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1 Thin crust and exposed mantle control sulfide
2 differentiation in slow-spreading ridge magmas

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16 **ABSTRACT**

17 Gabbroic veins enclosed in mantle peridotite from ocean core complexes next to
18 oceanic transform faults demonstrate sub-crustal crystallization of silicate minerals from
19 a MORB-like melt. Cooler lithosphere there may also affect sulfide crystallization and
20 the metal budget of the lower and upper crust but the related sulfide behavior is poorly
21 understood. Here, we use chalcophile elements to trace sulfide crystallization in a suite of
22 MORBs erupted at the Kane Megamullion south of the Kane Fracture Zone along the

23 Mid-Atlantic Ridge. Cool lithosphere there is inferred from a low magma supply, and
24 lithostratigraphic evidence for thin crust with abundant mantle rock exposed to the
25 seafloor (Dick et al., 2008). We show that the concentrations of Cu, Zn, As, Ga, Pb, Sb
26 and Tl in the Kane Megamullion MORBs rise linearly with melt differentiation expressed
27 by decreasing MgO and Ni content. The low-pressure fractional crystallization within the
28 crust thus occurs at sulfide-undersaturated conditions. Sulfide-undersaturated MORBs are
29 unusual. At the Kane Megamullion, however, the thin crust allows melt to more
30 extensively interact with the shallow and serpentinized mantle. We argue that sulfur and
31 chalcophile elements have been lost from the melt due to sulfide crystallization during
32 melt-rock reaction in the shallow mantle.

33 **INTRODUCTION**

34 Mid-ocean ridge basalts (MORB) are both the most abundant and the most-
35 studied rocks from the Earth's oceans, and represent 75% of the Earth's annual magma
36 production (Crisp, 1984). The main process controlling MORBs differentiation is low-
37 pressure fractional crystallization of olivine, plagioclase, and clinopyroxene within the
38 crust (White and Klein, 2013). Sulfides also appear to form there as chalcophile element
39 concentrations decrease gradually with MORB differentiation (Jenner and O'Neill, 2012;
40 Francis, 1990). This implies that, on average, cumulates in the lower ocean crust would
41 be richer in chalcophile elements than the overlying lavas and dikes. However, the global
42 average gabbro Cu concentration (71 ± 19 ppm, σ ; Coogan, 2014) appears lower than the
43 global average MORB Cu concentration (81 ± 25 ppm, σ ; White and Klein, 2013), and
44 much lower than in the primitive MORBs (~ 120 ppm Cu; Lee et al. 2012). An appealing
45 way to explain this discrepancy would be to assume that a significant portion of sulfide

46 crystallization occurs in the shallow mantle. The general concept of sub-crustal
47 crystallization is already well known for silicate minerals (White and Klein, 2013). Early
48 crystallization can be triggered by a thicker cooler lithosphere at slow-spreading ridges,
49 particularly in regions with lower magma supply as in the vicinity of fracture zones
50 (Herzberg, 2004; Villiger et al., 2007). However, little is known about: 1) the extent to
51 which sulfides are involved in sub-crustal differentiation; 2) what the principle
52 crystallization mechanism is; and 3) what the implications for the subsequent
53 differentiation of chalcophile elements in the crust are.

54 In order to understand the effect of a cooler lithosphere on sub-crustal sulfide
55 crystallization, we investigated a suite of MORBs from a region of thin crust indicative of
56 low magma supply from the slow-spreading Mid-Atlantic Ridge (MAR). We find they
57 have an anomalous pattern of chalcophile element differentiation with respect to typical
58 MORBs. We interpret this pattern as caused by sub-crustal sulfide precipitation during
59 melt interaction with the shallow mantle.

60 **SAMPLES**

61 The studied MORBs come from the Kane Megamullion ocean core complex
62 (OCC) adjacent to the Kane Fracture Zone (23°38'N) at the MAR (Dick et al., 2008). As
63 with other OCC's, Kane Megamullion exposes lower crust and mantle rocks in the
64 footwall of a detachment fault. Oceanic detachment faults are long-lived low-angle
65 plutonic growth faults that usually form along slow-spreading ridges during periods of
66 low to intermediate magma supply (Cann et al., 1997; Tucholke et al., 1998). Basalt
67 carapace on the seafloor is discontinuous. Dick et al. (2008) mapped the extent of the
68 lavas and interpret it to have either erupted off axis, or to be a remnant of the hanging

69 wall. We have selected nine cogenetic MORBs collected during Jason II Dives 110 and 111,
70 and Dredge 1 from one pillow basalt formation (23°34'N, 45°19'W) located ~5 km south of
71 the Kane Fracture Zone (Dick et al. 2008). All our samples are undeformed, minimally
72 seafloor weathered to fresh, aphyric (cryptocrystalline) to 1%-olivine-phyric basalts. Two
73 samples preserve glassy rims. The cryptocrystalline matrix is largely plagioclase, olivine
74 and clinopyroxene with minor titanomagnetite and ilmenite.

75 **METHODS**

76 Whole-rock major element contents were analyzed by X-ray Fluorescence (XRF)
77 spectroscopy at the Federal Institute for Geosciences and Natural Resources, Hanover,
78 Germany. An ELTRA CS 800 carbon/sulfur Analyzer (Institute of Mineralogy, Leibniz
79 University of Hanover, Germany) was used to determine whole-rock sulfur contents
80 using the analytical procedure of Lissner et al. (2014). Chalcophile element
81 concentrations were determined by a combination of instrumental neutron activation
82 analysis (INAA), and inductively coupled plasma - mass spectrometry (ICPMS), both
83 conducted by Activation Laboratories Ltd., Ontario, Canada with the Ultratrace 5
84 analytical package. Mineral major and trace element compositions were determined with
85 a Cameca SX100 electron microprobe (EPM) and an ELEMENT-XR (Thermo Scientific,
86 Germany) fast-scanning sector field inductively coupled plasma ICPMS coupled to a
87 femtosecond laser ablation (fs-LA) system (Solstice, Spectra-Physics, USA) at the
88 Institute of Mineralogy, Leibniz University of Hanover, Germany.

89 **RESULTS**

90 Major and trace element compositions of the whole-rock samples as well as for
91 olivine, plagioclase, and clinopyroxene are reported in the Data Repository (Tables DR1–

92 4). Our glasses and whole-rock samples have MgO contents between 8.3% and 6.1%
93 (Fig. 1) suggesting that the basalts represent moderately evolved mid-ocean ridge melts.
94 Compositions of both investigated glasses are consistent within 5% with the respective
95 whole-rocks (Fig. 1). A high Na₈ of 3.1% (Na₂O content normalized to 8 wt.% MgO;
96 Klein and Langmuir, 1987) is in agreement with the high Na₈ found in other MORBs
97 formed under the thin crust at the Southwest Indian Ridge, the Gakkel Ridge, and the
98 MAR from 13° to 35°N (White and Klein, 2013).

99 The basalts display a Cu trend that contrasts with the global MORB trend:
100 between 8.3–6.0 wt.% MgO, Cu increases linearly from 60 to 100 ppm with a coefficient
101 of determination (R^2) of 0.90, whereas non-plume-related MORBs from the global
102 reference data set of Jenner and O'Neill (2012) show the Cu concentrations decreasing
103 from 80 to 60 ppm over the same MgO range (Fig. 1). The increasing Cu trend in the
104 Kane Megamullion MORBs is matched by increasing Zn, As, Pb, Tl, Sb, and Ga. For
105 example, Zn rises from 85 to 115 ppm with decreasing MgO ($R^2 = 0.94$; Fig. 2). Similar
106 trends are observed against another differentiation index, the Ni content, with R^2 values
107 of 0.86 for Cu, and 0.71 for Zn. Chalcophile elements thus behaved incompatibly during
108 the differentiation of the Kane Megamullion MORBs, implying that this occurred under
109 sulfide-undersaturated conditions. These observations are critical as sulfur in MORBs is
110 often lost by degassing during eruption (e.g., Alt and Shanks, 2011). This can be also the
111 case for the Kane Megamullion MORBs as suggested by increasing Cl/S ratio upon
112 cooling (Fig. DR1; cf. Lesne et al., 2011).

