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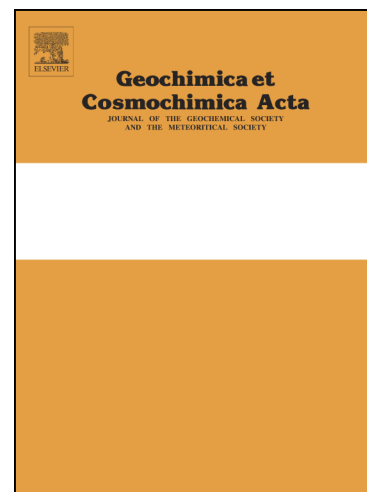
PII: S0016-7037(18)30071-1
DOI: <https://doi.org/10.1016/j.gca.2018.02.002>
Reference: GCA 10644

To appear in: *Geochimica et Cosmochimica Acta*

Received Date: 2 May 2017
Accepted Date: 2 February 2018

Please cite this article as: Stracke, A., Tipper, E.T., Klemme, S., Bizimis, M., Mg isotope systematics during magmatic processes: inter-mineral fractionation in mafic to ultramafic Hawaiian xenoliths, *Geochimica et Cosmochimica Acta* (2018), doi: <https://doi.org/10.1016/j.gca.2018.02.002>

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1 Mg isotope systematics during magmatic processes: inter-mineral 2 fractionation in mafic to ultramafic Hawaiian xenoliths

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12 Abstract

13 Observed differences in Mg isotope ratios between bulk magmatic rocks are small, often on a sub per
14 mill level. Inter-mineral differences in the ²⁶Mg/²⁴Mg ratio (expressed as δ²⁶Mg) in plutonic rocks are
15 on a similar scale, and have mostly been attributed to equilibrium isotope fractionation at magmatic
16 temperatures. Here we report Mg isotope data on minerals in spinel peridotite and garnet pyroxenite
17 xenoliths from the rejuvenated stage of volcanism on Oahu and Kauai, Hawaii. The new data are
18 compared to literature data and to theoretical predictions to investigate the processes responsible for
19 inter-mineral Mg isotope fractionation at magmatic temperatures. Theory predicts up to per mill level
20 differences in δ²⁶Mg between olivine and spinel at magmatic temperatures and a general decrease in
21 $\Delta^{26}\text{Mg}_{\text{olivine-spinel}} (= \delta^{26}\text{Mg}_{\text{olivine}} - \delta^{26}\text{Mg}_{\text{spinel}})$ with increasing temperature, but also with increasing Cr# in
22 spinel. For peridotites with a simple petrogenetic history by melt depletion, where increasing depletion
23 relates to increasing melting temperatures, $\Delta^{26}\text{Mg}_{\text{olivine-spinel}}$ should thus systematically decrease with
24 increasing Cr# in spinel. However, most natural peridotites, including the Hawaiian spinel peridotites
25 investigated in this study, are overprinted by variable extents of melt-rock reaction, which disturb the
26 systematic primary temperature and compositionally related olivine-spinel Mg isotope systematics.
27 Diffusion, subsolidus re-equilibration, or surface alteration may further affect the observed olivine-

28 spinel Mg isotope fractionation in peridotites, making $\Delta^{26}\text{Mg}_{\text{olivine-spinel}}$ in peridotites a difficult-to-apply
29 geothermometer. The available Mg isotope data on clinopyroxene and garnet suggest that this mineral
30 pair is a more promising geothermometer, but its application is restricted to garnet-bearing igneous
31 (garnet pyroxenites) and metamorphic rocks (eclogites). Although the observed $\delta^{26}\text{Mg}$ variation is on a
32 sub per mill range in bulk magmatic rocks, the clearly resolvable inter-mineral Mg isotope differences
33 imply that crystallization or preferential melting of isotopically distinct minerals such as garnet, spinel, and
34 clinopyroxene should cause Mg isotope fractionation between bulk melt and residue. Calculated Mg
35 isotope variations during partial mantle melting indeed predict differences between melt and residue,
36 but these are analytically resolvable only for melting of mafic lithologies, that is, garnet pyroxenites.
37 Contributions from garnet pyroxenite melts may thus account for some of the isotopically light $\delta^{26}\text{Mg}$
38 observed in ocean island basalts and trace lithological mantle heterogeneity. Consequently, applications
39 for high-temperature Mg isotope fractionations are promising and diverse, and recent advances in
40 analytical precision may allow the full petrogenetic potential inherent in the sub per mill variations in
41 $\delta^{26}\text{Mg}$ in magmatic rocks to be exploited.

42

43 **Keywords: Mg isotopes, peridotite, bulk earth, mantle, basalt.**

44

45 1. Introduction

46 Over the past 15 years, variations in Mg isotope ratios have become an important tool for investigating
47 Mg cycling in Earth's surface environments. Early research focused on low temperature processes
48 because of the associated large (ca. 5‰) Mg isotope variation (e.g., Brenot et al., 2008; Galy et al., 2002;
49 Hippler et al., 2009; Pogge von Strandmann et al., 2008a; 2008b; Shen et al., 2009; Teng et al., 2010b;
50 Tipper et al., 2006a; 2006b; Tipper et al., 2008a; 2006c; Young and Galy, 2004).

51 Recently, there is a growing body of work on Mg isotopes at high temperature, sparked by the
52 expectation that isotope ratios of Mg –the second most abundant element in the bulk silicate earth–
53 directly mirror planetary compositions and trace global (bio)geochemical cycles. It has been shown, for

54 example, that there is broad overlap between different types of chondrites, lunar and martian rocks
55 (Bourdon et al., 2010; Handler et al., 2009; Norman et al., 2006; Pogge von Strandmann et al., 2011;
56 Schiller et al., 2010; Sedaghatpour et al., 2013; Teng et al., 2010a; Wiechert and Halliday, 2007; Young
57 and Galy, 2004). The Earth's mantle contains ca. 99.9% of Earth's Mg. Its average Mg isotope ratio is
58 thus representative of the bulk earth and is similar to those of meteorites (Bizzarro et al., 2011;
59 Bourdon et al., 2010; Dauphas et al., 2010; Handler et al., 2009; Huang et al., 2011; Liu et al., 2011;
60 Pogge von Strandmann et al., 2011; Schiller et al., 2010; Teng et al., 2010a; Xiao et al., 2013; Yang et al.,
61 2009). Hence Mg isotope fractionation during planetary accretion and differentiation is difficult to
62 resolve. The average Mg isotope composition of Earth's mantle (peridotite) and its derivative melts
63 (MORB and OIB) is identical (Bourdon et al., 2010; Dauphas et al., 2010; Huang et al., 2011; Teng et
64 al., 2010a; Teng et al., 2007). Most previous studies have therefore concluded that there is no clearly
65 resolvable Mg isotope fractionation on a bulk sample scale during mantle melting and melt
66 differentiation, which contrasts with observations from other major elements such as Fe (Teng et al.,
67 2013; Weyer and Ionov, 2007; Williams and Bizimis, 2014).

68 In contrast, recent studies have documented clearly resolvable Mg isotope fractionation between
69 minerals in mantle peridotites (e.g., Handler et al., 2009; Hu et al., 2016; Huang et al., 2011; Li et al.,
70 2011; Liu et al., 2011; Pogge von Strandmann et al., 2011; Wang et al., 2016; Wang et al., 2012;
71 Wiechert and Halliday, 2007; Xiao et al., 2013; Yang et al., 2009; Young et al., 2009). These inter-
72 mineral Mg isotope differences in mantle peridotites (and eclogites) are generally thought to reflect
73 equilibrium magmatic fractionation, but in some cases were attributed to metasomatism (Hu et al.,
74 2016; Huang et al., 2011; Xiao et al., 2013; Young et al., 2009), or to diffusion (e.g., Huang et al., 2011;
75 Oeser et al., 2015; Pogge von Strandmann et al., 2011; Sio et al., 2013). Here we report Mg isotope data
76 on minerals in spinel peridotite and garnet pyroxenite xenoliths from the rejuvenated stage of
77 volcanism on Oahu and Kauai, Hawaii. The new data are compared to literature data and to theoretical
78 predictions to investigate the processes responsible for inter-mineral Mg isotope fractionation at
79 magmatic temperatures, with a special focus on the relative roles of temperature and composition. In
80 light of the observed inter-mineral Mg isotope differences, it would be expected that partial mantle

81 melting, which preferentially consumes the isotopically distinct phases clinopyroxene and garnet, may
82 lead to resolvable differences between melt (basalt) and residue (peridotite). Indeed, Zhong et al. (2017)
83 recently suggested that small, $<0.2\%$, differences in $\delta^{26}\text{Mg}$ occur during partial mantle melting, but the
84 magnitude of this fractionation relies on the inferred isotope fractionation factor between residual
85 source (peridotite or garnet pyroxenite) and melt. Here, we present a general model for partial melting
86 that accounts for isotopic changes in melt composition due to variable contribution of isotopically
87 diverse minerals to the melt. We show that partial melting of mantle peridotite does not generate
88 resolvable Mg isotope fractionation, consistent with the general overlap in $\delta^{26}\text{Mg}$ between peridotite
89 and basalt (Bourdon et al., 2010; Dauphas et al., 2010; Huang et al., 2011; Teng et al., 2010a; Teng et al.,
90 2007). In contrast, melting of garnet-bearing mafic source lithologies (garnet pyroxenites) produces
91 larger Mg isotope fractionation between source and melt. In the absence of experimentally determined
92 mineral–melt isotope fractionation factors, however, the overall offset between bulk melt and residual
93 rock remain uncertain, but low $\delta^{26}\text{Mg}$ at high Sm/Yb observed in some ocean island basalts hint at a
94 possible signature of garnet pyroxenite melting, and may thus trace lithological mantle heterogeneity.

95

96

97 2. Samples and analytical techniques

98 2.1. Sample selection and systematics

99 Five spinel peridotite and five garnet pyroxenite xenoliths from two locations on the Hawaiian islands
100 were analyzed. All xenoliths are found within the rejuvenated stage alkali lavas from Oahu (Honolulu
101 Volcanics (Clague and Frey, 1982)) and Kauai, Hawaii (Koloa volcanics (Garcia et al., 2010)). Samples
102 labeled 77SL-x or Pa-x are from the Presnal collection, the 114954-x pyroxenites are from the Jackson
103 collection, both housed at the Smithsonian Institution, Washington (Table 1). The 07Hana-001
104 peridotite is from the Hanapepe location, Kauai, Hawaii. The 77SL-x samples are exceptionally fresh,
105 while the olivines in the 007Hana-001 and Pa27 samples show minor signs of alteration. Only the
106 cleanest minerals, free of inclusions or blemishes, were handpicked for the Mg isotope analyses.

