

4 **The distribution of lead and thallium in mantle rocks: Insights**
5 **from the Balmuccia peridotite massif (Italian Alps)**

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16 **ABSTRACT**

17 Sulfides in mantle rocks sometimes have unradiogenic Pb isotopic compositions
18 and assuming specific conditions, may represent a low U/Pb reservoir that might balance
19 the radiogenic Pb isotope reservoirs of the silicate Earth. A critical requirement to test
20 this hypothesis is knowledge of typical Pb contents in sulfides from different types of
21 mantle rocks and estimates of their contribution to the Pb budget of the mantle rocks.
22 However, data on the distribution of Pb between mantle minerals in mantle rocks from
23 different geologic settings are scarce. In this study, new Pb and Tl concentration data
24 from well-characterized unserpentinized spinel-facies peridotites and pyroxenites from
25 the Balmuccia mantle tectonite (Ivrea-Verbano Zone, Italian Alps) are presented as an
26 example to better understand the Pb distribution in minerals and rocks of the upper
27 mantle.

28 Most peridotites display variable bulk rock Pb contents (13-97 ng/g), which tend to
29 be lower than Pb contents in the websterites (60-254 ng/g) and clinopyroxenites (174-657
30 ng/g). The pyroxenites show broadly positive correlations of Pb with Al₂O₃, Ce and also
31 S contents. In-situ laser ablation ICP-MS data indicate low Pb contents in olivine,
32 orthopyroxene and spinel (mostly below the detection limits of 50 ng/g); whereas Pb
33 contents are higher in clinopyroxene (from < 50 to 920 ng/g) and in sulfides (typically a
34 few µg/g and sometimes higher in chalcopyrites). Mass balance calculations indicate that
35 silicates predominantly control Pb contents in bulk rocks (> 70-80% of the Pb), with a
36 minor role for sulfides (mostly < 20%). This result from Phanerozoic subcontinental
37 lithosphere mantle rocks is consistent with data on abyssal peridotites. As in some
38 previous studies, bulk rock Pb contents calculated from constituent phases of peridotites
39 are often lower than the measured values. This imbalance mainly reflects trapped fluid
40 inclusions in silicate minerals and, perhaps also fine-grained crystallization products of
41 trapped melt along grain boundaries. Bulk rock Tl contents in peridotites (0.05-3.5 ng/g)
42 are lower than in pyroxenites (0.66-7.9 ng/g) and display no correlations with Al₂O₃ and
43 S contents. The bulk rock data probably reflect the highly heterogeneous distribution of
44 Tl in sulfides (< 0.01-110 µg/g), and, as for Pb, the effect of trapped fluid inclusion.
45 Because the Pb budget in mantle rocks is mainly controlled by silicates, mantle sulfides
46 with unradiogenic Pb isotopic compositions likely cannot balance radiogenic Pb isotopic
47 compositions of oceanic basalts.

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49 Keywords: peridotite, pyroxenite, sulfide, lead, thallium

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INTRODUCTION

52 The geochemical behavior of lead in the Earth is notable for some longstanding
53 paradoxes, some of which are still debated until recent time. The Pb isotopic composition
54 of the bulk silicate Earth model is more radiogenic (e.g., $^{207}\text{Pb}/^{204}\text{Pb} = 15.50$ and
55 $^{206}\text{Pb}/^{204}\text{Pb} = 18.29$, according to Burton et al. 2012) than models of the Pb isotopic
56 evolution of the Earth over the last 4.56 Ga (e.g., Allegre, 1969; Burton et al., 2012; Hart
57 and Gaetani, 2006; Hofmann, 2008). The existence of a complementary unradiogenic Pb
58 reservoir with low U/Pb has been a common explanation for these discrepancies (e.g.,
59 Allegre, 1969). It has been suggested that during formation of the Earth, Pb may have
60 partitioned into the metallic core (e.g., Allegre, 1969; Hart and Gaetani, 2006; Oversby
61 and Ringwood, 1971; Wood and Halliday, 2010; Wood et al., 2008) or was vaporized
62 during accretion (e.g., Lagos et al., 2008). Alternatively, some authors proposed that
63 significant quantities of Pb reside in plagioclase-rich cumulates of the lower continental
64 crust, leading to a low U/Pb of this reservoir (e.g, Kramers and Tolstikhin, 1997;
65 Moorbath et al., 1969; Newsom et al., 1986; Reid et al., 1989; Rudnick and Goldstein,
66 1990). Recent studies have documented unradiogenic Pb isotopic compositions (e.g.,
67 $^{206}\text{Pb}/^{204}\text{Pb} = 16.5$) in mantle rocks from the Horoman mantle tectonite in Japan
68 (Malaviarachchi et al., 2008) and in sulfide inclusions in olivine and pyroxene of abyssal
69 peridotites (Blusztajn et al., 2014; Burton et al., 2012; Warren and Shirey, 2012). Thus, it
70 is possible that the mantle itself may contain significant reservoirs of unradiogenic Pb.
71 The sizes of these reservoirs and their significance for basalt generation and the mantle-
72 crust mass balance are poorly constrained.

73 Quantitative balancing of the radiogenic Pb isotopic composition of the BSE via the
74 unradiogenic Pb in mantle sulfides has been suggested (Burton et al., 2012). The
75 feasibility of this explanation strongly depends on the abundance of sulfides in mantle
76 rocks and on the Pb content in mantle sulfides. For instance, if 0.08 wt.% sulfides with 47
77 $\mu\text{g/g}$ Pb occur in the mantle, 70% of the Pb budget of the mantle would be controlled by
78 sulfides (Burton et al., 2012). However, evaluation of the Pb mass balance of minerals in
79 abyssal peridotites from the Gakkel Ridge and the Southwest Indian Ridge has indicated
80 that mantle sulfides host less than 4 % of the Pb in mantle rocks at these locations
81 (Warren and Shirey, 2012). Bulk rock Pb contents reconstructed from silicate minerals of
82 mantle peridotites are commonly lower than measured values (e.g., Carignan et al., 1996;
83 Ionov et al., 2006; Meijer et al., 1990; Simon et al., 2007). The missing Pb fraction was
84 often thought to be hosted by sulfides. Mass balance calculations based on this
85 assumption suggested that sulfides in mantle peridotite xenoliths contain about 75 $\mu\text{g/g}$
86 Pb (e.g., Hart and Gaetani, 2006; Meijer et al., 1990). Such high Pb contents in sulfides
87 could be sufficient to balance the radiogenic Pb component of the mantle, if a large
88 fraction of bulk mantle Pb is unradiogenic (Burton et al., 2012). However, sulfide
89 separates and in-situ analyses of Pb contents in different sulfide phases in abyssal
90 peridotites show low Pb contents, typically $< 10 \mu\text{g/g}$ (Blusztajn et al., 2014; Burton et al.,
91 2012; Warren and Shirey, 2012; Warren et al., 2017). While sulfide inclusions in olivine
92 and pyroxenes of refractory peridotites sometimes show elevated Pb contents of up to 52
93 $\mu\text{g/g}$ (Burton et al., 2012), the proportion of such sulfides in peridotites seems to be too
94 low to account for a large fraction of the Pb budget. Consequently, according to studies

95 of abyssal peridotites, silicate phases are likely the primary host of Pb in rocks of the
96 upper mantle (e.g., Warren and Shirey, 2012).

97 Because of the limited data and mantle heterogeneity, it is unclear if the
98 subcontinental lithospheric mantle may also display chemical and isotopic
99 heterogeneities of Pb, involving low- and high U/Pb components (e.g., Malaviarachchi et
100 al., 2008; Meijer et al., 1990; Mukasa and Shervais, 1999). A potential problem with
101 studies of the Pb systematics of mantle peridotites is that Pb and other highly
102 incompatible elements are easily affected by mantle metasomatism, serpentinization and
103 other forms of contamination by late-stage processes (e.g., Deschamps et al., 2012;
104 Hanghøj et al., 2010; Harvey et al., 2012; Nielsen et al., 2015; Simon et al., 2007; Wittig
105 et al., 2009). Therefore, careful examination of the distribution and budget of Pb in
106 mantle rocks is of importance to understand if low-U/Pb phases such as sulfides can
107 balance the radiogenic Pb isotopic reservoirs of the silicate Earth.

108 The Balmuccia mantle tectonites (Ivrea-Verbano Zone, IVZ, Italian Alps) comprise
109 spinel-facies lherzolites and less abundant harzburgites and dunites, with different
110 generations of pyroxenite dikes that during the Paleozoic and Mesozoic were part of the
111 subcontinental lithospheric mantle. The rock association reflects open system partial
112 melting with coeval and subsequent melt infiltration processes during extension of
113 continental lithosphere. According to Re-Os model age distributions and Sm-Nd
114 errorchrons, the latter processes occurred during the Paleozoic and Mesozoic (e.g., Handy
115 et al., 1999; Mazzucchelli et al., 2009; Mukasa and Shervais, 1999; Obermiller, 1994;
116 Rivalenti et al., 1995; Shervais and Mukasa, 1991; Sinigoi et al., 1983; Voshage et al.,
117 1988; Wang and Becker, 2015a; Wang et al., 2013). The Balmuccia mantle tectonites

118 permit sampling of fresh rocks with negligible serpentinization and weathering (e.g.,
119 Mukasa and Shervais, 1999; Obermiller, 1994; Shervais and Mukasa, 1991; Wang et al.,
120 2013). Previous studies have constrained petrological features and the distribution of
121 other chalcophile elements in these rocks and offer a solid basis to understand the
122 distribution of Pb in these rocks. This study presents Pb and Tl contents in bulk rocks
123 (supplemented by data on other incompatible trace elements) and minerals in
124 unserpentinized mantle peridotites and pyroxenites from Balmuccia. Thallium is highly
125 incompatible and also sensitive to the effect of fluids (e.g., McGoldrick et al., 1979;
126 Nielsen et al., 2014, 2015), thus Tl data, as well as other incompatible trace elements may
127 aid understanding the Pb distribution in these rocks.