113 In a correlation matrix of Zn, Cu, Pb, As, Sb and Tl, coefficients of determination
114 between element pairs are all above 0.7 (Table DR5), with the exception of Tl ($R^2 =$

115 0.24–0.52). These strong correlations imply that the chalcophile element contents are
116 controlled by a common parameter. In the absence of sulfide this parameter is likely
117 element partitioning between melt and clinopyroxene, where $D_{\text{Ni}} > D_{\text{Ga}} > D_{\text{Zn}} > D_{\text{Cu}} >$
118 D_{Sb} (Fig. 3; Jochum et al., 2011). Indeed, Ni/Ga, Ga/Zn, Zn/Cu and Cu/Sb all fall with
119 decreasing Mg# in our basalts. Ni/Ga falls from 7.8 to 5.9 ($R^2 = 0.92$), and the others
120 from 0.20 to 0.15 ($R^2 = 0.90$), from 1.3 to 1.0 ($R^2 = 0.72$) and from 309 to 72 ($R^2 = 0.83$),
121 respectively. Therefore, the Sb concentration in the most evolved Kane Megamullion
122 MORBs is ~15 times larger than the initial Sb concentration at 8.3 MgO wt.%. In
123 contrast, Cu, Zn, and Ga concentrations increase more modestly, and Ni decreases (Fig.
124 3).

125 **DISCUSSION**

126 Data summarized on Figures 1-3 is consistent with Kane Megamullion MORBs
127 having evolved by low-pressure fractional crystallization under sulfide-undersaturated
128 conditions, and with other MORBs from the Kane area (22–25°N, Fig. DR2; Bryan et al.,
129 1981). Differentiation of chalcophile elements under sulfide-undersaturated conditions is
130 known from plume-related MORBs of Jenner and O'Neill (2012). The plume-related
131 MORBs differ, however, from the Kane Megamullion MORBs by their elevated Cu
132 contents, with Cu_8 (Cu content at 8 wt.% MgO) ranging from 130 to 160 ppm.

133 In principle, Cu-poor MORBs could be derived from a sulfide-poor mantle (Fig.
134 1: Model A). A primitive melt with only 25 ppm Cu formed at a typical degree of mantle
135 partial melting at the Kane Megamullion (11%–14%; Dick et al., 2010) would require a
136 mantle source with ~8 ppm Cu at 1.8 GPa or ~12 ppm Cu at 4.5 GPa (Lee et al., 2012).
137 Cu-poor depleted mantle is known for example from the Finero orogenic peridotites with

138 7 ppm average Cu (Garuti et al., 1984). At Kane Megamullion, however, Cu-poor mantle
139 is unrealistic as spinel harzburgites there contain on average 28 ppm Cu (Table DR6).

140 Assuming that a typical mantle source with ~30 ppm Cu produces primitive basalt
141 melts with ~120 ppm Cu (Lee et al., 2012; Fig. 1), an initial depletion process driving Cu
142 concentrations from 120 to 60 ppm Cu is required. We thus propose an alternative model
143 involving two steps of magmatic differentiation (Fig. 1: Model B; Fig. 4). In the first
144 step, chalcophile elements are removed from the melt during its ascent through the
145 mantle (orange color in Figures 1 and 4). The second step is exactly the same as in model
146 A, with low-pressure sulfide-undersaturated fractional crystallization in the crust (red
147 color in Figures 1 and 4).

148 We propose that melt-mantle reaction is the differentiation mechanism that drove
149 the chalcophile elements concentrations to low levels during the first step. The Kane
150 Megamullion dunites, plagioclase harzburgites, and mantle-gabbro contacts, which all
151 interacted with MORB-like melt (Dick et al., 2010), contain enhanced Cu concentrations
152 (57–230, 90–209, up to 305 ppm, respectively). Sulfides have been found in mantle
153 samples from a variety of other settings that underwent melt-rock reaction, including in
154 mantle xenoliths (Lorand et al., 2003; Wang et al., 2009; Chen et al., 2014), orogenic
155 mantle sections (Rehkämper et al., 1999; Lorand et al., 1993) abyssal peridotites
156 (Rehkämper et al., 1999; Lorand et al., 1993) and potentially slow-spreading ridge
157 ophiolites (Madrigal et al. 2015; Schwarzenbach et al., 2016). Such an enrichment of
158 mantle in various elements, including chalcophile elements, due to melt-mantle reaction
159 is called refertilization (e.g., Niu, 2004).

160 The mechanism of sulfide crystallization from a melt interacting with mantle has
161 not yet been fully explained. The aforementioned broad spectrum of tectonic settings,
162 encompassing a wide range of temperatures and pressures, suggests that neither
163 temperature nor pressure is crucial for controlling the refertilization of mantle by
164 chalcophile elements. The difference in Fe content between a melt and the mantle,
165 though, could be a common factor for all the settings and trigger sulfide crystallization
166 during mantle-melt reaction. The sulfur concentration at sulfide saturation (SCSS)
167 strongly decreases with the decreasing iron content of the melt, especially in the range of
168 5–15 wt.% FeO (O'Neill and Mavrogenes, 2002; Haughton et al., 1974; Ariskin et al.,
169 2013). The FeO content in average MORB is ~10.5 wt.% (Gale et al., 2013), and FeO₈
170 (the FeO content at an MgO value of 8 wt.%) for the Kane Megamullion MORB is 10.6
171 wt.% FeO (Table DR1). By contrast, the average mantle peridotite contains 8.0 wt.% FeO
172 (Lyubetskaya and Korenaga, 2007), and the median FeO content in the Kane
173 Megamullion spinel harzburgites is 7.6 wt.%. Based on the model of Ariskin et al.
174 (2013), SCSS should fall from 1500 to 900 ppm if FeO content of a melt would decrease
175 from 10.6 to 7.6 wt.% FeO. A further drop of SCSS is expected by increasing the Ni
176 content of the melt (Ariskin et al., 2013). Fe and Ni in melt are buffered by the exchange
177 reaction with large amount of olivine on the conduit walls that causes Fe loss (Dick and
178 Natland, 1996; Falloon et al., 2001) and Ni gain (Hart and Davis, 1978) in the melt, both
179 of which could lead to sulfide crystallization. The Fe loss causing sulfide crystallization
180 could also be achieved by simple olivine or spinel crystallization as proposed by Luguét
181 and Lorand (1999) and Luguét et al. (2003). Both would, however, trigger a simultaneous
182 Ni loss, which could possibly cancel the effect of Fe loss.

183 Refertilization of the mantle with sulfides is only moderate in most of the tectonic
184 settings listed above. For example, typical refertilized orogenic mantle contains a
185 moderately elevated Cu concentrations of ~50 ppm Cu (Lorand et al., 2013), whereas the
186 Cu content of the Kane Megamullion re-fertilized mantle is enhanced up to ~300 ppm.
187 This excessive enrichment and the accompanied depletion of Kane Megamullion MORBs
188 thus seem to be setting-specific, and linked to the very thin crust and the shallow mantle
189 in the area. The additional conductive cooling brought by hydrothermal circulation in this
190 ultrashallow mantle accelerates melt solidification upon reaction with the mantle (Fig. 4).
191 In addition, hydrothermal circulation introduces high amounts (up to ~15 wt.%, Table
192 DR7) of water into the shallow mantle. High water content of the Kane Megamullion
193 MORBs (up to 1.8 wt.% in glass, and up to 2.7 wt.% in bulk-rocks), and possible
194 crystallization of clinopyroxene before plagioclase (Fig. 3, cf. Danyushevsky, 2001) may
195 indicate that the water was partially stored in the altered peridotite already before mantle-
196 melt reaction. We have documented contact metamorphism along the recovered
197 serpentinite-gabbro contacts at the Kane Megamullion, which suggests the melt-
198 serpentinite reaction in fact takes place (Fig. DR3). The water lowers the solidus
199 temperature of the melt-mantle reaction allowing a yet larger amount of melt to react with
200 the conduit walls, and yet more efficient FeO loss. Consequently, sub-crustal sulfide
201 crystallization from the Kane Megamullion MORBs can be excessive with respect to
202 MORBs erupted on a completely developed oceanic crust.

