Selenium isotope and S-Se-Te elemental systematics along the Pacific-Antarctic ridge: Role of mantle processes

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Abstract

The selenium stable isotope system emerges as a new potential tracer of volatile origin and evolution in the terrestrial planets. Accurate determination of the mantle Se isotope composition requires an assessment of Se isotopic behavior in magmatic processes and potential variations across all mantle reservoirs. Here we report the first high-precision Se isotope compositions and Se–Te abundances of a suite of basaltic glasses from the Pacific–Antarctic ridge. These MORBs display a narrow range in $\delta^{82/76}$Se values (deviation of ^{82}Se/^{76}Se relative to NIST SRM 3149) between -0.30 ± 0.09‰ and -0.05 ± 0.09‰, with an average of -0.16 ± 0.13‰ (2 s.d., n = 27). We quantify the main processes relevant to MORB petrogenesis in order to better understand the Se–Te elemental behavior in the mantle and investigate if these are systematically related to Se isotope variations.

We show that both Se isotopes and S–Se–Te abundances of MORB melts remain unaffected by assimilation of high-temperature hydrothermal fluids and sulfides, whereas the latter has been shown to overprint the ^{34}S/^{32}S ratios. MORB differentiation involving sulfide segregation (sulfide liquid and monosulfide solid solution) significantly fractionates Se and Te (Se/Te ratio ~45 to 190), with no systematic Se isotope variation. The Se–Te contents of the primary MORB melt corrected for magmatic differentiation can be successfully reproduced by near-fractional decompression melting of a mantle with 170–200 µg g^{-1} S (as sulfide liquid), which has either (1) "fertile lherzolite-like" Se–Te contents (80 ± 17 and 11 ± 1.7 ng g^{-1}, respectively; 1 s.d.) or (2) distinctly lower Se (49 ± 11 ng g^{-1}) and Te (3.5 ± 1.3 ng g^{-1}) contents depending on the choice of experimental partition coefficients published by different studies. Regardless, our model shows that Se–Te systematics of "fertile" lithospheric peridotites preserve little primary melt depletion signatures and reflect significant, if not complete, metasomatic overprinting. Finally, based on the observed negligible Se isotopic fractionation between sulfide phase and silicate melt, we suggest that MORBs preserve their mantle source isotopic signature ($\delta^{82/76}$Se $= -0.16 \pm 0.13$‰). Our MORB average is similar within uncertainty to chondritic values but

35 significantly lighter than previously published $\delta^{82/76}$Se data for basalts from a variety of geodynamic settings.

36 The subtle but significant Se isotope variation observed within the investigated MORB suite (up to ~0.25‰) and

37 between other mantle samples analyzed so far may reflect intrinsic source heterogeneity and potential isotopic

38 differences across various mantle reservoirs.

1. Introduction

40   The current primitive mantle (PM) abundances of the moderately volatile and chalcophile elements

41 Se (~80 ng g^{-1}) and Te (~11 ng g^{-1}) are 35–45 times lower compared to the Earth's general volatile depletion

42 trend (McDonough and Sun, 1995; Allègre et al., 2001; McDonough, 2003; Wang and Becker, 2013; Palme and

43 O'Neill, 2014). Because extrapolation of metal–silicate partitioning experiments at 1–19 GPa to core formation

44 conditions predicts near-complete Se–Te removal from the silicate mantle (Rose-Weston et al., 2009), the mantle

45 abundances of Se–Te, together with that of S, have been explained to be established by a chondritic late veneer

46 addition after core formation (Morgan, 1986; McDonough and Sun, 1995; Rose-Weston et al., 2009; Wang and

47 Becker, 2013). However, the non-chondritic $^{34}S/^{32}S$ ratio of the mantle and recent S partitioning experiments

48 suggest that a major fraction of mantle S budget reflects metal–silicate equilibration (Labidi et al., 2013; Suer et

49 al., 2017). Meanwhile, it has been debated whether the broadly-chondritic relative abundances of S–Se–Te in

50 lherzolites are representative of the PM composition (Wang and Becker, 2013) since these samples from the

51 lithospheric mantle are often considered metasomatized, especially by Se–Te-rich base metal sulfides and

52 associated platinum-group minerals (Lorand and Alard, 2010; Lorand et al., 2003, 2004, 2010; Luguet et al.,

53 2003, 2004, 2015; König et al., 2014, 2015; Harvey et al., 2015). In this context, mantle-derived melts such as

54 mid-ocean ridge basalts (MORBs) may provide a complementary and broader picture regarding the composition

55 of the asthenospheric mantle, provided that Se–Te elemental behavior in mantle processes is well constrained.

56   There are only few studies concerning Se and/or Te elemental systematics in MORB (Hertogen et al., 1980;

57 Yi et al., 2000; Jenner et al., 2010, 2015; Lissner et al., 2014). Because of their strong partitioning into base

58 metal sulfides (Guo et al., 1999; Hattori et al., 2002; Peach et al., 1990; Barnes et al., 2009; Patten et al., 2013;

59 Brenan, 2015; Kiseeva et al., 2017), Se–Te abundances and ratios in basaltic melts are strongly controlled by

60 sulfide phase–silicate melt partitioning (Hertogen et al., 1980; Lissner et al., 2014). Hertogen et al. (1980) first

61 observed distinctly higher Se/Te ratios and broadly similar Te contents in worldwide MORBs compared to

62 mantle rocks and suggested a higher apparent compatibility of Te relative to Se during partial melting. This

63 appears consistent with observations from lherzolites, pyroxenites (Wang et al., 2013; Wang and Becker, 2013,

64 2015a), and sulfides in sub-arc mantle xenoliths (Hattori et al., 2002) but inconsistent with observations from

65 refractory harzburgites and platinum group minerals (König et al., 2012, 2014, 2015). Lissner et al. (2014)

66 investigated the Se–Te systematics in enriched- and depleted-MORBs from a restricted section of the southern

67 Mid-Atlantic Ridge and suggested an incompatible behavior of both elements and a higher incompatibility of Te

68 during partial melting. This relative partitioning seems to be reversed during magmatic differentiation (Lissner

69   et al., 2014). These observations might be partly attributed to contrasting relative partitioning of Se–Te in

70   different sulfide phases and platinum-group minerals (e.g., Helmy et al., 2010; Liu and Brenan, 2015; Brenan,

71   2015; König et al., 2015) during different mantle processes. Previous evidence for Se and Te behavior in MORB

72   petrogenesis remains ambiguous and warrants further work.

73   On the other hand, Se isotopes might provide new perspectives on the origin of S–Se–Te as well as other

74   highly siderophile or volatile elements on Earth. Due to analytical difficulties (e.g., Yierpan et al. 2018), only

75   few studies reported Se isotope composition ($\delta^{82/76}$Se; deviation of ^{82}Se/^{76}Se relative NIST SRM 3149) of mantle

76   rocks/melts, which are limited to geological reference materials (Rouxel et al., 2002; Kurzawa et al., 2017;

77   Yierpan et al., 2018). Compared to the chondrite average $\delta^{82/76}$Se of -0.30 ± 0.39‰ (Vollstaedt et al., 2016) and

78   -0.21 ± 0.31‰ (2 s.d.; Labidi et al., 2018), previously analyzed basalts (n = 9) and one peridotite show heavier

79   $\delta^{82/76}$Se with some marginal overlap. Labidi et al. (2018) reported resolvable mass-dependent Se isotope

80   variations among main chondrite groups, ranging between -0.40 ± 0.07‰ (enstatite chondrite) and -0.01 ± 0.09‰

81   (CI-chondrite). Recent high-precision Se isotope analyses on a small number of different basalts show a rather

82   restricted range in $\delta^{82/76}$Se ($+0.21 \pm 0.15$‰, n = 4; Kurzawa et al., 2017; Yierpan et al., 2018). These rocks

83   originate from a variety of geodynamic settings and cover a wide range of Se contents (~15–170 ng g^{-1}) and

84   Se/Te ratios (~3–65), indicating various mantle sources and/or igneous differentiation histories (Yierpan et al.,

85   2018). It thus remains unclear whether their $\delta^{82/76}$Se values readily represent a mantle source signature.

86   In this study, we present the first Se isotope compositions and new Se–Te abundances for a total of 27 fresh

87   MORB glasses collected from the Pacific–Antarctic ridge (65–56°S and 53–41°S). Compared to the sampling

88   areas in previous Se–Te studies (Hertogen et al., 1980; Lissner et al., 2014), these ridge sections are free of

89   plume influence and represent melts derived from a source with first-order major element homogeneity (Vlastélic

90   et al., 2000; Moreira et al., 2008; Hamelin et al., 2010). It is thus an ideal sample set for (1) better understanding

91   Se–Te elemental behavior during mantle processes using recently published experimental sulfide–silicate melt

92   partitioning data and (2) investigating effects of such processes on potential Se isotope fractionation in order to

93   constrain the isotopic composition of the depleted mantle.

2. Samples and geological background

95   We have analyzed 27 on-axis MORB glasses from two sections of the Pacific–Antarctic ridge (PAR): 65–

96   56°S (n = 10) and 53–41°S (n = 17) (Supplementary Fig. S1). These samples were collected from the PAR by

97   the French research vessel *L'Atalante* during the cruises PACANTARCTIC 1 (65–56°S; Géli et al., 1997;

98   Vlastélic et al., 1999) and PACANTARCTIC 2 (53–41°S; Klingelhoefer et al., 2006; Moreira et al., 2008;

99   Hamelin et al., 2010). The PAR extends southward from the southern end of the Juan Fernandez microplate at

100 35°S,110°W (Francheteae et al., 1987) to the Macquarie triple junction at 62°S, 161°E (Falconer, 1972). The

101 studied ridge sections are located to the north of the Vacquier Fracture Zone (FZ; ~53°S) and south of Udintsev

102 FZ (~56–57°S; Supplementary Fig. S1), respectively, with the Eltanin FZ System in between (Watts et al., 1988;

103 Géli et al., 1997; Castillo et al., 1998). The northern section is separated by the Menard FZ (~50°S), which is the

104 major geological feature along the sampling area (Hamelin et al., 2010). Two ridge sections have half-spreading

105 rates of 46–50 mm/year between 52 and 42°S (Lonsdale, 1994) and 27–37 mm/year between 65 and 55°S

106 (Hamelin et al., 2010). The northern ridge section is one of the fastest spreading mid-ocean ridges (Moreira et

107 al., 2008) and, therefore, shows a uniform axial high morphology along the crest (Klingelhoefer et al., 2006). In

108 contrast, the southern section (slow to intermediate spreading ridge) displays variable axis morphologies, ranging

109 from axial valley to axial high (Vlastélic et al., 2000; Ondréas et al., 2001). The oceanic crust beneath the PAR

110 is estimated to be 6–7 km (Adams, 1964).

111   Previous analyses of He, Sr, Nd, Hf, and Pb isotopes show that the studied PAR sections are free from any

112 plume-ridge interactions and reflect a regional-scale first-order mantle source homogeneity (Vlastélic et al., 1999,

113 2000; Moreira et al., 2008; Hamelin et al., 2010, 2011). However, the ridge sections display clear latitudinal

114 variations of radiogenic isotopes, with gradually increasing recycled crust component northwards (Hamelin et

115 al., 2011). This is interpreted to be a subtle yet intrinsic source heterogeneity resulting from progressive mixing

116 of a depleted MORB mantle and recycled oceanic crust. Besides, almost all PAR samples have experienced

117 contamination by Cl-rich brines and/or hydrothermally altered crust during low-pressure magmatic

118 differentiation, which results in significantly heavier S isotope composition if it is associated with hydrothermal

119 sulfide assimilation (Clog et al., 2013; Labidi et al., 2014; Bezard et al., 2016).

3. Analytical methods

3.1. Selenium isotope and Se–Te elemental analyses

122   Most of the studied PAR basalts are in the form of fresh glass fragments. A few samples have plagioclase

123 phenocrysts (<3 mm) and slightly altered yellowish crusts. After they were crushed, fresh chips (1–5 mm) were

124 picked, washed with 18.2 MΩ·cm water in an ultrasonic bath and ground to fine powders. At least 2.5 g sample

125 was used for grinding in order to preclude any potential effect of sample heterogeneity (Wang et al., 2015;

126 Yierpan et al., 2018). One sample (PAC2 DR01-1) is represented by both glass rims and pillow interior, which

127 were processed and analyzed separately.

128   All analyses were conducted at the University of Tübingen. Selenium isotope and Se–Te concentrations

129 were determined from the same sample digest. Details of the chemistry and instrumental procedures are given

130 in Kurzawa et al. (2017) and Yierpan et al. (2018). Briefly, Se contents of most sample unknowns were first

131 determined via isotope dilution by estimating a spike–sample ratio of ~1 based on a general Se vs MgO or S

132 trend previously shown for MORB (Lissner et al., 2014). For this procedure, only ~0.025 g of sample was

133 digested and analyzed directly after separating Fe (see below; but with 2.5 mL resin and 6 N HCl). After Se

134 content was determined, ~0.15–0.4 g of sample was mixed with ^{74}Se–^{77}Se double spike and ^{125}Te single spike

135 to yield Se and Te spike–sample ratios of ~1 and ~0.6–1, respectively. Samples were then digested in a HF–

136 HNO$_3$ mixture at 85°C and evaporated at 65°C. This is followed by heating in 6 N HCl at 130°C and complete

137 evaporation at 85°C. In order to remove Ge while minimizing evaporative Se losses, samples were additionally

138 dissolved and dried down twice with 10.5 N HCl at 85°C in the presence of rock matrix. Selenium was purified

139 by a two-stage column chemistry using 7 mL of Eichrom AG1-X8 and AG 50W-X8 (both 100–200 mesh) ion

140 exchange resins (collected in 4 N HCl and 0.1 N HNO₃, respectively). The dry Se cuts were subsequently

141 dissolved and evaporated in 10.5 N HCl. Tellurium was collected in 0.4 N HCl from the first column after eluting

142 Se and most matrix elements with 4 N HCl and Fe with a 2 N HCl–5 N HF mixture. Finally, the dry Se and Te

143 fractions were taken up in 1 mL 2 N HCl for analysis. Total procedural recoveries of Se and Te for MORBs are

144 systematically ~85–95%, higher than that for reference materials (~80%; Yierpan et al., 2018). Procedural blanks

145 (n = 5) yield signal intensities for each isotope indistinguishable from the background (2 N HCl), which are

146 equivalent to ~0.05 and 0.01 ng for Se and Te, respectively.

147   Selenium isotopes were measured on a ThermoFisher Scientific NeptunePlus multi-collector inductively

148 coupled plasma mass spectrometer (MC-ICP-MS) connected to a HGX-200 hydride generator. The double spike

149 method was used to correct for isotopic fractionation during the chemistry and instrumental analysis. Each

150 analysis was bracketed by 30 ng mL^{-1} spiked NIST SRM 3149 standard. The Se isotope composition is

151 expressed using δ-notation relative to the international reference material NIST SRM 3149 following:

152
$$\delta^{82/76}\text{Se}_{\text{Sample}} = \frac{\left(^{82}\text{Se}/^{76}\text{Se}\right)_{\text{Sample}}}{\left(^{82}\text{Se}/^{76}\text{Se}\right)_{\text{NIST SRM 3149}}} - 1 \tag{1}$$

153     $\delta^{82/76}$Se values are reported in ‰ units by multiplication with a factor of 1,000. In order to fully eliminate

154 residual Ge that represents a significant isobaric interference (Stüeken et al., 2013; Pogge von Strandmann et al.,

155 2014), post-chemistry Se fractions were additionally evaporated (1–2 times) in HCl at 85–90°C and monitored

156 for Ge using sample aliquots before analysis (Luais, 2012; Yierpan et al., 2018). Each analyzed sample has

157 ^{72}Ge/^{82}Se<0.0002 (with <~10% evaporative Se loss). Hydride interferences of Se, Br, and ArAr are generally

158 insignificant owing to the methane addition (Floor et al., 2011; Kurzawa et al., 2017) and associated corrections

159 (mainly SeH) on $\delta^{82/76}$Se are typically ≤0.04‰. For most sample analyses, ~20–40 ng Se was used and the

160 internal error (2 standard error, 2 s.e.) of a single measurement over 40 cycles is mostly <0.05‰. Analytical

161 accuracy and precision were monitored by analyses of inter-laboratory standard MH-495 (30 ng mL^{-1};

162 Supplementary Table S1) and three reference materials (Table 1; Fig. 1). The MH-495 yields an average $\delta^{82/76}$Se

163 of −3.24 ± 0.07‰ (2 s.d., n = 20), in excellent agreement with literature values (Zhu et al., 2008; Kurzawa et al.,

164 2017; Labidi et al., 2018; Yierpan et al., 2018). The $\delta^{82/76}$Se values of BHVO-2 (+0.10 ± 0.11‰; 2 s.d., n = 4)

165 and W-2a (0.00 ± 0.04‰; 2 s.e., n = 1) are comparable to the previously reported values of +0.18 ± 0.10‰ (2

166 s.d., n = 8) and −0.09 ± 0.11‰ (2 s.d., n = 6), respectively (Yierpan et al., 2018; Fig. 1). Two BCR-2 digestions

167 yield $\delta^{82/76}$Se values (+0.18 ± 0.09‰ and +0.15 ± 0.07 ‰; 2 s.e.) that are identical to the average value from

168 Kurzawa et al. (2017) (+0.18 ± 0.11‰; 2 s.d., n = 3) but somewhat lower than that from Yierpan et al. (2018)

169 (+0.29 ± 0.10‰; 2 s.d., n = 5; Fig. 1). BCR-2 yields an overall average $\delta^{82/76}$Se of +0.23 ± 0.14‰ (2 s.d., n =

170 10), whose uncertainty is slightly higher than a typical external reproducibility of 0.10 to 0.12‰ (2 s.d.) on other

171 reference materials (Fig. 1; Yierpan et al., 2018). Note that all these analyses were performed in the same lab

172 (Fig. 1). Considering potentially smaller sample heterogeneity in a glass matrix relevant to this study, the external

173 reproducibility for MORB was assessed by replicate analyses of a randomly selected moderately evolved sample

174 (PAC2 DR33-1; 6.63 wt.% MgO) with different sample amounts (0.15–0.4 g; Table 1). We obtain a 2 s.d.

175 uncertainty of 0.09‰ from 7 digestions and 9 measurements (4 different sessions over 6 months).

176   The isotope dilution concentrations for Te (and when necessary, also for Se; Table 2) were determined on

177 a ThermoFisher Scientific iCAP-Qc quadrupole ICP-MS connected to an ESI hydrideICP hydride generator.

178 Only ~0.1–0.3 ng Te and 0.5–1 ng Se (in 1 mL 2 N HCl) were used for each analysis. The analytical precision

179 of our method was previously reported to be ~2–3% r.s.d. (relative standard deviation) for both Se and Te. All

180 reference materials yield Se–Te concentrations that are in general agreement with the recently published data

181 (Table 1; Lissner et al., 2014; Wang et al., 2015; Yierpan et al., 2018). The Se concentrations of MORBs obtained

182 by double spike inversion and isotope dilution are always comparable within 2% and both reproduce at ~2% r.s.d.

183 (Tables 1 and 2).

3.2. Trace element analysis

185   Only a few trace element data have been published for the PAC1 samples (latitude 65–56°S), whereas the

186 data for PAC2 samples (latitude 53–41°S) are relatively complete (Supplementary Table S2; Vlastélic et al.,

187 2000; Hamelin et al., 2010; Clog et al., 2013; Labidi et al., 2014; Bezard et al., 2016). To fully characterize the

188 samples, we report a more complete set of trace element data (43 elements). The measurements were performed

189 at the University of Tübingen by solution ICP-MS following the method previously described by Babechuk et

190 al. (2010) and Albut et al. (2018). About 0.02 g of sample powder was digested and diluted with 2% HNO_3

191 containing an internal standard solution (^{6}Li, In, Re, and Bi) to the analyte solution with a final dilution factor

192 of ~10,000. Reproducibility and accuracy of trace element determinations were evaluated from the average data

193 of BHVO-2 (quality control standard) from 14 analyses of 6 separate digestions (4 digested together with the

194 PAR samples). Our BHVO-2 results (Supplementary Table S3) show uncertainties better than ~5% r.s.d. for all

195 elements except for Mo, Sb, W, and Tl (~8–20%). Most data agree within ~5% with previously reported values

196 (GeoReM; Jochum et al., 2005).

4. Results

4.1. Major/trace element composition

199   The trace element concentrations determined here, together with all available major/trace element,

200 radiogenic/stable isotope data, are compiled in Supplementary Table S2. All samples are typical N-MORB

201 (normal MORB) with $(La/Sm)_N$ ratios of 0.461–0.965 (normalized to PM; McDonough and Sun, 1995), except

202 PAC2 DR27-1 ($(La/Sm)_N = 1.227$), which is the most evolved sample (4.52 wt.% MgO) and dredged from a

203   seamount-ridge transition zone (Hamelin et al., 2010). The PM-normalized trace element patterns of PAR glasses

204   are similar to that of the average N-MORB compiled by Gale et al. (2013) (Supplementary Fig. S2). Variations

205   in major element compositions of the studied samples span the entire spectrum observed in PAR basalts from

206   65–56°S and 53–41°S, with MgO content from 8.85 to 4.52 wt.% (Supplementary Fig. S3). This MgO range is

207   larger than that of MORBs previously investigated for Se–Te systematics (7.02–9.23 wt.%; Hertogen et al., 1980;

208   Lissner et al., 2014). The most evolved glasses (MgO <5 wt.%; n = 3) have experienced titanomagnetite

209   fractionation, evidenced by a decrease in Ti and Fe from the general trend after 5 wt.% MgO (Supplementary

210   Fig. S3; Vlastélic et al., 2000; Hamelin et al., 2010). Similar abrupt drops are also consistently observed for

211   concentrations of Zn, Ga, Mn (not shown), V, Sc, and Co in these evolved samples (e.g., Supplementary Fig. S2),

212   probably resulted from the magnetite saturation and/or the induced sulfide segregation due to their strong

213   partitioning into these phases (Nielsen et al., 1994; Toplis and Corgne, 2002; Righter et al., 2006; Dare et al.,

214   2012, 2014; Labidi et al., 2014; Jenner et al., 2010, 2012, 2015).

4.2. Selenium isotope composition and Se–Te abundances

216   The selenium isotope composition and Se–Te concentrations of the studied PAR samples are reported in

217   Table 2 together with S (Labidi et al., 2014) and selected major element data. The uncertainties on $\delta^{82/76}$Se and

218   Se–Te abundances throughout the text are given in 2 and 1 s.d., respectively. The PAR glasses display $\delta^{82/76}$Se

219   values ranging between -0.30 ± 0.09‰ and -0.05 ± 0.09‰, with an average of $\delta^{82/76}$Se = -0.16 ± 0.13‰ (n =

220   27; Fig. 2 and 3). The differences in $\delta^{82/76}$Se between sample duplicates (n = 12) never exceeded the 2 s.d.

221   external reproducibility of 0.09‰ (Table 1). The glassy rim and pillow interior of PAC2 DR01-1 that were

222   analyzed separately yield identical $\delta^{82/76}$Se values within uncertainty (-0.13 ± 0.09‰ and -0.18 ± 0.09‰,

223   respectively; Table 2). However, small but resolvable isotopic variations (up to 0.25 ± 0.13‰ in $\delta^{82/76}$Se) are

224   observed between different samples (e.g., between PAC1 DR06-g and PAC2 DR29-1, with $\delta^{82/76}$Se of $-0.30 \pm$

225   0.09‰ and -0.05 ± 0.09‰, respectively). These variations are not systematically related to the sample latitude

226   or ridge axial depth (Fig. 2a and b). The average $\delta^{82/76}$Se of the two PAR sections (Fig. 2a) are identical within

227   uncertainty: -0.14 ± 0.12‰ north of the Vacquier FZ (n = 17) and -0.19 ± 0.14‰ south of the Udintsev FZ

228   (n = 10). $\delta^{82/76}$Se values of the samples are fairly constant over the wide range of Se abundances observed (158–

229   219 ng g^{-1}; Fig. 2c).