107 Major, trace element, and Hf, Nd, Sr, and Os isotopes compositions of the spinel peridotites from
108 the Salt Lake Crater (SLC) and Pali vents in Oahu have been reported by Bizimis et al. (2007; 2004),
109 and by a series of publications for the garnet pyroxenites (Bizimis et al., 2013; Bizimis et al., 2005;
110 Keshav and Sen, 2001; Keshav et al., 2007; Sen et al., 2010; 2011). The peridotites are either fragments
111 of the in-situ Pacific mantle lithosphere (Sen et al., 2005), or ancient recycled oceanic lithospheric
112 components of the plume Hawaiian source (Bizimis et al., 2007). The garnet pyroxenite xenoliths are
113 interpreted as high-pressure (2-3 GPa) cumulates from melts erupted during the rejuvenated phase of
114 volcanism (Bizimis et al., 2005; Sen et al., 2005). Further details on the composition and origin of the
115 analyzed samples are discussed in the supplementary information 1. In summary, the selected Hawaiian
116 peridotites cover almost the entire range of depletions observed in abyssal peridotites and have a wide
117 range of isotope and trace element compositions. Hence, they are ideally suited for investigating
118 whether there is a compositional effect on inter-mineral Mg isotope fractionation at magmatic P-T
119 conditions. In addition, the selected garnet pyroxenites provide a unique opportunity to investigate Mg
120 isotope variability in non-peridotitic lithologies of the oceanic mantle, and for evaluating the Mg
121 isotope fractionation between clinopyroxene and garnet as a potential geothermometer (Huang et al.,
122 2013).

123

124

125 **2.2. Analytical techniques**

126 The employed analytical techniques are identical to those described in detail in Bourdon et al. (2010)
127 and Tipper et al., (2008b), but are summarized below.

128 Powdered mineral separates were digested in a 1:1 concentrated HF-HNO₃ mixture for a minimum of
129 24 hours at ~150°C, with the exception of the spinels, which were digested under high-pressure in Parr
130 bombs in HF-HNO₃ for 3-4 days to ensure complete dissolution. Afterwards, sample solutions were
131 dried down and redissolved in 6N HCl, the latter step was repeated twice to eliminate any remaining
132 fluorides. An aliquot of these solutions containing 20 µg of Mg (<1% by weight) was evaporated and
133 dissolved in 12N HCl to be loaded on a 2 ml BioRad AG1-X8 anion column, Cl⁻ form, 200-400 mesh.
134 Mg was eluted in 12N HCl, and the Mg fraction was evaporated, redissolved in 0.4N HCl and loaded
135 onto a 1 ml cation exchange column (Biorad AG50W-X12). Mg was collected in 1N HCl, and this
136 column procedure was repeated to obtain a pure Mg fraction. The solutions were evaporated and
137 heated to 170°C in aqua regia for 24hrs before redissolving in 16N HNO₃ to convert to a nitric salt,
138 then evaporated, and dissolved in 2% HNO₃ at ~20 ppm, ready for final dilution immediately prior to
139 analysis. Total procedural blanks were less than 10 ng (< 0.05% of the total Mg processed).

140 Mg isotope ratios were measured on a Nu Plasma MC-ICPMS at IGMR, ETH Zurich, using an APEX
141 Q sample introduction system coupled to an ESI ACM membrane. The samples were aspirated using a
142 PFA nebulizer with nominal uptake of 20 µl/min, resulting in excess of 14V total beam of Mg for a
143 200 ppb solution at an actual uptake of ca. 10 µl/min. Prior to introduction of the samples into the
144 mass spectrometer, all solutions were centrifuged, and diluted to within 10% of the concentration of
145 the DSM3 reference standard (200 ppb).

146 Measurements were made using a standard bracketing protocol identical to that of Tipper et al. (2008b).

147 External reproducibility (precision) of mono-elemental standards over the 14-month period of analysis
148 was 0.095‰ (2 S.D.) for δ²⁶Mg. Based on the total number of procedural replicate analyses of both
149 mono-elemental and multi-elemental standards, the maximum 2 S.D. uncertainty was estimated as
150 0.094‰ for δ²⁶Mg and 0.052‰ for δ²⁵Mg (Bourdon et al., 2010).

151 **3. Results**

152 Olivine (ol) and clinopyroxene (cpx) have been analyzed in all five spinel peridotites, orthopyroxene
 153 (opx) from four of the five peridotites, and isolated spinel (sp) grains suitable for Mg isotope analyses
 154 could be recovered from three peridotite samples. Garnet (grt) and cpx have been analyzed in all five
 155 pyroxenites (Table 1, Fig. 1).

156 In the peridotites, the $\delta^{26}\text{Mg}$ values of the olivine, orthopyroxene and clinopyroxene are similar
 157 (Table 1 and Fig. 1), with $\delta^{26}\text{Mg}_{\text{ol}} = -0.24$ to -0.17‰ , $\delta^{26}\text{Mg}_{\text{opx}} = -0.22$ to -0.15‰ , and $\delta^{26}\text{Mg}_{\text{cpx}}^{\text{peridotite}} = -$
 158 0.32 to -0.11‰ . The $\delta^{26}\text{Mg}$ values in the spinels range to more positive values with $\delta^{26}\text{Mg}_{\text{sp}} = -0.03$ to $+$
 159 0.07 . Although the $\delta^{26}\text{Mg}$ values in clinopyroxene from peridotites and pyroxenites overlap, the
 160 $\delta^{26}\text{Mg}_{\text{cpx}}$ in the pyroxenites range to more positive values with $\delta^{26}\text{Mg}_{\text{cpx}}^{\text{pyroxenite}} = -0.13$ to $+0.02$. The
 161 garnets from the pyroxenites have overall the most negative $\delta^{26}\text{Mg}$ values ranging from -0.58 to $-$
 162 0.38‰ .

163 Calculated bulk rock $\delta^{26}\text{Mg}$ values for the peridotites ($\delta^{26}\text{Mg} = -0.24$ to -0.16) and pyroxenites
 164 ($\delta^{26}\text{Mg} = -0.26$ to -0.08) are close to the average value calculated for mantle-derived rocks (peridotites
 165 and basalts: $\delta^{26}\text{Mg} = -0.244 \pm 0.062$, 2 S.D., supplementary data; (Handler et al., 2009; Hu et al., 2016;
 166 Huang et al., 2011; Li et al., 2011; Liu et al., 2011; Pogge von Strandmann et al., 2011; Wang et al.,
 167 2014; Wang et al., 2016; Wang et al., 2012; Wiechert and Halliday, 2007; Xiao et al., 2013; Yang et al.,
 168 2009; Young et al., 2009; Zhong et al., 2017). In three-isotope plots of $\delta^{25}\text{Mg}'$ versus $\delta^{26}\text{Mg}'$ ($\delta^{2x}\text{Mg}' =$
 169 $1000 \cdot \ln((\delta^{2x}\text{Mg} + 1000)/1000)$; (Young and Galy, 2004)) the Hawaiian data define a line with a slope of
 170 0.527 ± 0.087 ($r^2 = 0.994$), which is within error of the slope of 0.521 expected for equilibrium isotope
 171 fractionation (Young and Galy, 2004).

172

173 Table 1: Mg isotope data for the Hawaiian spinel peridotites and garnet pyroxenites

Sample	Mineral	^{26}Mg	2 S.D.	^{25}Mg	2 S.D.	$\Delta^{25}\text{Mg}^{\dagger}$
<i>Spinel peridotites</i>						
07Han001	ol	-0.21	0.02	-0.1	0.03	0.005
07Han001	cpx	-0.16	0.01	-0.07	0.03	0.008
07Han001	sp	0.07	0.04	0.05	0.01	0.015
Pa27	ol	-0.24	0.04	-0.12	0.02	0.001
Pa27	opx	-0.22	0.06	-0.11	0.03	-0.001
Pa27	cpx	-0.32	0.03	-0.17	0.04	-0.001
Pa27	sp	-0.03	0.16	0	0.07	0.009
77SL405	ol	-0.17	0.07	-0.08	0.02	0.006
77SL405	opx	-0.16	0.1	-0.09	0.03	-0.009
77SL405	cpx	-0.13	0.11	-0.07	0.04	-0.003
77SL466	ol	-0.2	0.03	-0.11	0.06	-0.003
77SL466	opx	-0.2	0.05	-0.12	0.04	-0.009
77SL466	cpx	-0.15	0.1	-0.08	0.06	-0.001
77SL466	sp	0.04	0.03	0.02	0.03	0
77SL470	ol	-0.22	0.04	-0.11	0.02	0.005
77SL470	opx	-0.15	0.06	-0.09	0.02	-0.012
77SL470	cpx	-0.11	0.02	-0.06	0.01	0.001
<i>Garnet pyroxenites</i>						
77SL582	cpx	-0.1	0.03	-0.05	0.04	-0.001
77SL582	grt	-0.52	0.07	-0.27	0.06	-0.001
77SL620	cpx	0	0.19	0	0.08	-0.004
77SL620	grt	-0.38	0.09	-0.2	0.02	-0.004
77SL744	cpx	0.02	0.08	0.01	0.02	-0.005
77SL744	grt	-0.39	0.03	-0.21	0.03	-0.008
114954-20A	cpx	-0.03	0.06	-0.01	0.02	0.003
114954-20A	grt	-0.42	0.04	-0.21	0.04	0.005
114954-28A	cpx	-0.13	0.02	-0.05	0.04	0.014
114954-28A	grt	-0.58	0.03	-0.29	0.01	0.008

174 $\Delta^{25}\text{Mg}^{\dagger} = \delta^{25}\text{Mg}^{\dagger} - 0.521 * \delta^{26}\text{Mg}^{\dagger}$, with $\delta^{2x}\text{Mg}^{\dagger} = 1000 * \ln((\delta^{2x}\text{Mg} + 1000)/1000)$ (Young and Galy, 2004)

175

176

177

178 Inter-mineral fractionation factors for the peridotite minerals $\Delta^{26}\text{Mg}_{x-y}$, calculated as $\delta^{26}\text{Mg}_x - \delta^{26}\text{Mg}_y$
 179 –where x and y are different mineral phases– show no resolvable Mg isotope fractionation between ol
 180 and opx ($\Delta^{26}\text{Mg}_{\text{ol-opx}} = -0.07$ to 0 ; Fig. 2). $\delta^{26}\text{Mg}$ values in the clinopyroxenes, however, are slightly
 181 higher than those in ol or opx (e.g., $\Delta^{26}\text{Mg}_{\text{ol-cpx}} = -0.11$ to $+0.08$). Clearly resolvable, and uniform inter-
 182 mineral fractionation is observed between the spinels and other peridotite minerals (e.g., $\Delta^{26}\text{Mg}_{\text{ol-sp}} = -$
 183 0.28 to -0.21). These inter-mineral Mg isotope fractionations are within the range of previously
 184 reported values in peridotites: $\Delta^{26}\text{Mg}_{\text{ol-opx}} = -0.39$ to $+0.07$, $\Delta^{26}\text{Mg}_{\text{ol-cpx}} = -0.42$ to $+0.08$, and $\Delta^{26}\text{Mg}_{\text{ol-sp}} =$
 185 -0.88 to -0.16 (Fig. 2; (Liu et al., 2011; Wang et al., 2016; Xiao et al., 2013; Young et al., 2009)). In the
 186 pyroxenites, $\delta^{26}\text{Mg}_{\text{grrt}}$ is consistently lower than $\delta^{26}\text{Mg}_{\text{cpx}^{\text{pyroxenite}}}$, by -0.45 to -0.38% ($\Delta^{26}\text{Mg}_{\text{grrt-cpx}}$). This is
 187 about a factor of 2.7 less than reported for metamorphic garnet–omphacite pairs ($\Delta^{26}\text{Mg}_{\text{grrt-cpx}} = -1.65$ to
 188 -1.10) in eclogites reported by Li et al. (2011) and Wang et al. (2014) (Fig. 2), but within the range of
 189 values reported for eclogites from the South African subcontinental lithospheric mantle by Wang et al.
 190 (2012) ($\Delta^{26}\text{Mg}_{\text{grrt-cpx}} = -0.68$ to -0.38).

