Draft Manuscript for Review

Effect of water activity on reaction kinetics and intergranular transport:
Insights from the Ca(OH)2 + MgCO3 → CaCO3 + Mg(OH)2 reaction at 1.8 GPa

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2 **Insights from the Ca(OH)$_2$ + MgCO$_3$ → CaCO$_3$ + Mg(OH)$_2$ reaction at 1.8 GPa**

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5 **Authors**

6 Julien Gasc[1]

7 Laboratoire de Géologie, École normale supérieure, CNRS-UMR8538, Paris, France

8

9 Fabrice Brunet[✉]

10 Université Grenoble Alpes, CNRS, ISTERRE, Grenoble, France

11

12 Nicolas Brantut

13 Earth Sciences Department, University College London, UK

14

15 Jérôme Corvisier

16 Centre de Géosciences, Mines ParisTech, Fontainebleau, France

17

18 Nathaniel Findling

19 Université Grenoble Alpes, ISTERRE, Grenoble, France

20

21 Anne Verlaguet

22 ISTeP, – Université Pierre et Marie Curie, 4 place Jussieu, Paris, France

23

24   Christian LATHE

25   GFZ, Telegraphenberg, D-14473 Potsdam, Germany

26

27   [1] Current Address: Géosciences Montpellier, Université de Montpellier-CNRS, Montpellier, France

28   ✉ TEL : +33 476 514 106, Fax: +33 476 635 252 e-mail : fabrice.brunet@univ-grenoble-alpes.fr

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30 **ABSTRACT**

31   The kinetics of the irreversible reaction $Ca(OH)_2 + MgCO_3 \rightarrow CaCO_3 + Mg(OH)_2$ were investigated

32   at high pressures and temperatures relevant to metamorphic petrology, using both in-situ synchrotron

33   X-ray diffraction and post-mortem analysis of reaction rims growth on recovered samples. Reaction

34   kinetics are found to strongly depend on water content; comparable bulk-reaction kinetics are obtained

35   under water *saturated* (excess water, ca. 10 wt.%) and under *intermediate* (0.1-1 wt.% water) conditions

36   when temperature is increased by ca. 300 K. Whereas, similar reaction kinetics were observed at ~673 K

37   and 823 K between *intermediate* and *dry* experiments, respectively, where *dry* refers to a set of

38   experiments with water activity below one (no free water), as buffered by the $CaO-Ca(OH)_2$ assemblage.

39   Given the activation energies at play, this gap –corresponding to the loss of no more than 1 wt.% of

40   water by the assemblage– leads to a difference of several orders of magnitude in reaction kinetics at a

41   given temperature.

42   Further analysis, at the microscopic scale, of the *intermediate* and *dry* conditions samples, shows

43   that intergranular transport of calcium controls the reaction progress. Grain boundary diffusivities could

44   be retrieved from the classic treatment of reaction rim growth rate. In turn, once modeled, this rate was

45   used to fit the bulk kinetic data derived from XRPD, offering an alternative mean to derive calcium

46   diffusivity data. Based on a comparison with effective grain boundary data for Ca and Mg from the

47   literature, it is inferred that both *dry* and *intermediate* datasets are consistent with a water saturated

48   intergranular medium with different levels of connectivity. The very high diffusivity of Ca in the $CaCO_3$ +

49   $Mg(OH)_2$ rims, in comparison that of Mg in enstatite rims [Gardés et al., *Contributions to Mineralogy and*

50   *Petrology* 164; 2012], emphasizes the prominent role of the interactions between diffusing species and

51   mineral surfaces on diffusion kinetics. Furthermore, we show that the addition of water is likely to

52   change the relative diffusivity of Mg and Ca in carbonate aggregates. On a qualitative point of view, we

53   confirm, in a carbonate-bearing system, that small water content variations within the 0 - 1 wt. % range,

54   have tremendous effects on both intergranular transport mechanisms and kinetics. We also propose

55   that the water-content dependent diffusivity of major species (Mg, Ca) in low-porosity metamorphic

56   rocks is strongly dependent of the interaction between diffusing species and mineral surfaces. This

57   parameter which will vary from one rock-type to the other, needs also to considered when extrapolating

58   (P,T,t, xH_2O) laboratory diffusion data to metamorphic processes.

59   **Keywords**: metamorphic reaction, kinetics, intergranular transport, water, calcium diffusion

60   **INTRODUCTION**

61

62   The kinetics of metamorphic reactions is strongly dependent on temperature, grain size and

63   water availability. The latter parameter is probably the most difficult to quantify, especially over the

64   course of a whole metamorphic cycle. The ubiquity of fluid during metamorphism has long been a

65   subject of controversy (Rubie, 1986, Thompson, 1983) and it is widely accepted now that variations of

66   water availability and content, in metamorphic rocks, is likely to account for the discrepancy between

67   natural reaction kinetics and those extrapolated from experimental data (Baxter, 2003). On the field, the

68   prominent role of water availability is supported by occurrences of partially eclogitized high-grade rocks

69   in which eclogitization took place in shear zones, where fluid infiltrated (Austrheim, 1987, John &

70   Schenk, 2003, Molina *et al.*, 2002). At a larger scale, by combining petrological and geophysical

71   constraints, Hetenyi et al. (2007) have suggested that the eclogitization of the Indian lower crust

72   beneath Tibet is delayed due to equilibrium overstepping until it is catalyzed by the release of water

73   from hydrous minerals.