230   The MORBs show systematic offset towards lighter Se isotope composition compared to all previously

231   analyzed basalts (average $\delta^{82/76}$Se between $+0.21 \pm 0.15$‰ and $+0.30 \pm 0.32$‰; n = 9) and one peridotite ($+0.24$

232   ± 0.32‰), with some marginal overlap with the latter (Fig. 3; Rouxel et al., 2002, 2004; Kurzawa et al., 2017;

233   Yierpan et al., 2018; this study). The MORB average $\delta^{82/76}$Se (-0.16 ± 0.13‰) lies in the range of chondritic

234   values of -0.30 ± 0.39‰ (n = 14; Vollstaedt et al., 2016) and -0.21 ± 0.31‰ (n = 20; Labidi et al., 2018) (Fig.

235   3). Specifically, it is similar within uncertainty to $\delta^{82/76}$Se values of ordinary chondrites (-0.21 ± 0.10‰; n = 9)

236   and CO (-0.19 ± 0.07‰; n = 2), CV (-0.25 ± 0.12‰; n = 2), and CI (-0.01 ± 0.09‰; n = 2) carbonaceous

237   chondrites, but distinct from that of enstatite chondrites (-0.40 ± 0.07‰; n = 3; Labidi et al., 2018; Fig. 3).

238   Fig. 4 presents the variation of Se, Te, S, and Cu abundances and/or their ratios versus MgO contents of
239   PAR basalts. The generally negative correlation of Se (from 158 ± 1 to 219 ± 4 ng g^{-1}) and positive correlations
240   Te (from 4.10 ± 0.12 to 1.16 ± 0.03 ng g^{-1}) with MgO show their apparently contrasting compatibilities (Fig. 4a
241   and b), which result in significant Se/Te fractionation (increasing from 42.9 ± 1.1 to 188.8 ± 4.7 with decreasing
242   MgO content; Fig. 4c). Selenium in PAR MORBs seems to behave as an apparently incompatible element,
243   opposite to observations from the southern Mid-Atlantic Ridge (SMAR) basalts (Lissner et al., 2014). At a given
244   MgO, PAR MORBs tend to have higher Se content than SMAR N-MORBs (Fig. 4a). Two samples from the
245   Indian ocean have anomalously high Se contents (~330 ng g^{-1}) compared to the range in PAR and SMAR, but
246   these samples have probably been affected by assimilation of wall-rock sulfide cumulates (Fig. 4a; Hertogen et
247   al., 1980). Tellurium displays similarly apparent compatibility in a global context (Fig. 4b; Hertogen et al., 1980;
248   Yi et al., 2000; Lissner et al., 2014). It is noteworthy, however, that Te contents in SMAR E-MORBs (i.e.,
249   enriched- and transitional-type MORBs) are generally higher than in N-MORBs, attributed to Te enrichment
250   (relative to Se) in an E-MORB mantle source (Lissner et al., 2014). This is in agreement with the distinctly lower
251   Se/Te and S/Te ratios of E-MORBs compared to N-MORBs over almost the entire melt evolution in both PAR
252   and SMAR (Fig. 4c and e). Besides, the S/Se variations in these settings (Fig. 4d) appear to follow two distinct
253   trends, with Se being more compatible relative to S in the SMAR melts than in PAR melts. The Cu/Se ratios in
254   both PAR and SMAR for MgO contents above ~7–7.5 wt.% remain fairly constant and identical (418 ± 24 and
255   408 ± 22, respectively; Fig. 4f). The constant Cu/Se ratios were previously interpreted to reflect a similar
256   geochemical behavior of these elements based on a relatively small data set (MgO ~7–9 wt.%; Lissner et al.,
257   2014). Below ~7 wt.% MgO, the Cu/Se ratios of PAR basalts smoothly decrease from 346 to 178, indicating an
258   overall higher compatibility of Cu.

5. Discussion

5.1. Effects of non-magmatic processes on Se isotopes and S–Se–Te abundances

261   Non-magmatic processes that may potentially affect the S–Se–Te systematics of MORB melts generally
262   include eruption-related degassing and assimilation of hydrothermal fluids during and/or after MORB
263   differentiation in crustal magma chambers (Jenner et al., 2010; Floor and Román-Ross, 2012; Labidi et al., 2014;
264   Lissner et al., 2014). All the studied PAR glasses are sulfide saturated as evidenced by the systematically
265   observed immiscible sulfide droplets and the correlation between S and FeO contents (Labidi et al., 2014). The
266   latter, together with the lack of correlation between S content and eruption depth (~2220–2950 m; Supplementary
267   Table S2), also argues against eruptive S degassing (Moore and Fabbi, 1971; Moore and Schilling, 1973; Mathez,
268   1976; Wallace and Edmonds, 2011; Labidi et al., 2014). Little is known about the Se–Te gaseous species and
269   their formation conditions in igneous systems. Similar to S, Se and Te are possibly dissolved in a silicate melt
270   as Se^{2-} and Te^{2-} and/or Se^{4+} and Te^{4+} depending on the prevailing oxygen fugacity (e.g., Nagamori and Mackey,
271   1977; Fang and Lynch, 1987; Choi and Cho, 1997; Wykes et al., 2011). In the case of (PAR) MORB, S occurs

272 almost exclusively as reduced S^{2-} and retained in the glass during submarine quenching (Labidi et al., 2014).

273 Since transition of selenide and telluride to oxyanions requires higher redox potential relative to sulfide

274 (Se>Te>S at a given temperature and pH; Yamamoto 1976; Brookins, 1988; McPhail, 1995; Johnson, 2004;

275 König et al., 2019), we suggest that Se and Te are dissolved in MORB melts in the form of Se^{2-} and Te^{2-} and

276 are (also) unlikely to degas during submarine eruption (also see Yi et al., 2000; Jenner et al., 2010; Lissner et al.,

277 2014). This would be in accordance with the lack of a systematic variation of Se isotopes (Fig. 2b) and Se–Te

278 contents (not shown) with the ridge axial depth (>2220 m).

279   The majority of PAR basalts have experienced interaction with chlorine-rich brines and/or hydrothermally

280 altered materials during magmatic differentiation (Clog et al., 2013; Labidi et al., 2014). We have examined the

281 potential effect of hydrothermal fluid contamination on Se isotopes and Se–Te concentrations using Cl/K ratio

282 as an indicator of the extent of chlorine contamination because Cl and K are not fractionated during magmatic

283 processes (Fig. 5; Michael and Cornell, 1998; Clog et al., 2013; Labidi et al., 2014). Previous studies on PAR

284 samples show that this process did not significantly affect D/H ratios and stable Mo isotope compositions (Clog

285 et al., 2013; Bezard et al., 2016), but systematically shifted the S isotope compositions towards heavier values

286 (>−0.5‰ in $\delta^{34}S_{V\text{-}CDT}$) when the chlorine contamination was associated with high-temperature (>300°C)

287 hydrothermal sulfide assimilation (Fig. 5a; Labidi et al., 2014). Volcanogenic massive sulfides from sediment-

288 starved environments (such as hydrothermal systems at mid-ocean ridges) show highly variable and mostly

289 negative $\delta^{82/76}Se$ values from −4.75‰ to +0.7‰ (Rouxel et al., 2002, 2004; Layton-Matthews et al., 2013).

290 However, we do not observe any systematic deviations in $\delta^{82/76}Se$ values of the samples that show variable S

291 assimilation (i.e., $\delta^{34}S_{V\text{-}CDT}$ heavier than −0.5‰; n = 7) from the general variation trend along Cl/K or $\delta^{34}S_{V\text{-}CDT}$

292 (Fig. 5b and d). The sample PAC2 DR20-1 with the highest $\delta^{34}S_{V\text{-}CDT}$ value of +0.60 ± 0.10‰ (1 s.d.;

293 Supplementary Table S2), which represents the highest amount of S assimilation, shows "typical" $\delta^{82/76}Se$ of

294 −0.15 ± 0.09‰ (Table 2; Fig. 5d). Average $\delta^{82/76}Se$ values of the two sample subsets (i.e., with and without

295 sulfide assimilation) are identical within 2 s.d. uncertainty (−0.14 ± 0.12‰ and −0.16 ± 0.14‰, respectively).

296 Also, there is no clear covariation between the Se isotope composition and degree of Cl contamination (Fig. 5b).

297   On the other hand, there seems to be an apparent increase in S/Se ratio with Cl/K from 0.06 to 0.41 (Fig.

298 5c). Highest S/Se ratios (~8,000) are also observed in two samples (PAC2 DR20-1 and PAC2 DR27-1) that have

299 experienced S assimilation (Fig. 4d and 5c). Compared to MORBs (~3,800–9,200; Fig. 4d; Lissner et al., 2014;

300 this study) and magmatic sulfides (~2,700–8,700; Patten et al., 2013, 2016), massive sulfides from sediment-

301 starved hydrothermal systems have much more variable S/Se ratios (500–500,000), with lower values typical for

302 sulfides near mid-ocean ridges due to the formation of selenide or Se-rich sulfides at high temperature conditions

303 (Rouxel et al., 2004; Hannington et al., 2002; Layton-Matthews et al., 2008, 2013; Keith et al., 2016). Sulfur

304 assimilation would not increase S abundance (hence S/Se ratio) of the melt due to sulfide saturation (Labidi et

305 al., 2014; also see Section 5.2.2), but it may potentially increase the Se abundance because a MORB melt with

306 ~8–14 wt.% FeO can dissolve ~0.15–0.25 wt.% Se (Wykes et al., 2015). Labidi et al. (2014) show that the

307 highest $\delta^{34}S_{V\text{-}CDT}$ value (+0.60 ± 0.10‰; 1 s.d.) can be reproduced by mixing a MORB melt having 1,000 μg g^{-1}

308 S and $\delta^{34}S_{V\text{-}CDT}$ = −1‰ with a maximum of 3.5 wt.% wall-rock having 10,000 μg g^{-1} S and $\delta^{34}S_{V\text{-}CDT}$ = +5‰.

309 Assuming that the original melt has ~168 ng g^{-1} Se (at 1,000 μg g^{-1} S; from the general S–Se covariation), a

310 final melt with the lowest S/Se = 5,867 ($\delta^{34}S_{V\text{-}CDT}$ = −0.31‰) observed in the contaminated samples (Fig. 5a

311 and c) would require only ~3 ng g^{-1} increase in Se concentration to be associated with an assimilation of

312 ~1.35 wt.% wall-rock. Note that a typical uncertainty of MORB Se concentration is also ~3 ng g^{-1} (Table 2).

313 Therefore, we argue that the observed variation in S/Se ratios of PAR basalts (Fig. 5c) are not influenced by

314 high-temperature hydrothermal sulfide assimilation but rather reflects magmatic differentiation (Fig. 4d; see

315 below). Note that Cl contamination broadly scales with the degree of magmatic differentiation (Labidi et al.,

316 2014), which readily accounts for the seemingly increasing S/Se with increasing Cl/K (Fig. 5c). The same

317 conclusion may be reached for S/Te ratios (not shown) and hence the observed Te abundances. Lastly, alteration

318 by seawater after the eruption (e.g., Lissner et al., 2014) or during magmatic differentiation are not likely to

319 influence the Se isotope or Se–Te elemental systematics of MORBs because of extremely low Se and Te

320 concentrations in modern seawater at relevant depths (~200 and ~0.2 ng kg^{-1}, respectively; Cutter and Bruland,

321 1984; Cutter and Cutter, 2001; Lee and Edmond, 1985; Measures and Burton, 1980).

5.2. Se–Te elemental systematics during MORB differentiation

323 As chalcophile elements, Se and Te, together with S and Cu, are sensitive to progressive MORB

324 differentiation involving a concurrent precipitation of immiscible sulfides (Fig. 4). This process accounts for the

325 observed abundances and relative fractionation of Se–Te–S–Cu (Fig. 4) because these elements are all highly

326 incompatible in silicate minerals but show different partitioning into sulfides (Barnes et al., 2009; Patten et al.,

327 2013; Labidi et al., 2014; König et al., 2015; Brenan, 2015; Wang and Becker, 2015a; Kiseeva et al., 2017). Our

328 data shows a relative compatibility into sulfides (prior to magnetite saturation; see below) in the order of

329 Te>Cu>Se>S (Fig. 4; Cu/Te ratio increases with decreasing MgO; not shown), consistent with earlier studies.

330 The difference in the relative compatibility of Se and Cu above and below ~7 wt.% MgO (see Section 4.2 and

331 Fig. 4f) may be attributed to different FeO content of the silicate melt (Brenan, 2015).

332 All these elements are affected by magnetite saturation-triggered sulfide segregation after ~5 wt.% MgO

333 (Fig. 4; also see Section 4.1), as previously observed for S in PAR MORB (Fig. 6a; Labidi et al., 2014) and other

334 chalcophile elements in glasses from worldwide arc settings (Jenner et al., 2010, 2012, 2015) and Kilauea Iki

335 lava lake (Greaney et al., 2017). One exception is PAC2 DR27-1, which is the most evolved sample (MgO

336 4.52 wt.%; Table 2) yet remains largely unaffected (Labidi et al., 2014). Compared to the extrapolated general

337 differentiation trends prior to 5 wt.% MgO, there is a consistent decrease in S–Se and increase in Te

338 concentrations in samples that have experienced magnetite-induced sulfide segregation (Fig. 4a, 4b, and 6a;

339 Supplementary Fig. S3). This is amplified by consistent and abrupt decrease in Se/Te and S/Te (Fig. 4c and e).

340 Selenium and tellurium likely segregate from the silicate melt as Fe–Se and Fe–Te complexes analogous

341 to Fe–S and thus their abundances in the melt should (also) be directly related to the FeO content. This is

342 evidenced by the significant effect of FeO on the Se solubility in silicate melts (Fang and Lynch, 1987; Wykes

343 et al., 2015) and on the partitioning of Se–Te between sulfide and silicate melts (Choi and Cho, 1997; Brenan,

344 2015; Kiseeva et al., 2017). Indeed, PAR MORBs display strong covariations between FeO_T and Se–Te contents

345 (Fig. 6b and c), similar to that observed for S (Labidi et al., 2014). Note that FeO_T monotonically increases with

346 deceasing MgO prior to magnetite saturation (Supplementary Fig. S3). In the following sections, we first model

347 Se–Te variations during MORB differentiation using FeO_T content as an index of crystal fractionation. We then

348 estimate the primary melt Se–Te contents by correcting the observed concentrations for crystal + sulfide

349 fractionation.

350 5.2.1. Modelling Se–Te variations and implications for chalcophile element partitioning

351 Details of the model calculations are given in Supplementary Material. Major element variations were

352 modelled by alphaMELTS (fractional crystallization; Ghiorso and Sack, 1995; Smith and Asimow, 2005). The

353 model curves for FeO_T yield the best match with the observed variation at 3 kbar and the resulting parameters

354 were used subsequently (Supplementary Fig. S3). Bulk partition coefficients of Se and Te ($D_{Se\ or\ Te}^{bulk}$) were

355 calculated using the mean sulfide fraction in the bulk segregated minerals ($X_{sulf}^{bulk\ min} = 0.14 \pm 0.04$ wt.%; based

356 on S systematics; Labidi et al., 2014) and two sets of experimentally determined sulfide liquid–silicate melt

357 partition coefficients ($D_{Se\ or\ Te}^{sulf\ liq-sil}$) considering the range of FeO contents of our samples: 450–650 for Se and

358 2600–3200 for Te (Kiseeva et al., 2017) and 1560 ± 410–1035 ± 360 for Se and 14430 ± 1680–9570 ± 1150 for

359 Te (1 s.d.; $D_{Se\ or\ Te}^{sulf\ liq-sil}$ decreases with increasing FeO; Brenan, 2015). The Se–Te variations were then modelled

360 by a combination of the fractional and batch crystallization laws because partitioning of a chalcophile element

361 between the fractionated sulfide and silicate melt is probably an intermediate (between pure fractional and batch)

362 equilibrium process (Rehkämper et al., 1999; Bézos et al., 2005; Yang et al., 2014; Lissner et al., 2014; Kiseeva

363 and Wood, 2015). The partitioning mode is described by the parameter S_b, which is the mass fraction of sulfide

364 displaying batch partitioning (Rehkämper et al., 1999).

365 Dependency of the modelled Se–Te variations on the mode of sulfide–silicate melt partitioning (i.e., S_b) is

366 relatively small compared to that of other highly chalcophile elements (e.g., Rehkämper et al., 1999). This is

367 indicated by similar observed sulfide phase–silicate melt partition coefficients ($D_{Se\ or\ Te}^{sulf-sil}$) at S_b of 0 and 1 (by

368 inversion; Supplementary Material Eq. 2, 4, and 5; also see Bézos et al., 2005; Lissner et al.,2014), which yields

369 $D_{Se}^{sulf-sil}$ of ~560 ± 190 and 530 ± 180 and $D_{Te}^{sulf-sil}$ of ~1600 ± 600 and 2200 ± 950, respectively (1 s.d.). With

370 $S_b = 0.5$ and $D_{Se\ or\ Te}^{sulf\ liq-sil}$ from Kiseeva et al. (2017), the calculated trends well reproduce the observed Se–Te

371 variations across the PAR magmatic differentiation (Fig. 6b and c). On the other hand, the modelled trends using

372 $D_{Se\ or\ Te}^{sulf\ liq-sil}$ from Brenan (2015) predict much higher $D_{Se\ or\ Te}^{bulk}$ and cannot properly describe the observed patterns

373 with any S_b values (not shown). Based on the experiments of Brenan (2015), a lower apparent $D_{Te}^{sulf-sil}$ can be

374 predicted if a significant fraction of the segregating sulfides is crystalline monosulfide solid solution (MSS) in

375 which Te is significantly more incompatible relative to sulfide liquid ($D_{Te}^{MSS-sulf\ liq} \approx 0.02–0.08$ and $D_{Te}^{MSS-sil} = 729$;

376 also see Helmy et al., 2010; Liu and Brenan, 2015); in this case, our observed $D_{Te}^{sulf-sil}$ at $S_b = 1$ would require

377 $87 \pm 6\%$ of the sulfide phase to be MSS using an average $D_{Te}^{sulf\ liq-sil} = 11960 \pm 1400$ (see above). Such a high

378 MSS fraction is however unlikely. At a pressure–temperature (P–T) range relevant to MORB differentiation

379 (e.g., from ~1280 to 1160°C at 2–5 kbar until ~70% crystallization in most PAR melts; Fig. 7), segregated sulfide

380 is at its liquidus near ~1050–1125°C according to sulfide melting experiments (Bockrath et al., 2004; Zhang Z.

381 and Hirschmann, 2016) and empirical approximations on natural sulfides in MORB glasses (Patten et al., 2012).

382 Although there is geochemical evidence that a certain proportion of MSS needs to be present in fractionating

383 sulfides to explain the variations of some chalcophile elements (Li and Audétat, 2012), sulfide liquid is still the

384 main (if not dominant) sulfide phase during much of MORB differentiation that occurs above the sulfide liquidus

385 (e.g., Bézos et al., 2005; Jenner et al., 2010; Li and Audétat, 2012; Lissner et al., 2014; Brenan, 2015). Besides,

386 the fact that the observed Se–Te variations are well reproduced with $D_{Se\ or\ Te}^{sulf\ liq-sil}$ from Kiseeva et al. (2017) argues

387 against a significant control of MSS fractionation on Se–Te systematics of PAR glasses. Another alternative

388 explanation for the observed low $D_{Te}^{sulf-sil}$ compared to $D_{Te}^{sulf\ liq-sil}$ from Brenan (2015) could be poor equilibration

389 between sulfides and silicate melt (i.e., $R_{eff}<1$) as previously proposed for partitioning of platinum-group

390 elements in MORBs (Rehkämper et al., 1999; Bézos et al., 2005; Yang et al., 2014). However, the extent of

391 sulfide–silicate equilibration in our case might not be properly assessed due to the difference in the experimental

392 $D_{Se\ or\ Te}^{sulf\ liq-sil}$ published by Brenan (2015) and Kiseeva et al. (2017) for the range of FeO content of PAR basalts.

393 Finally, only for the highly evolved MORB melts (PAC1 DR10-1g and PAC2 DR20-1) that have

394 experienced >70% crystallization and magnetite-triggered sulfide segregation (Fig. 6a; Supplementary Fig. S3),

395 we suggest crystalline MSS to be the dominant fractionating sulfide phase to account for the observed abrupt

396 drop in Se/Te (and S/Te) ratios (Fig. 4), considering $D_{Se}^{sulf\ liq-sil}<D_{Te}^{sulf\ liq-sil}$ and $D_{Se}^{MSS-sil}>D_{Te}^{MSS-sil}$ (Brenan, 2015).

397 This was previously proposed for sulfide-saturated arc magmas based on Cu–Ag systematics (Jenner et al., 2010,

398 2012, 2015).

399 ### 5.2.2. Primary melt Se–Te contents: Consideration of sulfide saturation

400 The primary melt major element composition was calculated following Lee et al. (2009) by adding liquidus

401 olivine back into primitive samples with MgO >~8.5 wt.% (n = 10; Vlastélic et al., 2000; Hamelin et al., 2010)

402 until the melts reach equilibrium with mantle olivine containing Mg# = 0.90 (Mg#: molar Mg/(Mg + Fe^{2+})).

403 Assuming the glasses have Fe^{2+}/ΣFe = 0.87 (e.g., Bézos and Humler, 2005; Zhang H. L. et al., 2018), we obtain

404 an average primary melt composition of ~11.8 wt.% MgO and ~8.8 wt.% FeO$_T$ at ~10.2 kbar and ~1325°C after

405 ~8.7% olivine addition. For the Se–Te contents, we applied a two-step correction. Considering all studied glasses

406   are sulfide-saturated, based on the strong covariation paths of Se–Te with FeO_T (Fig. 6b and c) and FeO_T with

407   MgO (Supplementary Fig. S3), the Se–Te contents were first corrected to FeO_T content (8.49 wt.%) of the most

408   primitive sample (PAC1 DR12-1g; 8.85 wt.% MgO) following a linear regression scheme previously used for

409   other elements (e.g., Klein and Langmuir, 1987; Bézos et al., 2005; Kelley et al., 2006; Lissner et al., 2014).

410   This yields 164 ± 8 and 3.4 ± 0.4 ng g^{-1} Se and Te, respectively (melts experiencing magnetite saturation were

411   excluded; see Fig. 4 and Supplementary Fig. S2 and S3). Further corrections (from 8.85 to 11.8 wt.% MgO)

412   along some linear slope with MgO or Mg# depend on whether the more primitive melts are sulfide-saturated.

413   Several global MORBs with MgO >9 wt.% (Jenner and O'Neill, 2012; Jenner et al., 2015) seem to display a

414   clear absence of fractionation between chalcophile elements that have quite different $D^{sulf\,liq–sil}$ (e.g., Cu, As, Se,

415   Ag, In, Sn, Tl, and Pb; Li and Audétat, 2012; Patten et al., 2013; Kiseeva and Wood, 2015; Kiseeva et al., 2017),

416   which might indicate a sulfide undersaturation in high-MgO basalts (also see Ding and Dasgupta, 2017).

417   In this regard, we calculated the S solubilities of the primary PAR melts at their last equilibration with the

418   mantle (see above) using the recent sulfur content at sulfide saturation (SCSS) model of Smythe et al. (2017)

419   while taking into account the effect of equilibrium sulfide chemistry (Fig. 6a). It shows that, with a wide range

420   of sulfide compositions (42–51 wt.% Fe, 9–18 wt.% Ni, and 0.4–10 wt.% Cu; Bockrath et al., 2004; Patten et

421   al., 2013; Kiseeva and Wood, 2015; Zhang Z. and Hirschmann, 2016; Keith et al., 2017), SCSS of the primary

422   melts range from 1117 ± 44 to 1394 ± 55 µg g^{-1}, which decreases with decreasing X_{Fe} in sulfides (X_{Fe} = Fe/(Fe

423   + Ni + Cu) molar ratio). Even the lowest SCSS seems to be still higher than the S contents of the primitive PAR

424   glasses (932–968 µg g^{-1}; Labidi et al., 2014), implying that primary melts might be sulfide-undersaturated. The

425   modelled SCSS (Smythe et al., 2017) across the entire magmatic evolution (with X_{Fe} = 0.65 at 3 kbar and fO_2 of

426   FMQ − 0.18; Supplementary Material) shows that MORBs may have reached sulfide saturation during early

427   differentiation (P from ~10.2 to 3 kbar and T from ~1325 to 1248°C; Fig. 7) due to the decreasing S solubility

428   as well as olivine crystallization; they then remained sulfide-saturated, which also matches the model of Ariskin

429   et al. (2013, 2018) that considers the effect of sulfide chemistry using Ni contents of the silicate melts (Fig. 6a).

