1   **Si-metasomatism in serpentinized peridotite: the effects of talc-alteration**

2   **on strontium and boron isotopes in abyssal serpentinites from Hole 1268a,**

3   **ODP Leg 209**

4

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Abstract

Ultramafic rocks recovered from Hole 1268a, Ocean Drilling Program Leg 209, to the south of the 15° 20' N Fracture Zone on the Mid-Atlantic ridge have experienced a complex history of melt depletion and subsequent interaction with a series of fluids under varying temperature and pH conditions. After intense melt depletion, varying degrees of serpentinization at 100-200 °C took place, initially under seawater-like pH conditions. Subsequently, interaction with a higher temperature (300-350 °C) fluid with low (4-5) pH and low MgO/SiO_2 resulted in the heterogeneous alteration of these serpentinites to talc-bearing ultramafic lithologies. The proximity of the currently active, high temperature Logatchev hydrothermal field, located on the opposite flank of the Mid-Atlantic ridge, suggests that unlike more distal localities sampled during ODP Leg 209, Hole 1268a has experienced Si-metasomatism (i.e. talc-alteration) by a Logatchev-like hydrothermal fluid. Serpentinite strontium isotope ratios were not materially shifted by interaction with the subsequent high-T fluid, despite the likelihood that this fluid had locally interacted with mid-ocean ridge gabbro. $^{87}Sr/^{86}Sr$ in the ultramafic lithologies of Hole 1268a are close to that of seawater (c. 0.709) and even acid leached serpentinites retain $^{87}Sr/^{86}Sr$ in excess of 0.707, indistinguishable from Logatchev hydrothermal fluid. On the other hand, boron isotope ratios appear to have been shifted from seawater-like values in the serpentinites ($\delta^{11}B$ = c. +40 ‰) to much lighter values in talc-altered serpentinites ($\delta^{11}B$ = +9 to +20 ‰). This is likely a consequence of the effects of changing ambient pH and temperature during the mineralogical transition from serpentine to talc. Heterogeneous boron isotope systematics have consequences for the composition of ultramafic portions of the lithosphere returned to the convecting mantle by subduction. Inhomogeneities in $\delta^{11}B$, [B] and mineralogy introduce significant uncertainties in the prediction of the composition of slab fluids released during the early- to mid-stages of subduction.

1. Introduction

Mid-ocean ridges are responsible for the production of modern-day oceanic lithosphere; material that will, along with pelagic sediments, be re-introduced into the mantle at convergent margins. Around a third of the 55,000 km ridge system is thought to have a full spreading rate of less than 25 mm yr^{-1} (Dick et al., 2003; Escartín et al., 2003), with the Mid-Atlantic ridge (MAR; Lagabrielle et al., 1998), the Southwest Indian ridge (e.g. Sauter et al., 2004) and the Gakkel ridge in the Arctic Ocean (e.g. Cochran et al., 2003) all containing slow-spreading ridge segments. These segments are often characterized by thin or absent mafic sections, i.e. they are bereft of an igneous crust. Here, peridotite outcrops at the ocean floor and is vulnerable to a wide range of alteration processes such as seafloor weathering (Snow and Dick, 1995) and serpentinization (e.g. Janecky and Seyfried, 1986).

Probably the most significant modifications experienced by peridotite at the seafloor are the chemical and mineralogical changes associated with serpentinization. Several studies over the past decade or so have revealed much about the driving forces behind serpentinization reactions. Analyses of vent fluids from peridotite hosted hydrothermal systems (Kelley et al., 2001; Charlou et al., 2002; Douville et al., 2002), petrographic studies (e.g. Mével 2003 and references therein), geochemical investigations (e.g. Paulick et al., 2006; Godard et al., 2008) and the results of experiments and modelling (e.g. Allen and Seyfried, 2003; Foustoukos et al., 2008), have provided valuable insights into the mechanism and chemical consequences of serpentinization at mid-ocean ridges. Primary, anhydrous minerals, such as olivine and orthopyroxene, become hydrated as they are replaced by serpentine minerals (mainly lizardite and chrysotile; e.g. Allen and Seyfried, 2003, but also antigorite, e.g. Kodolányi and Pettke, 2011). Changes in mineral structure associated with the transition from nesosilicates (olivine) and inosilicates (orthopyroxene) to ferro-magnesian

72 phyllosilicates (serpentine minerals) and / or brucite allow the uptake of up to 20 weight %

73 H_2O, although more typically 13-14 wt % H_2O in serpentinites (e.g. Bach et al., 2004;

74 D'Antonio and Kristensen, 2004; Savov et al., 2005) and fluid-mobile elements (e.g. B, Cs,

75 As, I, Br), which can be structurally incorporated into the serpentine crystal lattice (e.g.

76 Scambelluri et al., 2004a; Palmer and Swihart, 1996; Liu and Tossell, 2005; Pabst et al.,

77 2011; Deschamps et al., 2011; Kodolányi et al., 2012), or within the interior of chrysotile

78 scrolls (Wunder et al., 2010). These mineralogical and chemical changes convert a dense,

79 nominally anhydrous, trace element-poor, melt-depleted peridotite protolith into a buoyant,

80 hydrous repository for many trace elements not normally hosted in olivine and

81 orthopyroxene; the minerals that constitute >90% of typical depleted mid-ocean ridge basalt

82 (MORB)-source peridotite. This, in turn, generates a potential geochemical reservoir capable

83 of introducing elemental and isotopic heterogeneity into the sub-arc mantle at active

84 subduction zones and provides an additional source of fluid-mobile elements, over and above

85 that supplied by hydrated meta-basic crust and pelagic sediment, potentially liberated at sub-

86 arc depths (e.g. Morris and Ryan, 2003; Scambelluri et al., 2004b; Savov et al., 2007;

87 Tonarini et al., 2007; Hattori and Guillot, 2007; Deschamps et al., 2011). In addition, the

88 interaction between high-temperature hydrothermal fluid and a serpentinite protolith

89 represents a further opportunity to modify oceanic lithosphere and provide a chemically

90 variable feedstock to the subduction factory in the form of talc (+/- amphibole)-altered

91 serpentinite (e.g. Bach et al., 2004; Paulick et al., 2006; Boschi et al., 2008).

92 Ultramafic-hosted hydrothermal systems have been identified at several locations

93 along amagmatic spreading centres (e.g. Bach et al., 2002). Chemical (e.g. CH_4, Mn) and

94 mid-water light back-scattering anomalies (Charlou et al., 1993; German et al., 1998;

95 Edmonds et al., 2003) suggest that hydrothermal activity at divergent plate margins is

96 commonplace. Ocean Drilling Program Leg 209 recovered significant amounts of

97 serpentinite from five drill sites (Holes 1268a, 1270a, 1271a, 1272a and 1274a) to the north

98 and south of the 15° 20' N fracture zone on the Mid-Atlantic ridge (Shipboard Scientific

99 Party, 2004). Of these, the material recovered from Holes 1272a and 1274a comprise

100 serpentinized abyssal peridotite (60 to 100 % serpentinization; Bach et al., 2004). Hole

101 1268a, located c.10 km from the actively venting Logatchev black-smoker hydrothermal field

102 (Batuev et al., 1994; Krasnov et al., 1995; Bogdanov et al., 1997; Shipboard Scientific Party,

103 2004) differs in its mineralogy, bulk rock and mineral geochemistry due to interaction with c.

104 350 °C hydrothermal fluids (Bach et al., 2004; Paulick et al., 2006; Barnes et al., 2009). This

105 study presents a comprehensive assessment of the effects of high-temperature hydrothermal

106 fluid on the composition of a suite of serpentinites. Specifically, new bulk-rock and mineral

107 chemistry and boron and strontium isotope systematics and elemental abundances are used to

108 assess the effects of fluid compositions, fluid / rock ratios, and temperature and pH conditions

109 necessary to transform Hole 1272a- and 1274a-like serpentinites into the talc-bearing

110 lithologies recovered from Hole 1268a. In addition, the implications of subducting such

111 diverse lithospheric material is explored.

112

2. Geological setting and sample petrology

114

115 The region of the Atlantic Ocean that includes the 15° 20′ N fracture zone has been

116 the subject of extensive geophysical (Fujiwara et al., 2003) and submersible surveys (Cannat

117 et al., 1997; Escartín and Cannat, 1999) and has been systematically sampled by dredging and

118 drilling (Cannat et al., 1997; Shipboard Scientific Party, 2004). The flanks either side of the

119 MAR expose serpentinized peridotite (serpentinite hereafter) and gabbro; the result of

120 extensive crustal thinning on low-angle faults, low magmatic input and the formation of an

121 oceanic core complex (e.g. Ildefonse et al., 2007).

122   Hole 1268a was drilled at 14° 50′ N on the western flank of the MAR axial rift; a

123   locality in flat terrain lying upslope of a steep scarp where gabbro-dyke-intruded serpentinites

124   have been identified (Figure 1). Drilling penetrated to a depth of 147.6 metres below sea floor

125   (mbsf) and a total of 78.7 metres of core was recovered. The recovered material comprises

126   harzburgite and dunite that has experienced varying degrees of serpentinization (60 to 100 %)

127   with localized late-stage gabbro/pyroxenite dykes and mylonitic shear zones. The lowermost

128   c. 50 metres, are dominated by microgabbro / gabbronorite that ranges from fresh to highly

129   (40-80 %) altered compositions. (Figure 2; Shipboard Scientific Party, 2004). Details of the

130   samples examined in this study can be found in Table 1. The Logatchev hydrothermal field is

131   located nearby, on the opposite wall of the axial rift at 14° 45′ N, within faulted blocks of

132   serpentinite (Figure 1). The presence of strong CH_4 and Mn anomalies in the water column at

133   14° 45′ N are indicative of high-temperature interaction between hydrothermal fluid and

134   ultramafic basement (Klinkhammer et al., 1985; Bougault et al., 1993; Rona et al., 1992) and

135   is characterized by the copious outpouring of high-temperature hydrothermal fluid (Schmidt

136   et al. (2007) and references therein).

137   The petrology of Hole 1268a samples has already been discussed extensively

138   (Shipboard Scientific Party, 2004; Bach et al., 2004). The serpentinites have been variably,

139   but extensively (60 to 100 %), serpentinized by hydration of olivine and pyroxene, leading to

140   the formation of serpentine minerals (Seyfried and Dibble, 1980; Seyfried and Ding, 1995;

141   Bach et al., 2004), i.e. "serpentinization *senso stricto*" (Miyashiro et al., 1969; Wicks and

142   Whittaker, 1977; Komor et al., 1985; Janecky and Seyfried, 1986; O'Hanley, 1996). In

143   addition, varying degrees of talc-alteration overprint the serpentinite minerals (e.g.

144    $Mg_3Si_2O_5(OH)_4 + 2SiO_2(aq) = Mg_3Si_4O_{10}(OH)_2 + H_2O$), a consequence of interaction of

145   serpentinite with a subsequent high-T, low-pH, low-MgO/SiO₂ fluid (Shipboard Scientific

146   Party, 2004; Bach et al., 2004). The intensity of alteration is generally high, with 98-100% of

147   the recovered ultramafic material being serpentinite and / or talc-bearing serpentinite.

148   Serpentinites typically preserve pseudomorphic mesh and hourglass textures, but transitional

149   ribbon textures and non-pseudomorphic interlocking textures are also locally present

150   (Shipboard Scientific Party, 2004; Bach et al., 2004). Evidence for a second period of

151   alteration by a higher temperature (300-350 °C) fluid is preserved in the static overprinting of

152   serpentine structure by talc. This manifests itself as a simple overprint, where earlier textures

153   attributable to serpentinization are still recognizable, as multiple generations of talc veins

154   cross-cutting predominantly serpentinite areas, and as finely disseminated talc not visible at

155   the hand specimen scale. A comprehensive account of the petrology of Hole 1268a can be

156   found in Shipboard Scientific Party (2004), and the interaction of serpentine with subsequent

157   fluids and the resultant talc alteration are well described in Bach et al. (2004) where these

158   phase relations and textures are particularly well documented (e.g. Figure 3 in Bach et al.,

159   2004). Samples from this study were divided into serpentinites and talc-bearing serpentinites

160   based upon their physical appearance, e.g. obviously talc-bearing on a hand specimen scale,

161   and on their loss on ignition (LOI wt. %, Table S1 in online supplementary material) obtained

162   during major element analyses. Samples with LOI greater than 10 wt. % were deemed to be

163   talc-free, whereas samples with less than 10 wt. % LOI were categorized as talc-bearing,

164   although the low MgO/SiO_2 compared to similar serpentinites suggests that despite their high

165   LOI, samples initially identified as serpentinites may in fact contain finely dispersed talc. In

166   addition, during sample categorization, 3 samples (10R1 35-41, 18R3 87-93 and 19R2 104-

167   110) were found to be chlorite-bearing.

168   In addition to the textural evidence, several lines of geochemical evidence suggest

169   that samples from Holes 1272a and 1274a share a common peridotite protolith with those

170   recovered from Hole 1268a (Shipboard Scientific Party, 2004; Bach et al., 2004; Paulick et

171   al., 2006; Godard et al., 2008). Similarities in major and trace element characteristics of

172　material from Holes 1268a, 1272a and 1274a are consistent with a shared melt-depletion

173　history prior to serpentinization. Low Al_2O_3 (< 1 wt. %) and high bulk rock Mg# (> 91.5;

174　where Mg# = atomic Mg/(Mg + Fe) x 100), is consistent throughout the three Holes and

175　indicative of similarly high degrees of melt depletion (Paulick et al., 2006; Godard et al.,

176　2008). On board CO_2 measurements during ODP Leg 209 revealed that talc-altered rocks

177　contain CO_2 of <0.04–0.11 wt. %, which completely overlaps with the serpentine-altered

178　rocks (0.05–0.20 wt. %).