128 **GEOLOGICAL SETTING AND SAMPLES**

129 The Balmuccia peridotite massif is a fragment of subcontinental lithospheric mantle
130 located in the Ivrea-Verbano Zone (IVZ), western Italian Alps. The mantle tectonite was
131 emplaced into lower crustal granulite facies metabasites of the IVZ during the late
132 extensional stage of the Hercynian orogeny, and was further exhumed in the course of the
133 Mesozoic extension and subsequent Alpine compression (Handy et al., 1999; Handy et al.,
134 2010; Mukasa and Shervais, 1999; Peressini et al., 2007; Shervais and Mukasa, 1991;
135 Zingg et al., 1990). The massif comprises predominantly spinel-facies lherzolites, minor
136 dunite, harzburgite and is cross-cut by various generations of pyroxenite, late gabbro and
137 hornblendite dikes. These rocks and their geological history have been studied in great
138 detail for several decades (e.g., Handy et al., 1999; Mazzucchelli et al., 2009; Mukasa

139 and Shervais, 1999; Obermiller, 1994; Rivalenti et al., 1995; Shervais and Mukasa, 1991;
140 Sinigoi et al., 1983; Voshage et al., 1988; Wang et al., 2013).

141 In the mantle, the lherzolites from Balmuccia underwent different extents of
142 chemical and isotopic re-equilibration with infiltrating melts in an open system
143 environment during the late Paleozoic (Mazzucchelli et al., 2009; Mukasa and Shervais,
144 1999; Obermiller, 1994; Rivalenti et al., 1995; Shervais and Mukasa, 1991; Voshage et
145 al., 1988; Wang et al., 2013). Later focused melt flow led to formation of replacive
146 dunites which show discordant relationships with the lherzolites and harzburgite-dunite
147 reaction zones (Mazzucchelli et al., 2009; Wang et al., 2013). Discordant layers of
148 websterites and spinel clinopyroxenites represent magmatic reaction products transitional
149 to cumulates, which formed during the Paleozoic and Mesozoic (Mazzucchelli et al.,
150 2010; Mukasa and Shervais, 1999; Rivalenti et al., 1995; Wang and Becker, 2015b). At
151 least some of the pyroxenites formed from melts that also infiltrated the peridotites. Both
152 bulk rocks and clinopyroxene separates of peridotites, pyroxenites and gabbros in
153 Balmuccia show depletion of light rare earth elements (LREE) relative to heavy REE
154 (Mazzucchelli et al., 2009; Mukasa and Shervais, 1999; Obermiller, 1994; Rivalenti et al.,
155 1995). The occasional presence of traces of phlogopite and amphibole in some
156 pyroxenites, variable enrichment of Cs, Rb and Ba relative to the REE, and enrichment of
157 LREE relative to HREE in some dunites suggest that some of the rocks were affected by
158 metasomatism to different extents (Mazzucchelli et al., 2010; Obermiller, 1994; Voshage
159 et al., 1988). Because of the MORB to OIB like initial Sr-Nd isotopic composition of the
160 rocks (e.g., $^{87}\text{Sr}/^{86}\text{Sr}_i$ at 250 Ma ranges between 0.7027 and 0.7037, Mazzucchelli et al.,
161 2009; Mukasa and Shervais, 1999; Obermiller, 1994), we infer that the occasional traces

162 of phlogopite or amphibole that occur in some peridotites and pyroxenites were likely
163 caused by melt stagnation in the lithospheric mantle.

164 The samples of this study include 13 fresh peridotites of variable fertility, 4
165 replacive dunites, an orthopyroxenite (crosscutting tabular dunite), 5 websterites and 11
166 spinel clinopyroxenites. The peridotites were collected > 0.3 m away from dikes. The
167 pyroxenite dikes show variable widths (a few cm to > half meter) and some show
168 reaction zones with surrounding peridotites. A detailed description of the samples has
169 been given before and major elements and many trace elements have been reported in
170 previous studies of these samples (Obermiller, 1994; Rivalenti et al., 1995; Wang and
171 Becker, 2015a, 2015b; Wang et al., 2013). Figure 1 shows typical microscopic features of
172 these samples.

173 ANALYTICAL METHODS

174 In this study, we used isotope dilution ICP-MS to determine bulk rock contents of
175 Pb and Tl in the above-mentioned samples. Bulk rock contents of Ba, Cs, Rb and other
176 trace elements also have been determined by ICP-MS. In addition, contents of Pb and
177 some other elements in sulfides (Tl contents) and in different silicate phases (Ce and Ba
178 contents) were determined for seven thin sections of peridotites (n=4) and pyroxenites
179 (n=3).

180 Bulk rock analytical methods

181 Bulk rock Pb and Tl contents were determined by isotope dilution ICP-MS at Freie
182 Universität Berlin on the same digestion aliquots. Sample digestion in Parr bombs using
183 HF-HNO₃ and subsequent chromatographic separation has been established previously

184 for concentration determinations of Tl and other trace elements (Wang et al., 2015). A
185 brief outline of the Pb separation method is reported here. Suitable amount of spike
186 solutions containing ^{203}Tl and ^{208}Pb , and 0.2-0.4 gram of sample powder were weighted
187 into 15 ml Savillex PFA beakers, followed by 1 ml $14 \text{ mol l}^{-1} \text{ HNO}_3$ and 4 ml 24 mol l^{-1}
188 HF. Digestions were performed in Parr bombs at $190 \text{ }^\circ\text{C}$ for 3 days. Sample solutions
189 were dried down, converted into chloride form and loaded on 2 ml pre-cleaned 100-200
190 mesh Eichrom 1-X8 anion resin. Solutions containing Pb (in $0.4 \text{ mol l}^{-1} \text{ HCl}$) and Tl (in
191 $0.7 \text{ mol l}^{-1} \text{ HNO}_3$ with 1% H_2O_2) were collected. The Tl fraction was dried down and
192 dissolved in $0.28 \text{ mol l}^{-1} \text{ HNO}_3$ for measurement. The Pb fraction was further purified by
193 adding ascorbic acid to remove Fe (Wang et al., 2015).

194 As the method formed part of a multi-element separation procedure, the total Pb
195 yields ranged from 10% to 30% only. However, because of the application of the isotope
196 dilution method, the low yields were not detrimental to the analytical results. Three mafic
197 reference materials (BHVO-1, BHVO-2 and MRG-1) were digested to evaluate Pb data
198 precision and accuracy in this study (Table 1). Eight replicates of peridotites (n=5) and
199 pyroxenites (n=3) are also included to evaluate data reproducibility (Table 2).

200 The solutions of separated elements were measured by sector field ICP-MS
201 (Thermo Scientific Element XR) with an Aridus-I desolvator at low oxide formation ratio
202 ($\text{CeO}^+/\text{Ce}^+ < 0.003$). Because the different rock types from the Balmuccia massif have
203 very similar measured Pb isotopic compositions (Mukasa and Shervais, 1999), average
204 isotopic ratios from the literature ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$: 18.550, 15.598
205 and 38.326, respectively) were used for calculation of Pb contents by isotope dilution.
206 Concentration results obtained from $^{204}\text{Pb}/^{208}\text{Pb}$ and $^{207}\text{Pb}/^{208}\text{Pb}$ show limited variations

207 (mostly < 2%, Table 2). Data reduction of Tl followed established methods (Wang et al.,
208 2015). During the measurement period, total procedural blanks (n=12, 1sd) were
209 0.36±0.28 ng for Pb and 0.019±0.016 ng for Tl. Blank corrections were always applied
210 and are mostly insignificant (< 1%) for both Pb and Tl. A few samples with low
211 concentrations of these elements required blank corrections of at most a few percent. The
212 combined uncertainties are shown in Table 2.

213 Precision and accuracy of the methods have been evaluated for Tl by the analysis of
214 different reference materials (Wang et al., 2015). The Pb contents of three mafic
215 reference materials were analyzed in this study (Table 1). Aliquots of these samples have
216 a relatively large uncertainty due to under-spiking (4%, 2sd). Concentrations obtained
217 from $^{204}\text{Pb}/^{208}\text{Pb}$ and $^{207}\text{Pb}/^{208}\text{Pb}$ show a difference of 1-3%. Replicate analysis of
218 BHVO-2 agrees within uncertainty (< 4%, 2sd). The Pb concentrations obtained for the
219 reference materials BHVO-1, BHVO-2 and MRG are similar to compiled values from the
220 GeoReM database and other values determined by isotope dilution (Jochum et al., 2005,
221 Table 1). Lead contents of replicates of peridotite (n = 5) and pyroxenite (n = 3) samples
222 show relative deviations ranging between 3 and 14 % (Table 2). Most replicates show a
223 similar level of variation for Tl contents. Two samples with very low Tl contents display
224 a larger variation (Table 2, 0.18 ng/g and 0.40 ng/g for BM90-5 and 1.07 and 0.66 ng/g
225 for BM11-14). These variations probably partially reflect the heterogeneous distribution
226 of accessory host phases of these elements (sulfides, melt and/or fluid inclusions, see
227 Discussion) and the rather low element concentrations. However, these issues will not
228 compromise the main conclusions drawn from the data.

229 Bulk rock trace elements were measured by quadrupole ICP-MS on an Agilent
230 7700 system at State Key Laboratory of Geological Processes and Mineral Resources,
231 China University of Geosciences (Wuhan). Reference materials UB-N (n=1), BHVO-2
232 (n=2), BCR-2 (n=1), W-2a (n=1) and OKUM (n=1) were analyzed. The uncertainty on
233 Ba, Cs, Rb and LREE contents were typically within 10 % (2sd) and reference materials
234 were reproducible within that range. Samples with low contents of these elements have
235 uncertainties of about 20 % (2sd, Supplementary Table S1). The replicates of peridotites
236 (n=5) and pyroxenites (n=3) from Balmuccia show a similar level of uncertainty as
237 reference materials (Supplementary Table S1).