430   Both predictions are consistent with the observed sulfide saturation in the PAR as well as global spreading-ridge

431   glasses (Jenner et al., 2012, 2015; Labidi et al., 2014; Smythe et al., 2017; but see Shimizu et al., 2016). Although

432   primitive basalts (MgO >9–10 wt.%) were also suggested to be S undersaturated based on a variety of S solubility

433   models, these models can result in significant differences in SCSS (up to 1,000 µg g^{-1}) at a given condition (Saal

434   et al., 2002; Ding and Dasgupta, 2017; and references therein). The model of Smythe et al. (2017), which we

435   applied for our model primary melts, also carries large uncertainties (~25%). Here, we tentatively assume that

436   parental PAR melts (MgO >8.85wt.%) are sulfide undersaturated and accordingly the Se–Te concentrations after

437   the first-step correction were further corrected for ~8.7% olivine fractionation only. This yields average Se and

438   Te concentrations of 150 ± 8 and 3.1 ± 0.4 ng g^{-1}, respectively, for PAR primary melts (Se/Te = 48.4 ± 6.8; n =

439   24; Fig. 6b and c). This Se/Te ratio would represent an upper limit if the primary melts are S saturated. These

440   estimates are significantly lower than for the SMAR N-MORB primary melts (230–254 and 9.0–11.3 ng g^{-1},

respectively; Se/Te = 22–26; Lissner et al., 2014). This discrepancy may be attributed to the difference in the observed Se–Te variations (Fig. 4a, b, and c; Section 4.2) as well as the correction approach used between two studies. Additional uncertainties may also result from other complexities during MORB differentiation (e.g., Coogan and Dosso, 2016; Lissenberg and MacLeod, 2016; O'Neill and Jenner, 2012). Most importantly, the clear negative slope in Te versus MgO in PAR MORBs is not resolved in SMAR N-MORBs (Lissner et al., 2014) due to the smaller MgO range of the latter (Fig. 4b). A wider compositional range of N-MORB now proves to be more appropriate (this study) than coupled N- and E-MORB arrays (Lissner et al., 2014) in order to adequately correct for differentiation and recover the primary melt Se–Te contents.

5.3. Role of partial melting on Se–Te systematics and inferences on composition of the upper mantle

5.3.1 Partitioning behavior of Se–Te during mantle melting

In the upper mantle, Se and Te are mainly hosted by Fe–Ni–Cu base metal sulfides and platinum-group minerals (Guo et al., 1999; Hattori et al., 2002; Lorand and Alard, 2010; König et al., 2015; Lorand and Luguet, 2016). The behavior of Se–Te during mantle melting is thus predominantly controlled by fractionation between these phases and silicate melt. However, their absolute and relative partitioning during melting has been debated. Based on the apparent variation in Se–Te abundances of peridotites, some authors suggest a slightly more incompatible behavior of Se compared to Te, with both being moderately incompatible (Wang and Becker, 2013; Wang et al., 2013). This relative partitioning is however opposite to observations from highly depleted harzburgites (König et al., 2012, 2014, 2015; Luguet et al., 2015). Hertogen et al. (1980), from the MORB perspective, suggest that Se is much more incompatible than Te during melting, with Te being rather compatible. This was based on the observed lack of clear Se/Te fractionation during magmatic differentiation and distinctly higher Se/Te ratios of global MORBs compared to mantle rocks (Hertogen et al., 1980; and references therein). In fact, as shown for PAR and SMAR MORBs (Fig. 4c), significant Se/Te fractionation occurs during MORB differentiation. This was not evident from the relatively small sample suite of Hertogen et al. (1980) probably due to (1) different source composition (Section 4.2) and (2) different mode and rate of sulfide fractionation during low-P magmatic differentiation in different spreading ridges (e.g., Bézos et al., 2005; Yang et al., 2014; Lissner et al., 2014), which may result in different apparent fractionation of Se/Te among genetically unrelated samples. Lissner et al. (2014) propose that both Se–Te are apparently incompatible during melting, with Te being more incompatible, although the empirical $D_{Se\ or\ Te}^{sulf\ liq-sil}$ they applied for modelling seem to suggest the opposite at low- to moderate-degree melting. Besides, both PAR and SMAR MORB data show that Te is much more compatible than Se during magmatic differentiation (Fig. 4c; Section 5.2.1), in accordance with experimental or empirical constraints (Peach et al., 1990; Patten et al., 2013; Lissner et al., 2014; Brenan, 2015; Wang and Becker, 2015a; Kiseeva et al., 2017).

474   These discrepancies have been explained by the presence of different equilibrium sulfide assemblages

475   (sulfide liquid and crystalline MSS) during MORB differentiation and mantle melting, which involve sulfide

476   liquid–silicate melt partitioning and MSS–sulfide liquid/silicate melt partitioning, respectively (Lorand and

477   Alard, 2010; Lissner et al., 2014; König et al., 2014, 2015; Brenan, 2015). This is because Te is much more

478   incompatible in MSS relative to sulfide liquid than Se (with $D_{Se\ or\ Te}^{MSS-sulf\ liq}$ of ~0.56–0.75 and ~0.02–0.08 for Se

479   and Te, respectively; Helmy et al., 2010; Liu and Brenan, 2015; Brenan, 2015). The presence of MSS in the

480   MORB mantle was also experimentally shown and used to explain the partitioning behavior of chalcophile and

481   highly siderophile elements during melting (e.g., Bockrath et al., 2004; Bézos et al., 2005; Ballhaus et al., 2006;

482   Fischer-Gödde et al., 2011; Brenan, 2015). However, the sulfide liquidus (Fig. 7) determined by Bockrath et al.

483   (2004) has been questioned (Hart and Gaetani, 2006; Fonseca et al., 2012; Mungall and Brenan, 2014; Zhang Z.

484   and Hirschmann, 2016). Recent sulfide melting experiments using the same sulfide composition as in Bockrath

485   et al. (2004) show that crystalline MSS is not stable in the convecting upper mantle (Fig. 7; Zhang Z. and

486   Hirschmann, 2016; Zhang Z. et al., 2018), which indicates that behavior of chalcophile elements during the

487   partial melting might be entirely controlled by sulfide liquid–silicate melt partitioning, in favour of earlier

488   conclusions based on Cu–Ag systematics of mantle rocks and melts (Wang and Becker, 2015b; Jenner et al.,

489   2015).

490   5.3.2 Melting model

491   In order to further understand the role of partial melting on the Se–Te systematics of MORB melts and

492   mantle residues, we modelled the behavior of Se–Te in a triangular passive-flow near-fractional melting regime,

493   which was previously used to explain the Se–Te and highly siderophile element systematics of MORBs (e.g.,

494   Rehkämper et al., 1999; Lissner et al., 2014; Brenan, 2015). The modelling procedures and parameters are

495   detailed in Supplementary Material and summarized in Table 3. Briefly, the melt major element compositions

496   and P–T conditions for calculating the SCSS (Smythe et al., 2017) and $D_{Se\ or\ Te}^{sulf\ liq-sil}$ (as a function of FeO; Brenan,

497   2015; Kiseeva et al., 2017) were modelled with alphaMELTS front end (pMELTS mode; Ghiorso et al., 2002;

498   Smith and Asimow, 2005) at a mantle potential temperature of 1350°C following a similar approach used by

499   Ding and Dasgupta (2017) (Fig. 6). The depleted mantle composition was taken from Salters and Stracke (2004)

500   assuming 0.2 wt.% Fe_2O_3 (e.g., Cottrell and Kelley, 2011). The average melting degree (F_B; Langmuir et al.,

501   1992; Plank et al., 1995) of the samples was estimated using differentiation-corrected incompatible trace element

502   concentrations by (1) solving the simple batch melting equation for F_B (e.g., Kelley et al., 2006) and (2)

503   comparing the concentrations to the result from pMELTS (near-fractional melting). These two approaches yield

504   consistent F_B of ~6.6–11.7% (average 8.5 ± 1.5%) and 6.5–9.5% (Supplementary Fig. S4), respectively, in

505   agreement with the previous estimates for global MORBs (e.g., Klein and Langmuir, 1987; Salters and Stracke,

506   2004; Workman and Hart, 2005; Kimura et al., 2017). Three different upper mantle sulfide compositions were

507   considered when calculating the SCSS of the partial melts (X_{Fe} = 0.44–0.74 and Ni/(Fe + Ni) = 0.25–0.53 at a

508   constant (Fe + Ni + Cu)/S = 0.93; Supplementary Fig. S5). Considering a large number of input parameters in

509 our model, in order to assure an internal consistency and reliability of our MORB mantle Se–Te estimates, we
510 first modelled the variation of S and Cu during partial melting (Fig. S5) because their mantle abundances
511 (McDonough and Sun, 1995; Salters and Stracke, 2004; Lorand et al., 2013; Lorand and Luguet, 2016; Palme
512 and O'Neill, 2014; Wang and Becker, 2013, 2015b) and behavior during mantle melting are relatively well
513 established (e.g., Lee et al., 2009; Li and Audétat, 2012; Kiseeva and Wood, 2013, 2015; Ding and Dasgupta,
514 2017).

515   Our result shows that the PAR primary melt S concentrations are well reproduced for the estimated F_B of
516 the samples using a range of source S content from "PM-like" 200 μg g^{-1} (e.g., Palme and O'Neill, 2014; Wang
517 and Becker, 2013) to slightly lower 150 μg g^{-1} as estimated for the depleted MORB mantle (e.g., Luguet et al.,
518 2003; Bézos et al., 2005; Nielsen et al., 2014; Lorand and Luguet, 2016) in combination with the SCSS model
519 of Smythe et al. (2017) and equilibrium "sulfide B" (Fig. S5a). Note that this sulfide chemistry is typical for
520 lherzolite-hosted sulfides (e.g., Lorand and Luguet, 2016; Kiseeva et al., 2017) and consistent with the suggested
521 range of Ni/(Fe + Ni) value for a shallow mantle Cu-free sulfide liquid (0.4–0.6) by recent experiments (Zhang
522 Z. et al., 2018) at the range of melting depth (~50–20 km; Fig. 7) and fO$_2$ (~FMQ; Cottrell and Kelley, 2011;
523 Zhang H. L. et al., 2018) estimated for the PAR basalts. The corresponding model curves also show an excellent
524 fit to the primary melt Cu concentrations with 170–200 μg g^{-1} S and 30 (or 24) μg g^{-1} Cu in the source (Fig. S5b
525 and c).

5.3.3 Modelling Se–Te variations in mantle melts and residues

527   Fig. 8 and Fig. 9a show that the Se–Te systematics of PAR primary melts (150 ± 8 and 3.1 ± 0.4 ng g^{-1} Se
528 and Te, respectively; Se/Te = 48.4 ± 6.8; n = 24) can be successfully reproduced by melting of a sulfide liquid-
529 bearing MORB mantle which has "fertile lherzolite-like" Se and Te contents (80 and 11 ng g^{-1}, respectively;
530 estimated at 3.52 wt.% Al$_2$O$_3$; Wang and Becker, 2013) using experimental $D_{Se\,or\,Te}^{sulf\,liq-sil}$ from Brenan (2015)
531 calculated at each 1% equilibrium melting (Table 3). With the same SCSS, the polybaric aggregate melts reach
532 S-undersaturation at F_B from ~9.5% to 11.5%, increasing with increasing initial S content from 170 to 200 μg g^{-1}
533 (also see Supplementary Fig. S5a). This corresponds to an extent of melting F from ~19% to 23% in the central
534 melting column (i.e., F_{max}; Supplementary Material) and is consistent with the conclusion of previous studies
535 using other empirical or experimental SCSS models (Luguet et al., 2003; Bézos et al., 2005; Lee et al., 2012;
536 Lissner et al., 2014; Brenan, 2015). In the case of 180 μg g^{-1} S, a mantle column becomes sulfide-exhausted
537 after ~20% melting. At any stage before sulfide exhaustion, Se is apparently much more incompatible than Te,
538 with contrasting $D_{Se\,or\,Te}^{bulk}$ values of ~0.69–0.01 and ~6.38–0.11 for Se and Te, respectively (decreasing with
539 ongoing partial melting). Therefore, a large Se/Te fractionation occurs between the melt and residue as long as
540 sulfide liquid is present in the system (Fig. 8c). The estimated F_B for PAR MORBs (~6.6–11.7%) indicates that
541 the primary aggregate melt is a mixture of melt increments derived from both sulfide-bearing (low-F) and
542 sulfide-exhausted (high-F) mantle columns (also see Ding and Dasgupta, 2017), and therefore, the observed

543   Se/Te fractionation in primary melts with respect to their source is largely accounted for by melting. This is in
544   contrast to the observations from the primary SMAR melts, in which the relative partitioning of Se and Te is
545   suggested to have played a minor role on the observed Se–Te variation (Lissner et al., 2014). This is because the
546   SMAR partial melts are mostly derived from sulfide-free mantle owing to the relatively high F_B (12.8–17.2%)
547   estimated by the authors, whereas sulfide exhaustion in their model occurs at around $F_B \approx 9\%$. However, as noted
548   by Kinzler and Grove (1993), the model of Niu and Batiza (1991) applied by Lissner et al. (2014) to estimate
549   the melting extent of the SMAR MORB tends to produce somewhat higher values compared to other models
550   using major element systematics. This may partly explain the different observations between our study and
551   Lissner et al. (2014) regarding the effect of partial melting on the observed Se/Te fractionation in MORB. The
552   modelling was also performed using experimental $D_{Se\ or\ Te}^{sulf\ liq–sil}$ of Kiseeva et al. (2017), from which the highest
553   values were taken (850 and 3800 for Se and Te, respectively) considering the FeO content of the equilibrium
554   melts (8.3–5.4 wt.%; Supplementary Material). However, these $D_{Se\ or\ Te}^{sulf\ liq–sil}$ overestimate the Se–Te contents of
555   the melts with a "fertile lherzolite-like" starting Se–Te contents (with 180 µg g^{-1} S; Fig. 8a and b). A good match
556   is obtained only after the source Se and Te contents are lowered to 48_{-8}^{+5} and $3.5_{-0.9}^{+0.5}$ ng g^{-1}, respectively (Fig. 8
557   and 9a). With this set of $D_{Se\ or\ Te}^{sulf\ liq–sil}$, we obtain 49 ± 11 ng g^{-1} Se and 3.5 ± 1.3 ng g^{-1} Te on average for the PAR
558   mantle having 170–200 µg g^{-1} S. Considering the difference in experimental $D_{Se\ or\ Te}^{sulf\ liq–sil}$ between Brenan (2015)
559   and Kiseeva et al. (2017), it is uncertain which Se–Te contents actually represent the mantle source composition
560   (Fig. 9a).

561   The role of MSS–silicate melt partitioning on the behavior of Se–Te was investigated by incorporating
562   varying proportions of MSS and sulfide liquid into the bulk sulfide assemblage in the mantle (180 µg g^{-1} S)
563   using experimental $D_{Se\ or\ Te}^{MSS–sil}$ from Brenan (2015) and "fertile lherzolite-like" Se–Te contents for consistency
564   (Supplementary Fig. S6). Due to the similar $D_{Se\ or\ Te}^{MSS–sil}$ of Se and Te (883 and 729, respectively), there is little
565   Se/Te fractionation during the entire melting interval if crystalline MSS is the only controlling sulfide phase
566   (also see Brenan, 2015); besides, both Se–Te concentrations are highly overestimated owing to their high
567   apparent incompatibilities, with $D_{Se\ or\ Te}^{bulk}$ values of ~0.43–0.01 and 0.35–0.01 for Se and Te, respectively
568   (Supplementary Fig. S6). It shows that Se–Te systematics of the melt can only be reproduced if sulfide liquid is
569   the major controlling phase (>50%; in the case of 180 µg g^{-1} S in the source; Fig. 9a and Supplementary Fig.
570   S6).

571   On the other hand, the modelled Se–Te contents of the residue shows that the variations of Se–Te
572   abundances and Se/Te ratios of worldwide lherzolites (Fig. 9b and c) can be reproduced only when MSS is the
573   dominant, if not only, sulfide phase (>90%) in the mantle. In this case, both Se and Te would be (apparently)
574   incompatible, with Te being more incompatible (e.g., Brenan, 2015). As mentioned earlier, this absolute and
575   relative partitioning during partial melting are in line with the conclusion of some studies (Lissner et al., 2014;
576   König et al., 2014, 2015) but cannot be reconciled with our observations from the perspective of partial melts,

577   which does not require the presence of "residual" crystalline MSS controlling Se–Te partitioning (Fig. 9a) as
578   previously suggested by the Cu–Ag systematics (Jenner et al., 2015; Wang and Becker, 2015b) as well as recent
579   sulfide melting experiments (Zhang Z. and Hirschmann, 2016; Zhang Z. et al., 2018; Fig. 7; Section 5.3.1). We
580   argue that, from the melt perspective, secondary refertilization processes such as addition of metasomatic base
581   metal sulfides and platinum-group minerals have significantly, if not completely, overprinted the original melt
582   depletion signature of lherzolites (i.e., sulfide liquid–silicate melt fractionation; Fig. 9b and c), in line with the
583   conclusions from studies of peridotites (Lorand and Alard, 2010; König et al., 2014, 2015; Luguet et al., 2015;
584   Harvey et al., 2015). Note that this argument is independent of the choice of source Se–Te contents and published
585   experimental $D_{Se\,or\,Te}^{sulf\,liq-sil}$. For instance, the residue composition was also calculated with a source having the
586   maximum "fertile mantle" Se and Te contents (101 and 12.5 ng g^{-1}, respectively; estimated at 4.45 wt.% Al$_2$O$_3$;
587   Wang and Becker, 2013) using $D_{Se\,or\,Te}^{bulk}$ from both studies (Brenan, 2015; Kiseeva et al., 2017). Results show
588   that the modelled residue composition still hardly reconciles with the observed Se–Te variation in lherzolites,
589   which likely represent a post-melt depletion refertilization trend (Fig. 9b and c). As for the highly depleted
590   residue after sulfide exhaustion, little is known regarding the quantitative control of Se–Te host phases.
591   Nevertheless, the increasing Se/Te ratios (>15; suprachondritic relative to CI chondrites; Lodders et al., 2009)
592   with progressive melt depletion in refractory harzburgites, which represent the least metasomatically influenced
593   peridotites (König et al., 2014; Luguet et al., 2015), probably reflects the relatively compatible behavior of Se
594   that is preferentially incorporated in platinum-group minerals formed upon sulfide exhaustion (Luguet and
595   Reisberg, 2016; Luguet et al., 2007; Fonseca et al., 2012; König et al., 2015).

5.4. Role of magmatic processes on Se isotope systematics of MORB

597   Having established the Se (and Te) elemental behavior during partial melting and MORB differentiation,
598   we now discuss the role of these magmatic processes on Se isotopes and estimate a reliable mantle source
599   composition. Note that none of the (secondary) non-magmatic processes, including high-T hydrothermal
600   fluid/sulfide assimilation during magmatic differentiation and volcanic degassing, have measurable effects on
601   Se isotope composition of PAR glasses (Section 5.1).

602   Previous experiments reported significant Se isotopic fractionation (up to 19‰ in ^{82}Se/^{76}Se) during abiotic
603   reduction of Se oxyanions (SeO$_3^{2-}$ and SeO$_4^{2-}$) at low temperature conditions (e.g., Krouse and Thode, 1962;
604   Rees and Thode, 1966; Rashid and Krouse, 1985; Johnson et al., 1999; Johnson and Bullen, 2003; Mitchell et
605   al., 2013). In contrast, there is little isotopic fractionation (<0.5‰) associated with oxidation of reduced Se
606   species (Johnson et al., 1999; Johnson, 2004). As discussed in Section 5.1, Se is very likely dissolved in MORB
607   melts as reduced Se^{2-}. Since MORB forms and evolves at fO$_2$ around FMQ buffer (Ballhaus, 1993; Bézos and
608   Humler, 2005; Cottrell and Kelley, 2011; Labidi et al., 2014; Zhang H. L. et al., 2018), transition between Se^{4+}
609   (with/without Se^{6+}) and Se^{2-} and hence associated Se isotopic fractionation, if any, is expected to be very subtle
610   across the entire MORB evolution starting from the mantle source region.

611   Despite the narrow range in $\delta^{82/76}$Se values of the PAR glasses (-0.16 ± 0.13‰), subtle but resolvable

612 differences (up to ~0.25‰ vs the external reproducibility of 0.09‰) is observed between some samples (Fig. 3).

613 These differences seem to be unrelated to the sample latitude, tectonic discontinuity, or ridge axial depth (Fig.

614 2a and b; Supplementary Fig. S1). Hamelin et al. (2011) demonstrated clear latitudinal variations in radiogenic

615 isotopes (He–Sr–Nd–Hf–Pb) along the studied PAR segments (65–56°S and 53–41°S), which is interpreted to

616 result from progressive mixing of the depleted Pacific upper mantle and gradually increasing amount of recycled

617 oceanic crust component northwards. However, Se isotope compositions of the northern and southern PAR

618 segments are essentially the same (-0.14 ± 0.12‰ and -0.19 ± 0.14‰, respectively; 2 s.d.) and show no clear

619 latitudinal variation (Fig. 2a). There is also no covariation between $\delta^{82/76}$Se (or Se–Te contents) and radiogenic

620 isotope ratios of the samples (not shown). Furthermore, the Se isotopic variations are not correlated with (1) Se

621 content of the melt (158–219 ng g^{-1}; Fig. 2c), (2) magmatic differentiation index Mg# (0.68–0.40; Fig. 10a), or

622 (3) Se/Te ratio (~43–189) that is demonstrated above as a direct indicator of sulfide liquid–silicate melt

623 fractionation (Fig. 4c and 10b; Section 5.2.1). Besides, two highly evolved PAR glasses that show clear evidence

624 of magnetite-triggered sulfide fractionation (PAC1DR10-1g and PAC2 DR20-1; Fig. 4c and e) have Se isotope

625 compositions (-0.24 ± 0.09‰ and -0.15 ± 0.09‰) indistinguishable from those of less evolved samples

626 (MgO >5wt.%). As discussed earlier, the predominantly fractionating sulfide phase in response to liquidus

627 magnetite appearance after MgO <5wt.% is very likely crystalline MSS. Altogether, we suggest that there is no

628 resolvable Se isotopic fractionation within uncertainty (0.09‰; 2 s.d.) during shallow-level magmatic

629 differentiation that involves segregation of silicate crystals and sulfide liquid and/or MSS (i.e., $\Delta^{82/76}$Se$_{sulf-sil} \approx$

630 0.00‰). Effects of pressure on Se isotopic partitioning at mantle conditions relevant to MORB petrogenesis (Fig.

631 7) is expected to be negligible (Young et al., 2015), as in the case of S isotopes (Labidi and Cartigny, 2016). We

632 therefore argue that there is negligible ^{82}Se/^{76}Se fractionation during partial melting of the upper mantle, which

633 also involves equilibrium partitioning of Se between sulfide liquid (probably without MSS) and silicate melt

634 (Fig. 8 and 9; Supplementary Fig. S5; see Section 5.3.3). Accordingly, we use the observed PAR MORB average

635 $\delta^{82/76}$Se (-0.16 ± 0.13‰; n = 27) to represent the Se isotope composition of the primary melts (Mg# = 0.73) as

636 well as the mantle source (Fig. 10a and b). The apparent Se isotope variation along the PAR (up to 0.25 ± 0.13‰;

637 e.g., Fig. 2 and 3) thus likely reflects intrinsic mantle heterogeneity.

