1 Revision 3: Experimental formation of pyroxenite veins by reactions
2 between olivine and Si, Al, Ca, Na and Cl-rich fluids at 800 ºC and 800
3 MPa; implications for fluid metasomatism in the mantle wedge.

4

5 Thomas B. Grant[1,2], Daniel E. Harlov[1], Dieter Rhede[1]

6

7 [1]Deutsches GeoForschungsZentrum

8 Telegrafenberg

9 D-14473 Potsdam

10 FR Germany

11

12 [2] Department of geology and mineral resources engineering,

13 Norwegian University of Science and Technology (NTNU)

14 7491 Trondheim, Norway

15

16 **ABSTRACT**

17 Fluids buffered by a plagioclase matrix are experimentally reacted with olivine

18 megacrysts at 800 ºC and 800 MPa (piston cylinder press, CaF_2 assembly) to form

19 secondary veins of orthopyroxene ± clinopyroxene in the olivine. Fluids utilized were

20 varied in both amount (0 – 2 wt.%) and salinity (0 – 8M NaCl). Assuming equilibrium

21 with the plagioclase matrix, they are presumed enriched in Si, Al, Ca, Na, and Cl and

22 are thereby similar in composition to slab derived fluids. The experiments provide

23 controlled, multicomponent analogues of Si-metasomatism in the mantle wedge

24 above subduction zones. The veins are dominated by orthopyroxene with minor

25 clinopyroxene and form complex interconnected networks along fractures in the

26 olivine. The reaction is rate limited by interfacial process of dissolution and

27   precipitation. Porosity is developed throughout the veins and along sub grain

28   boundaries in the olivine megacrysts. These veins strongly resemble the textures

29   observed in secondary metasomatic orthopyroxene veins widely reported in upper

30   mantle xenoliths within arc magmas. A review of literature data on natural samples

31   and experiments suggests that orthopyroxene ± clinopyroxene veins primarily form

32   between 750 – 950 ºC and over a large pressure range from 0.8 – 3.4 GPa. The

33   abundance and composition of these metasomatic veins may vary as a function of

34   pressure, variances in the fluid-rock partition coefficients, and/or by modification of

35   the metasomatic fluid during the reaction.

36

37

38   **INTRODUCTION**

39   During partial melting or dehydration of subducting oceanic lithosphere, Si-rich melts

40   (Schiano et al., 1995; Prouteau et al., 2001), aqueous fluids (Manning, 2004), or

41   supercritical liquids (Hermann et al., 2006) are released into the overlying mantle

42   wedge. This leads to Si metasomatism in the mantle wedge by the consumption of

43   olivine and the precipitation of secondary orthopyroxene (as well as other phases).

44   This form of metasomatism can be most simply expressed by the following

45   relationship: $(Mg,Fe)_2SiO_4 + SiO_2 = 2(Mg,Fe)SiO_3$. Metasomatic orthopyroxene,

46   formed by infiltrating Si rich melts or fluids in the sub arc mantle, have been observed

47   in mantle xenoliths within arc lavas (Smith and Riter; 1997; Smith et al., 1999;

48   Grégoire et al., 2001; McInnes et al., 2001; Franz et al., 2002; Arai et al., 2003; Arai

49   et al. 2004; Downes et al., 2004; Bell et al., 2005; Berly et al., 2006; Ishimaru et al.,

50   2007; Grégoire et al., 2008; Ishimaru and Arai, 2009; Soustelle et al., 2010; Ishimaru

51   and Arai, 2011; Soustelle et al., 2011) and peridotite complexes (Morishita et al.,

52   2003; Malaspina et al., 2006; Vrijmoed et al., 2013). Experimental studies involving

53   melts (Rapp et al., 1999; Rapp et al., 2010; Malik et al, 2015) or crystalline quartz +

54   fluid (Yund et al., 1997; Milke et al., 2009; Milke et al., 2011; Gardés et al., 2012;

55   Milke et al., 2013) have also shown that olivine will be consumed to form secondary

56   orthopyroxene.

57   Reactions between slab derived fluids or melts and the mantle wedge have

58   significant implications for the recycling of elements at subduction zones and the

59   compositions of arc lavas. It is therefore vital to understand the exchange of major

60   and trace elements during reactions between Si-rich fluids and olivine dominated

61   peridotite rocks. For example, how do the compositions of pyroxenite veins vary and

62   how are metasomatic fluids modified by reactions in the mantle wedge? These

63   processes are poorly understood (Spandler and Pirard, 2013).

64   In terms of major element chemistry, slab derived fluids are thought to be rich

65   in Si, Al, Na, K, Ca, and Cl as well as fluid mobile elements such as LILE, Sr and Pb

66   but poor in Mg and Fe (Manning, 2004; Berly et al., 2006). Due to large similarities

67   in the trace elements and isotopic signatures of arc magmas and the short time scales

68   of recycling from oceanic crust, it is thought that slab derived fluids are primarily

69   transported through the mantle wedge by channelized flow (Zack and John, 2007).

70   However, pervasive flow of fluids has also been observed (Malaspina et al., 2006),

71   and it is likely that some pervasive flow may occur perpendicular to the main channel.

72   In such a scenario the majority of the fluid may pass unmodified for substantial

73   distances in the mantle wedge, but the peridotite wall rocks become partially modified

74   by the influx Si-rich fluids. Furthermore, diapiric mélange zones may also bring felsic

75   material in contact with mafic peridotite rocks (Marschall and Schumacher, 2012).

76   Exchange of elements between them, via channelized, Si-rich fluids, can result in the

77   formation of vein sequences such as those observed in the Svartberget peridotite,

78   Norway which shows a series of zones from peridotite to pyroxenite, garnetite and

79   eclogite towards the country rock migmatite gneiss (for further details see Vrijmoed

80   et al., 2013).

81   In order to gain further understanding of how these metasomatic processes

82   proceed in the mantle wedge, a series of experiments have been conducted in which

83   Si-rich fluids are reacted with olivine megacrysts in a plagioclase matrix to form

84   orthopyroxene and clinopyroxene veins within the olivine megacrysts at conditions

85   applicable to the lower crust and upper mantle (800 °C and 0.8 GPa). These

86   experiments expand on a set of simpler experiments involving the reaction between

87   olivine and quartz $\pm$ H_2O to form secondary orthopyroxene (Yund et al., 1997; Milke

88   et al., 2009; Milke et al., 2011; Gardés et al., 2012; Milke et al., 2013). As slab

89   derived aqueous fluids are typically rich in Si, Al, Na, K, and Ca and low in Mg and

90   Fe (Manning, 2004), to a broad extent the use of anorthite-albite plagioclase as a

91   buffer for the fluids in these experiments is an appropriate analogue for complex

92   natural metasomatic fluids in the sub arc mantle. Variable amounts of fluid (0–2

93   wt.%) and variable fluid compositions (pure H_2O; 2M NaCl and 8M NaCl solutions)

94   are added to test how these parameters affect the vein mineralogy and composition.

95   This experimental data is then compared with naturally occurring, metasomatically

96   induced orthopyroxene and clinopyroxene veins in peridotitic mantle xenoliths. For

97   these same samples, compositional trends are also explored to see if there are any

98   potential indicators of fluid evolution, in terms of Mg, Fe, Al, Ca, and Cr, over small

99   (meter) and long (kilometer) length scales as they pass through the overlying mantle

100   wedge.

101

ELECTRON PROBE MICRO-ANALYSES (EPMA)

Chemical analyses were taken using a JEOL Hyperprobe JXA-8500F with a field-emission cathode at the GFZ Potsdam. For olivine, orthopyroxene, and clinopyroxene operating conditions were 15 kV accelerating voltage and 20 µA beam current. For plagioclase and chlorapatite operating conditions were 10 kV accelerating voltage and 10 µA. Silicate, oxide, and metal standards (both synthetic and natural) were used. A 5 µm beam diameter was used for plagioclase and chlorapatite analyses whereas beam sizes of 0 – 1 µm were used for olivine, orthopyroxene, and clinopyroxene.

EXPERIMENTAL METHODS

All experiments were conducted at the Deutsche GeoForschungsZentrum Potsdam using Johannes type piston cylinder apparatus (Johannes et al. 1971; Johannes, 1973). Pressures of 800 MPa, temperatures of 800°C and run durations of 8 days were used. Seven experiments were conducted in total. In each experiment, the sample charge consisted of isolated single San Carlos olivine crystal fragments in a plagioclase matrix (+ minor chlorapatite) with an added fluid component. Added fluid ranged from 0-2 wt.% (of sample charge) double distilled water and 2 wt.% of either 2 M or 8 M NaCl solution. Compositions of starting materials are given in Table 1 and the details of the run conditions are given in Table 2.

A single crystal of inclusion-free San Carlos olivine was crushed using a metal pestle and mortar. Crystal fragments with sizes of 250–500µm were separated from the crushed material using sieves. To prepare the matrix, plagioclase grains were hand-picked from a sample of partially crushed gabbro from the Bamble Sector, SE Norway. The plagioclase grains were ground to a fine powder (<50 µm) in ethanol

6

126   using an agate pestle and mortar. This powder consisted of > 96% anorthitic

127   plagioclase, 2 – 3% chlorapatite and 1 – 2% Cl-rich calcic amphibole.

128   All sample materials were loaded into platinum capsules with dimensions of 1

129   cm x 3 mm with wall thicknesses of 0.3 mm. The capsules were not pre-saturated

130   with Fe. A Lampert PUK 3 arc welder was used to seal all capsules at both ends.

131   Fluids (double distilled water, 2 M or 8 M NaCl solution) were added to the capsule

132   first via a micro-syringe. The capsules were then half filled with the plagioclase

133   powder, before several single olivine crystal fragments were added. The remainder of

134   the capsule was then filled with more plagioclase powder. All capsules were weighed

135   after the final weld, placed in a 100 °C oven for over an hour, and then weighed

136   again. No weight loss was observed. In the case of experiment OP001, where no fluid

137   was added, the plagioclase powder was dried at 100°C for 24 hours before being

138   added to the capsule.

139   All experiments were conducted in Johannes type piston cylinder apparatus

140   using CaF_2 pressure media, cylindrical graphite ovens, and Ni/Ni-Cr thermocouples

141   (Fig. 1). The graphite ovens are expected to buffer the fO_2 of the experiments to

142   between CCO and CCO-4 (Médard et al. 2008), although the high aH_2O in the most

143   hydrous experiments could potentially increase the fO_2 due to dissociation of H_2O and

144   H^- loss through the capsule walls (Botcharnikov et al 2005). The CaF_2 parts were

145   machined to accommodate four capsules within a single run. Each capsule was

146   separated by a sheet of biotite. Pressure was initially loaded to ~650 MPa before

147   heating to 800 °C. The experiment was then raised up to the desired pressure of 800

148   MPa. Temperature fluctuations were within 1 – 3 °C. After each experiment, the

149   capsules were cleaned and weighed again. None of the capsules were reduced in

150   weight, indicating no observable loss of volatiles during the experiment.