238 **LA-ICP-MS analytical methods**

239 Seven thin sections of lherzolites (BM11-02A, BM11-10, BM11-11 and BM11-18),
240 clinopyroxenites (BM11-16A and BM11-28B) and orthopyroxenite (BM11-07B,
241 crosscutting dunite BM11-07A) were analysed in-situ for trace element concentrations in
242 silicates (Cu, Pb, Ba and Ce) and sulfides (Cu, Pb and Tl). Because of very low signal
243 intensities in silicates, Tl concentrations in silicates (< 2 ng/g) were not determined. The
244 analyses were performed at the Institut für Mineralogie, Leibniz Universität Hannover
245 with a UV (194 nm) femtosecond laser system (Spectra Physics Solstice, USA) coupled
246 to a Thermo Finnigan Element XR ICP-MS (Lazarov and Horn, 2015; Oeser et al., 2014).
247 A Ni skimmer X cone and a Ni sampler cone were used. Thin sections of samples and the
248 reference material were ablated under a helium stream. The spot diameter was 30-40 μm ,
249 and laser repetition rate was between 14 and 20 Hz with a laser energy of around 1.3
250 J/cm². In each sequence consisting of 20 measurements, the reference materials NIST 610,
251 PGE-A (a Ni sulphide standard) or the Lombard iron meteorite (Gilbert et al., 2013;

252 Jochum et al., 2011; Pearce et al., 1997) were measured repeatedly. Evaluation of the
253 measurements was performed off-line by the SILLS (Version 1.3.2) MATLAB program
254 (Guillong et al., 2008). The first 30-40 seconds of background measurement were
255 subtracted from 120 seconds of sample measurement and the evaluated signal intervals
256 were integrated. For the internal standardization, concentrations of specific major element
257 determined by microprobe were used (Si for olivine and orthopyroxene, Al for spinel, Ca
258 for clinopyroxene, Ni for pentlandite, Fe for pyrrhotite and Cu for chalcopyrite and
259 cubanite). Data accuracy and precision were evaluated with reference materials and were
260 consistently within a few percent (Supplementary Tables S2 and S3).

261 **RESULTS**

262 **Concentrations in bulk rocks**

263 The bulk rock trace element data show depletion of light REE relative to heavy
264 REE for peridotite and pyroxenites (Figure 2). In the most LREE-depleted samples, the
265 fluid-mobile elements Cs, Rb and Ba are enriched compared to the LREE (Figure 2). In
266 all rock types Cs, Rb and Ba typically show strong inter element fractionation. These
267 results are similar to previous data obtained by spark source mass spectrometry
268 (Obermiller, 1994).

269 Most lherzolites from Balmuccia display variable, but typically low Pb contents
270 ranging from 13 to 97 ng/g (Table 2). Most values are similar to the Pb content of 30-40
271 ng/g in the depleted mantle estimated by Salters and Stracke (2004) and Warren and
272 Shirey (2012). Three peridotites (BM11-11, BM11-04 and BM11-03B) with relatively
273 high Ba contents of several $\mu\text{g/g}$ also show high Pb contents (400-700 ng/g), which were

274 confirmed by replicate analyses (Table 2). Lead contents in websterites are 60-254 ng/g
275 Pb, whereas Pb contents in clinopyroxenites tend to be even higher (174-657 ng/g, Figure
276 3). The pyroxenites show broadly positive correlations of Pb with Al₂O₃, Ce and S
277 contents, whereas the peridotites display scattered concentration values (Figure 3). Ce/Pb
278 ratios of bulk rocks (mainly 2-6) are significantly lower than data of MORB and OIB
279 (20-30, Figures 2 and 4). Even if dunites and peridotites with high Pb and Ba contents are
280 excluded, other peridotites also show low Ce/Pb, consistent with previous results
281 (Obermiller, 1994).

282 Thallium contents in peridotites with high Ba and Pb contents are noticeably higher
283 (2-3 ng/g) than Tl in peridotites with low Pb and Ba contents (mostly < 1 ng/g Tl, Table 2
284 and Figure 5). The dunites also show low Tl concentrations (0.16 to 0.94 ng/g).
285 Websterites and clinopyroxenites have higher Tl contents of 0.66-7.9 ng/g (Figure 5).
286 Thallium contents in pyroxenites are uncorrelated with Al₂O₃ and S contents (Figure 5).
287 Overall, Tl contents in peridotites and pyroxenites increase with Pb and Ba contents.
288 However, the Pb/Tl ratios are variable ranging from MORB-like values of 40-50 to much
289 higher values of 100-200 (Figure 6).

290 **Petrographic constraints**

291 Microscopic observations indicate the presence (2-4 vol.%) of fine-grained
292 pyroxene and olivine assemblages along grain boundaries in some peridotites (Fig. 1c).
293 Other peridotites show lower proportions (< 1 vol.%) of such interstitial phases and lower
294 Pb contents (Figures 1e and 3). Replacive dunites (n=4) with negligible fine-grained
295 aggregates (Figure 1d) also have enhanced Pb contents of 69-248 ng/g. Some pyroxenites
296 also contain fine-grained interstitial pyroxenes (mostly < 2 vol.%). In addition, planar

297 features of small dark inclusions (a few μm), perhaps fluid or melt inclusions, widely
298 occur inside of pyroxenes and olivines in the pyroxenites, lherzolites and dunites with
299 variable volumes (e.g., Figure 1a, b, d, e). Aside from these microscopic features,
300 samples display no macroscopic evidence for serpentinization or other forms of low-
301 temperature alteration (Figure 1 and also see Wang et al., 2013).

302 **Concentrations in minerals**

303 Olivine, orthopyroxene and spinel in peridotites and pyroxenites all have very low
304 Pb, Ba and Ce contents (mostly below detection limits, e.g., < 50 ng/g for Pb, see details
305 in Supplementary Table S4). Clinopyroxene has higher Pb, Ba and Ce contents, e.g., Pb
306 ranging from < 50 ng/g to 920 ng/g. The in-situ Pb contents in clinopyroxenes display a
307 range similar to clinopyroxene separates from Balmuccia peridotites and pyroxenites (50-
308 400 ng/g, Mukasa and Shervais, 1999). In-situ data on clinopyroxenes in peridotites and
309 pyroxenites show similar or higher Ce/Pb than bulk rocks (Supplementary Table S4 and
310 Figure 4). A single clinopyroxene grain in the replacive dunite BM11-07A contains 9.3
311 $\mu\text{g/g}$ Pb, as well as high contents of Ba (190 $\mu\text{g/g}$) and Ce (8.5 $\mu\text{g/g}$). Except for this
312 grain, the Ba contents in silicate phases are mostly < 0.2 $\mu\text{g/g}$ (Supplementary Table S4).

313 Sulfides in Balmuccia peridotites and pyroxenites are dominated by pentlandite,
314 with a smaller fraction of pyrrhotite, chalcopyrite and cubanite. These sulfides often
315 occur as intergrown assemblages with typical grain sizes between 50 and 1000 μm
316 (Figure 1f, Supplementary Figure S1 and Wang et al., 2013). The sulfide assemblages
317 result from the exsolution of immiscible sulfide phases during cooling of the mantle
318 rocks (e.g., Lorand et al., 2010; Luguét et al., 2004). Most sulfides in peridotites and
319 particularly in pyroxenites occur interstitial between main minerals (Supplementary

320 Figure S1 and Wang et al., 2013). The sulfides are very fresh (no significant oxidation to
321 Fe oxides), which is consistent with negligible low-temperature alteration of the bulk
322 rocks (Figure 1). Peridotites contain only a minor amount of sulfide inclusions in silicate
323 minerals, and given their small sizes (10-30 μm , Wang et al., 2013), they have not been
324 analyzed in this study.

325 Lead contents in 102 analyzed interstitial sulfide grains are highly variable (Figures
326 7 and 8, Supplementary Table S3 and Figure S1). In a given sample, chalcopyrites (0.6-
327 113 $\mu\text{g/g}$ Pb) commonly have higher Pb contents than pentlandites and pyrrhotites
328 (mostly $< 10 \mu\text{g/g}$, Figure 7, Supplementary Table S3). The average Pb contents in these
329 sulfides and standard deviations are given in Table 3. Similarly, Tl contents in sulfides
330 are also highly variable ($< 0.01 \mu\text{g/g}$ to $110 \mu\text{g/g}$) and chalcopyrites tend to have higher
331 Tl contents than pentlandites and pyrrhotites in the same thin sections (Figure 7,
332 Supplementary Table S3).

333

DISCUSSION

334 **Lead distribution between mineral phases of mantle rocks**

335 Clarification of the fraction of Pb that resides in sulfides of mantle rocks is critical
336 to evaluate the Pb budget of mantle rocks. Because bulk rock and in-situ data of S, Cu, Pb
337 and other elements are available for samples of this study, the new data yields improved
338 constraints on sulfide abundances and the budget of Pb in mantle rocks.

339

340 **Lead and Tl contents in mantle sulfides.** In a classic study, Meijer et al (1990)
341 showed that Pb concentrations in silicate mineral separates of peridotite xenoliths from

342 Dish Hill, California and San Carlos, Arizona were lower than bulk rock values. Acid
343 leaching experiments on bulk samples showed high Pb contents in leachates, and the
344 ‘missing’ fraction was thus inferred to be hosted in acid-soluble sulfides, with an
345 estimated 75 $\mu\text{g/g}$ Pb (Hart and Gaetani, 2006; Meijer et al., 1990). However, sulfide
346 separates and in-situ concentration data on sulfides in abyssal peridotites indicate much
347 lower Pb contents in these rocks, mostly $< 10 \mu\text{g/g}$ (Blusztajn et al., 2014; Burton et al.,
348 2012; Nielsen et al., 2014; Warren and Shirey, 2012; Warren et al., 2017). Only a few
349 sulfide inclusions in silicates of refractory peridotites show higher Pb concentrations of
350 up to 52 $\mu\text{g/g}$ (Burton et al., 2012). Lead contents of sulfides in peridotites and
351 pyroxenites from Balmuccia are highly variable, ranging from 0.1 $\mu\text{g/g}$ to 113 $\mu\text{g/g}$.
352 These results overlap the range of values reported from other peridotites extending
353 previous data to a larger range (e.g., Blusztajn et al., 2014; Burton et al., 2012; Nielsen et
354 al., 2014; Warren and Shirey, 2012). Sulfide melt that is stable at high-temperature
355 mantle conditions commonly exsolves different sulfide phases during ascent and slow
356 cooling of mantle rocks (e.g., Lorand et al., 2010; Luguet et al., 2004). This process leads
357 to redistribution of Pb between different sulfide minerals and preferential enrichment of
358 Pb in late exsolved sulfides, e.g., chalcopyrites (e.g., Brenan, 2015; Dare et al., 2011; Liu
359 and Brenan, 2015). In a given sample from Balmuccia, chalcopyrites tend to have higher
360 Pb contents than pentlandites and pyrrhotites (Figure 7, Supplementary Table S3),
361 consistent with experimental studies.