74   Beyond the notion of water availability, which describes the intermittent presence of water in

75   the course of the metamorphic reaction process, the question of the effect of water content on the

76   reaction kinetics also appears to be relevant. In fact, most of the dataset of mineral reaction kinetics

77   available in the literature (phase relationship, dissolution, etc.) is based on experiments performed

78   under hydrothermal conditions with large water/rock ratios. Consequently, when extrapolated to

79   nature, assuming permanent water availability, this type of experimental data predicts that

80   metamorphic reaction rates are fast and that the preservation of metastable mineral assemblages

81   (reaction equilibrium overstep) is short with respect to metamorphic timescales (Wood & Walther,

82   1983). Although possibly valid for metapelites transforming along their prograde path, this conclusion

83   does not necessarily hold for high-grade rocks (e.g., upper amphibolite or granulite facies rocks) reacting

84   back with water. Under these latter circumstances, Yardley and Valley (1997) showed, on

85   thermochemical grounds, that excess water conditions (i.e.; water saturation) are not met and that

86   water activity must be below unity (taking as reference state pure water at T and P). In parallel, it has

87   been shown recently that even minute amounts of water can have a drastic effect on the kinetics of

88   mineral reactions through the enhancement of mass transport (Milke *et al.*, 2013; Gardés *et al.*, 2012,

89   Joachim *et al.*, 2012, Carlson, 2010, Milke *et al.*, 2009). In fact, a full range of intergranular diffusion

90   regimes has been identified as a function of water content (Farver & Yund, 1995, Rubie, 1986) between

91   the "dry" and the "water saturated" end member cases. These regimes are characterized by a range of

92   grain boundary diffusivities that can span over seven orders of magnitude in the case of aluminum

93   (Carlson, 2010). Even though Gardés et al. (2012) proposed a microscopic description for each of these

94   intergranular diffusion regimes, the physical state of water below the 1 wt.% level remains largely

95   unknown under metamorphic pressures and temperatures. Furthermore, studies addressing the effect

96   of low water contents on intergranular transport and its implications for mineral reaction rates are

97   scarce although of high geological relevance. The in-situ characterization at high pressure and

98   temperature (PT) of the physico-chemical properties of intergranular water present in very low

99   concentrations is obviously a difficult task. Gasc et al. (2011), for example, used in-situ impedance

100   spectroscopy at 2 GPa to characterize the electrical properties (diffusivity of electrical charge carriers) of

101   the intergranular region of a brucite polycrystal as a function of temperature for various water contents.

102   Using the $CaO - Ca(OH)_2$ and $MgO - Mg(OH)_2$ equilibria to buffer the water activity in the samples, the

103   authors were able to show that grain-boundary conductivity can vary by seven orders of magnitude

104   upon water content. In the present study, we propose to use a similar water buffering strategy to

105   address the effect of low water content variation on intergranular transport in the course the $Ca(OH)_2 +$

106   $MgCO_3 \rightarrow CaCO_3 + Mg(OH)_2$ reaction at 1.8 GPa. A special attention will be paid to bridge bulk and

107   microscopic approaches so that reaction kinetics derived from time-resolved x-ray powder diffraction

108   (XRPD) will be compared to growth rate of $CaCO_3 + Mg(OH)_2$ rims around coarse magnetite ($MgCO_3$)

109   grains dispersed in a fine portlandite, $Ca(OH)_2$, matrix. All terms and symbols used throughout the text

110   are defined in Table 1.

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112 **EXPERIMENTAL**

113 **Experimental strategy**

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115   Cubic multi-anvil (DIA) experiments were performed at 1.8 GPa in a range of temperatures (393 –

116 873 K), run durations and water contents on the non-reversible exchange reaction:

117 $$Ca(OH)_2 + MgCO_3 \rightarrow Mg(OH)_2 + CaCO_3 \qquad (1).$$

118
119 This reaction was chosen for its relatively fast kinetics, even under severely dry conditions, in order to

120 allow investigation of its kinetics *in situ* from time-resolved synchrotron diffraction. Additional

121 experiments were also performed in a piston-cylinder (PC) apparatus to investigate the kinetics of

122 reaction (1) under water-saturated conditions at the same pressure, in sealed gold containers.

123   The recovered MA samples (i.e., *dry* and *intermediate*) were characterized using Scanning

124 Electron Microscopy (SEM) with a Zeiss® Field-effect SEM (FE-SEM), which showed the presence of

125 reaction rims around coarse residual magnesite grains. The kinetics of chemical transport across the rim-

126 forming polycrystalline material, composed of brucite, $Mg(OH)_2$, and aragonite, $CaCO_3$, was

127 characterized from the determination of rim growth rates as well as from one-dimension diffusion

128 experiments performed with the same starting material in the PC apparatus. Grain boundary diffusion

129 coefficients, $\overline{D}^{GB}\delta$, were retrieved from both datasets using a segregation factor set to one, since major

130 element diffusion is involved.

131   Finally, the two approaches (i.e., bulk reaction kinetics and chemical transport at the reaction

132 rim scale) were bridged. Grain boundary diffusion coefficients were refined to fit the time-resolved

133 synchrotron diffraction data; the diffusion coefficients obtained in this fashion were then compared to

134 those retrieved from the growth rate of reaction rims and reaction fronts (FE-SEM data), in order to test

135 the consistency between microscopic and bulk datasets.

136

137 **Starting materials**

138

139   The starting material was a mixture of natural magnesite, $MgCO_3$, and synthetic portlandite,

140 $Ca(OH)_2$. Portlandite was synthesized hydrothermally (623 K, 150 MPa, 45 h) in a cold-seal vessel from

141 CaO, which was obtained by decarbonation of reagent grade calcite (Merck 2066 with <1% impurities) at

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142   1273 K. Magnesite was extracted from a natural single crystal containing less than 1 wt.% CaO and FeO;

143   the absence of mineral impurity was checked by XRPD. Portlandite and magnesite were grinded

144   together in an agate mortar in equimolar proportions. SEM showed that the starting material was

145   composed of a fine-grained matrix (grain diameter less than 1 μm) with, sporadically, coarser magnesite

146   grains (~10 μm). These larger grains are less reactive but, as described hereafter, are suitable for the

147   measurement of reaction rim growth rates.

