy, spongy rims near a kinked olivine; (b) clinopyroxene with cloudy, spongy rims; (c)
882 reaction areas surrounding a spinel, constituted by small crystals of olivine, clinopyroxene, spinel
883 and rare glass; (d) orthopyroxene crystals showing a reaction rim composed of secondary
884 clinopyroxene and olivine.

885

886 Fig. 3. Compositional variations vs $mg\# [=MgO/(MgO+FeO)mol\%]$ for MG xenoliths, Lessini Mts.
887 peridotites (from Beccaluva et al., 2001; Gasperini et al., 2006; Morten et al., 1989; Siena and
888 Coltorti, 1989), Val d'Adige xenoliths (from Gasperini et al., 2006): (a) modal olivine
889 compositional variation (wt.%) vs Fo, the "oceanic trend" (from Boyd, 1989) is also shown (b)
890 olivine compositional variation in terms of Ni (ppm) vs. Fo; fields of olivines from Archean craton
891 peridotites, both garnet and spinel facies (Kelemen et al., 1998) and Phanerozoic mantle array
892 (Takahashi, 1987) are also plotted; (c) orthopyroxene compositional variation in terms of Al_2O_3 vs.
893 $mg\#$; (d) clinopyroxene compositional variation in terms of Al_2O_3 vs. $mg\#$; (e) clinopyroxene
894 compositional variation in terms of Na_2O vs. $mg\#$; (f) clinopyroxene compositional variation in
895 terms of TiO_2 vs. $mg\#$; (g) spinel compositional variation in terms of Cr_2O_3 vs. $mg\#$. In b, d, e, f
896 hypothetical trend of interaction with M. Glosio host lava is shown. In d, e, f black crosses represent
897 average major element compositions of cpx ~~crystallised~~ crystallized from silica-bearing carbonatite

898 melts (from Dasgupta et al., 2009), they are plotted for defining metasomatic agents of MG
899 xenoliths. Filled and open symbols are for lherzolite (Lh) and harzburgite (Hz), respectively.

900

901 Fig. 4. Chondrite-normalized (Sun and McDonough, 1989) incompatible trace elements diagrams
902 for opx in MG lherzolites (a) and harzburgites (b).

903

904 Fig. 5. Chondrite-normalized (Sun and McDonough, 1989) incompatible trace elements diagrams
905 of cpx group-1 (a) and cpx group-2 (b). Chondrite-normalized (Sun and McDonough, 1989) REE
906 patterns of cpx group-1 (c) and cpx group-2 (d).

907

908 Fig. 6. Comparison of chondrite-normalized (Sun and McDonough, 1989) trace element
909 distributions of MG cpx (this study) and primary, spongy, secondary cpx from VVP xenoliths
910 (Beccaluva et al., 2001) that exhibit comparable cpx modal contents and cpx-opx mg# values.
911 Patterns of VVP cpx (Beccaluva et al., 2001) are represented with shadowed areas.

912

913 Fig. 7. Temperatures and $\Delta\log f_{O_2}$ relative to the buffer reaction fayalite-quartz-magnetite ($\Delta\log f_{O_2}$
914 FQM). Temperatures are calculated using the approach of Brey and Köhler (1990). $\Delta\log f_{O_2}$
915 estimates are calculated with the method of Ballhaus et al., 1991. P is fixed at 1.5 GPa. Filled and
916 open symbols are for lherzolite (Lh) and harzburgite (Hz), respectively. $T_j f_{O_2}$ conditions of Lessini
917 and Val d'Adige lherzolites are calculated using EMP data from Gasperini et al., 2006. Shadowed
918 area represents the $T_j f_{O_2}$ range of highly metasomatized Lessini xenoliths previously reported in
919 Siena and Coltorti (1989).

920

921 Fig. 8. Comparison of chondrite-normalized REE patterns of MG cpx (this study),
922 carbonatitic/ CO_2 -rich silicate melt experimentally obtained at pressure 6.6GPa in equilibrium with

923 garnet (Dasgupta et al., 2009) and modeled cpx formed by a carbonatite/CO₂-rich silicate melt
924 applying ^{cpx/cab}D calculated at 2 GPa 1100-1150°C (Klemme et al., 1995) (shadowed area).
925 Chondrite compositions for the normalisation of all compositions are from Sun and McDonough
926 (1989).

927
928 Fig. 9. Orthopyroxene Ti (ppm) and Al₂O₃ (wt.%) contents are consistent with depletion due to melt
929 extraction followed by Ti enrichment due to and CO₂-rich silicatic metasomatism (from Scott et al.,
930 2016).

931
932 Fig. 10. Oxygen fugacity (Δlog/O₂) vs. temperature for MG xenoliths. Stability fields of diamond,
933 graphite and carbonates are delineated by the graphite/diamond transition and the EMOD/G and
934 D/GCO oxygen buffers (Goncharov et al., 2012 and references therein). Almost all the Marosticano
935 peridotites straddle the fields for carbonatite and CO₂ fluid suggesting that the Marosticano
936 geothermobarometric conditions record the interaction between matrix and carbonatite/CO₂-rich
937 silicate metasomatic melts.

938
939 Fig. 11. Summary sketch of the model presented of the processes significant in the VVP mantle
940 during the European/Adria collision. Purple denotes the cratonic keel preserved beneath the
941 Marosticano district, and blue represents the refertilized cratonic portions due to the infiltration of
942 asthenospheric-derived melts beneath the Lessini Mts. and Val d'Adige districts.

943 **Supplementary material**

944

945 **I. Analytical methods**

946

947 Major element compositions of minerals from xenoliths and host lavas were analyzed at the Istituto
948 di Geoscienze e Georisorse, CNR, Padua (Italy) on Electron MicroProbe (EMP), using ZAF on-line
949 data reduction and matrix correction procedure. An acceleration voltage of 20 keV and sample
950 currents of 20 nA with 10-20 s counting time on peak position was used. Synthetic oxide standards
951 (MgO, FeO, MnO, ZnO, NiO, Al₂O₃, Cr₂O₃, TiO₂ and SiO₂) were used. Analytical precision is
952 better than ±2% for elements in the range of >10 wt.%, better than 5% for elements in the range 2-
953 10 wt.%, and better than 10% for elements in the range 0.5-2 wt.%.

954

955 Trace element concentrations in cpx and opx were obtained by Laser Ablation Inductively Coupled
956 Plasma Mass Spectrometry (LA-ICP-MS) at the Department of Earth Sciences, University of New
957 Hampshire (USA) using an Analyte Excite 193 nm excimer laser plumbed into a Nu instruments
958 AttoM high resolution inductively coupled plasma mass spectrometer. Typical spot size was 65 µm,
959 and laser operating conditions were 6.0 mJ at 80% output, fluence of 8.1 J/cm² and repetition rate of
960 5 Hz. Silicate glass MPI-Ding standard, ML3B-G (Jochum et al., 2006), was used as the calibration
961 standard every four sample spots to correct for within-run instrumental drift. Resulting data were
962 then processed with the Lolite software package, using calcium data from EMPA as an internal
963 standard. Precision and accuracy were assessed to be within 10% for ppm-level concentrations by
964 repeated measurements of KH-1 and KL2-G as independent standards. Results of the repeated
965 “blind” standard results are present in Supplementary material Table G.

966

967 Two out of five samples only were suitable for bulk rock analyses. Major elements were determined
968 by Wavelength Dispersive X-Ray Fluorescence Spectrometry (WDXRF) on pressed powder pellets

969 at the Dipartimento di Fisica e di Scienze della Terra, Università di Ferrara (Italy), using an ARL
970 Advant-XP spectrometer, following the full matrix correction method proposed by Traill and
971 Lachance (1966). Accuracy is generally lower than 2% for major oxides.