638   The $\delta^{82/76}$Se values of the PAR MORBs are systematically lighter than that of all other basaltic lavas from

639 various geological settings (e.g., oceanic/continental intraplate basalts and plume-influenced ocean ridge basalts;

640 Fig. 3; Rouxel et al., 2002; Kurzawa et al., 2017; Yierpan et al., 2018; this study). Four subaerial basalts analyzed

641 by the same technique as in this study have variable Se (~15–170 ng g^{-1}) and Te (1.0–14.2 ng g^{-1}) contents with

642 Se/Te ratios ~3–65 (Fig. 10b; Yierpan et al., 2018), implying that they may have different source compositions

643 and/or experienced different degrees of partial melting and igneous differentiation (see Section 5.2 and 5.3).

644 These petrogenetic processes however should result in no Se isotopic fractionation as discussed above. Their

645 non-chondritic and significantly heavier $\delta^{82/76}$Se ($+0.21 \pm 0.15$‰) compared to MORB could thus reflect (1) so

646 far unidentified effects of non-magmatic processes (such as subaerial eruption-related degassing; e.g., Floor and

647 Román-Ross, 2012; Floor et al., 2013) and/or (2) Se isotopic variability among terrestrial igneous reservoirs

648 ($\delta^{82/76}$Se between −0.16 ± 0.13‰ and +0.21 ± 0.15‰; Fig. 3 and 10b).

5.5. Implications for the origin of Se and Te in the mantle

650   The upper mantle abundances of Se, Te, and S have been suggested to be primarily established by addition

651 of volatile-rich chondritic late veneer after core formation (Wang and Becker, 2013) because these elements are

652 predicted to behave as highly siderophile elements during core–mantle differentiation based on the extrapolation

653 of low-P (1–19 GPa) metal–silicate partitioning experiments (Rose-Weston et al., 2009; Steenstra et al., 2017).

654 However, this simple late-veneer origin of S cannot explain the non-chondritic S isotope composition of the

655 mantle, which requires a significant portion of S in the pre-late veneer mantle (Labidi et al., 2013, 2016). This

656 is further supported by more recent partitioning experiments on S (Boujibar et al., 2014; Suer et al., 2017). Suer

657 et al. (2017) showed that S becomes less siderophile with increasing pressure than previously predicted, with the

658 observed $D_S^{metal-silicate}$ of ~10–55 versus ~1000 predicted by Rose-Weston et al. (2009), at core forming condition

659 (~40–55 GPa; Jackson et al., 2018). In this context, if the late veneer consisted of volatile-rich materials (e.g.,

660 McDonough and Sun, 1995; Wang and Becker, 2013), suprachondritic S/Se and S/Te ratios should be expected

661 for the mantle because the Se–Te budget was primarily accounted for by late veneer; alternatively, if the pressure

662 dependence of $D_{Se\ or\ Te}^{metal-silicate}$ determined at <20 GPa (Rose-Weston et al., 2009; Steenstra et al., 2017) was

663 lowered at higher pressure (or temperature) to some extent as in the case of S (Suer et al., 2017) and other

664 elements (e.g., Siebert et al., 2013), the possibility that mantle Se–Te budget represents metal–silicate

665 equilibration would remain open (as suggested for the Moon; Steenstra et al., 2017).

666   As discussed earlier, lithospheric lherzolites that were used to estimate PM Se–Te abundances (Wang and

667 Becker, 2013) preserve little primary melt depletion signature and very likely represent refertilized (previously-

668 depleted) harzburgites (Fig. 9b and c; also see Le Roux et al., 2007; König et al., 2014). Unlike Cu and Ag that

669 show limited fractionation during different petrogenetic processes (e.g., mantle melting, refertilization, and melt

670 transport; Wang and Becker, 2015b), different and non-systematic Se–Te fractionation occurs during these

671 processes depending on the host assemblages controlling the Se–Te behavior (Fig. 4, 6, and 9b and c; Section

672 5.3.3). This implies that the near-chondritic Se/Te ratios (7.9 ± 1.6) in worldwide "fertile lherzolites", despite

673 the broad correlation between Se–Te and lithophile elements such as Al and Ca (Wang and Becker, 2013), should

674 be considered with great caution as primitive signature of PM.

675   Mantle melts provide an alternative approach to estimate composition of the asthenospheric mantle. The

676 MORB mantle abundances of Se–Te and other strongly chalcophile elements (e.g., Cu; Supplementary Fig. S5)

677 would be essentially identical to that of PM (Fig. 9b and c) because average depleted MORB mantle is only ~2–

678 3% melt-depleted from PM (Menzies et al., 1977; Salters and Stracke, 2004; Workman and Hart, 2005; Bodinier

679 and Godard, 2014). However, this approach critically depends on the modelling parameters (Section 5.2.2 and

680   5.3.3) and hence leads to different results (Fig. 8 and 9). We obtain two distinct possible source compositions

681   for the PAR MORB: 80 ± 17 ng g^{-1} Se and 11 ± 1.7 ng g^{-1} Te (source 1; "fertile lherzolite-like"; Wang and

682   Becker, 2013) vs 49 ± 11 ng g^{-1} Se and 3.5 ± 1.3 ng g^{-1} Te (source 2) due to the difference in $D_{Se\ or\ Te}^{sulf\ liq-sil}$

683   published by Brenan (2015) and Kiseeva et al. (2017), respectively (Table 3; Fig. 9 and 10). Note that only

684    $D_{Se\ or\ Te}^{sulf\ liq-sil}$ from the latter study successfully reproduces the observed Se–Te variation during MORB

685   differentiation (Fig. 6b and c; Section 5.2.1).

686   On the other hand, $\delta^{82/76}$Se of PAR MORB mantle (-0.16 ± 0.13‰) is well within the range of chondritic

687   values of -0.30 ± 0.39‰ (Vollstaedt et al., 2016) and -0.21 ± 0.31‰ (Labidi et al., 2018) (Fig. 3). Combined

688   with the possible Se/Te ratios (7.9 ± 1.6 and 14.0 ± 6.1 for source 1 and 2, respectively), $\delta^{82/76}$Se of the PAR

689   mantle appears to overlap with that of both CI chondrites and volatile-depleted carbonaceous (CV and CO) and

690   ordinary chondrites but show a significant offset from enstatite chondrites (Fig. 10b). Yet, the latter have been

691   suggested to be the main constituent of the late veneer based on Ru and Os isotopes (e.g., Meisel et al., 1996;

692   Dauphas, 2017; Fischer-Gödde and Kleine, 2017). Interestingly, all terrestrial rocks/melts show distinctly

693   heavier $\delta^{82/76}$Se relative to enstatite chondrites (Fig. 3). At this stage, it is difficult to link the late veneer material

694   to certain chondrite groups because a robust mantle $\delta^{82/76}$Se value remains to be established and little is known

695   regarding the role of planetary processes on moderately volatile Se isotopes (e.g., metal–silicate equilibration

696   and vapor loss during accretionary growth of small planetesimals; Labidi et al., 2016; Hin et al., 2017; Norris

697   and Wood, 2017). Our result obtained here however highlights the potential of Se isotopes to contribute new

698   constraints on planetary accretion models regarding the Earth's volatile delivery.

699 6. Conclusion

700   We present the first high-precision Se isotope and Se–Te elemental data for MORB glasses from the PAR

701   (65–56°S and 53–41°S) using recently developed analytical techniques (Kurzawa et al., 2017; Yierpan et al.,

702   2018). Almost all PAR basalts have experienced high-temperature hydrothermal fluid assimilation during

703   magmatic differentiation, which significantly overprints the S isotope composition when it is associated with

704   assimilation of hydrothermal sulfides (Labidi et al., 2014). However, neither of these processes affects the Se

705   isotope composition and S–Se–Te abundances. The observed S–Se–Te variation is dominantly controlled by

706   MORB differentiation involving segregation of immiscible sulfide liquid, which are successfully reproduced

707   using the experimentally determined $D_{Se\ or\ Te}^{sulf\ liq-sil}$ values from Kiseeva et al. (2017); in the highly evolved melts at

708   magnetite saturation, the dominant fractionating sulfide phase is very likely crystalline MSS, indicated by the

709   abrupt drop in Se/Te and S/Te ratios. The differentiation-corrected Se–Te contents of the primary MORB melts

710   are well reproduced by near-fractional decompression melting of a mantle using experimental $D_{Se\ or\ Te}^{sulf\ liq-sil}$ (Brenan,

711   2015; Kiseeva et al., 2017) with a mantle source containing 170–200 µg g^{-1} S but distinct Se–Te contents ("fertile

712   lherzolite-like" 80 ± 17 and 11 ± 1.7 ng g^{-1} vs 49 ± 11 and 3.5 ± 1.3 ng g^{-1} Se and Te, respectively) due to the

713   significant difference in $D_{Se\ or\ Te}^{sulf\ liq-sil}$ reported by these groups. Nevertheless, our model suggests that sulfide

liquid–silicate melt partitioning, rather than MSS–sulfide liquid or MSS–silicate melt partitioning, predominantly controls the partitioning behavior of chalcophile elements during melting of a MORB mantle, in accordance with recent sulfide melting experiments (Zhang Z. and Hirschmann, 2016; Zhang Z. et al., 2018). This reinforces the notion that Se–Te variations (with broadly-chondritic Se/Te ratios) in "static" lithospheric lherzolites reflect significant, if not complete, metasomatic overprinting (e.g., König et al., 2014), which in turn requires a reassessment of the current PM composition (Wang and Becker, 2013).

The observed Se isotope variation along the PAR ($-0.30 \pm 0.09‰$–$-0.05 \pm 0.09‰$; 2 s.d., n = 27) is not systematically related to magmatic differentiation involving sulfide liquid/MSS–silicate melt partitioning or other geochemical parameters, indicating negligible $^{82}Se/^{76}Se$ fractionation within uncertainty during decompression melting. The Se isotope composition of the Pacific mantle is thus represented by the average $\delta^{82/76}Se$ of all MORBs ($-0.16 \pm 0.13‰$). This value is significantly lighter than previously reported $\delta^{82/76}Se$ for basalts and one peridotite from diverse geodynamic settings (Rouxel et al., 2002; Kurzawa et al., 2017; Yierpan et al., 2018); meanwhile, it overlaps with $\delta^{82/76}Se$ of carbonaceous (CI and volatile depleted CV and CO) and ordinary chondrites but shows a distinct offset from that of enstatite chondrites (Labidi et al., 2018). Selenium isotope variations between different mantle reservoirs and in additional non-magmatic processes can be resolved and further investigated in order to contribute constraints on the accretion history of terrestrial volatiles.

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Captions for Tables and Figures

Table 1. Selenium isotope composition and Se–Te abundances of geological reference materials and a randomly

selected PAR MORB glass reported in this study and literature.

Table 2. Selenium isotope composition, S–Se–Te abundances, and selected major element composition of the

studied PAR glasses.

Table 3. Summary of model parameters used for the near-fractional melting of a MORB mantle.

Fig. 1. Measurements of geological reference materials and a randomly selected moderately evolved PAR glass

(PAC2 DR33-1; 6.63 wt.% MgO; Table 1) for assessing the external reproducibility (2 s.d.) on the sample

$\delta^{82/76}$Se (left panel). Each symbol represents an individual measurement with the associated internal precision

(2 s.e.; over 40 cycles). All sample digests were analyzed once, except for two MORB glass digestions that were

aliquoted and analyzed twice. Our analytical accuracy and precision is evaluated by the long-term reproducibility

of inter-laboratory standard MH-495 (open circles; right panel), which yields −3.26 ± 0.12‰ and −3.25 ± 0.07‰

(2 s.d.) for 15 and 30 ng mL^{-1} solutions, respectively (Supplementary Table S1; this study; Kurzawa et al., 2017;

Yierpan et al., 2018). Shown for comparison are literature data on reference materials reported by Kurzawa et

al. (2017), Yierpan et al. (2018) (measurements in both studies were performed over the course of ~18 months

at the University of Tübingen; all circles), and Rouxel et al. (2002) (diamonds). Interlaboratory comparison of

$\delta^{82/76}$Se data on silicate samples remains difficult due to the limited Se isotope studies, and therefore BHVO-2

and BCR-2 are compared here with BHVO-1 and BCR-1 (only BE-N has been analyzed by two working groups).

$\delta^{82/76}$Se from Rouxel et al. (2002) that were originally reported relative to MERCK standard are converted

relative to NIST SRM 3149 following Carignan and Wen (2007) considering error propagation (analytical and

conversion errors of 0.25‰ and 0.20‰, respectively).

Fig. 2. Variation of Se isotope composition of PAR glasses with (a) sample latitude, (b) dredging depth, and (c) Se abundance. Two ridge sections (north of the Vacquier FZ and south of the Udintsev FZ) display identical average $\delta^{82/76}$Se values within uncertainty (a).

Fig. 3. Compilation of Se isotope compositions of PAR MORBs, terrestrial rock standards (7 basalts and 1 peridotite; Rouxel et al., 2002; Kurzawa et al., 2017; Yierpan et al., 2018; this study), basalts from a lava lake near the Lucky Strike hydrothermal field (n = 2; Rouxel et al., 2004), and main chondrite classes (Vollstaedt et al., 2016; Labidi et al., 2018). See Fig. 1 and Yierpan et al. (2018) for details on the measured basaltic rock standards. The peridotite analyzed by Rouxel et al. (2002) is a partially serpentinized harzburgite (PCC-1; Jain et al., 2000). Each shaded field represents the average $\delta^{82/76}$Se (black dashed line) with 2 s.d. uncertainties of chondrite and terrestrial rocks. Red dashed line denotes $\delta^{82/76}$Se = 0‰. The overall chondrite average $\delta^{82/76}$Se from Labidi et al. (2018) includes all chondrite groups analyzed (enstatite, ordinary, and carbonaceous) except three weathered CV chondrites. The data from Rouxel et al. (2002, 2004) is converted relative to NIST SRM 3149 following the approach of Carignan and Wen (2007) while considering error propagation (analytical and conversion uncertainties); the light and dark grey fields represent the uncertainties of the mean with (0.32‰) and without (0.17‰) error prorogation, respectively.

Fig. 4. Variations of Se, Te, S, and Cu abundances and/or their ratios with MgO content. Also shown for comparison are SMAR N- and E-MORBs (Lissner et al., 2014; E-MORB refers to all enriched- and transitional-type MORBs), as well as global MORBs from Hertogen et al. (1980) and Yi et al. (2000). The SMAR E-MORBs display distinctly lower Se/Te and S/Te ratios than that of N-MORBs from both PAR and SMAR over almost the entire magmatic differentiation (c and e), reflecting the Te-enrichment in E-MORB mantle source (Lissner et al., 2014). The Cu/Se ratio (f) in PAR and SMAR remains fairly constant and remarkably similar prior to ~7–7.5 wt.% MgO and PAR samples show a smooth decrease afterwards. The change of relative compatibility of Cu–Se may be related to the FeO content of the silicate melt as noted by Brenan (2015). The vertical dashed lines represent the onset of magnetite saturation (5 wt.% MgO) and associated sulfide segregation. Prior to this, the observed apparent compatibilities of these chalcophile elements (Te>Cu>Se>S) in the PAR suite indicate that they are predominantly controlled by fractionation of sulfide liquid, consistent with previous studies. At magnetite saturation, except the most evolved sample (PAC2 DR27-1) whose S solubility remains largely unaffected (Labidi et al., 2014), other two samples show consistent decrease in Se (a) and increase in Te (b) from the general trend (note the consistent decreases in FeO$_T$ and TiO$_2$; Supplementary Fig. S3). The strong abrupt decrease in their Se/Te and S/Te ratios (c and e) is argued here as an indicator of the predominant appearance of crystalline MSS in the segregating sulfide assemblage from the MORB melt (see the text for details).

Fig. 5. Variations of δ^{34}S$_{V-CDT}$ (a), $\delta^{82/76}$Se (b) and S/Se ratios (c) with Cl/K that is used as a proxy for the extent of Cl contamination due to the interaction of the magma with brines and hydrothermally altered materials during magmatic differentiation (Michael and Cornell, 1998; Clog et al., 2013; Labidi et al., 2014). Note that Cl/K The grey shaded field represents the Cl/K ratio (0.01–0.08) of global MORBs that are unaffected by hydrothermal

1240 fluid assimilation (Michael and Cornell, 1998). The studied PAR basalts that have experienced high-T

1241 hydrothermal sulfide assimilation based on S isotope systematics (Labidi et al., 2014) are shown in red. Other

1242 PAR glass data (Labidi et al., 2014) are shown in grey circles (a). (d) shows the variation of $\delta^{82/76}$Se with δ^{34}S$_{V-}$

1243 $_{CDT}$. Two shaded fields in (d) represent the average $\delta^{82/76}$Se of two subsets of samples with and without

1244 assimilating hydrothermal sulfides.

1245 **Fig. 6.** Variations of S, Se, and Te abundances with MgO and/or FeO$_T$ contents in PAR glasses. (a) shows the

1246 calculated SCSS (Smythe et al., 2017) for the primary melts (n = 10) as well as across the entire PAR magmatic

1247 differentiation following a similar approach of Ding and Dasgupta (2017). The primary melt major element

1248 compositions and their P–T conditions (on average ~10.2 kbar and 1325°C) of last equilibration with mantle

1249 olivine (Mg# = 0.90) are calculated using the algorithm of Lee et al. (2009). At this condition, their SCSS are

1250 calculated in combination with a variety of equilibrium sulfide compositions (X_{Fe} = 0.65–0.82; X_{Fe} = Fe/(Fe +

1251 Ni + Cu) atomic ratio) that might be found in the shallow mantle. It shows that even the lowest SCSS value with

1252 X_{Fe} = 0.63 (calculated sulfide composition in equilibrium with the most primitive glass PAC1 DR12-1g

1253 following Kiseeva and Wood (2015)) is still higher than the observed S contents of primitive PAR MORBs,

1254 implying that primary melts may be sulfide-undersaturated. The modelled SCSS (Smythe et al., 2017) across the

1255 entire PAR magmatic differentiation (from ~11.8 wt.% MgO) is calculated at 3 kbar (also see Fig. 7 and

1256 Supplementary Fig. S3) with X_{Fe} = 0.65 using major element compositions from alphaMELTS. Also shown for

1257 comparison is the SCSS from COMAGMAT (Ariskin et al., 2013, 2018) for the observed magmatic

1258 differentiation using Ni contents of the silicate melts (other parameters from alphaMELTS; Supplementary Fig.

1259 S3). Both models are in good agreement with the observed S abundances in sulfide-saturated MORBs from the

1260 PAR and global oceanic spreading ridges (Jenner et al., 2012, 2015; Labidi et al., 2014; global MORB data from

1261 Jenner and O'Neill (2012); n = 233). (b) and (c) show the modelled Se–Te variations with the calculated $X_{sulf}^{bulk\ min}$

1262 (based on S systematics; Labidi et al., 2014) and the experimentally determined $D_{Se\ or\ Te}^{sulf\ liq–sil}$ for basaltic melts with

1263 8–11 wt.% FeO from Kiseeva et al. (2017), which well reproduces the observed Se–Te variations. Calculation

1264 assumes that Se–Te partitioning between the fractionated sulfide liquid and silicate melt is an intermediate

1265 equilibrium process between fractional and batch partitioning, with S_b = 0.5 (Rehkämper et al., 1999). The

1266 observed/empirical trends using the observed $D_{Se\ or\ Te}^{bulk}$ values with S_b of 0 and 1 were shown for comparison.

1267 Each tick mark represents 10% crystal fractionation step. Also shown in (b) and (c) are the primary PAR melt

1268 (~11.8 wt.% MgO) Se–Te contents corrected for sulfide + crystal fractionation during later differentiation (S-

1269 saturated; MgO <8.85 wt.%) and for olivine fractionation during early differentiation (S-undersaturated; 11.8–

1270 8.85 wt.% MgO).

1271 **Fig. 7.** P–T diagram showing the sulfide phase relations determined on a single sulfide composition (X_{Fe} = 0.74,

1272 metal/S = 0.93, and Ni/(Fe + Ni) = 0.25 molar ratio; Bockrath et al., 2004; Zhang Z. and Hirschmann, 2016) and

1273 modelled conditions of PAR MORB differentiation (isobaric fractional crystallization; also see Supplementary

1274 Fig. S3) and near-fractional isentropic decompression melting path of a depleted MORB mantle (Salters and

1275 Stracke, 2004) to the base of the PAR crust (6.5 Km; alphaMELTS; Ghiorso and Sack, 1995; Ghiorso et al.,

1276 2002; Smith and Asimow, 2005). Each tick mark indicates 10% crystal fractionation or 2% melting extent.

1277 Anhydrous lherzolite solidus and bulk melt fraction (F_B) isopleths are calculated after Katz et al. (2003). The P–

1278 T condition of primary melt–mantle equilibration was obtained by the thermobarometer of Lee et al. (2009)

1279 using primitive PAR MORBs (>8.5 wt.% MgO; n = 10; Vlastelic et al., 2000; Hamelin et al., 2010), suggesting

1280 that melting at a mantle potential temperature (T_P) of 1350°C (also see Ding and Dasgupta (2017) for other

1281 MORBs) may be adequate for our modelling purpose because each data point for an aggregate primary melt

1282 represents weighted average P–T of melt extraction from all mantle parcels across the triangular melting zone

1283 and thus lies below the polybaric melting path (Asimow and Longhi, 2004; Lee et al., 2009). The primary melt

1284 P–T of MORBs from the Pacific (n = 55; Jenner and O'Neill, 2012) and other spreading-ridges (n = 157; PetDB)

1285 is shown for comparison. Both sulfide melting experiments (Bockrath et al., 2004; Zhang Z. and Hirschmann,

1286 2016) suggest that sulfide liquid is the dominant fractionating phase across much of low-P MORB differentiation

1287 (red arrow), consistent with previous inferences from behavior of chalcophile elements (see Section 5.2.1).

1288 However, the sulfide liquidi estimated by these experiments distinctly vary at P–T conditions relevant to melting

1289 of a depleted mantle with typical T_P between ~1275°C and 1400°C. Under these conditions, a mantle sulfide

1290 may have similar metal/S ratio but much higher Ni/(Fe + Ni) (~0.40–0.65) compared to the sulfide mentioned

1291 above, resulting in an even lower solidus (Zhang Z. and Hirschmann, 2016; Zhang Z. et al., 2018). This implies

1292 that chalcophile element behavior during decompression melting is entirely controlled by sulfide liquid–silicate

1293 melt fractionation rather than MSS–sulfide liquid or MSS–silicate melt fractionation.

1294 **Fig. 8.** Variations of Se (a) and Te (b) contents and Se/Te ratios (c) of the primary PAR melts (also see Fig. 6b

1295 and c) with their average degree of melting (F_B) estimated by batch melting equation using incompatible trace

1296 element systematics (~6.6–11.7%; Supplementary Fig. S4). The vertical and horizontal shaded field represent

1297 the range of F_B (6.5–9.5%) estimated from the forward modelling (near-fractional melting; pMLETS) and

1298 average primary melt composition (150 ± 8 and 3.1 ± 0.4 ng g^{-1} Se and Te, respectively; Se/Te = 48.4 ± 6.8).