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Reaction kinetics from in-situ synchrotron x-ray diffraction

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151   High PT experiments with in-situ energy dispersive XRPD were carried out using the MAX80 DIA

152   press (6 anvils cubic type multi-anvil) installed on beamline F2.1 at Hasylab. The starting powder was

153   pressed to a pellet (2 mm in diameter) and fitted into a boron nitride (BN) sleeve, which purpose was to

154   insulate chemically the sample from the graphite furnace but was not designed to retain water. The BN

155   sleeve was then fitted into a cylindrical graphite furnace and sandwiched between two dried NaCl

156   pellets used as pressure marker (Decker, 1971). Temperature was measured with a Type-N

157   thermocouple, the junction of which was located at a NaCl / sample interface. Boron-epoxy cubes with

158   8 mm edges were used as pressure medium in conjunction with 6 mm truncation WC anvils. Details of

159   the cell assembly and the MAX80 press can be found in Mueller (2003). Note that in order to minimize x-

160   ray absorption no sealed noble-metal container was used. Therefore, as described hereafter, water

161   saturated experiments were achieved separately in the PC using sealed gold container.

162   Two types of hydration levels were tested in the DIA experiments. The starting material was

163   either equilibrated with the air moisture before being loaded into the BN sleeve, or was dried at 383 K

164   and mixed together with about 5 wt.% CaO, a hygroscopic compound. In the former case, the amount of

165   adsorbed water onto the starting material can be estimated by weight loss through heating at 383 K and

166   was found to reach ca. 1 wt.%. These hydration conditions are referred to as *intermediate* hereafter.

167   Gasc et al. (2011) showed, using in-situ impedance spectroscopy on an $Mg(OH)_2$ aggregate at 2 GPa, that

168   in a similar set-up where the sample is only partly sealed, such absorbed water mostly remains in the

169   sample for several hours at temperature below ca. 980 K. In the case where CaO (lime) was added to

170   the oven-dried sample powder, residual free-water from the sample and its close environment was

171   removed below the set-point temperature by chemical drying following the reaction:

172

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (2)$$

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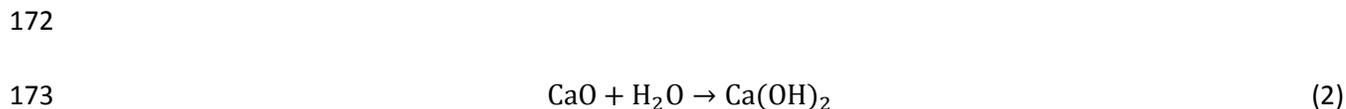
175 This method has been successfully used in Gasc et al. (2011), who showed progressive sample drying,

176 through CaO hydroxylation, as evidenced by a drop of the sample bulk electrical conductivity upon

177 heating at temperatures as low 673 K. Lime hydroxylation was similarly evidenced here by the

178 pronounced decrease of the CaO reflections intensity upon heating at T > 500 K, i.e., while the reaction

179 of interest (1) had not yet started (Figure 1). As long as CaO and $Ca(OH)_2$ are present in the sample, the

180 starting water activity is buffered to a value that depends on the free enthalpy of Reaction (2) and

181 therefore on temperature. The water activity was calculated using Wintwq 2.34 (Berman & Aranovich,

182 1996) in the 823–873 K temperature range corresponding to our experiments and was found to vary

183 from 0.1 to 0.15. These experiments, which involve chemical drying, will be called *dry* in the following.

184 A white x-ray beam provided by the DORIS III storage ring was used to collect energy dispersive

185 XRPD data. The spectra were collected continuously with acquisition times of 45 or 60 seconds (Figures

186 1 and 2) with a 2048 channels solid-state Ge detector. The Bragg reflection of highest intensity typically

187 varied from 2×10^3 to 5×10^3 detector counts.

188 Reaction progress, $\xi(t)$, was calculated for each spectrum collected at a time, t, from the

189 intensity, $I(t)$ of selected diffraction peaks, assuming that $\xi(t) = I(t)/I_{max}$ for products and that $\xi(t) = 1-$

190 $(I(t)/I_{max})$ for reactants, where I_{max} is the maximum intensity of the considered reflection (Lathe *et al.*,

191 2005, Zinn *et al.*, 1995). Therefore, for reactants, at $t = 0$, $\xi(t) = 0$ and $I(0) = I_{max}$. We calculated reaction

192 progress either from the intensity of the (104) reflection of $MgCO_3$ or the (011) reflection of $Ca(OH)_2$

193 (Figure 2). Because of its larger grain size distribution, magnesite is less suitable for quantification

194 purposes using X-ray powder diffraction than portlandite, which was thus preferentially used to

195 calculate $\xi(t)$. Note that, with the use of white synchrotron light, the beam is collimated and the volume

196 sampled is relatively small, which, in some cases, may translate as an insufficient number of grains

197 sampled for proper quantitative analysis. This can cause the relative intensities of the diffraction peaks

198 to fluctuate and not represent the actual phase proportions. Therefore, whenever possible, reaction

199 progress was additionally retrieved from the (111) and (011) reflection intensities of $CaCO_3$ and

200 $Mg(OH)_2$, respectively. In all cases, intensities, I, were also subtracted a background that was estimated

201 for each t. The ratio between maximum peak intensity and background level was typically ~30. In some

202 instances, after collection of kinetic data at a certain constant temperature, the experiment was

203 terminated by increasing further the temperature until $\xi(t) = 1$ was achieved, which allows retrieving I_{max}

204 values for the reaction products and enables their use for calculating $\xi(t)$. In addition, the incident beam

205 intensity decayed with time due to the decrease of the storage ring current. In order to account for this

206 effect on peak intensities, and since the irradiated sample zone relative to the x-ray detector remains

207 unchanged during an experiment, the peak intensities were normalized to the BN (100) reflection

208 (Figure 2).