362 On the basis of bulk rock S contents (Wang and Becker, 2015a; Wang et al., 2013)
363 and assuming 35 wt. % S in a nominally homogeneous sulfide phase, sulfide abundances
364 were calculated for the analyzed peridotites (0.03 wt.% to 0.11 wt.% sulfide) and

365 pyroxenites (0.31 wt.%-0.46 wt.% sulfide, Table 3). Because chalcopyrite plays an
366 important role for the Pb budget, it is useful to determine its fraction based on Cu
367 contents in bulk rocks. Olivine, orthopyroxene, clinopyroxene and spinel contain < 0.5 -
368 3 $\mu\text{g/g}$ Cu and thus provide only a small fraction of the Cu in pyroxenites and lherzolites.
369 Pentlandite and pyrrhotite typically contain several hundreds of $\mu\text{g/g}$ Cu, however,
370 because of their low abundances, they only account for < 5 % of bulk rock Cu contents in
371 peridotites and pyroxenites (Supplementary Tables S3-S5). For sample BM11-11 which
372 has a low Cu content of 8 $\mu\text{g/g}$ in the bulk rock, the proportion of Cu provided by
373 chalcopyrite is still 88% (Supplementary Table S5).

374 Based on bulk rock Cu contents and assuming that all Cu resides in chalcopyrites,
375 the maximum calculated abundance of chalcopyrite is 0.003 wt.% to 0.017 wt.% for
376 peridotites and 0.05 wt.% to 0.07 wt.% for pyroxenites, which accounts for 9-25 wt.% of
377 the sulfide fraction (Table 3). Using the proportion of chalcopyrite in sulfides and the
378 mean Pb contents of chalcopyrites, pentlandites and pyrrhotites, the contribution of
379 sulfides to the bulk rock Pb budget is 0.2 ng/g to 9.8 ng/g for peridotites and 11-36 ng/g
380 for pyroxenites (Table 3). The calculated Pb contents of the sulfides are 0.6-22.2 $\mu\text{g/g}$ in
381 the peridotites and 3.6-12.9 $\mu\text{g/g}$ in the pyroxenites. These values are comparable to
382 typical Pb concentrations in sulfides from abyssal peridotites and peridotites elsewhere
383 (e.g., Blusztajn et al., 2014; Burton et al., 2012; Nielsen et al., 2014; Warren and Shirey,
384 2012; Warren et al., 2017). For comparison, slightly higher mean Pb concentrations of
385 $18.5 \pm 3.6 \mu\text{g/g}$ (1sd, n=7) were determined for sulfide droplets in MORBs (Patten et al.,
386 2013).

387 Thallium contents in sulfides from Balmuccia peridotites and pyroxenites are also
388 highly variable from below detection limits of about 0.01 $\mu\text{g/g}$ to 110 $\mu\text{g/g}$ (Figure 7). In
389 a given sample, chalcopyrites show higher Tl contents than pentlandites and pyrrhotites.
390 Thus, Tl also should be concentrated in late exsolved sulfides (Figure 7). Sulfides in
391 different samples from Balmuccia display different Tl contents (Supplementary Table S3),
392 suggesting heterogeneous distribution of Tl in mantle rocks and their sulfides. The results
393 are consistent with literature data on lherzolites which show heterogeneous distribution of
394 Tl in sulfides with contents of 0.023-0.43 $\mu\text{g/g}$ (Nielsen et al., 2014).

395

396 **Lead contents in silicate phases of mantle rocks.** Previous studies on Pb
397 concentrations in separated mantle minerals by isotope dilution have shown that olivine,
398 orthopyroxene and spinel typically host very little Pb, e.g., 10-15 ng/g, 20-25 ng/g and 60
399 ng/g, respectively (e.g., Burton et al., 2012; Carignan et al., 1996; Meijer et al., 1990).
400 Because in-situ Pb contents in olivine, orthopyroxene and spinel were below detection
401 limits (about 50 ng/g in this study), the specific Pb contents of these phases are not
402 available. Therefore, we refer to the above-mentioned literature data for olivine,
403 orthopyroxene and spinel (Table 3).

404 Clinopyroxene separates from the literature show highly variable Pb contents,
405 ranging from low values of a few tens of ng/g (e.g., Galer and O'Nions, 1989; Meijer et
406 al., 1990) to several hundreds and in rare cases even thousands of ng/g (e.g., Burton et al.,
407 2012; Carignan et al., 1996; Mukasa and Shervais, 1999; Wittig et al., 2010). Lead
408 concentration data obtained *in situ* on clinopyroxenes in peridotites from different
409 localities often show several hundreds of ng/g Pb (e.g., Lazarov et al., 2012a; Simon et al.,

410 2007). Clinopyroxene separates from Balmuccia peridotites contain 130-300 ng/g Pb
411 (Mukasa and Shervais, 1999) and the in-situ data on clinopyroxene in this study lie
412 mostly within this range with some analyses below detection limits (50 ng/g).

413 The peridotites analyzed in this study contain about 58-62 % olivine, 21-27 %
414 orthopyroxene, 10-15 % clinopyroxene and 2-5 % spinel (Table 3), which is similar to
415 previous estimates of modal abundances (Mukasa and Shervais, 1999; Shervais and
416 Mukasa, 1991). According to these mineral proportions and corresponding Pb contents,
417 the calculated Pb contents in the main mineral fraction (silicates + spinel) of the
418 peridotites are 18-32 ng/g (Table 3).

419 While sulfides have higher Pb contents, the low proportion of sulfides in peridotites
420 leads to a range of 0.2 ng/g to 5.9 ng/g Pb hosted by sulfides, which are only about 1-
421 16 % of the calculated bulk rock Pb contents from the constituent phases (Table 3). We
422 note that one peridotite (BM11-18) shows a somewhat higher contribution of sulfide-
423 hosted Pb (35%), which, in this particular case, is mainly due to high Pb contents in
424 chalcopyrites (Figure 8 and Table 3). Calculated bulk rock Pb concentrations determined
425 from abundances in sulfides, silicates and spinel yield a range of 19 and 38 ng/g, a level
426 similar to the estimated Pb content of the depleted mantle based on oceanic basalt and
427 abyssal peridotite data (e.g., Salters and Stracke, 2004; Warren and Shirey, 2012).

428 The pyroxenites formed from magmatic accumulation of clino- and orthopyroxenes,
429 spinel and sulfides (Wang and Becker, 2015a). In-situ Pb contents on clinopyroxene of
430 clinopyroxenites are 170 ± 50 and 670 ± 80 (1sd) ng/g (Table 3 and Supplementary Table
431 S4), similar to Pb concentrations in clinopyroxene separates from Balmuccia pyroxenites
432 (100-400 ng/g Pb, Mukasa and Shervais, 1999). The Pb concentration data for the two

433 clinopyroxenites studied with *in situ* methods indicates that the Pb hosted in sulfides
434 represents only 5-20 wt.% of the calculated bulk rock contents, although these samples
435 contain a relatively high proportion of sulfides of 0.29-0.44 wt.% (Table 3). Mass balance
436 based on the new data indicates that Pb abundances in clinopyroxenites are
437 predominantly controlled by clinopyroxene rather than sulfides (Table 3, Figure 9). This
438 result is consistent with the positive correlations of Pb with Al₂O₃ and Ce contents in
439 pyroxenites, because the latter elements are mainly controlled by clinopyroxene (Figure
440 3). Lead and S contents in pyroxenites also show a positive correlation. This behavior
441 apparently reflects the precipitation of similar proportions of clinopyroxene and sulfide
442 melt (e.g., Nielsen et al., 2014) during the crystallization of sulfide-bearing mantle
443 pyroxenites.

444 In conclusion, the Pb budget of sulfides in peridotites and pyroxenites from
445 Balmuccia accounts for only 1-20 wt.% fraction of the Pb contents in bulk rocks if the
446 latter are calculated from Pb abundances in constituent mineral phases (Table 3 and
447 Figure 9). This conclusion is consistent with the observation that silicates host the main
448 fraction of Pb in some abyssal peridotites (Warren and Shirey, 2012). In addition, we
449 note that in 5 of 7 analyzed peridotites and pyroxenites, calculated Pb concentrations are
450 lower than the measured bulk rock values of this study (Table 3 and Figure 9). The
451 significance of these results will be discussed further below.

452

453 **Partitioning of Pb between coexisting sulfides and clinopyroxenes.** Based on
454 average Pb contents in sulfide and clinopyroxene from the clinopyroxenites BM11-16A
455 and BM11-28B (Table 3), the apparent partition coefficients $D_{Pb}^{\text{sulfide-clinopyroxene}}$ between

456 sulfide and clinopyroxene (the ratio of Pb contents in sulfide to clinopyroxene) are 5-137.
457 The data from peridotites in Table 3 display a similar level of $D_{\text{Pb}}^{\text{sulfide-clinopyroxene}}$. Lead
458 contents in chalcopyrites, which have higher Pb contents than pentlandites and
459 pyrrhotites, suggest a maximum empirical $D_{\text{Pb}}^{\text{sulfide-clinopyroxene}}$ of about 540 (Figure 7).
460 Data from a garnet peridotite (Lashaine, Tanzania, Burton et al., 2012) show a much
461 lower $D_{\text{Pb}}^{\text{sulfide-clinopyroxene}}$ of < 10 (5.75 $\mu\text{g/g}$ Pb in sulfide and 1.12 $\mu\text{g/g}$ in clinopyroxene,
462 Figure 7). These $D_{\text{Pb}}^{\text{sulfide-clinopyroxene}}$ based on natural samples are far lower than an
463 experimentally determined $D_{\text{Pb}}^{\text{sulfide-clinopyroxene}}$ value of about 3300 (Hart and Gaetani,
464 2016).