972

973 **References**

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979

980

981

982

983 **On-line Supplementary material (Excel file)**

984 Major (wt.%) abundances of representative olivine (Table A), orthopyroxenes (Table B),
985 clinopyroxenes (Table C) and spinel (Table D) in MG spinel peridotite xenoliths. Trace element
986 (ppm) abundances of representative orthopyroxenes (Table E), clinopyroxenes (Table F) in MG
987 spinel peridotite xenoliths. Table G: Standard used for LA-ICP-MS analyses. The values are in ppm.

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Figure 1

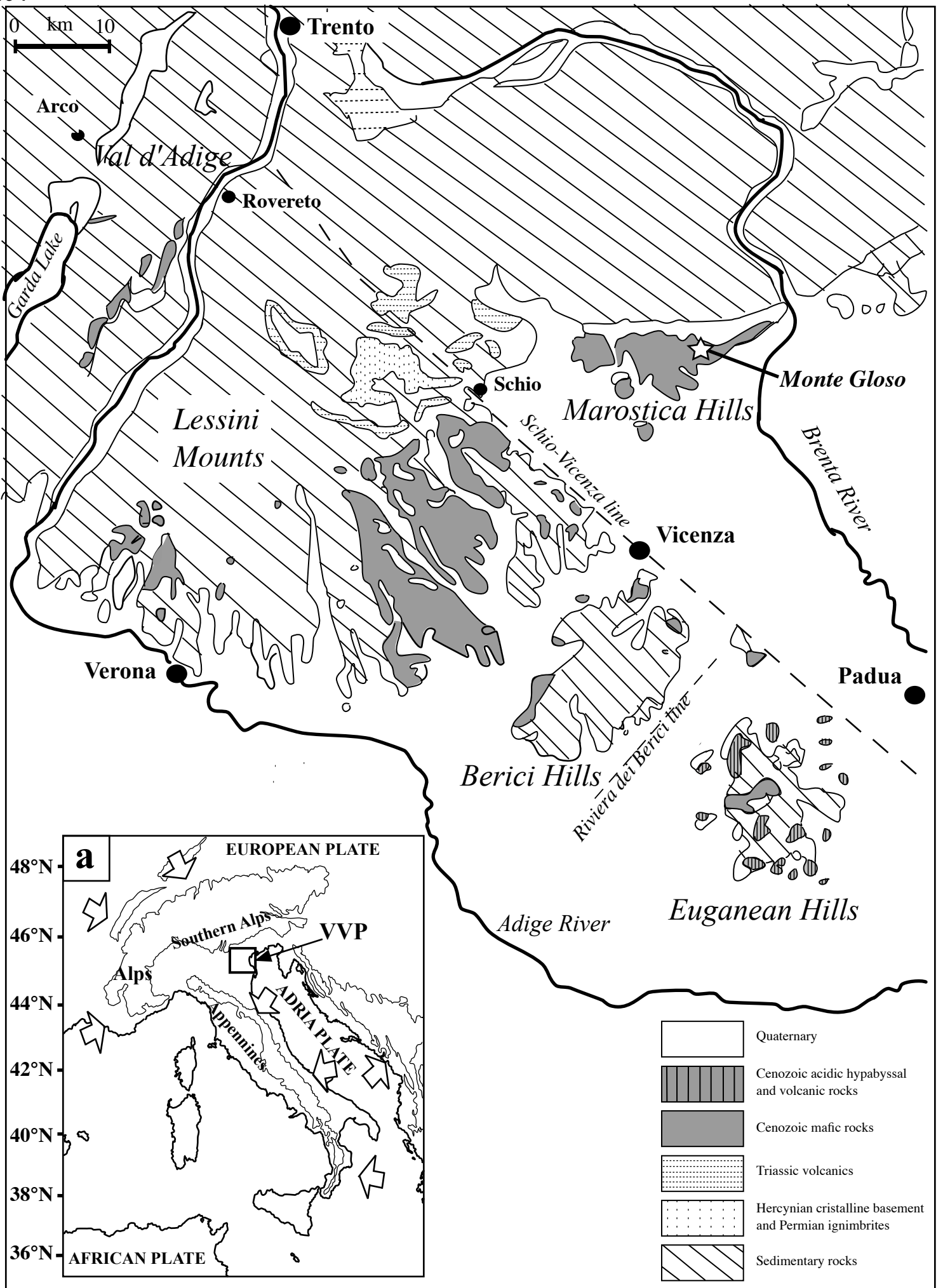


Figure 2

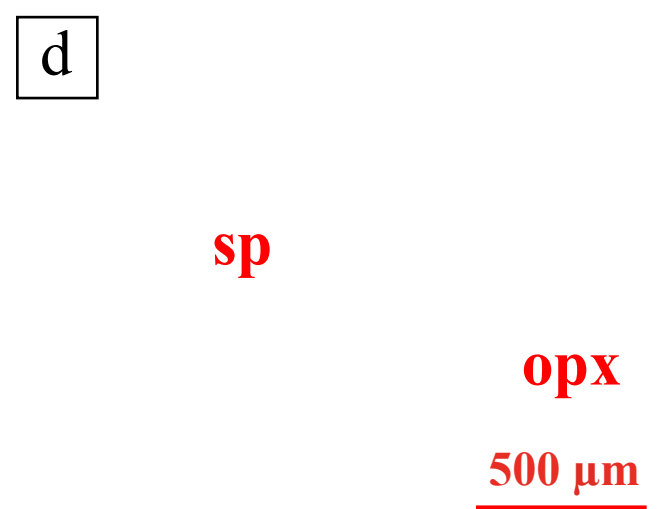
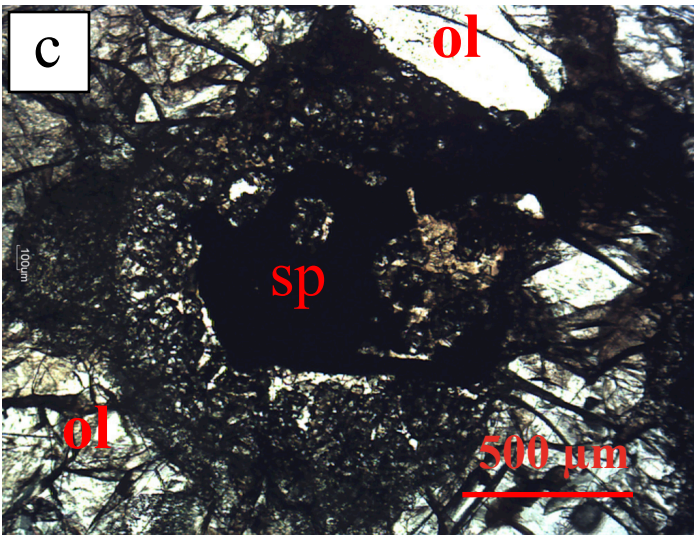
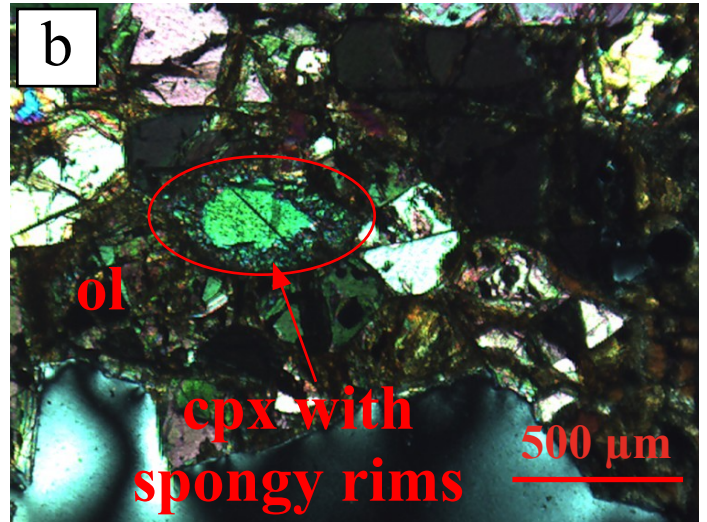
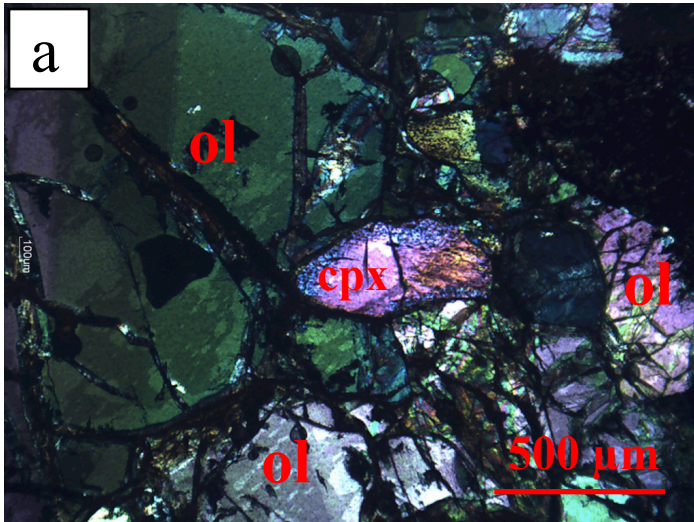