Reaction kinetics with excess water

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211 The kinetics of the reaction was also investigated at lower temperatures by performing off-beam

212 PC experiments, for which both longer run durations and excess water (i.e., water saturated) conditions

213 could be more easily achieved. For these experiments, the solid starting material was loaded together

214 with 10 wt.% deionized water in a gold capsule welded shut. This type of hydration conditions will be

215 referred to as *saturated* hereafter. Low-friction NaCl-based pressure cells (1/2 inch) were used. More

216 details on the pressure assembly can be found in Brunet et al. (2003). The temperature was measured

217 with an S-type thermocouple and regulated within 1 K with a Eurotherm^{TM} controller.

218 Angle dispersive XRPD patterns were collected on quenched products with a Rigaku

219 diffractometer (Ultrax18hf-RINT2500) equipped with a Cu rotating anode (300 mA, 40 kV). XRPD data

220 were collected using 0.02° steps at a speed of 2°/min. In this case, the reaction extent, $\xi(t)$, could be

221 determined from reactant/product molar proportions in the quenched samples as follows. First, phase

222 proportions were calculated using the following relation:

223
224
$$\frac{\chi_P}{\chi_B} = \varphi \frac{I_P}{I_B} \tag{3}$$

225

226 where φ is a constant, χ is the weight fraction of a given phase in the sample, I is the height (i.e.,

227 counts) of a selected diffraction peak, and the subscripts P and B stand for portlandite and brucite,

228 respectively. The value of φ was calibrated from mixtures of known portlandite to brucite weight

229 proportions using the height of the (001) reflection of each phase. The reaction progress, $\xi(t)$,

230 corresponding to the molar fraction of the forming phase, brucite, was then estimated from the

231 relation:

232 $$\frac{\xi}{1-\xi} = \frac{\chi_B M_B}{\chi_P M_P}$$ (4),

234 where M_P and M_B are the molar masses of portlandite and brucite, respectively.

One-dimension diffusion experiments under *intermediate* hydration level

238 The kinetics of Reaction (1) was further investigated in a one-dimension set-up using the piston-
239 cylinder apparatus (1D-PC experiments) by measuring the width of the reaction zone, which developed
240 at the interface between magnesite and portlandite polycrystals. This set-up aimed at characterizing
241 grain-boundary transport with the simplest geometry. Contrary to the kinetic experiments described in
242 the previous section, individual magnesite and portlandite powders (same material as for DIA and PC
243 experiments but unmixed) were loaded one after the other in a gold capsule. As much as possible, the
244 contact between these two materials was made planar (Figure 5a). No water was added to the capsule
245 nor was the sample dried beforehand. The hydration level can therefore be considered here as
246 *intermediate*. As for multi-anvil experiments, the run products of 1D-PC experiments were embedded in
247 epoxy, cut and hand polished with diamond paste. After carbon coating, these samples were also
248 characterized using the FE-SEM.

249 In order to investigate the temperature dependency of the chemical transport kinetics, these
250 experiments were performed in the 773–873 K temperature range. Typical reaction front widths of
251 ~ 1 mm were obtained for durations of a several days.

EXPERIMENTAL RESULTS

255 Bulk kinetic data from time-resolved XRD

257 In total, 16 experiments have been successfully performed on Reaction (1) with time-resolved
258 in-situ XRPD at 1.8 GPa and for temperatures ranging from 573 to 873 K (Table 2). It must be noted that
259 each dataset is composed of tens to hundreds of diffraction patterns, each represented by a data point
260 in left and middle panels of Figure 3. Water saturated conditions were investigated at two single

261   temperatures (393 and 423 K) through four and five PC experiments (Figure 3), respectively, which

262   therefore correspond to two kinetic data points for *saturated* conditions in Figure 4. Hundreds of PC

263   experiments would have been required to achieve a time resolution on the reaction progress similar to

264   that of the synchrotron-based experiments, which clearly emphasizes the advantage of using an in-situ

265   technique for kinetic purposes.

266   The scattering observed in the kinetic data obtained from synchrotron XRPD indicates a

267   precision of +/- 10% on the reaction progress (Figure 3). However, the precision on the reaction kinetics

268   is better owing to the averaging of the large number of data at each PT conditions. For PC experiments,

269   the precision on the determination of the reaction progress is expected to be better than 5 %; in

270   particular, sample heterogeneity is averaged out by x-ray diffraction pattern collected on a larger

271   sample volume

272   As one can observe from the shape of the reaction curves, the reaction rate is the fastest when

273   the reaction starts and slows down as the reaction proceeds. Heterogeneous reactions, such as the one

274   studied here, do not generally comply with simple kinetic laws such as zero- or first-order. Furthermore,

275   the presence of a grain size distribution instead of single grain size in the starting material will influence

276   the shape of the kinetic curve if the reaction process is dependent on the reactive-surface area of the

277   reactants. Finally, change of hydration conditions from one set of experiments to another may lead to a

278   change in the reaction process (e.g., dissolution – crystallization in the water saturated case). The overall

279   shape of the kinetic curves can be successfully fitted to an empirical Avrami law (Avrami, 1939) with an

280   exponent value of 0.4, which, according to Christian (1975), would reflect a diffusion limited reaction

281   process. However, due to the truly empirical character of these fits, following (Brown *et al.*, 1962), we

282   decided to merely compare half-reaction times (i.e., the time needed to reach $\xi = 0.5$) between all

283   datasets in order to grasp the effect of water as a whole on the reaction kinetics (Table 2, Figure 4). Note

284   that for the particular case of the PC experiments performed with 10 wt.% water (*water saturated*

285   conditions), dissolution-precipitation process is expected to occur. However, aqueous species transport

286   rate – rather than dissolution rate – may well be the rate limiting process. Diffusivity of aqueous species

287   in bulk water is not within the scope of the present study. These "saturated" experiments should be

288   seen as representative of the water-excess experiments usually carried out in experimental petrology.