191

192

193 4. Discussion

194 $\delta^{26}\text{Mg}$ values in constituent minerals in peridotites and garnet pyroxenites or eclogites deviate
 195 considerably from the mantle average calculated from the available peridotite and oceanic basalt data
 196 ($\delta^{26}\text{Mg} = -0.245 \pm 0.119$, 2 S.D., $n = 349$; Fig. 1; supplementary data). Calculated or measured whole
 197 rock values in peridotites and garnet pyroxenites or eclogites, however, are in most cases within
 198 uncertainty of the mantle average. Inter-mineral Mg isotope variability in mantle derived rocks is thus
 199 expected to reflect temperature–dependent equilibrium isotope fractionation during magmatic
 200 processes. Especially mineral pairs with comparatively large isotopic differences, such as olivine and
 201 spinel could therefore be useful geothermometers (Liu et al., 2011; Macris et al., 2013; Schauble, 2011;
 202 Xiao et al., 2013; Young et al., 2009). However, compositional effects on inter-mineral isotope
 203 fractionation may affect the underlying temperature driven Mg isotope fractionation (e.g., Liu et al.,

204 2011; Macris et al., 2013; Schauble, 2011; Young et al., 2009). Additional complexity –on the mineral or
 205 whole rock scale– may be introduced by diffusion (e.g., Huang et al., 2011; Oeser et al., 2015; Pogge
 206 von Strandmann et al., 2011; Sio et al., 2013), metasomatic processes (Hu et al., 2016; Huang et al.,
 207 2011; Xiao et al., 2013; Young et al., 2009), and subsolidus re-equilibration of mineral phases. In light
 208 of these potential complications we will discuss the applicability of the two most promising mineral
 209 pairs for Mg isotope geothermometry: olivine–spinel (Liu et al., 2011; Macris et al., 2013; Schauble,
 210 2011; Xiao et al., 2013; Young et al., 2009) and garnet–clinopyroxene. To minimize potential
 211 disequilibrium effects by natural or analytical processes, the following discussion will only use literature
 212 data where $\Delta^{25}\text{Mg}'$ indicates $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ within 3% of equilibrium (i.e., $-0.03 < \Delta^{25}\text{Mg}' < 0.03$;
 213 where $\Delta^{25}\text{Mg}' = \delta^{25}\text{Mg}' - 0.521 * \delta^{26}\text{Mg}'$ (Young and Galy, 2004)).

214

215 4.1 Inter-mineral Mg isotope fractionation in mantle rocks

216 4.1.1. Mg isotope fractionation between olivine and spinel

217 Theoretical and experimental studies predict up to per mill level Mg equilibrium isotope
 218 fractionation between olivine and spinel at magmatic temperatures, caused by differences in Mg–O
 219 bond length for the six-fold coordinated Mg^{2+} in olivine and mostly four-fold coordinated Mg^{2+} in
 220 spinel (Macris et al., 2013; Schauble, 2011). In spinels –with a general composition of AB_2O_4 – theory
 221 predicts that Mg–O bond length of the tetrahedral A site depends on which cation occupies the
 222 octahedral B site (Schauble, 2011). The Mg–O bond length in MgAl_2O_4 (1.964Å) is shorter than in
 223 MgCr_2O_4 (2.001Å) (Schauble, 2011), leading to a preference for the heavy Mg isotope in MgAl_2O_4
 224 relative to MgCr_2O_4 . In addition to the general temperature dependence, therefore, $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ should
 225 vary systematically with the relative amount of Cr in the octahedral B site, that is, the Cr# in spinel (Fig.
 226 3). The theoretically predicted range in Mg–O bond lengths (1.964 – 2.001 for Cr# 0-1, (Schauble,
 227 2011)) is on the same order as the Mg–O bond length in natural spinels (1.945 – 1.965 for Cr# 0 – 0.3;
 228 (Princivalle et al., 1989)), suggesting that theoretical predictions should also apply to natural spinels, at
 229 least qualitatively. As shown in Fig. 3a, high Cr# and high temperature for olivine–spinel equilibration
 230 predict low $\Delta^{26}\text{Mg}_{\text{ol-sp}}$.

231 In peridotites, the Cr# in spinel increases with the extent of melting experienced (Dick and Bullen,
232 1984). In absence of volatile induced, or redox partial melting, larger degrees of melting occur at higher
233 temperatures. In this case, peridotites with increasing Cr# should reflect higher melting temperatures,
234 and show progressively decreasing $\Delta^{26}\text{Mg}_{\text{ol-sp}}$. For peridotites with a simple petrogenetic history of melt
235 depletion, a strong inverse coupling between $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ and Cr# would thus be expected (Fig. 3a).
236 However, few, if any of the peridotites analyzed for Mg isotope ratios preserve such a simple
237 petrogenetic history (Fig. 4). The only likely candidate are peridotites from the North China Craton
238 investigated by Liu et al. (2011). These rocks preserve the expected correlation between Al_2O_3 (whole
239 rock) or Cr# in spinel with Mg# (olivine) for variably depleted residual peridotites (Fig. 4), although
240 their rare earth element patterns also show variable metasomatic overprint (Wu et al., 2006). All other
241 peridotite suites that include data for $\delta^{26}\text{Mg}$ in spinel have experienced considerable post-depletion
242 metasomatism by interaction with silicate melts (Liu et al., 2011; Xiao et al., 2013; Young et al., 2009),
243 including the Hawaiian peridotites investigated in this study (Bizimis et al., 2004). Melt-peridotite
244 reaction incongruently dissolves pyroxenes and forms olivine, spinel, and a modified melt (Kelemen et
245 al., 1990). Melt-rock reaction, especially at lower temperature than for the primary depletion by partial
246 melting, can therefore disturb the primary, partial melting-related $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ and Cr# signatures (Fig.
247 3a). Hence a first-order control by temperature on $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ is difficult to establish in natural
248 peridotites investigated for Mg isotopes thus far, because of the almost ubiquitous and variable
249 overprint by post-melting metasomatism (e.g., Hu et al., 2016; Huang et al., 2011; Xiao et al., 2013;
250 Young et al., 2009). Note that even for the suite of spinel peridotites from the North China Craton, the
251 inferred temperature control on $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ by Liu et al. (2011) is difficult to establish given analytical
252 uncertainty and superimposed compositional effects due to variable Cr#, which make it difficult to
253 assign the observed variation in $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ solely to temperature (Fig. 3a).

254 Moreover, a discrepancy of several hundred °C is observed between temperatures predicted from
255 $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ (Schauble, 2011) and mineral equilibria (e.g., cpx-opx, (Brey and Köhler, 1990), compare Fig.
256 3a and b). This discrepancy is observed for the Hawaiian peridotite xenoliths, but also for the
257 peridotites investigated previously (Liu et al., 2011; Xiao et al., 2013; Young et al., 2009), and may point

258 either to an offset in calculated temperatures from $\Delta^{26}\text{Mg}_{\text{ol-sp}}$, or different closure temperatures of Mg
 259 isotope exchange between olivine and spinel relative to Fe–Mg exchange between orthopyroxene and
 260 clinopyroxene (Brey and Köhler, 1990; Wells, 1977). It should also be considered that, owing to the
 261 shallow slope of the predicted $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ – temperature curves (Fig. 3b; (Macris et al., 2013; Schauble,
 262 2011)), the uncertainties in predicted temperatures from Mg isotope variations are several hundred °C
 263 at temperatures $>1000^\circ\text{C}$, assuming an uncertainty of $\pm 0.10\%$ (2 S.D.) on $\delta^{26}\text{Mg}_{\text{ol}}$ and $\delta^{26}\text{Mg}_{\text{sp}}$, and
 264 thus a propagated uncertainty on $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ of $\pm 0.14\%$ (2 S.D.). For current analytical uncertainties,
 265 therefore, temperatures predicted from $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ are less precise, and may also be less accurate than
 266 those derived from conventional mineral–mineral thermometers (e.g., (Roeder et al., 1979; Wan et al.,
 267 2008)), although different geothermometers may also diverge by over 200°C , even in well-equilibrated
 268 peridotite and pyroxenite mantle xenoliths (Nimis and Grütter, 2010).

269

270 *4.1.2 Mg isotope fractionation between garnet and clinopyroxene*

271 Mg occupies the 8–fold coordinated A site in garnet with a general formula $\text{A}_3\text{B}_2\text{Si}_3\text{O}_{12}$. The 3+ cations
 272 Fe, Al, and Cr occupy the octahedral B site in garnet. Huang et al. (2013) inferred from theory that Mg–
 273 O bond length, and thus Mg isotope fractionation in garnet, is largely insensitive to variable cation
 274 composition on both the A and B sites, and could thus serve as a thermobarometer (Huang et al.,
 275 2013).

276 For the eclogites studied by Wang et al. (2012), which are interpreted as metamorphosed altered
 277 oceanic crust, temperatures estimated from Fe–Mg exchange in clinopyroxene–garnet (Ellis and Green,
 278 1979) and those predicted by $\Delta^{26}\text{Mg}_{\text{cpx-grt}}$ (Huang et al., 2013) agree within uncertainty (Fig. 5). The
 279 eclogites from the Dabie orogen investigated by Li et al. (2011) are ultra-high-pressure (UHP)
 280 metamorphic eclogites with gabbroic protoliths. The temperatures estimated from $\Delta^{26}\text{Mg}_{\text{cpx-grt}}$ (Huang
 281 et al., 2013) for these samples are $100\text{--}200^\circ\text{C}$ higher than the Fe–Mg exchange temperatures (549--
 282 614°C). At these low temperatures, uncertainties in predicted temperatures are little influenced by the
 283 analytical uncertainty on $\Delta^{26}\text{Mg}_{\text{cpx-grt}}$ ($\pm 0.14\%$, see above) and are ca. $\sim 50\text{--}70^\circ\text{C}$, (Fig. 5a). Hence the
 284 observed discrepancy likely arises from uncertainties in estimating Fe^{3+} contents from Fe_{total} in these

285 mineral phases, which leads to anomalously low Fe–Mg exchange temperatures well outside the
 286 calibrated temperature range of this empirical thermobarometer (Ellis and Green, 1979).

287 The Hawaiian garnet pyroxenites analyzed in this study are interpreted as high–pressure (2–3 GPa)
 288 cumulates from melts erupted during the rejuvenated phase of volcanism (Bizimis et al., 2005; Sen et
 289 al., 2005). The temperatures of last equilibration estimated from Fe–Mg exchange (Bizimis et al., 2005)
 290 and Mg isotope fractionation for three out of five Hawaiian samples are within 40–80°C, and therefore
 291 considered in good agreement. The other two samples show larger deviations: 140 and 260°C,
 292 respectively. The largest difference of 260°C is for sample 77SL-620 with a $T \sim 1160^\circ\text{C}$ based on Fe–
 293 Mg exchange (Bizimis et al., 2005), but a $T \sim 1420^\circ\text{C}$ based on $\Delta^{26}\text{Mg}_{\text{cpx-grt}} = 0.38$ (Table 1, Fig. 5).
 294 Although a seemingly large difference, it should be considered that uncertainties of $\pm 0.14\text{‰}$ on
 295 $\Delta^{26}\text{Mg}_{\text{cpx-grt}}$ (see above) translate into uncertainties in temperature of $\sim 150\text{--}250^\circ\text{C}$ at $T \sim 1200^\circ\text{C}$ (Fig.
 296 5a). Considering analytical uncertainties on $\Delta^{26}\text{Mg}_{\text{cpx-grt}}$, temperatures estimated from Fe–Mg exchange
 297 and $\Delta^{26}\text{Mg}_{\text{cpx-grt}}$ therefore mostly agree within uncertainty (Fig. 5a).