465 Incomplete equilibration of sulfides and co-existing clinopyroxenes in mantle rocks
466 might be a possible explanation for low apparent $D_{\text{Pb}}^{\text{sulfide-clinopyroxene}}$ in natural samples
467 compared to experimental data. This discrepancy may also reflect variable partitioning of
468 Pb in clinopyroxene in mantle rocks. Until now only a single value of experimentally
469 determined $D_{\text{Pb}}^{\text{sulfide-clinopyroxene}}$ has been reported (Hart and Gaetani, 2016). The
470 experiment yielded $D_{\text{Pb}}^{\text{sulfide melt-silicate melt}}$ of 67 and $D_{\text{Pb}}^{\text{clinopyroxene-silicate melt}}$ of 0.02. The
471 former is close to the required $D_{\text{Pb}}^{\text{sulfide melt-silicate melt}}$ of 30-60 to explain constant Ce/Pb (or
472 Nd/Pb) in ocean ridge and ocean island tholeiites (e.g., Hofmann et al., 1986; Kiseeva
473 and Wood, 2013). Similar $D_{\text{Pb}}^{\text{sulfide melt-silicate melt}}$ were calculated based on Pb
474 concentrations in coexisting sulfide globules and MORB glass (Patten et al., 2013).

475 Thus, it is likely that the inconsistency of $D_{\text{Pb}}^{\text{sulfide-clinopyroxene}}$ between natural
476 samples and experimental values does not result from $D_{\text{Pb}}^{\text{sulfide melt-silicate melt}}$ but from
477 variations in $D_{\text{Pb}}^{\text{clinopyroxene-silicate melt}}$. Reported experimental $D_{\text{Pb}}^{\text{clinopyroxene-silicate melt}}$ are
478 highly variable, for instance 0.01 (Hauri et al., 1994), 0.02 (Hart and Gaetani, 2016),

479 0.028 (Schmidt et al., 1999), 0.014 - 0.058 (Adam and Green, 2006) and up to 0.13
480 (Klemme et al., 2002). The combination of $D_{\text{Pb}}^{\text{clinopyroxene-silicate melt}}$ of 0.12 with $D_{\text{Pb}}^{\text{sulfide}}$
481 $D_{\text{Pb}}^{\text{melt-silicate melt}}$ of 44 would be consistent with constant Ce/Pb in ocean ridge basalts
482 (Kiseeva and Wood, 2013). A $D_{\text{Pb}}^{\text{clinopyroxene-silicate melt}}$ value of 0.02 would be too low to
483 explain the Ce/Pb of oceanic basalts. As discussed earlier, the Pb contents in
484 clinopyroxene in natural mantle rocks vary by two orders of magnitude, from a few tens
485 of ng/g to thousands of ng/g. The high Pb contents in clinopyroxenes from the
486 pyroxenites at Balmuccia cannot reflect high Pb contents of parental melts. If low
487 $D_{\text{Pb}}^{\text{clinopyroxene-silicate melt}}$ of 0.02 (Hart and Gaetani, 2016) were applied, the parental melts
488 would contain a few tens of $\mu\text{g/g}$ Pb, which is higher than Pb concentrations in MORBs
489 and ocean island basalts, which range between (0.2 to 10 $\mu\text{g/g}$, Figure 4). Therefore, it is
490 likely that other processes affecting mantle rocks result in highly variable and lower
491 apparent $D_{\text{Pb}}^{\text{sulfide-clinopyroxene}}$ than experimentally determined values.

492

493 **Location and origin of the ‘missing’ Pb in calculated bulk rock compositions**

494

495 **Correlated enrichment of Pb, Ba and Tl.** Reconstructed whole rock
496 concentrations of Pb based on mineral proportions and corresponding Pb concentrations
497 are sometimes similar to measured abundances in whole rocks of, e.g., 16-40 ng/g (this
498 study; Carignan et al., 1996; Warren and Shirey, 2012). However, measured Pb contents
499 in both sulfides and silicate minerals of peridotites cannot explain bulk rock Pb contents
500 that are higher than 30-40 ng/g. Ten of thirteen peridotites from Balmuccia display Pb
501 contents > 40 ng/g, with concentrations as high as 400 and 700 ng/g in three peridotites

502 (Figure 3 and Tables 2 and 3). We note that the replacive dunites contain low proportions
503 of pyroxenes and sulfides (low Al₂O₃, Sm and S contents), but at the same time show
504 relatively high Pb contents in their measured bulk rocks (69-248 ng/g, Table 2). Similarly,
505 the measured bulk rock Pb contents in pyroxenites show discrepancies compared with
506 those calculated from *in situ* data on mineral phases (e.g., BM11-28B and BM11-07B,
507 Table 3 and Figure 9). These features indicate a deficit of Pb contents in calculated values
508 based on mineral modes compared to measured values in most bulk rocks. The
509 uncertainty of mineral modes and the variation of in-situ Pb data, particularly on sulfides,
510 may contribute to the imbalance of measured and calculated compositions (e.g., BM11-
511 16A in Figure 9). However, it should be not the main cause because 5 of 7 samples in this
512 study show very large differences between calculated and measured abundances of Pb
513 (e.g., 37-94%, Table 3).

514 Similarly, the low Ba contents in silicates (mostly < 0.2 µg/g) cannot balance the
515 high measured contents of Ba in bulk rocks of most peridotites (e.g., 0.3-7.5 µg/g Ba,
516 Supplementary Table S4, Tables 2 and 3), indicating that like for Pb, bulk rock Ba
517 contents calculated from in-situ analyses of silicate phases are also mostly lower than the
518 measured values.

519 Thallium is a highly incompatible element, and its content in the depleted mantle
520 was estimated to be about 0.4-0.5 ng/g (Nielsen et al., 2014; Salters and Stracke, 2004).
521 The Tl contents in many peridotites from Balmuccia (Table 2) are similar to or slightly
522 higher than the values of the depleted mantle model composition and abundances in
523 harzburgites from other tectonic settings (Nielsen et al., 2015). Three peridotites (BM11-

524 11, BM11-04 and BM11-03B) show high Tl contents of 2-3 ng/g (Figure 5), as well as
525 noticeable enrichments of Pb and Ba.

526 Because of low Tl intensities at detection limits, Tl contents in silicates were not
527 obtained in this study. Other work showed < 1 ng/g Tl in silicate phases of lherzolites
528 (Nielsen et al., 2014). Thallium contents in sulfides are highly variable and chalcopyrites
529 have the highest Tl contents among different constituent phases of mantle rocks
530 (Supplementary Table S3 and Figure 7). As for Pb, the low proportion of sulfides results
531 in a small contribution of sulfides to the bulk rock budget of Tl. For example,
532 chalcopyrites (0.003 wt.%) in the peridotite BM11-11 have the highest Tl contents of 28-
533 85 $\mu\text{g/g}$ in this study (Table 3 and Supplementary Table S3). These minerals contribute
534 only 64 % (1.4 ng/g) of the 2.5 ng/g Tl in the measured bulk rock. Thallium contents in
535 sulfides of other samples are mostly < 0.5 $\mu\text{g/g}$ (Figure 7) and in these samples sulfides
536 contribute a maximum of 0.5 ng/g or < 30 % to the bulk rock budgets. In summary,
537 contributions of Tl from sulfides and silicate phases are obviously lower than the
538 measured bulk rock Tl contents of some peridotites and most pyroxenites (typically 2-8
539 ng/g) from Balmuccia. Thallium contents in bulk rocks show positive correlations with
540 Ba and Pb contents (Figures 5 and 6), implying that a common process may be
541 responsible for their overabundances at the bulk rock scale.

542 In order to explain the correlated excesses of Pb, Ba and Tl in most measured bulk
543 rocks compared to calculated bulk rocks, the unaccounted fraction of these elements must
544 reside in trace phases included in main minerals, or on grain boundaries (e.g., Bedini and
545 Bodinier 1999).

546

547 **Trace phases as hosts of Pb, Ba and Tl excess concentrations in bulk rocks.** As
548 noted before, the peridotites and pyroxenites analyzed in this study lack macroscopic
549 mineralogical effects of serpentinization and weathering (Figure 1). The entrapment of
550 ‘exotic’ phases along grain boundaries and as micron-size inclusions in main minerals
551 could provide a viable explanation for the common enrichment of Pb, Ba and Tl in
552 measured bulk samples of mantle rocks (e.g., Hanghøj et al., 2010; Harvey et al., 2012;
553 Niu, 2004; Wittig et al., 2009). The highly labile characteristics and enrichment of Pb in
554 acid leachates of mantle rocks supports this view (Carignan et al., 1996; Meijer et al.,
555 1990; Wittig et al., 2009).

556 Both harzburgite BM11-03B and dunite BM11-03A are from the same outcrop and
557 reflect gradual dissolution of pyroxenes by percolating melts during the formation of
558 replacive dunites (Mazzucchelli et al., 2009; Wang et al., 2013). The harzburgite has 396
559 ng/g Pb, 3100 ng/g Ba and 2.5 ng/g Tl; the dunite also shows high contents (205 ng/g Pb,
560 1440 ng/g Ba, 0.59 ng/g Tl). The harzburgite and another two peridotites with high Ba
561 and Pb contents (BM11-11 and BM11-04) show an assemblage of fine-grained silicate
562 phases (pyroxenes and olivine) along grain boundaries of larger silicate grains (Fig. 1c).
563 The fine-grained assemblage may represent crystallization products of late infiltrating
564 basic melts (Figure 1c). In contrast, Balmuccia peridotites with relatively low Pb, Ba and
565 Tl contents, such as most of the lherzolites, display less abundant or no interstitial micro-
566 phases (e.g., BM11-10, Figure 1e). Some pyroxenites also show evidence for fine-grained
567 interstitial pyroxene assemblages. Consequently, the coupled enrichment of Ba, Pb and Tl
568 in some Balmuccia peridotites (Table 2, Figure 5) can be interpreted to result from melt
569 infiltration and entrapment of interstitial melts (Figure 1). However, the fine-grained

570 silicate assemblages can only be the source of the unaccounted fraction of Pb if they have
571 much higher concentrations of incompatible elements than other silicates in the rock.
572 Alternatively, the aggregates may contain not yet identified trace phases that contain a
573 large fraction of the budget of Pb, Tl and Ba. As no concentration data on these fine-
574 grained minerals are available, this issue still remains open.