179

180　**3. Analytical methods**

181

182　　　Based upon observations of recovered core made during ODP Leg 209 and the

183　isotopic, elemental and mineralogical information recorded in previous studies of Hole 1268a

184　(Bach et al., 2004; Paulick et al., 2006; Moll et al., 2007; Barnes et al., 2009), samples were

185　carefully selected from sections of core unaffected by melt infiltration and / or serpentine /

186　talc veining. Surface alteration and potential contamination were removed with a diamond

187　saw followed by repeated rinsing in ultrapure water, prior to drying and powdering in an

188　agate mortar. Whole rock major element abundances were obtained using XRF spectroscopy

189　on a ARL 8420+ dual goniometer wavelength dispersive XRF spectrometer at The Open

190　University and on a PANalytical Axios Advanced XRF spectrometer at the University of

191　Leicester. Major element and Ni data quality were assessed using WS-E and OUG-94 at The

192　Open University and a suite of ultramafic reference materials (including UM-1, UM-2, UM-

193　4, JP-1 and PCC-1) at the University of Leicester. Reproducibility of reference materials is

194　within 2% of recommended values at both laboratories. Loss on ignition was determined by

195　mass difference on powders dried at 110 °C and then fired in a furnace at c. 1000 °C. Mineral

196　major element analyses were performed at the University of Leeds using a Jeol JXL 8230

197   Superprobe. An accelerating voltage of 15 kV was used. Beam currents were typically 15 nA

198   and a beam size of 10 μm was used throughout the study, with reduced beam sizes (4-8 μm)

199   for particularly small areas of talc. Calcium, Mg, Al and Si abundances were all normalized

200   against in-house mineral standards. Reproducibility of all analytical techniques during the

201   course of this study is indistinguishable from the values given in the online supplementary

202   information of Harvey et al. (2010).

203   Strontium was extracted from unleached bulk-rock samples via conventional ion-

204   exchange chromatographic techniques in a clean laboratory facility at the University of

205   Leeds. The total Sr blank was negligible (< 100 pg) compared to the amount of material

206   processed (typically several hundred ng Sr). The analysis of SRM 987 standard during the

207   course of the measurements gave an average $^{87}Sr/^{86}Sr = 0.710248 \pm 4$ (2σ; n=11). Prior to

208   dissolution, 4 samples from the uppermost levels of Hole 1268a (2R2 27-35, 2R2 87-93, 4R1

209   44-55, 6R1 100-106) were leached, first with 10 % glacial acetic acid for 15 minutes and then

210   with 1.5M Romil UpA HCl. The leachates and residues were spiked using a highly enriched

211   ^{84}Sr solution before complete dissolution in Romil UpA HNO_3 and UpA HF, before a final

212   dissolution stage in 6M Romil UpA HCl. Strontium was extracted from the leachates and

213   residues using Sr-Spec resin in dilute UpA HNO_3, before drying prior to analysis by thermal

214   ionisation mass spectrometry (TIMS). Strontium isotope measurements were carried out at

215   the University of Leeds on a Thermo Scientific Triton TIMS instrument running in static

216   mode. The instrumental mass fractionation was corrected for by normalizing results to

217    $^{86}Sr/^{88}Sr = 0.1194$. Bulk rock strontium abundances were measured at The Open University

218   using an Agilent 7500a ICP MS after a HF + HNO_3 + HCl digestion. Reference materials

219   PCC-1, BHVO-1 and WS-E were also analysed as a check on reproducibility. Uncertainties

220   on bulk rock Sr abundances are < 3%. Strontium abundances of leached serpentinites and

221   leachates were obtained by isotope dilution, using the same enriched ^{84}Sr spike solution as

222   the respective $^{87}Sr/^{86}Sr$ measurements, as part of the strontium isotope ratio determinations.

223   The analytical blank on the Sr abundance measurements were 0.05 μg g^{-1}.

224   Boron isotopic compositions were measured at IGG (CNR-Pisa, Italy) using a VG

225   Isomass 54E positive ion thermal ionization mass spectrometer following boron extraction

226   and purification procedures described by Tonarini et al. (1997, 2003). The $^{11}B/^{10}B$ isotopic

227   ratio is reported in standard delta notation as permil (‰) deviation from the mean value for

228   the SRM-951 boric acid standard routinely passed through the same chemistry as the

229   samples. Precision and accuracy are estimated conservatively as ± 0.64 ‰, based on replicate

230   determinations for samples and for repeated analyses of reference material JB-2 ($\delta^{11}B$ = 7.25

231   ± 0.64 ‰ (2 σ), n=33 analyses with independent chemistry). Boron abundances were

232   determined on 10 g powder splits by ICP AES following a sodium peroxide digestion at

233   Acme Laboratories, Vancouver, Canada. Duplicate analyses of 6R1 100-106 were within 2

234   μg g^{-1} of each other. Analyses of reference materials LKSD-3 and C3 were within 2 μg g^{-1}

235   boron of the certified values. Detection limits of the method are 3 μg g^{-1} boron.

236

237   **4. Results**

238

239   *4.1 Bulk-rock major elements*

240

241   Full bulk-rock major element analyses can be found in Table S1 of the online

242   supplementary electronic material (see also Paulick et al. (2006) for analogous samples).

243   Serpentinized dunites and harzburgites of Sites 1268a typically possess low Al_2O_3

244   abundances (<1 wt. %; Table S1). Chlorite-bearing serpentinites 10R1 35-41, 18R3 87-93

245   and 19R2 104-110 and meta-gabbroic samples (27R1 102-109 and 29R1 123-129) contain

246   significantly more Al_2O_3; (10-20 wt. % and 15-18 wt. % Al_2O_3 respectively; Table S1).

247   MgO/SiO$_2$ values of Hole 1268a serpentinites typically fall below the "Terrestrial Array for

248   peridotites" of Jagoutz et al. (1979; MgO/SiO$_2$ = 0.8 to 1) and are significantly lower than

249   serpentinites from the other side of the 15° 20' N Fracture Zone (e.g. Harvey et al., 2006;

250   Godard et al., 2008). In contrast, talc-altered serpentinites have even lower MgO/SiO$_2$ values

251   (0.4 - 0.6; Figure 3a), in good agreement with similar samples studied by Paulick et al.

252   (2006). However, it is important to note that *all* of the Hole 1268a serpentinites lie beneath

253   the terrestrial array for peridotite, including serpentinites deemed to have experienced no

254   discernible *macro-scale* talc-alteration (i.e. visible at the hand specimen size). Loss on

255   ignition in Hole 1268a serpentinites is significantly higher ($\leq$ 13 wt. %; Table S1) than that in

256   talc-bearing serpentinites (4-8 wt. %; Table S1), i.e. where the presence of talc is obvious in

257   hand specimen. Two samples (18R3 87-93 and 19R2 104-110) possess >1 wt. % CaO and

258   also elevated TiO$_2$ ($\leq$ 0.9 wt. %) which suggests that in some isolated samples additional Ca-

259   and / or Ti-bearing phases may occasionally be present, but do not constitute a major part of

260   the altered lithologies. To date, no such phase has been identified petrographically at this

261   locality (Shipboard Scientific Party, 2004; Bach et al., 2004; Paulick et al., 2006; Harvey et

262   al., 2006; Godard et al., 2008; Barnes et al., 2009; this study). The major element

263   compositions of Hole 1268a meta-gabbros from this study are indistinguishable from similar

264   Hole 1268a samples of Paulick et al. (2006). The MgO/SiO$_2$ and LOI values of Hole 1268a

265   serpentinites and talc-altered serpentinites are also similar to analogous material recovered

266   from further north on the MAR at the Atlantis Massif (Boschi et al., 2008), although meta-

267   gabbros recovered from Atlantis Massif appear somewhat less hydrated and more SiO$_2$-rich

268   and MgO-poor than at Hole 1268a.

269

270   *4.2 Mineral major element compositions*

271

272   The major element composition of minerals from Hole 1268a serpentinites and talc-

273   bearing serpentinites (Table S2) have already been discussed in detail in Moll et al. (2007),

274   and only an overview of the analogous samples examined as part of this study will be given

275   here. The composition of serpentine after orthopyroxene, serpentine after olivine and talc are

276   indistinguishable from those of Moll et al. (2007) (Figure 3b). Curiously, when analysing

277   minerals that were identified petrographically and by EDS emission spectra as serpentine or

278   talc, quantitative analyses of many secondary minerals were found not to be consistent with

279   the phase initially identified, suggesting that even in samples where bulk-rock LOI indicates a

280   serpentine- or talc-dominated lithology, there is a strong possibility of serpentine-talc

281   intergrowth at a very fine scale. The analyses of Moll et al. (2007) support this assertion, as

282   they also appear to have experienced the same difficulty in unequivocally identifying end-

283   member serpentine and talc. The MgO/SiO_2 vs. Al_2O_3/SiO_2 of minerals from both studies are

284   plotted in Figure 3b. Both datasets demonstrate that minerals identified as either serpentine or

285   talc sometimes plot in the compositional field of the other mineral (or occasionally between

286   the two). Only by reducing the analyser beam size (see analytical methods above) were we

287   able to confidently analyse end-member serpentine and talc (Table S2). Chlorite

288   compositions of talc-altered serpentinites have not previously been reported (Table S2). In

289   MgO/SiO_2 vs. Al_2O_3/SiO_2 space they are similar to chlorites analysed in serpentinites from

290   Cerro del Almirez, Spain (Padrón-Navarta et al., 2011; Figure 3b), but are slightly richer in

291   MgO and Al_2O_3 by comparison.

292

293   *4.3 Strontium abundances and isotope analyses*

294

295   Strontium isotope analyses of the various lithologies recovered from Hole 1268a have

296   a wide range of values ($^{87}Sr/^{86}Sr$ = 0.702940 ± 9 to 0.71196 ± 15; Table 2; Figure 4a). With

297   the exception of the uppermost serpentinite (2R2 27-35; $^{87}Sr/^{86}Sr$ = 0.71196 ± 15) unleached

298   serpentinites and talc (± chlorite)-altered serpentinites of this study have Sr isotope ratios that

299   are indistinguishable from those of Boschi et al. (2008), where similar lithologies from the

300   MAR were analysed (i.e. $^{87}Sr/^{86}Sr$ = 0.707347 ± 16 to 0.709171 ± 13, Boschi et al., 2008), as

301   were the serpentinites of Delacour et al. (2008) from the same locality ($^{87}Sr/^{86}Sr$ = 0.70885 to

302   0.70918). The majority of the unleached ultramafic samples from this study have Sr isotope

303   ratios close to that of seawater ($^{87}Sr/^{86}Sr$ = 0.70916; Palmer and Edmond, 1989),

304   indistinguishable from many of the measurements of Logatchev hydrothermal fluids made by

305   Amini et al. (2008), and also overlap with the Sr isotope ratios obtained by Vils et al. (2009)

306   for variably serpentinized serpentinites from Holes 1272a and 1274a ($^{87}Sr/^{86}Sr$ = 0.70807 ± 1

307   to 0.70913 ± 4). There is no correlation between the depth from which the samples were

308   recovered and the Sr isotope ratio (Figure 4a). Similarly, the presence or absence of macro-

309   scale talc-alteration does not appear to be a major control on Sr isotope composition,

310   although two talc (± chlorite)-altered samples (18R3 87-93 and 19R2 104-110) possess the

311   lowest Sr isotope ratios of the ultramafic samples of this study.

312   Strontium abundances were determined in eleven serpentinites, nine talc-altered

313   serpentinites and two gabbro-norites. With the exception of the two gabbro samples ([Sr] =

314   72.8 to 86.9 µg g^{-1}) [Sr] ranges from 0.41 to 2.44 µg g^{-1}, with no clear distinction between

315   serpentinite and talc-altered serpentinite (Table 2; Figure 5). While strontium abundances are

316   close to those of similar serpentinite samples reported in Paulick et al. (2006) and Godard et

317   al. (2008), Sr abundances in the serpentinites from this study occupy a much smaller range

318   than those from the Atlantis Massif (up to 15 µg g^{-1}, Boschi et al., 2008; up to 90 µg g^{-1},

319   Delacour et al., 2008). Four samples (2R2 27-35, 2R2 83-89, 4R1 44-55, 6R1 100-106) were

320   sequentially leached first with 10 % glacial acetic acid for 15 minutes and then with 1.5 M

321   HCl for 15 minutes. The results of these leaching experiments can be found in Table S3.

322 Briefly, the combined leaching experiments removed up to 20 % of the original material but

323 account for c. 90 % of the Sr budget. The acetic acid leach liberated a Sr-rich component (50-

324 80 % of the Sr budget) with $^{87}Sr/^{86}Sr$ very similar to that of both seawater and the unleached

325 bulk-rock samples. In particular, the anomalously high $^{87}Sr/^{86}Sr$ of unleached bulk-rock 2R2

326 27-35 ($^{87}Sr/^{86}Sr$ = 0.71196 ± 15) appears to be due to an easily leached component; the acetic

327 acid leach of 2R2 27-35 is very radiogenic compared to the leached residue of that sample

328 ($^{87}Sr/^{86}Sr$ = 0.7172 ± 8 vs. 0.70763 ± 3 respectively) and has a relatively high Sr

329 concentration compared to the leached residue ([Sr] = 13 µg g^{-1} vs. 0.12 µg g-1 respectively).

330 HCl leaching also removed 10-20 % of the Sr, also with a seawater-like composition

331 ($^{87}Sr/^{86}Sr$ = 0.70901 ± 1 to 0.70918 ± 1), leaving a less radiogenic residue in all four cases

332 ($^{87}Sr/^{86}Sr$ = 0.70763 ± 3 to 0.70871 ± 6).