151

RESULTS

153   The olivine crystal fragments reacted with the surrounding plagioclase matrix to form

154   rim coronas of predominantly clinopyroxene and amphibole ± phlogopite. In the

155   olivine grains, vein assemblages of either secondary olivine + clinopyroxene,

156   clinopyroxene + orthopyroxene, and/or pore trails formed. The veins are the primary

157   focus of this study.

158

Textures

Pore trails

161   Small to medium sized pore trails are observed in the olivine grain interiors (Fig. 2;

162   Fig. 3c-d). Pores range from < 1–2 μm to 10–20 μm or greater. Smaller pores have

163   very round shapes and appear to be closely (1–2 μm apart) and regularly spaced (Fig.

164   2a). Small pore trails have also been observed along interphase grain boundaries (see

165   Fig. 3b). Larger pores are much more irregularly shaped (elongate and oblong) and

166   are more widely spaced (up to tens of μm). For examples see Fig. 2b and 3d. Pore

167   trails tend to not extend completely across the olivine grain and may be curved or

168   straight forming a complex network (cf. Fig. 2). Similar trails of small fluid inclusions

169   have been described in olivine from mafic xenoliths (Hansteen et al., 1991),

170   clinopyroxene in peridotites (Frezzotti et al., 2010), and quartz in granites (Lespinasse

171   and Cathelineau, 1990). Open pore spaces have also been observed in sub-arc

172   xenoliths that have been metasomatised by hydrous fluids (see textures in McInnes et

173   al., 2001).

174

Secondary olivine patches

176   Irregular patches and linear veins of secondary olivine, that are richer in Mg

177   compared to the host olivine, are observed in sample OP002 (cf. Figure 2). The

178   interface between Mg-rich olivine and primary San Carlos (Mg-poorer olivine) appear

179   to be slightly diffuse (see Fig. 2b). However, an element line scan indicates that the

180   Mg-rich olivine, while variable in composition, has a sharp interface with the primary

181   olivine (Fig. 4). These patches and veins are typically associated with large and small

182   pores.

183

184   *Pyroxene veins*

185   A complex network of orthopyroxene ± clinopyroxene veins, often extending form

186   the rim to the center or across the whole olivine grain, formed in experiments OP003,

187   OP004, OP010, and OP016 (Fig. 3d). The thicknesses of the veins vary from several

188   μm to over 100 μm. The veins are dominated by orthopyroxene with minor

189   clinopyroxene. Clinopyroxene appears to be more abundant in samples with lower

190   water contents (OP002 and OP010) or with higher salinity (OP016), however, these

191   relationships are difficult to quantify. The vein network may include islands of

192   angular original olivine (Fig. 3d). Contacts between the olivine, orthopyroxene, and

193   clinopyroxene are compositionally sharp in texture (Fig. (Figs. 4, 5, and 6). Interphase

194   boundaries between the pyroxene and the olivine are typically lined with small (1–2

195   μm) round pores (Fig. 3b), although large pores are also common. Small pores are

196   also present within the orthopyroxene veins (Fig. 3d).

197   In natural samples, pyroxene typically replaces olivine in the form of (often

198   thin) pyroxenite veins (e.g., Fig. 2 in Morishita et al., 2003; 2001 Ishimaru et al.,

199   2007; Ishimaru and Arai, 2011), and along grain boundaries (see Grégoire et al.,

200   2001; McInnes et al., 2001). Very thin veins, which are typically <500 μm and as

201   small as ~40–60 μm, of orthopyroxene with complex cross-cutting structures through

202   olivine grains have also been observed (Soustelle et al., 2011; Bernard and Ionov,

203   2013). Thin orthopyroxene veins may also contain vesicles (Bernard and Ionov,

204   2013). Secondary orthopyroxene in natural xenoliths can also form radial aggregates

205   (Arai et al., 2004; Ishimaru et al., 2007) but these were not observed in our

206   experiments.

207

208   **Mineral chemistry**

209   *Secondary olivine*

210   Secondary olivine has an X_{Mg} of ~0.97 and is richer in Mg compared to the San

211   Carlos olivine (X_{Mg} ~0.91) (Table 3). The secondary olivine is also depleted in Al_2O_3,

212   CaO, and NiO but slightly enriched in P_2O_5 and SiO_2 relative to the San Carlos

213   olivine. High-Mg secondary olivine in pyroxenites (up to $X_{Mg} = 0.97$) have been

214   observed in metasomatised xenoliths from Avacha (Ishimaru and Arai, 2011).

215

216   *Orthopyroxene veins*

217   The secondary orthopyroxene veins are Mg rich ($X_{Mg} = 0.98–0.99$). In natural

218   samples, secondary metasomatic orthopyroxene is often characterized by low Al and

219   Ca (as well as Cr) compared to primary orthopyroxene (Smith and Riter, 1997; Smith

220   et al., 1999; McInnes et al., 2001; Franz et al., 2002; Arai et al., 2003; Arai et al.,

221   2004; Downes et al., 2004; Morishita et al., 2003; Berly et al., 2006; Ishimaru et al.,

222   2007; Grégoire et al., 2008; Ishimaru and Arai, 2011) although there is some

223   crossover between the two data sets. Secondary orthopyroxene from the experiments

224   in this study are richer in Al relative to secondary and primary orthopyroxenes from

225   natural samples (Fig. 7) but have comparable Ca contents to most of the natural data.

226   However, many natural secondary orthopyroxenes have extremely Ca depleted

227   compositions relative to primary and experimental orthopyroxenes. The

228   orthopyroxene is also enriched in P_2O_5 compared to the secondary olivine (see Table

229   4, and Figs. 5 and 6). This is a rather surprising result as it is well documented that P

230   preferentially partitions into olivine rather than orthopyroxene over a wide range of P-

231   T-X and fO_2 conditions (Bishop et al., 1978; Millman-Barris et al., 2008; Mallmann

232   and O'Neill, 2009; Mallmann et al., 2009; Konzett et al., 2012). It appears that

233    $D_P^{OPX/fluid)}$ is greater than $D_P^{Ol/fluid}$. The source of the P is presumably the small

234   amounts of chlorapatite in the plagioclase matrix.

235   No significant internal zoning patterns were observed within the

236   orthopyroxene veins. In addition, all elements show sharp step profiles at the interface

237   between olivine and orthopyroxene (Figs. 5 and 6). The composition of the vein

238   orthopyroxene also appears to vary with the molar amount of NaCl in the fluid

239   Increasing molar NaCl in the fluid is correlated with increasing Al_2O_3 and MnO and

240   decreasing CaO in the orthopyroxene (Figure 8). In contrast, no strong trends were

241   observed between the orthopyroxene compositions and the bulk water contents of the

242   samples.

243   The major elements (MgO, SiO_2, FeO) have sharp step function profiles when

244   crossing from olivine to orthopyroxene (Fig 5 and 6). This is also the same for minor

245   elements within the error of the analyses, e.g. NiO, Al_2O_3, CaO. For MnO there is a

246   near constant composition from olivine to orthopyroxene in Fig 5. In Fig. 6 there is a

247   trend of increasing MnO across the olivine-orthopyroxene interface. The

248   concentration of P_2O_5 increases within the orthopyroxene with increasing distance

249   from the olivine-orthopyroxene interface. Some scatter in NiO, MnO and P_2O_5 are

250   seen within the orthopyroxene veins in Fig 5. In some line scans (not shown) Al_2O_3

251   shows symmetrical zoning patterns on either side of the center of the vein, although

252   this was not a very common feature. In sample OP003, secondary orthopyroxene has

253   an MnO composition similar to the primary olivine, whereas in in sample OP010

254   MnO is slightly richer in the orthopyroxene. This was consistent in other line scans of

255   the same samples.

256

257   *Clinopyroxene veins*

258   Two types of Ca-bearing pyroxene were found in the experiments (Table 5). In

259   sample OP016 (8M NaCl solution) the clinopyroxene is richer in Al_2O_3, FeO, MnO,

260   and Na_2O compared to the clinopyroxene from samples OP003 and OP010 (pure

261   H_2O). Augite/pigeonite was only observed in sample OP010 where it coexists in the

262   same vein with clinopyroxene. It is higher in Al_2O_3, TiO_2, and Na_2O but lower in

263   FeO.

264

265   **DISCUSSION**

266   **Formation of veins, pore trails and cracks**

267   *Pore trails*

268   Crushing of the San Carlos olivine crystal and loading of pressure onto the sample

269   during the initial stages of the experiment will introduce micro-fractures into the

270   olivine grains. These have a structure similar to low angle olivine-olivine grain

271   boundaries or sub-grain boundaries, i.e. they are planar fractures with a low angle of

272   mis-orientation that have faster rates of diffusion compared to the adjacent olivine

273   lattices. Fluid within the experimental charge can then hydrate these fractures during

274   the experiment. Hydration of grain and interphase boundaries has been demonstrated

275   in a large number of experimental studies (e.g. Gardés et al. 2012; Milke et al., 2013).

276 Sommer et al. (2008) noted that fluids can become concentrated along dislocation

277 structures and grain boundaries in olivine. Fluid along fractures in olivine has also

278 been shown to allow for exchange of H_2O between melt inclusions and the host

279 magma (Bakker and Jansen, 1994; Massare et al., 2002; Portnyagin et al., 2008). The

280 presence of pores in our experiments strongly suggests that a free fluid was present

281 along the micro-fractures. Inclusion trails in olivine adjacent to secondary

282 orthopyroxene veins have also been observed by McInnes et al. (2001).

283 Small fluid pores are effective agents for the enhanced dissolution of olivine

284 and the precipitation of orthopyroxene (Milke et al., 2013; also see the review by

285 Putnis (2009) for numerous other examples). In systems controlled by grain boundary

286 diffusion, increasing the fluid to rock ratio significantly enhances the rates of reaction

287 (Rubie 1986, Gardés et al., 2012; Milke et al., 2013). This is because the diffusion

288 mechanism changes with increasing hydration of grain boundaries. Diffusion in 'Dry'

289 grain boundaries involves breaking of Si-O bonds, which requires high activation

290 energies. Partially hydrated grain boundaries contain weaker O-H bonds and therefore

291 the activation energies for diffusion are lower and diffusion rates are higher (Rubie

292 1986). The development of (interconnected) free-fluid along grain boundaries results

293 in another change in diffusion mechanism where diffusion rates significantly increase

294 (Gardés et al., 2012). The development from near dry micro-fractures to partially

295 hydrated grain boundaries to pores trails shows the various stages of grain boundary

296 hydration. The pores then become sites of both dissolution of olivine and precipitation

297 of secondary olivine, orthopyroxene, and clinopyroxene.