298

299 4.2 Bulk rock Mg isotope fractionation during magmatic processes

300 Mantle–derived rocks (i.e., peridotites, basalts) exhibit a small range in $\delta^{26}\text{Mg}$ from -0.48 to about 0
 301 (Fig. 6; supplementary data). The global averages of peridotites ($\delta^{26}\text{Mg} = -0.243\text{‰} \pm 0.135$, 2 S.D., $n =$
 302 184), mid ocean ridge basalts (MORB; $\delta^{26}\text{Mg} = -0.239\text{‰} \pm 0.102$, 2 S.D., $n = 74$) and ocean island
 303 basalts (OIB; $\delta^{26}\text{Mg} = -0.252\text{‰} \pm 0.096$, 2 S.D., $n = 91$) are identical within uncertainty and have
 304 similar variance (supplementary figure 2). Accordingly, previous studies have concluded that neither
 305 partial melting nor crystal fractionation significantly affect the Mg isotope variability of oceanic basalts
 306 on the bulk sample scale (Bourdon et al., 2010; Dauphas et al., 2010; Huang et al., 2011; Teng et al.,
 307 2010a; Teng et al., 2007). Magmatic differentiation at shallow depths (< 1 GPa) in basaltic melts
 308 dominantly involves phases whose Mg isotope composition is similar to that of the bulk rock (olivine,
 309 Fig. 1), or phases that contain little Mg (plagioclase). Thus, fractional crystallization of basaltic melts
 310 does not produce significant Mg isotope fractionation (e.g., Teng et al., 2007), unless large amounts of
 311 clinopyroxene with slightly different Mg isotope composition compared to the bulk rocks (Fig. 1)

312 dominate the fractionating assemblage. Partial melting in Earth's mantle, however, preferentially
 313 consumes clinopyroxene and garnet, which have $\delta^{26}\text{Mg}$ significantly different from the average bulk
 314 mantle (Fig. 1), and may therefore induce isotopic differences between melt (basalt) and residue
 315 (peridotite) (Zhong et al., 2017). If so, this needs to be reconciled with the identical average $\delta^{26}\text{Mg}$ of
 316 basalts and peridotites.

317 In the following, Mg isotope fractionation during partial melting of mantle lithologies is investigated
 318 using an incremental non-modal melting model, equivalent to fractional melting (Shaw, 1970). For
 319 details of the modeling see the supplementary information. In the absence of experimentally
 320 determined mineral–melt isotope fractionation factors, $\alpha_{\text{mineral-melt}}$, these can be estimated from known
 321 inter–mineral isotope fractionation factors (Fig. 2), and one known or estimated $\alpha_{\text{mineral-melt}}$ (cf. Williams
 322 and Bizimis, 2014; Zhong et al., 2017) as a reference point. Olivine and orthopyroxene are isotopically
 323 almost identical to bulk peridotite and basaltic melts, and thus have $\alpha_{\text{ol,opx-melt}} \sim 1$ (Fig. 1, 2, and
 324 supplementary figure 2). Moreover, Mg occurs in five to six–fold coordination in silicate melts (George
 325 and Stebbins, 1998; Shimoda et al., 2007), similar to Mg in olivine and orthopyroxene, providing
 326 additional support for the assumption that little, if any, isotope fractionation between olivine or
 327 orthopyroxene and melt occurs. Alternatively, minimum $\alpha_{\text{mineral-melt}}$ can be calculated from known inter–
 328 mineral isotope fractionation factors (Fig. 2) and assuming an initial $\alpha_{\text{source-melt}} = 1$, which appears
 329 reasonable for Mg, because peridotites and basalts have, on average, almost identical $\delta^{26}\text{Mg}$ (Fig. 1,
 330 supplementary figure 2). The latter approach anchors the initial melt at the initial $^{26}\text{Mg}/^{24}\text{Mg}$ of the
 331 residue (initial $\alpha_{\text{source-melt}} = 1$, Fig. 7), but would offset the initial $^{26}\text{Mg}/^{24}\text{Mg}$ of the melt from its source
 332 for $\alpha_{\text{source-melt}} \neq 1$. The former approach for calculating initial $\alpha_{\text{source-melt}}$ offsets the initial $^{26}\text{Mg}/^{24}\text{Mg}$ of
 333 the melt to that of the peridotite source proportional to the difference between the $^{26}\text{Mg}/^{24}\text{Mg}$ of
 334 olivine (orthopyroxene) and the bulk peridotite. For melting garnet pyroxenite sources, $\alpha_{\text{cpx,grt-melt}}$ can

335 also be calculated from known inter-mineral isotope fractionation factors (Fig. 2) and assuming $\alpha_{\text{source-}}$
 336 $\text{melt} = 1$, or, $\alpha_{\text{cpx,grt-melt}}$ similar to those derived for peridotite-melt can be used. Similar to the peridotite
 337 case, the initial melt is either anchored or slightly offset from the initial $^{26}\text{Mg}/^{24}\text{Mg}$ of the garnet
 338 pyroxenite. It should be stressed that the inherent assumptions for calculating $\alpha_{\text{source-melt}}$ are critical for
 339 assessing the overall isotopic offset between source and melt (cf. Williams and Bizimis, 2014; Zhong et
 340 al., 2017). Importantly, the magnitude of isotope fractionation between source and melt remains
 341 uncertain in the absence of experimentally determined $\alpha_{\text{mineral-melt}}$, but the relative changes in $^{26}\text{Mg}/^{24}\text{Mg}$
 342 ($\delta^{26}\text{Mg}$) of melt and residue with progressive melting are independent of their initial values and are thus
 343 a robust feature for any given melting scenario. The following discussion of the effect of partial melting
 344 on the $\delta^{26}\text{Mg}$ of the derivative melts will therefore focus on these relative changes in $\delta^{26}\text{Mg}$ with
 345 progressive melting. In Fig. 6, all $\alpha_{\text{mineral-melt}}$ are estimated assuming the initial $\alpha_{\text{source-melt}} = 1$, hence are
 346 initially anchored at their source value, but it should be kept in mind that larger offsets between melt
 347 and residue would occur for initial $\alpha_{\text{source-melt}} \neq 1$.

348 Figure 6 shows that for melting garnet peridotite at high P-T (OIB melting), melts evolve to slightly
 349 lower $\delta^{26}\text{Mg}$ compared to their initial value, but only by $< 0.01\%$. The changing $\delta^{26}\text{Mg}$ of the partial
 350 melts with increasing extent of melting (F) reflect the changing contribution of Mg of each mineral to
 351 the melt. For the melt reactions assumed here, formation of orthopyroxene, and consumption of
 352 clinopyroxene and garnet characterize the melting of garnet peridotite at high P and low F. During this
 353 early stage of melting, clinopyroxene delivers approximately four times more Mg to the melts than
 354 garnet, thus outweighs the effect of melting garnet with $\delta^{26}\text{Mg}$ lower than the bulk peridotite. During
 355 the rapid transition from garnet to spinel peridotite, spinel (and orthopyroxene) is formed at the
 356 expense of garnet (and olivine) and a large amount of Mg from garnet enters the melt, thus decreasing
 357 its $\delta^{26}\text{Mg}$. Eventually, after garnet disappears from the residue, almost only clinopyroxene delivers Mg

358 to the produced melt, which slightly increases the $\delta^{26}\text{Mg}$ in the incremental melts. During melting of
359 peridotite at comparatively lower P-T (MORB melting), garnet is residual only during the initial stages,
360 or absent from the residual assemblage. In this latter case, melting is dominated by clinopyroxene, and
361 the $\delta^{26}\text{Mg}$ of the produced melts increase in $\delta^{26}\text{Mg}$, but still remains within $<0.01\%$ of its starting value
362 (Fig. 6). Overall, partial melting of peridotite therefore does not produce resolvable Mg isotope
363 variation, unless the assumption inherent in calculating $\alpha_{\text{source-melt}}$ lead to values substantially different
364 from 1 (cf. Zhong et al., 2017). The reason is that the $\alpha_{\text{source-melt}}$ is buffered ~ 1 by residual olivine and
365 orthopyroxene, which together host ca. 90% of the Mg and have $\alpha_{\text{ol,opx-melt}} \sim 1$ (Fig. 1).

366 More significant Mg isotope fractionation during partial melting is expected only if the predominant
367 contribution of Mg is from phases with $\delta^{26}\text{Mg}$ significantly different from that of the bulk rock. Melting
368 of mafic lithologies, such as garnet pyroxenite, imposes a pronounced garnet signature onto the
369 derivative melts, and thus results in $\delta^{26}\text{Mg}$ variability in excess of that for peridotite melting (Fig. 6).
370 Melts of G2 pyroxenite are dominated by melting garnet at low extent of melting, but are increasingly
371 dominated by melting clinopyroxene with progressive extent of melting (Pertermann and Hirschmann,
372 2003a, b). Owing to the persistent strong garnet influence, the $\delta^{26}\text{Mg}$ of garnet pyroxenite melts remains
373 lower than their starting value, by ca. 0.03–0.04‰, even for extents of melting $>50\%$ (Fig. 6). However,
374 the $\delta^{26}\text{Mg}$ of garnet pyroxenite melts strongly depend on the relative contribution of Mg from
375 clinopyroxene and garnet. Below ca. 12% of melting, garnet delivers more Mg to the melt than
376 clinopyroxene, which is reversed at $F > 12\%$ (Fig. 6), and garnet pyroxenite melts then deviate less from
377 that of the bulk residue, similar to what is observed for peridotite-derived melts.

378 In the OIB investigated thus far, the lowest $\delta^{26}\text{Mg}$ in OIB occur in rocks with the highest Sm/Yb
379 and tend to decrease with increasing Sm/Yb (Fig. 7). This observation is consistent with the greater
380 influence of residual garnet during melting predicted by our model. Some scatter is induced by variable
381 amounts of clinopyroxene accumulation or fractionation (Fig. 7), but the available data hint at a
382 possible decrease of $\delta^{26}\text{Mg}$ with progressively lower degrees of melting in the garnet–stability field, that

383 is, higher Sm/Yb (Fig. 7). As discussed above, $\delta^{26}\text{Mg}$ significantly lower than their initial source are only
384 expected for melting garnet pyroxenite, and this observation could therefore be indicative of an
385 increasing garnet pyroxenite melt component in OIB with increasingly lower $\delta^{26}\text{Mg}$. Confidently
386 resolving this effect, however, would require larger absolute values of $\alpha_{\text{mineral-melt}}$ than the minimum
387 values assumed for the modeling in this study, or, alternatively more precise Mg isotope data (see
388 discussion above and Fig. 7). Whereas the data for Hawaiian alkali basalts compared to tholeiites by
389 Zhong et al. (2017) are compatible with such an interpretation, the data for Hawaiian tholeiites reported
390 previously (Teng et al., 2010a) do not show any systematic variation in Figure 7. Although this
391 observation is consistent with the small variability of Sm/Yb and $\delta^{26}\text{Mg}$ at the similarly large degrees of
392 melting expected for Hawaiian tholeiites, significant analytical uncertainty in the $\delta^{26}\text{Mg}$ and the trace
393 element data compiled for the Hawaiian tholeiites (see Fig. 7 and supplementary data) –but also
394 variable amounts of clinopyroxene fractionation– may obscure an inherent systematic relationship as
395 observed by Zhong et al. (2017). In MORB (including Iceland) the invariably low Sm/Yb reflect large
396 amounts of melting in the spinel–stability field (Fig. 6 and 7). $\delta^{26}\text{Mg}$ in MORB scatter around the
397 MORB average ($-0.239\text{‰} \pm 0.102$, S.D., $n = 74$; supplementary data), probably mostly due to analytical
398 uncertainty in $\delta^{26}\text{Mg}$, but some low $\delta^{26}\text{Mg}$ could also be consistent with a garnet pyroxenite melt
399 component. It should also be noted that the relatively large extents of melting for MORB and the
400 Hawaiian tholeiites make it difficult to resolve potential pyroxenite $\delta^{26}\text{Mg}$ signatures. For melting of
401 lithologically heterogeneous mantle sources, the relative contribution of pyroxenite–derived melt to the
402 erupted melt decreases with increasing extent of (peridotite) melting (c.f. Stracke and Bourdon, 2009).
403 Large overall extents of partial melting also minimize any variation in Sm/Yb, thus making it more
404 difficult to resolve correlated small differences in $\delta^{26}\text{Mg}$ in pyroxenite versus peridotite–derived melts,
405 especially in light of the current analytical uncertainty on $\delta^{26}\text{Mg}$.