Figure 3

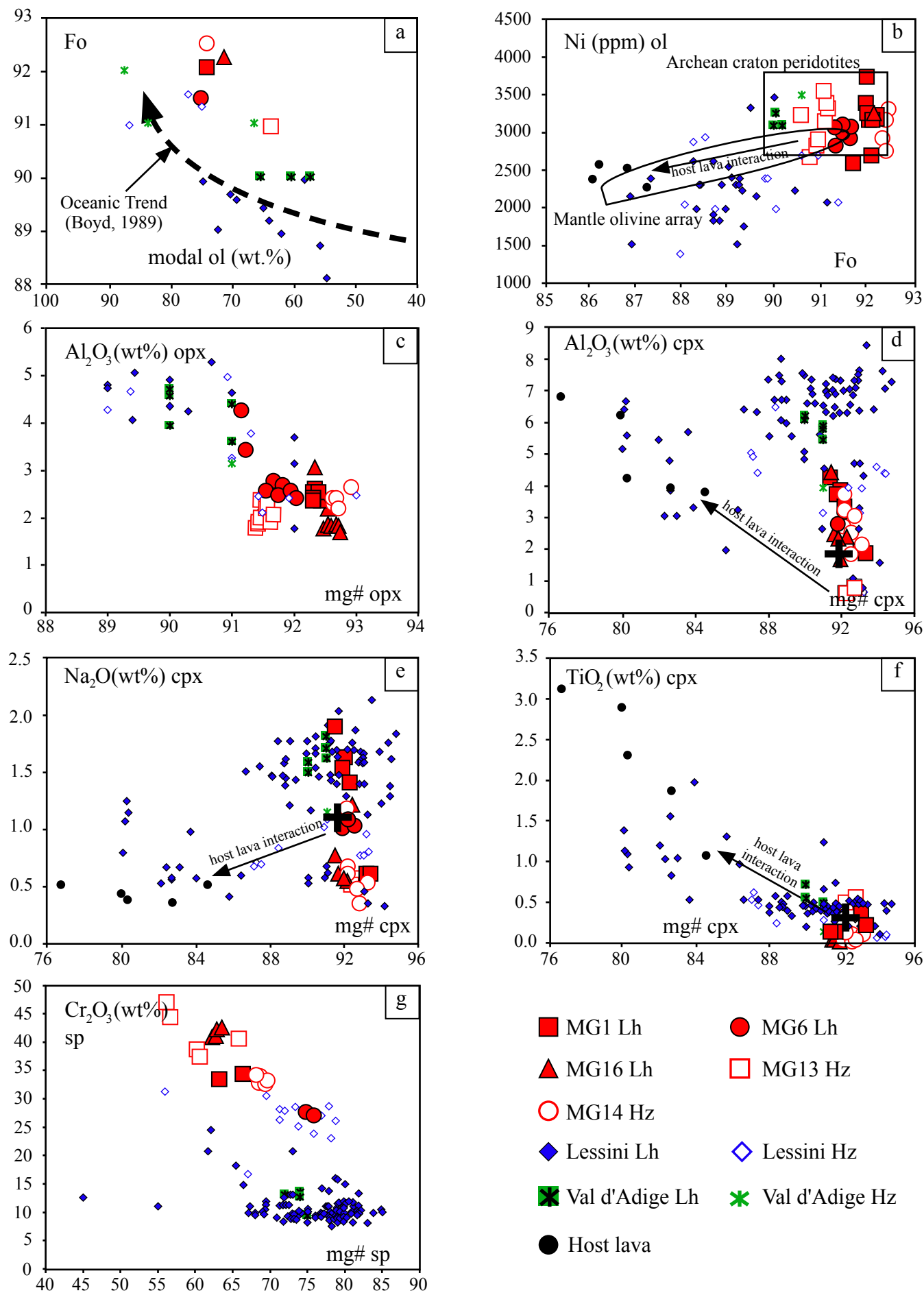
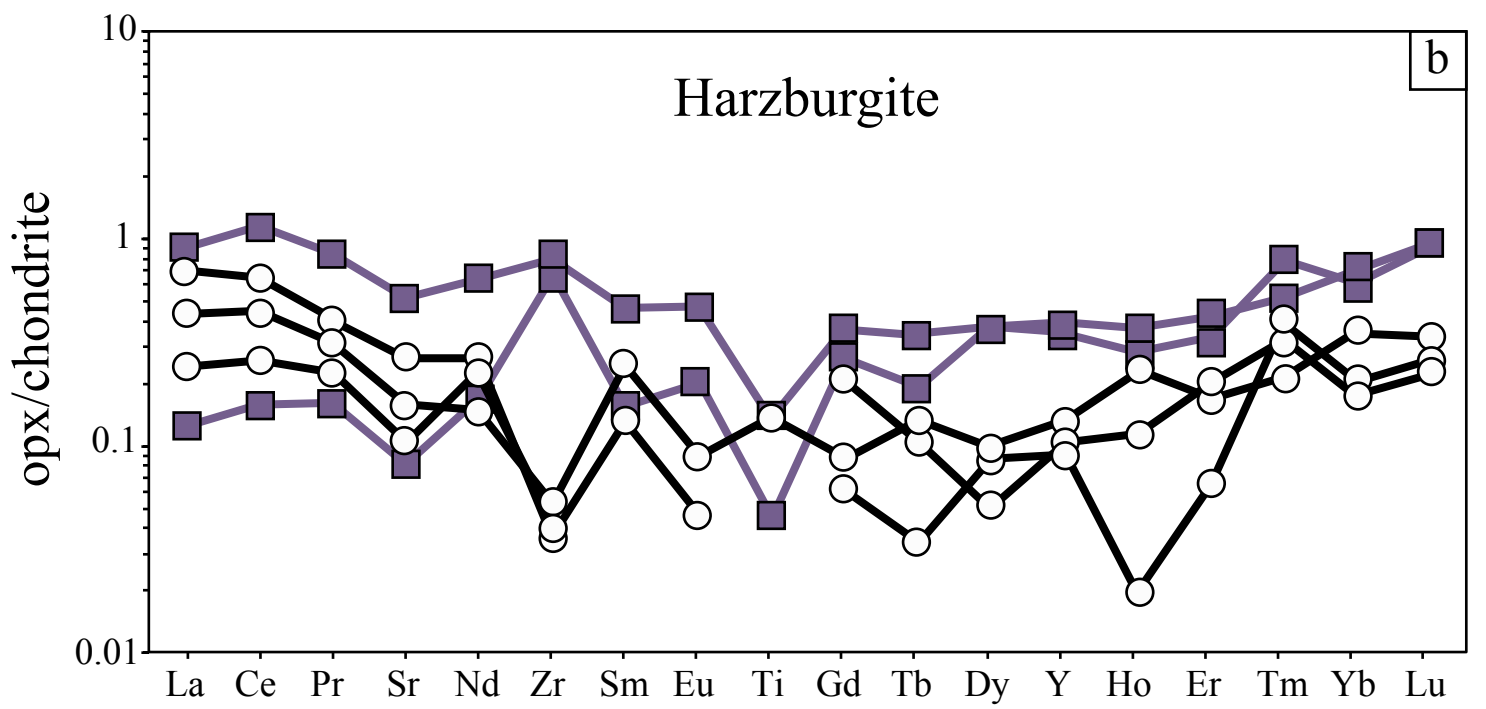
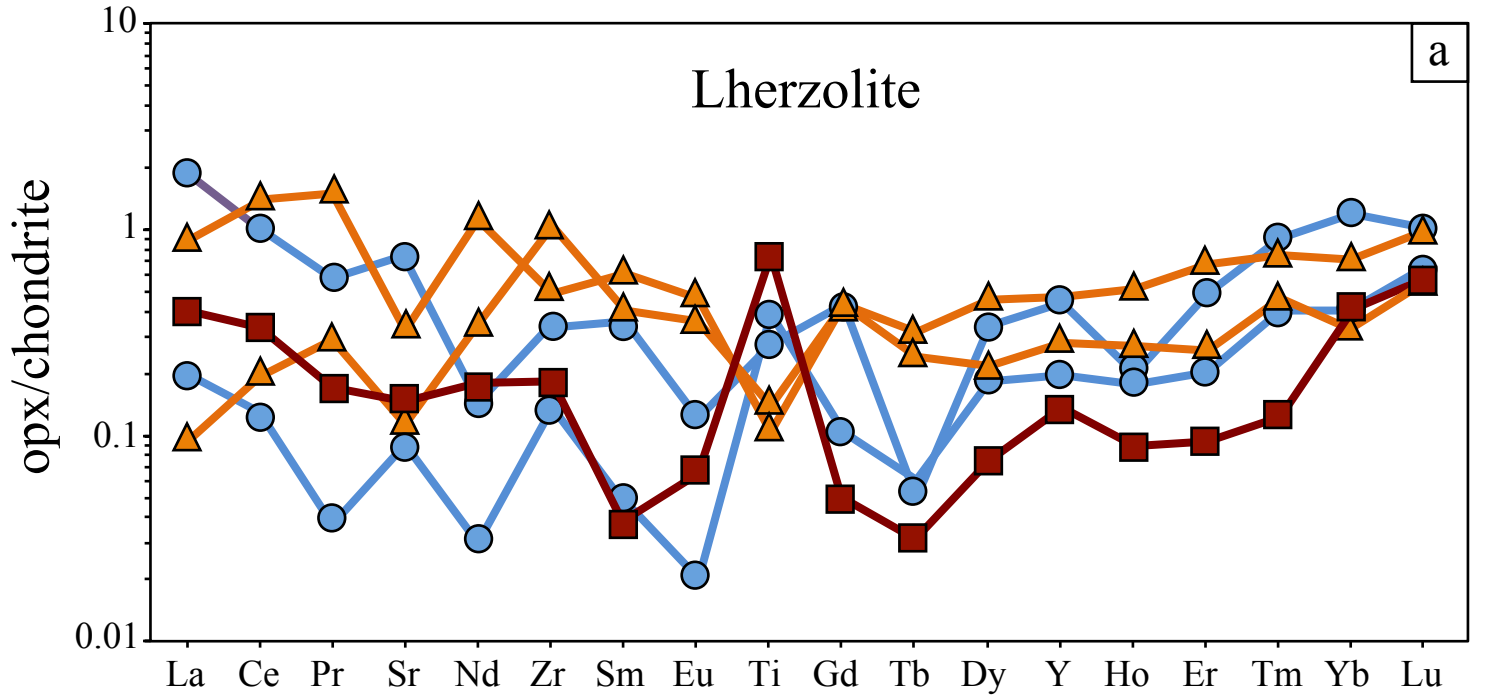