575 We also note that many planar features of tiny dark inclusions exist in the replacive
576 dunites (e.g., BM11-24A, Figure 1d), in some lherzolites and in pyroxenites (Figure 1a, b,
577 e). These planar inclusion features may represent late fluid or melt inclusions trapped in
578 healed fractures of silicate minerals. The excess of abundances of Pb, Tl and Ba in
579 measured bulk rocks and the positive correlation of these elements may also be caused by
580 the trapped fluid or melt inclusions (Figures 1 and 4). In a few cases, the rims of olivine
581 and pyroxene have higher Ba contents than the interiors of these mineral grains
582 (Supplementary Table S4). These different concentrations may reflect sampling of such
583 fluid or melt inclusions near the rims of these silicate grains.

584 Similar to Pb, concentrations of the highly incompatible and fluid-mobile elements
585 Tl, Ba, Cs and Rb can be modified easily by fluids (e.g., Deschamps et al., 2012; Jochum
586 and Verma, 1996; McGoldrick et al., 1979; Nielsen et al., 2015). Abundances and ratios
587 of Ba, Cs and Rb can be used to evaluate and to distinguish the effects of metasomatism
588 by basaltic melts or solute rich fluids on Pb and Tl contents. In the most LREE-depleted
589 samples (the peridotites), the fluid-mobile elements Cs, Rb, Ba and Pb are enriched
590 compared to the LREE, indicative of metasomatism by a fluid phase (Figures 2-3). In-situ
591 data on clinopyroxenes in peridotites and pyroxenites tend to show higher Ce/Pb than the
592 bulk rocks (Supplementary Table S4 and Figure 4), consistent with two components with

593 different Ce/Pb, at least in some of the rocks. Given nearly constant ratios of Cs, Rb and
594 Ba of MORBs and OIBs (Hofmann and White, 1983), the enrichment of Cs relative to Rb
595 and Ba in Balmuccia peridotites and pyroxenites necessitates to consider continental
596 fluids, which may have been present during the exhumation of the mantle rocks to
597 granulite-amphibolite facies lower crustal conditions (Metasomatism of mantle by
598 continental fluids and the effects on alkali metals was discussed in Becker, et al., 1999).
599 Moreover, given similar bulk incompatibilities of Pb and Tl as indicated by nearly
600 constant ratios of Pb/Tl in oceanic basalts (Figure 6), the higher Pb/Tl in many peridotites
601 and clinopyroxenites than in oceanic basalts (Figure 6) should reflect the additional effect
602 of fluid infiltration. The enrichment of Pb compared to Tl suggests that under these
603 conditions, the former is probably more fluid mobile than the latter. Consequently,
604 correlated enrichment of Pb, Tl, Cs, Rb and Ba in the bulk rocks thus suggests that these
605 elements show similar behavior and were controlled by fluid-mineral equilibria.

606 Clinopyroxenes from peridotites and pyroxenites of the Balmuccia massif show
607 radiogenic $^{207}\text{Pb}/^{204}\text{Pb}$ relative to their $^{206}\text{Pb}/^{204}\text{Pb}$ and MORB compositions (Mukasa and
608 Shervais, 1999), suggestive of a fluid component with the signature of upper continental
609 crust. Such fluids might have been released from ambient gneisses of the kinzigite
610 formation during the intrusion of the mafic complex. It is worth noting that Sr and Nd
611 isotopic compositions of clinopyroxenes are consistent with a depleted mantle-like
612 composition of the peridotites and pyroxenites (Mukasa and Shervais, 1999), suggesting
613 that Pb is decoupled from the other tracers. This observation represents further indirect
614 evidence for the hypothesis that Pb in these rocks was strongly affected by ‘continental’
615 fluids.

616 As previous studies of peridotite xenoliths have shown, significant differences
617 between measured and calculated bulk-rock contents of Pb, Ba and other highly
618 incompatible lithophile elements are common (e.g., Burton et al., 2012; Harvey et al.,
619 2012; Ionov et al., 2005; Lazarov et al., 2012a, 2012b; Simon et al., 2007; Wittig et al.,
620 2009). Detailed work has indicated the presence of entrapped melts, amorphous material,
621 or ‘spongy’ reaction rims around minerals (e.g., Harvey et al., 2012; Ionov, 2007; Ionov
622 et al., 2005). Neglecting the substantial fraction of Pb in these materials may be the main
623 reason for the previous inference that sulfides should have high Pb contents (Hart and
624 Gaetani, 2006; Meijer et al., 1990). We note however that these previous studies often
625 concerned mantle xenoliths in which the contamination with melt and fluid inclusions
626 may record transient processes related to xenolith transport. Lead enrichment is also
627 commonly present in serpentinized abyssal peridotites (Godard et al., 2008; Niu, 2004)
628 and in serpentinized peridotites from ophiolites (Hanghøj et al., 2010). However, because
629 these rocks often show strong serpentinization, the specific reasons of Pb enrichments
630 were difficult to specify. In the case of the Balmuccia mantle rocks, it appears that a
631 variable and often significant fraction of the budget of Pb, Ba and Tl (e.g., variable from
632 10% to 94% for Pb, Table 3) is controlled by unaccounted trace phases.

633

634 **IMPLICATIONS AND CONCLUSIONS**

635 Most mantle sulfides in peridotites and pyroxenites from Balmuccia contain < 20
636 $\mu\text{g/g}$ Pb. These abundances are much higher than abundances in silicate phases (typically
637 < 50 ng/g). However, because of the low abundances of sulfides in peridotites (0.03-0.1

638 wt.%) and in pyroxenites (0.29-0.44 wt.%), sulfides in most cases contribute only < 20%
639 to bulk rock Pb budgets calculated based on the composition of silicates, spinel and
640 sulfides. Silicate phases and fluid inclusions therein host the predominant fraction of Pb
641 in the peridotites and pyroxenites (> 70-80 wt.%, Table 3). Therefore, the results from
642 Balmuccia, representing Phanerozoic subcontinental mantle and data from abyssal
643 peridotites (Harvey et al., 2016; Warren and Shirey, 2012) both indicate that silicates
644 rather than sulfides are the major reservoir for Pb in the upper mantle. Mantle
645 metasomatism and in particular late-stage crustal fluids introduce a variable, often
646 significant fraction of Pb, Ba, Tl and other highly incompatible fluid-mobile elements
647 such as Cs and Rb along grain boundaries and as fracture-controlled inclusions in main
648 minerals (e.g., Figures 1 and 2), thus affecting bulk rock element budgets of mantle
649 tectonites and xenoliths (e.g., Bedini and Bodinier 1999; Carignan et al., 1996; Harvey et
650 al., 2012; Ionov et al., 2006; Meijer et al., 1990; Simon et al., 2007 and this study). The
651 data on natural sulfides from both subcontinental (this study) and oceanic lithospheric
652 mantle (Warren and Shirey, 2012) do not support the assumed high Pb contents in mantle
653 sulfides proposed in earlier work (Hart and Gaetani, 2006).

654 The identification of unradiogenic Pb in some mantle sulfides (Burton et al., 2012)
655 was used to argue that mantle sulfides may represent an unaccounted reservoir of
656 unradiogenic Pb in the mantle if they are shielded during the formation of mantle derived
657 magmas such as MORB. The validity of this proposition strongly depends on the
658 abundance of mantle sulfides and the content and isotopic composition of Pb in mantle
659 sulfides. The main control of the Pb budget in mantle rocks by silicates (predominantly
660 clinopyroxene) rather than sulfides suggests that sulfides in the mantle likely do not

661 represent a major reservoir of unradiogenic Pb. Burton et al (2012) suggested that
662 assuming 0.08 wt.% sulfides (equivalent to 250 $\mu\text{g/g}$ S) in the mantle containing on
663 average 47 $\mu\text{g/g}$ Pb with an unradiogenic isotopic composition ($^{206}\text{Pb}/^{204}\text{Pb}$ of 16.23),
664 sulfides may account for 70% of the Pb in the upper mantle and may balance the
665 radiogenic Pb isotopic composition of the silicate Earth model composition ($^{206}\text{Pb}/^{204}\text{Pb}$
666 of 18.29). However, according to the data from abyssal peridotites (Warren and Shirey,
667 2012) and from subcontinental mantle rocks at Balmuccia, mantle sulfides very likely
668 have typical Pb contents of $< 20 \mu\text{g/g}$ and contribute $< 20\%$ of Pb in mantle rocks. These
669 data indicate that typical Pb abundances in mantle sulfides are too low to balance the
670 radiogenic Pb of current BSE models (Burton et al., 2012). Because S is an incompatible
671 element during mantle melting, the abundances of sulfides in refractory peridotites where
672 the unradiogenic Pb commonly resides should be lower than 0.08 wt.%. Moreover, not all
673 mantle sulfides in mantle peridotites contain unradiogenic Pb (Blusztajn et al., 2014;
674 Burton et al., 2012; Warren and Shirey, 2012). These results suggest that mantle sulfides
675 with unradiogenic Pb isotopic compositions (low time integrated U/Pb) likely cannot
676 effectively balance reservoirs with higher time-integrated U/Pb in the upper mantle and
677 require additional unradiogenic reservoirs such as the core (e.g., Wood and Halliday,
678 2010).