1299 The variation in Se–Te concentrations were modelled for a triangular near-fractional melting regime (e.g.,

1300 Rehkämper et al., 1999; Lissner et al., 2014; Brenan, 2015) using "fertile lherzolite-like" Se and Te contents (80

1301 and 11 ng g^{-1}; Wang and Becker, 2013) and a range of S contents (150–200 μg g^{-1}) previously estimated for the

1302 primitive and/or depleted upper mantle (e.g., Luguet et al., 2003; Lorand et al., 2013; Lorand and Luguet, 2016;

1303 Bézos et al., 2005; Wang and Becker, 2013; Nielsen et al., 2014; Palme and O'Neill, 2014). $D_{Se\ or\ Te}^{sulf\ liq–sil}$ values are

1304 from Brenan (2015) and Kiseeva et al. (2017) (Table 3). The melt major element compositions and P–T

1305 conditions were modelled with pMELTS (see Fig. 7) and used to calculate $D_{Se\ or\ Te}^{sulf\ liq–sil}$ (as a function of FeO

1306 content of each equilibrium melt) and SCSS of the melt (Smythe et al., 2017) assuming the melt is in equilibrium

1307 with a calculated upper mantle sulfide (Fe$_{0.50}$Ni$_{0.36}$Cu$_{0.07}$S$_{1.00}$; Supplementary Fig. S5). (a), (b), and (c) show that

1308 the Se–Te systematics of the primary PAR melts can be broadly reproduced using the selected "fertile lherzolite-

1309 like" Se–Te contents (with 170–200 μg g^{-1} S) and $D_{Se\ or\ Te}^{sulf\ liq-sil}$ from Brenan (2015) (black lines). S-undersaturation

1310 in the aggregate melt occurs at slightly different F_B (~9.5% to 11.5%) depending on the source S content (see

1311 Supplementary Fig. S5a). With the same starting composition, calculation using $D_{Se\ or\ Te}^{sulf\ liq-sil}$ of Kiseeva et al. (2017)

1312 overestimates the Se–Te contents of the melts (only shown for 180 μg g^{-1} S in the source for simplicity; red

1313 dashed lines) and only reproduces the observed variations with a significantly lowered source Se and Te contents

1314 (48 and 3.5 ng g^{-1}, respectively; red solid lines).

1315 **Fig. 9.** Variations of Se/Te against (a) Te contents of the primary aggregate melts and (b) Te and (c) Al$_2$O$_3$

1316 contents of the mantle residue. The red solid lines and all black lines correspond to the modelled melt

1317 composition with different proportions of sulfide liquid and crystalline MSS in the mantle having 180 μg g^{-1} S

1318 but two distinct Se and Te concentrations: (1) 80 ± 17 and 11 ± 1.7 ng g^{-1}, respectively ("fertile mantle";

1319 estimated at 3.52 wt.% Al$_2$O$_3$; Wang and Becker, 2013), in combination with $D_{Se\ or\ Te}^{sulf\ liq-sil}$ (changing as a function
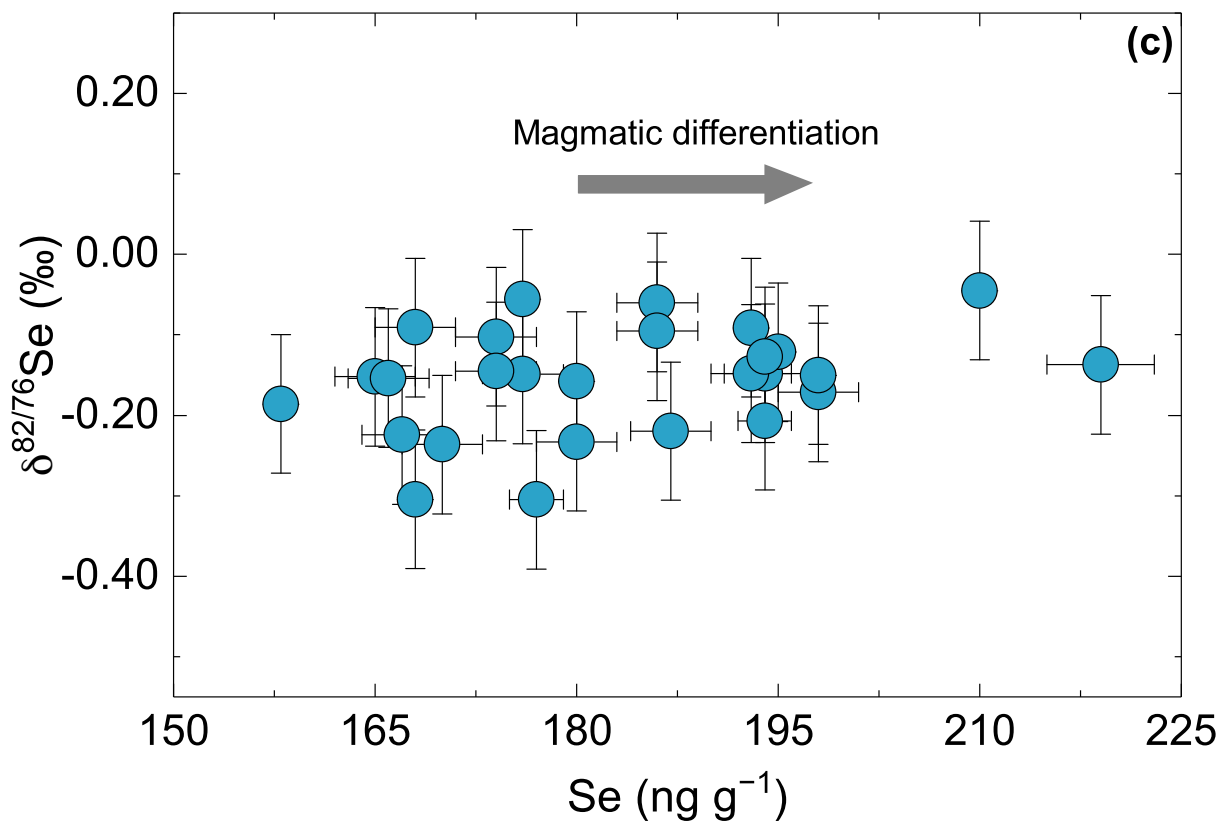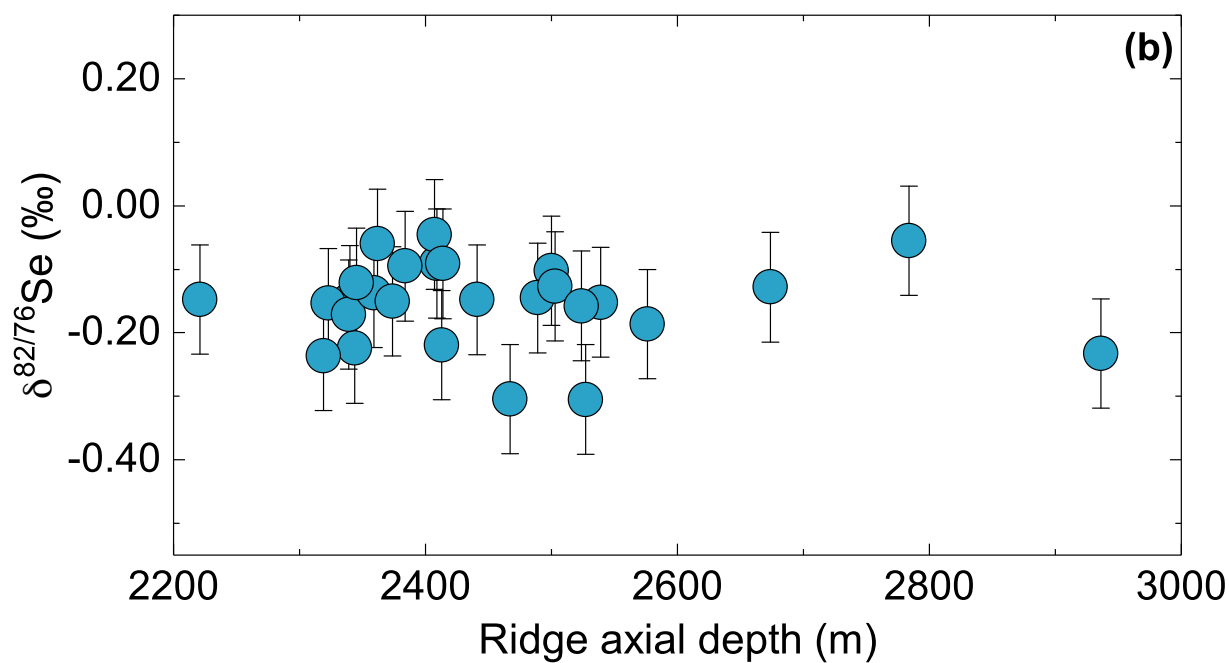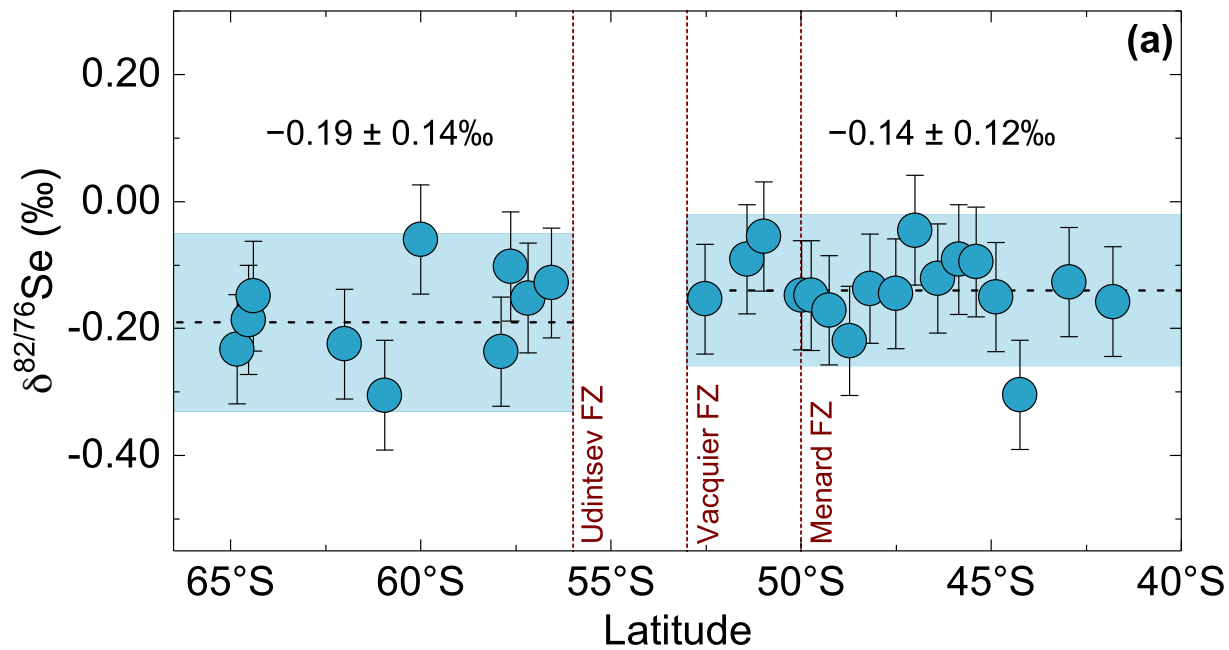
1320 of FeO contents of equilibrium melts) and/or $D_{Se\ or\ Te}^{MSS-sil}$ (constant) from Brenan (2015); and (2) 48 ± 8 and 3.5 ±

1321 0.9 ng g^{-1}, respectively, which are the best-fit values from the modelling in combination with $D_{Se\ or\ Te}^{sulf\ liq-sil}$ (constant)

1322 from Kiseeva et al. (2017) (see Fig. 8 and Supplementary Fig. S6 for the modelling of partial melt composition).

1323 Each tick mark indicates 2% F_B (average degree of melting over a triangular melting zone) for the melts and 4%

1324 melting for a residual melting column (only shown for curves with 100% sulfide liquid or MSS). The modelling

1325 results are only shown until a mantle column becomes sulfide-exhausted, after which the remaining Se–Te

1326 budget is controlled by platinum-groups minerals (PGM; see the light blue shaded area in (c); Luguet et al., 2007;

1327 König et al., 2015). Additionally shown are the melting curves of a source with the maximum "fertile mantle"

1328 Se and Te contents (101 and 12.5 ng g^{-1}, respectively; estimated at 4.45 wt.% Al$_2$O$_3$ by Wang and Becker (2013))

1329 using experimental $D_{Se\ or\ Te}^{sulf\ liq-sil}$ of (1) 1086 and 8789 (used in the melting model of Brenan (2015)) and (2) 850

1330 and 3800 (same as above; Kiseeva et al., 2017) for Se and Te, respectively. For this modelling, major element

1331 compositions are from PM of McDonough and Sun (1995) and SCSS is calculated accordingly using parameters

1332 from pMELTS. The light yellow shaded areas in (c) are the range of residue compositions with a typical fertile

1333 mantle S content (200 ± 40 μg g^{-1}; e.g., Lorand, 1991; Palme and O'Neill, 2014). Our result shows that,

1334 regardless of the choice of source Se–Te contents and experimental $D_{Se\ or\ Te}^{sulf\ liq-sil}$ data, the Se–Te pattern displayed

1335 by lherzolites is inconsistent with melt depletion involving sulfide liquid–silicate melt fractionation (all solid

1336 black and red lines; b and c), which is suggested here to control Se–Te partitioning during mantle melting (D_{Se}^{bulk}

1337 $<< D_{Te}^{bulk}$; see text for more details). Shown for comparison are the Se–Te contents for the SMAR N- and E-

1338 MORB primary melts and mantle sources (Lissner et al., 2014). Lherzolite (>1.5 wt.% Al$_2$O$_3$) and harzburgite

1339 (<1.5 wt.% Al$_2$O$_3$) data are from Morgan (1986), Lorand and Alard (2010), Wang and Becker (2013), Wang et

1340 al. (2013), König et al. (2012, 2014, 2015), Luguet et al. (2015), and Harvey et al. (2015).

1341 **Fig. 10.** δ$^{82/76}$Se plotted against (a) Mg# and (b) Se/Te ratio across the entire MORB evolution according to our

1342 models of magmatic differentiation and partial melting. Also shown for comparison are δ$^{82/76}$Se (± 2 s.d.) and

1343   Se/Te (± 1 s.d.) data for basaltic reference materials and main chondrite groups (also see Fig. 3). Each shaded

1344   field represents the average $\delta^{82/76}$Se with 2 s.d. uncertainty and range of Mg# (a) or Se/Te (b). The mass fractions

1345   of the fractionated crystals and sulfides are relative to the initial primary melt (a). Selenium isotope compositions

1346   of the primary PAR melt and MORB mantle source are represented by the average $\delta^{82/76}$Se value of all PAR

1347   glasses (−0.16 ± 0.13‰; 2 s.d., n = 27) based on the demonstrated absence of Se isotope fractionation during Se

1348   partitioning between sulfide (liquid and/or crystalline MSS) and silicate melt ($\Delta^{82/76}$Se$_{sulf–sil} \approx 0.00$‰). Both

1349   mantle source compositions estimated for PAR MROBs were shown: 80 ± 17 and 11 ± 1.7 ng g^{-1} (source 1) and

1350   49 ± 11 and 3.5 ± 1.3 ng g^{-1} (source 2) Se and Te, respectively (also see Fig. 8 and 9; symbols in (a) were slightly

1351   staggered for clarity). $\delta^{82/76}$Se and Se/Te ratios of all basaltic reference materials are from this study and Yierpan

1352   et al. (2018) and $\delta^{82/76}$Se of BCR-2 is also taken from Kurzawa et al. (2017) (also see Fig. 1). For chondrites,

1353 $\delta^{82/76}$Se are from Labidi et al. (2018) and the Se/Te ratios from Wasson and Kallemeyn (1988), Lodders et al.

1354   (2009), Schaefer and Fegley (2010), and Wang and Becker (2013).

−0.21 ± 0.31‰
(n = 20)

0.30 ± 0.32‰
(n = 6)

0.21 ± 0.15‰
(n = 4)

−0.16 ± 0.13‰
(n = 27)

Chondrites:
All (Vollstaedt et al., 2016)
Labidi et al. (2018):
CI
CV
CO
Ordinary
Enstatite

Peridotite (PCC-1):
Rouxel et al. (2002)
Worlwide basaltic lavas:
Rouxel et al. (2002, 2004)

This study
Kurzawa et al. (2017)
Yierpan et al. (2018)

PAR MORB:
This study

$\delta^{82/76}$Se (‰)

(a)

X_{Fe} of equilibrium sulfide used for the primary melt SCSS:
- 0.82 (average MORB sulfide; Keith et al., 2017)
- 0.74 (calculated typical upper mantle sulfide; Bockrath et al., 2004; Zhang & Hirschmann, 2016)
- 0.72 (typical MORB sulfide; Patten et al., 2013)
- 0.65 (calculated sulfide following Kiseeva & Wood (2015))

Modelled SCSS (3 kbar and buffered fO$_2$ of FMQ − 0.18):
- Smythe et al. (2017)
- Ariskin et al. (2013, 2018)

Magnetite saturation

Decreasing X_{Fe} in sulfide

S-undersaturated parental melts?

(b)

- PAR MORB
- Primary melts
- Average primary melt

Sulfide fractionation
$X_{sulf}^{bulk\ min}$ = 0.14 ± 0.04 wt.%

$D_{Se}^{sulf\ liq-sil}$ = 450–650

MgO (wt.%)
11.8

Primary melts

8.82
FeO$_T$ (wt.%)

(c)

- S_b = 0
- S_b = 1 } Observed trend (this study)
- S_b = 0.5; $D_{Se\ or\ Te}^{sulf\ liq-sil}$ (Kiseeva et al., 2017)

Sulfide fractionation
$X_{sulf}^{bulk\ min}$ = 0.14 ± 0.04 wt.%

$D_{Te}^{sulf\ liq-sil}$ = 2600–3200

MgO (wt.%)
11.8

Primary melts

8.82
FeO$_T$ (wt.%)

(a)

Average F_B
(pMELTS)

180

150

170

180

200

180

Average primary
melt composition

Source composition:

80 ng g^{-1} Se, 11 ng g^{-1} Te
("fertile lherzolite"; Wang & Becker, 2013)

48 ng g^{-1} Se, 3.5 ng g^{-1} Te
(This study)

D$_{Se\ or\ Te}^{sulf\ liq-sil.}$:

Constant
(Kiseeva et al., 2017)

Changing with FeO
(Brenan, 2015)

(b)

150

170

180

200

180

180

(c)

Average F_B
(pMELTS)

Average primary
melt composition

180

150

170

180

200

180

Lherzolites

(a) Melts

(b) Mantle residues

(c)

Legend:

Primary melts:
- PAR
- SMAR N-MORB
- SMAR E-MORB

Equilibrium sulfides:
- 100% sul liq
- 75% sul liq
- 50% sul liq
- 90% MSS
- 100% MSS

MORB source mantle Se–Te contents:
- PAR source 1 ("fertile lherzolite"; Wang & Becker, 2013)
- PAR source 2 (low Se & Te; this study)
- SMAR N-MORB } Lissner et al. (2014)
- SMAR E-MORB

"Fertile lherzolite" max. Se–Te contents (at 4.45 wt.% Al_2O_3):
- Wang & Becker (2013)

Literature peridotite data:
- Lherzolites
- Harzburgites

(a)

Magnetite-triggered sulfide fractionation

Fractionation of ~65% crystal and ~0.12% sulfide

Fractionation of ~8.7% olivine

Partial melting (~6.5–9.5%)

$D_{Se}^{MSS-sil}$

$D_{Se}^{sulf\ liq-sil}$

$D_{Se}^{sulf\ liq-sil}$

$\Delta^{82/76}Se_{sulf\ liq/MSS-sil} \approx 0.00‰$

$\delta^{82/76}Se\ (‰)$

Mg#

- ● PAR MORB
- ◆ PAR average primary melt
- ⬢ PAR mantle source 1 ("fertile lherzolite"; Wang & Becker, 2013)
- ⬢ PAR mantle source 2 (low Se & Te; this study)

(b)

$\delta^{82/76}Se\ (‰)$

Se/Te

BIR-1a   BHVO-2   BCR-2   BE-N

Chondrites:
- ■ CI
- ■ CV
- ■ CO
- ■ Ordinary
- ■ Enstatite

Magmatic differentiation

Electronic Annex Supplementary Material for

Selenium isotope and S-Se-Te elemental systematics along the Pacific-Antarctic ridge: Role of mantle processes

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This Supplementary Material includes

Supplementary Text (S1 and S2)

Supplementary Table Captions (Tables S1–S3 are uploaded separately as an Excel file)

Supplementary Figures (Fig. S1–S6) and Figure Captions

S1. Modelling Se–Te variations during MORB differentiation

The observed major element systematics were first constrained using a simple fractional crystallization model, which is generally considered as a dominant process during low-pressure magmatic evolution, especially in fast spreading ridges (Grove et al., 1992; Sinton and Detrick, 1992; Perfit, 2001) as in the case of the studied PAR segments (see Main Text Section 2). The liquid lines of descents (LLDs) were modelled with alphaMELTS front end (MELTS mode; Version 1.8) run in isobaric mode (Ghiorso and Sack, 1995; Smith and Asimow, 2005). Calculations were performed starting from the most primitive glass PAC1 DR12-1g (Electronic Annex 2 Table S1) at 2–7 kbar along a buffered fO_2 of 0.18 log units below the FMQ buffer (Zhang H. L. et al., 2018). The modelled trends at 2–5 kbar broadly reproduce the observed variations of most major elements (Fig. S3), reflecting a comagmatic origin of the entire PAR on-axis (Vlastélic et al., 2000; Hamelin et al., 2010). The observed Se–Te variations were subsequently modelled using FeO_T as an index of differentiation due to their tight covariations as mentioned in Main Text Section 5.2 (also see Main Text Fig. 6). Note that FeO_T content of the PAR samples monotonically increases with ongoing crystal fractionation prior to magnetite saturation (Fig.

S3). The modelled LLDs for FeO$_T$ yields the best match with the observed trend at 3 kbar and the resulting parameters were used in the subsequent modelling.

The Se–Te partitioning between the bulk fractionated minerals (i.e., silicate crystals + sulfide phase) and silicate melt ($D^{bulk}_{Se\ or\ Te}$) is described by

$$D^{bulk}_{Se\ or\ Te} = \frac{X_{sulf}}{1-f}D^{sulf-sil}_{Se\ or\ Te} + \frac{X_{cryst}}{1-f}D^{cryst-sil}_{Se\ or\ Te} \tag{1}$$

where f, X_{sulf}, and X_{cryst} are the mass fractions of remaining silicate melt, fractionated immiscible sulfide phase, and silicate crystals, respectively, relative to the initial system (i.e., PAC1 DR12-1g); $D^{sulf-sil}_{Se\ or\ Te}$ and $D^{cryst-sil}_{Se\ or\ Te}$ are the sulfide phase–silicate melt and silicate crystal–silicate melt partition coefficients, respectively. As Se–Te are essentially incompatible in silicate crystals (assuming $D^{cryst-sil}_{Se\ or\ Te} = 0.001$; Brenan, 2015), Eq. (1) can be approximated as

$$D^{bulk}_{Se\ or\ Te} = \frac{X_{sulf}}{1-f}D^{sulf-sil}_{Se\ or\ Te} \tag{2}$$

Considering that all fractionated S is exclusively partitioned into sulfide due to its incompatibility in silicate crystals (Labidi et al., 2014), the mass balance allows calculation of X_{sulf} at a given f (directly obtained from alphaMELTS) following

$$X_{sulf} = \frac{C^0_S - fC^l_S}{C^{sulf}_S} \tag{3}$$

where C^0_S, C^l_S, and C^{sulf}_S are the S concentrations of the initial high-MgO melts (on average 968 ± 26 µg g^{-1}; Main Text Table 2 and Fig. 6a), remaining melt, and segregated sulfides, respectively. The term $\frac{X_{sulf}}{1-f}$ in Eq. (2) represents the proportion of sulfide in the bulk fractionated minerals ($X^{bulk\ min}_{sulf}$). For the studied PAR glasses that have not experienced magnetite saturation-triggered sulfide segregation (see Main Text Section 5.2 and Fig. 6a), we obtain $X^{bulk\ min}_{sulf}$ ranging between 0.09 and 0.20 wt.% averaging at 0.14 ± 0.04 wt.%, consistent with the previous estimate for a larger set of samples (0.19 ± 0.07 wt.%; assuming $C^{sulf}_S = 35$ wt.%; Labidi et al., 2014).