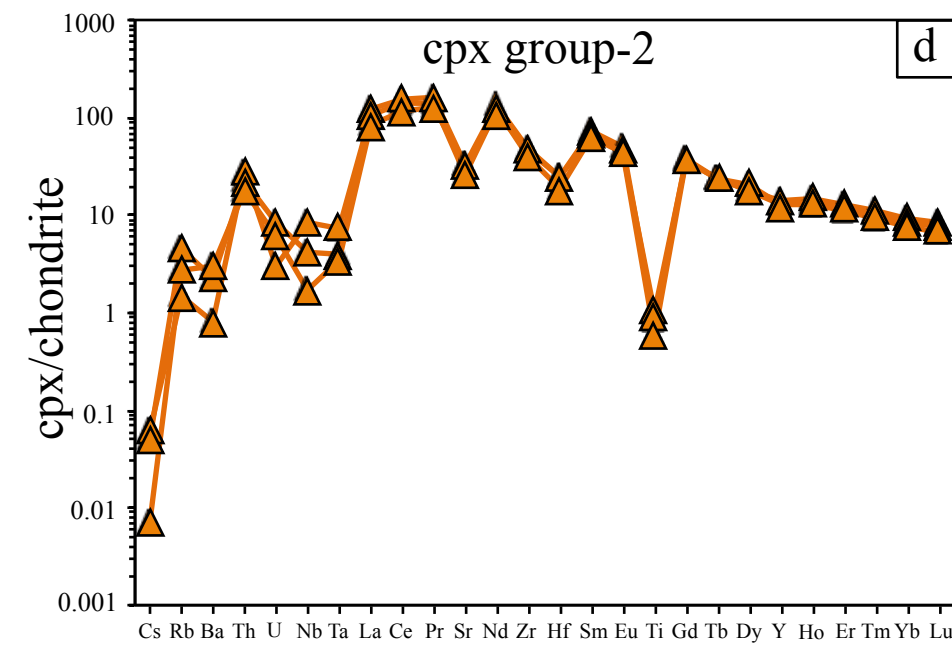
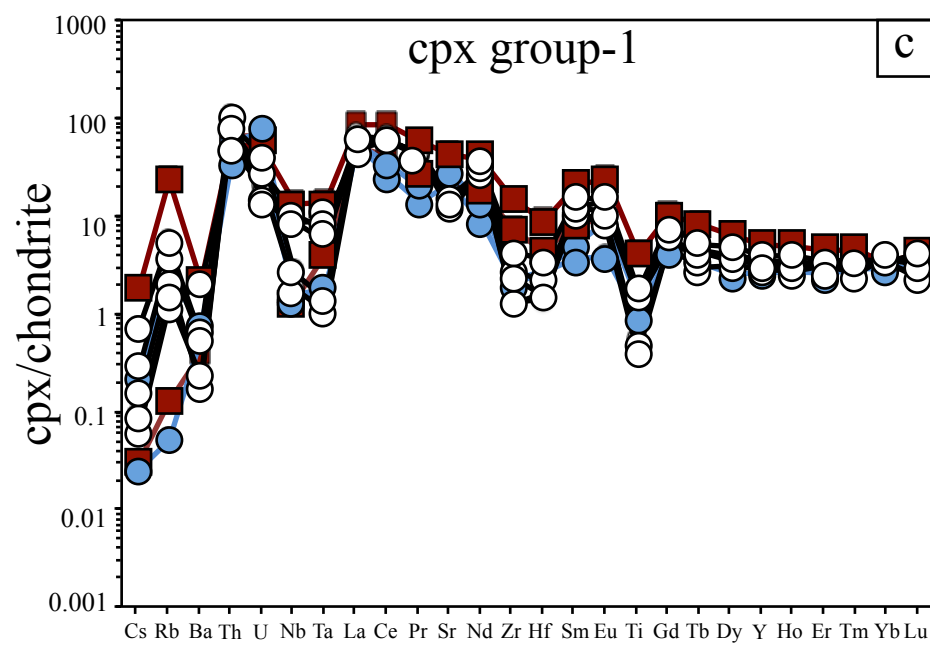
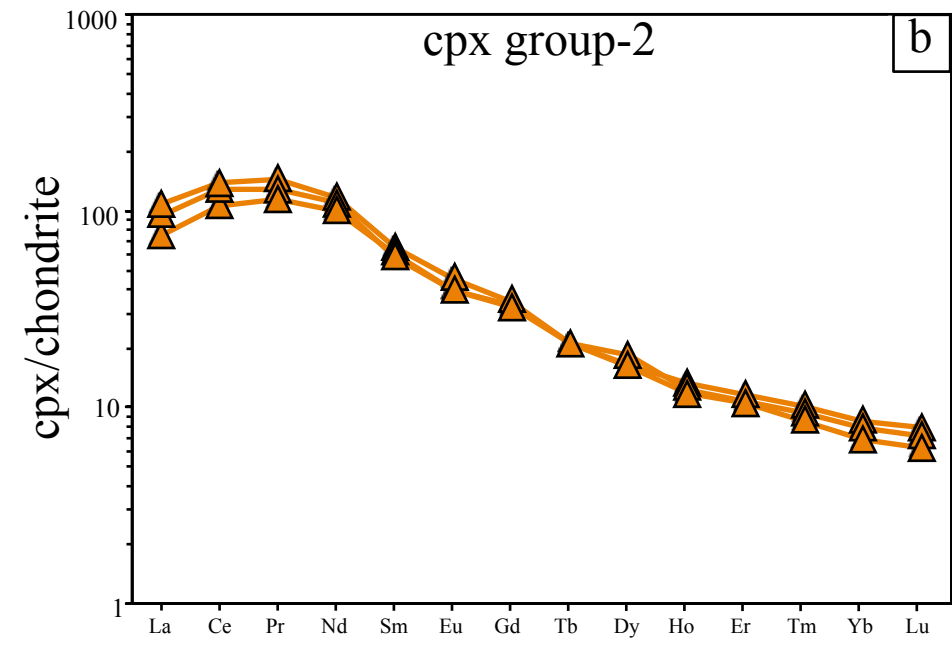
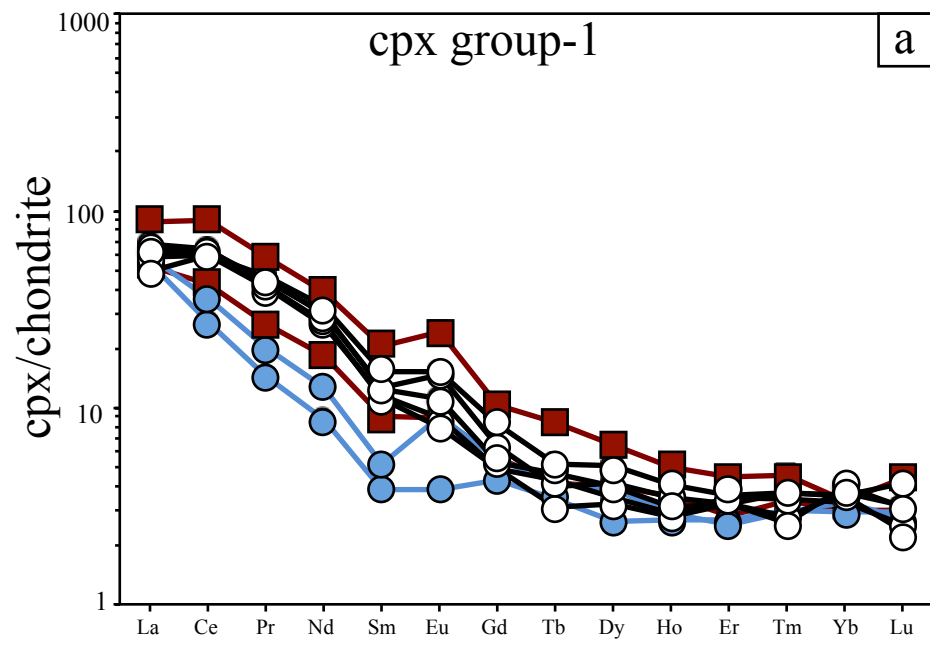