298

299 *Secondary olivine*

300   Secondary, Mg-richer olivine was only observed in several samples (OP002) It forms

301   in locations that are close to or extend from the individual pores or pore tails. The

302   interface between secondary and primary olivine appears to be sharp (< 1 μm) with a

303   sudden change in major element chemistry. Compositional zoning is then observed in

304   the secondary olivine. The sharp interface suggests that dissolution and precipitation

305   are involved in the formation of secondary olivine but that diffusion was not efficient

306   enough at 800 °C and 800 MPa to create a homogenous secondary olivine zone. It is

307   presumed that secondary olivine in the immediate vicinity of the pore formed first and

308   that the reaction front moved in a direction perpendicular to the fluid-olivine interface

309   replacing the primary olivine with secondary olivine. As the length scales increased,

310   the flux of components across the olivine reaction zone was reduced leading to

311   diffusion profiles.

312

313   *Pyroxene veins*

314   Step function concentration profiles across the olivine-orthopyroxene interfaces and

315   (generally) flat concentrations profiles across the orthopyroxene veins and within

316   olivine (Figs, 5 and 6) suggest that the reaction was limited by interfacial processes

317   (dissolution and precipitation) and not by diffusion. The association of large pores

318   with the secondary veins strongly suggests that a free fluid phase was involved in the

319   reaction. Although line scans across orthopyroxene veins in natural samples have not

320   been reported, the similar textures and the presence of associated fluid inclusions

321   suggest that pyroxene veins in the upper mantle are also rate limited by fluid mediated

322   interfacial processes (particularly at lower temperatures).

323   The orthopyroxene veins have $X_{Mg} = 0.98 - 0.99$ (Table 4). This is close to the

324   expected equilibrium value for the partitioning of Fe/Mg between olivine and

325   orthopyroxene with the secondary olivine composition of $X_{Mg} = 0.97$ (Koch-Muller et

326   al. 1992; von Seckendorff and O'Neill 1993).

327

328   **Balanced reaction for formation of orthopyroxene veins**

329   The textures indicate that olivine is replaced by orthopyroxene and pore space, and

330   the chemical data shows that both olivine and orthopyroxene have homogenous

331   compositions (although there are some small variations). It is possible that some of

332   the pore space along sub-grain boundaries in olivine could represent initial added

333   fluid and formed prior to reaction. However, the presence of pores along interphase

334   boundaries between olivine and orthopyroxene (Figure 3D), along interphase

335   boundaries between secondary orthopyroxene and clinopyroxene (Figure 3B) and

336   within secondary orthopyroxene (Figure 3D) demonstrates that porosity forms during

337   reaction. The relative proportions of orthopyroxene and pore space were determined

338   from area percentages of BSE images using ImageJ software. Three different regions

339   in the orthopyroxene veins within sample OP016 (Fig 3D) gave an orthopyroxene to

340   pore space ratio of 87:13. The results were consistent over areas with minimal (30%

341   of total area) and extensive (55% of total area) vein formation. Therefore, in a volume

342   balanced reaction (an area with thickness of 1 μm), 1 μm^3 volume unit of olivine

343   appears to form approximately 0.87 μm^3 of orthopyroxene + 0.13 μm^3 of pore space.

344   The reaction can be described by the equation;

345

346    $(Mg,Fe)_2SiO4 + SiO_2 = (Mg,Fe)_2Si_2O_6$
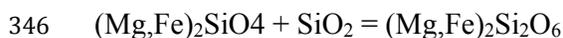
347

348   Using the molar volumes of olivine (43.67 cm^3/mol) and orthopyroxene (62.76

349   cm^3/mol – calculated using Brey et al 1999), the following, volume balanced reaction,

350   describes the proportions of orthopyroxene and pore space observed;

351

352   0.7 olivine + 0.3 pore space = 0.87 orthopyroxene + 0.13 pore space

353

354   As the reaction has a positive ΔV, porosity should be consumed during the formation

355   of orthopyroxene. The presence of porosity could mean that there are two stages to

356   the reaction whereby olivine first dissolves, forming porosity, and then orthopyroxene

357   is precipitated and porosity is consumed. The presence of pores along sub-grain

358   boundaries in the samples could indicate the presence of an initial dissolution

359   dominated first stage to the reaction. An alternative explanation is that not all of the

360   dissolved olivine forms orthopyroxene and that a loss of mass during reaction results

361   in pore space. It has been shown that in many other reactions porosity forms in both

362   positive and negative ΔV (Putnis 2002; Putnis 2009). Porosity is not only related to

363   volume changes but also the solubility of phases in the fluid (Putnis 2002).

364

365

366   **Formation conditions of metasomatic orthopyroxene in the mantle wedge by**

367   **slab-derived fluids**

368   Reactions between slab derived Si-rich fluids and olivine dominated mantle

369   lithologies in the mantle wedge will inevitably lead to the consumption of olivine and

370   the formation of orthopyroxene. This has been demonstrated in experimental studies

371   (Keller et al., 2008; Perchuk and Yapaskurt, 2013), and in natural samples of sub-arc

372   xenoliths (Smith and Riter, 1997; Smith et al., 1999; McInnes et al. 2001; Franz et al.,

373   2002; Arai et al., 2003; Downes et al., 2004; Berly et al., 2006; Morishita et al., 2006;

374   Ishimaru and Arai, 2011; Vrijmoed et al., 2013). Pressure and temperature data from

375   these studies are given in Table 6. Pressures range from 0.8–3.4 GPa indicating that

376   these reactions can occur from top slab conditions to mid to lower crustal conditions

377   following the geotherm in the mantle wedge. Most temperature estimates for the

378   reactions in natural samples are approximately 800–900 ºC (table 6), suggesting that

379   metasomatic orthopyroxene forms within a relatively narrow temperature range.

380   Our experiments, although at the lower end of this pressure range, are

381   consistent with these estimates. The experiments in this study also show that the

382   orthopyroxene veins will form in fluids consisting of both NaCl poor fluids (no added

383   NaCl) and NaCl-richer brines (2 M and 8 M) as long as a high fluid : rock ratio is

384   maintained (>1 wt% fluid). Reactions are also concentrated at grain boundaries and

385   fractures in the primary olivine. This is also observed in many natural examples

386   (Grégoire et al., 2001; McInnes et al., 2001). Increasing the fluid amount, salinity

387   (Fig. 8), fractures, and total grain surface area will increase the amounts of the

388   reaction.

389

390   **Fluid evolution from slab to crust**

391   *Al, Ca, and Cr*

392   Metasomatic orthopyroxene is often characterized by having lower Al, Ca, and Cr

393   than primary orthopyroxenes (for examples see Smith and Riter, 1997; Smith et al.,

394   1999; McInnes et al. 2001; Downes et al., 2004; Morishita et al., 2003). Figure 7

395   shows that this is generally the case but there is a significant amount of scatter in the

396   data with secondary and primary orthopyroxenes often having similar Al, Ca, and Cr

397   contents (Table 4). Secondary orthopyroxene in our experiments is generally much

398   higher in Al than secondary orthopyroxene from natural samples. Experimental

399   orthopyroxenes have Ca contents that are comparable to most of the natural

400   orthopyroxene data except for some extremely Ca depleted natural samples. Higher

401   Al in secondary orthopyroxene has also been observed for other experiments in the

402   same system at higher pressures of 1.8 GPa (Keller et al., 2008). From these

403   experiments there are no clear trends or variations in Al, Ca, and Cr in orthopyroxene

404   or clinopyroxene with pressure and temperature. As Al appears to decrease and Ca

405   appears to increase in the presence of NaCl brines, variations in Al and Ca in

406   secondary orthopyroxenes are unlikely to be explained by variations in the NaCl

407   content in the metasomatizing fluids (Tables 1, 4, and 5).

408   One potential explanation for the variance in Al and Ca (and also perhaps Cr)

409   in secondary orthopyroxene is that concentrations of these elements may vary in the

410   metasomatizing fluids from one location to another or that the fluid compositions are

411   modified during reaction with the peridotite. Consider a fracture zone acting as a

412   conduit for fluid flow. The fluid composition is not dramatically altered as it passes

413   within the fracture zone (Zack and John, 2007). However, fluid percolation through

414   the surrounding wall rock perpendicular to the fracture zone may react with olivine in

415   the peridotite to form orthopyroxene. Precipitation of a zone of Al and Ca rich phases

416   in the form of garnet and clinopyroxene, close to the fluid source, with a more

417   orthopyroxene rich zone at the peridotite contact, has been observed by both

418   Vrijmoed et al. (2013) and Keller et al. (2008). In these experiments, amphibole and

419   clinopyroxene that form at the contact with the plagioclase matrix represent the more

420   Al and Ca rich reaction zone. With greater length scales (meters) in natural

421   metasomatized peridotite (Vrijmoed et al., 2013), the orthopyroxene contains much

422   less Al_2O_3 (0.53-0.9) and CaO (0.21-0.24) compared to Al_2O_3 (3.03-4.68) and CaO

423   (0.61-0.73) in orthopyroxene from the experiments of Keller et al. (2008) and this

424   study (Al_2O_3 = 3.39 and CaO = 0.51), which have much smaller length scales

425   (microns). This would appear to explain why the Al and Ca contents of secondary

426   orthopyroxenes vary so much.

427

428   *Mg and Fe*

429   The very high xMg contents of the product phases raise concerns that some Fe might

430   have been lost to the Pt capsules during the experimental runs, whilst we cannot rule

431   this out our results are consistent with the relationship between pressure and xMg for

432   natural samples (Fig. 9). Very high xMg values have been observed in several studies

433   of natural samples (Morishita et al. 2003; Ishimaru and Arai 2011) also imply that our

434   results are not extraordinary. Additionally, it seems unlikely that during dissolution of

435   olivine Fe can instantaneously be diffused to the capsule walls several hundred

436   microns away but not incorporated into the product phases across the reaction

437   interface that can be less than a micron, unless the partitioning of Fe/Mg between the

438   product phases and fluid is low.

439   Using the data in Table 6, XMg appears to decrease with increasing pressure

440   in both orthopyroxene and clinopyroxene (Figure 9a). This trend fits both the natural

441   and experimental data, but is unlikely to represent phase stability over pressure as

442   ferrosilite has a greater molar volume relative to enstatite. It could be related to the

443   composition of the metasomatic fluid changing with pressure, i.e. indicating a

444   possible signature of fluid evolution as it passes from the slab through the mantle

445   wedge. Experimental peridotite – fluid partitioning experiments by Ayers et al. (1997)

446   showed that the rock / fluid partition coefficients appear to change with pressure. At

447   2.0 GPa and 900 °C $D_{Mg}^{rock/fluid}$ = 82.5 and $D_{Fe}^{rock/fluid}$ = 32.1. At 3.0 GPa and 900 °C,

448    $D_{Mg}^{rock/fluid}$ = 10.1 and $D_{Fe}^{rock/fluid}$ = 9.3. Although this represents a very limited data

449   set, this does suggest that at higher pressures pyroxene bearing vein assemblages will

450   be more Fe rich than at lower pressures. This might explain the trends shown in

451   Figure 9. Therefore, slab derived fluids should produce increasingly Mg rich

452   pyroxenite veins as they move to shallower pressures. $D^{rock/fluid}$ for Mg also increases

453   relative to Fe as temperature increases (Ayers et al., 1997), although it appears to have

454   a lesser effect compared to pressure.