406

407 4.3 Applications for Mg isotope fractionation during magmatic processes

408 Several studies highlighted the potential application of large inter–mineral olivine–spinel
409 fractionation as a geothermometer in peridotites (Liu et al., 2011; Schauble, 2011; Xiao et al., 2013;
410 Young et al., 2009). A dominant effect of temperature on $\Delta^{26}\text{Mg}_{\text{ol-sp}}$, however, can only be expected for
411 refractory peridotites with a simple petrogenetic history by melt depletion. In this case a superimposed
412 compositional effect on Mg isotope fractionation in spinel, that is, decreasing $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ with increasing
413 Cr# in spinel (Fig. 3, (Schauble, 2011)), should further diminish the decreasing $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ with
414 increasing temperature. However, most of the peridotites analyzed for Mg isotopes so far do not
415 preserve such a simple petrogenetic history, but have $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ that are variably overprinted by
416 metasomatism (melt–rock reaction, Fig. 4). A possible exception may be the peridotites from the North
417 China Craton investigated by Liu et al. (2011). Even in this latter case, however, disentangling
418 temperature and compositionally related effects on $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ proves complicated (Fig. 3a), making
419 olivine–spinel Mg isotope fractionation in peridotites a difficult-to-apply geothermometer. Moreover,
420 in addition to melt–rock reaction (metasomatism) subsolidus re-equilibration, diffusion (e.g., Huang et
421 al., 2011; Oeser et al., 2015; Pogge von Strandmann et al., 2011; Sio et al., 2013), or surface alteration
422 may also affect the Mg isotope composition of olivine and spinel in mantle peridotites.

423 In contrast to olivine–spinel, inter–mineral Mg isotope fractionation between co–existing
424 clinopyroxene and garnet (Li et al., 2011; 2014; Wang et al., 2012); and this study) is a more promising
425 geothermometer (see also Huang et al., 2013). However, significant deviations between temperatures
426 estimated from Mg isotope fractionation and Fe–Mg exchange between cpx and grt are observed,
427 mostly at $T < 800^\circ\text{C}$, probably due to anomalously low Fe–Mg exchange temperatures resulting from
428 uncertainties in estimating Fe^{3+} – Fe^{2+} contents (Ellis and Green, 1979). Uncertainties on temperature
429 estimates from $\Delta^{26}\text{Mg}_{\text{cpx-grt}}$ at higher magmatic temperatures may arise mostly from analytical uncertainty
430 in $\Delta^{26}\text{Mg}_{\text{cpx-grt}}$ ($\sim \pm 0.14\%$) which is several 100°C at $T > 1100$ – 1200°C (Huang et al., 2013), Fig. 5).
431 Precise temperature estimates based on $\Delta^{26}\text{Mg}_{\text{cpx-grt}}$ are thus only possible within a small temperature
432 range between $T \sim 800$ – 1100°C , restricting its use to garnet–bearing igneous and metamorphic rocks. It
433 should also be assessed whether the potential information to be derived from Mg isotope
434 thermobarometry warrants the substantially larger analytic effort compared to conventional Fe–Mg

435 exchange thermobarometers.

436 Applications of Mg isotope fractionation on the bulk sample scale in magmatic rocks have so far
437 been elusive, because of the associated small range of $\delta^{26}\text{Mg}$. Zhong et al. (2017) recently argued that
438 partial melting leads to Mg isotope fractionation on a level of tenths of per mill. However, the
439 observation that olivine and orthopyroxene have similar $\delta^{26}\text{Mg}$ as both average peridotite and basalts
440 (Fig. 1, 2, and supplementary figure 2) indicates that $\alpha_{\text{ol, opx-melt}} \sim 1$. Given the predominance of olivine
441 and orthopyroxene on the Mg budget of peridotite, partial melting of peridotite does not result in
442 resolvable Mg isotope fractionation, in good agreement with the identical average $\delta^{26}\text{Mg}$ in peridotites
443 and basalts (supplementary figure 2). More variable $\delta^{26}\text{Mg}$ may only result from melting mafic source
444 lithologies such as garnet pyroxenite, consistent with a tendency of lower $\delta^{26}\text{Mg}$ with higher Sm/Yb
445 (Fig. 7). At current levels of analytical precision, however, this effect is only resolvable with confidence
446 for larger absolute values of $\alpha_{\text{mineral-melt}}$ than assumed for the modeling in this study (Fig. 6). Low $\delta^{26}\text{Mg}$
447 at high Sm/Yb observed in some alkaline OIB, however, hint at a possible signature of garnet
448 pyroxenite melting, in which case $\delta^{26}\text{Mg}$ trace lithological mantle heterogeneity. In contrast, the higher
449 extents of melting inferred for tholeiitic OIB and especially MORB, lead to much less variable Sm/Yb
450 than in the low degree alkaline OIB, making it difficult to resolve potentially correlated sub per mill
451 variations in $\delta^{26}\text{Mg}$.

452 Owing to the general lack of offset in $\delta^{26}\text{Mg}$ between mantle sources and melt (supplementary figure
453 2), Mg isotope ratios in mantle-derived rocks should accurately reflect bulk planetary composition.
454 Hence, comparison of $\delta^{26}\text{Mg}$ in meteorites and bulk planets could provide valuable information about
455 the provenance of planet forming materials, and the processes that lead to Mg isotope fractionation
456 during planet formation and early differentiation. However, while some earlier studies invoke a
457 difference between silicate Earth and chondrites (Wiechert and Halliday, 2007; Young et al., 2009),
458 most recent studies have argued for a broadly similar Mg isotope composition (Bizzarro et al., 2011;
459 Bourdon et al., 2010; Handler et al., 2009; Huang et al., 2011; Liu et al., 2011; Schiller et al., 2010; Teng

460 et al., 2010a; Yang et al., 2009). A compilation of the available data yields average values of -0.270 (\pm
461 0.074 , S.D., $n = 102$) and -0.247 (± 0.064 , S.D., $n = 389$) for $\delta^{26}\text{Mg}$ in chondrites and terrestrial
462 mantle-derived rocks (basalts, eclogites, and peridotites), respectively (supplementary data). As pointed
463 out by Pogge von Strandmann et al. (2011), these averages are statistically different based on a student's
464 t-test. Recent, more precise Mg isotope measurements have substantiated this small difference in
465 $\delta^{26}\text{Mg}$ between chondritic meteorites and the bulk silicate Earth and attributed it to vapor loss from
466 growing planetesimals (Hin et al., 2017).

467 In summary, in addition to being potential geothermometers (especially clinopyroxene-garnet),
468 stable Mg isotope variations in magmatic rocks may be a useful tool for identifying lithological
469 heterogeneity in the mantle. Analysis of peridotitic garnets and the investigation of specifically targeted
470 OIB suites should allow further constraints on the potential variation in $\delta^{26}\text{Mg}$ in response to partial
471 melting. Most crucial in this respect, however, is to determine isotope fractionation factors between
472 mantle minerals and melt, $\alpha_{\text{mineral-melt}}$, which would determine the actual offsets in $\delta^{26}\text{Mg}$ between melt
473 and source, and thus further constrain the respective influence of different source lithologies on the
474 $\delta^{26}\text{Mg}$ of mantle melts. Applications for high-temperature Mg isotope fractionation are thus diverse,
475 but further improving the analytical precision of Mg isotope measurements (e.g., Hin et al., 2017) has
476 proven crucial for planetary scale applications, and also holds promise for investigating a diverse range
477 of magmatic processes at higher resolution.

478

479 Acknowledgments

480 We would like to thank the reviewers, Jasper Konter, Merlin Méheut, and the associate editor Nicolas
481 Dauphas for their helpful and constructive comments, which significantly improved parts of the
482 discussion. Marc Norman is thanked for editorial handling. ETT was supported by a Marie-Curie Inter-
483 European-Fellowship No. 41189 at ETH Zürich for research on global budgets of Ca and Mg and a
484 Cambridge NERC Fellowship (NE/G013764/1) at the University of Cambridge. MB acknowledges
485 NSF grants OCE-0622827 and OCE - 0852488 for sample collection and processing.

486

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- 668
- 669

670 **Figure and Table captions:**

671 **Fig. 1:** $\delta^{26}\text{Mg}$ values in minerals from the Hawaiian spinel peridotite (olivine, orthopyroxene,
 672 clinopyroxene, spinel) and garnet pyroxenite (garnet, clinopyroxene) xenoliths investigated in this
 673 study (colored symbols) compared to $\delta^{26}\text{Mg}$ values in minerals from peridotites and eclogites
 674 reported in the literature (gray symbols). Literature data are from (Handler et al., 2009; Huang et al.,
 675 2011; Li et al., 2011; Liu et al., 2011; Pogge von Strandmann et al., 2011; Wang et al., 2014; Wang et
 676 al., 2016; Wang et al., 2012; Wiechert and Halliday, 2007; Xiao et al., 2013; Yang et al., 2009; Young
 677 et al., 2009).

678

679 **Fig. 2:** Inter-mineral fractionation factors $\Delta^{26}\text{Mg}_{\text{g-X}} = \delta^{26}\text{Mg}_{\text{g}} - \delta^{26}\text{Mg}_{\text{X}}$ for minerals from Hawaiian
 680 spinel peridotites (olivine, orthopyroxene, clinopyroxene, spinel) and garnet pyroxenites (garnet,
 681 clinopyroxene) (colored symbols) compared to $\Delta^{26}\text{Mg}_{\text{g-X}}$ values in minerals from spinel peridotites
 682 and eclogites reported in the literature (gray symbols). Literature data are from (Handler et al., 2009;
 683 Huang et al., 2011; Li et al., 2011; Liu et al., 2011; Pogge von Strandmann et al., 2011; Wang et al.,
 684 2014; 2016; 2012; Wiechert and Halliday, 2007; Xiao et al., 2013; Yang et al., 2009; Young et al.,
 685 2009).