Figure 4



■ MG1 Lh
 ● MG6 Lh
 ▲ MG16 Lh
 ■ MG13 Hz
 ○ MG14 Hz

Figure 5



■ MG1 Lh
 ● MG6 Lh
 ▲ MG16 Lh
 ○ MG14 Hz

Figure 6

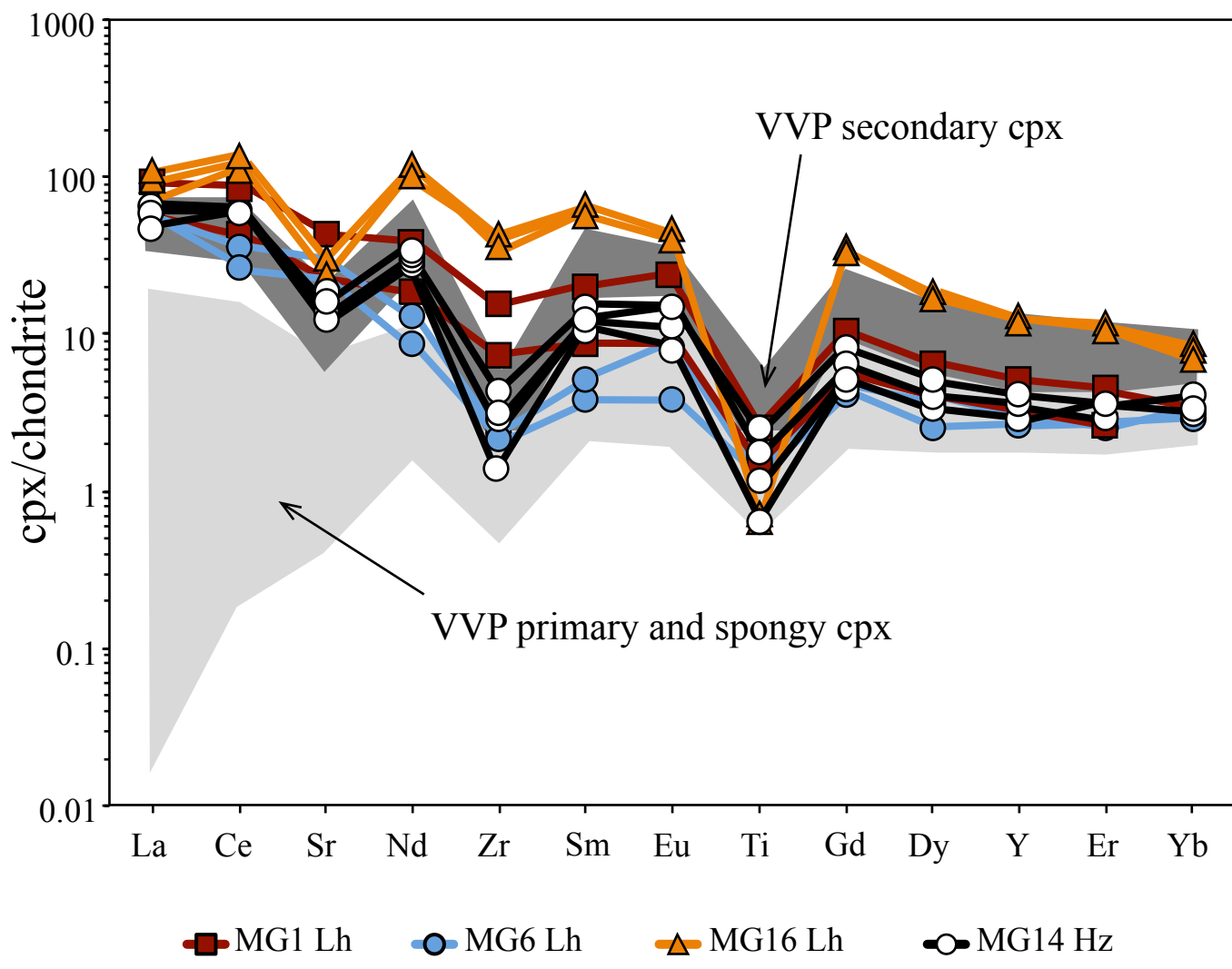
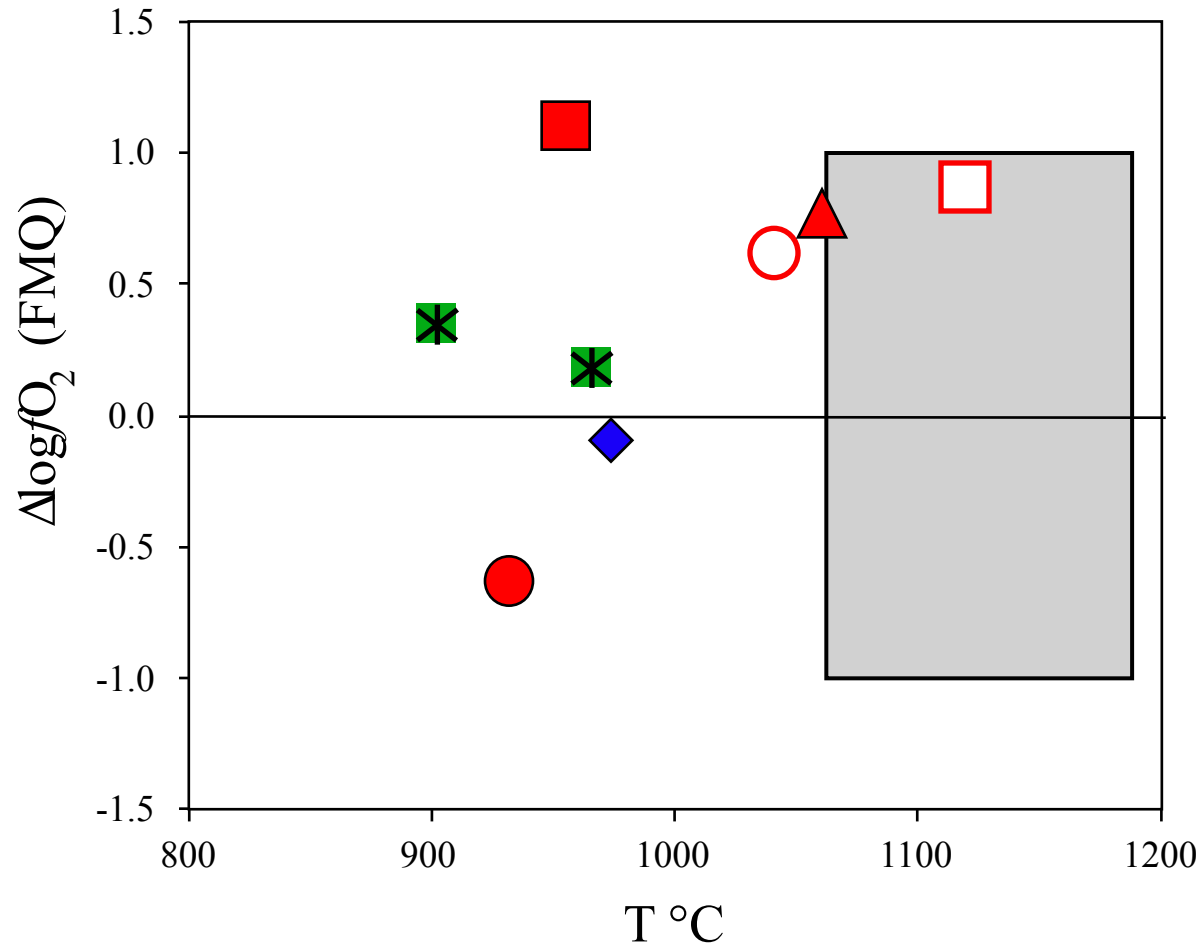