203 **CONCLUSIONS**

204 MORBs at slow and ultraslow-spreading ridges with low magma supply rates
205 may become sulfide-undersaturated due to extensive sub-crustal sulfide crystallization

206 following melt reaction with the mantle. The crystallization of sulfides during melt-
207 mantle reaction could be achieved by lowering the level of sulfide concentration at
208 sulfide saturation in the portion of melt that was depleted in FeO. This process may be
209 global, but it becomes increasingly significant at ridge segments with thin crust, where
210 the melt-mantle reaction can proceed to very shallow depths. In addition, conductive
211 cooling related to hydrothermal circulation and high water content of the serpentinized
212 peridotite boost the intensity of the melt-rock reaction.

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367

368 FIGURE CAPTIONS

369

370 Figure 1. Cu versus MgO contents of the Kane Megamullion MORBs (red) compared to
371 non-plume-related MORBs from the reference data set of Jenner and O'Neill (2012;
372 gray). Models A and B are two possible scenarios for the early MORB differentiation
373 (see Discussion). Modified after Jenner and O'Neill, 2012.

374

375 Figure 2. Chalcophile element versus MgO contents of the Kane Megamullion MORBs.

376

377 Figure 3. Ratios of actual to initial (for MgO wt.% = 8.3) chalcophile element contents
378 versus MgO contents of the Kane Megamullion MORBs. Note that element
379 concentrations grow proportionally fast to the decreasing clinopyroxene-melt partition
380 coefficients (D_{cpx}), which are <0.02 for Sb, 0.07–0.36 for Cu, 0.41–0.50 for Zn, 0.74 for
381 Ga, and 2.6–4.4 for Ni (Jochum et al., 2011).

382

383 Figure 4. Lithosphere profile in the Kane area as proposed by Cannat et al. (1995) along
384 with the Cu concentration observed in the Kane Megamullion basalts (red) and the

385 predicted Cu concentrations at the first stage of differentiation (orange). Modified after

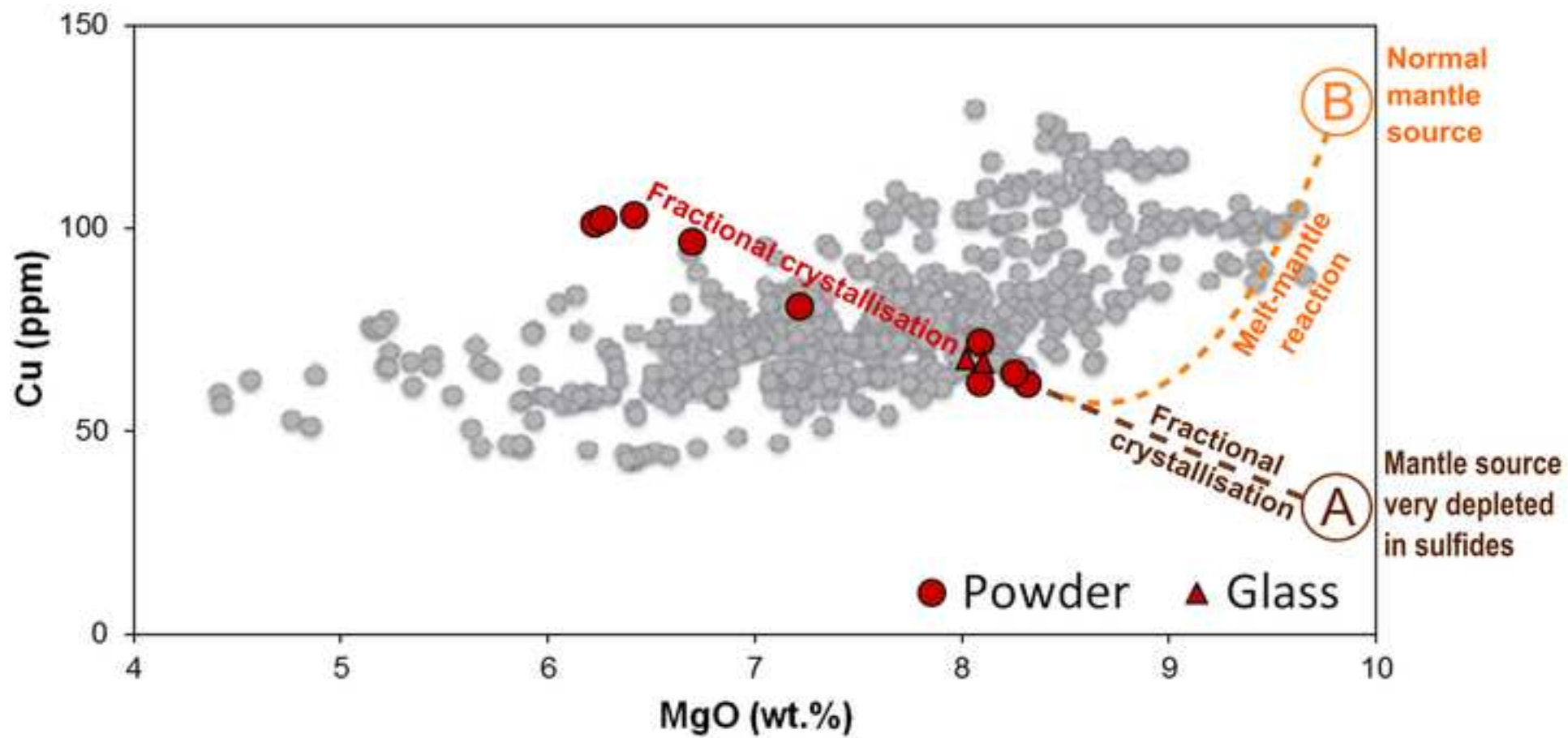
386 Dick et al., 2006.

