An experimental investigation of C-O-H fluid-driven carbonation of serpentinites under forearc conditions

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Abstract

The carbonation of serpentinites in the forearc region of the mantle wedge in subduction zones and of serpentinites within the subducting slab by fluids derived from prograde dehydration and decarbonation have important implications for the deep Earth carbon cycle. This study shows that the carbonation of serpentinites under the forearc can establish, over time, a significant reservoir for carbon within a partially hydrated mantle wedge and that carbonation of (ultra-) mafic rocks within the subducting slab contributes to C-transfer to greater depths and might supply carbon for arc volcanism or the deep mantle.

We report a new high pressure experimental investigation of the interactions between oxidised C-O-H fluids and serpentinite and model the reaction progress with time series experiments. The CO_2, H_2O and alkane (C_nH_{2n+2}, n=1-6; e.g. methane, ethane) contents in the fluid phase from quenched experimental run products have been analysed by gas chromatography and the results are compared with thermodynamic calculations. With progressive carbonation, the formation of magnesite + chlorite together with quartz, quartz + talc or talc at 1-2 GPa and 500-650 °C was observed. At temperatures above antigorite stability (T$\gtrsim$700 °C and 2 GPa) magnesite + chlorite is stable together with talc, talc + enstatite, enstatite or enstatite + forsterite for decreasing CO_2-content in the fluid.

Carbonation of serpentinite is a rapid process where magnesite forms within the first hour of the experiments, filtering CO_2 from the fluid effectively and equilibrium is approached within 48 h. The CO_2-sequestration and magnesite production are less pronounced at higher temperatures. Therefore, C-O-H fluids released under subarc conditions might migrate through the mantle with only minor changes in their carbon budget whereas significant carbonation likely occurs under the forearc. Furthermore, partition coefficients for Ca, Ba, Sr and Pb between magnesite and a C-poor aqueous fluid have been established to demonstrate the potential of newly formed magnesite to sequester fluid mobile elements.

Highlights

Quantitative C-O-H analyses of fluids after piston cylinder experiments

Carbonation of serpentinites in the forearc region of the mantle wedge

Carbonation is rapid and occurs within the first hour of the experiments

Magnesite is a good monitor for Ca, Ba, Sr and Pb in subduction zone fluids

Keywords

Deep carbon cycle

Carbonation

Serpentinites

Forearc

C-O-H fluid

Partitioning

1. Introduction

A key aspect of the deep carbon cycle is how exogene carbon may be fixed in oceanic lithosphere via hydrothermal alteration of oceanic crust, subducted into the mantle and then recycled within subduction zones (Berner, 1999; Hayes and Waldbauer, 2006; Kelemen and

48 Manning, 2015). Large amounts of carbon stored in marine sediments and altered oceanic

49 crust are transported into the Earth's mantle at subduction zones. Through decarbonation,

50 carbonate dissolution and partial melting, a poorly constrained fraction of carbon is released

51 into fluids and melts during subduction (Poli, 2015) and some carbon is returned to shallower

52 reservoirs (e.g. crust, biosphere and atmosphere), but some carbon is subducted deeper and

53 may be sequestered in the deep mantle (Yaxley and Green, 1994). The magnitudes of the

54 various carbon fluxes and reservoirs have been investigated in several studies (see

55 discussions in Collins et al. (2015); Dasgupta and Hirschmann (2010); Kelemen and Manning

56 (2015)) but remain controversial.

57 In the absence of fluids and for typical subducting slab geotherms, carbonates are stable and

58 refractory. The stability of carbonates at high pressures has been demonstrated in

59 experimental studies on carbonated peridotites and eclogites (Brey et al., 2008; Yaxley and

60 Brey, 2004; Yaxley and Green, 1994). The transport of carbon to greater depths has further

61 been evidenced by stable isotope and mineral inclusions data in some diamonds (Stachel and

62 Harris, 2008).

63 However, carbonates can dissolve into aqueous fluids (Caciagli and Manning, 2003; Dolejs

64 and Manning, 2010), released during subduction. The capacity of the slab to produce such

65 aqueous fluids is pronounced at an early stage of subduction, because prograde

66 metamorphism leads to dehydration reactions. Thermodynamic models have shown that

67 carbon is released as CO_2 from carbonated rocks especially when externally derived hydrous

68 fluids infiltrate them (Gorman et al., 2006; Kerrick and Connolly, 2001a; Kerrick and

69 Connolly, 2001b). The amount of CO_2 in fluids is higher under forearc ($X_{CO_2} \leq 0.7$) compared

70 to subarc ($X_{CO_2} \leq 0.21$) conditions as shown in experimental studies

71 ($X_{CO_2} = \frac{n_{CO_2}[mol]}{n_{CO_2}[mol]+n_{H_2O}[mol]}$; Molina and Poli (2000); Poli (2015); Poli et al. (2009)). Such

C-O-H fluids might interact with the surrounding slab lithologies and (ultra-) mafic rocks in the overlying mantle wedge causing carbonation. Field observations demonstrate the importance of C-O-H-fluid driven carbonation in the slab and overlying mantle wedge (Ague and Nicolescu, 2014; Beinlich et al., 2012; Bjerga et al., 2015; Piccoli et al., 2016; Scambelluri et al., 2016).

This study focuses on the potential capacity of serpentinites to store carbon as carbonates when C-O-H bearing fluids released from the slab migrate into and interact with the partially serpentinized mantle and serpentinites in the slab (Hyndman and Peacock, 2003; Kerrick and Connolly, 1998; Tumiati et al., 2013). Carbon concentrations in fluids are poorly constrained, because earlier experimental studies were often inhibited by the inability to precisely measure the volatile compositions in equilibrium with the solid phases. To analyse the volatile species in C-O-H fluids from experimental capsules Tiraboschi et al. (2016) used a mass spectrometer based technique and computed the obtained mass/charge signal into volatile concentrations.

In this study, we measured directly the C-O-H fluid species in quenched experimental fluids by gas chromatography using an inlet system, that allows the experimental capsule to be pierced under vacuum and the gas phase to be extracted (Martin and Hermann, in press). We compare the measured volatile fluid compositions with thermodynamic calculations and show to what extent the behaviour of real fluids containing dissolved species like CO_3^{2-}, Si^{4+} and Mg^{2+} can be approximated by pure CO_2-H_2O fluids assumed in the model. We demonstrate how fast the formation of carbonates reduces the amount of CO_2 in the fluids by investigating the kinetics of the carbonation reaction through time series experiments. We further show the potential of newly formed magnesite to sequester Ca and fluid mobile trace elements such as Ba, Sr and Pb and show to what extent they may become enriched in carbonated ultramafic rocks. Our results are important to constrain carbon fluxes in subducted ultramafic rocks and

the mantle wedge as we demonstrate that the forearc mantle may, over time, become an important and previously unrecognised reservoir for carbon, whereas carbonation in the subarc is less pronounced.

2. Experimental methods

Piston cylinder experiments were performed using powdered natural serpentinite (>98% antigorite, traces of magnetite and no sulfides according to XRD) mixed with various amounts of oxalic acid dihydrate (OAD; abbreviations are listed in the supplementary information) as the main source of H_2O and CO_2. Four starting mixes (SP1-4) with various serpentinite/fluid ratios were used (Table 1). Ba, Pb, Sr and Ca-carbonate were added in trace and minor abundances (Table 1). See supplementary information for details of preparation and performance of the piston cylinder experiments.

Table 1

Experiments were run at 1 and 2 GPa, between 500-750ºC for 48 h. Two sets of time series experiments, both using SP1, were performed at 600ºC, 2 GPa for 24, 48 and 72 h and at 550ºC, 1 GPa for 0.1, 0.42, 0.85, 1, 48 and 192 h.

3. Analytical Methods

After the piston cylinder experiments, the composition of the fluid in the recovered capsules was analysed by gas chromatography (GC-TCD). Then the capsules were mounted, polished and C-coated for electron microscopy (SEM and EPMA). Afterwards, LA-ICP-MS was used to determine the trace element composition of the solid assemblage on selected runs. The presence of particular mineral phases was verified by powder X-ray diffraction (XRD) for selected samples. The details of these techniques are reported in the supplementary information.