686

687 **Fig. 3: a)** Diagram showing $\Delta^{26}\text{Mg}_{\text{olivine-spinel}}$ versus Cr# in spinel, and **b)** $\Delta^{26}\text{Mg}_{\text{olivine-spinel}}$ versus $10^6/T_{\text{BKN}}^2$
 688 for the peridotites with reported Mg isotope ratios in spinel. The Cr# is the molar ratio $\text{Cr}/(\text{Cr}+\text{Al})$,
 689 Mg# is the molar ratio $\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$, and T_{BKN} is the Mg-Fe exchange temperature between clino-
 690 and orthopyroxene, estimated after Brey and Köhler (1990) for an assumed equilibration pressure of
 691 15 kb, and $\Delta^{26}\text{Mg}_{\text{olivine-spinel}} = |(\delta^{26}\text{Mg}_{\text{ol}} - \delta^{26}\text{Mg}_{\text{sp}})|$. There is no systematic decrease in $\Delta^{26}\text{Mg}_{\text{olivine-spinel}}$
 692 with Cr# in spinel, as would be expected based on theoretical predictions for refractory peridotites,
 693 nor a systematic relation between $\Delta^{26}\text{Mg}_{\text{cpx-grt}}$ and $10^6/T_{\text{BKN}}^2$, suggesting that secondary processes
 694 (post-melting metasomatism) have disturbed these predicted primary relations. Gray lines are drawn
 695 using predictions by Schauble, (2011) and Macris et al., (2013). The $\Delta^{26}\text{Mg}_{\text{olivine-spinel}}$ for peridotites

696 with different Cr# are linearly interpolated between the predicted $\Delta^{26}\text{Mg}_{\text{olivine-spinel}}$ for pure MgCr_2O_4
 697 and MgAl_2O_4 (Schauble, 2011; Macris et al., 2013). Note that there is an offset between the
 698 temperatures inferred for $\Delta^{26}\text{Mg}_{\text{olivine-spinel}}$ from theoretical models (Schauble, 2011, Macris et al.,
 699 2013) and Mg-Fe exchange equilibria in pyroxenes (T_{BKN} , Brey and Köhler; 1990). Error bars for
 700 $\Delta^{26}\text{Mg}_{\text{olivine-spinel}}$ are drawn assuming an uncertainty of $\pm 0.10\text{‰}$ (2 S.D.) on $\delta^{26}\text{Mg}_{\text{ol}}$ and $\delta^{26}\text{Mg}_{\text{sp}}$, and
 701 thus a propagated uncertainty on $\Delta^{26}\text{Mg}_{\text{ol-sp}}$ of $\pm 0.14\text{‰}$ (2 S.D.) for all samples. Data and
 702 references for the major element data are given in the supplementary data.

703

704 **Fig. 4:** Diagram showing **a)** Cr# in spinel versus Mg# in olivine, and **b)** Al_2O_3 (wt.%) in the whole rock
 705 versus Mg# in olivine for the peridotites with reported Mg isotope ratios in spinel. For peridotites
 706 with a simple history of depletion by partial melting, a positive correlation in Fig. 4a and a negative
 707 correlation in Fig. 4b would be expected. With the possible exception of the peridotites investigated
 708 by Liu et al. (2011), the lack of such correlations indicate that the investigated peridotite suites are
 709 affected by post-melting melt-rock reaction (metasomatism, see also Fig. 4). Further explanations are
 710 given in the main text. Data and references for the major element data are given in the
 711 supplementary data.

712

713 **Fig. 5:** Diagram showing $\Delta^{26}\text{Mg}_{\text{cpx-grt}}$ versus temperatures estimated based Fe-Mg exchange (Ellis and
 714 Green, 1979). The gray curves show the $\Delta^{26}\text{Mg}_{\text{cpx-grt}} - T$ parameterization of Huang et al. (2013) for
 715 pressures between 2 and 5 GPa. The Hawaiian pyroxenites equilibrated at a mean pressure of ~ 2.5
 716 GPa (Bizimis et al., 2005), the pressure of equilibration for the data from Li et al. (2011) is 3 GPa
 717 and 5 GPa for the eclogites studied by Wang et al. (2012). Data from Hu et al. (2016) are omitted,
 718 because their clinopyroxene-garnet isotope ratios indicate isotopic disequilibrium.

719

720 **Fig. 6:** Diagram showing the deviation in $\delta^{26}\text{Mg}$ of instantaneous and accumulated melts and residue
 721 from the initial source composition for melting spinel peridotite (MORB), garnet peridotite (OIB),

722 and garnet pyroxenite. F is the extent of melting, i.e., the mass of melt generated relative to the mass
723 of the source. The $\delta^{26}\text{Mg}$ of the partial melts become different from their source value owing to the
724 changing contribution of Mg from the different source minerals to the melt. Garnet has a large
725 influence on the $\delta^{26}\text{Mg}$ of the partial melt, but the calculated variation in $\delta^{26}\text{Mg}$ is small ($\sim 0.03\%$)
726 relative to the typical analytical uncertainty of $\sim 0.1\%$. Note that $\alpha_{\text{mineral-melt}}$ used in the calculations
727 are calculated from known inter-mineral isotope fractionation factors (Fig. 2) and assuming an initial
728 $\alpha_{\text{source-melt}} = 1$, hence the calculated deviations from the initial source are minimum deviations, and
729 the overall offset to the initial source could be larger for any initial $\alpha_{\text{source-melt}} \neq 1$. Further details of
730 the partial melting calculations are described in the text and the supplementary information.

731

732 **Fig. 7:** Observed variation between bulk rock $\delta^{26}\text{Mg}$ and Sm/Yb in OIB and MORB. Data are grouped
733 in (1) OIB from the South Pacific and South Atlantic, which are created by small amounts of
734 melting in the garnet stability field (colored circles), (2) OIB created by large amounts of melting in
735 the garnet stability field with intermediate Sm/Yb (Hawaii, diamonds), and (3) ridge basalts (squares)
736 including those from Iceland (green squares), which are dominated by melting in the spinel stability
737 field with Sm/Yb ~ 1 (Fig. 7c). The Mg isotope data are taken from ref. 1: Bourdon et al. (2010),
738 ref. 2: Teng et al. (2010a), and Zhong et al. (2017). Data and references for the trace element data are
739 given in the supplementary data.

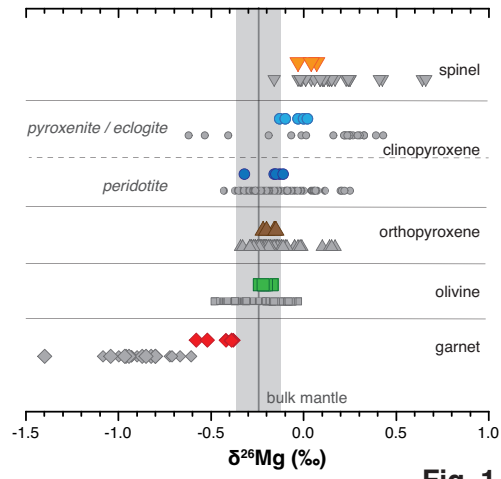


Fig. 1

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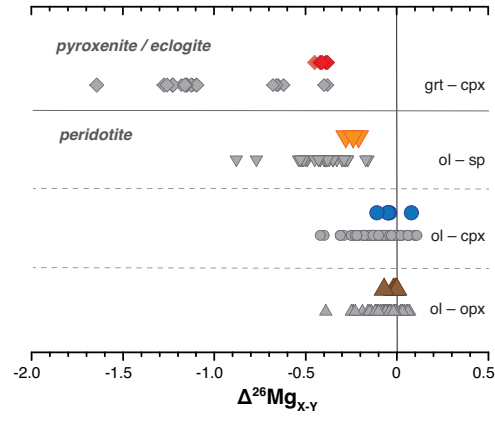