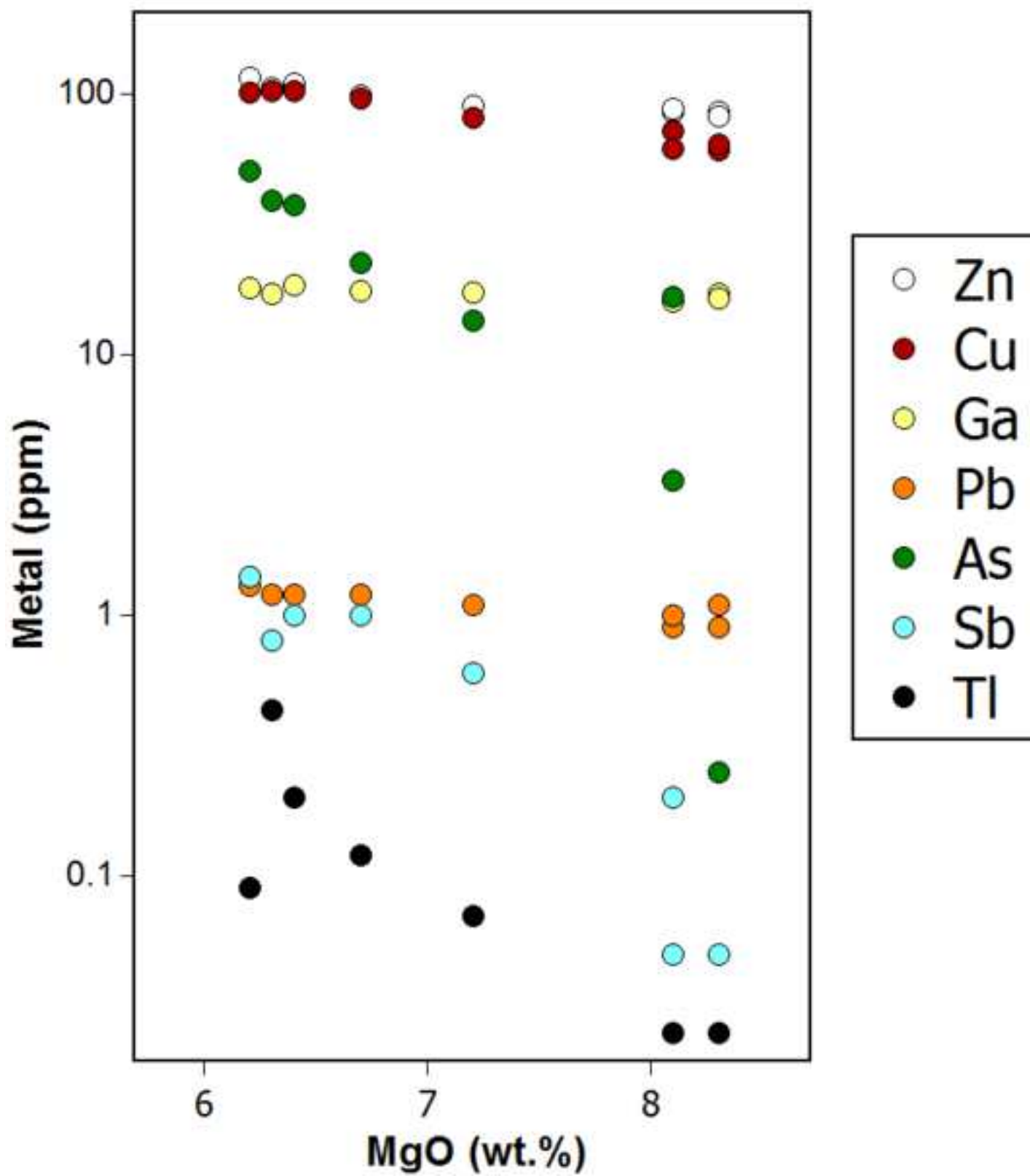
387

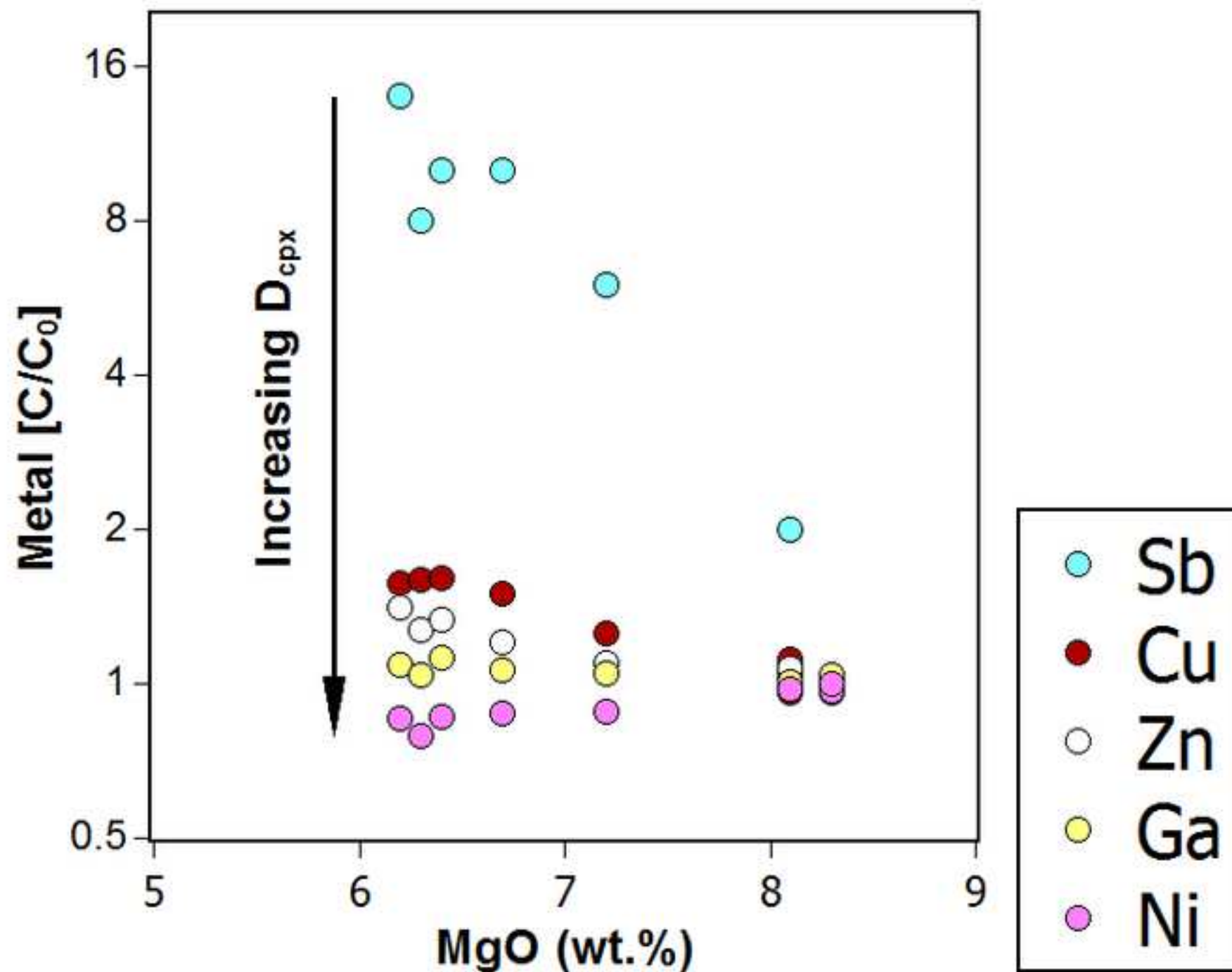
388 1GSA Data Repository item 2017xxx, xxxxxxxx, is available online at

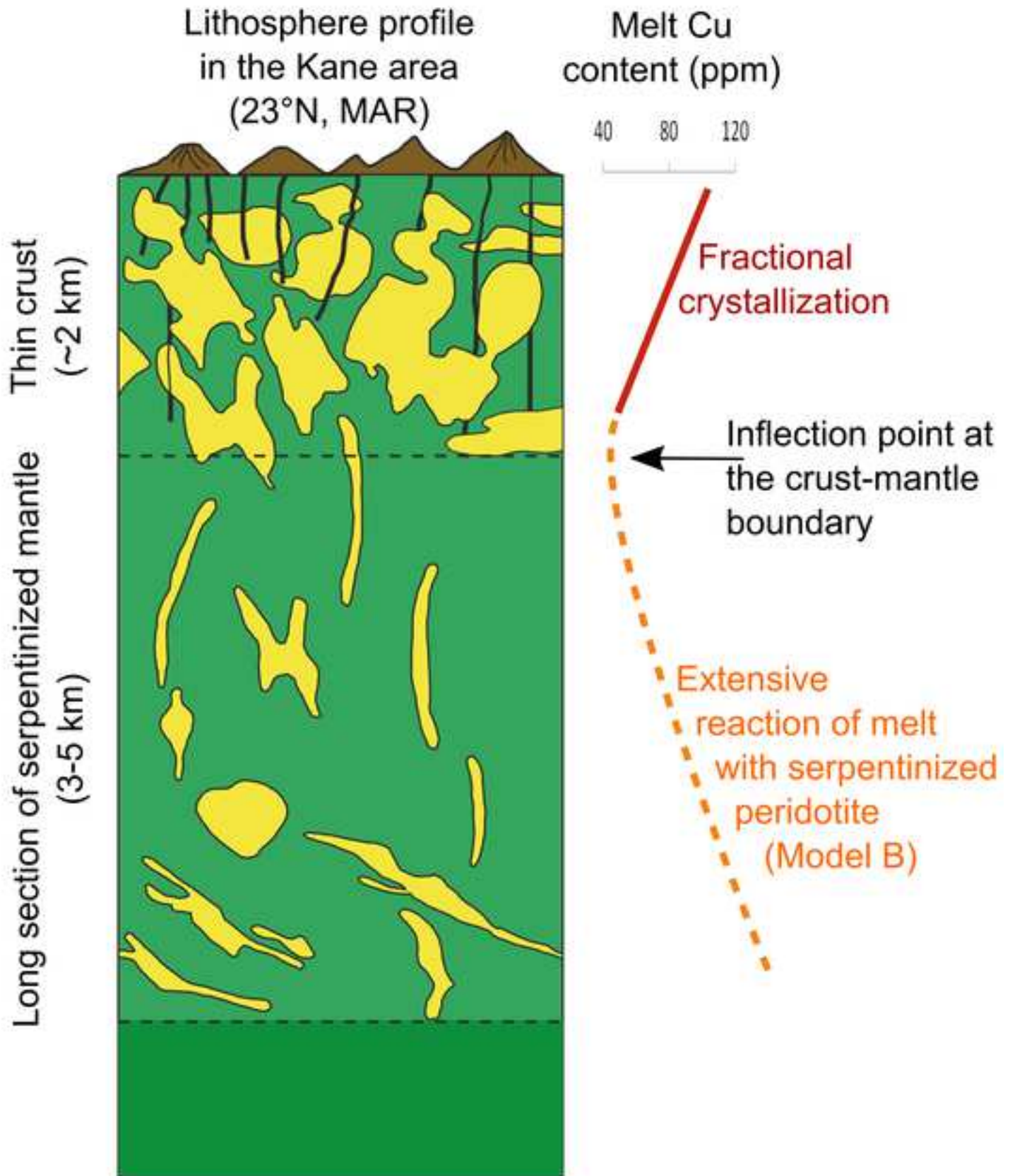
389 <http://www.geosociety.org/datarepository/2017/> or on request from