Figure 7



- MG1 Lh
- MG6 Lh
- MG16 Lh
- MG13 Hz
- MG14 Hz
- Lessini Lh
- Val d'Adige Lh

Figure 8

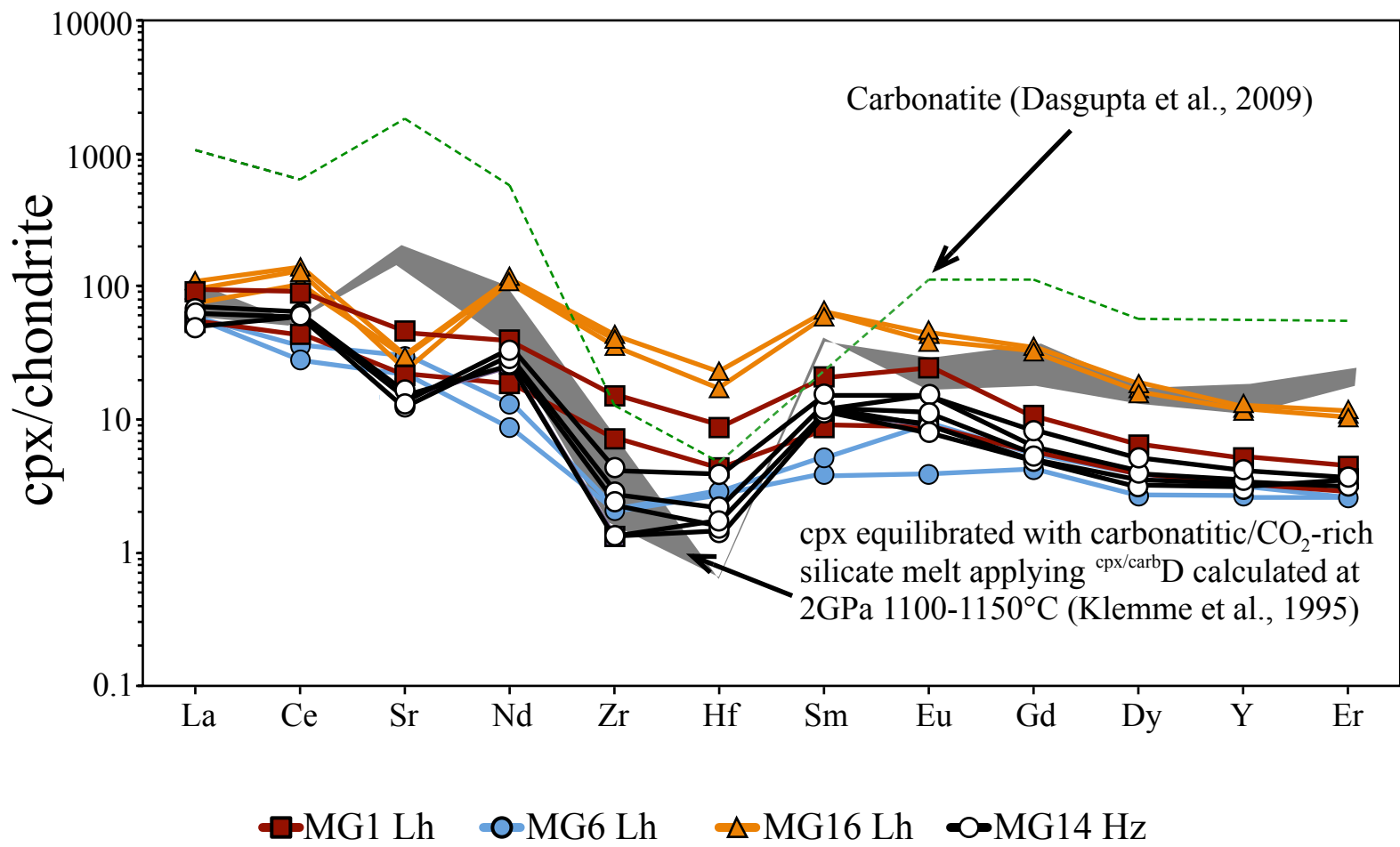
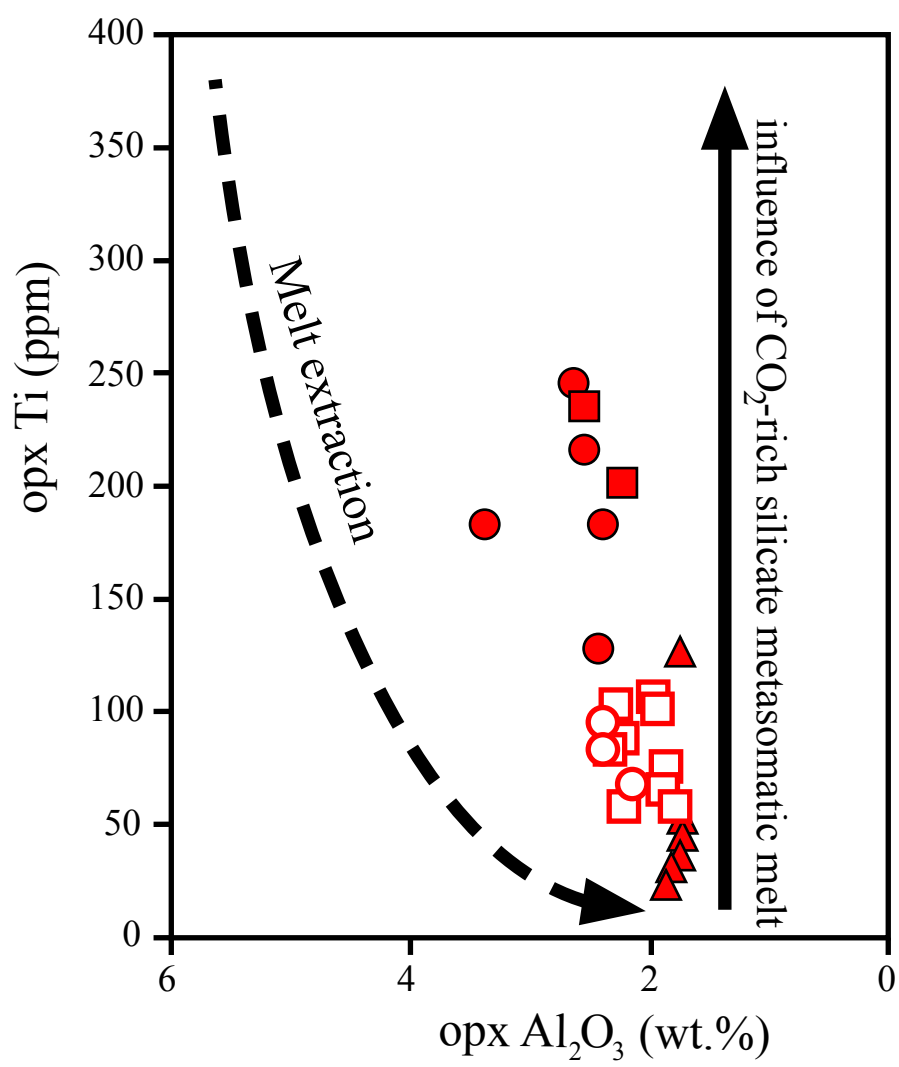
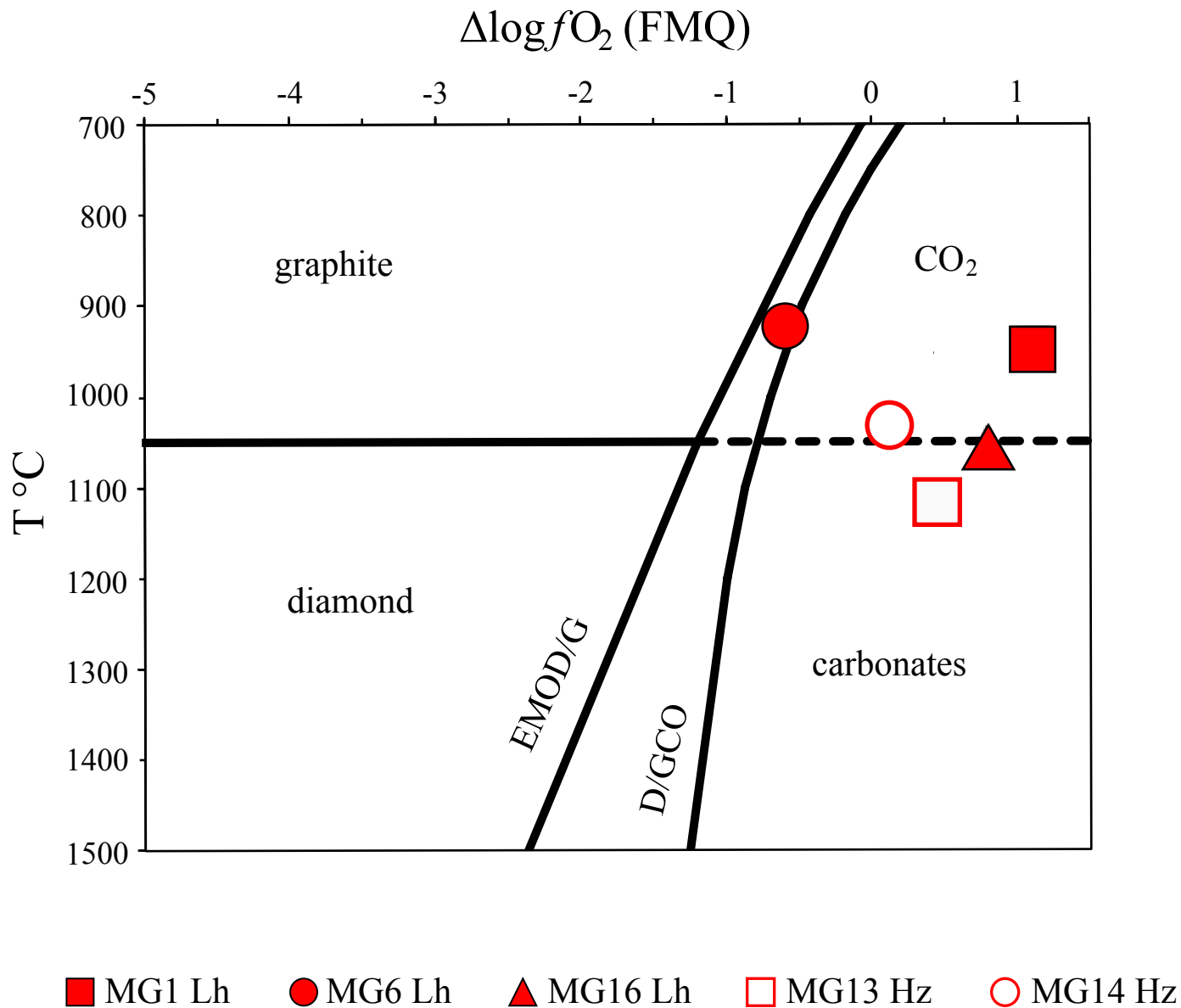