5

3.1. Gas Chromatography – Thermal Conductivity Detector *(GC-TCD)*

Gas-chromatography was applied to identify and quantify the amount and composition of the volatile species in post-run fluids. A sample-inlet system connected to a gas-chromatograph allows capsules recovered after piston cylinder experiments to be pierced under vacuum and the released gas can be analysed (Figure S1 in the supplementary information). For analysing the gas composition of post-run fluids, the sample holder is first heated to ~150°C for ~10 min and then pierced under vacuum. Heating is necessary to guarantee that all volatiles can escape from the sample. The pressure is sensed at constant temperature (ΔT~2°C per analytical session; temperature range over all analyses ~130-160°C) and volume. This pressure is proportional to the amount of the released sample gas according to the ideal gas law. The sample gas is then topped up with pure He gas to above atmospheric pressure (~140 kPa). The gas mixture (sample plus He) is homogenized after waiting ~60 min at constant temperature. Aliquots of this gas mixture are then progressively introduced into, and analysed with the connected GC-TCD 5-7 times showing a reproducibility of ~19%. This routine was used for measuring both standards and samples.

CO_2 was calibrated using pure CO_2 as a standard and alkanes were calibrated using a certificated standard containing 1000 ppm of each component (C_nH_{2n+2}, n=1-6) in helium. For the H_2O-calibration, Pt-capsules filled with Milli-Q water were prepared in the same fashion as the experimental capsules. The standard calibration was performed with similar concentrations to those expected to be measured from the samples. The standard gases were therefore strongly diluted with pure He (Figure 1 and supplementary for absolute concentrations). The relation between standard present in the sample inlet chamber and the GC-TCD signal intensity is shown in Figure 1 for H_2O and CO_2 and in Figure S2 for the alkanes. The GC settings have been optimized to separate and satisfactorily resolve CO/air, CH_4, CO_2, C_2H_6, H_2O, propane, n-butane, n-pentane and hexane (Figure S3). The peak area is

145 a function of the amount of elute in a gas. Gas behaviour was found to be ideal at any stage

146 (see supplementary information).

147 Figure 1

148 The post-run fluids in this study contain only two volatile compounds (CO_2 and H_2O). The

149 CO_2 calibration has been used to determine the molar proportion of CO_2 in the fluid. H_2O

150 subsequently makes up the remaining fluid. The total molar amount of the extracted fluid was

151 calculated using the ideal gas law from the measured sample pressure and hence the absolute

152 concentrations of H_2O and CO_2 in the fluid can be calculated from the molar proportions (see

153 formula in the supplementary information).

4. Thermodynamic calculations

155 Temperature-X_{CO_2} sections have been calculated with Perple_X using a gridded

156 minimization strategy and linear programming for optimization (Connolly, 2005) to constrain

157 the reactions of serpentine with a CO_2-H_2O fluid. The calculations were simplified to the

158 FMASCH-system using the volatile-free bulk composition (FeO-MgO-SiO_2-Al_2O_3) of the

159 primary antigorite as measured with EPMA (Table S1) saturated with a CO_2+H_2O fluid.

160 Magnetite (<<2 wt%) was not considered in the modelling, because it did not participate in

161 the reactions (see discussion). Minor amounts of Ca (introduced by the fluid) were also

162 excluded (see supplementary). The Holland and Powell (1998) database and the Holland and

163 Powell (1991) and (1998) model for the fluid equation of state were used. Solid solution

164 models for phase A, brucite, chlorite, clinohumite, olivine, orthopyroxene, magnesite, talc,

165 staurolite, wuestite (Holland and Powell, 1998), antigorite (Padrón-Navarta et al., 2013) and

166 clino- and ortho-amphibole (Diener et al., 2007) have been used in the thermodynamic

167 calculations. This consistent set of solution models takes Fe-Mg exchange between magnesite

168 and silicates into account, as well as the tschermak exchange in chlorite, talc and antigorite.

169 Calculations were performed at 1 and 2 GPa between 400-800ºC for $0 \leq X_{CO_2} \leq 0.2$.

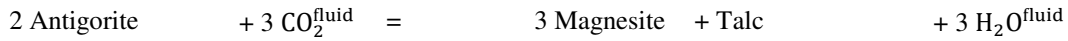## 5. Results

5.1. Textures

172 The reaction of serpentine with CO_2-rich fluids produced a variety of secondary phases

173 depending on pressure, temperature and fluid/rock ratio. Magnesite is commonly fine grained

174 (<10 µm) with a few exceptions (<30 µm). Talc is usually fibrous and fine-grained chlorite

175 occurs interstitially. Quartz forms small, subhedral crystals and occurs in a granular texture

176 together with magnesite. Orthopyroxene crystals are often elongated with maximum

177 dimensions ranging between ~15-30 µm. Remaining antigorite, if present, is coarser grained

178 (>25 µm) than any secondary phases and anhedral. Primary magnetite shows unreacted grain

179 boundaries (Figure S4 in supplementary). The porosity is generally high as the fluid volume

180 varies between ~6-16 vol% (fluid volume was calculated assuming the fluid behaves as an

181 ideal gas at high pressure and temperature, and therefore reflects an estimate of the maximum

182 volume).The textures of selected runs are illustrated with BSE-images and overlapping EDS

183 element maps of Mg, Si and Al distributions in Figure 2.

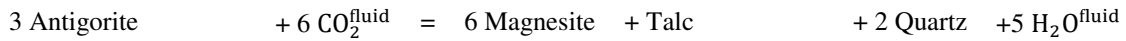184 Figure 2

5.2. Phase assemblages

186 Starting mixture SP1 was used for all experiments at 1 GPa (temperature ranging from

187 500-650°C). Magnesite + talc + chlorite + antigorite were observed in all experiments at

188 1 GPa, where equilibrium was reached (run time $\geq$ 48 h, Figure 3a). The reaction (1) forming

189 this assemblage in a simplified MSHC system is as follows:

$$2\ Mg_3Si_2O_5(OH)_4 \quad +\ 3\ CO_2 \quad = \quad 3\ MgCO_3 \quad +\ Mg_3Si_4O_{10}(OH)_2 \quad +\ 3\ H_2O \qquad (1)$$

$$2\ \text{Antigorite} \quad +\ 3\ CO_2^{\text{fluid}} \quad = \quad 3\ \text{Magnesite} \quad +\ \text{Talc} \quad +\ 3\ H_2O^{\text{fluid}}$$
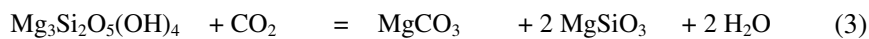
Note that chlorite formed in all experiments due to the presence of minor aluminium in the natural antigorite used in the starting mixtures.

For experiments at 2 GPa, four different starting mixtures were used with various H_2O+CO_2-fluid to serpentinite ratios (Table 1), but maintaining X_{CO_2} at 0.5 in the starting fluid. The measured fluid compositions are shown together with the observed reaction products in Figure 3. Depending on the starting composition and temperature, different phase assemblages were observed (Figure 3b). Magnesite + talc + chlorite + quartz was observed at 550°C using SP1 and at 600°C and 650°C using SP2. This assemblage is formed via reaction (2) in the simplified MSCH-system:

$$3\ Mg_3Si_2O_5(OH)_4 \quad +\ 6\ CO_2 \quad = \quad 6\ MgCO_3 \quad +\ Mg_3Si_4O_{10}(OH)_2 \quad +\ 2\ SiO_2 \quad +5\ H_2O \qquad (2)$$

$$3\ \text{Antigorite} \quad +\ 6\ CO_2^{\text{fluid}} \quad = \quad 6\ \text{Magnesite} \quad +\ \text{Talc} \quad +\ 2\ \text{Quartz} \quad +5\ H_2O^{\text{fluid}}$$

Quartz-free assemblages of magnesite + talc + chlorite (1) were crystallised at 600°C for SP1, 630°C for SP4, 650°C for SP3 and at 700°C and 750°C for SP2. Within these experiments relicts of primary antigorite persisted below 650°C and at 650°C for the experiment with higher X_{CO_2}. In the experiments ≥700°C using SP3 and SP4, enstatite was found for $X_{CO_2} <$ 0.1. At 700°C magnesite + talc + chlorite + enstatite + antigorite were present. Using SP4 as starting material, a talc-free assemblage of magnesite + chlorite + enstatite was observed that can be explained via reaction (3).

$$Mg_3Si_2O_5(OH)_4 \quad +\ CO_2 \quad = \quad MgCO_3 \quad +\ 2\ MgSiO_3 \quad +\ 2\ H_2O \qquad (3)$$

$$\text{Antigorite} \quad +\ CO_2^{\text{fluid}} \quad = \quad \text{Magnesite} \quad +\ 2\ \text{Enstatite} \quad +2\ H_2O^{\text{fluid}}$$

206 At higher temperatures (750°C) the assemblage using SP4 was likewise free of talc but

207 contained forsterite (magnesite + chlorite + enstatite + forsterite). All experiments contain

208 some relicts of minor, primary magnetite.