289   Both series of experiments performed under *dry* and *intermediate* conditions seem to display an

290   Arrhenius-type behavior (i.e., the logarithm of half reaction times have a linear dependency to reciprocal

291   temperature) although, comparatively, experimental data obtained for an *intermediate* hydration level

292   are much more scattered (Figure 4). The dependency of the reaction kinetic with water content is likely

293   causing the important scattering observed in the *intermediate* dataset (see Discussion section). The

294   present results illustrate a drastic effect of water content on the kinetics. We note that similar half

295   reaction times (ca. 1 hour) were obtained at ~823, 648 and 423 K, for *dry*, *intermediate* and *saturated*

296   conditions, respectively, although the gap between *intermediate* and *dry* conditions seems to shrink

297   towards higher temperatures due to an apparently larger activation energy of the kinetic under *dry*

298   conditions.

299   **Chemical transport through the $CaCO_3$ + $Mg(OH)_2$ reaction rims**

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301   FE-SEM images of the recovered 1D-PC samples show mineral intergrowth in reaction zones

302   composed of $Mg(OH)_2$ and $CaCO_3$ (Figure 5a). Energy dispersive spectrometry data collected with the FE-

303   SEM indicated that the Ca/Ca+Mg molar ratio remains constant and equal to 0.5 across the reaction

304   zones. In all of the DIA samples, partly reacted magnesite grains are surrounded by reaction rims (Figure

305   5b) within which the grain size of the reaction products is found to gradually increase from the

306   Ara+Bru│Mag to the Port│Ara+Bru interfaces. These reaction rims are composed of equimolar $Mg(OH)_2$

307   (brucite) + $CaCO_3$ (aragonite) and show the same textural characteristics (grain size distribution,

308   symplectite intergrowth) as the reaction fronts in 1D-PC experiments. For 1D-PC and DIA experiments,

309   the grain size of the reaction products varies between 30 nm and a few µm (Figure 5d and 5e),

310   depending on temperature, water content and run duration. The constant stoichiometry

311   (CaO/H_2O = MgO/CO_2 = 1) throughout the reaction zones in both 1-D experiments and DIA samples,

312   implies the equality of Ca (CaO) and H (H_2O) fluxes through the Port│Ara+Bru interface. Similarly, the

313   Mg (MgO) and C (CO_2) fluxes must be identical through the Ara+Bru│Mag interface. In experiment

314   PC_180, a Pt chip was positioned at the interface between portlandite and magnesite. The Pt chip

315   (Figure 5a) remained at the Port│Ara+Bru interface in the course of the diffusion process. Its presence

316   at the interface appears to have hindered the transport of species from the Port│Ara+Bru interface to

317   the Ara+Bru│Mag interface, as indicated by the depression of the reaction front opposite to the Pt chip.

318   Therefore, CaO and H_2O are the mobile species in the system, whereas MgO and CO_2 remained

319   comparatively immobile. This conclusion is in line with the grain size gradient observed across the

320   reaction zones, where grains situated next to the Port│Ara+Bru interface formed first and are therefore

321   larger.

322

$\overline{D}_{CaO}$ **retrieval from 1D experiments**

We showed in the previous section that the reaction zone growth in 1D-PC and DIA samples is controlled (i.e., limited) by the diffusion of CaO, assuming that H_2O diffusion is not limiting. The growth rate of the reaction zone (front or rim) depends on the molar flux of the limiting diffusing species, i.e., J_{CaO} in the present case, perpendicular to the reaction zone. Let us consider the equimolar mix of brucite and aragonite as a single phase having an effective molar volume corresponding to V_r (Figure 6a). In the planar geometry of our 1D-PC experiments, since each mole of CaO diffusing through the front results in the creation of one mole of said hypothetical phase, the growth rate of the reaction front thickness, ΔX, can be written:

$$\frac{d\Delta x}{dt} = J_{CaO}V_r \tag{5},$$

According to the formalism developed by Fisler and Mackwell (1994), the first Fick's law for diffusion can be used to write the CaO flux across the reaction zone, J_{CaO}, as a function of the CaO chemical potential gradient, $d\mu_{CaO}/dx$, as follows:

$$J_{CaO} = -\frac{D_{CaO}C_{CaO}}{RT}\frac{d\mu_{CaO}}{dx} \tag{6}.$$

Fisler and Mackwel (1994) also showed that this latter expression can be integrated using the mean-value theorem, introducing the mean diffusion coefficient, $\overline{D}_{CaO}$, which represents the mean value for the diffusion across the reaction front or rim. The flux can then be written:

$$J_{CaO} = -\frac{\overline{D}_{CaO}C_{CaO}}{RT}\frac{\Delta\mu_{CaO}}{\Delta x} \tag{7},$$

349   where $\Delta\mu_{CaO} = \mu'_{CaO} - \mu^0_{CaO}$ and therefore represents the chemical potential difference across the

350   reaction zone.