390 editing@geosociety.org.









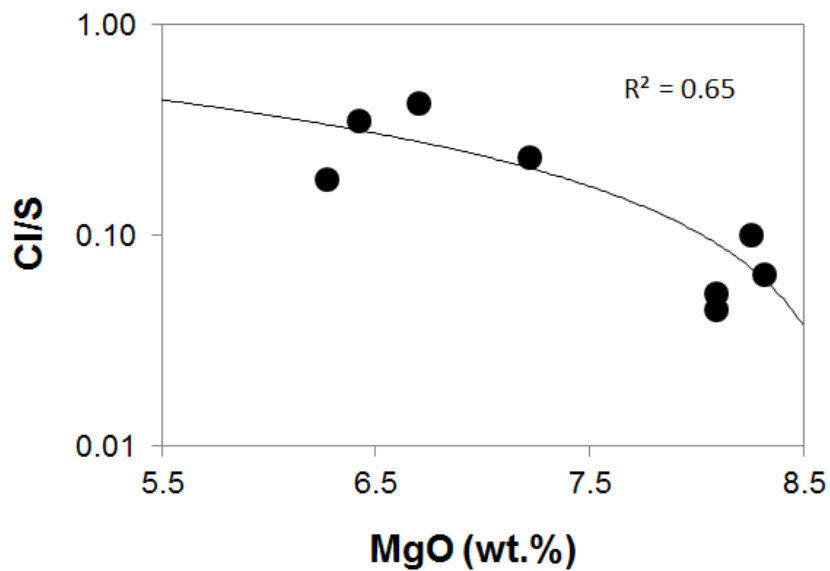


Figure DR1. Bulk-rock Cl/S ratios versus bulk-rock contents of MgO in the Kane Megamullion MORBs.

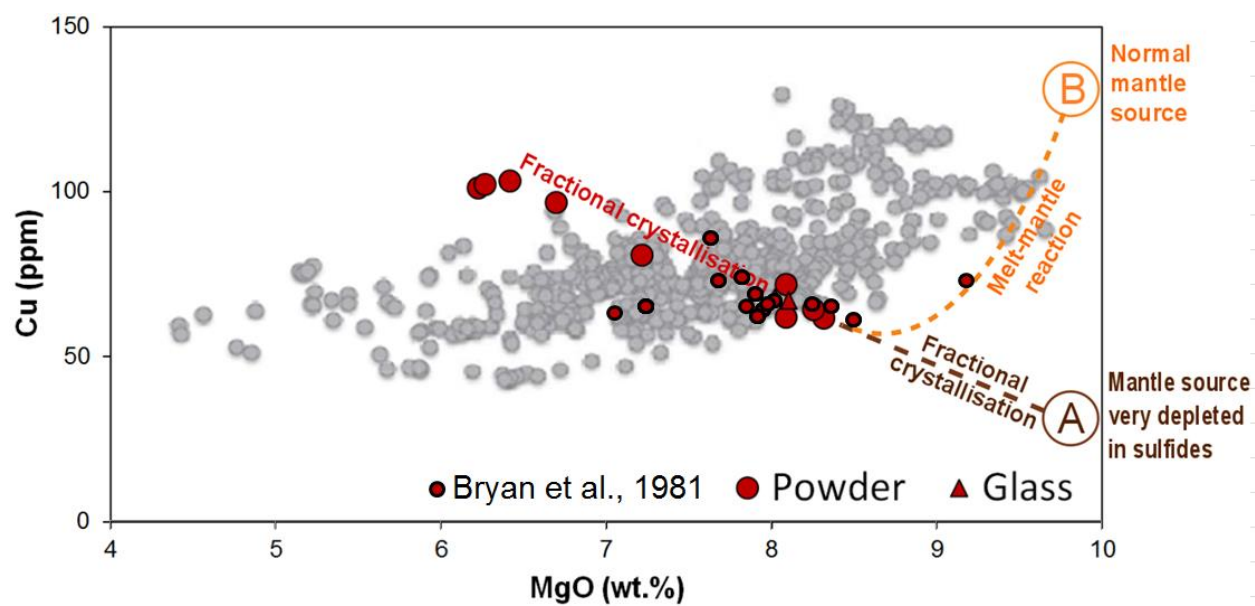


Figure DR2. Bulk-rock copper content versus bulk-rock MgO in the Mid Atlantic Ridge Kane MORB's (22-25°N, Bryan et al., 1981) plotted on top of Figure 1.

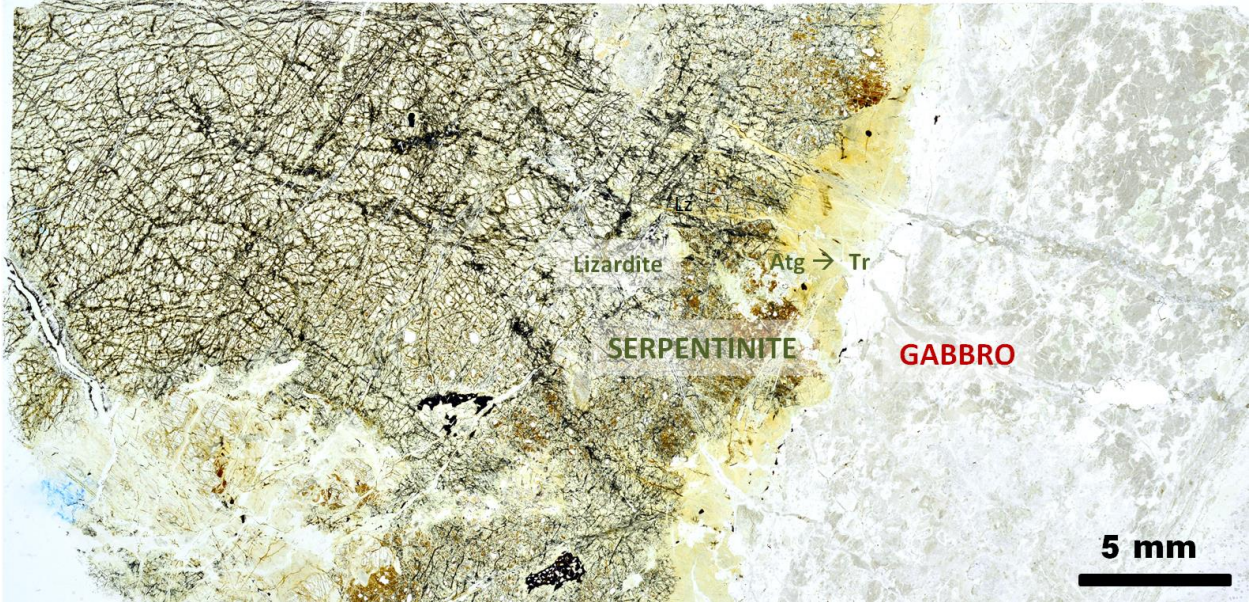


Figure DR3. Thin-section microphotography of a serpentinite-gabbro contact with a distinct zone of contact metamorphism (yellow) between the serpentinite host rock and the gabbro vein. Sample 21-9. Plane-polarized transmitted light. Atg, Antigorite. Tr, Tremolite.