209 Figure 3

210 ### 5.3. Gas chromatograph results

211 An innovative aspect and significant advantage of this study is the direct analysis of the gas

212 present in the capsule after the experiment by gas chromatography. From the occurrence and

213 abundances of different C-O-H species such as CH_4, CO_2 and H_2O, conclusions about the

214 redox conditions, reaction progress and approach to equilibrium can be obtained. The fluid in

215 this study is exclusively comprised of CO_2 and H_2O and in the following, X_{CO_2} refers to the

216 molar proportion of CO_2 in the fluid. Figure 3 shows the phase assemblages as a function of

217 measured post-run X_{CO_2} and temperature for 1 and 2 GPa.

218 At 1 GPa, magnesite + talc + chlorite + antigorite (Figure 3a) are stable with X_{CO_2} increasing

219 from 0.017 to 0.14 as temperature increases from 500 to 650°C. Likewise at 2 GPa, this

220 assemblage of secondary phases (Figure 3b) is stable at higher X_{CO_2} (0.022-0.116) with

221 increasing temperature (600-750°C). Quartz is additionally present when the fluid contains

222 more CO_2 at the same PT. At temperatures $\gtrsim$ 700°C (at 2 GPa) antigorite starts to dehydrate

223 to enstatite and forsterite. At 700°C and $X_{CO_2} = 0.053$, talc (and antigorite) are still present

224 together with enstatite + magnesite + chlorite. At lower $X_{CO_2} = 0.031$ talc (and antigorite)

225 are absent and the proportion of chlorite is strongly reduced due to the incorporation of Al

226 into enstatite. Magnesite + enstatite + forsterite + chlorite are stable at 750°C and $X_{CO_2} =$

227 0.076.

228 ### 5.4. Major element compositions

229 The Mg-number [Mg#=100*atomicMg/(Mg+Fe)] of antigorite used in the starting material is

230 92.1±0.5 and is maintained in the bulk assemblage after the experiment (Table S3). Relicts of

231 antigorite and magnetite in the post-run assemblages are chemically and texturally

232 indistinguishable from the starting material and likely represent unreacted phases (Table S1,

233 Figure S4).

234

235 Magnesite shows the largest range in Mg# over all runs (Mg#=91.7, 2σ=5.4) and in

236 individual runs with a variation over a similar range. Nevertheless, single magnesite grains

237 are homogenous. No systematic correlation between the Mg# of magnesite and the phase

238 assemblage could be found. The variation in Mg# in talc over all runs is, in comparison to

239 magnesite, more restricted to Mg#=93.9±1.5 (2σ). Enstatite shows Mg# between 88.2-93.8

240 and forsterite has Mg# of 91.7±3.9 (2σ) (Table S1 and S3).

241 Chlorite (Mg#=93.3; 2σ=2.9) takes up most of the Al, although talc contains a median of

242 1.5±1.1 wt% Al_2O_3. The fine grain size and interstitial texture of chlorite makes it

243 challenging to obtain a pure chlorite analysis by EPMA. Overlap with surrounding phases

244 (e.g. talc, antigorite) might affect chlorite analyses as shown in Figure S5. This makes it

245 difficult to determine the true extent of solid solutions in chlorite and only a fraction (marked

246 with small cyan stars in Figure S5) of all chlorite analyses close to the clinochlore

247 endmember were considered as clean analyses. The presence of chlorite was verified in all

248 XRD scans on selected runs.

249   5.5. Mass balance and phase proportions

250 The gas analyses not only allow the calculation of the molar proportion of CO_2 in the fluid,

251 but also give the absolute abundances of CO_2 and H_2O in the fluid if all fluid can be extracted

252 from the capsule. This allows mass balance calculations including solid and fluid phases

253 assuming that the amount of dissolved solutes in the fluid is minor. The measured amount of

254 fluid, however, represents a minimum value, but the relative modal amounts of CO_2 and H_2O

255 are unaffected by incomplete fluid-extraction. Therefore, mineral and fluid proportions were

256 established by processing BSE-images and elemental maps using the software ImageJ for

257 solid phases and the measured X_{CO_2} combined with mass balance for the fluid phase (Table

258 2). The solid phase proportions obtained by image processing are within uncertainty

259 consistent with the results from the full mass-balance approach using the amount of extracted

260 fluid. For the calculations, the median major element abundance as measured by EPMA and

261 SEM for each phase in each individual run was used (see Table S3). The exception to this

262 was chlorite, for which the median composition over all accepted EPMA analyses (stars in

263 Figure S5) was used if precise analyses were not obtained. The listed absolute errors in X_{CO_2}

264 (Table 2) were calculated using Gaussian error propagation including the errors from the

265 balance, GCTCD and EPMA measurements.

266 Table 2

267 The abundances of magnesite formed at equilibrium most importantly depend on the bulk

268 CO_2-concentration to serpentinite ratio. Therefore, experiments performed using SP2 are

269 highest in magnesite and SP4 lowest (Figure 4, Table 2). The CO_2-fluid composition at

270 equilibrium (as a function of temperature and pressure) further determines the amount of

271 magnesite in an inverse correlation. The abundances of other solid phases are determined by

272 the chemical reactions (1-3) that describe the transition from the starting antigorite to the

273 observed equilibrium assemblage.

274 Figure 4

275   5.6. Time series

276 Two time-series were performed to investigate the reaction progress and fluid evolution over

277 time. The same starting mix (SP1) was used in both time-series; one was performed at 600°C,

278   2 GPa for 24, 48 and 72 h and the second at 550ºC, 1 GPa for 0.1, 0.42, 0.85, 1, 48 and 192 h.

279   The measured fluid compositions and obtained phase assemblages are displayed as a function

280   of time in Figure 5.

281   Figure 5

282   The assemblages and measured fluid compositions in the runs at 1 and 2 GPa do not differ

283   from each other within error, suggesting that equilibrium was approached after 48 h. The

284   shorter experiments ($\leq$1 h) at 1 GPa have significantly higher CO_2 concentrations in the fluid

285   and more primary antigorite remained (Table 2), implying that carbonation was not

286   completed. Note that the amount of CO_2 in SP1 is insufficient to completely carbonate all

287   antigorite present. In these short runs, quartz is present and the abundances of quartz and

288   magnesite increase together from the 0.1 h to the 0.42 h run while X_{CO_2} and the abundances

289   of primary antigorite simultaneously decrease. Already after 6 min of run duration, the X_{CO_2}

290   changed from 0.5 to 0.26 and 14 wt% of magnesite has formed. The carbonation is complete

291   after 1 h (24 wt% magnesite present) and no further changes in fluid compositions occur with

292   longer run durations. However, the silicate phases still change proportions. In comparison to

293   the 0.1 and 0.42 h experiments, we can observe that at 0.85 and 1 h quartz becomes less

294   abundant and talc starts to crystallise. Talc abundances then further increase significantly

295   between 1 to 48 h run while antigorite abundance decrease and magnesite remains constant.

296   No changes to the fluid composition and phase abundances are observed after 48 h indicating

297   that equilibrium has been reached.

298   5.7. Trace elements and partition coefficients

299   Partition coefficients for Sr, Pb, Ba and Ca between magnesite and a CO_2-poor fluid with

300    $0.02 \leq X_{CO_2} \leq 0.15$ have been established in the range of 500-750°C and 1-2 GPa.

301   Magnesite is too fine grained to be measured individually by LA-ICP-MS. Therefore, 'bulk'

13

302 compositions were analysed by LA-ICP-MS and the proportion of magnesite in the solid

303 assemblage was used to obtain the trace element concentrations in magnesite. The local

304 'bulk' compositions have been determined using a laser spot size of 47 μm, which is much

305 larger than any grain size. Ca was used during data reduction as the reference element. The

306 bulk Ca-concentration was previously determined by EPMA using a defocused beam. For

307 each sample 10 single LA-ICP-MS and EPMA spots were averaged. The abundances of

308 magnesite (Table 2) were used to calculate the trace element composition of magnesite,

309 assuming that negligible amounts of trace elements are incorporated into talc, chlorite and

310 quartz (Figure S6). The trace element concentrations in the post-run fluid were subsequently

311 established via a mass balance approach, knowing the amount of traces in the starting

312 material, the proportions of magnesite and fluid after the experiment (Table 2) and the trace

313 element concentration in magnesite (Table S2 and formula in the supplementary

314 information). The partition coefficients between magnesite and fluid are within errors

315 consistent between individual experiments in the investigated P, T and X_{CO_2} range.