333   Two Hole 1268a meta-gabbros were also analysed as part of this study. Samples 27R1

334 102-108 and 29R1 123-129 yielded $^{87}Sr/^{86}Sr$ values of 0.702940 ± 9 and 0.703094 ± 11,

335 respectively, i.e. only moderately elevated compared to the mean value for MORB recovered

336 north of 17° 10′ N on the MAR ($^{87}Sr/^{86}Sr$ = 0.70238 ± 4; Dosso et al., 1993).

337

338 *4.4 Boron abundance and isotope analyses*

339

340   Boron abundances were determined on nine serpentinites and six talc-altered

341 serpentinites. Serpentinite boron abundances range from 19 ± 2 to 36 ± 2 µg g^{-1}, significantly

342 higher than the talc-altered serpentinites ([B] = <3 to 12 ± 2 µg g^{-1} (Table 3; Figure 5). With

343 the exception of a single talc-altered serpentinite with [B] of almost 40 µg g^{-1}, the

344 serpentinites of Boschi et al. (2008) possess similarly high boron abundances when compared

345 to talc-altered serpentinites from the same locality. Boron isotope analyses of Hole 1268a

346 serpentinites and talc (± chlorite)-altered samples are presented in Table 3 and illustrated in

347   Figure 4b. Measured values of $\delta^{11}B$ range from $+9.35 \pm 0.35$ ‰ to $+19.56 \pm 0.32$ ‰ (where

348   $\delta^{11}B_{sample} = ((^{11}B/^{10}B_{sample})/(^{11}B/^{10}B_{SRM-951}) -1) *1000)$. Similar to the Sr isotope ratios of the

349   same samples, there is no obvious relationship between $\delta^{11}B$ and depth below seafloor,

350   although the samples with the highest $\delta^{11}B$ tend to be found towards the lower half of Hole

351   1268a. Again, like the Sr isotope values, there is no clear distinction between talc ($\pm$

352   chlorite)-altered serpentinites and those that lack macro-scale talc-alteration in terms of $\delta^{11}B$

353   (Figure 4b). The majority of the ultramafic samples from Hole 1268a overlap in $\delta^{11}B$ values

354   with serpentinites, talc-altered serpentinites and amphibolite-schists of Boschi et al. (2008),

355   but are considerably lighter than the $\delta^{11}B$ of Vils et al. (2009) which extend up to $\delta^{11}B$ +40

356   ‰, i.e. the value of seawater (Foster et al., 2010).

357

5. Discussion

359

360   A long history of melt depletion is evident in the rocks recovered from ODP Leg 209

361   (Harvey et al., 2006). Extensive serpentinization subsequent to melt depletion, and localized

362   talc-alteration, i.e. Si-metasomatism are also observed. This is indicative of a wide range of

363   pH and temperature conditions during the petrogenesis of the Hole 1268a samples and the

364   evolution of fluid compositions and fluid/rock ratios necessary to induce these characteristics.

365   Any model that explains the boron and strontium isotope systematics must also be consistent

366   with the following observations: (i) the $\delta^{11}B$ of Hole 1268a samples are consistently lighter

367   than those of Hole 1272a and Hole 1274a, but (ii) are very similar to talc-bearing

368   serpentinites from the Atlantis Massif (Boschi et al., 2008). (iii) There is no clear difference

369   in $\delta^{11}B$ between the serpentinites and talc-altered serpentinites of Hole 1268a. (iv) The LOI in

370   Hole 1268a samples appears to be bimodal. i.e. there is no continuous variation in the relative

371   proportions of talc and serpentine. In the following sections the evidence for these processes,

372   and the physical and chemical conditions under which they occurred are explored.

373

374   *5.1 The effect of serpentinization and Si-metasomatism on Sr isotope ratios*

375

376   Sequential leaching of the uppermost samples (2R2 27-35 to 6R1 100-106) revealed

377   an easily mobilized component of the Sr budget which, once removed, leaves a residual

378   serpentinite with 1-2 orders of magnitude less Sr and less radiogenic $^{87}Sr/^{86}Sr$ than the

379   corresponding unleached serpentinite (Table 2). However, it is evident from Figure 4a that

380   leaching of the uppermost samples from Hole 1268a simply shifts the Sr isotope ratio from

381   values that resemble the unleached samples of Vils et al. (2009) to those of Boschi et al.

382   (2008), also unleached, i.e. although the $^{87}Sr/^{86}Sr$ of the leached rocks are noticeably less

383   radiogenic than unleached examples, both unleached and leached samples span a continuum

384   of radiogenic compositions from $^{87}Sr/^{86}Sr$ = c 0.707 to 0.709, indistinguishable from many of

385   the measurements of Logatchev hydrothermal vent fluids (e.g. Amini et al., 2008). However,

386   it should be noted that the more aggressive HCl leach performed on these samples continued

387   to remove a radiogenic component, which implies that the range of Sr isotope ratios for more

388   aggressively leached samples could be pushed to more unradiogenic values. Notwithstanding

389   this observation, the source of the easily-leachable Sr is somewhat equivocal. On board

390   measurements during ODP Leg 209 revealed that talc-altered rocks contain CO_2 of <0.04–

391   0.11 wt. %, which completely overlaps with the serpentinites (0.05–0.20 wt. %). In the

392   serpentinites that lack macro-scale talc-alteration a positive correlation is evident between

393   CO_2 and H_2O (Shipboard Scientific Party, 2004). However, a general absence of carbonate

394   veining (Bach et al., 2011) and the lack of any significant correlation between volatile content

395   and depth below sea floor suggests that late-stage carbonate formation is unlikely to be

396   responsible for the readily leached, seawater-like Sr reservoir ($^{87}Sr/^{86}Sr$ seawater = 0.70916;

397   Palmer and Edmond, 1989). The presence of an easily leachable Sr component also has some

398   implications for calculated water / rock ratios necessary to account for the observed

399   alteration.

400   Water / rock ratios (W/R) were calculated for the Hole 1268a samples using the

401   "single pass" model employed by Vils et al. (2009), which is based upon, and uses the same

402   parameters as Taylor (1977) and McCulloch et al. (1980). The highly melt depleted protolith

403   has particularly low [Sr] (1.75 µg g-1 ; Harvey et al., 2006; Paulick et al., 2006; Godard et al.,

404   2008; Vils et al., 2009; Barnes et al., 2009). Mixing calculations suggest that the

405   transformation of peridotite to a serpentinite with seawater-like Sr isotopic characteristics

406   requires only low W/R (2-8 for the Hole 1268a samples) due to the low Sr concentration in

407   highly depleted serpentinite compared to seawater. Bearing in mind that the structurally

408   bound Sr constitutes only a small percentage of the Sr budget of unleached samples (<20 %),

409   and the process of near complete serpentinization shifted $^{87}Sr/^{86}Sr$ of unleached samples to

410   values of c. 0.709 then the calculated W/R ratios for Hole 1268a can be considered a

411   maximum.

412   The Hole 1268a serpentinites, calculated to have experienced relatively low W/R

413   ratios compared to Hole 1272a and Hole 1274a serpentinites (cf. Vils et al., 2009), appear to

414   possess a radiogenic Sr isotope composition despite interaction with the later high-

415   temperature hydrothermal fluid. This, in itself, is curious. It is inferred that the high-

416   temperature fluid with which serpentinite must have interacted to produce talc-bearing rocks

417   had acquired its high-Si composition through interaction with local gabbro (Bach et al., 2004;

418   Paulick et al., 2006; Barnes et al., 2009). Given that relatively unaltered gabbros from Hole

419   1268a retain a mantle-like Sr isotope ratio and contain 1-2 orders of magnitude more Sr than

420   the serpentinites ($^{87}Sr/^{86}Sr$ = 0.702940 to 0.703094, [Sr] = 73 to 87 µg g-1 ; this study),

421 interaction between serpentinite, with a seawater-like Sr isotope ratio, and a high

422 temperature, high-Si fluid that has partially broken down MORB-like gabbro should quickly

423 reduce the $^{87}Sr/^{86}Sr$ of the talc-altered serpentinites. Indeed, strontium isotope ratios as low as

424 $^{87}Sr/^{86}Sr = 0.70477$ have been recorded in Logatchev hydrothermal fluids (Amini et al.,

425 2008), suggesting that some fluids have equilibrated more completely with the local gabbro

426 than others, but $^{87}Sr/^{86}Sr$ as low as this appears to be exceptional. The majority of Sr that

427 could be derived from the gabbro is plagioclase-hosted and it is not clear whether plagioclase

428 alteration is synchronous with the breakdown of orthopyroxene, i.e. it is not certain that the

429 Sr-rich fluid released during plagioclase breakdown was also the source of the high-Si

430 signature. There are several possible explanations for why the final talc-altered Sr isotope

431 ratio is not significantly reduced (i.e. to values of < 0.707 in leached samples, or < 0.709 in

432 unleached samples) by interaction with the high-Si, high-T fluid. Preferential breakdown of

433 orthopyroxene versus plagioclase would minimize the amount of unradiogenic Sr released

434 during the hydrothermal alteration of gabbro, while still releasing sufficient SiO_2 to produce

435 the necessary seawater-Sr-dominated, high-Si fluid. Alternatively, hydrothermal interaction

436 with a previously altered gabbro, i.e. one that has interacted with large volumes of seawater,

437 and whose plagioclase has acquired a seawater-like Sr isotope signature, may subsequently

438 provide a high temperature fluid with a more radiogenic Sr isotope ratio, which would not

439 necessarily dramatically lower the $^{87}Sr/^{86}Sr$ of the final talc-altered serpentinite, although this

440 would require highly altered plagioclase to co-exist with relatively unaltered orthopyroxene.

441 Core descriptions of gabbro from ODP Leg 209 (Shipboard Scientific Party, 2004) show that

442 plagioclase in Core 27R1 to 29R1 is largely unaltered, whereas orthopyroxene is often

443 completely replaced. This favours the former explanation for the lack of a drastic reduction in

444 $^{87}Sr/^{86}Sr$ (i.e. < 0.707) during Si-metasomatism; even if unradiogenic Sr is hosted within the

445 unaltered orthopyroxene this mineral is not a significant source of Sr. However, it should be

446   noted that on a local scale, the degree of alteration of the gabbro is not homogeneous and

447   likely to be the result of local heterogeneity in available fluid pathways, i.e. one of these "end

448   member" hypotheses is unlikely to account for all the Sr isotope systematics of all the Hole

449   1268a serpentinites.

450   Based upon our interpretations, we can propose the following scenarios to account for

451   the observed Sr isotope systematics. (i) Serpentinization of a highly melt-depleted peridotite

452   protolith results in a serpentinite with Sr isotope characteristics similar to seawater, after Sr

453   exchange at low W/R ratios. (ii) Limited exchange of Sr between serpentinite and a

454   subsequent high-Si, high temperature fluid with a mantle-like Sr isotope ratio lowers the

455   serpentinite $^{87}Sr/^{86}Sr$ to values similar to those observed in leached serpentinites (i.e. $\leq$

456    $^{87}Sr/^{86}Sr$ 0.707). (iii) Late-stage interaction with seawater near to the surface of the seafloor

457   adds an easily-leachable, i.e. not structurally bound, seawater-like Sr component that

458   dominates the bulk-rock Sr budget and returns the bulk-rock Sr isotope ratio to seawater-like

459   values ($^{87}Sr/^{86}Sr \sim 0.709$). Despite requiring a three-step process this seems the most likely

460   sequence of events as it does not rely upon the simultaneous release of Si from orthopyroxene

461   with the retention of most of the gabbro-bearing Sr in unaltered plagioclase.

462

463   *5.2 The effects of serpentinization and Si-metasomatism on B isotope systematics*

464

465   This study benefits from the prior knowledge of B and Sr isotope systematics of a

466   local, likely precursor to talc-altered serpentinite - the material recovered from Hole 1272a

467   and 1274a (Shipboard Scientific Party, 2004; Bach et al., 2004; Paulick et al., 2006; Godard

468   et al., 2008; Vils et al. 2009; Barnes et al., 2009). The $\delta^{11}B$ values of Hole 1272a and 1274a

469   serpentinites (Vils et al., 2009), range from seawater-like, where seawater $\delta^{11}B = +39.61 \pm$

470   0.04 ‰; Foster et al. (2010) to a $\delta^{11}B$ of c.+30 ‰, significantly heavier than the samples of

471 this study ($\delta^{11}B$ = +9 to +20 ‰) (Table 3). However, irrespective of lithology, the Hole

472 1268a samples yield $\delta^{11}B$ values that are close to the range of the talc-altered serpentinites

473 described by Boschi et al. (2008) with $\delta^{11}B$ values of +9 to +16 ‰, who interpreted the $\delta^{11}B$

474 of the Atlantis Massif talc-serpentinites as being the result of an interaction with a moderate

475 temperature (c. 250 °C) fluid under mostly open system conditions and highly variable W/R

476 ratios (0.5 to > 100). From Figure 4b it can be seen that the Hole 1272a and 1274a

477 serpentinites have much higher $\delta^{11}B$ than the 1268a samples and those from the Atlantis

478 Massif. This suggests that the $\delta^{11}B$ of serpentinites and talc-altered serpentinites of Hole

479 1268a are the result of a multi-stage alteration process at this locality, where low temperature

480 (100-200 °C) serpentinization raised $\delta^{11}B$ (and $^{87}Sr/^{86}Sr$) to seawater-like values before a

481 subsequent high temperature event reduced the B isotope ratio of the serpentinites and talc-

482 altered serpentinites, while leaving Sr isotope ratios largely unaffected. This contrasts with

483 the scenario described by Boschi et al. (2008) for the Atlantis Massif talc-bearing

484 serpentinites where serpentine and talc generation was synchronous.