Fig. 2

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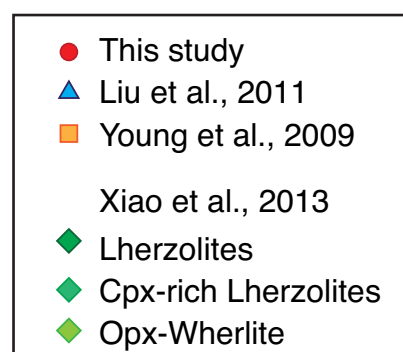
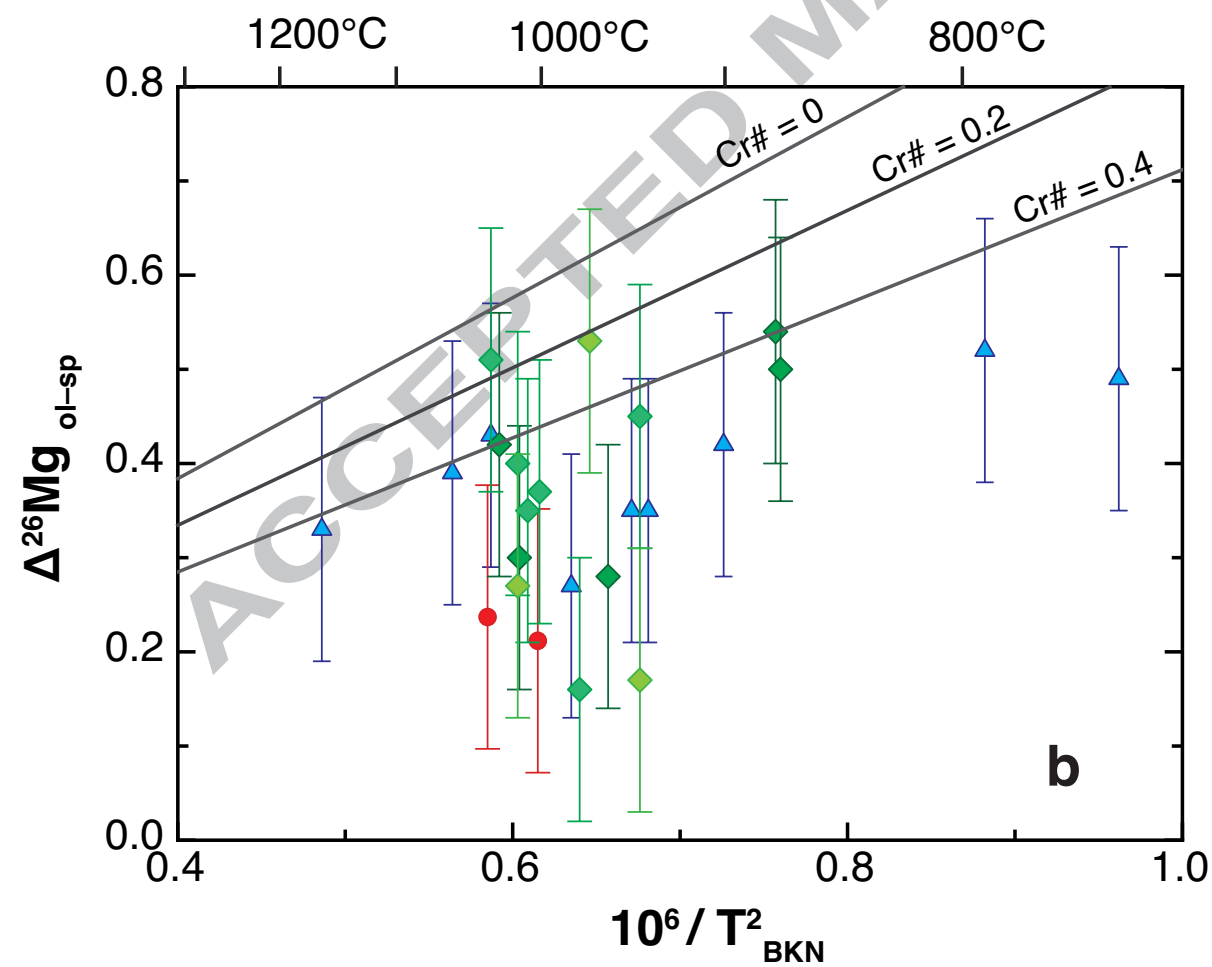
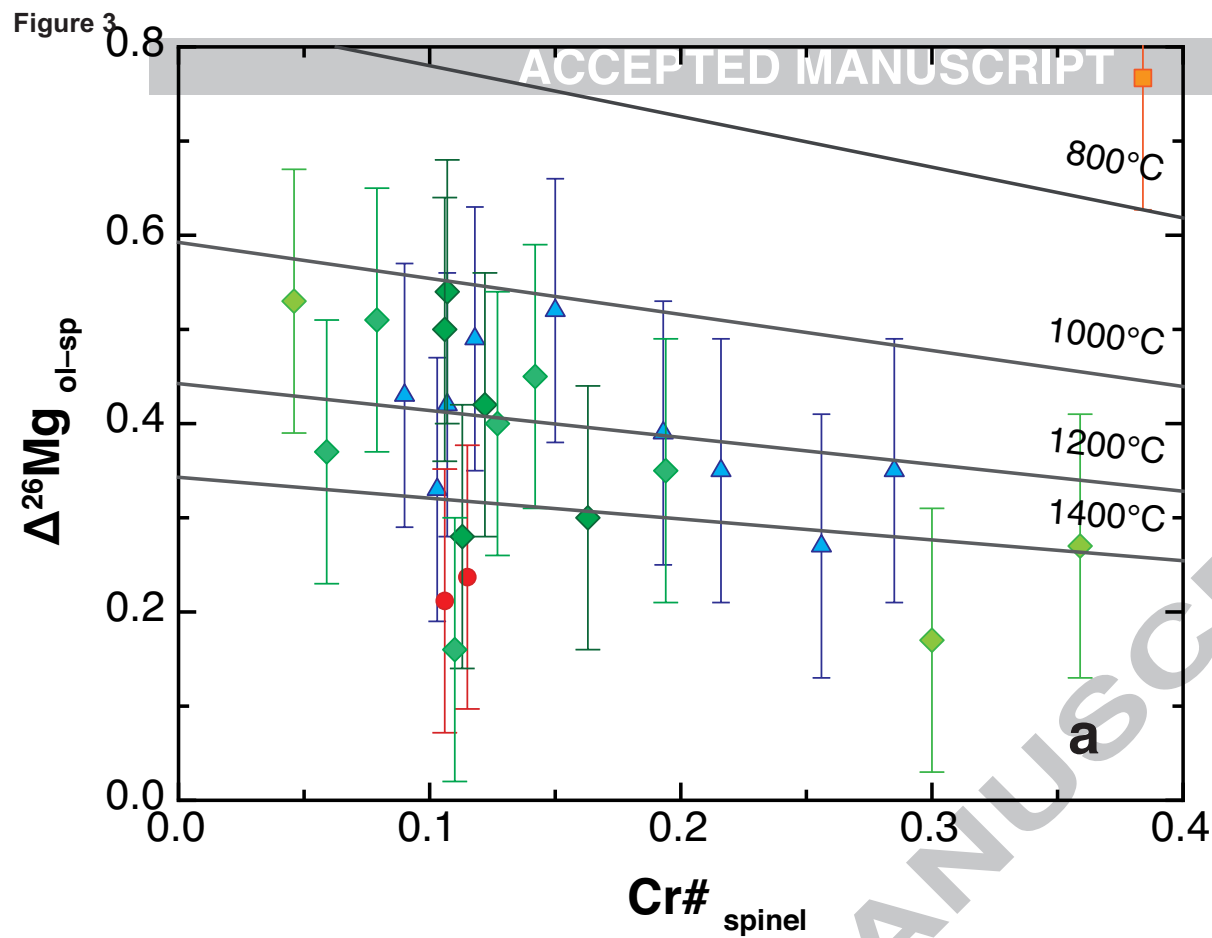