316 Magnesite is the main host for Ca, as verified by SEM and EPMA measurements (Table S1).

317 The positive correlation between the counts per second of Ca compared to Ba, Sr and Pb

318 during LA-ICP-MS analyses suggests that Ba, Sr and Pb are likewise enriched in magnesite

319 (Figure S6). Ca provided the most consistent partition coefficient with a $D_{Ca}^{magnesite/fluid} =$

320 0.8 ± 0.1 (Table S2) showing that Ca is mildly incompatible in magnesite compared to the

321 aqueous fluid. Similar but slightly more scattered values of Sr and Pb resulted in partition

322 coefficients varying between 0.4 and 2.2 for Sr and 0.2 to 9.8 for Pb, with medians of

323 $D_{Sr}^{magnesite/fluid} = 1 \pm 0.2$ and $D_{Pb}^{magnesite/fluid} = 0.8 \pm 0.2$, respectively. It was more difficult

324 to determine the partition coefficient for Ba, as the concentrations in magnesite are more

325 variable and often so high, that the fluid phase is strongly depleted in Ba. In four

326 experiments (run 15b, 16, 16c, 30) the Ba concentration in magnesite was so high, that no Ba

327 was left over for the fluid phase. To obtain a lower limit for these experiments, an arbitrary

328 low Ba concentration of 200 ppm in the fluid was assumed. The overall observations indicate

329 that Ba is compatible in magnesite and partition coefficients ranged between 0.4-9.7. The

330 median of all experiments resulted in a $D_{Ba}^{magnesite/fluid}$ of about 2.

331   5.8. <u>Thermodynamic modelling</u>

332 Using the thermodynamic software package perple_X (Connolly, 2005) the binary

333 equilibrium phase diagrams shown in Figure 6 were computed for a fixed

334 FeO-MgO-Al$_2$O$_3$-SiO$_2$ composition corresponding to the primary antigorite at 1 and 2 GPa

335 between 400-800°C assuming the system is saturated with a CO$_2$-H$_2$O fluid. The

336 magnesite-in reaction boundary (red solid line) marks the minimum required molar

337 proportion of CO$_2$ in the fluid for the carbonation to start. The magnesite-in reaction (and

338 most reactions within the magnesite stability field) has a positive slope in a T-X$_{CO_2}$ isobaric

339 diagram. Thus, at any given pressure, the required amount of CO$_2$ in the fluid increases with

340 increasing temperature to produce magnesite.

341 Magnesite is stable with quartz and an Al-rich phase at temperatures ≲550°C, 1 GPa and

342 elevated X$_{CO_2}$. Above ~420°C the Al-rich phase is kyanite or chlorite. At either higher

343 temperature at constant X$_{CO_2}$ or lower X$_{CO_2}$ at constant temperature, quartz is no longer

344 stable and the assemblage consists of magnesite + talc + chlorite.

345 If the CO$_2$ concentration in the fluid is too low, carbonation will not occur. Antigorite breaks

346 down to olivine+talc+chlorite at 1 GPa above 550°C. Talc stays stable until ≲660°C and

347 orthopyroxene becomes abundant when temperature increases further. The assemblage of

348 orthopyroxene + chlorite + olivine is stable towards high X$_{CO_2}$. A completely volatile free

349 crystalline assemblage is present above ≳770°C for 1 GPa.

350 The systematics of the equilibrium phase stabilities at 2 GPa are similar. When carbonation

351 occurs, magnesite + quartz are stable together with kyanite at elevated X_{CO_2} ($X_{CO_2} \gtrsim 0.01$ at

352 500°C, respectively). Analogously to the 1 GPa diagram, talc becomes stable and quartz

353 disappears with either increasing temperature at constant X_{CO_2} or lower X_{CO_2} at constant

354 temperature. In contrast to the low-pressure diagram, magnesite + talc can be stable together

355 with kyanite at 2 GPa when $X_{CO_2} \gtrsim 0.06$. Kyanite is replaced by chlorite at lower X_{CO_2}

356 (under constant temperature). At low X_{CO_2} antigorite breaks down to

357 olivine+orthopyroxene+chlorite above 650°C. The magnesite-free assemblages occur at

358 lower X_{CO_2} at 2 GPa compared to 1 GPa.

359 Besides the main stability fields described above, restricted divariant fields exist due to solid

360 solutions relating to Mg-Fe partitioning and tschermak exchange between coexisting phases.

361 Figure 6

362 **6. Discussion**

363 Our study aims to constrain the reactions and mass transfers involved in the C-O-H fluid

364 driven carbonation of serpentinite in the slab and the forearc of subduction zones. We will

365 first consider the approach to equilibrium of the experiments and compare the experimental

366 results with the thermodynamic calculations. Then we discuss how equilibrium is reached,

367 debate the potential of magnesite as monitor for trace element compositions of slab-derived

368 fluids, and point out the implications for the deep Earth's carbon cycle.

369 6.1. Approach to equilibrium

370 Equilibrium was reached in runs with durations ≥48 h. This is demonstrated in the time series

371 experiments, because the assemblages crystallised and measured fluid compositions in runs

372 with durations ≥48 h are identical within analytical uncertainty (Figure 5). The water and

373   CO_2 contents in the starting mixes determine the equilibrium phase assemblage, X_{CO_2} in the

374   post-run fluid and the proportion of magnesite crystallised at a given pressure and

375   temperature (Figure 3). One assumption is that no graphite or carbonate is formed upon

376   quenching. Matveev et al. (1997) showed that graphite saturated C-O-H fluids preserve their

377   equilibrium C-O-H speciation during quenching from 2.4 GPa and 1000°C.

378   There is no evidence that the liberation of H_2 in the dissociation of OAD has influenced the

379   phase relations. Although H_2 can diffuse out through the Pt-capsule wall (Chou et al., 1978;

380   Harvie et al., 1980) it must be evaluated, whether significant reduction of run products occur

381   as a result of remaining H_2 in the charge. Note that the experiments were not externally

382   buffered, but previous experiments have shown that the applied assembly imposes an f_{O_2}

383   close to the nickel-nickel oxide buffer (Hermann and Spandler, 2008). Reaction of magnetite

384   with H_2 would result in additional FeO available for uptake in silicate phases or formation of

385   alloys with the Pt-capsule. The bulk Mg# of product minerals overlaps with the Mg# of the

386   starting antigorite (Table S3) indicating negligible changes in the FeO content. Additionally,

387   neither graphite in the solids nor methane in the quenched fluid was observed. These

388   observations indicate that carbonation occurred in the presence of a CO_2-H_2O fluid.

389   6.2. Comparison of experimental and thermodynamic results

390   Overall the experimental results (measured X_{CO_2}, observed assemblages and composition) are

391   in agreement with the thermodynamic calculations. The measured and calculated post-run

392   fluid compositions correlate well (Figure 7), providing evidence that the post-run analyses of

393   experimental volatiles via gas-chromatography is a viable technique (see also Martin and

394   Hermann (in press)). Nevertheless, there are some minor discrepancies that are worth noting.

395   The observed phase assemblage (and hence abundances) diverges from the

396   thermodynamically calculated assemblages, in relation to the Al-rich phase in 7 out of 21

397 experiments. Kyanite is predicted by the modelling to comprise 2-4 wt% of the solid

398 assemblage at high X_{CO_2} (>0.03 at 2 GPa, 600°C), but was never observed in the

399 experimental run products, which might be related to inhibited nucleation of kyanite. Instead

400 chlorite was detected as the main Al phase implying that chlorite may be stable at lower

401 water activities than thermodynamically predicted. Chromium, present in trace amounts in

402 the serpentinite, but not considered in the thermodynamic calculations, may extend the

403 stability of chlorite to higher X_{CO_2}. Cr in chlorites has found to increase with increasing

404 CO_2-concentrations in the fluid. The Mg# of chlorite is higher compared to computed Mg#

405 (Table S3 for comparison of the measured and computed Mg# and Al-content of solid

406 phases). Further, the uptake of Al in talc may also affect chlorite stability. Although the solid

407 solution model used for talc considers the substitution of Al onto the tetrahedrally

408 coordinated site, the measured talc stoichiometry implies that Al occurs in both the octahedral

409 (Al^{VI}=0.03±0.05 apfu for 11 oxygens) and tetrahedral sites (Al^{IV}=0.08±0.05 apfu) and

410 consequently substitutes for both silicon and magnesium (supplementary information for

411 calculation of mineral stoichiometry). Talc has incorporated more Al than thermodynamically

412 predicted (Table S3). That talc can incorporate significant amounts of Al at elevated

413 pressures has been shown previously (e.g. Al=0.12-0.24 apfu at 2-1 GPa; Hoschek (1995)).