485   The speciation of boron in a fluid is strongly dependent upon pH, with alkaline

486 conditions being favourable for boron removal from solution (Foustoukos et al,, 2008; Figure

487 6a). At low temperature (0-25 °C) and at seawater pH (7.5 to 8.4) c. 80 % of boron in a

488 seawater-like solution is trigonally coordinated (Figure 6a), with the remainder being

489 tetrahedrally coordinated (Hemming and Hanson, 1992). The models of Benton et al. (2001)

490 and Boschi et al. (2008) demonstrate that continuing increases in fluid pH at moderate

491 temperatures (c. 250 °C) during the uptake of boron by serpentine minerals results in heavy,

492 trigonally coordinated boron and the incorporation of ^{11}B-rich tetrahedrally coordinated

493 boron into serpentine minerals (Figure 6b). With their calculated fluid-mineral fractionation

494 factors Boschi et al. (2008) calculate that a solution dominated by trigonally coordinated

495 boron with $\delta^{11}B$ of c. +55 to +60 ‰, i.e. in equilibrium with serpentine minerals dominated

496   by tetrahedrally coordinated boron with $\delta^{11}B$ of c. +40 ‰, is attained for solutions at c. 250

497   °C at a pH of c. 10. This is consistent with the measured $\delta^{11}B$ of Hole 1272a and 1274a

498   serpentinites (Vils et al., 2009) and broadly consistent with the "single pass" model for fluid-

499   rock interaction (Vils et al., 2009).

500   It has been clearly demonstrated that during the changes in mineralogy associated

501   with low-temperature alteration and serpentinization B is rapidly accumulated in

502   phyllosilicates (Pabst et al., 2011), increasing both the $\delta^{11}B$ and [B] as serpentinization

503   progresses (e.g. Wunder et al., 2005). This accounts for the high [B] and $\delta^{11}B$ of the

504   serpentinites of Hole 1272a and 1274a as reported by Vils et al. (2008, 2009, respectively)

505   (Figure 6a). By way of contrast, the high-T, high-Si fluid associated with talc-alteration has

506   been calculated to have had a pH of 4 to 5 (Bach et al., 2004). Under these pH conditions B is

507   entirely trigonally coordinated with little propensity for incorporation of ^{11}B into tetrahedrally

508   coordinated sites within the stable mineral phases. Thus any B incorporated during changes in

509   mineralogy will have a much lower $\delta^{11}B$ than minerals formed under higher pH conditions

510   (Figure 6b). The net effect is a pH-controlled fractionation that differs markedly from the

511   prevailing conditions during low temperature serpentinization (Figure 6b). As trigonally

512   coordinated B is less easily incorporated into silicates (e.g. Williams et al., 2001), otherwise

513   identical minerals will have lower boron abundances and $\delta^{11}B$ than minerals formed at high

514   pH. This is consistent with the offset to lower $\delta^{11}B$ in talc-altered serpentinites of this study

515   and those from the Atlantic Massif (Boschi et al., 2008), and also the lower [B] measured in

516   talc-altered serpentinites versus low-temperature serpentinites (Boschi et al., 2008 vs. Vils et

517   al., 2008, respectively).

518   Superimposed upon the pH-influenced fluid-mineral fractionation of $\delta^{11}B$ is an

519   additional temperature effect (Figure 6b). As predicted from Figure 6b, the maximum fluid-

520   mineral fractionation of B isotopes occurs at the lowest pH. Although the fluids associated

521   with Si-metasomatism at Hole 1268a are likely to have been in the region of pH 4 to 5, the

522   maximum fluid-mineral fractionation occurs at a pH of c. 6, where all B present is trigonally

523   speciated; a further reduction on fluid pH has no additional effect on fluid-mineral

524   fractionation. Similarly, the maximum degree of fluid-mineral B isotope fractionation occurs

525   at low temperatures (Figure 6b). With increasing temperature the potential range of fluid-

526   mineral induced fractionation contracts. However, at the temperatures associated with Si-

527   metasomatism (300 to 350 ^{o}C; Bach et al., 2004; Paulick et al., 2006) and pH of <6 there

528   remains the potential for a significant fluid-mineral fractionation of B isotopes during the

529   talc-alteration of pre-existing serpentine. Figure 6b demonstrates that under the conditions of

530   Si-metasomatism at Hole 1268a this could have been as great as -19 ‰; a degree of

531   fractionation that encompasses most of the differences observed between the serpentinites

532   from Hole 1272a and 1274a (δ^{11}B = + 29.72 to +40.66 ‰; Vils et al., 2009) and talc-altered

533   serpentinites of this study (δ^{11}B = +9.65 to +19.56 ‰) and from the Atlantis Massif (δ^{11}B =

534   +8.78 to +16.21 ‰; Boschi et al., 2008). Moreover, this large degree of fluid-mineral

535   fractionation is only possible at the low pH associated with Si-metasomatism. The

536   synchronous occurrence of serpentinization during talc-alteration would buffer the low pH of

537   the silicic high-T fluid and thus restrict the possible range of fractionation of boron isotopes

538   to a value below that observed in the Hole 1268a serpentinites.

539

540   *5.3 The consequences of mineralogical changes during serpentinization and subsequent Si-*

541   *metasomatism*

542

543   The multi-stage evolution of the 1268a talc-altered serpentinites is summarized in

544   Figure 7. Changes in [Sr], [B], δ^{11}B and ^{87}Sr/^{86}Sr during the sequential transition from melt

545   depleted peridotite to serpentinite to talc-altered serpentinite are not only controlled by fluid

546 composition and ambient pH-T conditions, but also the change in mineralogy during the

547 evolution of the Hole 1268a material. Melt-depleted peridotite lithologies are dominated by

548 olivine and orthopyroxene with simple nesosilicate and inosilicate orthorhombic structures,

549 respectively. Their structures are not conducive to large-scale substitution of major cations by

550 Sr and / or B, hence the low abundances of these elements in peridotitic lithologies (e.g. [Sr]

551 and [B] in the primitive mantle are estimated at 20 $\mu g \ g^{-1}$ and <0.25 $\mu g \ g^{-1}$ respectively;

552 Palme and O'Neill, 2003; Chaussidon and Jambon, 1995, respectively). In contrast, the

553 ferromagnesian, phyllosilicate serpentine $[Mg_3Si_2O_5(OH)_4]$ is a trioctahedral sheet silicate

554 comprising stacked layers of a pseudo-hexagonal network of linked SiO_4 tetrahedra

555 interspersed with brucite-like $[Mg(OH)_2]$ layers (Deer et al. 1992). Thus, there is a much

556 greater potential for the incorporation of Sr and / or B either within the pseudo-hexagonal

557 network itself, or between the sheets during the process of serpentinization, which in turn

558 accounts for the large differences in B and Sr systematics between unaltered mafic-ultramafic

559 material and serpentinites (e.g., Bonatti et al. 1984; Ryan and Langmuir 1993; Benton et al.

560 2001; Snyder et al. 2005; Vils et al. 2008, 2009; Deschamps et al. 2010; Pabst et al., 2011).

561 Melt-depleted peridotite which still retains its mantle-like Sr and B isotope signatures

562 ($^{87}Sr/^{86}Sr$ = 0.7025 e.g. Hofmann, 1997; $\delta^{11}B$ = c. -5 ‰, e.g. Chaussidon and Marty, 1995) is

563 systematically serpentinized through interaction with a high-pH, seawater-dominated fluid.

564 The inherently low [Sr] (1 to 3 $\mu g \ g^{-1}$, Paulick et al., 2006; Godard et al., 2008) and

565 especially low [B] (0.06 $\mu g \ g^{-1}$, Salters and Stracke, 2004) of the melt depleted peridotite

566 means that $\delta^{11}B$ in particular will rapidly shift to heavier $\delta^{11}B$ with increased seawater /

567 peridotite interaction. Simple binary mixing calculations demonstrate that during

568 serpentinization a depleted peridotite pre-cursor will acquire seawater-like $\delta^{11}B$ after

569 interacting with c. 10 % of the fluid necessary to impart seawater Sr isotopic characteristics

570 (Figure 7). However, this is reliant upon certain assumptions regarding the uptake of B into

571   the serpentinizing peridotite, i.e. the trajectory assumed in Figure 7 for the change in both B

572   and Sr isotope systematics relies upon the rapid uptake of B by serpentine minerals and the

573   complete exchange of B between the serpentine phases and seawater. Pabst et al. (2011)

574   demonstrate that there is strong evidence for incorporation of B into the serpentine mineral

575   structure itself. The mechanism of B incorporation into serpentine is independent of the

576   serpentine polymorph or textural type (e.g., Pelletier et al. 2008; Pabst et al., 2011). Highly

577   charged ($^{+3}$) B should be readily accommodated within the Si and / or Al crystallographic

578   sites. For example in both chlorite-group and mica-group minerals, B^{3+} either partly replaces

579   Al in tetrahedral coordination ($^{[4]}Al^{3+}$) (Foord et al. 1991; Zagorsky et al. 2003), or enters the

580    $^{[4]}Si^{4+}$ site (Ranorosoa et al. 1989). From these observations, Pabst et al. (2011) hypothesize

581   that B is directly incorporated into the serpentine crystal structure in tetrahedral coordination.

582   Thus, the rate of increase of [B] and $\delta^{11}B$ is likely to be dependent upon kinetics of serpentine

583   production rather than a simple W/R ratio calculation with an assumed 100 % exchange of B

584   between the fluid and the rock undergoing serpentinization. Vils et al. (2009) clearly showed

585   that there is no straightforward relationship between degree of serpentinization and either [B]

586   or $\delta^{11}B$. Under open system conditions, where the supply of seawater-derived B is effectively

587   unlimited, the supply of B to rapidly serpentinizing peridotite is unlikely to be a limiting

588   factor. As both Boschi et al. (2008) and Vils et al. (2009) note, there is a significant fluid-

589   mineral fractionation factor under these pH-T conditions (Figure 6b). At some point, in order

590   to produce serpentine minerals with seawater-like $\delta^{11}B$, closed system distillation of seawater

591   must occur (Vils et al., 2009), with pH evolving over time from seawater-like pH to the high

592   pH (c.10) necessary to incorporate heavy $\delta^{11}B$ ($\delta^{11}B$ = c. +40 ‰) in serpentine minerals. In

593   essence, if serpentinization commenced under open-system conditions it would appear that it

594   culminated under closed system conditions.

595   It is clear that there is a marked offset in δ^{11}B of up to 20 ‰ between the Hole 1272a

596   and Hole 1274a serpentinites of Vils et al. (2009) and the Hole 1268a samples. As discussed

597   above, Hole 1268a samples have Sr isotope ratios that are indistinguishable from those of

598   Hole 1272a and Hole 1274a. Furthermore, both leached and unleached Hole 1268a samples

599   overlap completely with the serpentinites and talc-altered serpentinites of Boschi et al.

600   (2008), suggesting that 75-100 % of the peridotite-protolith Sr budget has been exchanged

601   with seawater-derived Sr. Where these two sample suites appear to differ is in the acquisition

602   of the final δ^{11}B signature in both serpentinites and talc-altered serpentinites, which is

603   probably related to the differences in the exact settings of the two localities, despite their

604   seemingly similar mid-ocean ridge locations.

605   Serpentinites contain significantly more B than talc-altered serpentinites (Boschi et

606   al., 2008; Vils et al., 2008, 2009; this study Table 3) so whatever mechanism is responsible

607   for the shift from seawater-like δ^{11}B to significantly lighter values must also account for the

608   evident decrease in boron abundance and be consistent with the mechanisms that account for

609   the observed Sr isotope systematics. Pabst et al. (2011) observe that boron hosted along grain

610   boundaries, in microfractures, or in between serpentine sheets, would be removed by

611   infiltrating hydrous fluids irrespective of temperature. However, this highly mobile

612   component is not likely to affect the overall B systematics of serpentine to any great extent.

613   In addition, Pabst et al. (2011) report that serpentine mesh centres and mesh rims contain by

614   far the most B in lizardite-dominated serpentinite lithologies (up to 197 μg g^{-1} and 97 μg g^{-1}

615   respectively), i.e. the majority of serpentine-hosted B is structurally bound and can only be

616   extracted as a result of serpentine recrystallization, breakdown through changes in P-T-X

617   conditions, or significant shifts in fluid pH (e.g., Palmer et al. 1987; Spivack and Edmond

618   1987; Ulmer and Trommsdorff 1995; Hawthorne et al. 1996; Palmer and Swihart 1996;

619   Peacock and Hervig 1999; Hattori and Guillot 2003; Schmidt et al. 2005).

620   The pervasive talc-alteration / Si-metasomatism present throughout the Hole 1268a

621   samples of this study is clear evidence for a mineralogical change in response to the presence

622   of a high-T, low-pH fluid (Bach et al. 2004; Paulick et al., 2006). The change from a tri-

623   octahedral sheet silicate (serpentinite) with relatively high MgO/SiO_2 to monoclinic / triclinic

624   talc with a distinctly lower MgO/SiO_2 requires a significant re-ordering of the crystal

625   structures. This has the potential to not only allow B to be removed from formerly

626   structurally bound $^{[4]}Al^{3+}$ and $^{[4]}Si^{4+}$ sites during recrystallization but is also accompanied by a

627   dehydration reaction where the amount of structurally bound water is reduced from up to 14

628   wt. % in serpentinite (Vils et al., 2009; this study) to 4-8 wt. % in talc-bearing serpentinites

629   (Boschi et al., 2008; this study). As boron is considered to be a particularly fluid-mobile

630   element (e.g. Ryan and Langmuir, 1993; Palmer and Swihart, 1996; Ryan et al., 1996;

631   Ishikawa and Tera, 1997; Savov et al., 2007) this presents a viable mechanism for the

632   reduction in [B] during the transition from serpentinite to talc-altered serpentinite. Moreover,

633   the change in fluid composition relative to that responsible for serpentinization (higher T,

634   lower pH, higher Si content) induces a fluid-mineral fractionation that is distinctly different

635   to that induced during serpentinization. For example, Figure 6b illustrates that at c.350 °C

636   and in the presence of a fluid of pH 6, mineral compositions can be shifted to $\delta^{11}B$ c. 10 ‰

637   lighter than the results of interaction with a seawater-like fluid at 200 °C. This does not take

638   into account any differences in the actual starting composition of the higher temperature fluid

639   which may (or may not) have a distinctly lighter $\delta^{11}B$ than the lower temperature

640   serpentinizing fluid. However, it seems unlikely that the higher temperature fluid would

641   possess a heavier $\delta^{11}B$ than the earlier serpentinizing fluid, given the evidence presented by

642   Vils et al. (2009) suggesting that closed-system refinement of fluid composition is required in

643   order to precipitate serpentine minerals with $\delta^{11}B$ of c. +40 ‰.