Figure 9



- MG1 Lh ● MG6 Lh ▲ MG16 Lh
- MG13 Hz ○ MG14 Hz

Figure 10



Figure

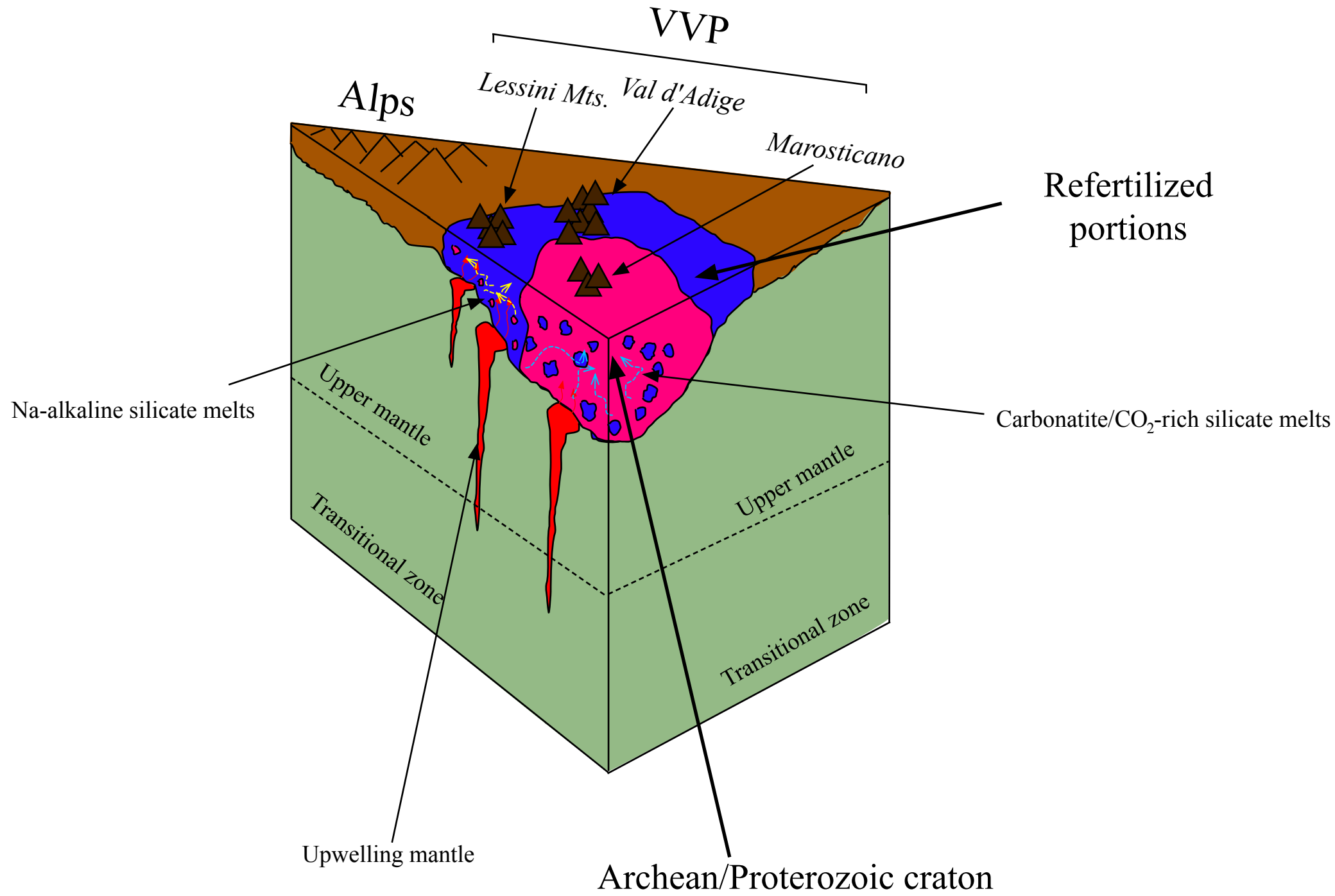


Table 1: Modal composition (%) of MG spinel peridotite xenoliths.

Samples	Lherzolites			Harzburgites	
	MG1	MG6	MG16	MG13	MG14
Ol	73	74	70	63	73
Opx	12	14	20	31	19
Cpx	13	9	6	4	4
Sp	2	3	4	2	4
Gl	trace	trace		trace	trace
Alteration	trace	trace	trace	trace	trace

Ol= olivine; Opx= orthopyroxene; Cpx= clinopyroxene; Sp= spinel; Gl= glass.

Table 2: Average temperature (T) and oxygen fugacity ($\Delta\log f_{O_2}$) for MG spinel-peridotites from Marosticano, ~~spinel-peridotites from Val d'Adige~~ and ~~spinel-lherzolites from Lessini~~ calculated at 1.5 GPa. Estimated T_s are from geothermometers of Brey & Köhler (1990); T_{BK} of Taylor (1998; T_T) and of Wells (1977; T_W). ~~Estimated $\Delta\log f_{O_2}$ (FMQ) is provided from the method of Ballhaus et al. (1991) using T_{BK} and a uniform equilibration pressure of 1.5 GPa.~~ T_{BK} and $\Delta\log f_{O_2}$ (FMQ) of spinel-peridotites from Val d'Adige and Lessini were calculated using EMP data from Gasperini et al. (2006). CO_2 mole fractions are calculated by equation of Stagno and Frost (2010) using the estimated T_{BK} and $\Delta\log f_{O_2}$ (FMQ).

	n	Average T_{BK} (°C)	2 σ uncertainty T_{BK} (°C)	Average T_T (°C)	2 σ uncertainty T_T (°C)	Average T_W (°C)	2 σ uncertainty T_W (°C)	Average $\Delta\log f_{O_2}$ (FMQ)	2 σ uncertainty $\Delta\log f_{O_2}$ (FMQ)	CO_2 mole fractions
Sp-lherzolite (Marosticano)										
MG1	2	949	36	912	60	954	46	1.1	0.00	1.19
MG6	2	923	25	898	12	940	12	-0.6	0.08	0.02
MG16	2	1058	21	1022	19	1041	10	0.8	0.08	1.03
Sp-harzburgite (Marosticano)										
MG13	2	1117	20	1069	22	1109	22	0.9	0.44	1.85
MG14	3	1033	30	1010	28	1029	29	0.6	0.12	0.65
Sp-lherzolite (Val d'Adige)										
56B	1	902		836		914		0.3		
F56-7	1	966		888		956		0.2		
Sp-harzburgite (Val d'Adige)										
F56-5	1	896		842		909				
Sp-lherzolite (Lessini)										
25	1	975		969		998		-0.1		
25C	1	885		883		926				

n= number of analyses per sample.

Table 3: Major oxide (wt.%) abundances of MG lherzolites (Lh).

Sample	MG 1	MG 6
Host Rock	Lh	Lh
SiO ₂	44.66	46.94
TiO ₂	0.02	0.02
Al ₂ O ₃	0.41	1.03
Fe ₂ O ₃	0.00	0.00
FeO	7.44	8.15
MnO	0.11	0.12
MgO	45.72	42.61
CaO	1.57	1.12
Na ₂ O	0.00	0.00
K ₂ O	0.07	0.02
P ₂ O ₅	0.00	0.00
Tot	100.00	100.00
mg#	91.64	90.31



Table A: Major oxide (wt.%) abundances of representative olivine in MG spinel peridotite xenolit

Sample	MG1	MG1	MG1	MG1	MG1	MG1
Lithology	Lh	Lh	Lh	Lh	Lh	Lh
SiO₂	40.87	41.08	41.04	39.82	40.19	40.71
FeO	7.83	7.84	8.28	8.08	7.95	7.91
MnO	0.15	0.09	0.12	0.12	0.14	0.11
MgO	51.58	51.25	51.07	51.84	51.74	51.08
CaO	0.04	0.06	0.05	0.05	0.09	0.07
NiO	0.41	0.46	0.33	0.43	0.34	0.4
Tot	100.96	100.83	100.92	100.42	100.61	100.44
Si	0.99	0.99	0.99	0.97	0.98	0.99
Fe	0.16	0.16	0.17	0.16	0.16	0.16
Mn	0.00	0.00	0.00	0.00	0.00	0.00
Mg	1.86	1.84	1.84	1.88	1.87	1.85
Ni	0.01	0.01	0.01	0.01	0.01	0.01
Fo	92.15	92.09	91.66	91.96	92.06	92.01

Abbreviations: Lh= lherzolite; Hz= harzburgite; b.d.l.= below detection limit.