414 Magnesite has slightly higher Mg# than predicted by the model (Table S3) and, in contrast to

415 the model, no correlation between the Mg# of magnesite and the phase assemblage could be

416 observed. A further difference is that experimental magnesite contains ~1 wt% CaO,

417 whereas thermodynamic calculations were performed in a Ca-free system.

418 Although measured and calculated X_{CO_2} in the fluid correlate well, it appears that the

419 measured values are slightly higher (Figure 7). The calculated fluids are pure H_2O-CO_2

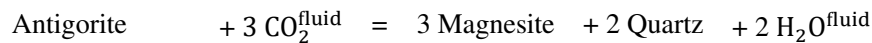420 fluids, whereas in the experiments other species might be present as well. Sverjensky et al.

421 (2014) demonstrated that in a silicate environment, fluids are more complex and can contain

422 additional species such as HCO_3^-, dissolved methane or even more complex hydrocarbon

423 molecules. HCO_3^- could potentially be present as an additional species for the given P-T and

424 oxygen fugacity (Sverjensky et al., 2014). Methane was not observed in quenched fluids,

425 indicating that methane, if present, has a concentration of $\ll 1$ wt% in the fluid (see

426 supplementary information). Another difference between the experimental and modelled fluid

427 compositions relates to the likely occurrence of additional, dissolved cations (e.g. Si^{4+}, Mg^{2+},

428 Fe^{2+} etc.) in the experimental fluids, which is not considered in the thermodynamic

429 calculations. The next section shows that there is evidence for dissolved Si in the

430 experimental fluids.

431 Figure 7

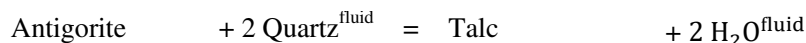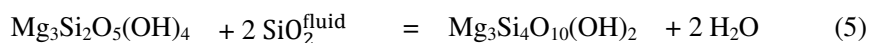432 ## 6.3. Reaction progress and fluid composition

433 Unlike the thermodynamic calculations, the time series experiments coupled with the

434 analyses of the fluid composition provide evidence on how the carbonation reactions proceed

435 and how the equilibrium state is reached. The high amount of CO_2 in the starting fluid is the

436 driving force of the carbonation reaction. With progressive reaction, the CO_2 concentration in

437 the fluid decreases as magnesite (sink of CO_2) is produced and simultaneously antigorite is

438 consumed (source of H_2O). Observed phase abundances confirm the decreasing antigorite

439 and increasing magnesite abundances with time (Table 2). The abundance of magnesite

440 further depends on the fluid/rock ratio (OAD to serpentinite ratio) and to a lesser extent, on

441 pressure and temperature. The time series shows that most magnesite is formed within less

442 than 1 h from the start of the experiment. Measured X_{CO_2} in the fluid changes quickly within

443 the first hour as magnesite is formed (Figure 5). Afterwards the abundance of magnesite and

444 X_{CO_2} in the fluid change insignificantly (Table 2).

Quartz was only observed in runs <1 h. This indicates that antigorite breaks down initially into quartz+magnesite (4) at high CO_2-concentrations in the fluid. The reaction at this point is incomplete considering that experiments that reached equilibrium contain less unreacted antigorite (Table 2).

$$Mg_3Si_2O_5(OH)_4 + 3\,CO_2 = 3\,MgCO_3 + 2\,SiO_2 + 2\,H_2O \qquad (4)$$

$$\text{Antigorite} + 3\,CO_2^{fluid} = 3\,\text{Magnesite} + 2\,\text{Quartz} + 2\,H_2O^{fluid}$$

The amount of quartz found is less than expected from reaction (4). The abundance of quartz increases initially (≤ 0.42 h) and then decreases (run 59; 0.85 h) until quartz completely disappears. In contrast, magnesite is continuously formed within the first hour. This implies that quartz solubility increases as the fluid becomes more aqueous.

High amounts of antigorite ($\gtrsim 50$ wt%) are still present in the shortest runs, but antigorite abundance decreases over time. As carbonation seems to be completed after ~1 h, this suggests that the fluid, enriched in SiO_2, reacts with antigorite to form talc according to reaction (5) until equilibrium is reached.

$$Mg_3Si_2O_5(OH)_4 + 2\,SiO_2^{fluid} = Mg_3Si_4O_{10}(OH)_2 + 2\,H_2O \qquad (5)$$

$$\text{Antigorite} + 2\,\text{Quartz}^{fluid} = \text{Talc} + 2\,H_2O^{fluid}$$

The mass balance calculations (Table 2) additionally imply that some Si is dissolved in the fluid. The enrichment of Si in the fluid was further constrained by measuring the 'local' bulk composition of the solids by EPMA using a 50 µm diameter defocused electron beam. The results show that the 'bulk'-solids are depleted in silica compared to the starting material by ~10-20%. Dissolution of silicates (eg. quartz, forsterite and olivine) in COH-fluid is further supported by the experimental study of Tumiati et al. (2017) conducted under similar pressure and temperatures.

6.4. Trace element partitioning

In addition to CO_2 and dissolved silica, fluids derived from subducted altered oceanic crust and sediments contain Ca and fluid mobile elements like Ba, Sr and Pb (Bebout et al., 2013). Ba, Sr and Pb concentrations in the forearc mantle are low, but these elements are generally enriched in arc lavas compared to MORB, and isotopic studies have convincingly shown that Pb and Sr derive from the subducted crust (Elliott et al., 1997). Our study shows that CO_2 might be efficiently sequestered in newly formed magnesite in the mantle wedge. An important matter is then to what extent also divalent Ca, Ba, Sr and Pb that can substitute for Mg could be retained in magnesites.

We have determined partition coefficients for Ca, Ba, Sr and Pb between magnesite and a CO_2 poor hydrous fluid ($X_{CO_2} < 0.15$) for 1-2 GPa and 500-750ºC. In this range, the partitioning is, within an uncertainty of ~20% (Table S2), unaffected by a change in X_{CO_2}, temperature, pressure, the phase assemblage and proportions of minerals. The Ca, Sr and Pb partitioning is close to unity, suggesting little Ca, Sr and Pb fractionation between fluid and magnesite. Magnesite therefore can be used as a monitor for determining Ca, Sr and Pb concentrations in fluids. Ba seems to be more compatible. As an example, if a fluid with an initial X_{CO_2} of 0.27 (SP1; Table 1), liberated from altered oceanic crust at forearc conditions (Molina and Poli, 2000), interacts with mantle wedge serpentinites, about 30 wt% magnesite can be formed (Table 2). This magnesite can potentially retain about half of the original Ca, Sr and Pb and about 70% of the initial Ba in the fluid. The carbonation of serpentinites thus may partially sequester fluid mobile elements from slab fluids in magnesite.

6.5. Implications for carbon fluxes and carbon budget in the forearc

488 The reaction of C-O-H bearing fluids with serpentinites in the slab and under the forearc has

489 been investigated in this study and the results have important implications for carbon fluxes

490 and carbon storage in the mantle.

491 Firstly, C-O-H fluids released from the subducting slab that migrate into the

492 overlying, partially serpentinized mantle cause carbonation in the forearc. We have shown

493 that carbonated serpentinite contains ~30 wt% magnesite filtering ~70 to 95% of the initial

494 CO_2 content out of the fluid and that the carbonation of serpentinites occurs almost

495 instantaneously. A serpentinised mantle wedge will not be coupled to the down going slab

496 (Arcay et al., 2005) and thus over time, significant amounts of carbon can potentially be

497 accumulated in this cold part of the mantle wedge (Figure 8).