644   Despite strong evidence for a significant dehydration event, and the likely

645   fractionation of boron that accompanied the transition from serpentine to talc, the apparent

646   lack of offset in $\delta^{11}B$ between the Hole 1268a serpentinites and the talc-bearing serpentinites

647   needs to be reconciled with the theoretical framework discussed above. All of the Hole 1268a

648   samples plot below the Terrestrial Array for peridotite (Figure 3a), implying that at least

649   some shift to a lower MgO/SiO_2 has occurred through interaction with the late-stage high-

650   temperature Si-bearing fluid. Despite this observation, many Hole 1268a samples retain high

651   LOI values, which suggests that while some talc may be present in all of the Hole 1268a

652   samples, in serpentinites where talc has not been observed on a macro-scale it may only be

653   present in small amounts as a micron-scale intergrowth with serpentine. This is consistent

654   with the apparent difficulty in identifying talc-free serpentine during electron microprobe

655   analyses (Moll et al., 2007; this study). For all of the Hole 1268a samples to shift from

656   seawater-like $\delta^{11}B$ (cf. Vils et al., 2009) to those observed in this study (and those of Boschi

657   et al., 2008), implies that the $\delta^{11}B$ of serpentinite changes almost completely at the onset of

658   talc formation and that significant further changes in $\delta^{11}B$ are unlikely with increasing

659   degrees of talc growth. In this case, at least, the dominant factor controlling the $\delta^{11}B$ may be

660   the different fluid-mineral fractionation that prevails at low-pH and high-temperature, acting

661   in concert with a fluid produced under open-system conditions. This fluid has not

662   experienced the in-situ distillation process described by Vils et al. (2009) necessary to

663   produce particularly heavy $\delta^{11}B$ in minerals and provides a source of lighter $\delta^{11}B$ than that

664   with which the serpentinite lithologies of Hole 1272a and 1274a were in equilibrium.

665   This also helps to reconcile the measured B isotope ratios with the suggested

666   sequence of events that account for the Sr isotope systematics of the Hole 1268a samples.

667   The return to seawater-like Sr isotope signatures through interaction with seawater at ocean

668   floor ambient conditions is not mimicked by the boron isotope systematics because, at the

669   low temperatures at the surface of the seafloor, fluid-mineral fractionation of boron isotopes

670   will be at a maximum. Any boron incorporated into mineral phases under these conditions

671   will be particularly light. For example, at pH 8.2 and at temperatures of <100 °C, fluid-

672   mineral fractionation factors would be at least -24 ‰ (Figure 6b), resulting in a shift in

673   mineral hosted B to $\delta^{11}B = +16$ ‰ (assuming equilibrium with seawater with $\delta^{11}B$ +40 ‰)

674   which is in good agreement with the measured values of Hole 1268a samples.

675

676   *5.4 Implications of talc-bearing lithologies at convergent margins.*

677

678   The significance of talc-bearing ultramafic lithologies exhumed at convergent

679   margins has been recognised for decades. Hydration of the mantle wedge (e.g. Bebout and

680   Barton, 1989; Fryer et al., 1999; Marschall and Schumacher, 2012), generation of chemical

681   and isotopic heterogeneity in the mantle wedge (e.g. Gerya and Yuen 2003; Hyndman and

682   Peacock, 2003; Grove et al., 2009), and erosion, entrainment and transport of heterogeneous

683   serpentinite and its derivatives have resulted in lively debate regarding the ultimate fate of

684   boron-bearing lithologies contained within the downgoing slab versus that removed from the

685   mantle wedge through subduction erosion (e.g. Peacock and Hervig, 1999; Benton et al.,

686   2001; Savov et al., 2005; Tonarini et al., 2011; Scambelluri and Tonarini, 2012; Marschall

687   and Schumacher, 2012). Despite the lower boron concentrations in talc compared to

688   serpentinite (Boschi et al., 2008; Vils et al., 2008), the stability of talc to greater depths and

689   higher pressures during subduction (Pawley and Wood, 1995) has the potential for the

690   delivery of boron, sometimes isotopically lighter than its precursor serpentinite (cf. Boschi et

691   al., 2008; Vils et al., 2009; this study), to deeper regions beneath evolving arcs, and possibly

692   even beyond the arc in cold subduction zones.

The talc-altered serpentinites of ODP Leg 209 Hole 1268a represent a rare example of serpentinite that has been recently and variably altered by interaction with a high-T, low-pH, high-Si fluid at a mid-ocean ridge setting. Although likely restricted to areas of mid-ocean ridges that are experiencing mid- to high-temperature hydrothermal activity, such as the area around the Logatchev hydrothermal field, processes such as those observed during this study may occur in many spreading centre settings where anomalous concentrations of CH_4, H_2 and / or Mn are detected, or mid-water light back scattering anomalies are observed in the overlying water column. While the generation and subduction of talc-bearing serpentinite produced as a result of prograde metamorphism is well known at convergent margins (e.g. Sorensen and Grossman, 1993; Bebout and Barton, 2002; King et al., 2003, 2007; Spandler et al., 2008; Marschall and Schumacher, 2012) little effort has been dedicated to the quantification of the effects of subducting talc generated at mid-ocean ridge settings. This is inevitably a function of the (im)practicalities of sampling peridotite at mid-ocean ridges and the lack of knowledge regarding the abundance and spatial extent of these lithologies. As more information is gathered regarding the distribution of high-temperature, ultramafic-hosted hydrothermal systems, then the relative contributions of convergent-margin- versus mid-ocean ridge-generated talc to boron transport at, and beyond, subduction zones will become clearer.

6. Concluding remarks

The ultramafic samples recovered from Hole 1268a, ODP Leg 209 have experienced high degrees of prior melt depletion, most of which occurred in antiquity, followed by multiple episodes of fluid / rock interaction and hydrothermal alteration. The sequential transformation from melt-depleted peridotite to serpentinite to talc-altered serpentinite has

718   imparted distinctive δ^{11}B signatures, similar to talc-altered serpentinites seen elsewhere on

719   the Mid-Atlantic ridge. Assuming that serpentinites from nearby Hole 1272a and Hole 1274a

720   are reasonable analogues for Hole 1268a lithologies, a likely sequence of events can be

721   constructed to account for the present day boron and strontium isotope systematics of Hole

722   1268a serpentinites and talc-bearing serpentinites. Low temperature (c. 200 °C) interaction

723   with seawater resulted in intense to complete serpentinization of a nominally anhydrous

724   peridotite protolith, accompanied by a shift in δ^{11}B to seawater-like values and a shift in Sr

725   isotope ratios to significantly more radiogenic values. Subsequent interaction with a high-

726   temperature (300-350 °C), low-pH, Si-bearing hydrothermal fluid induced varying degrees of

727   talc-alteration, i.e. Si-metasomatism, causing a shift to lighter δ^{11}B (likely accompanied by a

728   significant loss of boron) but no significant change in Sr isotope systematics. Although talc

729   formation under these conditions results in an ultramafic lithology with a reduced boron

730   concentration compared to serpentinite, it potentially provides a feedstock to subduction

731   zones with a more variable, and lighter δ^{11}B than previously expected based upon the

732   subduction of serpentinite.

733

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1211 **Figure captions**

1212

1213 Figure 1. (a) Location of the 15° 20′ N Fracture Zone, sampled by Ocean Drilling Program

1214 Leg 209, in the Atlantic Ocean. (b) Location of ODP Sites 1268a, 1272a, and 1274a. The

1215 location of the active Logatchev Hydrothermal Field is also shown. Bathymetry from

1216 Lagabrielle et al. (1998).

1217

1218 Figure 2. Downhole variation in metres below seafloor (mbsf) of primary lithology, intensity

1219 of alteration, loss on ignition (LOI) and SiO_2 wt. %. Modified after Bach et al. (2004) and

1220 Paulick et al. (2006).

1221

1222 Figure 3. The mineralogical control of Hole 1268a bulk-rock compositions. (a) Bulk-rock

1223 MgO/SiO_2 vs. Al_2O_3/SiO_2. Solid line is the "Terrestrial Array for peridotite" of Jagoutz et al.

1224 (1979). Hole 1272a and 1274a serpentinites from Harvey et al. (2006) and Godard et al.

1225 (2008). Large oval symbols denote Hole 1268a samples from this study, small round symbols

1226 denote equivalent Hole 1268a lithologies of Paulick et al. (2006). Talc- (± chlorite-) altered

1227 serpentinites are labelled according to the core section they were recovered from. (b) Mineral

1228   major element compositions of serpentine (lizardite), bastite pseudomorphs of orthopyroxene,

1229   chlorite and talc. Bulk-rock compositions in (a) are readily accounted for by simple mixing of

1230   mineralogical components in (b). Endmember mineral compositions from Yalçin and

1231   Bozkaya, (2006) (talc), Harvey et al. (2012) (opx and cpx), Padrón-Navarta et al. (2011)

1232   (chlorite). Large symbols = this study. Small symbols = Moll et al. (2007). * = analyses of

1233   talc after olivine from this study with reduced beam size (4-8 μm).

1234

1235   Figure 4. Strontium and boron isotope variation with depth at Hole 1268a. (a) $^{87}Sr/^{86}Sr$ versus

1236   depth (mbsf). Oval symbols as in Figure 3a. White squares are the leached residues of 2R2

1237   27-35 (A), 2R2 83-89 (B), 4R1 44-55 (C) and 6R1 100-110 (D). Leached samples are tied to

1238   their respective unleached sample by dotted lines. Hashed field denotes range of values

1239   reported by Vils et al. (2009). Light grey field denotes range of compositions obtained for

1240   serpentinites from Atlantis Massif (Boschi et al., 2008). Dark grey field denotes talc- and talc

1241   + chlorite-altered serpentinites from Atlantis Massif (Boschi et al., 2008). (b) Boron isotope

1242   variability with depth. Symbols and fields as in (a) above.

1243

1244   Figure 5. Boron and strontium abundances in Hole 1268a serpentinites and talc-altered

1245   serpentinites. Concentrations expressed in μg g^{-1}.

1246

1247   Figure 6. Fluid-mineral fractionation as a function of pH and temperature. (a) Relative

1248   speciation of boric acid versus borate as a function of pH at 25 °C (Hemming and Hanson,

1249   1992). Stippled area denotes possible range of seawater pH (after Boschi et al., 2008). Dark

1250   grey shading denotes pH conditions prevalent during Si-metasomatism / talc-alteration (Bach

1251   et al., 2004). Light grey shading denotes likely range of pH conditions experienced during the

1252   serpentinization of ODP Leg 209 serpentinites (Vils et al., 2009). (b) Despite the contraction

1253 of the possible magnitude of fluid-mineral fractionation with increasing temperature, under

1254 the conditions prevalent during Si-metasomatism, a fluid-mineral fractionation factor of for

1255 $\delta^{11}B$ of c. +19 ‰ is still possible, independent of any differences in initial fluid composition

1256 between the early serpentinizing fluid and the later talc-alteration-related fluid. Modified after

1257 Foustoukos et al., 2008; Boschi et al. (2008).

1258

1259 Figure 7. Strontium and boron isotope evolution diagram for Hole 1268a serpentinites. A

1260 melt-depleted peridotite precursor is progressively serpentinized at c. 200 °C (Process 1),

1261 resulting in a rapid increase in $\delta^{11}B$ and likely accompanied by an equally rapid increase in

1262 [B] (not illustrated). At relatively low fluid / rock ratios, i.e. when < 10% of the peridotite Sr

1263 budget has been exchanged with seawater, the serpentinite has already acquired a seawater-

1264 like $\delta^{11}B$. Continued fluid / rock interaction has little further effect upon $\delta^{11}B$ but continues to

1265 increase serpentinite $^{87}Sr/^{86}Sr$ by exchanging 75 to 100 % of the original mantle-like Sr.

1266 Subsequent interaction with a low-pH, high-T fluid (> 300 °C; Bach et al. 2004) and the

1267 consequent alteration to a talc-bearing lithology results in dehydration, loss of B and a shift to

1268 lighter $\delta^{11}B$ (Process 2; see text for details). The large grey arrow with solid outline denotes

1269 the shift in $\delta^{11}B$ possible starting from the most ^{11}B-rich of the precursor samples of Vils et

1270 al. (2009) whereas the large grey arrow with the dashed outline denotes range of possible

1271 $\delta^{11}B$ using the least ^{11}B-rich sample of Vils et al. (2009) as a precursor. Both arrows span a

1272 range of 19 ‰ − the possible range calculated in Figure 6b for these pH-temperature

1273 conditions. This differs from the inferred process of talc-alteration and acquisition of boron

1274 isotope signatures suggested by Boschi et al. (2008). Small numbers near narrow dashed,

1275 dotted and solid curves indicate modelled water / rock ratios. Figure modified after Boschi et

1276 al. (2008).