As for $D^{sulf-sil}_{Se\ or\ Te}$, previous studies reported a wide range of values (Peach et al., 1990; Barnes et al., 2009; Patten et al., 2013; Brenan, 2015; Kiseeva et al., 2017). Two partitioning experiments show that $D^{sulf-sil}_{Se\ or\ Te}$ strongly depends on the fractionating sulfide phase (crystalline monosulphide solid solution (MSS) and sulfide liquid) and FeO content of the silicate melt (Brenan, 2015; Kiseeva et al., 2017). Both elements are highly compatible in sulfides relative to silicates, whereas Te is more compatible in sulfide liquid and Se is more compatible in MSS (Brenan, 2015). For sulfide liquid–silicate melt partitioning ($D^{sulf\ liq-sil}_{Se\ or\ Te}$), these studies reported significantly different values. For a basaltic melt with 8–11 wt.% FeO, Kiseeva et al. (2017) reported $D^{sulf\ liq-sil}_{Se} = 450$–650

and $D_{Te}^{sulf\,liq-sil} = 2600–3200$, much lower than $D_{Se}^{sulf\,liq-sil} = 1050 \pm 360–1460 \pm 400$ and $D_{Te}^{sulf\,liq-sil} = 9720 \pm 1170–$ 13640 ± 1590 (1 s.d. propagated error) expected from the formula of Brenan (2015), respectively ($D_{Se\,or\,Te}^{sulf\,liq-sil}$ decreases with increasing FeO content of the silicate melt). In the case of the evolving PAR melts with FeO$_T$ from 8.49 to 12.78 wt.% (Main Text Fig. 6b and c; MgO from ~8.85–5.5 wt.%; Fig. S3), assuming Fe^{2+}/ΣFe = 0.87 (Bézos and Humler, 2005; Zhang H. L. et al., 2018), we obtain $1560 \pm 410–1035 \pm 360$ for $D_{Se}^{sulf\,liq-sil}$ and $14430 \pm 1680–9570 \pm 1150$ for $D_{Te}^{sulf\,liq-sil}$ (both 1 s.d.) following Brenan (2015). Both these values and $D_{Se\,or\,Te}^{sulf\,liq-sil}$ from Kiseeva et al. (2017), together with $X_{sulf}^{bulk\,min} = 0.14 \pm 0.04$ wt.%, are used to derive $D_{Se\,or\,Te}^{bulk}$ using Eq. (2). Finally, the model Se–Te concentrations were calculated using the fractional (Eq. 4) and/or batch crystallization (Eq. 5) laws following

$$C_{Se\,or\,Te}^{l} = C_{Se\,or\,Te}^{0} f^{D_{Se\,or\,Te}^{bulk} - 1} \tag{4}$$

and/or

$$C_{Se\,or\,Te}^{l} = \frac{C_{Se\,or\,Te}^{0}}{f + D_{Se\,or\,Te}^{bulk}(1 - f)} \tag{5}$$

where $C_{Se\,or\,Te}^{l}$ and $C_{Se\,or\,Te}^{0}$ are Se-Te concentrations of the remaining melt at a given f and the initial melt (PAC1 DR12-1g; Main Text Table 2), respectively.

S2. Modelling Se–Te variations during partial melting

The variations of Se–Te during partial melting were modelled for a triangular passive-flow near-fractional melting regime, which has been previously used to explain the Se–Te and highly siderophile element systematics of MORB melts (Rehkämper et al., 1999; Bézos et al., 2005; Mungall and Brenan, 2014; Lissner et al., 2014; Brenan, 2015). The procedures of our model basically follow that detailed by Rehkämper et al. (1999) and Brenan (2015). Briefly, we assume a simplified two-phase mineralogy for the mantle source, which consists of sulfides (sulfide liquid with/without MSS) and bulk silicate minerals. The Se–Te concentrations of each melt increment (1%; relative to the initial system mass) and the residue are calculated by the batch melting equation (Shaw, 1970) with $D_{Se\,or\,Te}^{bulk}$ using experimentally determined $D_{Se\,or\,Te}^{sulf\,liq-sil}$ and/or $D_{Se\,or\,Te}^{MSS-sil}$ values while assuming $D_{Se\,or\,Te}^{cryst-sil} = 0.001$ (Brenan, 2015; Kiseeva et al., 2017; see Section S1). After each equilibrium melting step, 0.1% of the fractional melt is retained (by simple batch mixing) to refertilize the residual mantle column and the rest is extracted. The mineral modes (sulfide and silicate) and composition (S–Se–Te contents) of the residue (i.e., the source for the next melting step) are recalculated accordingly. Finally, the polybaric column-melts produced over the entire two-dimensional melting zone are pooled completely and produce the PAR primary melts at a mean extent of melting F_B (defined as the mass fraction of all melts relative to the initial solid entering the melting region), which is approximated as $\frac{F_{max}}{2}$, where F_{max} is the maximum extent of melting achieved in the

central melting column (Langmuir et al., 1992; Plank et al., 1995; Rehkämper et al., 1999). Sulfur contents of the residue and partial melts at each step depend on the initial S content of the source and SCSS of the aggregate melt in a specific melting column. When the S content of the residue is insufficient to keep the equilibrium melt S-saturated, S starts to behave as an incompatible element (with $D_S^{cryst-sil} = 0.001$; Labidi et al., 2014). Upon sulfide exhaustion in a column, S content of the aggregate melt is simply diluted as the subsequent melt increments essentially become S-free. We note that this may be an oversimplification in some cases. For instance, S systematics in the Garrett transform fault lavas, which might have formed by re-melting of a depleted MORB source ($F_B \approx 10\%$ for both melting events; see discussion and Fig. S5a for the typical F_B of S undersaturation in aggregate MORB melts), are similar to those observed in global sulfide-saturated MORBs, requiring that their source (after the first MORB melting event) kept the melts sulfide-saturated (Labidi and Cartigny, 2016). However, generally, MORB melts produced in a triangular melting regime typical for fast-spreading ridges (e.g., Langmuir and Forsyth, 2007; Langmuir et al., 1992; Lin and Morgan, 1992; Brown and Lesher, 2016; and references therein) represent a mixture of S-saturated partial melts (coming from low-F sulfide-bearing mantle columns) and S-undersaturated partial melts (from high-F (e.g., ~20%) S-exhausted mantle columns) (also see Ding and Dasgupta, 2017).

The model parameters used here are summarized in Main Text Table 3. The melt major element compositions and pressure-temperature (P–T) conditions for calculating the SCSS of the aggregate melt in a melting column (Smythe et al., 2017) and $D_{Se\ or\ Te}^{sulf\ liq-sil}$ (as a function of FeO; for each incremental/equilibrium melt; Brenan, 2015; Kiseeva et al., 2017) were modelled with alphaMELTS front end run in pMELTS mode (Ghiorso et al., 2002; Smith and Asimow, 2005), following a similar approach used by Ding and Dasgupta (2017). The relevant mantle potential temperature (T_P) for the PAR MORBs was estimated based on the previously determined primary melt–mantle equilibration P–T (on average ~10.2 kbar and 1325°C; Main Text Section 5.2.2), which falls between 1275 and 1350°C, in accordance with the previous estimates for global MORBs (Main Text Fig. 7; Lee et al., 2009; Ding and Dasgupta, 2017). The pMELTS calculation with $T_P = 1350$°C may be adequate for our purpose because each P–T data for the aggregate PAR primary melts represents the weighted average P–T of melt extraction from all mantle parcels across the triangular melting zone and thus lies below the polybaric melting path (Main Text Fig. 7; Asimow and Longhi, 2004; Lee et al., 2009). The composition of the depleted MORB mantle were taken from Salters and Stracke (2004) assuming 0.2 wt.% Fe_2O_3 (e.g., Cottrell and Kelley, 2011). We obtain a range of temperature from 1389 to 1294°C for the extent of melting F from 0 to 20%, with the corresponding extraction pressures 17.5 to 5.4 kbar for the incremental melts and 17.5 to 9.4 kbar for the aggregate melts (1-D integration over a single melting column). Under these conditions, the calculated $D_{Se\ or\ Te}^{sulf\ liq-sil}$ values following Brenan (2015) at each melting step are 1414 ± 401–1900 ± 435 for $D_{Se}^{sulf\ liq-sil}$ and 13199 ± 1541–16811 ± 1940 for $D_{Te}^{sulf\ liq-sil}$ (1 s.d. propagated uncertainty), increasing with progressive melting due to the decreasing FeO content of the fractional melts (~8.34–5.37 wt.%). These values are considerably higher than that used by Brenan (2015) for the melting model, which are 1086 and 8789 for Se

and Te, respectively (chosen at an empirical FeO content of 10 wt.%). At this range of FeO content, $D_{Se\ or\ Te}^{sulf\ liq-sil}$ values of Kiseeva et al. (2017) should be 550–850 and 3000–3800 for Se and Te, respectively (see Section S1 for the different results between two studies).

As for estimating the average melting degree for the PAR MORBs, we used (incompatible) trace element systematics (Fig. S4). The primary melt compositions (on average ~11.8 wt.% MgO and Mg# = 0.73) were obtained by a similar method used for Se–Te (see Main Text Section 5.2.2). Briefly, measured concentrations (Electronic Annex 2 Table S1) were first corrected to MgO content (8.85 wt.%) of the most primitive glass by linear regression. This was followed by correcting for ~8.7% olivine fractionation considering that these elements are highly incompatible in olivine (e.g., Bédard, 2005). The average melting degree was then estimated in two different approaches: (1) by solving the simple batch melting equation for F_B using concentration of each trace element i (C_i^{melt}) for all primary melts (n = 24) and the source (C_i^{mantle}; depleted MORB mantle; Salters and Stracke, 2004) with empirical mantle–melt bulk partition coefficients ($D_i^{mantle-melt}$) following the approach of Kelley et al. (2006):

$$F_B = \frac{\dfrac{C_i^{mantle}}{C_i^{melt}} - D_i^{mantle-melt}}{1 - D_i^{mantle-melt}} \tag{5}$$

which yields F_B from ~6.6 to ~11.7% (average 8.5 ± 1.5%; 1 s.d., n = 24); and (2) comparing the results obtained from pMELTS for the accumulated melts (over the entire triangular melting region) to our calculated primary melt concentrations, which gives a best match if F_B ranges between 6.5 and 9.5% (Fig. S4). Both results are in excellent agreement and, meanwhile, consistent with the previous estimates for global MORBs (e.g., Klein and Langmuir, 1987; Salters and Stracke, 2004; Workman and Hart, 2005; Kimura et al., 2017). Besides, our calculated primary melt–mantle equilibration P–T for PAR glasses, together with most global MORBs, fall between 10–20% melt fraction isopleths estimated for a fertile lherzolite (Main Text Fig. 7; Katz et al., 2003; Lee et al., 2009). Lower melt fractions would be expected for a depleted MORB source mantle due to its relatively higher solidus (Lee et al., 2009), which may then be broadly consistent with our estimated F_B.

Three different mantle sulfides (Fe–Ni–Cu BMS) were used to calculate the SCSS of the partial melts considering that the equilibrium sulfide chemistry significantly affects the S solubility as FeS activity decreases due to the presence of Ni and Cu, i.e., SCSS decreases with decreasing $X_{Fe} = \dfrac{Fe}{Fe + Ni + Cu}$ (molar ratio) (e.g., Ariskin et al., 2013, 2018; Ding and Dasgupta, 2017; Ding et al., 2018; Smythe et al., 2017). The calculated chemical formulas are shown in Fig. S5. Sulfide A has a relatively refractory composition and was used in the melting experiments of Bockrath et al. (2004) and Zhang Z. and Hirschmann (2016) to obtain the sulfide solidus and liquidus as shown in Main Text Fig. 7. Sulfide B is calculated assuming 25 wt.% Ni + 5 wt.% Cu (used in the melting model of Ding and Dasgupta (2017)) and metal/S atomic ratio of 0.93 that is typical for shallow mantle sulfides under relatively oxidized conditions (e.g, MORB source mantle; Zhang Z. et al., 2018; also see

Lorand and Luguet, 2016). For sulfide C, we first estimated its $\frac{Ni}{Ni+Fe}$ molar ratio using the Ni and FeO contents of olivine in the residue (~10.06–9.01 wt.% FeO and ~1964–2349 µg g^{-1} Ni for 0–20% melting; from pMELTS) and sulfide melt–olivine Fe–Ni exchange relations following Zhang Z. et al. (2018):

$$\frac{(Ni/Fe)_{sulf\,liq}}{(Ni/Fe)_{olivine}} = 14.33\frac{Ni}{Ni+Fe} + 39.45 \tag{6}$$

which yields 0.53–0.60 (increasing with increasing F). The weight fractions of Fe, Ni, and S are then calculated with a constant $\frac{Ni}{Ni+Fe}$ = 0.53 while taking metal/S ratio of 0.93 (Zhang Z. et al., 2018) and 5 wt.% Cu (Kiseeva et al., 2017).

Because there are a large number of model parameters, we first validate our model for the variation of chalcophile elements S and Cu during melting (Fig. S5) because (1) S and Cu abundances in the mantle are relatively well constrained using different approaches by several studies (e.g., Mcdonough and Sun, 1995; Salters and Stracke, 2004; Lorand and Luguet, 2016; Lorand et al., 2013; Wang and Becker, 2013, 2015b; Palme and O'Neill, 2014); (2) their behavior during partial melting has been systematically modelled using experimentally determined partition coefficients (e.g., Lee et al., 2009; Li and Audétat, 2012; Kiseeva and Wood, 2013, 2015; Brenan, 2015) and a large number of analyses in MORB melts (e.g., Jenner and O'Neill, 2012; Labidi et al., 2014) with a variety of SCSS models, source contents, and T$_P$ (Lee et al., 2009; Li and Audétat, 2012; Ding and Dasgupta, 2017). The S of contents used for the PAR MORB source mantle ranges from "PM-like" 200 µg g^{-1} (e.g., Lorand et al., 2013; Palme and O'Neill, 2014; Wang and Becker, 2013) to slightly lower 150 µg g^{-1} as estimated for the depleted MORB mantle (e.g., Luguet et al., 2003; Bézos et al., 2005; Nielsen et al., 2014; Lorand and Luguet, 2016). A starting Cu content of 30 ± 6 µg g^{-1} is used, as suggested for the PM (Mcdonough and Sun, 1995; Wang and Becker, 2015b) as well as the depleted MORB mantle (Salters and Stracke, 2004). Partition coefficients of Cu between silicate minerals and melt ($D_{Cu}^{cryst–sil}$) are taken from Lee et al. (2009). $D_{Cu}^{sulf\,liq–sil}$ is taken as 1000 (Li and Audétat, 2012), which has been used in several studies for modelling the behavior of Cu (e.g., Ding and Dasgupta, 2017; Wang and Becker, 2015b). The primary melt S and Cu contents (after correcting for sulfide + crystal fractionation) are calculated by the same approach used for Se and Te contents (Main Text Section 5.2.2). Our result (Fig. S5) shows that, with the SCSS model of Smythe et al. (2017) and equilibrium sulfide composition B (X_{Fe} = 0.54; $\frac{Ni}{Ni+Fe}$ = 0.42; Fig. S5a), the PAR primary melt S concentrations are very well reproduced with our partial melting model for the estimated F_B of the samples using a range of source S content (150–200 µg g^{-1}). Note that the chemistry of sulfide B used here is also consistent with typical lherzolite-hosted sulfide compositions (e.g., Lorand and Luguet, 2016) as well as the suggested range of $\frac{Ni}{Ni+Fe}$ value for a shallow mantle Cu-free sulfide (0.4–0.6) by Zhang Z. et al. (2018) at the range of melting depth (from ~50 to 20 km from pMELTS; Maint Text Fig. 7) and fO$_2$ (~FMQ; Cottrell and Kelley, 2011; Zhang H. L. et al., 2018) estimated for the Pacific–Antarctic MORB. The corresponding model curves also show

a very good fit to the primary melt Cu concentrations with 170–200 μg g^{-1} S and 30 (or 24) μg g^{-1} Cu in the source (Fig. S5b and c). The same parameters are then used for the modelling of Se and Te behavior during partial melting and estimation of the Pacific mantle composition (Fig. S6 and Main Text Fig. 8 and 9).

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Supplementary Table Captions

Table. S1 Selenium isotope analysis of MH-495 (inter-laboratory standard solution; 30 ng mL^{-1} Se) during the course of this study.

Table. S2 Compilation of trace element concentrations analyzed in this study (solution iQAP-Qc quadrupole ICP-MS) together with the major/trace element and radiogenic/stable isotope composition in the literature for the studied PAR glasses.

Table. S3 Trace element concentrations of BHVO-2 (USGS reference material) analyzed in this study as a quality control standard.

Supplementary Figure Captions

Fig. S1. Map showing the location of the studied MORB samples from the Pacific–Antarctic ridge (PAR; 65–56°S (n = 10) and 53–41°S (n = 17)). Also shown are the major fracture zones in the southern and northern ridge sections (Vlastélic et al., 2000; Hamelin et al., 2010). The map is generated using the GeoMapApp (http://www.geomapapp.org; and references therein).

Fig. S2. Primitive mantle-normalized (McDonough and Sun, 1995) trace element diagram of the studied PAR MORBs. The element order (with increasing compatibility to the right) is after Hofmann (1988) and Jenner et al. (2012). All samples show typical depleted MORB patterns similar to that of the average N-MORB from Gale et al. (2013). Three most evolved samples (blue line) that have experienced magnetite saturation and magnetite-triggered sulfide precipitation (Fig. S3; Main Text Fig. 4 and 6) display abrupt drops in apparently compatible elements Zn, Ga, Ti, V, Sc, and Co due to their strong partitioning into fractionating magnetite and/or sulfide (Nielsen et al., 1994; Toplis and Corgne, 2002; Righter et al., 2006; Dare et al., 2012, 2014; Labidi et al., 2014; Jenner et al., 2010, 2012, 2015).

Fig. S3. Major element variation diagrams versus MgO for all the PAR on-axis samples (between 65–56°S and 53–41°S; Electronic Annex 2 Table S1) as well as the modelled liquid lines of descents (LLDs). The TiO_2 data (a) for the studied glasses are obtained in this study together with other trace elements. All other data along the studied ridge segments are reported by Vlastélic et al. (2000) and Hamelin et al. (2010). The differentiation trends (isobaric fractional crystallization) are modelled with alphaMELTS front end (V 1.8; Ghiorso and Sack, 1995; Smith and Asimow, 2005) along a buffered fO_2 of 0.18 log units below the FMQ buffer (Zhang H. L. et al., 2018) at a variety of pressures (2, 3, 4, 5 and 7 kbar), starting from the most primitive glass PAC1 DR12-1g (8.85 wt.% MgO). Each tick mark indicates 10% crystal fractionation step. Before the magnetite saturation at ~5 wt.% MgO (Vlastélic et al., 2000; Hamelin et al., 2010; Labidi et al., 2014), most major element variations broadly follow the modelled LLDs at 2–5 kbar. The variation of FeO_T is best reproduced at 3 kbar, and the resulting parameters are used in the subsequent modelling in Main Text Fig. 6.

Fig. S4. Primitive mantle-normalized (McDonough and Sun, 1995) incompatible trace element pattern for the model PAR primary magmas (n = 24; at Mg# = 0.73) which were obtained after correcting the observed concentrations for fractional crystallization (see the text for details). Three samples (MgO <5 wt.%) that have experienced magnetite saturation were not included (Fig. S2 and S3 and Main Text Fig. 4). The curves show the best-matched primary melt composition obtained from (1) simple batch melting using average F_B (~8.5%) of the samples, which was first obtained by solving the batch melting equation for F_B for each sample (Eq. 5; following the approach of Kelley et al. (2006)) and (2) pMELTS (near-fractional melting) for the aggregate melts over the entire triangular melting region (F_B: 6.5, 8.0, and 9.5%). The source trace element compositions and empirical bulk partition coefficients were taken from Salters and Stracke (2004) and Kelley et al. (2006),

respectively. Both results are in excellent agreement with each other and used for modelling the Se–Te (additionally S–Cu) behavior during partial melting (Fig. S5 and 6; Main Text Fig. 8).

Fig. S5. Variations of S (a) and Cu (b) concentrations of the primary PAR melts with their average degree of melting (F_B; estimated by batch melting equation Eq. 5 using incompatible trace element systematics; ~6.6–11.7%). The S and Cu concentrations were corrected for sulfide + crystal fractionation by the same approach used for Se and Te concentrations (see Main Text Section 5.2.2 for details). The vertical and horizontal shaded field represent the range of F_B (6.5–9.5%; estimated from the forward modelling (near-fractional melting; pMLETS); also see Fig. S4) and average primary melt composition (874 ± 48 μg g^{-1} S and 68 ± 5 μg g^{-1} Cu), respectively. Superimposed are modelled S and Cu contents of the primary melt during a near-fractional melting of a depleted MORB mantle in a triangular melting regime (e.g., Rehkämper et al., 1999; Lissner et al., 2014; Brenan, 2015). The major element concentrations, mineral modes, and P–T parameters were obtained from the pMELTS modelling (see Main Text Fig. 7) and used for calculating the SCSS of the silicate melts (Smythe et al., 2017) and D_{Cu}^{bulk}. Three different equilibrium BMS compositions were used to calculate the SCSS (Smythe et al., 2017) of the partial melts (see Section S2 for details). A range of source S contents (150–200 μg g^{-1}) are used for the PAR MORB source mantle according to previous estimates for the primitive and depleted upper mantle (e.g., Luguet et al., 2003; Lorand et al., 2013; Lorand and Luguet, 2016; Bézos et al., 2005; Wang and Becker, 2013; Nielsen et al., 2014; Palme and O'Neill, 2014). The source Cu concentration used here (30 ± 6 μg g^{-1}) has been suggested for both the PM (Wang and Becker, 2015b) and depleted MORB mantle (Salters and Stracke, 2004). $D_{Cu}^{cryst-sil}$ (silicate minerals include olivine, orthopyroxene, clinopyroxene, and spinel) from Lee et al. (2009) and $D_{Cu}^{sulf\,liq-sil} = 1000$ from Li and Audétat (2012). The $D_{Cu}^{sulf\,liq-sil}$ value was used by Ding and Dasgupta (2017) and Wang and Becker (2015) for modelling the behavior of Cu during melting. It shows that our modelled S variation using the SCSS model of Smythe et al. (2017) combined with equilibrium sulfide B ($X_{Fe} = 0.54$; $\frac{Ni}{Ni+Fe} = 0.42$) successfully reproduces the primary melt S contents with 150–200 μg g^{-1} S in the mantle source (a); meanwhile, the model curves also perfectly match the Cu contents with 170–200 μg g^{-1} S (b and c; also see the light yellow shaded area in c). Additionally shown in (b) and (c) is the modelled Cu content with 24 μg g^{-1} Cu (previously used in the model of Ding and Dasgupta (2017)) and 180 μg g^{-1} S (dashed black line), in accordance with the source S content used for modelling the Se–Te variation during melting shown in Fig. S6 and Main Text Fig. 8 and 9.

Fig. S6. Variations of Se (a) and Te (b) contents and Se/Te ratios (c) of the primary PAR melts with their average degree of melting (F_B). Here, it shows the effect of varying proportions of sulfide phases (i.e., sulfide liquid and crystalline MSS; assuming congruent melting) in the source with 180 μg g^{-1} S. See Main Text Fig. 8 for details of the modelling parameters when the source has only sulfide liquid (e.g., different S–Se–Te contents of the mantle source). The grey shaded areas have the same meaning as in Main Text Fig. 8. $D_{Se\,or\,Te}^{sulf\,liq-sil}$ values are either calculated following Brenan (2015) at each incremental melt (black lines) or taken from Kiseeva et al. (2017)

(red lines; $D_{Se}^{sulf\,liq-sil}$ = 850 and $D_{Te}^{sulf\,liq-sil}$ = 3800) considering the FeO content of the melt increments (also see Section S1 for the difference of $D_{Se\,or\,Te}^{sulf\,liq-sil}$ values between these studies). $D_{Se}^{MSS-sil}$ = 883 and $D_{Te}^{MSS-sil}$ = 729 (both constant) from Brenan (2015). It shows that the Se–Te fractionation during entire F_B interval is limited if MSS is the only residual sulfide due to the similar $D_{Se\,or\,Te}^{MSS-sil}$ values (also see Main Text Fig. 9; Brenan, 2015). Sulfide liquid is required to be the dominant (>50%), if not only, residual sulfide phase in order to account for the observed Se–Te variations of the primary MORB melts based on the relative partitioning of these elements in sulfide liquid and crystalline MSS (see Main Text for discussion).