679

680

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FIGURE CAPTIONS

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923 Figure 1. Examples of microphotographs of Balmuccia peridotites and pyroxenites which
924 have not been affected by serpentinization. a-b) Clinopyroxenites (BM11-16A) often
925 display planar traces of dark inclusions in clinopyroxene (white arrows). These features
926 may represent fluid inclusions (see text in the Discussion). b) Magnified view of the red
927 box in a). c) A peridotite with high Ba and Pb content (BM11-04) shows interstitial fine-
928 grained silicates (yellow arrows) that may have been caused by late infiltration of
929 metasomatic melt. d) Replacive dunites (BM11-24A) are also very fresh, but contain
930 traces of tiny dark inclusions in olivine, presumably fluid inclusions (white arrows). e)
931 Peridotites with low Pb and Ba contents (BM11-10) are commonly very fresh and show
932 limited amounts of interstitial phases and planes of fluid inclusions (white arrows). f)
933 Typical sulfide assemblage of pentlandite (Pent) and chalcopyrite (Cpy) in peridotites
934 (BM11-10). White scale bars are 250 μm . a-e: cross-polarized light; f: reflected light. See
935 Wang et al (2013) and Supplementary Figure S1 for more microscopic observations.

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937

938 Figure 2. Bulk silicate Earth (BSE) normalized abundances of bulk rock concentration
939 data of trace elements in pyroxenites (a) and peridotites (b) from Balmuccia. The data
940 show depletion of light REE relative to heavy REE for peridotite and pyroxenites.
941 However, all peridotites and a few pyroxenites display strong Pb enrichment relative to
942 neighbor elements. Note that in the most LREE-depleted samples, the fluid-mobile
943 elements Cs, Rb, Ba and Pb are enriched compared to the LREE. BSE abundances from
944 (Palme and O'Neill, 2014).

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946

947 Figure 3. Diagrams of Pb contents with Al₂O₃ (a), Ce (b), S (c) and Ba (d) in Balmuccia
948 peridotites and pyroxenites. Most pyroxenites show positive correlations of Pb with
949 Al₂O₃, Ce and S, whereas the data for the peridotites appears scattered. A few peridotites
950 with fine-grained interstitial phases (e.g., Figure 1c) and replacive dunites show
951 noticeable Pb enrichment. Literature Pb and Ce data from the Balmuccia massif
952 (Obermiller, 1994) are included for comparison.

953

954

955 Figure 4. Lead and Ce contents of bulk rocks and in-situ data on clinopyroxenes in
956 Balmuccia peridotites (Per) and pyroxenites (Pyr). Note that the Pb contents of
957 clinopyroxenes determined *in situ* are variable and some are not shown because they were
958 below detection limits (50 ng/g). Ce/Pb of clinopyroxenes from Balmuccia peridotites
959 and pyroxenites are similar to or higher than those of bulk rocks, but in any case, the
960 values are lower than in oceanic basalts, confirming that Balmuccia peridotites and
961 pyroxenites have distinctly low Ce/Pb ratios (Obermiller, 1994). Oceanic basalts and arc
962 basalts are shown for comparison (Jenner and O'Neill, 2012; Nielsen et al., 2014; Norman
963 and Garcia, 1999; Miller et al., 1994). Fertile peridotites from the Horoman massif with
964 unradiogenic Pb isotopic compositions are also included (Malaviarachchi et al., 2008).

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966

967 Figure 5. Thallium contents in Balmuccia peridotites and pyroxenites. Overall, Tl
968 contents do not show correlations with Al₂O₃ and S contents (a and b) but broadly
969 correlate with Ba contents (c).

970

971 Figure 6. Contents of Pb and Tl in peridotites and pyroxenites from Balmuccia. The Pb/Tl
972 ratios in some peridotites and many clinopyroxenites with high Pb contents are higher
973 than those in oceanic basalts. Contents of Tl in the BSE (Palme and O'Neill, 2014)
974 (yellow circle) and MORBs (Jenner and O'Neill, 2012; Nielsen et al., 2014) are shown for
975 comparison. Note that many MORBs have higher Pb and Tl contents, which are not
976 shown because they are out of the range of the diagram (arrow).

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978

979 Figure 7. In-situ Pb and Tl contents in sulfides and clinopyroxenes (Cpx) of Balmuccia
980 peridotites and pyroxenites. a) Pb and Tl contents are highly variable in sulfides from the
981 same thin sections and also from different samples of peridotites and pyroxenites (see
982 details in Supplementary Table S3). Chalcopyrites (Cpy) in these samples tend to have
983 higher Pb and Tl contents relative to pentlandites and pyrrhotites (Pent + Pyrr). Note that
984 many sulfides have Tl contents below detection limits (about 0.01 $\mu\text{g/g}$, not shown, see
985 details in Supplementary Table S3). Thallium data of sulfides in lherzolites elsewhere
986 (Nielsen et al., 2014) are shown for comparison. b) Because of variable Pb contents in
987 sulfides, the ratios of Pb contents in sulfides to clinopyroxenes (i.e., empirical $D_{\text{Pb}}^{\text{sulfide-}}$
988 clinopyroxene), including from the same thin sections show large variations. These ratios are
989 considerably lower than partitioning data from an experimental study ($D_{\text{Pb}}^{\text{sulfide-clinopyroxene}}$
990 = 3300, Hart and Gaetani, 2016). Similarly, the ratio of Pb contents in sulfides (5.75 $\mu\text{g/g}$
991 Pb) and co-existing clinopyroxene (1.12 $\mu\text{g/g}$ Pb) in garnet peridotite from Lashaine,
992 Tanzania (Burton et al., 2012) is also lower than the experimental value.

993

994

995 Figure 8. Lead contents in pentlandites, pyrrhotites and chalcopyrites of Balmuccia
996 peridotites (n=4) and pyroxenites (n=3). a) shows the measured values (n=102) and b)
997 represents the distributions of concentrations within the gray area of a). The data are
998 listed in Supplementary Table S3.

999

1000

1001 Figure 9. The Pb contents of sulfides, clinopyroxene, olivine+orthopyroxene+spinel and
1002 the ‘missing’ fraction (the deficit of Pb contents calculated from constituent phases
1003 relative to measured bulk rock values) in Balmuccia peridotites and pyroxenites (a) and
1004 their percentage relative to measured Pb contents (b). The data are from Table 3. Note the
1005 calculated bulk rock Pb content of BM11-16A exceeds the measured value by 13%
1006 (above dashed line in b).

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1008

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DEPOSIT ITEMS

1010

The supplementary materials include Table S1-S5 and Figure S1.

1011

1012

TABLES (PLEASE SEE ATTACHED EXCEL FILES)

1013

1014 Table 1. Bulk rock Pb contents in reference materials determined by isotope dilution ICP-

1015 MS

1016

1017 Table 2. Bulk rock Pb and Tl contents and in-situ Ba, Pb and Ce contents of

1018 clinopyroxene in Balmuccia peridotites and pyroxenites

1019

1020 Table 3. Pb content and the relative percentage in different phases of Balmuccia

1021 peridotites and pyroxenites

1022

1023

Table 1. Bulk rock Pb contents in reference materials determined by isotope dilution ICP-MS

Samples	Comments	Pb ($\mu\text{g/g}^a$)	2sd	Pb ($\mu\text{g/g}^b$)	2sd	$\Delta\%$	Mean value ($\mu\text{g/g}$)	2sd
BHVO-2	Basalt	1.52	0.06	1.57	0.05	2.8%	1.54	0.06
BHVO-2	Replicate	1.48	0.06	1.50	0.05	1.2%	1.49	0.05
BHVO-1	Basalt	2.07	0.10	2.15	0.08	3.5%	2.11	0.09
MRG-1	Gabbro	5.38	0.19	5.43	0.22	0.9%	5.41	0.21

Note: a and b are based on $^{207}\text{Pb}/^{208}\text{Pb}$ and $^{204}\text{Pb}/^{208}\text{Pb}$, respectively, and $\Delta\%$ reflects the differences between the calculation method ID in GeoReM ranges indicates values obtained by isotope dilution.

GeoReM: <http://georem.mpch-mainz.gwdg.de/>

GeoReM ranges ($\mu\text{g/g}$)

1.55 \pm 0.28; ID: 1.52 \pm 0.24 or 1.82 \pm 0.16

2.06-2.6; ID: 2.10 \pm 0.08

4.4-5.3

ls.

Table 2. Bulk rock Pb and Tl contents and in-situ Ce, Ba and Pb contents of clinopyroxene in Balmuccia peridotites and pyroxenites