351   Let us now consider the Ara+Bru│Mag interface, where, by definition, $x = \Delta x$ (Figure 6a). If we

352   consider the equilibrium between $MgCO_3$, the reaction products and the diffusing components, CaO and

353   H_2O, we can write that:

354

355
$$\mu_{MgCO_3} + \mu'_{CaO} + \mu'_{H_2O} = \mu_{Mg(OH)_2} + \mu_{CaCO_3} \tag{8}.$$

356

357   In addition, at $x = 0$, $\mu^0_{CaO} = \mu_{Ca(OH)_2} - \mu^0_{H_2O}$. Assuming that water activity is constant across the whole

358   sample (due to supposedly faster diffusion kinetics), then $\mu^0_{H_2O} = \mu'_{H_2O}$. We can therefore write:

359

360
$$\mu'_{H_2O} = \mu_{Ca(OH)_2} - \mu^0_{CaO} \tag{9}.$$

361

362   Finally, combining equations (8) and (9) gives:

363

364
$$\mu'_{CaO} - \mu^0_{CaO} = \mu_{Mg(OH)_2} + \mu_{CaCO_3} - \mu_{MgCO_3} - \mu_{Ca(OH)_2} \tag{10},$$

365

366   from which we find that $\Delta\mu_{CaO} = \Delta_R G$. In addition, it can be noticed that, in the present case $C_{CaO}.V_r = 1$.

367   The combination of (5) and (7) then yields:

368
$$\frac{d\Delta x}{dt} = -\frac{\bar{D}_{CaO}}{RT}\frac{\Delta_R G}{\Delta x} \tag{11}.$$

369

370   We note here that the mean diffusion coefficient, $\bar{D}_{CaO}$, is an effective (i.e., apparent) diffusion

371   coefficient, considering the brucite + aragonite aggregate in the reaction zone as a homogeneous

372   diffusing medium. Effective and grain boundary diffusion coefficients are related to one another by a

373 ratio that depicts the shape and the volume fraction of grain boundaries available for intergranular

374 diffusion. For example, in the ideal case where grain boundaries are planar (i.e., devoid of tortuosity)

375 and parallel to the diffusion flux, the following relation applies (Brady, 1983):

376

377
$$\overline{D}^{GB} = \overline{D}\,\frac{2l}{\pi\delta} \tag{12},$$

378

379 where l is the distance separating the diffusion planes, i.e., the grain size (Figure 6a), and δ is the grain

380 boundary width. Since this latter parameter is virtually impossible to determine, most authors choose to

381 report the product of the grain boundary diffusivity $\overline{D}^{GB}$ and the grain boundary width, δ. However,

382 during the diffusion process and the growth of reaction rims or fronts, l is not constant but obeys an

383 exponential grain growth law (Joesten, 1991):

384

385
$$l = (\rho t)^{1/n} \tag{13},$$

386

387 where ρ and n are the grain coarsening rate constant and exponent, respectively. Combining relations

388 (12) and (13) yields the expression:

389

390
$$\overline{D}^{GB} = \overline{D}\,\frac{2(\rho t)^{1/n}}{\pi\delta} \tag{14}.$$

391

392 It has been shown indeed that the growth of reaction fronts limited by grain boundary diffusion is no

393 more proportional to the square root of time, but that it slows down further with time due to grain

394 coarsening, and therefore decreasing availability of grain boundaries (Gardes & Heinrich, 2011). In that

395 case, Δx is proportional to $(t^{1-1/n})^{1/2}$, where n is the grain coarsening exponent. Here, the combination of

396 Equations (11) and (14) gives the relation between rim thickness and time as a function of the grain

397 boundary diffusion coefficient:

398

$$\frac{d\Delta x}{dt}\Delta x = -\overline{D}^{GB}\delta\frac{\Delta_R G}{RT}\frac{\pi}{2\rho^{\frac{1}{n}}}t^{-\left(\frac{1}{n}\right)} \qquad (15).$$

399

400

401 Integrating the above equation, noting that for $t = 0$ then $\Delta x = 0$, we obtain the relation:

402

$$\Delta x = \sqrt{\left(-\overline{D}^{GB}\delta\frac{\Delta_R G}{RT}\frac{\pi}{\rho^{\frac{1}{n}}}\left(\frac{n}{n-1}\right)\right)}t^{\frac{n-1}{2n}} \qquad (16).$$

403

404

405 In the present case (see Appendix 1), the grain size of the reaction products was analyzed using SEM

406 imaging to constrain the grain coarsening parameters, ρ and n. Relation (16) was then used to derive

407 $\overline{D}^{GB}\delta$ from 1D-PC experiments (Table 2), where a planar geometry applies (Figure 6a).

408   Generally speaking, the presence of water may impact $\overline{D}_{CaO}$ values by affecting any of the other

409 parameters included in Equation (14), namely CaO mobility in the intergranular medium (i.e., $\overline{D}^{GB}_{CaO}$),

410 grain boundary width and grain growth. This holds for experimentally grown coronae and for natural

411 metamorphic reactions as well and since these latter parameters are difficult to estimate, one might

412 also want to compare effective diffusivity values, $\overline{D}_{CaO}$. This approach was chosen by Carlson (2010),

413 where Al effective diffusion coefficients were retrieved in the case of natural metamorphic coronae; it

414 allows evaluating the overall effects of water content variations on the growth of reaction zones and

415 visualizing how they affect metamorphic reaction kinetics in general.

416

417 **$\overline{D}_{CaO}$ retrieval from reaction coronae (spherical setting)**

418

419   Similar to our 1D-PC experiments, SEM examination of the DIA samples evidenced that the

420 reaction proceeds via the development of reaction rims around magnesite grains. This is nicely

421 illustrated by the coronae observed around coarser residual magnesite grains in some samples (Figure

422 5b). The dimensions of these reaction rims can be used to calculate effective diffusion coefficients

423 according to the model shown in Figure 6b. We note however that, in the initial setting (at $t = 0$),

424 magnesite grains are not surrounded strictly by portlandite only, but rather by a mix of finer magnesite

425 grains and portlandite. This may result in low Ca availability for diffusion and growth of the reaction

426   rims, which, in turn, implies that the diffusion values retrieved may be underestimated. Unfortunately, it

427   is impossible to measure the impact of this bias on the values retrieved.