498 In the following we roughly estimate the storage potential for C in the North Cascadia

499 forearc mantle. We selected the North Cascadia subduction zone, because our experimentally

500 investigated PT conditions correspond to 'hot' subduction zone geotherms likely present in

501 the North Cascadia (Stern, 2002; Wada and Wang, 2009). For colder subduction geotherms,

502 the X_{CO_2} of fluids in equilibrium with serpentinites at the same depth is expected to be even

503 lower (Figure 6; Kerrick and Connolly (1998)). Geophysical studies have suggested that the

504 depression in seismic velocities would correspond to 20-30 vol% of serpentinization of the

505 North Cascadia forearc mantle (500-1,000 km^2*1,000 km) (Hyndman and Peacock, 2003;

506 Wada and Wang, 2009). This provides the potential to store ~1-4E+07 MtC if 30 wt%

507 magnesite is formed (on average the solid post-run assemblage consists of ~30 wt%

508 magnesite). This amount of carbonates is presumably not detectable by seismic investigations

509 (Sanchez-Valle et al., 2011; Yang et al., 2014). A global C-flux of 0.2-1.3 Mt/y into the

510 leading edge of the mantle wedge has been proposed by Kelemen and Manning (2015). With

511 a cumulative length of convergent plate margins of 55,000 km (Lallemand, 1999), the

512   proportion of C-flux at the 1,000 km long North Cascadia subduction is 0.004-0.024 Mt/y.

513   Using this annual C-flux and the lower C-storage capacity (1E+07 MtC) it would take

514   100 My to carbonate ~3-20% of the serpentinites in the North Cascadia forearc mantle

515   (Table S4) assuming pervasive fluid flow. This illustrates the potential capacity of the mantle

516   wedge to sequester CO_2 derived from the subducting slab. However, if fluid flow is

517   channelized carbonation is likely to be less pronounced, because infiltration of subsequent

518   fluids into unreacted serpentinites may be limited. The extent of carbonation of ultramafic

519   rocks in the context of channelized fluid flow needs to be addressed with future studies.

520   Secondly, carbonation of serpentinites (and other ultramafic lithologies) within the

521   subducting slab contributes to C-retention in the slab, because carbonates are refractory and

522   stable even at high pressures (Brey et al., 2008; Kerrick and Connolly, 2001a; Kerrick and

523   Connolly, 2001b; Molina and Poli, 2000; Poli et al., 2009; Yaxley and Brey, 2004; Yaxley

524   and Green, 1994). Hence, trapping carbon first released into fluids as carbonates in the slab

525   can supply carbon for arc magmatism and/or can lead to even deeper subduction into the

526   convecting mantle. The mobilization of C into fluids and precipitation of carbonates along the

527   fluid paths at high pressures has been inferred from several field studies of blueschist and

528   eclogite facies rocks (Ague and Nicolescu, 2014; Collins et al., 2015; Piccoli et al., 2016;

529   Scambelluri et al., 2016) investigating for example metacarbonate rocks, ophicarbonates or

530   eclogite-facies marbles from the Syros and Tinos Island, Northern Apennines, Alpine Corsica

531   or Ligurian Alps.

532   Thirdly, fluid driven carbonation at the subarc will be less pronounced compared to

533   the forearc, because fluids released under the subarc already contain smaller amounts of CO_2

534   with $X_{CO_2} \leq 0.21$ (Molina and Poli, 2000; Poli et al., 2009). Additionally, our study shows

535   that CO_2-sequestration is less efficient at higher temperatures. For example, in experiments

536   performed at 2 GPa and 700-750°C (run 15b, 17) the post-run fluids show $X_{CO_2} > 0.1$,

537   whereas in experiments at lower temperatures and/or pressures fluids have $X_{CO_2} \ll 0.1$

538   (Table 2). At mantle wedge conditions of 3 GPa, 900°C Tumiati et al. (2013) constrained an

539   X_{CO_2} of 0.15 in fluids coexisting with a magnesite bearing garnet-peridotite and discuss

540   possible scenarios for carbon transfer from the slab to the mantle wedge. These findings

541   together imply that C-O-H-fluids travelling through the subarc mantle are less affected by a

542   change in their carbon content and therefore most of the CO_2, released into fluids under the

543   subarc, may be transported to the source region of arc-lavas. This finding may also imply that

544   CO_2-sequestration has been less pronounced in ancient subduction zones, because ambient

545   mantle temperatures are believed to have been higher (Nisbet et al., 1993).

7. Conclusions

By performing piston cylinder experiments on the C-O-H fluid driven carbonation of serpentinites at pressure and temperatures corresponding to the forearc this study shows that:

- the CO_2, H_2O and alkane (C_nH_{2n+2}, n=1-6; e.g. methane) composition of experimentally derived fluids can be successfully quantified by gas-chromatography.

- the X_{CO_2} fluid composition and stable mineral assemblage can be predicted by thermodynamic modelling. Minor deviations between the modelled and observed results, however, relate to the Al-bearing phases and the assumption of a binary CO_2-H_2O fluid in the model compared to a more complex fluid composition containing dissolved Si for instance.

- carbonation of serpentinite is a rapid process, filtering CO_2 from the fluid involved effectively within the first hour of the experiment. Full equilibrium is attained within 48 hours.

Our experiments have three main implications for estimating the deep Earth's carbon fluxes (Figure 8): (1) carbonation of a partially hydrated mantle wedge may establish, over time, a significant C-reservoir; (2) carbonation of serpentinite within the subducted slab contributes to C-transfer to the deeper mantle (3) CO_2-sequestration from fluids released under the subarc is likely to be less pronounced compared to the forearc and thus C-O-H fluids may migrate through the subarc mantle with only minor changes in their C-content.

Figure 8

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672   melt in the subduction regime. Earth and Planetary Science Letters, 128(3–4), 313-325.

673

674 Figure 1: Relation between amount of H_2O and CO_2 present in the sample inlet chamber to

675 the median signal intensity, which is the peak area of 5-7 GCTCD analyses of aliquots of the

676 sample gas (=standard in He).

677 Figure 2: SEM-EDS elemental maps (left) and BSE-images (right) of four selected runs with

678 variable observed magnesite abundances. The distribution of Mg in red, Si in green and Al in

679 blue are overlayed in each elemental map. Phases present are also indicated (ant: antigorite;

680 chl: chlorite; enst: enstatite; mt: magnetite; qtz: quartz).

681   Figure 3: Fluid composition (X_{CO_2}=n_{CO_2}/(n_{CO_2}+n_{H2O})) measured by GC-TCD in the

682   experiments at 1 GPa (left) and 2 GPa (right). Symbols refer to mineral assemblages

683   crystallised in the experiments (mag: magnesite; chl: chlorite; ant: antigorite; qtz: quartz;

684   enst: enstatite; fo: forsterite). Magnesite was observed in all experiments. Grey-dots

685   represents quartz-in, yellow-dashes stands for talc-in, green-dashes/dots for the enstatite-out

686   reaction and black points for forsterite-out (in/out in respective to increasing X_{CO_2}).

687   Figure 4: Ternary diagram for the H_2O-SiO_2+MgO-CO_2 system, showing the starting

688   compositions used (SP1-4; orange circles), which are mixtures between antigorite (green

689   triangle) and oxalic acid dihydrate (~start fluid composition; blue rectangle). Observed solid

690   run products (talc: yellow triangle; quartz + enstatite + olivine: purple triangle; magnesite:

691   orange triangle) and X_{CO_2} in post run fluids (blue diamonds) are included.

692   Figure 5: Measured X_{CO_2} in post run fluid and change in solid assemblage over time in

693   performed time series. Carbonation is completed after 1 h and full equilibrium has been

694   reached after ≥ 48 h.