Hole	Core	Section	Lithology	Interval - top	bottom	Piece no.	Depth (mbsf)
1268a	2R	2	S	27	35	4	15.19
1268a	2R	2	S	83	89	10	15.67
1268a	4R	1	S	44	55	9	25.24
1268a	6R	1	S	100	106	15	35.40
1268a	8R	1	T	28	35	8	44.28
1268a	8R	1	T	108	114	25	45.08
1268a	8R	2	S	14	20	3	45.64
1268a	10R	1	S	35	41	7	53.95
1268a	11R	1	T	39	45	8	58.99
1268a	12R	1	S	41	46	3	63.61
1268a	13R	1	S	46	55	6	68.66
1268a	14R	1	T	90	96	16	73.70
1268a	15R	3	T	38	44	1	80.78
1268a	16R	2	T	88	94	4	84.49
1268a	18R	3	T	87	93	9	95.59
1268a	18R	1	T	100	110	10	95.72
1268a	19R	1	S	34	44	1	97.34
1268a	19R	2	S	104	110	14	98.04
1268a	19R	4	S	61	67	1	101.41
1268a	20R	1	S	100	110	8	102.60
1268a	23R	3	S	92	98	4	119.83
1268a	27R	1	G	102	108	8	136.53
1268a	29R	1	G	123	129	14	146.33

Table 1. Samples from ODP Leg 209 Site 1268 used in this study. Site 1268 is located at 14°50.755 N, 45°04.641 W, and commenced at a water depth of 3007 m. The Hole penetrated to a depth of 146.7 metres below seafloor (mbsf) and 78.7 m of material was recovered, with primary lithologies comprising 63 % harzburgite, 11 % dunite and 26 % gabbro. Lithologies sampled were serpentinite (S), talc-altered serpentinite (T), and gabbro / micro-gabbro (G). Core images of the samples can be found at http://www-odp.tamu.edu/publications/209_ir/volume/cores/cor_1268.pdf.

Sample	Lithology		$^{87}Sr/^{86}Sr$	2 σ	[Sr]
1268a 2R2 27-35	serpentinite	bulk rock	0.71196	0.00015	2.44
		acetic leach	0.71727	0.00088	13.00
		HCl leach	na	na	na
		leached residue	0.707630	0.000030	0.12
1268a 2R2 83-89	serpentinite	bulk rock	0.709012	0.000005	1.97
		acetic leach	0.70912	0.00002	10.81
		HCl leach	0.70918	0.00001	4.10
		leached residue	0.70871	0.00007	0.37
1268a 4R1 44-55	serpentinite	bulk rock	0.708995	0.000009	2.01
		acetic leach	0.70921	0.00001	8.51
		HCl leach	0.70906	0.00002	2.03
		leached residue	0.707668	0.000008	0.14
1268a 6R1 100-106	serpentinite	bulk rock	0.709004	0.000007	2.18
		acetic leach	0.70916	0.00003	10.70
		HCl leach	0.70901	0.00001	1.34
		leached residue	0.70784	0.00005	0.14
1268a 8R1 28-35	talc-altered serpentinite	bulk rock	0.709102	0.000009	na
1268a 8R1 108-114	talc-altered serpentinite	bulk rock	0.708731	0.000009	2.38
1268a 8R2 14-20	serpentinite	bulk rock	0.70882	0.000009	1.02
1268a 10R1 35-41	talc-altered serpentinite	bulk rock	0.708912	0.000007	1.77
1268a 11R1 39-45	talc-altered serpentinite	bulk rock	0.709149	0.000006	0.41
1268a 12R1 41-46	serpentinite	bulk rock	0.708857	0.000006	1.43
1268a 13R1 46-55	serpentinite	bulk rock	0.708978	0.000008	1.03
1268a 14R1 90-96	talc-altered serpentinite	bulk rock	0.708928	0.000011	0.62
1268a 15R3 38-44	talc-altered serpentinite	bulk rock	0.708805	0.000005	1.03
1268a 16R2 88-94	talc-altered serpentinite	bulk rock	0.709093	0.000006	1.38
1268a 18R3 87-93	talc-altered serpentinite	bulk rock	0.707466	0.000050	2.23
1268a 18R3 100-110	talc-altered serpentinite	bulk rock	0.709054	0.000006	1.55
1268a 19R1 34-43	serpentinite	bulk rock	0.709236	0.000022	0.88
1268a 19R2 104-110	talc-altered serpentinite	bulk rock	0.707318	0.000006	1.69
1268a 19R4 61-67	serpentinite	bulk rock	0.708416	0.000007	0.95
1268a 20R1 100-110	serpentinite	bulk rock	0.709054	0.000008	1.16
1268a 23R3 92-98	serpentinite	bulk rock	0.709110	0.000010	1.13
1268a 27R1 102-108	(micro) gabbro-norite	bulk rock	0.70294	0.000009	72.8
1268a 29R1 123-129	(micro) gabbro-norite	bulk rock	0.703094	0.000011	86.9

Table 2. Strontium isotope and abundance analyses of ODP Leg 209 Hole 1268a serpentinites, talc-altered serpentinites and gabbro. Instrumental mass fractionation corrected for by normalizing results to $^{86}Sr/^{88}Sr = 0.1194$ for isotope measurements. Sr blank was negligible compared to the amount of material processed (typically several hundred ng Sr). SRM 987 reference material (n = 11) during the course of the measurements gave an average $^{87}Sr/^{86}Sr = 0.710248 ± 4$. 2R2 27-35, 2R2 87-93, 4R1 44-55 and 6R1 100-106 were sequentially leached (10 % glacial acetic acid then, 1.5M Romil UpA HCl). Strontium abundance expressed in µg g^{-1}.

Sample	Lithology	^{11}B/^{10}B	δ^{11}B	2σ	[B]
1268A 2R2 27-35	serpentinite	4.1004	11.60	0.32	29
1268A 2R2 83-89	serpentinite	4.1080	15.93	0.24	36
1268A 4R1 44-55	serpentinite	4.0951	10.29	0.25	28
1268A 6R1 100-106	serpentinite	4.0847	10.16	0.37	26
1268A 8R1 28-35	talc-altered serpentinite	na	na	na	na
1268A 8R1 108-114	talc-altered serpentinite	4.0981	13.47	0.74	12
1268A 8R2 14-20	serpentinite	na	na	na	na
1268A 10R1 35-41	talc-altered serpentinite	4.087	10.73	2.97	<3
1268A 11R1 39-45	talc-altered serpentinite	na	na	na	na
1268A 12R1 41-46	serpentinite	4.0946	12.60	0.19	20
1268A 13R1 46-55	serpentinite	4.0909	9.25	0.35	24
1268A 14R1 90-96	talc-altered serpentinite	na	na	na	na
1268A 15R3 38-44	talc-altered serpentinite	4.1171	18.17	0.40	4
1268A 16R2 88-94	talc-altered serpentinite	4.094	12.5	3.7	5
1268A 18R3 87-93	talc-altered serpentinite	4.0927	12.1	2.3	5
1268A 18R3 100-110	talc-altered serpentinite	4.0925	9.65	0.99	<3
1268A 19R1 34-43	serpentinite	na	na	na	na
1268A 19R2 104-110	talc-altered serpentinite	na	na	na	na
1268A 19R4 61-67	serpentinite	4.1227	19.56	0.32	20
1268A 20R1 100-110	serpentinite	4.1218	16.87	0.30	27
1268A 23R3 92-98	serpentinite	4.1157	17.83	0.37	19

Table 3. Boron isotope analyses of ODP Leg 209 Hole 1268a serpentinites, talc-altered serpentinites. ^{11}B/^{10}B isotopic ratio is reported in standard delta notation as permil (‰) deviation from the mean value for the SRM-951 boric acid standard. Boron abundances ([B]) expressed in μg g^{-1}.

Sample	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	MgO	CaO	Na$_2$O	K$_2$O	P$_2$O$_5$	SO$_3$	Cr$_2$O$_3$	NiO	LOI	Total
1268a 2R2 27–35	41.3	0.018	0.60	8.35	0.061	37.2	bdl	bdl	0.002	bdl	0.327	0.342	0.290	11.3	99.8
1268a 2R2 27–35*	41.5	0.019	0.62	8.08	0.057	37.1	0.03	0.11	0.013	0.011	na	na	na	11.8	99.3
1268a 2R2 83–89	40.0	0.018	0.64	7.88	0.092	38.6	bdl	bdl	bdl	bdl	0.157	0.388	0.272	11.8	99.9
1268a 4R1 44–55	42.8	0.006	0.29	6.63	0.056	37.4	bdl	bdl	0.002	bdl	0.640	0.239	0.291	12.3	100.7
1268a 4R1 44–55*	41.6	0.007	0.38	6.37	0.056	36.6	0.03	0.11	0.015	0.007	na	na	na	12.7	97.9
1268a 6R1 100–106	41.6	0.005	0.36	6.62	0.039	38.0	0.00	bdl	0.002	bdl	0.174	0.255	0.276	12.5	99.9
1268a 8R1 28–35*	59.3	0.016	0.90	5.69	0.085	28.1	0.10	0.24	0.019	0.008	na	na	na	4.4	98.7
1268a 8R1 108–114	56.8	0.105	0.88	7.08	0.074	28.5	0.18	0.20	0.010	0.024	0.075	0.259	0.245	5.4	99.8
1268a 8R2 14–20	43.5	0.006	0.45	6.42	0.108	37.3	0.01	bdl	bdl	bdl	0.137	0.285	0.284	11.3	99.8
1268a 10R1 35–41	29.7	0.350	19.7	14.4	0.383	24.5	0.01	0.13	0.009	bdl	bdl	0.083	0.036	10.5	99.8
1268a 11R1 39–45	59.1	0.006	0.16	5.61	0.062	29.1	bdl	0.02	bdl	bdl	0.258	0.158	0.201	5.1	99.9
1268a 12R1 41–46	40.8	0.121	0.89	8.25	0.122	36.5	bdl	0.01	0.002	bdl	0.162	0.331	0.267	12.0	99.4
1268a 13R1 46–55	42.5	0.005	0.42	6.90	0.060	37.6	bdl	bdl	bdl	bdl	0.155	0.302	0.281	11.7	100.0
1268a 14R1 90–96	60.9	0.019	0.25	6.21	0.095	28.3	bdl	0.01	bdl	bdl	0.007	0.056	0.240	4.4	100.5
1268a 15R3 38–44	56.6	0.005	0.30	5.12	0.093	31.0	bdl	bdl	bdl	bdl	0.124	0.151	0.220	6.0	99.6
1268a 16R2 88–94	59.7	0.006	0.66	5.07	0.059	29.1	0.00	0.10	bdl	bdl	0.047	0.174	0.230	4.9	100.1
1268a 18R1 100–110*	64.1	0.028	0.76	4.55	0.062	31.4	0.05	0.19	0.015	0.011	na	na	na	5.4	106.5
1268a 18R3 87–93	42.5	0.202	9.83	7.99	0.272	29.1	1.47	0.12	0.011	0.003	bdl	0.013	0.026	8.4	99.9
1268a 19R1 34–43	39.9	0.008	0.43	7.53	0.071	38.5	bdl	bdl	bdl	bdl	0.247	0.324	0.276	12.1	99.4
1268a 19R1 34–43*	40.4	0.011	0.44	7.55	0.070	38.8	0.03	0.08	0.012	0.005	na	na	na	12.6	100.1
1268a 19R2 104–110	33.7	0.878	14.2	12.4	0.502	27.3	1.02	0.06	bdl	bdl	0.029	0.019	0.020	10.0	100.0
1268a 19R4 61–67	39.9	0.006	0.66	7.57	0.063	38.8	bdl	bdl	bdl	bdl	0.246	0.577	0.287	11.8	99.9
1268a 20R1 100–110	40.6	0.005	0.63	7.02	0.071	38.8	bdl	0.02	bdl	bdl	0.178	0.479	0.265	12.0	100.1
1268a 20R1 100–110*	40.9	0.008	0.64	6.88	0.070	38.8	0.04	0.14	0.013	0.009	na	na	na	12.7	100.2
1268a 23R3 92–98	41.7	0.010	0.51	7.19	0.066	38.5	0.01	bdl	bdl	bdl	0.047	0.281	0.283	11.9	100.5
1268a 27R2 102–108	49.5	0.239	17.8	6.32	0.146	9.49	13.1	2.12	0.032	bdl	bdl	0.001	0.009	1.7	100.5
1268a 29R1 123–129	47.2	0.291	15.2	8.19	0.181	12.6	11.9	1.73	0.030	bdl	bdl	0.003	0.011	2.7	100.1

Table S1. Whole rock major element abundances expressed as weight percent (wt. %). ( ) Denotes XRF measurement made at The Open University, all others performed by XRF at the University of Leicester. Major element and Ni data quality was assessed using two WS-E and OUG-94 at The Open University and a suite of ultramafic reference materials (including UM-1, UM-2, UM-4, JP-1 and PCC-1) at the University of Leicester. Reproducibility of reference materials is within 2% of recommended values and in excellent agreement between the two laboratories. LOI = loss on ignition. bdl = below detection limit. na = not analysed.