Table DR1. Major and trace element composition of MORBs from the Kane Megamullion OCC

Sample	1-2	110-1	110-2	111-2	111-3	111-4	111-7	111-16	111-17
Mg#	0.51	0.53	0.55	0.54	0.61	0.57	0.60	0.61	0.60
major elements (wt.%)									
SiO ₂	46.3	46.6	47.8	47.4	49.0	48.1	49.0	49.4	47.8
TiO ₂	1.76	1.64	1.59	1.65	1.58	1.64	1.57	1.55	1.62
Al ₂ O ₃	17.2	16.4	15.9	16.4	15.7	16.0	15.6	15.6	16.1
Fe ₂ O ₃	11.7	11.0	10.6	10.9	10.6	10.7	10.5	10.4	10.8
MnO	0.17	0.19	0.18	0.16	0.18	0.18	0.18	0.18	0.18
MgO	6.23	6.27	6.70	6.42	8.32	7.22	8.09	8.26	8.09
CaO	11.5	11.4	11.1	11.2	11.2	11.5	11.0	11.1	11.4
Na ₂ O	2.94	3.02	3.03	3.08	2.71	2.83	2.79	2.74	2.78
K ₂ O	0.09	0.18	0.17	0.16	0.14	0.26	0.20	0.16	0.12
P ₂ O ₅	0.33	0.32	0.22	0.28	0.14	0.21	0.15	0.15	0.22
L.O.I.	1.6	2.7	2.5	2.1	0.1	1.0	0.4	0.1	0.5
Total	99.7	99.8	99.8	99.8	99.6	99.7	99.6	99.6	99.7
Chalcophile elements (ppm)									
Cu	101	102	96	103	61	81	72	64	62
As	50	39	23	37	-	14	3	-	17
Zn	116	105	99	110	85	90	86	82	88
Ga	17.9	17.2	17.6	18.5	17.2	17.3	16.6	16.5	16.1
Pb	1.3	1.2	1.2	1.2	0.9	1.1	0.9	1.1	1.0
Se	2	1.7	1.7	1.8	2.1	2	2.2	1.3	2.3
Sb	1.4	0.8	1.0	1.0	-	0.6	-	-	0.2
Tl	0.09	0.43	0.12	0.20	-	0.07	-	-	-
Ni	110	102	113	111	125	114	126	129	126
Ag	0.06	-	0.07	-	-	0.07	-	0.24	0.07
Bi	-	-	0.03	-	-	-	0.02	0.11	0.02
Cd	0.2	0.3	0.2	0.2	0.1	0.2	0.2	0.2	0.2
Te	-	0.4	-	-	-	-	0.2	0.2	0.2
Hg	30	10	-	-	-	20	-	10	10
Ge	0.2	0.6	0.3	0.3	0.2	0.5	0.2	0.2	0.3

LOI - loss-on-ignition

The estimates of analytical precision (1 SD) are as follows: Cu, $\pm 1.5\%$; Cd, $\pm 33.3\%$; Ge, $\pm 7.1\%$; Ga, $\pm 1.5\%$; Pb, $\pm 7.1\%$; Tl, $\pm 1.5\%$; major elements $\pm 1-2\%$, and were determined by repeated measurements of unknown samples. The estimates of analytical accuracy are as follows: As, $\pm 3.7\%$; Cu, $\pm 5.3\%$; Cd, $\pm 14.6\%$; Ge, $\pm 7.1\%$; Ga, $\pm 17.0\%$; Hg, $\pm 31.3\%$; Pb, $\pm 4.5\%$; Sb, $\pm 5.3\%$; Te, $\pm 11.7\%$; Tl, $\pm 10.6\%$ and were determined by measurements of various certified material (GXR-1, GXR-4, GXR-6, SDC-1, SAR-M (U.S.G.S), DNC, SBC-1, DMMAS).

Table DR2. Major and trace element composition of olivines from the Kane Megamullion MORBs

Sample	1-2		110-1		110-2		111-2		111-3		111-4		111-7		111-16		111-17		
	n	5	SD	5	SD	8	SD	7	SD	4	SD	6	SD	8	SD	4	SD	7	SD
major elements (wt%)																			
SiO ₂	39.8	0.4	39.9	0.1	40.0	0.3	40.1	0.1	40.0	0.5	39.9	0.3	40.1	0.3	40.2	0.3	39.8	0.4	
Al ₂ O ₃	0.01	0.02	0.02	0.04	0.0	0.0	0.04	0.05	0.07	0.08	0.02	0.04	0.01	0.04	0.14	0.15	0.17	0.17	
TiO ₂	0.02	0.04	0.0	0.0	0.0	0.0	0.01	0.02	0.0	0.0	0.0	0.0	0.01	0.04	0.04	0.05	0.06	0.05	
CaO	0.32	0.04	0.3	0.0	0.33	0.05	0.32	0.03	0.31	0.04	0.3	0.0	0.36	0.05	0.4	0.1	0.4	0.1	
FeO	13.7	0.7	13.4	0.2	13.2	0.3	13.5	0.3	13.7	0.8	13.4	0.3	14.0	0.4	13.5	0.4	14.1	1.1	
MnO	0.2	0.1	0.23	0.01	0.2	0.1	0.2	0.1	0.1	0.1	0.25	0.02	0.1	0.1	0.21	0.04	0.2	0.2	
MgO	45.9	0.8	46.2	0.3	46.6	0.2	46.6	0.3	45.4	0.6	45.4	0.2	45.1	0.4	44.8	0.6	45.0	1.3	
NiO	0.22	0.02	0.220	0.003	0.210	0.007	0.210	0.008	0.21	0.02	0.22	0.01	0.15	0.02	0.21	0.02	0.19	0.03	
Cr ₂ O ₃	0.04	0.06	0.0	0.0	0.0	0.0	0.02	0.05	0.0	0.0	0.0	0.0	0.0	0.0	0.03	0.06	0.04	0.06	
Total		100.0		100.0		100.4		100.8		99.6		99.3		99.8		99.4		99.7	
Fo (%)		85.1		85.5		85.7		85.5		85.1		85.2		84.7		84.9		84.4	
trace elements (µg/g)																			
Co (59)	148	15	168	1	164	7	157	6	160	13	162	4	130	18	155	6	140	12	
Ni (60, 61, 62)	1747	163	1771	22	1683	59	1656	64	1653	183	1731	101	1217	179	1680	137	1502	271	
Cu (63)	14	13	7	8	4	4	11	8	10	13	3	3	22	16	23	5	34	20	
Zn (67)	92	20	80	7	68	8	73	7	95	7	79	3	82	20	98	19	78	15	
Ga (71)	0.6	0.3	0.16	0.04	0.17	0.05	0.20	0.08	0.5	0.7	0.3	0.4	1.8	1.1	0.9	0.5	1.5	1.6	
Ge (74)	3.19	-	1.18	0.08	1.19	0.09	1.14	0.09	1.22	0.02	1.2	0.1	1.3	0.1	-	-	-	-	
As (75)	-	-	1.9	2.5	1.2	2.5	3.6	3.8	0.2	0.1	0.1	0.0	0.5	0.1	-	-	1.9	0.1	
Se (77)	-	-	4.7	0.3	5.4	0.7	5.0	0.4	4.0	0.6	4.3	0.3	4.0	0.5	-	-	-	-	
Pd (106)	0.014	-	0.004	0.003	0.004	0.002	0.003	0.000	0.004	0.002	0.003	0.001	0.005	0.002	-	-	-	-	
Cd (111)	-	-	0.021	0.004	0.023	0.004	-	-	0.03	0.01	-	-	0.051	0.009	-	-	-	-	
In (115)	-	-	0.028	0.001	0.022	0.002	0.025	0.002	0.016	0.006	0.024	0.004	0.027	0.008	-	-	-	-	
Sn (118)	2.1	0.8	5.8	0.3	4.6	0.2	5.4	0.6	2.2	1.0	4.4	0.3	2.7	1.1	3.1	1.5	3.9	0.3	
Sb (121)	-	-	0.20	0.09	-	-	0.09	-	0.12	0.05	-	-	-	-	-	-	-	-	
Te (125)	-	-	0.08	0.03	0.08	0.03	0.09	-	0.09	-	-	-	-	-	-	-	-	-	
Pt (195)	5.7	9.5	1.6	2.3	1.0	1.2	0.9	0.9	2.8	2.7	1.0	1.6	1.1	0.5	4.5	3.4	6.6	8.1	
Au (197)	1.1	-	0.11	0.09	0.09	0.04	-	-	0.11	0.06	-	-	0.1	-	0.4	-	0.4	-	
Pb (206, 208)	0.9	0.8	0.3	0.3	0.5	0.7	1.0	0.7	0.8	0.5	0.11	0.06	1.4	0.6	1.6	1.4	1.2	0.4	
Bi (209)	-	-	0.005	0.002	0.04	0.06	0.08	0.07	0.02	0.02	-	-	0.06	0.04	-	-	0.034	0.003	