695   Figure 6: Thermodynamically calculated pseudosections in the FMASCH-system using the

696   volatile-free bulk composition of primary antigorite (Table 1) saturated with a CO_2 and H_2O

697   fluid at 1 GPa (left) and 2 GPa (right) between 400-800 °C. Colour coded boundaries refer to

698   mineral in or out boundaries relative to increasing X_{CO_2} at given temperature. Abbreviations

699   are: Amph: Amphibole; Atg: Antigorite; Chl: Chlorite; dsp: diaspore; ky: kyanite; Mag:

700   Magnesite; Mcar: Mg-carpholite; Ol: Olivine; Opx: Orthopyroxene; prl: pyrophyllite; q:

701   quartz; Tlc: Talc. Phases written with a capital letter refer to solid solutions, small letters

702   indicate endmember composition. Numbers in brackets point to restricted fields: (1)

703   Opx+Chl+Tlc+Ol; (2) Amph+Chl+Tlc+Ol; (3) Chl+Tlc+Ol+Mag; (4) Chl+Tlc+Ol+Atg; (5)

704   Chl+Tlc+Mag+Atg;   (6)   Tlc+Ol+Mag+Atg;   (7)   Amph+Tlc+Ol+Atg;   (8)

Amph+Tlc+Mag+Atg; (9) Tlc+Mag+Atg; (10) Amph+Tlc+Atg; (11) Tlc+Atg; (12)

Chl+Tlc+Mag+Atg; (13) Chl+Mag+mcar+qtz; (14) Mag+mcar+qtz; (15)

Mag+mcar+prl+qtz; (16) Mag+ky+mcar+qtz; (17) Opx+Chl+Ol+Mag; (18)

Opx+Chl+Tlc+Mag; (19) Chl+Tlc+Mag+qtz; (20) Chl+Mag+ky+qtz; (21)

Opx+Chl+Tlc+Mag; (22) Opx+Chl+Ol+Atg; (23) Opx+Chl+Mag+Atg; (24) Opx+Ol+Ant;

(25) Opx+Mag+Ant; (26) Chl+Tlc+Mag+Atg; (27) Opx+Tlc+Mag+Atg; (28) Opx+Atg; (29)

Tlc+Mag+Atg; (30) Opx+Tlc+Atg; (31) Amph+Tlc+Atg; (32) Tlc+Atg; (33)

Chl+Tlc+Mag+qtz; (34) Tlc+Mag+mcar+qtz; (35) Mag+ky+mcar+qtz; (36) Mag+mcar+qtz;

(37) Chl+Mag+qtz; (38) Mag+mcar+qtz+dsp; (39) Opx+Chl+Ol+Mag; (40) Opx+Tlc+Mag;

(41) Opx+Tlc+Mag+ky; (42) Tlc+Mag+ky+qtz

Figure 7: Comparison of the fluid composition as measured by GC-TCD and per thermodynamic calculations for experiments where equilibrium has been reached. The X_{CO_2} values per thermodynamic modelling are obtained from Figure 6 for observed assemblages.

Figure 8 Illustration of the three main implications of the COH fluid driven carbonation of serpentinites under the forearc as investigated and discussed in this study. Fluids released under the forearc are high in $X_{CO_2} \leq 0.7$ (Molina and Poli, 2000) and will react with serpentinite filtering CO_2 effectively in the formation of magnesite. The remaining fluids are low in $X_{CO_2} \leq 0.15$ and ~30 wt% magnesite can be formed under the forearc. This study shows that (1) carbonation might be significant under the forearc, (2) carbonation within the slab contributes to C-transfer to the deeper mantle, (3) CO_2-sequestration is likely to be less pronounced at higher temperatures and pressures.

Table 1: Four starting mixes (SP1-4) with various serpentinite/fluid ratios have been used in this study. Oxalic acid dihydrate (OAD) is the main fluid source. Ba-, Sr-, Pb-, Ca-carbonate

728　　were added to the starting mix and are assumed to be present in the fluid in the beginning of

729　　the experiment in the listed concentrations.

730　　Table 2: Overview of performed piston cylinder experiments and measured volatile

731　　composition (X_{CO_2}) in the post-run fluids. The phase proportions were obtained by area

732　　analyses of BSE images and elemental maps of the solid post run assemblage in combination

733　　with the measured X_{CO_2} fluid composition (see text for details). XRD has been performed on

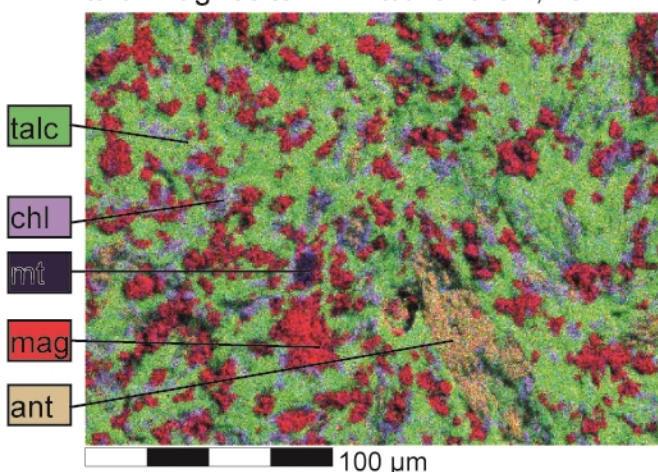734　　selected runs to confirm the occurrence of chlorite.

run23: SP4; 2 GPa 630 °C; 48 h
talc>ant>magnesite=16 wt%>chl,mt

ant
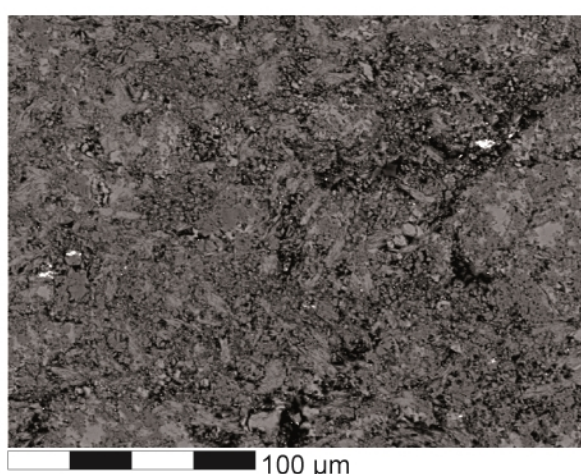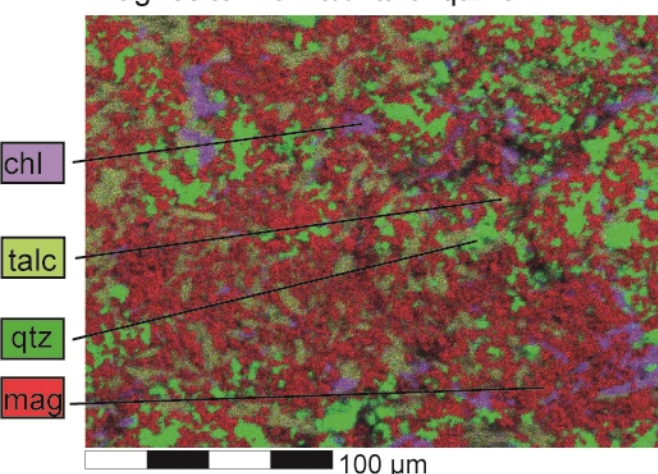**chl**
talc
mag
mt

100 µm

100 µm
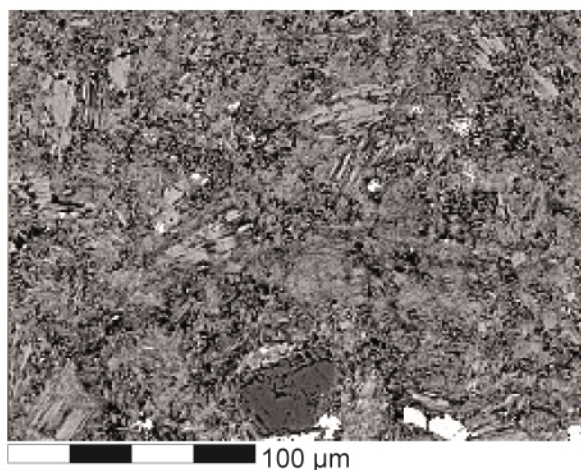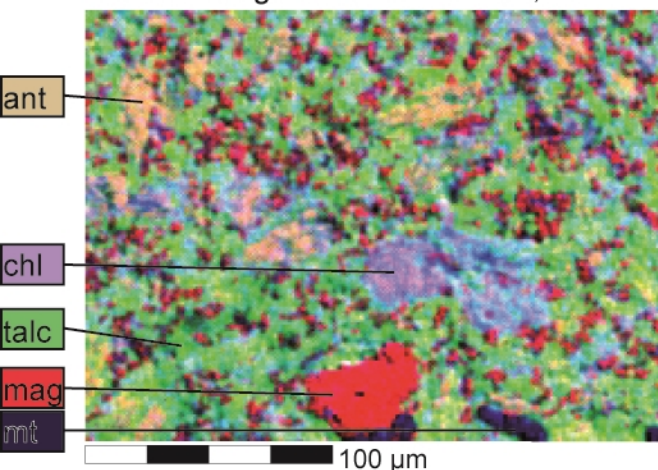
run24: SP4; 2 GPa; 700 °C;48 h
enst>magnesite=16 wt%>chl