	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Cr$_2$O$_3$	FeO	MnO	MgO	CaO	NiO	Na$_2$O	K$_2$O
10R1 35–41 chlorite spot 1	35.35	0.016	20.16	0.098	15.29	0.742	28.07	0.163	0.093	0.024	0.006
10R1 35–41 chlorite spot 2	35.96	0.001	19.47	0.094	15.88	0.828	27.54	0.140	0.053	0.017	0.007
10R1 35–41 chlorite spot 3	35.13	0.034	19.34	0.082	17.02	0.847	27.34	0.112	0.071	0.013	0.012
10R1 35–41 chlorite spot 4	35.51	0.030	19.41	0.161	16.34	0.839	27.43	0.124	0.117	0.033	0.010
10R1 35–41 chlorite spot 5	35.24	0.015	19.57	0.107	16.98	0.922	26.92	0.109	0.112	0.000	0.013
10R1 35–41 chlorite spot 6	35.61	0.018	18.99	0.088	16.74	0.899	27.48	0.116	0.037	0.023	0.005
10R1 35–41 chlorite spot 7	35.60	0.007	20.11	0.113	15.59	0.808	27.52	0.145	0.060	0.047	0.000
10R1 35–41 chlorite spot 8	35.51	0.009	19.93	0.350	15.76	0.874	27.24	0.153	0.081	0.075	0.019
10R1 35–41 chlorite spot 9	35.59	0.013	20.23	0.091	15.34	0.842	27.62	0.147	0.063	0.046	0.010
10R1 35–41 chlorite spot 10	35.55	0.000	19.65	0.097	16.44	0.926	27.17	0.136	0.000	0.025	0.009
10R1 35–41 chlorite spot 11	35.58	0.012	20.34	0.087	15.19	0.863	27.71	0.130	0.048	0.027	0.003
10R1 35–41 chlorite spot 12	34.65	0.014	21.89	0.047	14.34	0.656	28.20	0.134	0.041	0.020	0.003
10R1 35–41 chlorite spot 13	34.78	0.000	21.67	0.051	14.30	0.685	28.29	0.119	0.079	0.022	0.000
10R1 35–41 chlorite spot 14	35.26	0.042	21.50	0.064	14.20	0.623	28.09	0.156	0.030	0.030	0.005
10R1 35–41 chlorite spot 15	35.56	0.026	20.89	0.112	14.46	0.655	28.08	0.118	0.062	0.025	0.009
10R1 35–41 chlorite spot 16	35.10	0.002	21.11	0.093	14.60	0.682	28.20	0.139	0.068	0.000	0.008
10R1 35–41 chlorite spot 17	35.24	0.053	21.05	0.109	14.54	0.657	28.16	0.137	0.029	0.004	0.014
10R1 35–41 chlorite spot 18	35.03	0.022	22.68	0.255	12.44	0.334	28.98	0.147	0.056	0.061	0.000
10R1 35–41 chlorite spot 19	35.67	0.020	22.97	0.130	11.90	0.163	28.96	0.122	0.056	0.016	0.001
10R1 35–41 chlorite spot 20	34.88	0.018	21.50	0.247	13.61	0.666	28.88	0.085	0.079	0.037	0.004
10R1 35–41 chlorite spot 21	35.39	0.012	21.90	0.173	12.70	0.475	29.13	0.083	0.086	0.047	0.010
10R1 35–41 chlorite spot 22	34.88	0.004	21.09	0.228	14.25	0.847	28.49	0.097	0.078	0.029	0.013
10R1 35–41 chlorite spot 23	34.01	0.010	21.49	0.128	12.23	0.310	31.48	0.211	0.077	0.055	0.000
10R1 35–41 chlorite spot 24	35.32	0.020	23.24	0.017	12.47	0.271	28.34	0.156	0.074	0.061	0.026
10R1 35–41 chlorite spot 25	36.14	0.021	21.68	0.067	12.08	0.192	29.64	0.128	0.041	0.000	0.000
10R1 35–41 chlorite spot 26	35.43	0.000	21.69	0.253	12.38	0.403	29.70	0.128	0.000	0.008	0.002
10R1 35–41 chlorite spot 27	34.70	0.000	24.13	0.000	11.77	0.204	28.83	0.307	0.026	0.029	0.001

Table S2.1. Electron microprobe analyses of chlorite from sample 10R1 35-41, Hole 1268a. Analyses normalized to anhydrous composition. Operating conditions: Accelerating voltage of 15 kV, beam current 15nA, beam size 10 μm.

Serpentine after opx

	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	NiO	Na_2O	K_2O
6R1 100-106 spot 1	47.04	0.009	2.87	0.854	5.56	0.067	43.35	0.062	0.118	0.046	0.024
6R1 100-106 spot 2	47.63	0.023	2.25	1.331	7.67	0.096	40.66	0.129	0.133	0.044	0.025
6R1 100-106 spot 3	46.99	0.036	3.34	1.062	5.65	0.063	42.65	0.068	0.070	0.053	0.020
6R1 100-106 spot 4	47.85	0.020	1.93	1.441	7.69	0.103	40.59	0.035	0.151	0.114	0.076
6R1 100-106 spot 5	47.32	0.008	2.28	1.361	7.89	0.085	40.64	0.136	0.180	0.078	0.023
6R1 100-106 spot 6	47.01	0.028	1.57	0.979	9.12	0.099	40.92	0.081	0.128	0.055	0.003
6R1 100-106 spot 7	47.32	0.043	1.85	1.095	11.25	0.135	37.99	0.094	0.182	0.023	0.020
6R1 100-106 spot 8	47.02	0.000	1.88	1.038	11.83	0.124	37.77	0.120	0.169	0.019	0.028
6R1 100-106 spot 9	48.24	0.012	1.29	0.408	10.29	0.091	39.39	0.088	0.159	0.013	0.015
6R1 100-106 spot 10	47.25	0.026	1.70	0.899	11.22	0.156	38.37	0.149	0.121	0.069	0.042
6R1 100-106 spot 11	47.13	0.014	1.81	0.920	11.46	0.118	38.22	0.062	0.180	0.058	0.025
6R1 100-106 spot 12	46.87	0.006	1.95	1.006	11.40	0.051	38.48	0.077	0.105	0.035	0.033
6R1 100-106 spot 13	47.37	0.001	1.68	0.737	11.86	0.090	37.93	0.096	0.165	0.050	0.021
6R1 100-106 spot 14	47.39	0.000	1.70	0.773	11.57	0.141	38.08	0.074	0.210	0.033	0.027

Serpentine after olivine

	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	NiO	Na_2O	K_2O
6R1 100-106 spot 1	49.11	0.012	0.45	0.000	4.82	0.059	45.17	0.045	0.283	0.043	0.006
6R1 100-106 spot 2	49.17	0.000	0.37	0.016	4.41	0.033	45.72	0.031	0.218	0.020	0.010
6R1 100-106 spot 3	49.72	0.000	0.20	0.000	3.70	0.040	46.15	0.000	0.175	0.014	0.004
6R1 100-106 spot 4	49.75	0.003	0.31	0.000	3.93	0.036	45.69	0.033	0.257	0.002	0.000
6R1 100-106 spot 5	50.13	0.001	0.22	0.015	3.73	0.045	45.68	0.016	0.139	0.016	0.009
6R1 100-106 spot 6	49.03	0.017	0.25	0.013	4.90	0.021	45.33	0.038	0.343	0.042	0.011
6R1 100-106 spot 7	49.60	0.000	0.22	0.000	4.14	0.004	45.64	0.028	0.328	0.027	0.008
6R1 100-106 spot 8	49.44	0.009	0.23	0.002	4.48	0.040	45.43	0.036	0.318	0.000	0.006
6R1 100-106 spot 9	49.59	0.006	0.38	0.000	4.68	0.037	44.81	0.083	0.398	0.011	0.014
6R1 100-106 spot 10	49.56	0.013	0.42	0.000	4.24	0.037	45.39	0.075	0.242	0.021	0.003
6R1 100-106 spot 11	49.37	0.011	0.35	0.004	4.39	0.041	45.35	0.061	0.419	0.000	0.007

6R1 100-106 spot 12	49.74	0.014	0.41	0.000	4.24	0.030	45.18	0.057	0.293	0.015	0.013
6R1 100-106 spot 13	49.05	0.000	0.39	0.042	4.58	0.064	45.54	0.047	0.252	0.014	0.021
6R1 100-106 spot 14	49.58	0.015	0.24	0.001	3.55	0.022	46.18	0.038	0.335	0.047	0.000
6R1 100-106 spot 15	49.90	0.000	0.27	0.022	3.17	0.038	46.14	0.046	0.336	0.058	0.019
6R1 100-106 spot 16	49.99	0.000	0.33	0.009	2.92	0.034	46.37	0.027	0.304	0.005	0.019

Table S2.2. Electron microprobe analyses of serpentine after orthopyroxene (opx) and serpentine after olivine from sample 6R1 100-106, Hole 1268a, ODP Leg 209. Composition normalized to anhydrous composition. Analytical conditions as Table S2.1.

10 μm beam diameter

	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Cr$_2$O$_3$	FeO	MnO	MgO	CaO	NiO	Na$_2$O	K$_2$O
6R1 100-106 talc spot 1	62.62	0.01	0.317	0.028	5.69	0.036	31.16	0.009	0.073	0.04	0.013
6R1 100-106 talc spot 2	55.99	0.004	0.302	0	5.37	0.026	38.04	0.022	0.222	0.024	0.009
6R1 100-106 talc spot 3	49.68	0.005	0.61	0.03	4.23	0.042	45.05	0.063	0.258	0.024	0.011
6R1 100-106 talc spot 4	63.27	0.001	0.25	0.008	6.07	0.046	30.2	0.015	0.105	0.043	0
6R1 100-106 talc spot 5	54.02	0	0.347	0	5.35	0.014	39.85	0.05	0.363	0	0.009
6R1 100-106 talc spot 6	49.65	0	0.461	0.02	3.19	0.006	46.39	0.042	0.195	0.021	0.02
6R1 100-106 talc spot 7	50.1	0	0.559	0.023	3.93	0.035	45.08	0.008	0.214	0.03	0.015
6R1 100-106 talc spot 8	51.44	0	0.638	0.006	4.42	0.045	43.12	0.158	0.147	0.017	0.011
6R1 100-106 talc spot 9	49.88	0.012	0.405	0	4.38	0.045	45.01	0.072	0.164	0.015	0.008
6R1 100-106 talc spot 10	62.88	0.007	0.462	0.012	6.9	0.051	29.52	0.014	0.066	0.082	0
6R1 100-106 talc spot 11	49.46	0.017	0.299	0.005	3.7	0.048	45.4	0.721	0.325	0.018	0.001
6R1 100-106 talc spot 12	63.99	0	0.418	0.006	6.36	0.02	29.09	0.017	0.043	0.047	0.01
6R1 100-106 talc spot 13	64.4	0.001	0.244	0	6.73	0.048	28.46	0.022	0.043	0.051	0.004
6R1 100-106 talc spot 14	49.45	0.017	0.483	0.003	4.36	0.033	45.32	0.091	0.218	0.013	0.013
6R1 100-106 talc spot 15	61.81	0.003	0.299	0.014	6.06	0.077	31.61	0.005	0.082	0.028	0.014
6R1 100-106 talc spot 16	51.08	0.002	0.462	0	3.68	0.046	44.51	0.038	0.165	0.021	0.003
6R1 100-106 talc spot 17	49.54	0.02	0.294	0	5.72	0.067	43.96	0.038	0.302	0.045	0.006
6R1 100-106 talc spot 18	52.28	0.028	0.56	0	4.57	0.074	42.22	0.029	0.181	0.041	0.013

4-6 μm beam diameter

	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Cr$_2$O$_3$	FeO	MnO	MgO	CaO	NiO	Na$_2$O	K$_2$O
6R1 100-106 talc spot 1	64.39	0.01	0.15	0.02	6.86	0.05	28.36	0.02	0.05	0.05	0.02
6R1 100-106 talc spot 2	64.24	0	0.12	0	6.65	0.03	28.94	0	0.00	0.01	0
6R1 100-106 talc spot 3	64.20	0.02	0.15	0	6.74	0.06	28.69	0.01	0.09	0.01	0
6R1 100-106 talc spot 4	63.52	0	0.21	0.04	7.86	0.05	28.23	0.01	0	0.06	0.01

6R1 100-106 talc spot 5	64.02	0	0.20	0.01	7.74	0.03	27.87	0.01	0.06	0.03	0.02
6R1 100-106 talc spot 6	64.44	0	0.18	0	6.37	0.05	28.86	0	0	0.07	0.01
6R1 100-106 talc spot 7	63.45	0.01	0.15	0	7.24	0.05	28.98	0.01	0.03	0.06	0.01
6R1 100-106 talc spot 8	63.51	0	0.21	0	7.74	0.05	28.38	0	0.03	0.05	0.02
6R1 100-106 talc spot 9	62.91	0	0.19	0	7.57	0.04	29.22	0.02	0	0.01	0.03

Table S2.3. Electron microprobe analyses of talc from sample 6R1 100-106, Hole 1268a, ODP Leg 209. Composition normalized to anhydrous composition. Analytical conditions as Table S2.1.