PAR MORB (n = 27)

PAR MORB after magnetite saturation (n = 3)

Average N-MORB (± 1 s.d.; Gale et al., 2013)

(a) Average F_B (pMELTS)

S (μg g^{-1})

1350
1200
1050
900
750
600

Average primary melt composition

200 μg g^{-1} S
180 μg g^{-1} S
170 μg g^{-1} S
150 μg g^{-1} S

200 μg g^{-1} S
170 μg g^{-1} S
150 μg g^{-1} S
150 μg g^{-1} S
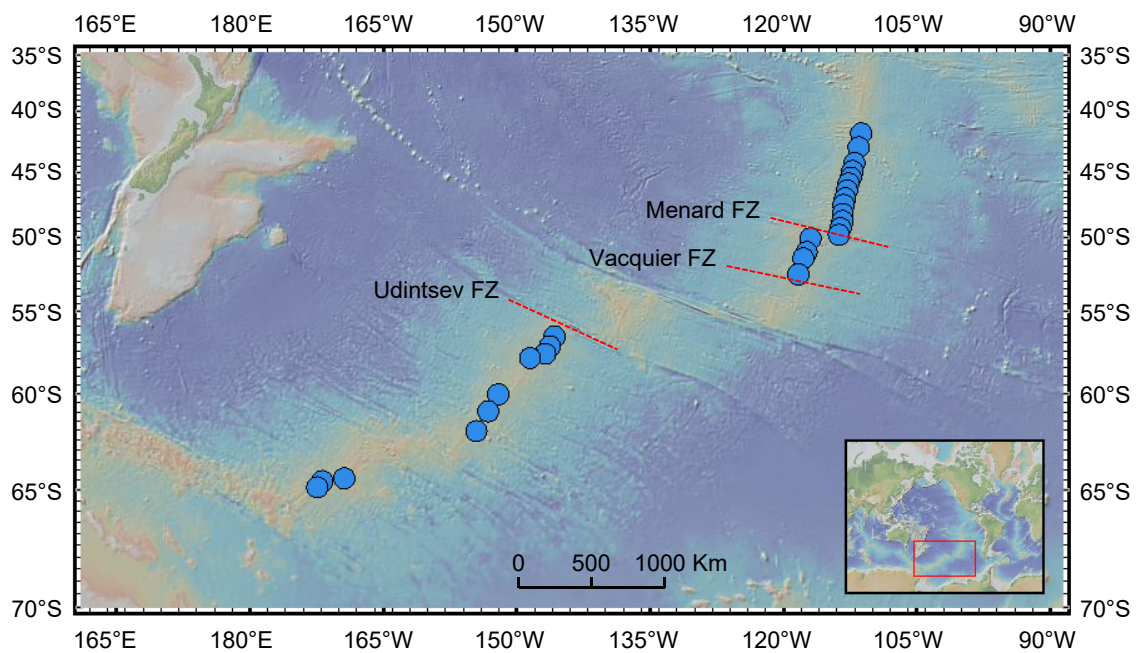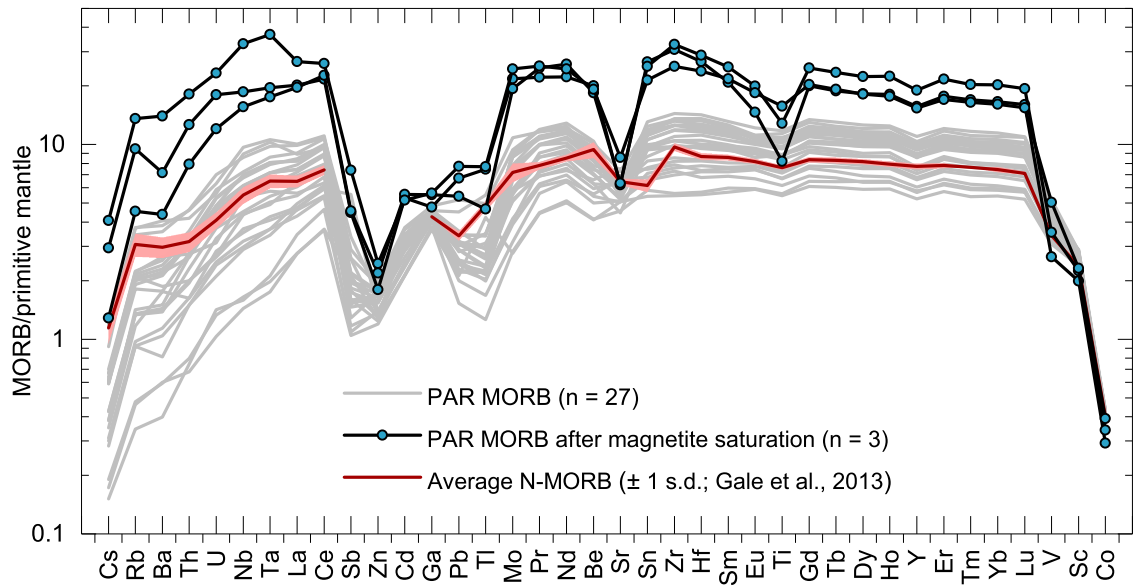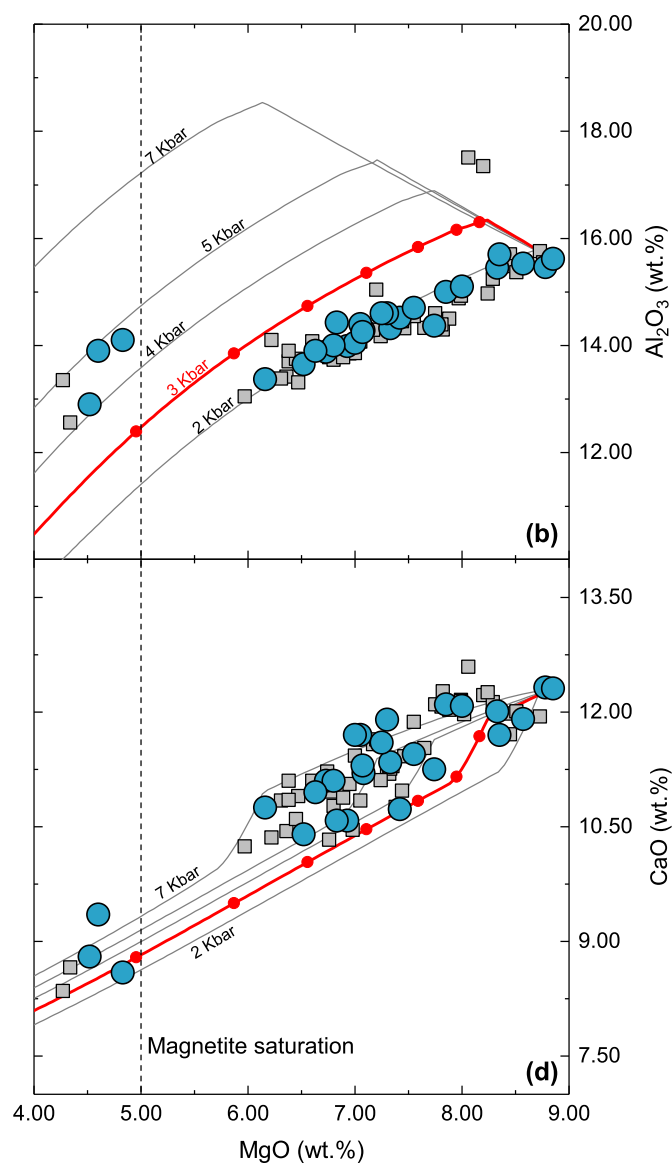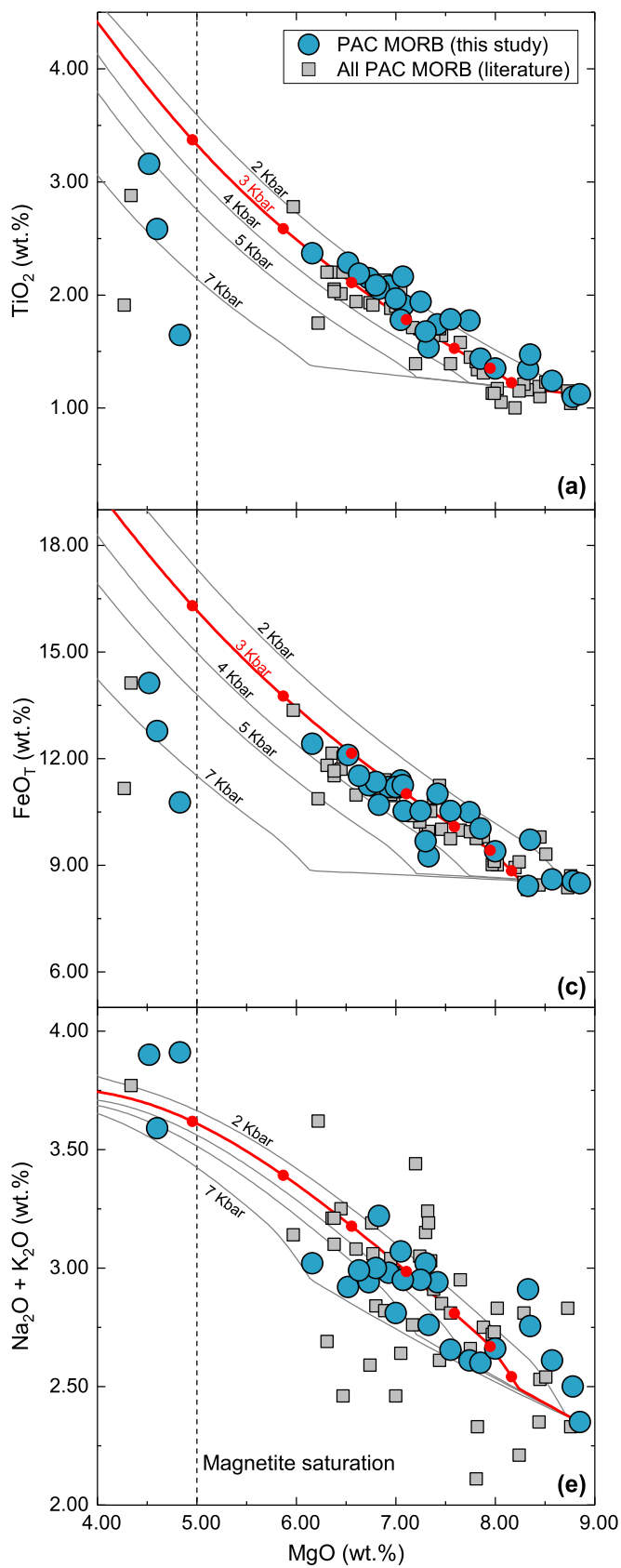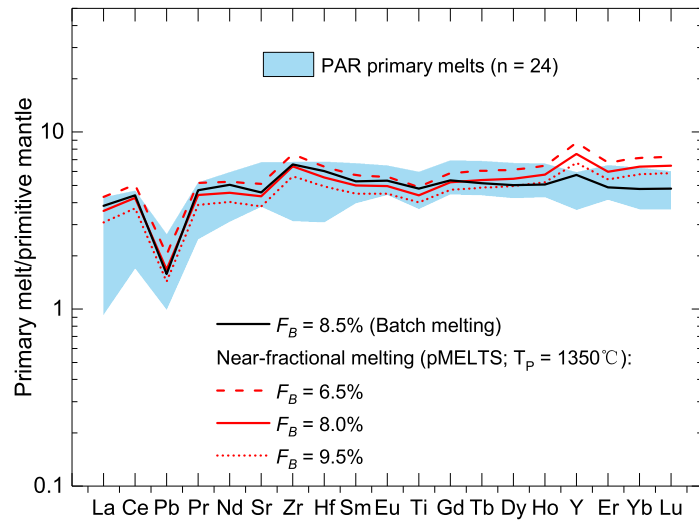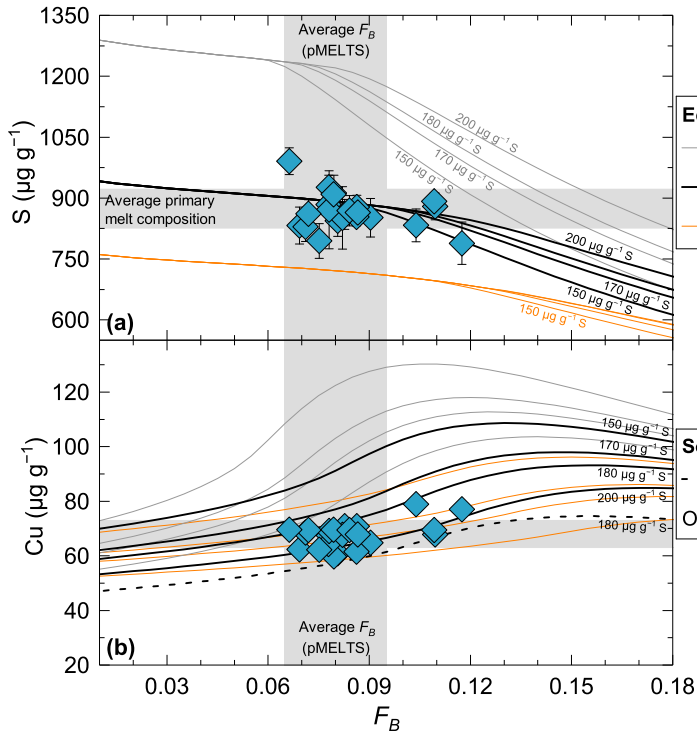
Equilibrium mantle sulfide:

A (Fe$_{0.69}$Ni$_{0.23}$Cu$_{0.01}$S$_{1.00}$)

B (Fe$_{0.50}$Ni$_{0.36}$Cu$_{0.07}$S$_{1.00}$)

C (Fe$_{0.41}$Ni$_{0.46}$Cu$_{0.07}$S$_{1.00}$)

Increasing $X_{Ni}/(X_{Ni} + X_{Fe})$
Decreasing X_{Fe}
Decreasing SCSS

(b)

Cu (μg g^{-1})

120
100
80
60
40
20

150 μg g^{-1} S
170 μg g^{-1} S
180 μg g^{-1} S
200 μg g^{-1} S
180 μg g^{-1} S

Average F_B (pMELTS)

Source Cu content:

24 μg g^{-1} } Salters & Stracke (2004)
Others: 30 μg g^{-1} } Wang & Becker (2015b)

0.03   0.06   0.09   0.12   0.15   0.18

F_B

(c)

Cu (μg g^{-1})

105
90
75
60
45

170–200 μg g^{-1} S and 30 μg g^{-1} Cu

180 μg g^{-1} S

180 μg g^{-1} S

600   750   900   1050

S (μg g^{-1})

Average F_B
(pMELTS)

100% MSS

90% MSS

50% sulf liq

75% sulf liq

100% sulf liq

100% sulf liq

Average primary
melt composition

Source composition:
80 ng g^{-1} Se, 11.0 ng g^{-1} Te
("fertile lherzolite"; Wang & Becker, 2013)
48 ng g^{-1} Se; 3.5 ng g^{-1} Te
(This study)

$D^{sulf\ liq-sil}_{Se\ or\ Te}$:
Changing with FeO
(Brenan, 2015)
Constant
(Kiseeva et al., 2017)

$D^{MSS-sil}_{Se\ or\ Te}$:
Constant
(Brenan, 2015)

Se (ng g^{-1})

400
300
200
100

(a)

Te (ng g^{-1})

40
20
10
4
2

100% MSS

90% MSS

50% sulf liq

75% sulf liq

100% sulf liq

100% sulf liq

(b)

Se/Te

75
60
45
30
15
0

100% sulf liq

75% sulf liq

50% sulf liq

90% MSS

Lherzolites

100% MSS

Average F_B
(pMELTS)

Average primary
melt composition

100% sulf liq

(c)

F_B

0.03   0.06   0.09   0.12   0.15   0.18

Supplementary Table S1

Selenium isotope analysis of MH-495 (inter-laboratory standard solution; 30 ng mL^{-1} Se) during the course of this study.

$\delta^{82/76}$Se (‰)	2 s.c. (‰)[a]
-3.20	0.04
-3.19	0.05
-3.27	0.05
-3.24	0.04
-3.22	0.06
-3.28	0.05
-3.26	0.05
-3.21	0.05
-3.17	0.07
-3.24	0.05
-3.24	0.05
-3.29	0.04
-3.25	0.06
-3.28	0.05
-3.25	0.06
-3.28	0.04
-3.17	0.05
-3.28	0.05
-3.24	0.05
-3.23	0.05

Average[b] **-3.24 ± 0.07**

Kurzawa et al. (2017)[b] -3.27 ± 0.13 (n = 100) (15 ng mL^{-1} Se)
-3.24 ± 0.10 (n = 46) (15 ng mL^{-1} Se)

Yierpan et al. (2018)[b] -3.26 ± 0.06 (n = 32) (30 ng mL^{-1} Se)

[a] Internal uncertainty of each individual measurement (40 cycles) given in 2 standard error.

[b] Uncertainty on the average given in 2 standard deviation.

References:

Kurzawa T., König S., Labidi J., Yierpan A. and Schoenberg R. (2017). A method for Se isotope analysis of low ng-level geological samples via double spike and hydride generation MC-ICP-MS. Chemical Geology, **466**, 219-228.
Yierpan A., König S., Labidi J., Kurzawa T., Babechuk M. G. and Schoenberg R. (2018). Chemical Sample Processing for Combined Selenium Isotope and Selenium-Tellurium Elemental Investigation of the Earth's Igneous Reservoirs. Geochemistry, Geophysics, Geosystems, **19**, 516-533.

Supplementary Table S2

Compilation of trace element concentrations analyzed in this study (solution iQAP-Qc quadrupole ICP-MS) together with the

Sample	Latitude (°S)	Longitude (°W)	Dredging Depth (m)	Major elements[a] (wt. %)	SiO$_2$	TiO$_2$	Al$_2$O$_3$	FeO$_T$	MnO	MgO	CaO
PAC1 CV02-g	*64.83*	*172.43*	*2936*		*50.8*	*1.77*	*14.4*	*10.5*	*0.19*	*7.74*	*11.3*
PAC1 CV03-g	*64.53*	*171.88*	*2576*		*50.7*	*1.24*	*15.5*	*8.60*	*0.16*	*8.57*	*11.9*
PAC1 CV04-g	*64.40*	*169.40*	*2340*		*50.3*	*1.10*	*15.5*	*8.55*	*0.16*	*8.78*	*12.3*
PAC1 DR05-1g	*62.00*	*154.54*	*2344*		*51.0*	*1.34*	*15.5*	*8.42*	*0.15*	*8.33*	*12.0*
PAC1 DR06-g	*60.94*	*153.21*	*2527*		*51.0*	*2.08*	*14.0*	*11.2*	*0.20*	*6.93*	*10.6*
PAC1 DR07-1g	*60.00*	*152.08*	*2362*		*50.8*	*2.05*	*14.4*	*10.7*	*0.22*	*6.83*	*10.6*
PAC1 DR10-1g	*57.89*	*148.50*	*2319*		*53.8*	*1.65*	*14.1*	*10.8*	*0.21*	*4.83*	*8.59*
PAC1 DR11-1g	*57.63*	*146.80*	*2500*		*50.2*	*1.53*	*14.3*	*9.25*	*0.17*	*7.33*	*11.3*
PAC1 DR12-1g	*57.18*	*146.29*	*2539*		*50.9*	*1.12*	*15.6*	*8.49*	*0.15*	*8.85*	*12.3*
PAC1 DR13-2g	*56.57*	*145.74*	*2674*		*50.5*	*1.74*	*14.5*	*11.0*	*0.19*	*7.42*	*10.7*
PAC2 DR01-1	*52.53*	*118.35*	*2323*		*50.2*	*1.68*	*14.6*	*9.67*	*0.18*	*7.30*	*11.9*
PAC2 DR04-2	*51.43*	*117.78*	*2409*		*50.4*	*1.91*	*14.3*	*10.5*	*0.20*	*7.08*	*11.2*
PAC2 DR05-2g	*50.98*	*117.40*	*2784*		*49.9*	*2.28*	*13.7*	*12.1*	*0.22*	*6.52*	*10.4*
PAC2 DR08-1	*49.99*	*116.97*	*2221*		*49.4*	*1.78*	*14.4*	*11.4*	*0.20*	*7.05*	*11.7*
PAC2 DR20-1	*49.73*	*113.78*	*2441*		*51.2*	*2.58*	*13.9*	*12.8*	*0.24*	*4.60*	*9.35*
PAC2 DR21-2	*49.26*	*113.60*	*2339*		*50.3*	*2.15*	*13.9*	*11.2*	*0.21*	*6.73*	*11.1*
PAC2 DR22-1	*48.73*	*113.37*	*2413*		*49.9*	*1.94*	*14.6*	*10.5*	*0.20*	*7.25*	*11.6*
PAC2 DR27-1	*48.18*	*113.34*	*2359*		*49.8*	*3.16*	*12.9*	*14.1*	*0.26*	*4.52*	*8.80*
PAC2 DR28-2	*47.51*	*113.25*	*2489*		*49.7*	*1.44*	*15.0*	*10.0*	*0.19*	*7.85*	*12.1*
PAC2 DR29-1	*47.01*	*113.09*	*2407*		*49.9*	*2.37*	*13.4*	*12.4*	*0.23*	*6.16*	*10.8*
PAC2 DR30-1	*46.40*	*112.87*	*2345*		*50.0*	*1.97*	*14.1*	*11.2*	*0.21*	*7.00*	*11.7*
PAC2 DR31-3	*45.85*	*112.69*	*2414*		*49.9*	*1.78*	*14.7*	*10.5*	*0.19*	*7.55*	*11.5*
PAC2 DR32-1	*45.39*	*112.43*	*2384*		*50.5*	*2.08*	*14.0*	*11.3*	*0.21*	*6.80*	*11.1*
PAC2 DR33-1	*44.87*	*112.25*	*2374*		*50.2*	*2.19*	*13.9*	*11.5*	*0.21*	*6.63*	*11.0*
PAC2 DR34-1	*44.24*	*112.04*	*2467*		*50.0*	*1.35*	*15.1*	*9.39*	*0.18*	*8.00*	*12.1*
PAC2 DR36-1	*42.95*	*111.56*	*2503*		*49.6*	*2.16*	*14.3*	*11.2*	*0.20*	*7.07*	*11.3*
PAC2 DR38-1	*41.80*	*111.27*	*2524*		*49.1*	*1.47*	*15.7*	*9.72*	*0.18*	*8.35*	*11.7*

Note: All literature data are shown in italics.

[a] From Vlastélic et al. (2000) and Hamelin et al. (2010).

[b] Literature trace element data are mostly from Vlastelic et al. (2000) and Hamelin et al. (2010); Cu, S and Cl data from Labidi et al. (2014); Mo data fro

[c] Uncertainties (Li to U) are estimated using relative standard deviations (r.s.d.) from 14 analyses of 6 BHVO-2 digestions (4 digested together with the

[d] From Labidi et al. (2014).

[e] From Vlastélic et al. (2000), Moreira et al. (2008) and Hamelin et al. (2010, 2011).

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major/trace element and radiogenic/stable isotope composition in the literature for the studied PAR glasses.