Fo=100*(molar Mg/(Mg+Fe+Ca+Mn)); NiO was determined using LA-ICPMS; SD - standard deviation

Table DR3. Major and trace element composition of plagioclase from the Kane Megamullion MORBs

Sample	1-2		110-1		110-2		111-2		111-3		111-4		111-7		111-16		111-17		
	n	2	SD	3	SD	4	SD	3	SD	5	SD	5	SD	6	SD	2	SD	3	SD
major elements (wt%)																			
SiO ₂	53.0	0.4	52.7	1.5	52.5	0.8	54.0	1.0	51.8	0.7	52.0	1.5	51.8	0.4	51.9	0.1	51.6	0.5	
Al ₂ O ₃	27.6	0.5	28.8	0.9	28.5	1.4	28.3	0.4	29.4	0.7	28.5	0.7	29.7	0.3	28.8	0.1	28.6	1.0	
K ₂ O	0.2	0.1	0.1	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TiO ₂	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.0
CaO	11.4	1.1	11.9	1.1	12.0	1.5	12.0	0.8	13.7	0.5	12.8	0.9	13.7	0.2	13.2	0.3	13.3	0.5	
FeO	1.4	0.4	0.8	0.3	1.4	0.8	1.2	0.1	0.7	0.1	0.8	0.1	0.8	0.1	0.9	0.1	1.1	0.4	
MnO	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Na ₂ O	4.5	0.5	4.8	0.5	4.8	0.5	4.8	0.3	3.6	0.3	3.9	0.5	3.7	0.1	3.8	0.1	3.9	0.3	
MgO	0.3	0.1	0.1	0.0	0.1	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.0	0.4	0.0	0.6	0.4	
Total		98.5		99.5		99.4		100.7		99.7		98.5		100.0		99.0		99.3	
Or (%)		1.1		0.3		0.4		0.3		0.2		0.3		0.2		0.2		0.2	
Ab (%)		41.2		44.9		41.7		41.1		33.0		34.3		32.8		34.2		35.0	
An (%)		57.7		54.8		57.9		58.6		66.8		65.5		67.0		65.6		64.7	
trace elements (µg/g)																			
Co (59)	13	-	57	77	46	57	19	15	11	7	41	58	6	5	14	18	28	13	
Ni (60)	81	-	26	-	75	38	36	15	48	16	45	34	39	32	119	43	135	167	
Cu (65)	71	95	42	32	140	90	55	37	61	42	48	18	34	23	87	16	61	24	
Zn (66)	54	6	58	10	66	8	64	17	42	26	48	17	44	13	85	8	87	44	
Ga (69, 71)	15	1	19.0	0.6	17.0	0.9	18	8	14	2	16.9	0.9	16	2	16.7	1.0	16.3	0.7	
Ge (74)	-	-	-	-	1.7	-	-	-	1.6	0.4	1.8	0.1	1.1	-	2.1	-	-	-	
As (75)	-	-	18	13	56	37	16	18	0.73	0.06	0.33	0.08	0.5	-	2.39	0.05	0.7	-	
Se (77)	-	-	-	-	12	8	-	-	5	2	6.3	0.7	-	-	9.3	-	-	-	
In (115)	-	-	-	-	0.11	0.03	-	-	0.063	0.003	0.07	0.01	0.04	-	0.07	0.003	0.06	-	
Sn (118)	7	1	6	1	7	1	6	1	5	2	5.5	0.3	3	1	3.6	0.6	5.6	0.8	
Pt (195)	0.64	0.09	8.9	-	12	12	3.8	-	2	2	2	2	2	3	3	2	9	7	
Tl (203,205)	-	-	-	-	-	-	-	-	0.0215	0.0007	0.05	0.03	0.03	-	0.04	-	-	-	
Pb (206,208)	1.1	0.5	2.0	0.7	3	1	2.4	0.5	1.8	0.5	1.3	0.6	1.6	0.8	1.6	0.1	2	-	
Bi (209)	-	-	0.07	-	0.11	0.07	0.09	0.03	0.05	0.01	0.020	0.003	0.11	0.09	0.04	-	-	-	

Or=100*(molar K/(Ca+Na+K)); Ab=100*(molar Na/(Ca+Na+K)); An=100*(molar Ca/(Ca+Na+K)); SD - standard deviation

Table DR4. Major and trace element composition of clinopyroxenes from the Kane Megamullion MORBs

Sample	n	1-2		110-1		110-2		111-2		111-3		111-4	
		4	SD	8	SD	5	SD	4	SD	5	SD	5	SD
major elements (wt%)													
SiO ₂		45.9	0.7	46.4	1.6	48.6	1.2	47.9	0.6	45.4	2.0	47.1	0.5
Al ₂ O ₃		5.9	1.3	5.0	1.0	3.6	0.8	5.3	0.7	6.2	1.9	5.8	0.3
K ₂ O		0.0	0.0	0.01	0.01	0.0	0.0	0.01	0.02	0.0	0.0	0.01	0.03
TiO ₂		3.3	0.3	2.5	0.6	2.1	0.6	2.3	0.2	3.3	0.7	2.5	0.1
CaO		21.1	1.1	19.4	1.0	19.8	0.8	19.7	1.1	20.5	1.0	20.4	0.2
FeO		10.7	1.7	11.9	1.9	10.4	1.4	10.7	0.8	12.3	0.8	8.7	0.8
MnO		0.1	0.1	0.3	0.1	0.3	0.1	0.2	0.2	0.1	0.2	0.20	0.03
Na ₂ O		0.6	0.2	0.5	0.1	0.5	0.1	0.5	0.2	0.5	0.1	0.4	0.1
MgO		11.2	0.5	12.2	0.9	13.6	1.1	13.2	0.7	10.2	0.7	12.9	0.5
Cr ₂ O ₃		0.04	0.08	0.0	0.0	0.1	0.1	0.2	0.2	0.1	0.1	0.2	0.1
Total			98.9		98.2		99.0		100.0		98.7		98.2
En (%)			37.6		41.3		43.5		42.9		36.0		41.7
Fs (%)			11.3		11.4		10.9		11.1		11.8		10.9
Wo (%)			51.0		47.3		45.6		46.0		52.1		47.4
trace elements (µg/g)													
Co (59)		32	5	54	35	35	5	46	14	37	7	43	8
Ni (60)		84	22	69	33	52	21	158	115	75	50	69	41
Cu (63)		33	16	45	31	28	17	27	8	78	35	33	12
Zn (66)		58	24	94	40	56	12	62	3	124	52	68	12
Ga (69, 71)		14	2	14	3	12	2	10	1	13	1	13	1
Ge (74)		3	-	11	-	3.3	1.0	-	-	3.8	-	3.30	0.04
As (75)		1.4	0.1	19	15	11	6	13	-	1	-	-	-
Pd (106)		0.025	0.006	-	-	0.03	0.01	-	-	-	-	0.02	-
In (115)		0.12	0.01	0.20	0.08	0.19	0.05	-	-	0.17	0.02	0.12	0.02
Sn (118)		6.7	0.7	7	2	5.6	1.0	6.5	-	4.0	0.5	5.0	0.7
Pt (195)		3	5	-	-	8	7	-	-	1.1	0.7	0.2	-
Pb (208)		0.6	0.5	1.8	0.6	2	1	2	1	3	2	0.7	0.2
Bi (209)		-	-	0.4	0.2	0.5	0.6	-	-	0.25	0.05	-	-