Sample	Original mass (g)	After leach (g)	Leached (g)	% leached
2R2 27-35 unleached	0.0301	0.0260	-0.0260	13.6
2R2 83-89 unleached	0.0358	0.0326	-0.0326	8.9
4R1 44-55 unleached	0.0282	0.0228	-0.0228	19.1
6R1 100-106 unleached	0.0302	0.0252	-0.0252	16.6

	$^{87}Sr/^{86}Sr$	+/-	[Sr] ppm	
2R2 27-35 unleached	0.711957	0.000152	2.44	
2R2 83-89 unleached	0.709012	0.000005	1.97	
4R1 44-55 unleached			2.01	
6R1 100-106 unleached	0.709004	0.000007	2.18	
2R2 27-35 leached residue	0.707627	0.000032	0.12	
2R2 83-89 leached residue	0.708710	0.000062	0.37	
4R1 44-55 leached residue	0.707656	0.000058	0.14	
6R1 100-106 leached residue	0.707842	0.000037	0.14	
2R2 27-35 acetic leach	0.717274	0.000843	13.003	
2R2 83-89 acetic leach	0.709125	0.000017	10.81	
4R1 44-55 acetic leach	0.709212	0.000012	8.51	
6R1 100-106 acetic leach	0.709161	0.000026	10.72	
2R2 27-35 HCl leach	lost sample during drying			
2R2 83-89 HCl leach	0.709181	0.000006	4.10	
4R1 44-55 HCl leach	0.709063	0.000014	2.03	
6R1 100-106 HCl leach	0.709013	0.00001	1.34	

Table S3. Leaching experiments for uppermost samples recovered from Hole 1268a. First leach: 10 % glacial acetic acid for 15 minutes. Second leach 1.5M UpA HCl, for 15 minutes.
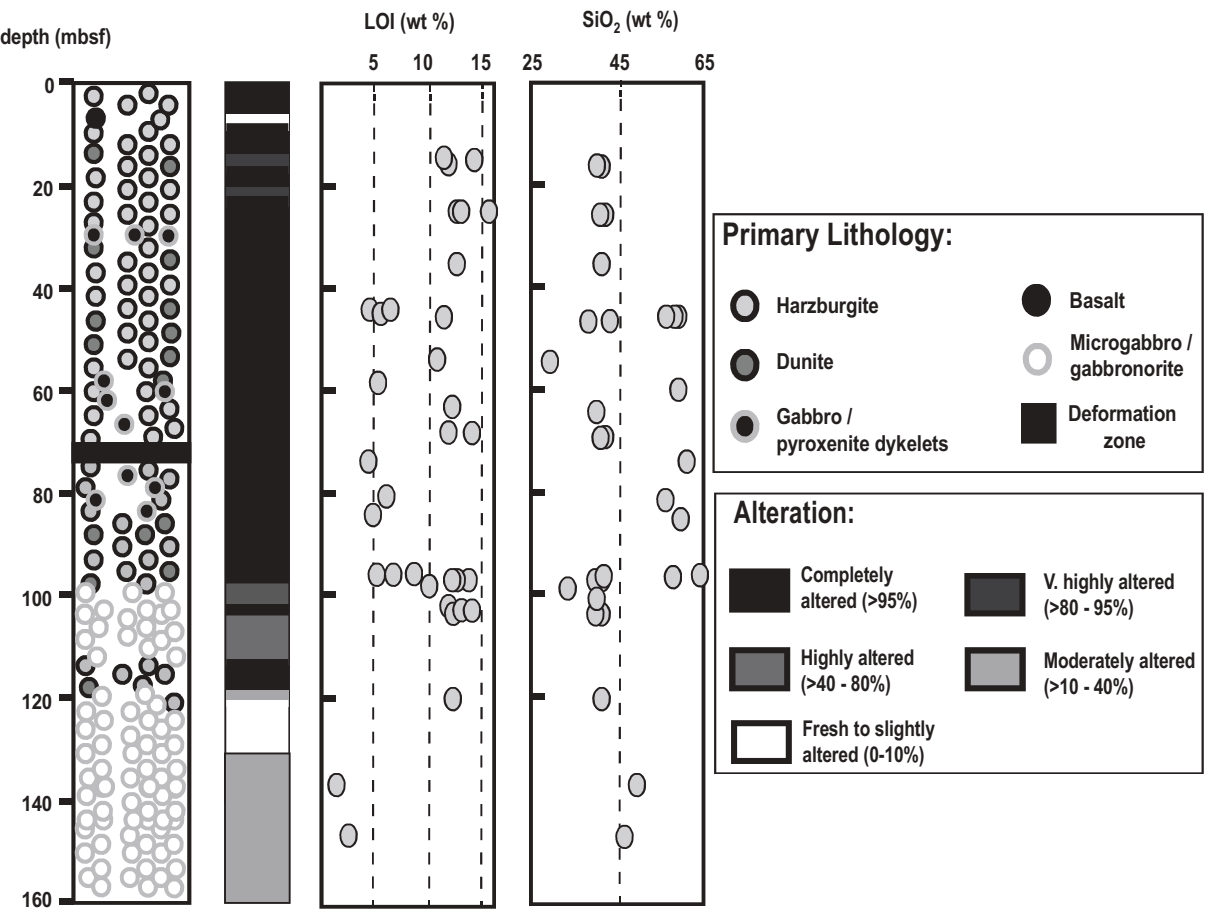
Figure 1

(a) Mid-Atlantic Ridge
15°20' FZ
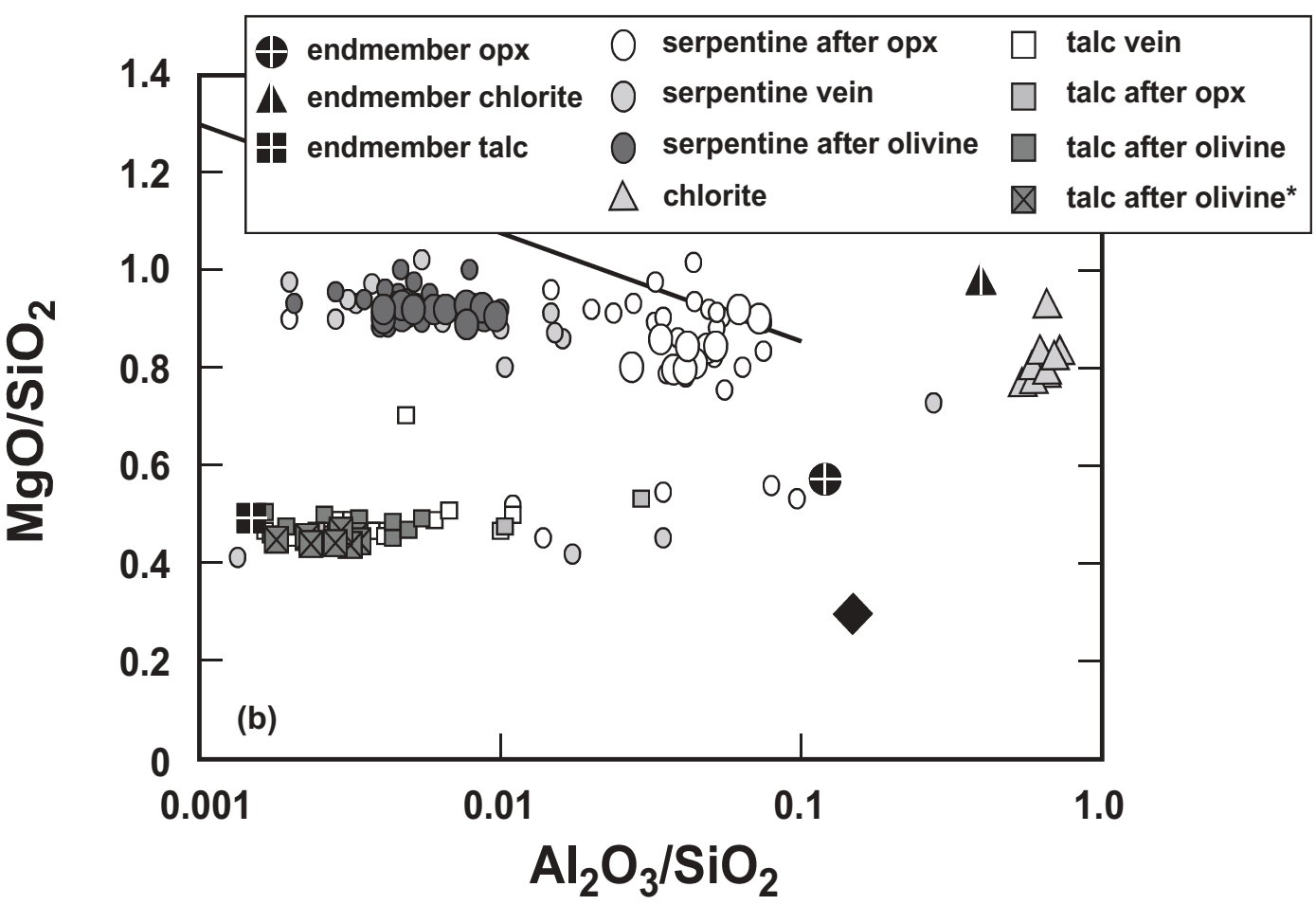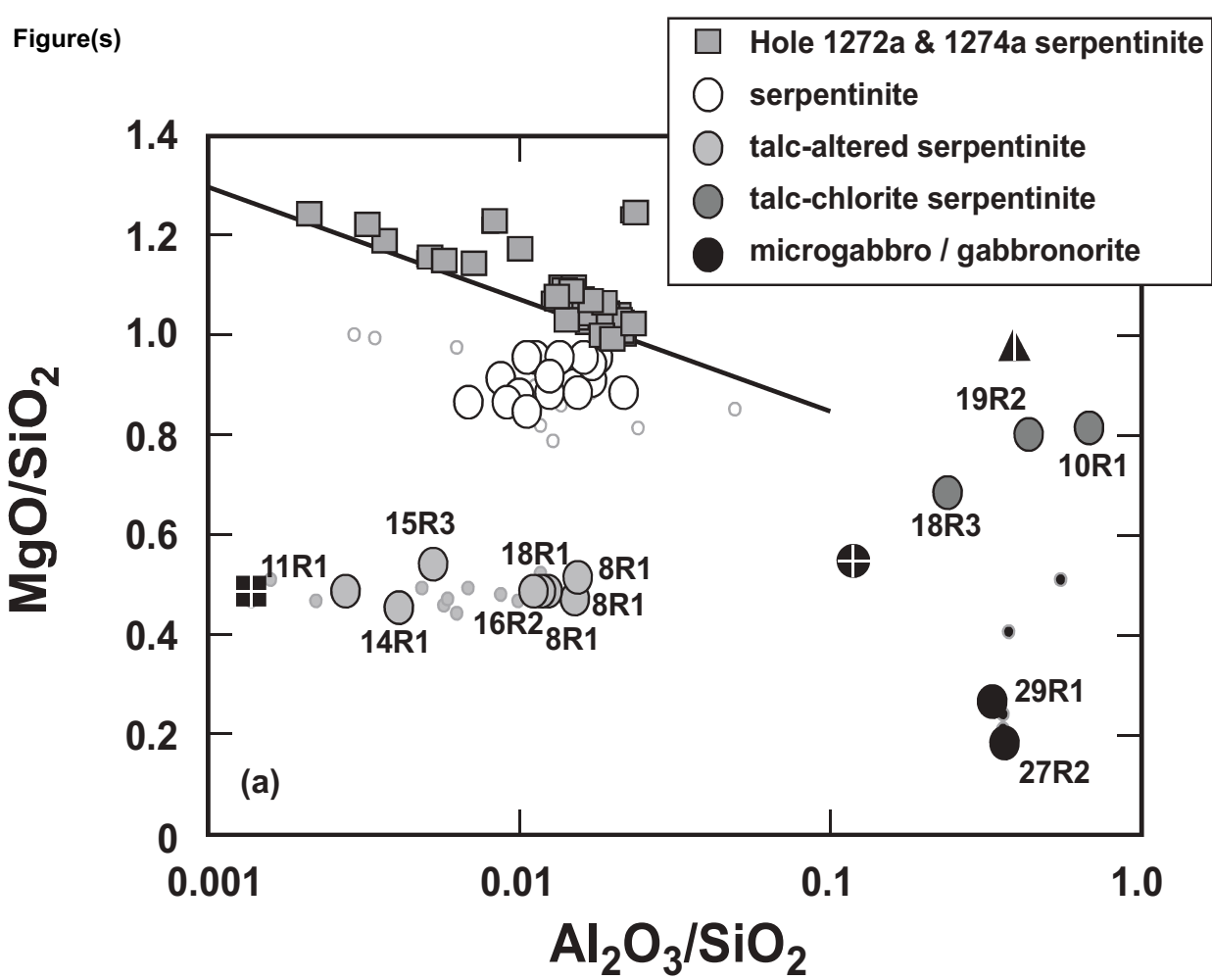
(b)
15°20'N
Hole 1274a
15°10'N
Hole 1272a
15°00'N
Hole 1268a
14°50'N
Logatchev hydrothermal field
10 km
14°40'N
45°00'W   44°50'W

Depth (m.b.s.f)
<2000
2000-2500
2500-3000
3000-3500
3500-4000
4000-4500
4500-5000
>5000

Figure 2

depth (mbsf)

LOI (wt %)

SiO$_2$ (wt %)

Primary Lithology:

Harzburgite

Basalt

Dunite

Microgabbro / gabbronorite

Gabbro / pyroxenite dykelets

Deformation zone

Alteration:

Completely altered (>95%)

V. highly altered (>80 - 95%)

Highly altered (>40 - 80%)

Moderately altered (>10 - 40%)

Fresh to slightly altered (0-10%)

(a)

(b)

Figure 3

Figure 4

Figure 5

Figure 5

(a)

B(OH)$_3$

talc-alteration & Si-metasomatism (Hole 1268a)

serpentinisation (Hole 1272a & 1274a)

seawa

B(OH)$_4^-$

time

Relative abundance

pH

(b)

pH >10

Hole 1272a and 1274a serpentinization

Si-metasomatism

pH = 8.2

pH = 7

pH = 6 (limit of mineral-seawater fractionation)

Fractionation ($^0/_{00}$)

Temperature (^{O}C)

Figure 7