455

456   **IMPLICATIONS**

457   Whilst both slab derived fluids and melts are important metasomatic agents in the

458   mantle wedge, this work specifically focuses on the role of fluid driven reactions. The

459   experiments presented here clearly demonstrate that the reaction between slab-derived

460   fluids and olivine will form orthopyroxene veins similar to those observed in

461   xenoliths from the mantle wedge. Sharp compositional changes across the interfaces

462   between olivine and orthopyroxene indicate that this reaction is rate limited by

463   interfacial processes (dissolution and precipitation). At high fluid : rock ratios, an

464   interconnected grain boundary facilitates fast diffusion rates of elements during

465   reaction (Rubie 1986; Gardés et al. 2012).

466   A review of the literature on orthopyroxene formed by fluids within the

467   mantle wedge shows that this reaction occurs over a narrow temperature range ~800-

468   900°C but a wide pressure range >0.8-3.4 GPa. This means that secondary

469   orthopyroxenite veins may develop by reaction with slab derived fluids at these

470   temperatures from the slab interface to the lower arc crust above a subduction zone.

471   The composition of secondary metasomatic phase is controlled by variation in fluid

472   compositions, which may vary over cm-m scales (Al + Ca + Cr) during reaction or

20

473   (Mg / Fe) due to differences in the partitioning behavior at different pressures (km

474   scale).

475   The results from these experiments enhance our understanding of the chemical

476   fluxes from slab to crust. Whilst channelized flow of slab fluids may pass rapidly

477   through the mantle with little modification, the mantle wall rock will become

478   significantly metasomatized and these reactions may control the composition of the

479   mantle source regions that arc-magmas are derived from.

480

481   **ACKNOWLEDGEMENTS**

487   **BIBLIOGRAPHY**

488   Arai, S., Ishimaru, S., and Okrugin, V.M. (2003). Metasomatized harzburgite

489   xenoliths from Avacha volcano as fragments of mantle wedge of the Kamchatka arc:

490   implication for the metasomatic agent. The Island Arc, 12, 233-246.

491   Arai, S., Takada, S., Michibayashi, K., and Kida, M. (2004). Petrology of peridotite

492   xenoliths from Iraya Volcano, Philippines, and its implication for dynamic mantle-

493   wedge processes. Journal of Petrology, 45, 369-389.

494   Ayers, J. C., Dittmer, S. K., and Layne, G. D. (1997). Partitioning of elements

495   between peridotite and H_2O at 2.0–3.0 GPa and 900–1100° C, and application to

496   models of subduction zone processes. Earth and Planetary Science Letters, 150, 381-

497   398.

498   Bakker, R.J., and Jansen, J.B.H., (1994). A mechanism for preferential H_2O leakage

499   from fluid inclusions in quartz, based on TEM observations. Contributions to

500   Mineralogy and Petrology, 116, 7-20.

501   Bell, D.R., Grégire, M., Grove, T.L., Chatterjee, N., Carlson, R.W., and Buseck, P.R.

502   (2005). Silica and volatile-element metasomatism of Archean mantle: a xenolith-scale

503   example from the Kaapvaal Craton. Contributions to Mineralogy and Petrology, 150,

504   251-267.

505   Bénard, A., and Ionov, D.A. (2013). Melt- and fluid-rock interaction in supra-

506   subduction lithospheric mantle: evidence from andesite-hosted veined peridotitic

507   xenoliths. Journal of Petrology, 54, 2339-2378.

508   Berly, T. J., Hermann, J., Arculus, R. J., and Lapierre, H. (2006). Supra-subduction

509   zone pyroxenites from San Jorge and Santa Isabel (Solomon Islands). Journal of

510   Petrology, 47, 1531-1555.

511   Bishop, F.C., Smith, J.V., and Dawson, J.B. (1978). Na, K, P and Ti in garnet,

512   pyroxene and olivine from peridotite and eclogite xenoliths from African kimberlites.

513   Lithos, 2, 155-173.

514   Botcharnikov, R.E., Kopke, J., Holtz, F., and Wilke, M. (2005). The effect of water

515   activity on the oxidation and structural state of Fe in a ferro-basaltic melt. Geochimica

516   et Cosmochimica Acta, 69, 5071-5085.

517   Brey, G.P., Doroshev, A.M., Girnis, A.V., and Turkin, A.I. (1999). Garnet-spinel-

518   olivine-orthopyroxene equilibria in the $FeO-MgO-Al_2O_3-SiO_2-Cr_2O_3$ system: I.

519   composition and molar volumes of minerals. European Journal of Mineralogy, 11,

520   599-617.

521 Downes, H., Macdonald, R., Upton, B.G.J., Cox, K.G., Bodinier, J-L., Mason, P.R.D.,

522 James, D., Hill, P.G., and Hearn, B.C. Jr. (2004). Ultramafic xenoliths from the

523 Bearpaw Mountains, Montana, USA: evidence for multiple metasomatic events in the

524 lithospheric mantle beneath the Wyoming craton. Journal of Petrology, 45, 1631-

525 1662.

526 Franz, L., Becker, K-P., Kramer, W., and Herzig, P.M. (2002). Metasomatic mantle

527 xenoliths from the Bismark Microplate (Papua New Guinea)- thermal evolution,

528 geochemistry and extent of slab-induced metasomatism. Journal of Petrology, 43,

529 315-343.

530 Frezzotti, M. L., Ferrando, S., Peccerillo, A., Petrelli, M., Tecce, F., and Perucchi, A.

531 (2010). Chlorine-rich metasomatic H_2O-CO_2 fluids in amphibole-bearing peridotites

532 from Injibara (Lake Tana region, Ethiopian plateau): Nature and evolution of volatiles

533 in the mantle of a region of continental flood basalts. Geochimica et Cosmochimica

534 Acta, 74, 3023-3039.

535 Gardés, E., Wunder, B., Marquardt, K., and Heinrich, W. (2012) The effect of water

536 on intergranular mass transport: new insights from diffusion-controlled reaction rims

537 in the MgO-SiO_2 system. Contributions to Mineralogy and Petrology, 164, 1-16.

538 Grant, T.B., Milke, R., Wunder, B., Wirth, R., and Rhede, D. (2014) Experimental

539 study of phlogopite reaction rim formation on olivine in phonolite melts; kinetics,

540 reaction rates and residence times. American Mineralogist,

541 Grégoire, M., McInnes, B.I.A., and O'Reilly, S.Y. (2001). Hydrous metasomatism of

542 oceanic sub-arc mantle, Lihir, Papua New Guinea Part 2. Trace element

543 characteristics of slab-derived fluids. Lithos, 59, 91-108.

544 Grégoire, M., Jego, S., Maury, R.C., Polve, M., Payot, B., Tamayo, R.A. Jr., and

545 Yumul, G.P.Jr. (2008). Metasomatic interactions between slab-derived melts and

546 depleted mantle: insights from xenoliths within Monglo adakite (Luzon arc,

547 Philippines). Lithos, 103, 415-430.

548 Hansteen, T.H., Andersen, T., Neumann, E.R., and Jelsma, H. (1991). Fluid and

549 silicate glass inclusions in ultramafic and mafic xenoliths from Hierro, Canary

550 Islands: implications for mantle metasomatism. Contributions to Mineralogy and

551 Petrology, 107, 242-254.

552 Herman, J., Spandler, C., Hack, A., and Korsakov, A.V. (2006). Aqueous fluids and

553 hydrous melts in high-pressure and ultra-high pressure rocks: implications for element

554 transfer in subduction zones. Lithos, 92, 399-417.

555 Ishimaru, S., Arai, S., Ishida, Y., Shirasaka, M., and Okrugin, V.M. (2007). Melting

556 and multi-stage metasomatism in the mantle wedge beneath a frontal arc inferred

557 from highly depleted peridotite xenoliths from the Avacha Volcano, Southern

558 Kamchatka. Journal of Petrology, 48, 395-433.

559 Ishimaru, S., and Arai, S. (2009). Highly silicic glasses in peridotite xenoliths from

560 Avacha volcano, Kamchatka arc; implications for melting and metasomatism within

561 the sub-arc mantle. Lithos, 107, 93-106.

562 Ishimaru, S., and Arai, S. (2011). Peculiar Mg-Ca-Si metasomatism along a shear

563 zone within the mantle wedge: inference from fine-grained xenoliths from Avacha

564 volcano, Kamchatka. Contributions to Mineralogy and Petrology, 161, 703-720.

565 Johannes W. (1973) Eine vereinfachte Piston-Zylinder-Apparatur hoher Genauigkeit.

566   Neues Jahrbuch Mineralogi 337-351

567 Johannes W., Bell P.M., Mao H.K., Boettcher A.L., Chipman D.W., Hays J.F.,

568 Newton R.C., and Seifert F. (1971) An interlaboratory comparison of piston-cylinder

569 pressure calibration using the albite-breakdown reaction. Contributions to Mineralogy

570 and Petrology, 32, 24-38

571 Keller, L.M., Wunder, B., Rhede, D., and Wirth, R. (2012). Component mobility at

572 900ºC and 18 kbar rom experimentally grown coronas in natural gabbro. Geochimica

573 et Cosmochimica Acta, 72, 4307-4322.

574 Koch-Müller M., Cemic L., and Langer K. (1992). Experimental and thermodynamic

575 study of Fe-Mg exchange between olivine and orthopyroxene in the system MgO-

576 FeO-SiO$_2$. European Journal of Mineralogy, 4, 115–135

577 Konzett, J., Rhede, D., and Frost, D.J. (2012). The high PT stability of apatite and Cl

578 partitioning between apatite and hydrous potassic phases in peridotite: an

579 experimental study to 19 GPa with implications for the transport of P, Cl and K in the

580 upper mantle. Contributions to Mineralogy and Petrology, 163, 277-296.

581 Lespinasse, M., and Cathelineau, M. (1990). Fluid percolations in a fault zone: a

582 study of fluid inclusion planes in the St Sylvestre granite, northwest Massif Central,

583 France. Tectonophysics, 184, 173-187.

584 Liu, Y., Olsen, A.A., and Rimstidt, J.D. (2006) Mechanism for the dissolution of

585 olivine series minerals in acidic solutions. American Mineralogist, 91, 455-458.

586 Malaspina, N., Herman, J., Scambelluri, M., and Compagnoni, R. (2006). Polyphase

587 inclusions in garnet-orthopyroxenite (Dabie Shan, China) as monitors for

588   metasomatism and fluid-related trace element transfer in subduction zone peridotite.