428   The spherical setting implies that Equations (5) through (7) defined above in a planar setting no

429   longer apply. We used the analytical solution given for a spherical geometry in Abart et al. (2009) that

430   relates the rim dimensions and the bulk diffusion coefficient. This relation was modified in order to take

431   grain coarsening for *intermediate* conditions into account; the *dry* case was treated assuming constant

432   grain size in the rim (see next section and Appendix 1 for details).

433   It should be noted that rim widths are determined from SEM images of sample sections which

434   do not necessarily pass through the center of the imaged magnesite grains. This can introduce a

435   measurement bias with apparently larger r_A/r_B ratios. Therefore, as much as possible, only rims with the

436   lowest r_A/r_B ratio were used for the present determination (i.e., largest residual grains were

437   preferentially picked). Additional errors may arise from the estimation of the inner and outer rim

438   dimensions, r_B and r_A respectively (see Table 2). Errors on those measurements are of 0.1-0.3 μm (Table

439   2). According to Equation (A5), $\overline{D}_{CaO}^{GB}\delta$ is proportional to the square of r_B/r_0., which is accounted for by

440   the error bars in the Arrhenius plot (Figure 7a).

441   Diffusivity values obtained for both 1D-PC and DIA (3D) experiments are listed in Table 2 and are

442   reported in Figure 7a (empty symbols). We note that the *intermediate* data, retrieved from 1D-PC, and

443   DIA experiments, although conducted over very different time scales, (i.e., a few hours and several days

444   respectively) show a good consistency. Despite the uncertainties discussed above, the results clearly

445   show a gap between *dry* and *intermediate* conditions, where comparable diffusivities are found at 823

446   and 673 K, respectively.

447

Numerical extraction of diffusivity values from bulk reaction kinetics

449   The bulk reaction progress, $\xi(t)$, represents the molar fraction of magnesite (or portlandite)

450   having reacted after a given run duration. At the scale of a single magnesite grain surrounded by

451   portlandite, the reaction progress, $X(t)$, is related to the inner rim radius, r_b, as follows:

452

$$X(t) = 1 - \frac{r_B{}^3}{r_0{}^3} = 1 - y^3 \tag{17}$$

454

455   If reaction rim growth is the limiting factor to the bulk reaction progress, then reaction kinetics

456   derived from in-situ diffraction should correspond to the magnesite rim growth kinetics (i.e., $X(t) =$

457     $\xi(t)$). However, the relation between $\xi(t)$ and $X(t)$ depends on the magnesite grain size distribution.

458   SEM images show that this distribution consists of a fine-grained fraction (<1 μm) along with coarser

459   grains, which size can be as large as several tens of microns. We assumed a log-normal grain size

460   distribution, typical of ground powders (Astrom, 2006, German, 2009, Sanchidrian *et al.*, 2012),

461   characterized by γ_0 and σ, which represent respectively the mean and the standard deviation of the

462   grain size natural logarithm. The grain size distribution was binned into 25 grain sizes with

463   corresponding proportions (p_i). Using, again, the analytical solution derived from Abart et al. (2009) in

464   Equation (A5), we could simulate reaction progress data, $X_i(t)$, for each grain size. Then kinetic curves

465   (i.e., $\xi(t)$), were obtained by calculating the weighted sum: $\sum_{i=1}^{25} p_i X_i(t)$ with $\sum_{i=1}^{25} p_i = 1$. For each

466   experimental data set, this approach was used to simulate kinetic data with varying values of $\overline{D}_{CaO}^{GB}\delta$.

467   The best fit to the experimental data was then obtained using a standard grid search algorithm and by

468   minimizing the absolute value of the difference between modeled and observed kinetic curves; this

469   method is also known as Least Absolute Deviations (LAD) method. The uncertainty on $\overline{D}_{CaO}^{GB}\delta$ introduced

470   by possible error on the initial grain size distribution is addressed in Appendix 2. It should be noted here,

471   that, as mentioned in the experimental section of the present study, the diffraction peak intensities

472   used to calculate reaction progress may not reflect the actual proportion of a phase in the sample at a

473   given time but may differ significantly. Based on observations of the standard deviation in our DIA

474   datasets, we inferred that this bias could result in errors of +/- 0.05 on $\xi(t)$, which impacts the values of

475     $\overline{D}_{CaO}^{GB}\delta$ retrieved by a factor of 3 at most.

476   All 10 DIA experiments under *intermediate* conditions were used to estimate the mean grain

477   boundary diffusivity, $\overline{D}_{CaO}^{GB}\delta$, in this fashion. However, for some experiments performed under *dry*

478   conditions, the model failed to fit the experimental data satisfactorily. This can be explained by the

479   minor amount of grain growth involved in *dry* conditions (maximum grain sizes in the reaction rims are

480   typically no larger than tens of nanometers), which is therefore difficult to characterize (see appendix 1).

481   Alternatively, we chose to fit the *dry* datasets without integrated grain growth, i.e., by using the

482   analytical solution given in Abart et al. (2009), which allowed us to retrieve mean bulk diffusivity values,

483     $\overline{D}_{CaO}$. Values of grain boundary diffusion, $\overline{D}_{CaO}^{GB}\delta$, were then calculated using equation (12) and an

484   estimated grain size of l = 120 nm, based on measurements made on two recovered samples (see

485 Appendix 1). The results are listed in Table 2 and, as a test of consistency between the bulk and the

486 microscopic datasets, both are reported on an Arrhenius plot in Figure 7a, along with $\overline{D}^{GB}_{CaO}\delta$ values from

487 the literature (Figure 7b). Test analysis of the retrieved diffusion values with varying grain growth

488 parameters, n and ρ, showed that the errors introduced by the estimation of these parameters are

489 negligible compared to other sources of errors (namely the initial grain size distribution and the

490 experimentally determined reaction progress).