chl
enst
mag

100 µm

100 µm
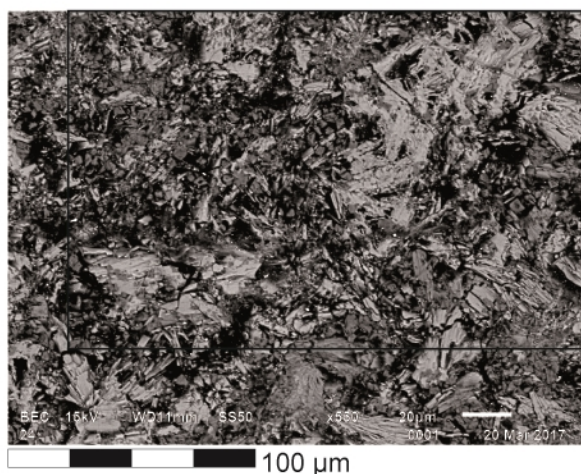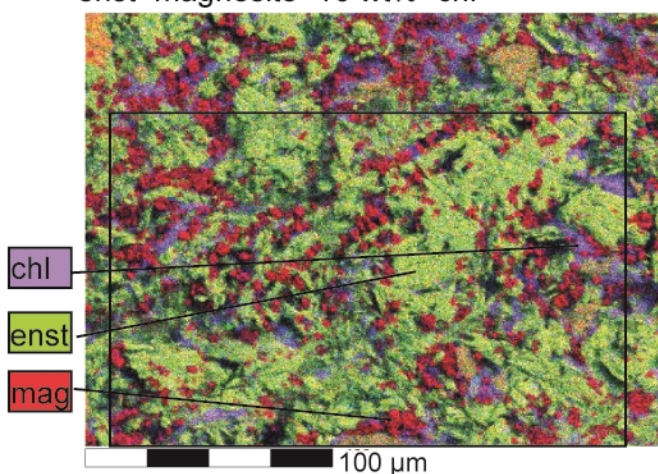
run7b: SP1; 2 GPa; 600 °C; 48 h
talc>magnesite=24 wt%>ant>chl,mt

talc
chl
mt
mag
ant

100 µm

100 µm
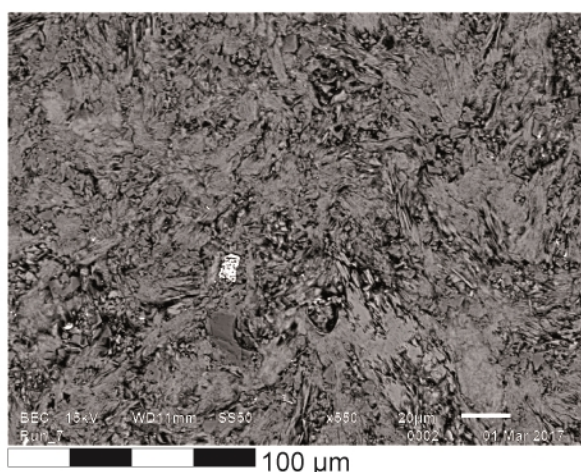
run21: SP2; 2 GPa; 600 °C; 48 h
magnesite=40 wt%>talc>qtz>chl

chl
talc
qtz
mag

100 µm

100 µm

Modified after Stern (2002; Fig. 9); [1] Molina and Poli, 2000; [2] Poli et al., 2009

Four starting mixes (SP1-4) with various serpentinite/fluid ratios have been used in this study. Oxalic acid dihydrate (OAD) is the main fluid source. Ba-, Sr-, Pb-, Ca-carbonate were added to the starting mix and are assumed to be present in the fluid in the beginning of the experiment in the listed concentrations.

Start mix			SP1	2*stdev	SP2	2*stdev	SP3	2*stdev	SP4	2*stdev
	Serpentinite	wt%	80,0	0,3	66,4	0,4	74,3	0,4	87,8	0,2
	OAD	wt%	19,3	0,3	33,0	0,4	25,1	0,3	11,5	0,2
Conc in fluid	Ba	ppm	2118	21	1050	11	1528	11	3803	38
	Ca	wt%	1,32	0,01	0,65	0,01	0,95	0,01	2,33	0,02
	Pb	ppm	2118	21	1050	11	1528	15	3803	38
	Sr	ppm	2101	21	1042	10	1516	15	3772	38
	X_{CO2} bulk*		0,27	0,004	0,35	0,005	0,31	0,005	0,2	0,004

Table 2

Overview of performed piston cylinder experiments and measured volatile composition (X_{CO2}) in the post-run fluids. The phase proportions were obtained by area analyses of BSE images and elemental maps of the solid post run assemblage in combination with the measured X_{CO2} fluid composition (see text for details). XRD has been performed on selected runs to confirm the occurrence of chlorite.

Run No	P [GPa]	T [°C]	duration [h]	start mix	start weight [mg]	X_{CO2} postrun fluid	ΔX_{CO2} postrun fluid	fluid [wt%]	magnesite [wt%]	talc [wt%]	chlorite [wt%]	quartz [wt%]	antigorite [wt%]	enstatite [wt%]	forsterite [wt%]	deviation total mass* [wt%]	XRD
30	1	500	48	SP1	8,9	0,017	0,004	22	24	39	2	n.o.	14	n.o.	n.o.	0	
58	1	550	0,1	SP1	6,5	0,256	0,013	12	14	n.o.	n.o.	7	67	n.o.	n.o.	-4	
61	1	550	0,42	SP1	2,5	0,128	0,015	13	21	n.o.	n.o.	9	58	n.o.	n.o.	0	
59	1	550	0,85	SP1	11,7	0,024	0,003	16	24	9	n.o.	2	49	n.o.	n.o.	0	
53	1	550	1	SP1	12,0	0,052	0,009	20	23	12	2	n.o.	43	n.o.	n.o.	-2	
31	1,2	550	48	SP1	8,2	0,030	0,005	23	23	43	2	n.o.	9	n.o.	n.o.	0	
52	1	550	192	SP1	8,0	0,025	0,003	28	24	40	1	n.o.	8	n.o.	n.o.	0	
32b	1	600	48	SP1	8,1	0,047	0,009	15	24	49	2	n.o.	10	n.o.	n.o.	1	
33	1	650	48	SP1	7,5	0,140	0,018	23	17	46	1	n.o.	13	n.o.	n.o.	0	
22	2	550	48	SP1	11,1	0,018	0,002	20	24	50	2	4	n.o.	n.o.	n.o.	0	
8	2	600	24	SP1	11,0	n.a.		n.a.	present	present	present	n.o.	present	n.o.	n.o.	u.c.	
7	2	600	48	SP1	12,5	n.a.		n.a.	present	present	present	n.o.	present	n.o.	n.o.	u.c.	
7b	2	600	48	SP1	9,6	0,022	0,002	24	24	44	2	n.o.	6	n.o.	n.o.	0	y
9	2	600	72	SP1	12,0	0,039	0,011	12	24	44	3	n.o.	18	n.o.	n.o.	3	
21	2	600	48	SP2	11,7	0,040	0,003	36	40	15	2	8	n.o.	n.o.	n.o.	-0,1	
23	2	630	48	SP4	12,6	0,005	0,001	11	16	64	4	n.o.	6	n.o.	n.o.	7	
19	2	650	48	SP3	8,6	0,031	0,004	16	34	48	2	n.o.	n.o.	n.o.	n.o.	9	y
19b	2	650	48	SP3	9,2	0,049	0,015	21	32	31	2	n.o.	14	n.o.	n.o.	6	
16	2	650	53	SP2	5,5	0,058	0,010	19	38	24	3	16	n.o.	n.o.	n.o.	0	
16c	2	650	48	SP2	6,6	0,077	0,012	21	39	17	3	20	n.o.	n.o.	n.o.	0	y
24	2	700	48	SP4	13,5	0,031	0,007	18	16	n.o.	2	n.o.	n.o.	64	n.o.	19	
20	2	700	48	SP3	14,3	0,053	0,019	19	29	45	0,4	n.o.	4	2	n.o.	0,4	y
15b	2	700	48	SP2	8,3	0,116	0,021	24	34	40	3	n.o.	n.o.	n.o.	n.o.	0,4	y
25	2	750	48	SP4	13,6	0,076	0,005	30	11	n.o.	3	n.o.	n.o.	36	20	9	
17	2	750	48	SP2	10,3	0,148	0,023	24	31	43	2	n.o.	n.o.	n.o.	n.o.	0	

*Deviation of the total mass after mass-balance compared to the start weight.

n.a.: not analysed; n.o.: not observed; y: XRD measurement has been performed and the occurrence of chlorite was verified