589   Earth and Planetary Science Letters, 249, 173-187.

590   Malik, A., Nelson, J., and Dasgupta, R. (2015). Partial melting of fertile peridotite

591   fluxed by hydrous rhyolitic melt at 2-3 GPa: implications for mantle wedge

592   hybridization by sediment melt and generation of ultrapotassic magmas at convergent

593   margins. Contributions to Mineralogy and Petrology, 169, 48.

594   Mallmann, G., and O'Neill, H.St.C. (2009). The crystal/melt partitioning of V during

595   mantle melting as a function of oxygen fugacity compared with some other elements

596   (Al, P, Ca, Sc, Ti, Cr, Fe, Ga, Y, Zr, Nb). Journal of Petrology, 50, 1765-1794.

597   Mallmann, G., O'Neill, H.St.C., and Klemme, S. (2009). Heterogeneous distribution

598   of phosphorus in olivine from otherwise well-equilibrated spinel peridotite xenoliths

599   and its implication for the mantle geochemistry of lithium. Contributions to

600   Mineralogy and Petrology, 158, 485-504.

601   Manning, C.E. (2004). The chemistry of subduction zone fluids. Earth and Planetary

602   Science Letters, 223, 1-16.

603   Marschall, H.R., and Schumacher, J.C. (2012). Arc magmas sources from melange

604   diapirs in subduction zones. Nature Geoscience, 862-867.

605   Massare, D., Metrich, N., and Clocchiatti, R. (2002). High-temperature experiments

606   on silicate melt inclusions in olivine at 1 atm: inference on temperatures of

607   homogenization and H_2O concentrations. Chemical Geology, 183, 87-98.

608   McInnes, B.I.A., Gregoire, M., Binns, R.A., Herzig, P.M., and Hannington, M.D.

609   (2001) Hydrous metasomatism of oceanic sub-arc mantle, Lihir, Papua New Guinea:

610   petrology and geochemistry of fluid-metasomatised mantle wedge xenoliths. Earth

611   and Planetary Science Letters, 188, 169-183.

612   Médard, E., McCammon, C.A., Barr, J.A., and Grove, T.L. (2008). Oxygen fugacity,

613   temperature reproducibility, and H_2O contents of nominally anhydrous piston-

614   cylinder experiments using graphite capsules. *American Mineralogist,* 93, 1838-1844.

615   Millman-Barris, M.S., Beckett, J.R., Baker, M.B., Hofmann, A.E., Morgan, Z.,

616   Crowley, M.R., Vielzeuf, D., and Stolper, E. (2008). Zoning of phosphorus in igneous

617   olivine. Contributions to Mineralogy and Petrology, 155, 739-765.

618   Milke, R., Kolzer, K., Koch-Müller, M., and Wunder, B. (2009) Orthopyroxene rim

619   growth between olivine and quartz at low temperatures (750-950°C) and low water

620   concentration. Mineralogy and Petrology, 97, 223-232.

621 Milke, R., Abart, R., Keller, L., and Rhede, D. (2011) The behavior of Mg, Fe, and Ni
622 during the replacement of olivine by orthopyroxene: experiments relevant to mantle
623 metasomatism. Mineralogy and Petrology, 103, 1-8.

624 Milke, R., Neusser, G., Kolzer, K., and Wunder, B. (2013) Very little water is
625 necessary to make a dry solid silicate system wet. Geology, 41, 247-250.

626 Morishita, T., Arai, S., and Green, D.H. (2003). Evolution of low-Al orthopyroxene in
627 the Horoman Peridotite, Japan: an unusual indicator of metasomatizing fluids. Journal
628 of Petrology, 44, 1237-1246.

629 Perchuk, A.L., and Yapaskurt. V.O. (2013). Experimental simulation of
630 orthopyroxene enrichment and carbonation in the suprasubduction mantle under the
631 influence of H_2O, CO_2 and SiO_2. Geochemistry International, 51, 257-268.

632 Pokrovsky, O.S. and Schott, J. (2000) Kinetics and mechanism of forsterite
633 dissolution at 25ºC and pH from 1 to 12. Geochemica et Cosmochimica Acta, 64,
634 3313-3325.

635 Portnyagin, M., Almeev, R., Matveev, S., and Holtz, F. (2008). Experimental
636 evidence for rapid water exchange between melt inclusions in olivine and host
637 magma. Earth and Planetary Science Letters, 272, 541-552.

638 Prouteau, G., Scaillet, B., Pichavant, M., and Maury, R. (2001) Evidence for mantle
639 metasomatism by hydrous silicic melts derived from subducted oceanic crust. Nature,
640 410, 197-200.

641 Putnis, A. (2002). Mineral replacement reactions: from macroscopic observations to
642 microscopic mechanisms. Mineralogical Magazine, 66, 689-708.

643 Putnis, A. (2009). Mineral replacement reactions. Reviews in Mineralogy and
644 Geochemistry, 70, 87-124.

645 Rapp, R.P., Shimizu, N., Norman, M.D., and Applegate, G.S. (1999). Reaction
646 between slab-derived melts and peridotite in the mantle wedge: experimental
647 constraints at 3.8 GPa. Chemical Geology, 160, 335-356.

648 Rapp, R.P., Norman, M.D., Laporte, D., Yaxley, G.M., Martin, H., and Foley, S.F.
649 (2010). Continent formation in the Archean and chemical evolution of the cratonic
650 lithosphere: melt-rock reaction experiments at 3-4 GPa and petrogenesis of Archean
651 Mg-diorites (sanukitoids). Journal of Petrology, 51, 1237-1266.

652 Rubie, D.C. (1986). The Catalysis of mineral reactions by water and restrictions on
653 the presence of aqueous fluid during metamorphism. Mineralogical Magazine,
654 50, 399-415.

655 Schiano, P., Clocchiatti, R., Shimizu, Maury, R.C., Jochum, K.P., and Hofmann,
656 A.W. (1995). Hydrous, silica-rich melts in the sub-arc mantle and their relationships
657 with erupted arc lavas. Nature, 377, 595-600.

658 Smith, D., and Riter, J.C.A. (1997). Genesis and evolution of low-Al orthopyroxene
659 in spinel peridotite xenoliths, Grand Canyon field, Arizona, USA. Contributions to
660 Mineralogy and Petrology, 127, 391-404.

661 Smith, D., Riter, J.C.A., and Mertzman, S.A. (1999). Water-rock interactions,
662 orthopyroxene growth, and Si-enrichment in the mantle: evidence in xenoliths from
663 the Colorado Plateau, southwestern United States. Earth and Planetary Science
664 Letters, 165, 45-54.

665 Spandler, C., and Pirard, C. (2013). Element recycling from subducting slabs to arc
666 crust: a review. Lithos, 170-171, 208-223.

667 Sommer, H., Regenauer-Lieb, K., Gasharova, B., and Siret, D. (2008). Grain
668 boundaries: a possible water reservoir in the Earth's mantle? Mineralogy and
669 Petrology, 94, 1-8.

670 Soustelle, V., Tommasi, A., Demouchy, S., and Ionov, D.A. (2010). Deformation and
671 Fluid-Rock Interaction in the Supra-subduction Mantle: Microstructures and Water
672 Contents in Peridotite Xenoliths from the Avacha Volcano, Kamchatka. Journal of
673 Petrology, 51, 363-394.

674 Soustelle, V., Tommasi, A., Demouchy, S., and Franz, L. (2011). Melt-rock
675 interactions, deformation, hydration an seismic properties in the sub-arc lithospheric
676 mantle inferred from xenoliths from seamounts near Lihir, Papua New Guinea.
677 Tectonophysics, 608, 330-345.

678 von Seckendorff V., and O'Neill H.S.C. (1993). An experimental study of Fe-Mg
679 partitioning between olivine and orthopyroxene at 1173, 1273 and 1423 K and 1.6
680 GPa. Contributions to Mineralogy and Petrology, 113, 196–207

681 Vrijmoed, J.C., Austrheim, H., John, T., Hin, R.C., Corfu, F., and Davies, G.R.
682 (2013). Metasomatism in the ultrahigh-pressure Svartberget garnet-peridotite
683 (Western Gneiss Region, Norway): implications for the transport of crust derived-
684 fluids within the mantle. Journal of Petrology, 54, 1815-1848.

685 Yund, R. (1997) Rates of grain boundary diffusion through enstatite and forsterite
686 reaction rims. Contributions to Mineralogy and Petrology, 126, 224-236.

687 Zack, T., and John, T. (2007). An evaluation of reactive fluid flow and trace element
688 mobility in subducting slabs. Chemical Geology, 239, 199-216.

689

690

691

692

693

694

695 **Figures**

696 **Figure 1:** Experimental set-up.

697

698 **Figure 2:** BSE images of cracks and veins in olivine. Figure 2 – Image from sample

699 OP004 shows different types of cracks or veins. These include unfilled cracks that

700 cross-cut other features and formed during unloading of pressure; trails of small <1

701 µm pores; and linear patches of secondary more Mg-rich olivine that are interspaced

702 with large pores 1-2 µm pores. For further details on these types see text. Figure 2b –

703 image of sample OP010 shows an area of secondary olivine formation near a crack

704 and large pores as well as a type 1 unfilled crack (contains some polishing material).

705 Line A-B indicates the line scan shown in Figure 4. Note the relatively sharp interface

706 between secondary olivine (dark grey) and the original olivine (lighter grey).

707

708 **Figure 3:** BSE images of orthopyroxene and orthopyroxene veins. Abbreviations are;

709 plag – plagioclase, amph – amphibole, cpx – clinopyroxene, opx – orthopyroxene.

710 Figure 3a – image from sample OP002 shows the reaction rim of amphibole +

711 clinopyroxene that has formed between olivine and the plagioclase matrix. A large

712 clinopyroxene vein extends across the olivine to the reaction rim. Secondary Mg-rich

713 olivine (olivine 2) has also formed in a small zone adjacent to the clinopyroxene vein.

714 Figure 3b shows a pyroxenite vein extending across the olivine grain from sample

715   OP010. Two clinopyroxene compositions are observed. A complex network of large

716   pores and cracks are associated within the olivine close to the vein. It is unclear if

717   these are formed during unloading or due to a fluid. Smaller trails along interphase

718   boundaries, such as the one highlighted with an arrow between the orthopyroxene

719   vein and CPX2, are common between each phase within the vein. Figure 3c –

720   complex vein structure of secondary Mg-rich olivine, clinopyroxene, and pores

721   observed within sample OP010. Figure 3d shows an interconnected network of

722   orthopyroxene veins through an olivine grain from sample OP016. The reaction rim

723   and contact with the matrix is $100 - 200$ μm above the top of this image. Some

724   clinopyroxene is also present in the vein network along with many pores of varying

725   size (< 1 μm up to 20 μm).