Fig. 3

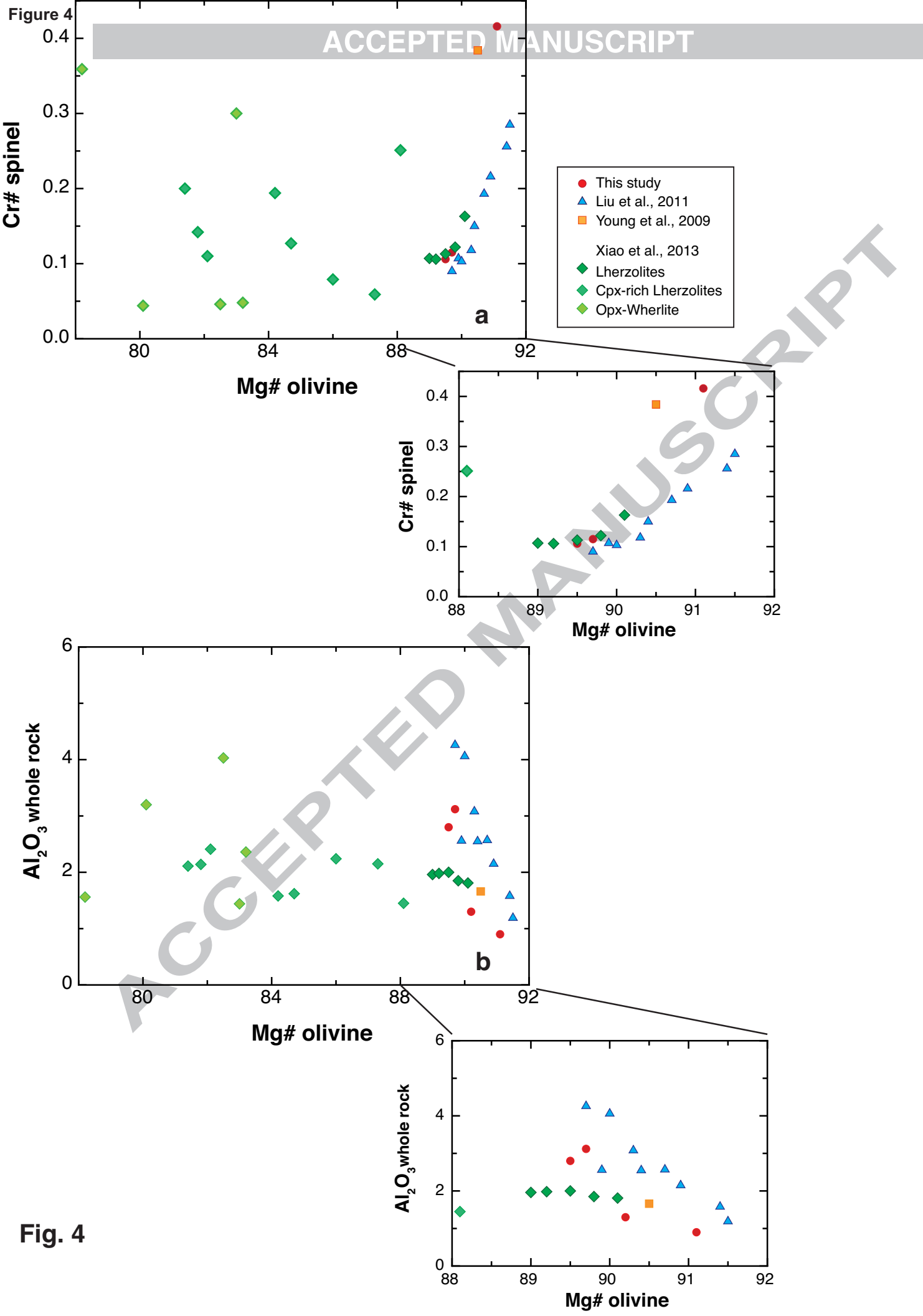


Fig. 4

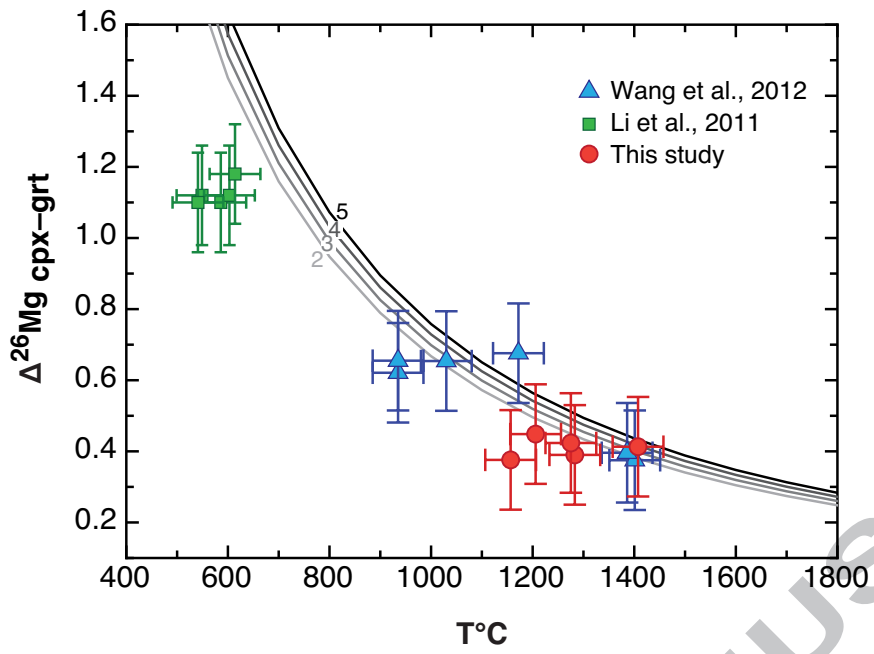


Fig. 5

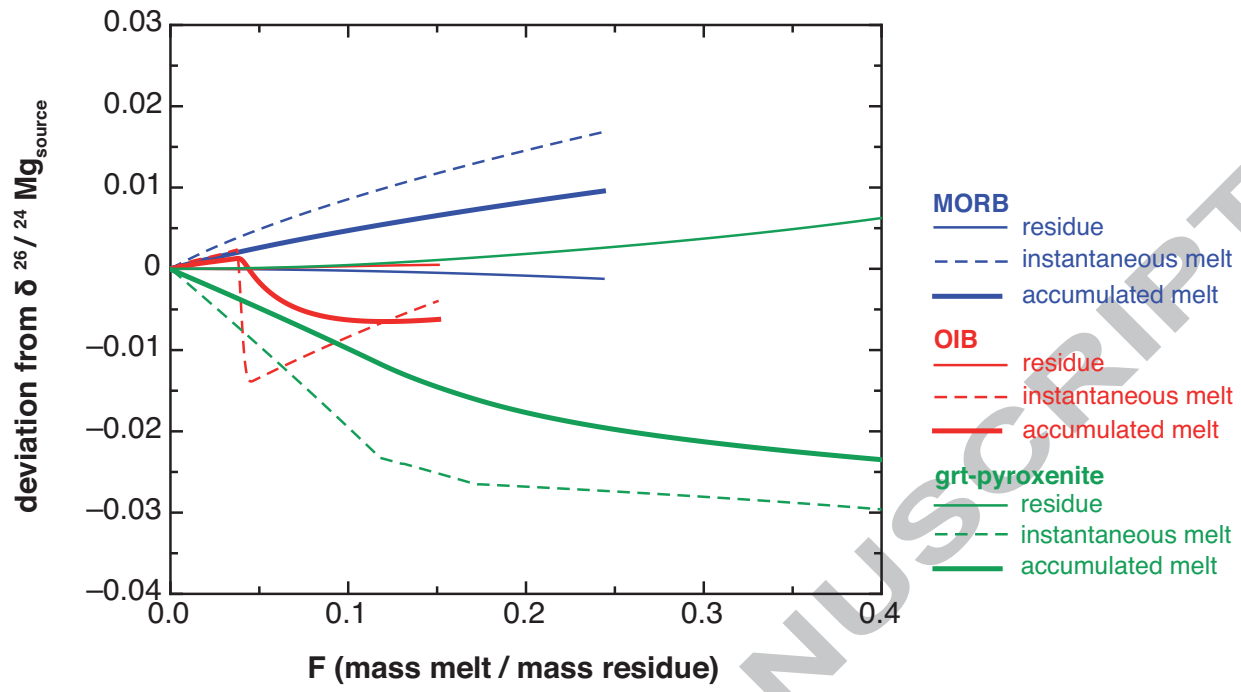


Fig. 6

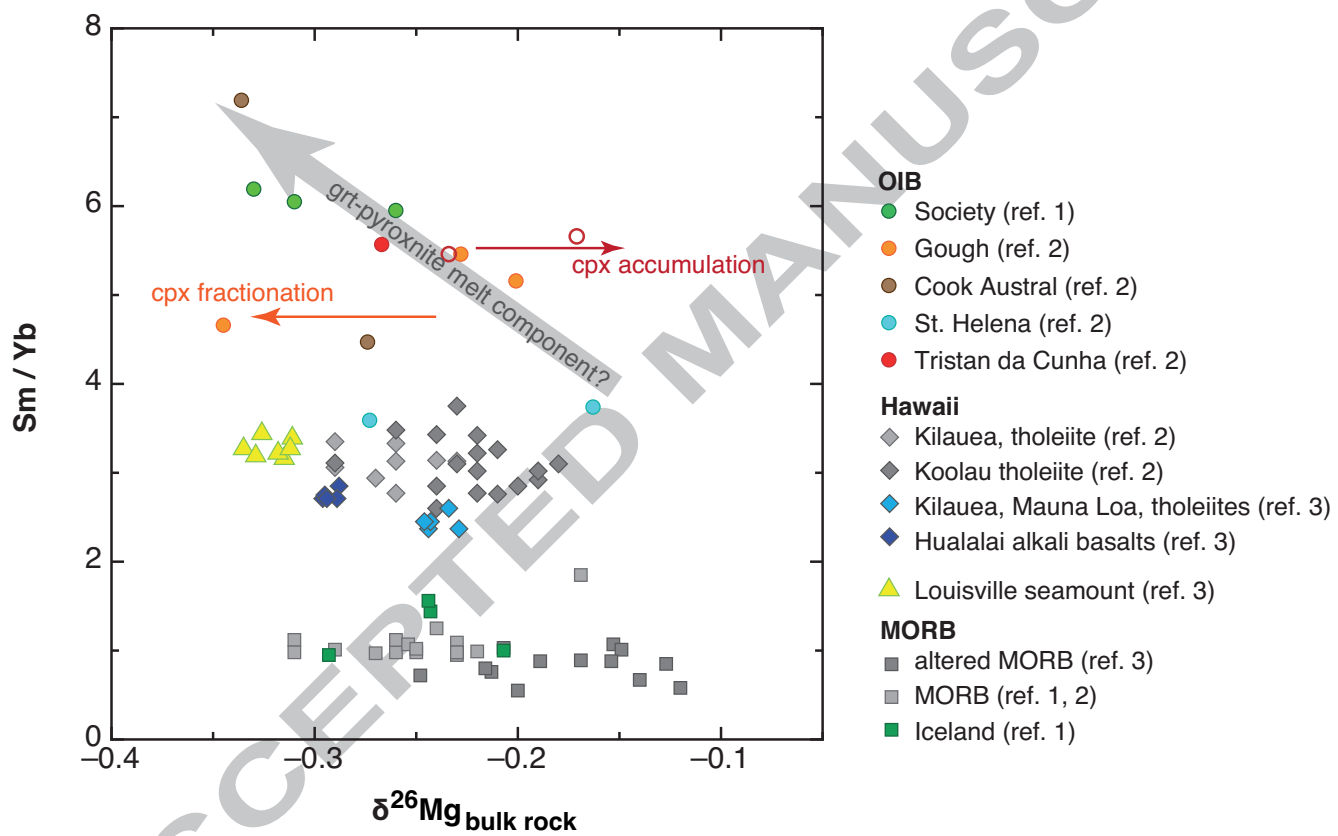
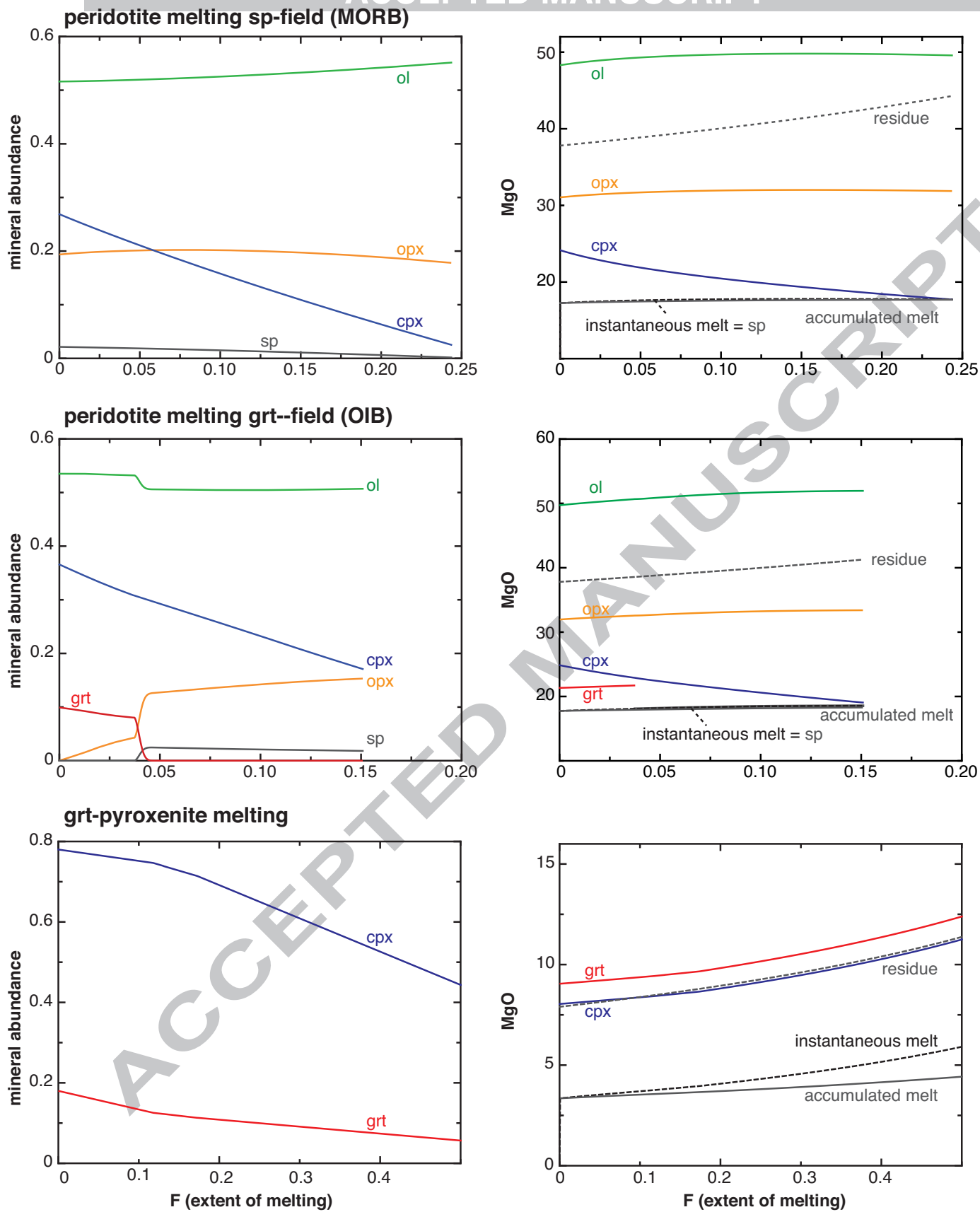
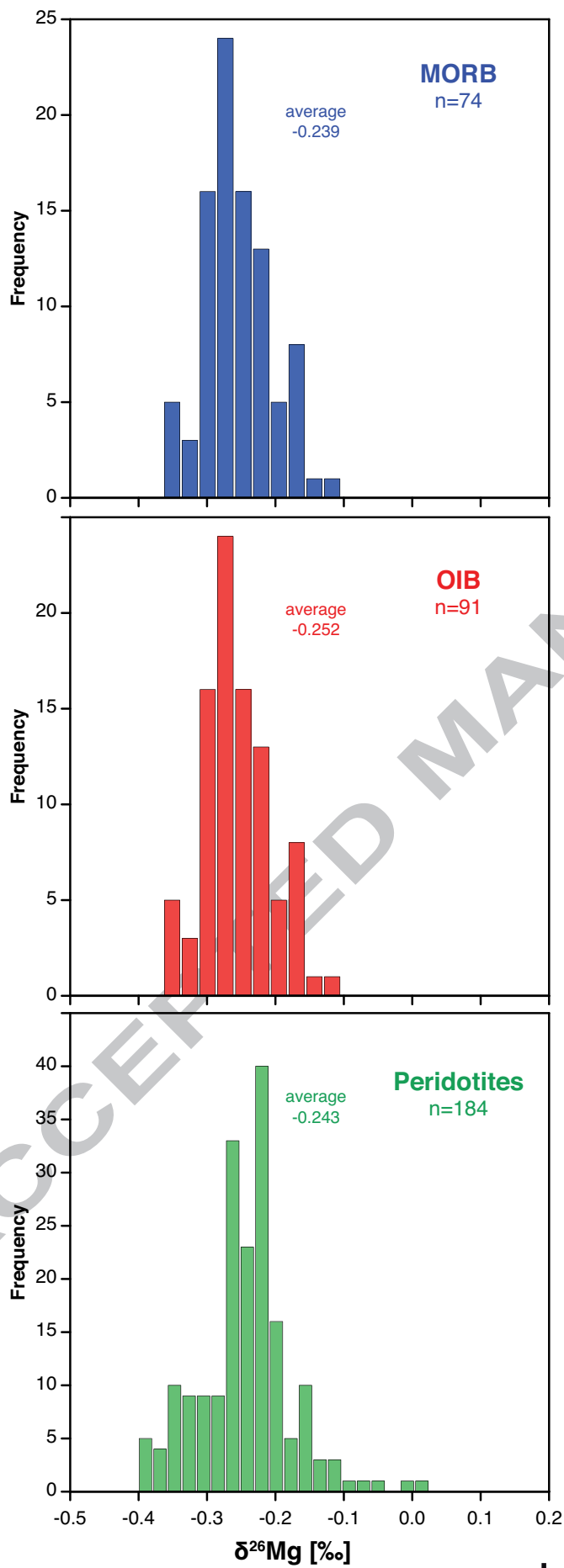


Fig. 7



supplementary Fig. 1



supplementary Fig. 2