Samples	Comments	Al ₂ O ₃ ^a	MgO ^a	S ^a	Ce	Ba	Pb ^b	Pb ^c		Pb Δ%	Tl		
		wt. %	wt. %	μg/g	μg/g	μg/g	ng/g	2sd	ng/g	2sd	ng/g	2sd	
Balmuccia peridotites													
BM90-5	Lherzolite	2.0	42.5		0.037	0.15	28	1	28	1	1%	0.18	0.06
BM90-5	<u>Replicate</u>				0.035	0.11	23	1	23	1	3%	0.40	0.06
BM90-25	Lherzolite	2.5	41.1		0.032	0.96	60	2	59	2	2%	0.59	0.06
BM90-41	Lherzolite	2.6	40.5		0.032	0.56	13	1	13	1	0%	0.35	0.06
BM90-15	Lherzolite	2.8	39.9		0.083	0.70	65	2	65	2	1%	0.37	0.06
BM11-11 ^d	Lherzolite	2.1	39.4	88	0.11	1.47	770	20	748	19	3%	2.67	0.07
BM11-11	<u>Replicate</u>				0.12	1.53	679	19	673	24	1%	2.32	0.07
	In-situ cpx				1.37±0.32	<0.05 to 0.52	0.09 to 0.20						
BM-09	Lherzolite	3.4	37.6	182	0.093	0.76	47	1	48	1	-2%	0.57	0.06
BM11-08	Lherzolite	3.2	38.6	170	0.046	1.14	97	2	98	2	-1%	0.92	0.06
BM11-09	Lherzolite	2.7	40.1	127	0.032	0.72	55	1	55	1	0%	0.55	0.06
BM11-03B	Harzburgite	1.1	44.1	76	0.14	2.37	394	9	396	9	0%	2.50	0.07
BM11-03B	<u>Replicate</u>				0.15	2.34	417	11	403	12	4%	2.09	0.07
BM11-04	Lherzolite	2.5	39.9	153	0.38	7.50	683	17	678	16	1%	3.27	0.07
BM11-04	<u>Replicate</u>				0.39	7.53	706	17	700	17	1%	3.05	0.07
BM11-18 ^d	Lherzolite	2.8	39.6	168	0.020	1.28	90	2	89	2	0%	3.55	0.07
	In-situ cpx				0.15±0.03	<0.12 to 1.88	<0.05						
BM11-10 ^d	Lherzolite	2.8	39.8	134	0.025	0.30	21	1	20	1	2%	0.05	0.06
	In-situ cpx				0.18±0.03	<0.090 to 0.18	<0.05						
BM11-02A ^d	Lherzolite	3.4	37.6	349	0.063	0.32	44	1	43	1	2%		
BM11-02A	<u>Replicate</u>				0.065	0.28	42	1	42	1	2%	0.66	0.06
	In-situ cpx				0.41±0.17	<0.08 to 0.13	0.09 to 0.14						
BM11-03A	Dunite	0.3	48.4	29	0.072	1.44	211	5	205	5	3%	0.59	0.06
BM11-05	Dunite	0.4	48.5	19	0.062	1.64	180	4	178	4	1%	0.73	0.06
BM11-07A	Dunite	0.3	48.1	73	0.028	0.98	248	6	239	6	4%	0.94	0.06
BM11-24A	Dunite	0.5	48.4	28	0.018	0.31	69	2	68	2	2%	0.16	0.06
Balmuccia pyroxenites													
BM11-28A	Clinopyroxenite	14.0	18.8	1456	2.51	1.64	522	18	522	16	0%	2.50	0.07
BM11-28B ^d	Clinopyroxenite	6.0	23.7	1509	1.43	0.70	318	10	318	9	0%	1.88	0.07
	In-situ cpx				2.35±0.56	<0.09 to 0.19	0.13 to 0.26						
BM11-28C	Clinopyroxenite	6.0	23.0	1490	1.42	0.73	355	13	357	11	0%	2.28	0.07
BM11-27	Clinopyroxenite	7.1	19.5	1559	1.20	2.94	481	21	477	17	1%	3.97	0.11
BM11-15	Clinopyroxenite	11.6	18.0	1250	3.33	1.03	657	33	644	26	2%	4.16	0.10
BM11-16A ^d	Clinopyroxenite	10.4	17.8	1532	3.39	0.87	535	24	531	20	1%	2.07	0.07
	In-situ cpx				4.02±0.46	<0.08 to 2.20	0.57 to 0.92						
BM11-20	Clinopyroxenite	5.4	20.7	537	1.14	4.61	180	6	179	5	1%	6.80	0.12
BM11-20	<u>Replicate</u>				1.14	4.54	187	5	181	5	3%	6.97	0.13
BM11-22	Clinopyroxenite	8.1	18.0	523	2.05	7.56	183	6	183	5	0%		
BM11-26	Clinopyroxenite	7.0	17.3	805	1.69	2.52	350	13	347	11	1%	3.06	0.11
BM11-26	<u>Replicate</u>						350	9	342	11	2%	3.07	0.07
BM11-23	Clinopyroxenite	11.0	17.9	1028	2.75	4.38	428	17	420	14	2%	5.71	0.13
BM11-29	Clinopyroxenite	6.6	17.3	323	1.45	4.29	174	4	173	4	1%	2.75	0.07
BM11-25	Websterite	4.9	21.4	722	1.16	1.13	246	6	246	6	0%	3.41	0.08
BM11-19	Websterite	5.1	21.8	611	1.78	1.93	254	6	255	6	0%	4.06	0.06
BM11-21	Websterite	2.7	21.9	1745	0.80	1.06	186	4	184	4	1%	2.31	0.06
BM11-12	Websterite	4.2	20.5	680	0.69	3.97	205	5	204	5	1%	2.97	0.06
BM11-14	Websterite	5.0	26.1	468	0.76	0.41	58	1	58	1	0%	1.07	0.06
BM11-14	<u>Replicate</u>				0.75	0.42	61	2	61	2	1%	0.66	0.06
BM11-07B ^d	Orthopyroxenite	5.4	30.6	1017	0.096	2.22	369	9	367	9	1%	7.86	0.11
	In-situ cpx				1.86±36	<0.11 to 0.82	0.37 to 0.70						

Note: a means published data (Wang et al., 2013, Wang and Becker 2015)

b and c are based on ²⁰⁷Pb/²⁰⁸Pb and ²⁰⁴Pb/²⁰⁸Pb, respectively, and Δ% reflects their differences.

d means those used for in-situ analyses and the data on clinopyroxene are shown (see Supplementary Tables for details).

Underlined samples indicate replicate analyses.

Note that Tl intensities in clinopyroxenes were very low and thus not monitored.

Table 3. Pb contents and the relative percentage in different phases of Balmuccia peridotites and pyroxenites

Samples	Bulk rock	Bulk rock	Bulk rock	Bulk rock	Bulk rock	Sulfide	Chalcopyrite	Constituent Phases	Phase mode	Average	Is.d.	Fraction of Pb budget of different phases	Apparent $D_{pb}^{clinopyroxene}$	Bulk rock Pb	Pb in Sulfides	Pb in	Unaccounted Pb fraction	Unaccounted Pb fraction relative to measured Pb in bulk rocks	
	Al_2O_3	S	Cu	Pb	Ba	abundances fraction	fraction			Pb content in phases				calculated from phases	relative to calculated bulk rock Pb	clinopyroxene fraction relative to calculated bulk rock Pb			
	wt. %	$\mu g/g$	$\mu g/g$	ng/g	$\mu g/g$	wt. %	wt. %			%	$\mu g/g$	$\mu g/g$	ng/g		ng/g	%	%	ng/g	%
BM11-02A Peridotite	3.4	349	54.7	42	0.30	0.10%	0.017%	OI	58%	0.011		6.3	14	27	5%	41%	15	37%	
								Opx	27%	0.02	5.4								
								Spinel	5%	0.05	2.5								
								Cpx	10%	0.11	0.02	11							
								Sulfides	Pent	0.08%	1.5	2.6							1.1
								Pyrr	0.5	0.2									
Cpy	0.02%	1.6	0.6	0.3															
BM11-10 Peridotite	2.8	134	31.1	21	0.30	0.04%	0.01%	OI	60%	0.011		6.5	14	19	1%	32%	2	10%	
								Opx	21%	0.02	4.2								
								Spinel	4%	0.05	2.0								
								Cpx	15%	<0.05	6.0								
								Sulfides	Pent	0.03%	0.4	0.2							0.1
								Pyrr	0.03%	0.5	0.4	0.1							
Cpy	0.01%	1.0	0.5	0.1															
BM11-11 Peridotite	2.1	88	8.0	679	1.50	0.03%	0.003%	OI	60%	0.011		6.5	119	38	16%	52%	641	94%	
								Opx	24%	0.02	4.8								
								Spinel	2%	0.05	1.0								
								Cpx	14%	0.14	0.03	20							
								Sulfides	Pent	0.023%	17	22							4.0
								Pyrr	0.003%	75	33	1.9							
Cpy	0.01%	75	48	7.7															
BM11-18 Peridotite	2.8	168	35.6	90	1.28	0.05%	0.01%	OI	62%	0.011		6.8	537	27	35%	20%	63	70%	
								Opx	22%	0.02	4.4								
								Spinel	2%	0.05	1.0								
								Cpx	14%	<0.05	5.6								
								Sulfides	Pent	0.04%	5.1	5.3							1.9
								Pyrr	0.01%	75	48	7.7							
Cpy	0.01%	75	48	7.7															
BM11-16A Pyroxenite	10.4	1532	151	535	0.87	0.44%	0.06%	Spinel	10%	0.05		5.0	5	605	5%	94%	-70	-13%	
								Cpx	85%	0.67	0.08	566							
								Opx	5%	0.02	1								
								Sulfides	Pent	0.37%	3.5	3.5							10.3
								Pyrr	0.06%	2.0	1.2	22.9							
								Cpy	0.06%	35.5	6.7	22.9							
BM11-28B Pyroxenite	6.0	1509	259	318	0.70	0.43%	0.07%	Spinel	2%	0.05		1.0	47	187	19%	79%	131	41%	
								Cpx	88%	0.17	0.05	149							
								OI	5%	0.011	1								
								Opx	5%	0.02	1								
								Sulfides	Pent	0.36%	7.9	13.9							18.6
								Pyrr	0.07%	2.1	1.0	17.3							
Cpy	0.07%	23.3	7.8	17.3															
BM11-7B Pyroxenite	5.4	1017	189	369	2.22	0.29%	0.05%	Opx	90%	0.02		17.9	4	52	20%	41%	317	86%	
								OI	2%	0.011	0.2								
								Spinel	4%	0.05	2.0								
								Cpx	4%	0.54	0.15	21.6							
								Sulfides	Pent	0.24%	2.2	2.2							5.2
								Pyrr	0.05%	2.5	8.3	5.2							
Cpy	0.05%	10.5	8.3	5.2															

The bulk rock Al_2O_3 , S and Cu contents have been reported before (Wang et al., 2013; Wang and Becker, 2015).

The sulfide fractions were calculated from bulk rock S contents, and chalcopyrite abundances from Cu contents in bulk rocks.

Note that Cu contents in chalcopyrites are maximum fractions due to a small fraction of Cu in pentlandites, pyrrhotites and clinopyroxene (Supplementary Tables S2 and S3). Cu fractions in the latter minerals overall comprise < 5 % (Supplementary Table S4). Mean Pb contents and the standard deviation (1s.d.) in clinopyroxene and sulfides are mean values of multiple analyses. For single analyses see data in Supplementary Tables 2 and 3.

In cases where measured Pb contents in cpx were < 50 ng/g, 40 ng/g Pb in clinopyroxene was assumed. The Pb contents of olivine, orthopyroxene and spinel in peridotites are commonly below detection limits of about 50 ng/g. Mean values as

in published data obtained by isotope dilution were assumed (11 ng/g, 20 ng/g and 50 ng/g respectively, e.g., Carignan et al., 1996; Meijer et al., 1990).

Because pentlandites and pyrrhotites have similar Pb contents, their modal abundances are not separated.

