726

727   **Figure 4:** Secondary olivine. Line scan across a zone of secondary Mg-rich olivine

728   from sample OP010. The location of line scan A-B is shown in Figure 2. The location

729   of the interface between Mg-rich olivine and primary olivine is shown by the grey

730   dashed lines. Secondary olivine is on the right hand side of the line scan A) and

731   primary olivine is on the left (B).

732

733

734   **Figure 5:** Line scan across an orthopyroxene vein from sample OP003, where the

735   left and right sections are olivine and the middle section is the orthopyroxene vein.

736

737   **Figure 6:** Line scan from olivine to orthopyroxene (left to right) from sample OP010.

738

739   **Figure 7:** Plot of Al vs. Ca for the orthopyroxene veins. OPX I (grey circles) is

740   primary orthopyroxene from sub-arc xenoliths and OPX II is secondary metasomatic

741   orthopyroxene in sub-arc xenoliths. Analyses are taken from Smith and Riter (1997),

742   Smith et al. (1999), McInnes et al. (2001), Franz et al. (2002), Arai et al. (2003), Arai

743   et al. (2004), Downes et al. (2004), Morishita et al. (2004), Berly et al. (2006),

744   Ishimaru et al. (2007), Grégoire et al. (2008) and Ishirau and Arai (2011). Exp =

745   analyses of orthopyroxenes from the experiments in this study.

746

747   **Figure 8:** Effects of a NaCl brine on orthopyroxene compositions. Average analyses

748   of orthopyroxenes from samples OP003 (~0 mol NaCl), OP004 (~2 mol NaCl) and

749   OP016 (~8 mol NaCl) were used and the error bars correspond to the standard

750   deviation of the data for each sample.

751

752   **Figure 9:** X_{Mg} of pyroxenes vs. pressure. X_{Mg} = (Mg/(Mg + Fe) of metasomatic

753   orthopyroxene and clinopyroxene from natural (Arai et al. 2003; Berly et al. 2006;

754   Downes et al. 2004; Franz et al. 2002; McInnes et al. 2001; Morishita et al. 2003;

755   Smith and Riter 1997; Vrijmoed et al. 2013) and experimental (Keller et al. 2008;

756   Perchuk and Yapaskurt 2013) samples plotted against the estimated pressure.

757   Standard deviations in X_{Mg} are the same as the standard deviations for analyses from

758   each study, and errors for pressure are the ranges, if given, in the literature.

Tables

Table 1. EPMA analyses (oxide wt%) of starting materials.

	Plagioclase		San Carlos olivine	Apatite
SiO_2	52.96	(50.01-54.54)	41.86	0.01
Al_2O_3	30.7	(29.53-32.71)	-	-
FeO	0.13	(0.00-0.42)	9.25	0.04
MnO	0.02	(0.00-0.12)	0.36	0.05
MgO	0.03	(0.00-0.15)	50.95	-
CaO	12.65	(11.44-14.57)	0.18	54.43
Na_2O	4.42	(3.40-5.16)	-	-
K_2O	0.05	(0.03-0.09)	0.04	0.03
P_2O_5	0.02	(0.00-0.04)	0.01	42.46
F	-	-	-	-
Cl	0.01	(0.00-0.04)	-	1.09
Total	100.99	-	102.65	98.12
An	0.61	(0.55-0.69)	-	-
Ab	0.39	(0.30-0.44)	-	-
Kfs	-	-	-	-
X_{Mg}	-	-	0.9	-

Table 2. Experimental conditions.

Experiment	Time(h)	T (°C)	P (MPa)	wt.% fluid	Fluid	Veins
OP001	192	800	800	0	-	-
OP002	192	800	800	0.51	H_2O	CPX, Ol2
OP003	192	800	800	2.04	H_2O	OPX
OP004	192	800	800	1.99	2M NaCl	OPX, Ol2
OP010	192	800	800	1.13	H_2O	OPX, CPX, Ol2
OP012	192	800	800	1.86	H_2O	-
OP016	192	800	800	1.98	8M NaCl	OPX, CPX

Table 3. Representative EPMA analyses (oxide wt%) of olivine.

	OL2	**OL2**	**Ol1**	**Ol1**
Experiment	OP010	OP010	OP010	OP010
SiO_2	41.981	42.03	40.661	40.7
TiO_2	0.006	0.011	0.014	-
Cr_2O_3	0.034	0.007	0.022	0.017
Al_2O_3	0.002	-	0.027	0.023
FeO	2.384	2.738	8.599	8.579
MnO	0.19	0.177	0.172	0.125
NiO	0.317	0.376	0.393	0.442
MgO	55.613	55.229	50.018	50.107
CaO	0.026	0.027	0.1	0.085
Na_2O	-	0.016	0.015	-
K_2O	0.008	-	-	0.002
CoO	0.011	0.014	-	0.002
P_2O_5	0.024	-	0.01	0.006
Total	100.595	100.625	100.03	100.089
X_{Mg}	0.971	0.967	0.905	0.906

Ol1 is primary San Carlos olivine, and Ol2 is secondary olivine in patches.
Structural formulae calculated based on four oxygens. $X_{Mg} = Mg/(Mg+Fe)$.

Table 4. Representative EPMA analyses (oxide wt%) of orthopyroxene.
$X_{Mg} = Mg/(Mg+Fe)$.

Experiment	OP003	OP003	OP004	OP004	OP010	OP010	OP010
SiO_2	56.36	56.39	57.17	57.24	58.29	57.72	58.03
TiO_2	0.02	0.02	0.06	0.03	0.04	0.04	0.05
Cr_2O_3	0.03	0.03	0.02	0.03	0.01	0.01	0.02
Al_2O_3	3.22	2.85	3.13	3.25	2.27	3.19	2.27
FeO	1.57	1.46	1.05	1.12	1	0.77	1.03
MnO	0.14	0.15	0.15	0.17	0.23	0.18	0.22
NiO	0.16	0.17	0.13	0.11	0.15	0.13	0.1
MgO	36.35	36.29	36.33	36.09	37.25	37.38	37.15
CaO	0.53	0.57	0.59	0.6	0.62	0.51	0.83
Na_2O	0.02	0.02	0.12	0.09	0.05	0.03	0.07
K_2O	0.01	-	0.01	0.01	-	-	-
CoO	0.02	0.03	0.01	-	-	-	0
P_2O_5	0.04	0.05	0.06	0.06	0.06	0.02	0.05
Total	98.47	98.02	98.83	98.8	99.97	99.99	99.82
X_{Mg}	0.98	0.98	0.98	0.98	0.99	0.99	0.98

'

Table 5. Representative EPMA analyses (oxide wt%) of clinopyroxene.
X_{Mg} = Mg/(Mg+Fe).

Experiment	OP003	OP010	OP010	OP016	OP016	OP016
SiO_2	55.09	55.22	56.26	51.67	53.89	53.51
TiO_2	0.11	0.08	0.25	-	-	-
Cr_2O_3	0.05	0.05	0.02	-	-	-
Al_2O_3	1.17	0.98	4.65	5.71	2.72	3.37
FeO	0.85	0.75	0.66	1.82	1.58	1.66
MnO	0.11	0.14	0.09	0.36	0.3	0.24
NiO	0.07	0.03	0.12	-	-	-
MgO	18.91	19.69	22.16	15.48	17.5	16.56
CaO	23.98	22.91	10.89	23.62	23.16	23.45
Na_2O	0.32	0.28	1.06	0.69	0.63	0.74
K_2O	-	0.03	0.18	-	-	-
CoO	0.02	-	-	-	-	-
P_2O_5	0.04	0.2	0.03	0.13	0.15	0.06
Total	100.72	100.36	96.37	99.48	99.94	99.59
X_{Mg}	1	0.96	0.98	0.99	0.99	0.98

Table 6.

Metasomatic OPX	Pressure (GPa)	Temperature	N	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Cr$_2$O$_3$	MgO	MnO	FeO	CaO	K$_2$O	Na$_2$O	x Mg
Smith et al. (1999)	-	800	2	58.50 (0)	0.03 (1)	0.58 (54)	0.06 (2)	35.20 (57)	0.16 (4)	5.84 (61)	0.39 (18)	-	0.01 (0)	0.91 (1)
Morishita et al. (2003)	>1,0	900	6	57.80 (91)	0.05 (0)	1.01 (119)	0.09 (7)	35.76 (104)	0.16 (1)	5.30 (38)	0.34 (28)	0.03 (0)	0.03 (1)	0.93 (1)
Franz et al. (2002)	1.3	650-950	9	58.50 (0)	0.03 (1)	0.58 (54)	0.06 (2)	35.20 (57)	0.16 (4)	5.84 (61)	0.39 (18)	-	0.01 (0)	0.91 (1)
Smith and Riter (1997)	1.45	800-850	3	57.93 (67)	0.02 (2)	0.12 (7)	0.06 (5)	35.33 (78)	0.30 (18)	6.59 (118)	0.17 (16)	-	0.01 (1)	0.92 (2)
Berly et al. (2006)	1.3-1.7	870	7	56.70 (61)	0.06 (6)	1.45 (48)	0.50 (9)	33.23 (75)	0.10 (4)	6.98 (70)	0.79 (16)	-	0.20 (9)	0.90 (1)
McInnes et al. (2001)	1.0-2.2	790-1034	3	57.79 (21)	0.01 (0)	1.05 (51)	0.36 (5)	34.25 (175)	0.14 (3)	5.65 (34)	0.30 (11)	-	0.02 (1)	0.92 (1)
Arai et al. (2003)	1.62	900	3	57.11 (53)	0.02 (3)	1.21 (27)	0.03 (4)	35.67 (95)	0.10 (3)	4.61 (59)	0.26 (22)	-	-	0.94 (1)
Arai et al (2006)	-		7	57.31 (71)	-	1.31 (47)	0.22 (15)	34.50 (65)	0.18 (6)	5.55 (69)	0.47 (22)	-	-	0.92 (1)
Ishimaru and Arai (2011)	-	845-980	10	57.98 (124)	0.01 (1)	0.97 (33)	0.20 (11)	36.67 (140)	0.08 (4)	3.67 (140)	0.55 (11)	-	-	0.96 (2)
Ishimaru et al. (2007)	-	890-1100	11	57.74 (86)	0.01 (2)	1.21 (50)	0.29 (16)	34.99 (78)	0.13 (4)	5.58 (25)	0.66 (32)	-	-	0.92 (1)
Downes et al. (2004)	2.0	830-1090	2	57.48 (24)	-	0.14 (12)	0.05 (5)	33.70 (62)	0.22 (8)	7.21 (5)	0.35 (48)	-	0.04 (1)	0.89 (0)
Vrijmoed et al. (2013)	3.4	800	109	56.6	0.02	0.53	0.03	30.8	0.23	12.2	0.24	-	0.01	0.82
Experimental														
This study	0.8	800	115	56.63 (63)	0.03 (2)	3.38 (71)	0.02 (2)	36.16 (77)	0.23 (9)	1.79 (59)	0.51 (10)	-	0.04 (3)	0.98 (1)
Keller et al. (2008)	1.8	900	8	56.48	0.01	3.03	0.01	32.78	0.08	8.72	0.61	-	0.06	0.88
Keller et al. (2008)	1.8	900	2	53.39	-	4.68	-	31.92	0.12	7.60	0.73	-	-	0.91
Perchuk and Yapaskurt (2013)	2.5	800	1	56.03	0.23	1.55	-	33.50	-	8.04	0.18	0.01	0.17	0.88