En=100*(molar Mg/(Mg+Fe+Ca)); Fs=100*(molar Fe/ (Mg+Fe+Ca)); Wo=100*(molar Ca/(Mg+Fe+Ca)).

SD - standard deviation

Table DR5. Correlation matrix for chalcophile elements of the Kane Megamullion MORBs

	Zn	Cu	Pb	As	Sb	Tl	Ni
Zn	1						
Cu	0.85	1					
Pb	0.71	0.72	1				
As	0.96	0.77	0.72	1			
Sb	0.90	0.85	0.83	0.85	1		
Tl	0.35	0.52	0.29	0.40	0.24	1	
Ni	0.71	0.86	0.59	0.72	0.71	0.71	1

The values represent coefficients of determination (R^2)

Table DR6. Chalcophile element contents (wt.%) of Kane Megamullion spinel harzburgites

Label	S	(ppm)								(ppb)			
		Cu	As	Zn	Ga	Pb	Se	Sb	Tl	Ni	Ag	Bi	Cd
5-1	159	40	35	68	1.6	0.5	2.6	1.5	0.24	1860	-	-	100
5-31A	142	17	3	56	11.7	0.6	0.5	-	0.06	1120	-	-	-
14-44	142	7	11	47	1.9	-	0.4	0.4	0.36	2050	-	-	-
14-70	81	9	5	43	3.9	-	0.3	-	0.13	1800	-	-	-
17-17	210	47	29	101	2.0	-	0.6	0.5	0.24	1590	-	-	-
19-10A	188	39	22	91	1.8	-	0.2	0.7	1.96	1810	-	20	100
19-11A	283	69	20	110	2.2	0.8	0.8	0.9	0.39	1720	-	-	-
19-18A	81	52	45	126	2.3	1.1	1.2	1.4	1.58	1870	-	70	-
19-31	215	59	45	111	2.4	0.7	-	2.1	1.71	1900	-	30	-
112-44A	241	11	5	72	1.2	0.7	1.6	0.3	0.14	1930	-	-	-
112-49	332	52	17	69	1.4	0.8	0.7	0.8	0.26	1670	-	20	-
112-71	84	21	23	82	2.1	0.9	-	1.4	0.28	1300	-	-	-
112-84	184	38	3	67	1.5	1.5	-	-	-	2030	-	-	-
113-40	129	14	25	50	1.2	0.6	0.1	0.3	0.63	1230	-	-	-
113-55A	561	21	22	127	3.0	1.0	-	1.8	3.30	1600	-	-	-
113-57A	32	25	10	115	1.8	0.8	-	0.4	0.41	1110	-	-	-
113-59A	45	23	9	171	1.6	0.9	-	0.4	0.70	1400	-	-	-
114-9	6	8	5	36	2.0	0.6	0.2	0.3	-	1380	-	20	-
114-19A	212	24	13	55	1.8	1.2	-	0.5	0.58	1610	90	100	-

The estimates of analytical precision (1 SD) are as follows: Cu, $\pm 1.5\%$; Cd, $\pm 33.3\%$; Ge, $\pm 7.1\%$; Ga, $\pm 1.5\%$; Pb, $\pm 7.1\%$; Tl, $\pm 1.5\%$; and were determined by repeated measurements of unknown samples. The estimates of analytical accuracy are as follows: As, $\pm 3.7\%$; Cu, $\pm 5.3\%$; Cd, $\pm 14.6\%$; Ge, $\pm 7.1\%$; Ga, $\pm 17.0\%$; Hg, $\pm 31.3\%$; Pb, $\pm 4.5\%$; Sb, $\pm 5.3\%$; Te, $\pm 11.7\%$; Tl, $\pm 10.6\%$ and were determined by measurements of various certified material (GXR-1, GXR-4, GXR-6, SDC-1, SAR-M (U.S.G.S), DNC, SBC-1, DMMAS). After Ciazela et al. (under review, *Geochimica et Cosmochimica Acta*).

Table DR7. Major element contents (wt.%) of Kane Megamullion spinel harzburgites

Label	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ *	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total
5-1	38.6	0.02	1.21	9.07	0.13	36	1.25	0.07	0.01	0.04	12.9	99.2
5-31A	38.9	0.12	1.41	10.15	0.13	36.4	0.56	0.02	0.02	0.02	11.6	99.3
14-44	39.1	0.01	1.33	8.29	0.09	36.2	0.62	0.11	0.02	0.01	13.3	99.3
14-70	40.0	0.05	2.06	9.83	0.12	34.7	1.12	0.15	0.05	0.01	11.1	99.3
17-17	38.7	0.02	1.33	8.00	0.10	36.8	0.29	0.06	0.02	0.02	13.8	99.3
19-10A	34.8	0.02	1.06	8.54	0.17	32.5	5.87	0.08	0.02	0.03	16.1	99.3
19-11A	39.3	0.02	1.68	8.31	0.13	35.9	0.34	0.1	0.03	0.03	13.3	99.2
19-18A	37.6	0.04	1.58	11.31	0.16	33.5	1.81	0.14	0.03	0.07	12.9	99.2
19-31	36.5	0.02	1.71	9.38	0.15	31.6	5.28	0.15	0.01	0.07	14.1	99.1
112-44A	39.4	0.01	1.04	8.20	0.12	37.7	0.3	-	-	0.01	12.5	99.3
112-49	39.7	0.02	1.37	8.47	0.11	37.1	0.54	0.02	0.01	0.02	11.9	99.3
112-71	40.4	0.02	1.35	8.25	0.15	36	0.33	0.11	0.03	0.03	12.6	99.3
112-84	42.2	0.02	1.45	8.51	0.13	40.3	1.16	-	0.01	0.00	5.4	99.2
113-40	36.1	0.01	1.09	7.80	0.07	34.3	4.66	0.07	0.03	0.02	15.1	99.3
113-55A	40.4	0.12	1.78	15.09	0.20	33.8	1.79	0.16	0.02	0.09	5.8	99.3
113-57A	39.3	0.02	1.37	8.16	0.12	37.6	0.06	0.08	0.01	0.01	12.6	99.3
113-59A	38.5	0.01	1.07	10.52	0.14	36.9	0.03	0.05	0.01	0.01	12.2	99.4
114-19A	39.3	0.02	1.33	8.23	0.11	37.5	0.40	0.02	0.01	0.01	12.4	99.3

Fe₂O₃* = Total Fe as Fe₂O₃. LOI – loss-on-ignition, (-) below detection limit.

The estimates of analytical precision (1 SD) are between 1 and 2% and were determined by repeated measurements of unknown samples. After Ciazela et al. (under review, *Geochimica et Cosmochimica Acta*).