Na$_2$O	K$_2$O	P$_2$O$_5$	Trace elements[b] (µg g^{-1})	Li	Be	Sc	Ti	V		Cr
			Uncertainty[c] (%)	1	2	1	2	1		1
2.55	0.06			7.02	0.43	42	10632	358	334	272
2.53	0.08			4.88	0.38	38	7428	261	255	413
2.46	0.04			4.69	0.28	39	6585	252	251	377
2.82	0.09			5.29	0.45	42	8041	267	243	400
2.86	0.12			7.89	0.60	41	12451	375	366	232
3.03	0.19			6.76	0.69	40	12308	354	344	143
3.43	0.48			11.63	1.36	32	9863	217	227	106
2.70	0.06			6.18	0.43	47	9199	333	294	334
2.32	0.03			5.16	0.28	38	6720	270	248	409
2.85	0.09			7.03	0.47	41	10433	325	309	219
2.82	0.20	0.17		5.56	0.50	44	10050	310		289
2.83	0.12	0.18		7.39	0.52	43	11451	343		224
2.74	0.18	0.24		8.45	0.62	42	13690	391		163
2.87	0.20	0.17		6.31	0.53	44	10660	323		207
3.34	0.25	0.42		11.16	1.25	36	15485	290		58
2.79	0.15	0.18		7.46	0.59	46	12873	375		134
2.78	0.17	0.18		6.96	0.57	44	11625	359		263
3.37	0.53	0.46		11.40	1.30	38	18926	414		18
2.52	0.08	0.12		5.91	0.37	45	8601	308		335
2.83	0.19	0.23		8.53	0.71	46	14192	427		94
2.64	0.17	0.20		7.19	0.56	45	11799	371		251
2.56	0.10	0.18		6.72	0.48	42	10688	351		320
2.84	0.16	0.21		7.37	0.63	46	12493	389		175
2.84	0.15	0.22		7.70	0.66	46	13113	401		135
2.60	0.06	0.12		5.82	0.34	42	8091	294		340
2.80	0.15	0.21		7.58	0.64	45	12952	385		298
2.67	0.09	0.14		5.54	0.40	40	8824	285		322

m Bezard et al. (2016). Ce data for PAC1 samples are from Clog et al. (201
PAR samples; see Table S3

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and statistical techniques. Earth and Planetary Science Letter **302**(1-2), 154-162.

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Co	Ni	Cu		Zn	Ga	Rb	Sr		Y	
1	1	1		4	1	1	1		1	
44	100	56	*57*	92	17	0.55	89		38	*37*
41	123	65	*72*	68	15	0.81	132		25	*24*
42	110	70	*85*	66	15	0.29	101		23	*23*
42	91	77	*85*	72	16	1.33	149		26	*25*
43	77	50	*57*	100	19	1.09	107		43	*42*
41	62	61	*69*	93	18	2.06	145		41	*40*
31	29	49	*68*	99	19	5.70	124		67	*71*
45	75	74	*76*	85	17	0.70	122		32	*29*
43	128	70	*82*	70	15	0.28	91		24	*24*
45	92	59	*64*	95	17	1.25	106		37	*35*
40	67	67	*82*	74	17	1.20	137	*144*	32	*39*
42	73	55	*65*	86	17	0.81	114	*116*	38	*43*
42	63	47	*66*	104	18	2.24	113	*115*	45	*50*
42	60	67	*88*	85	17	2.23	145	*142*	33	*36*
36	30	40	*52*	120	22	2.72	126	*137*	82	*89*
44	54	59	*62*	94	18	1.25	122	*123*	41	*44*
43	79	63	*76*	85	18	1.15	127	*122*	39	*43*
41	21	39	*29*	135	23	8.15	170	*164*	66	*72*
45	86	77	*93*	77	17	0.55	101	*103*	30	*32*
45	48	55	*71*	108	19	1.34	119	*117*	47	*51*
43	74	60	*69*	90	18	1.20	115	*119*	40	*45*
44	98	64	*73*	85	17	0.80	104	*102*	37	*41*
43	63	59	*66*	95	18	1.29	132	*138*	40	*45*
43	57	56	*63*	97	18	1.24	131	*130*	42	*47*
43	105	70	*74*	75	16	0.21	102	*93*	28	*32*
43	72	60	*67*	94	18	0.85	124	*124*	43	*49*
46	124	68	*67*	75	16	0.58	127	*131*	29	*33*

Zr		Nb		Mo		Cd	Sn	Sb	Cs	Ba
2		1		15		1	2	10	1	1
101	*105*	1.90	*2.13*	0.20		0.12	1.22	0.009	0.006	5.36
76	*77*	2.42	*2.21*	0.19	*0.18*	0.09	0.88	0.009	0.009	9.49
57	*64*	1.08	*1.03*	0.14		0.08	0.70	0.006	0.004	3.92
82	*86*	3.54	*3.43*	0.26		0.10	0.97	0.010	0.015	17.46
132	*140*	3.57	*3.65*	0.38		0.13	1.53	0.011	0.012	11.65
141	*148*	5.64	*5.77*	0.54		0.14	1.61	0.019	0.025	23.53
323	*355*	12.26	*13.62*	1.09		0.21	3.45	0.025	0.062	47.21
90	*89*	2.09	*1.93*	0.26	*0.19*	0.11	1.07	0.008	0.007	11.58
59	*62*	0.95	*0.82*	0.14		0.08	0.76	0.012	0.004	3.97
102	*107*	2.86	*2.86*	0.28	*0.26*	0.11	1.25	0.007	0.013	12.30
104	*112*	3.76	*3.74*	0.33	*0.32*	0.12	1.13	0.014	0.013	14.54
115	*120*	2.90	*3.13*	0.28		0.12	1.27	0.009	0.009	9.27
142	*153*	6.38	*6.83*	0.45		0.15	1.53	0.014	0.024	25.32
109	*116*	5.89	*6.03*	0.36		0.12	1.30	0.010	0.019	26.74
342	*305*	10.28	*10.70*	0.97	*0.80*	0.22	3.27	0.025	0.027	28.83
131	*139*	4.60	*4.92*	0.39		0.13	1.45	0.008	0.012	15.16
124	*128*	4.05	*4.28*	0.37	*0.46*	0.13	1.38	0.011	0.013	13.98
265	*279*	21.66	*22.42*	1.22	*1.19*	0.21	2.79	0.041	0.085	92.44
80	*83*	1.96	*2.36*	0.21		0.10	0.92	0.006	0.006	6.87
152	*161*	4.77	*5.12*	0.47		0.15	1.70	0.016	0.014	16.79
125	*133*	4.04	*4.40*	0.37		0.13	1.38	0.010	0.013	14.64
110	*117*	2.98	*3.15*	0.30	*0.28*	0.11	1.25	0.009	0.008	9.13
132	*138*	4.52	*4.61*	0.43		0.14	1.48	0.012	0.014	15.84
139	*145*	4.44	*4.79*	0.43		0.14	1.54	0.012	0.013	14.13
73	*77*	1.05	*1.17*	0.16		0.09	0.85	0.006	0.003	2.63
140	*149*	3.87	*4.23*	0.45	*0.39*	0.14	1.55	0.011	0.008	9.90
86	*91*	2.32	*2.32*	0.29	*0.23*	0.10	0.99	0.030	0.007	7.52

La		Ce		Pr		Nd		Sm		Eu
1		1		1		1		1		2
3.00	*3.01*	10.27	*10.5*	1.88		10.55		3.83	*4.03*	1.32
2.98	*2.88*	9.14	*8.7*	1.55		8.20		2.78	*2.83*	1.03
1.79	*1.97*	6.08	*6.3*	1.12		6.28		2.31	*2.51*	0.91
3.64	*3.77*	10.61		1.75		9.20		3.05	*3.08*	1.15
4.68	*4.58*	14.65	*5.2*	2.54		13.66		4.64	*4.67*	1.58
6.42	*6.11*	18.08	*10.5*	2.94		15.09		4.86	*5.02*	1.64
13.05	*14.27*	36.30	*39.6*	5.62		27.84		8.48	*9.50*	2.25
3.22	*3.11*	10.30	*9.6*	1.83		9.95		3.48	*3.45*	1.27
1.78	*1.87*	6.17	*6.0*	1.14		6.42		2.42	*2.58*	0.91
3.54	*3.79*	11.42	*11.1*	2.02		11.10		3.92	*3.92*	1.39
4.49	*4.94*	13.29	*14.4*	2.19	*2.22*	11.38	*12.32*	3.78	*3.94*	1.38
4.16	*3.98*	13.15	*12.8*	2.30	*2.14*	12.34	*11.94*	4.27	*4.13*	1.54
6.50	*6.37*	18.58	*17.6*	3.02	*2.82*	15.52	*15.10*	5.12	*4.89*	1.72
5.77	*5.57*	16.05	*15.8*	2.53	*2.41*	12.76	*12.29*	4.00	*3.87*	1.47
12.72	*11.92*	38.04	*34.2*	6.27	*5.69*	32.38	*28.95*	10.16	*9.29*	3.07
5.34	*4.64*	16.31	*14.0*	2.78	*2.32*	14.63	*12.61*	4.82	*4.41*	1.71
4.81	*4.81*	14.84	*14.6*	2.54	*2.41*	13.33	*12.94*	4.46	*4.42*	1.58
17.27	*16.13*	43.61	*40.3*	6.41	*5.87*	30.53	*28.60*	8.82	*8.49*	2.84
2.78	*2.77*	8.98	*8.6*	1.59	*1.50*	8.73	*8.40*	3.10	*3.02*	1.19
5.86	*5.61*	17.94	*17.1*	3.04	*2.79*	16.12	*14.87*	5.33	*5.14*	1.87
4.84	*4.79*	14.97	*14.9*	2.53	*2.43*	13.45	*13.16*	4.55	*4.51*	1.59
3.93	*3.91*	12.55	*12.7*	2.19	*2.09*	11.73	*11.46*	4.05	*4.00*	1.43
5.33	*5.26*	16.21	*16.2*	2.71	*2.68*	14.24	*14.33*	4.72	*4.77*	1.67
5.48	*5.44*	16.79	*16.2*	2.81	*2.70*	14.70	*14.32*	4.85	*4.83*	1.70
2.23	*2.27*	7.76	*8.1*	1.42	*1.43*	8.04	*8.24*	2.93	*3.03*	1.14
5.09	*5.15*	16.13	*16.2*	2.77	*2.75*	14.78	*14.80*	4.97	*4.99*	1.71
3.07	*3.14*	9.89	*10.2*	1.74	*1.74*	9.44	*9.64*	3.26	*3.34*	1.23

	Gd			Tb		Dy		Ho		Er	
	1			1		2		1		1	
	5.54			0.99		6.59		1.47		4.23	
	3.75			0.67		4.31		0.95		2.72	
	3.31			0.60		3.96		0.88		2.51	
	4.10			0.72		4.65		1.02		2.91	
	6.36			1.12		7.37		1.62		4.61	
	6.40			1.13		7.31		1.61		4.57	
	10.87			1.87		12.29		2.70		7.74	
	4.95			0.87		5.84		1.29		3.67	
	3.52			0.64		4.36		0.96		2.77	
	5.68			1.02		6.77		1.52		4.33	
1.56	5.11	*5.00*	0.90	*0.93*	5.88	*6.22*	1.29	*1.32*	3.70	*3.71*
1.54	6.02	*5.63*	1.06	*1.03*	7.03	*6.89*	1.56	*1.51*	4.44	*4.33*
1.74	7.08	*6.57*	1.23	*1.20*	8.15	*8.03*	1.81	*1.76*	5.14	*5.07*
1.38	5.31	*5.01*	0.93	*0.90*	6.07	*5.96*	1.35	*1.30*	3.81	*3.69*
2.78	13.46	*11.64*	2.32	*2.11*	15.04	*14.10*	3.34	*3.08*	9.50	*8.82*
1.60	6.68	*5.73*	1.18	*1.04*	7.65	*7.13*	1.72	*1.57*	4.85	*4.50*
1.55	5.95	*5.64*	1.05	*1.02*	6.91	*6.81*	1.52	*1.50*	4.32	*4.29*
2.65	11.06	*10.50*	1.90	*1.82*	12.24	*11.81*	2.63	*2.54*	7.47	*7.23*
1.19	4.47	*3.97*	0.81	*0.77*	5.43	*5.40*	1.20	*1.13*	3.48	*3.30*
1.78	7.32	*6.83*	1.29	*1.26*	8.48	*8.26*	1.86	*1.78*	5.29	*5.21*
1.60	6.16	*6.16*	1.10	*1.11*	7.24	*7.31*	1.60	*1.60*	4.53	*4.62*
1.42	5.59	*5.38*	0.99	*0.99*	6.58	*6.65*	1.45	*1.43*	4.13	*4.20*
1.70	6.30	*6.19*	1.12	*1.13*	7.30	*7.52*	1.61	*1.59*	4.54	*4.58*
1.70	6.49	*6.21*	1.15	*1.13*	7.50	*7.59*	1.66	*1.64*	4.70	*4.85*
1.19	4.22	*4.12*	0.76	*0.78*	5.06	*5.21*	1.12	*1.14*	3.18	*3.28*
1.74	6.75	*6.58*	1.19	*1.21*	7.85	*7.97*	1.73	*1.71*	4.90	*4.87*
1.29	4.47	*4.41*	0.80	*0.82*	5.26	*5.41*	1.15	*1.17*	3.29	*3.37*

Tm	Yb		Lu		Hf		Ta		W	Tl
2	2		2		3		2		20	8
0.63	4.09		0.60		2.74		0.13		0.11	0.007
0.40	2.57		0.38		1.92		0.15		0.09	0.007
0.37	2.39		0.35		1.56		0.07		0.09	0.015
0.42	2.70		0.40		2.08		0.21		0.11	0.008
0.69	4.38		0.65		3.37		0.23		0.09	0.009
0.66	4.25		0.63		3.53		0.36		0.12	0.019
1.15	7.32		1.08		7.53		0.72		0.14	0.026
0.54	3.45		0.51		2.36		0.14		0.06	0.009
0.41	2.61		0.39		1.61		0.06		0.08	0.004
0.64	4.12		0.60		2.78		0.19		0.06	0.008
0.55	3.48	*3.72*	0.51	*0.50*	2.70	*2.89*	0.24		0.04	0.008
0.67	4.18	*4.10*	0.63	*0.60*	3.16	*3.23*	0.18	*0.32*	1.17	0.011
0.76	4.84	*4.78*	0.73	*0.69*	3.84	*3.86*	0.39	*0.29*	0.06	0.010
0.55	3.50	*3.49*	0.53	*0.50*	2.85	*2.98*	0.38	*0.52*	0.07	0.008
1.38	8.93	*8.26*	1.31	*1.24*	8.14	*7.87*	0.65	*0.62*	0.15	0.016
0.70	4.53	*4.22*	0.68	*0.63*	3.59	*3.69*	0.30	*0.88*	0.09	0.012
0.64	4.11	*3.98*	0.61	*0.60*	3.29	*3.36*	0.26	*0.41*	0.04	0.010
1.12	7.11	*6.80*	1.04	*0.99*	6.73	*6.66*	1.36	*0.36*	0.23	0.027
0.52	3.31	*3.18*	0.49	*0.48*	2.20	*2.15*	0.14	*1.35*	0.59	0.008
0.79	5.06	*4.85*	0.74	*0.72*	4.03	*4.18*	0.32	*0.15*	0.07	0.017
0.68	4.36	*4.47*	0.64	*0.65*	3.34	*3.55*	0.26	*0.44*	0.10	0.009
0.62	3.97	*3.97*	0.58	*0.57*	2.97	*3.13*	0.20	*0.34*	1.37	0.008
0.67	4.37	*4.29*	0.63	*0.63*	3.48	*3.56*	0.30	*0.27*	0.80	0.012
0.70	4.47	*4.48*	0.65	*0.64*	3.59	*3.75*	0.29	*0.35*	1.23	0.012
0.47	3.02	*3.17*	0.44	*0.45*	2.05	*2.13*	0.08	*0.48*	0.71	0.006
0.73	4.68	*4.71*	0.69	*0.67*	3.75	*3.74*	0.27	*0.10*	1.39	0.010
0.49	3.13	*3.24*	0.46	*0.46*	2.33	*2.40*	0.16	*0.31*	0.02	0.008

Pb		Th		U		(La/Sm)$_N$	Se (ng g^{-1})	1 s.d. (ng g^{-1})	Te (ng g^{-1})
6		5		4					
0.37		0.12		0.04		0.490	180	4	1.99
0.34		0.16		0.05		0.671	158	1	3.19
0.32		0.06		0.03		0.485	176	4	4.10
0.43		0.22		0.06		0.747	167	3	3.06
0.47		0.22		0.09		0.632	177	2	1.61
0.68		0.37		0.14		0.828	186	4	2.23
1.01		1.01		0.37		0.965	170	3	2.68
0.48		0.13		0.05		0.579	174	3	3.06
0.23		0.05		0.02		0.461	165	3	3.70
0.37		0.16		0.06		0.566	194	2	1.95
0.36	*6.51*	0.21	*0.27*	0.09	*0.10*	0.744	166	3	2.45
0.42	*0.46*	0.15	*0.20*	0.07	*0.07*	0.610	168	3	2.33
0.54	*1.35*	0.37	*0.43*	0.13	*0.16*	0.796	176	4	1.43
0.43	*0.63*	0.33	*0.38*	0.11	*0.14*	0.904	194	4	2.76
0.81	*1.04*	0.63	*0.69*	0.24	*0.25*	0.785	193	4	1.68
0.45	*0.60*	0.24	*0.29*	0.10	*0.10*	0.693	198	4	1.97
0.47	*0.51*	0.25	*0.26*	0.10	*0.10*	0.675	187	4	2.47
1.16	*1.31*	1.44	*1.41*	0.47	*0.43*	1.227	219	4	1.16
0.33	*0.34*	0.12	*0.12*	0.05	*0.06*	0.562	174	3	3.32
0.78	*0.59*	0.29	*0.29*	0.12	*0.12*	0.688	210	4	2.07
0.46	*0.47*	0.25	*0.26*	0.10	*0.10*	0.667	195	1	2.21
0.38	*0.44*	0.18	*0.19*	0.08	*0.08*	0.608	193	4	3.17
0.51	*0.62*	0.26	*0.28*	0.11	*0.11*	0.708	186	4	1.97
0.52	*0.53*	0.25	*0.27*	0.11	*0.11*	0.708	199	1	2.20
0.30	*0.42*	0.06	*0.06*	0.03	*0.06*	0.476	168	1	2.63
0.47	*0.49*	0.21	*0.22*	0.09	*0.09*	0.642	194	1	2.26
0.34	*0.61*	0.13	*0.13*	0.06	*0.12*	0.590	180	1	3.12

1 s.d. (ng g^{-1})	S (μg g^{-1})	1 s.d. (ng g^{-1})	Cl (μg g^{-1})	Cl/K	δ$^{82/76}$Se$_{SRM\ 3149}$ (‰)	2 s.d. (‰)	δ^{34}S$_{V-CDT}$ (‰)[d]	1 s.d. (‰)[d]	Radiogenic[d] and stable isotopes
0.06	1171	50	49	0.10	-0.23	0.09	-0.91	0.14	
0.10	938	42	38	0.06	-0.19	0.09	-0.72	0.02	
0.12	940	52	75	0.22	-0.15	0.09	-0.83	0.04	
0.09	932	40	47	0.06	-0.22	0.09	-0.94		
0.05	1351	48	290	0.29	-0.30	0.09	-0.89	0.05	
0.07	1301	33	494	0.31	-0.06	0.09	-0.95	0.01	
0.08	1047	39	2163	0.54	-0.24	0.09	-0.14	0.03	
0.09	1153	44	162	0.32	-0.10	0.09	-0.29	0.03	
0.11	968	26	36	0.14	-0.15	0.09	-0.31	0.01	
0.06	1259	84	75	0.10	-0.21	0.09	-0.65	0.10	
0.07	1116	36	225	0.13	-0.16	0.09	-0.81	0.14	
0.07	1199	24	264	0.26	-0.09	0.09	-0.80		
0.04	1339	47	292	0.19	-0.06	0.09	-0.78	0.04	
0.08	1239	57	266	0.16	-0.15	0.09	-0.77	0.02	
0.05	1550	50	1475	0.71	-0.15	0.09	0.60	0.10	
0.06	1312	105	287	0.23	-0.17	0.09	-0.42	0.03	
0.07	1172	39	281	0.20	-0.22	0.09	-0.83	0.05	
0.03	1755	14	1047	0.24	-0.14	0.09	-0.10	0.08	
0.10	1112	44	223	0.33	-0.15	0.09	-0.80	0.01	
0.06	1471	32	404	0.25	-0.05	0.09	-0.20	0.01	
0.07	1348	21	373	0.26	-0.12	0.09	-0.72		
0.10	1208	37	435	0.52	-0.09	0.09	-1.02	0.01	
0.06	1321	41	335	0.25	-0.10	0.09	-0.70	0.04	
0.05	1340	25	277	0.22	-0.15	0.09	-0.86	0.01	
0.08	1094	22	77	0.15	-0.30	0.09	-0.99	0.30	
0.07	1381	32	514	0.41	-0.13	0.09	-1.11	0.08	
0.09	1244	36	141	0.19	-0.16	0.09	-1.12	0.02	

^{87}Sr/^{86}Sr	^{143}Nd/^{144}Nd	^{176}Hf/^{177}Hf	^{3}He/^{4}He (R/Ra)	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb
0.702568	0.513135	0.283175	7.6	18.395	15.491	37.916
0.702406	0.513117	0.283170		18.497	15.498	38.093
0.702512	0.513144	0.283173	8.1	18.152	15.453	37.596
0.702407	0.513132	0.283168		18.491	15.507	37.998
0.702502	0.513126		8.0	18.504	15.505	37.987
0.702472	0.513099	0.283144		18.632	15.498	38.074
0.702473	0.513112	0.283149		18.435	15.510	37.968
0.702435	0.513125	0.283171		18.401	15.494	37.862
0.702310	0.513150	0.283235		18.015	15.473	37.506
0.702556	0.513142	0.283204	7.6	18.500	15.497	37.966
0.702422	0.513090	0.283133	7.6	18.822	15.547	38.199
0.702367	0.513134	0.283163	7.7	18.531	15.513	37.942
0.702524	0.513098	0.283135	7.5	18.634	15.504	38.024
0.702483	0.513077	0.283132	7.3	18.796	15.550	38.237
0.702493	0.513092	0.283126	7.1	18.749	15.540	38.168
0.702483	0.513088	0.283125	7.1	18.768	15.544	38.189
0.702465	0.513100	0.283131	7.25	18.726	15.539	38.153
0.702643	0.513035	0.283094	6.1	19.174	15.585	38.634
0.702468	0.513070	0.283102	7.1	18.725	15.539	38.121
0.702504	0.513059	0.283117	7.2	18.798	15.538	38.208
0.702472	0.513060	0.283106	6.8	18.887	15.565	38.311
0.702479	0.513066	0.283112	7.3	18.858	15.580	38.300
0.702516	0.513078	0.283100	7.2	18.809	15.539	38.202
0.702488	0.513082	0.283111	7.3	18.817	15.562	38.236
0.702392	0.513108	0.283145	7.3	18.798	15.549	38.234
0.702479	0.513066	0.283119	7.5	18.724	15.538	38.117
0.702465	0.513108	0.283125	7.2	18.671	15.533	38.039

Supplementary Table S3

Trace element concentrations of BHVO-2 (USGS reference material) analyzed in this study as a quality control standard.

Trace elements	Concentration[a] (ng g^{-1})	Uncertainty[b] (%)
Li	4536	1
Be	1019	2
Sc	32716	1
Ti	16994990	2
V	325386	1
Cr	309103	1
Co	45747	1
Ni	119380	1
Cu	125876	1
Zn	100302	4
Ga	21049	1
Rb	9131	1
Sr	397697	1
Y	24508	1
Zr	165858	2
Nb	18450	1
Mo	4114	15
Cd	121	1
Sn	2016	2
Sb	101	10
Cs	96	1
Ba	131906	1
La	15330	1
Ce	37955	1
Pr	5421	1
Nd	24686	1
Sm	6098	1
Eu	2073	2
Gd	6307	1
Tb	944	1
Dy	5308	2
Ho	1012	1
Er	2547	1
Tm	341	2
Yb	1999	2
Lu	278	2
Hf	4302	3
Ta	1151	2
W	229	20
Tl	19	8
Pb	1580	6
Th	1159	5
U	416	4

[a] Average concentration of 14 analyses of 6 separate digestions (4 digested together with PAR glasses).

[b] Expressed as relative standard deviation.