Metasomatic CPX	Pressure (GPa)	Temperature	N	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Cr$_2$O$_3$	MgO	MnO	FeO	CaO	K$_2$O	Na$_2$O	x Mg
Morishita et al. (2003)	>1,0	900	3	54.36 (60)	0.12 (3)	0.78 (49)	0.49 (28)	17.65 (31)	0.10 (0)	1.78 (19)	24.26 (17)	0.07 (6)	0.25 (5)	0.97 (2)
Smith and Riter (1997)	1.3	650-950	1	54.40	0.04	0.80	0.09	18.50	0.06	1.85	23.90	-	0.08	0.97
Franz et al. (2002)	1.45	800-850	7	54.71 (102)	0.02 (2)	1.66 (131)	0.21 (21)	19.03 (140)	0.07 (2)	2.91 (115)	21.01 (264)	0.03 (4)	0.16 (8)	0.93 (4)
Berly et al. (2006)	1.3-1.7	870	8	54.10 (80)	0.11 (8)	1.37 (65)	0.68 (21)	17.20 (45)	0.05 (5)	2.81 (83)	24.15 (42)	-	0.26 (9)	0.94 (2)
McInnes et al. (2001)	1.0-2.2	790-1034	3	55.65 (41)	0.02 (1)	1.35 (14)	0.43 (11)	21.49 (82)	0.08 (1)	2.18 (18)	17.78 (158)	0.21 (11)	0.32 (12)	0.95 (0)
Downes et al. (2004)	2.0	830-1090	18	53.69 (66)	0.14 (10)	1.48 (89)	0.53 (40)	16.35 (120)	0.15 (6)	4.31 (190)	22.54 (59)	-	0.57 (24)	0.89 (5)
Vrijmoed et al. (2013)	3.4	800	117	54.90	0.03	1.20	0.42	15.70	0.11	4.53	21.80	0.01	1.07	0.86
Experimental														
This study	0.8	800	14	54.32 (118)	0.06 (4)	2.25 (160)	0.04 (2)	17.92 (135)	0.19 (10)	1.26 (47)	23.26 (55)	0.01 (2)	0.50 (21)	0.98 (1)

Table 6. Composition of secondary orthopyroxene and clinopyroxene from natural and experimental samples.

Figure 1.
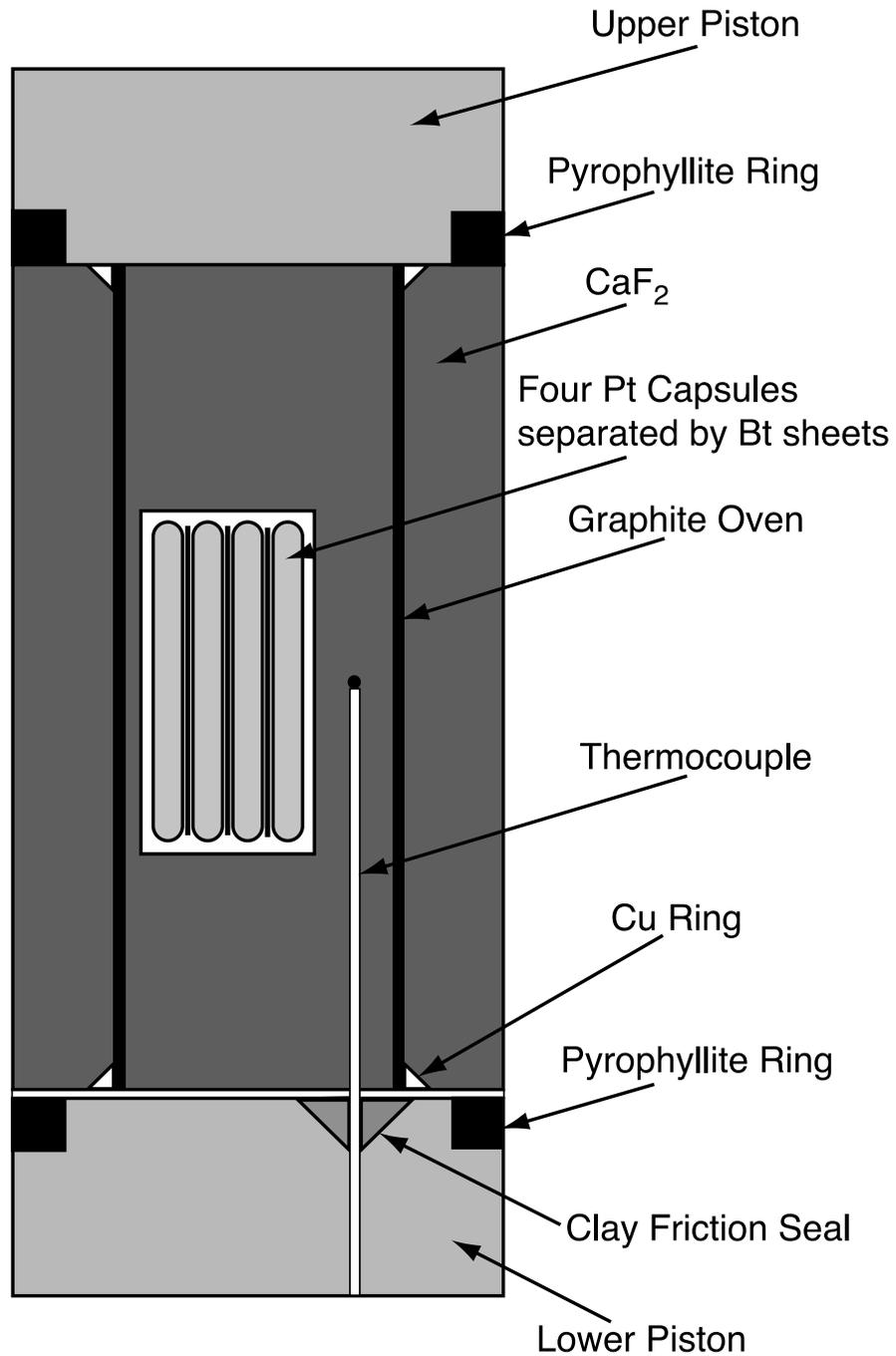
Figure 2.
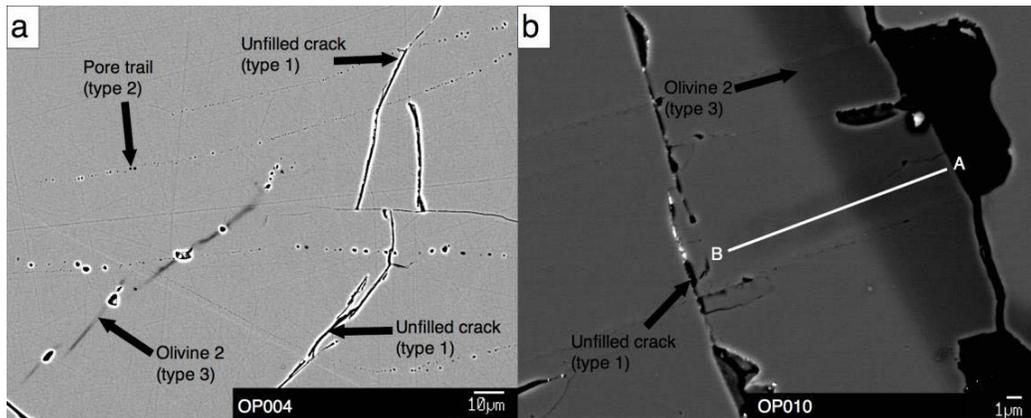
Figure 3.
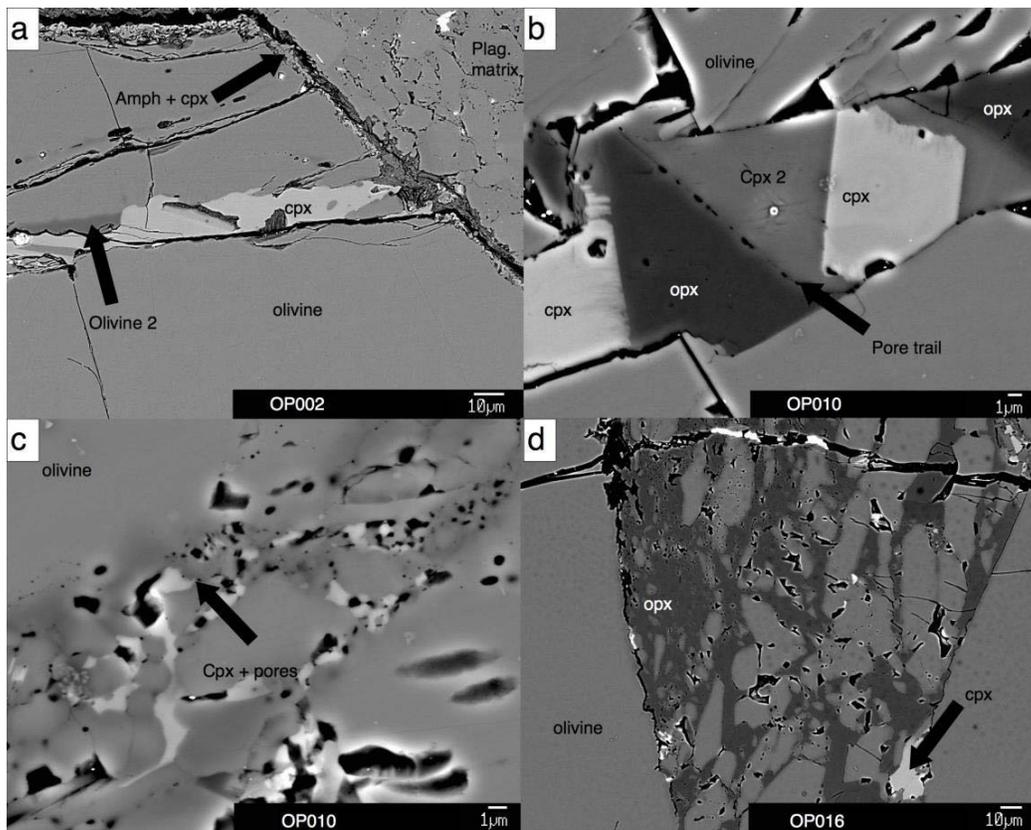
Figure 4.
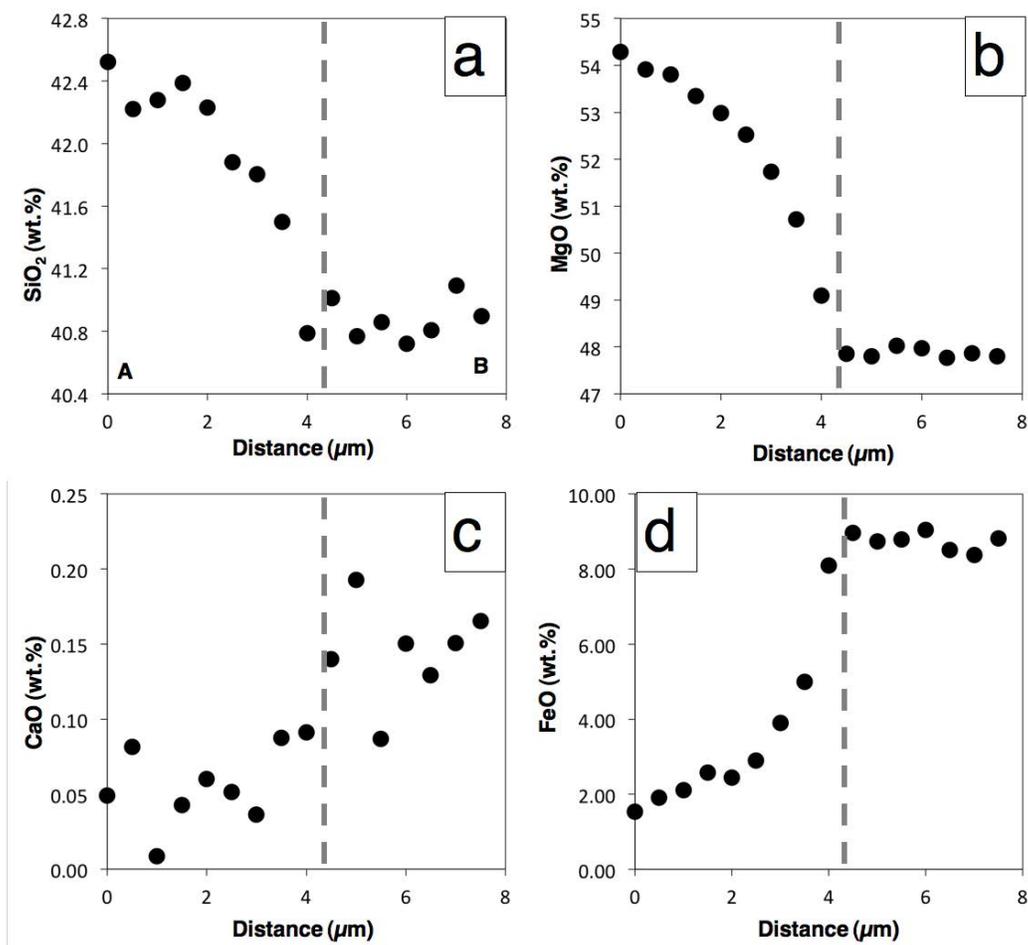
Figure 5.
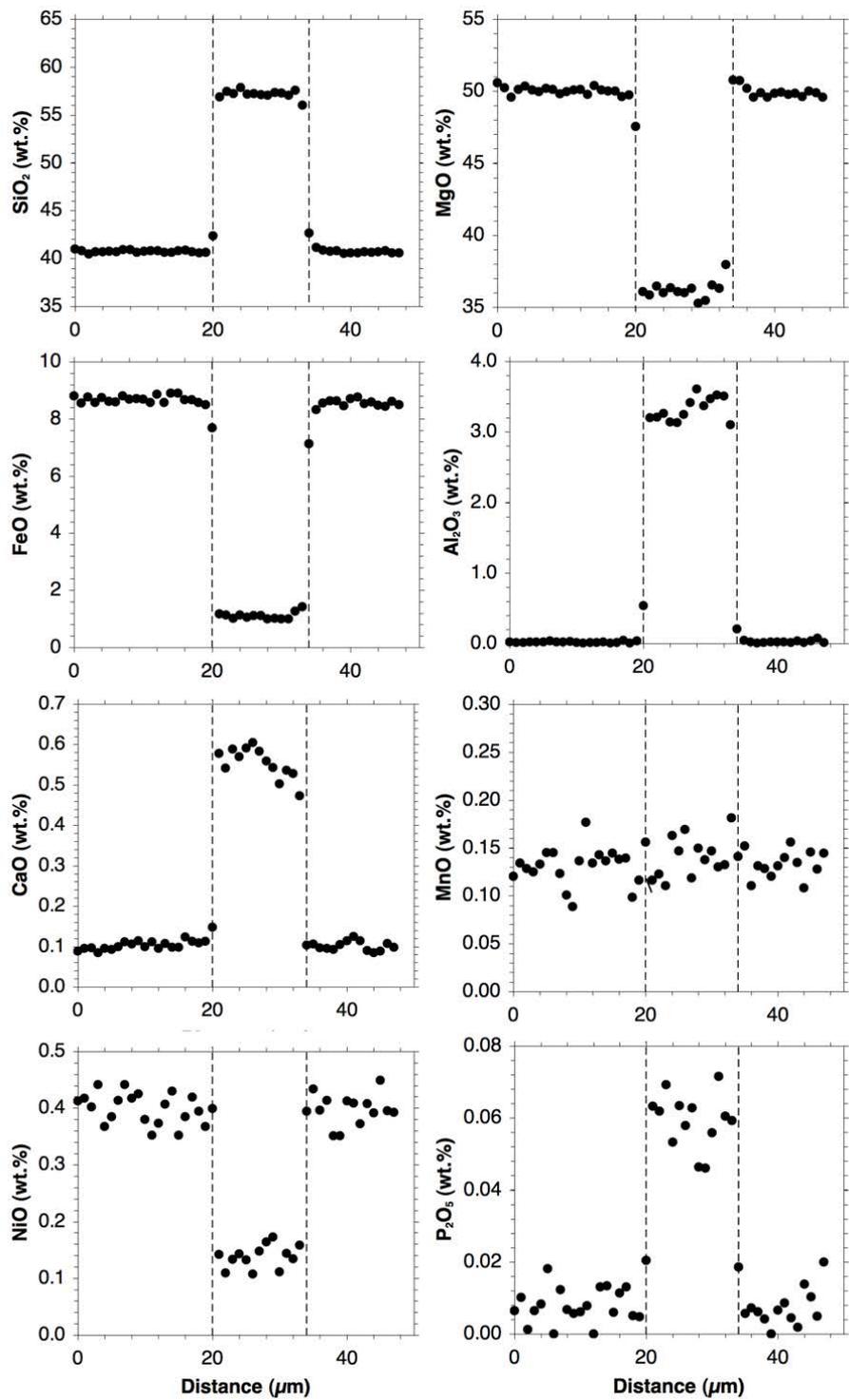
Figure 6.
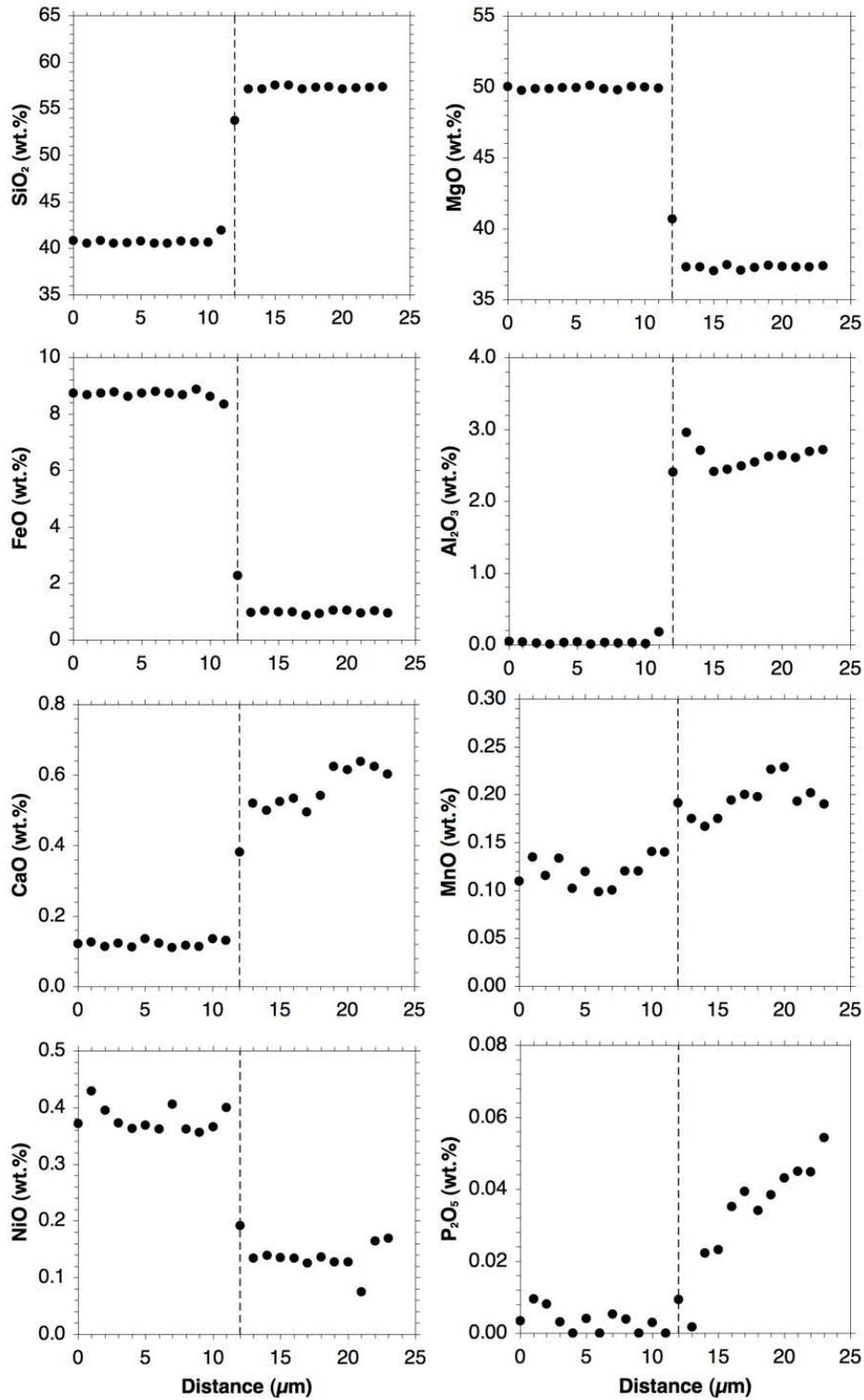
Figure 7.

Figure 8.

Figure 9.