491 For four experiments performed under *intermediate* conditions and two experiments performed

492 under *dry* conditions, diffusivities could be retrieved from both the microscopic approach and by

493 simulating kinetic curves (bulk approach). The largest difference observed between the two approaches

494 is of 1.33 log units. Although these differences seem significant at first sight, they are within the

495 uncertainties discussed above. In fact, the two datasets evidence a good consistency between the

496 microscopic (reaction rim and 1D diffusion fronts) and the macroscopic approaches, as highlighted by

497 the Arrhenius plot on Figure 7a.

498 A drastic difference is observed between *dry* and *intermediate* datasets, where similar values of

499 $\overline{D}^{GB}_{CaO}\delta$ are found at ~823 and 673 K, respectively, similar to the temperature gap observed when

500 comparing bulk reaction kinetics, i.e., half-reaction times (Figure 4). As for half-reaction times, the

501 diffusivity gap between *dry* and *intermediate* seems to shrink towards higher temperatures. The

502 activation energy returned by the Arrhenius fit in the *dry* case is 573 ± 208 kJ.mol^{-1}, which is indeed

503 considerably larger than for the *intermediate* case (291 ± 29 kJ.mol^{-1}). But, in the former case, due to

504 the narrower temperature range investigated, the uncertainty returned is too large to allow any

505 assertion regarding its absolute value. Conclusively, although our results strongly suggest a larger

506 activation energy in the *dry* case, they do not entirely exclude the possibility that the activation energy

507 be the same in both cases (i.e., around 300 kJ.mol^{-1}).

508

DISCUSSION

509

510

511 **Consistency between bulk and microscopic approaches**

512 In order to investigate the effect of water on the $MgCO_3$ + $Ca(OH)_2$ → $Mg(OH)_2$ + $CaCO_3$ reaction

513 at 1.8 GPa, we designed experiments where the starting material is composed of a grain size distribution

514 of the first reactant (i.e., magnesite with a log-normal distribution which includes grains > 10 μm)

515   reacting with a fine and homogeneous matrix of the second reactant (portlandite ≤ 1 μm). We show

516   here that this starting material is suitable for the estimation of mean diffusion coefficients from time-

517   resolved in-situ XRPD provided (1) that significant reaction extents be achieved with sufficient XRD

518   sensitivity, (2) that the grain-size distribution of the reactants can be approximated and (3) that the

519   texture of the reacted samples can be characterized post-mortem. Obviously, the conventional

520   approach, which consists in measuring the growth rate of reaction rims remains more accurate for the

521   determination of diffusion coefficients. However, the in-situ approach can be appealing in some

522   instances since it allows fast collection of large datasets as required when investigating a range of

523   hydration levels (or a range of pressures) at various temperatures. One obvious limitation of our in-situ

524   approach with respect to the effect of hydration on reaction kinetics is the absence of a sealed container

525   in order to ensure constant water concentration over the whole run duration. For example, in the case

526   of the present brucite-bearing system at 1.8 GPa, this limitation implies that the reaction kinetics of

527   samples containing a few thousands of ppm water cannot be reasonably investigated at temperature

528   above ca. 950 K at the hour timescale (Gasc et al., 2011). The noble metal often used as container

529   material strongly absorbs the x-ray radiation and therefore alters the XRD signal intensity. The use of

530   titanium as capsule material (Chollet *et al.*, 2009) for synchrotron diffraction experiments dealing with

531   water-bearing systems clearly opens the way to the collection of in-situ XRD data under controlled and

532   constant water content.

533

534   **Role of the geometry of the intergranular medium**

535   It is important to note that, in the present diffusion dataset, the effect of water content is

536   potentially twofold. Water content will modify the chemistry of the intergranular medium and impact

537   the effective intergranular diffusivity (here $\overline{D}_{CaO}^{GB}$). The presence of water can also modify the geometry

538   of the diffusion paths through grain growth or by controlling the grain boundary width. The impact of

539   grain coarsening on kinetics via the reduction of the intergranular medium available for diffusion can be

540   of several orders of magnitude (Carlson & Gordon, 2004). Therefore, the effect of grain growth has been

541   taken into account by introducing a grain-growth rate law (Appendix 1). However, it can be argued that

542   the diffusivity gap between *dry* and *intermediate* conditions results from variations of the effective grain

543   boundary width, δ. According to Relation (14), identical Ca diffusivity would imply that δ is at least 2

544   orders of magnitude greater in *intermediate* than in *dry* conditions at 823 K. This seems huge in

545   comparison to what we know about grain boundary width at ambient pressure. Although the effective

546   grain boundary width may be larger than the structural grain boundary width, even in the absence of

547   fluids (Marquardt *et al.*, 2011), in our *dry* conditions, the effective boundary width –which is the one of

548   anhydrous aggregates– should not exceed significantly the structural boundary width, generally

549   described as being equal to a few nanometers (Bons *et al.*, 1990, Farver *et al.*, 1994, Hiraga *et al.*, 1999,

550   Ricoult & Kohlstedt, 1983, (Marquardt *et al.*, 2011). On the other hand, studies of water-mineral

551   interface structures show that no more than two monolayers of water are adsorbed at the surface of

552   calcite grains with water being structured over a distance of approximately 15 Å (Cooke *et al.*, 2010,

553   Fenter & Sturchio, 2004). This implies that δ cannot vary by more than one order magnitude between

554   *dry* and *intermediate* conditions. Conclusively, even if intergranular diffusion may be enhanced by small

555   amounts of water through grain boundary widening, this effect alone cannot be responsible for the

556   tremendous differences observed between *dry* and *intermediate* cases, which are greater than two

557   orders of magnitude at the lowest temperatures of the present study (Figure 7a). As suggested by the

558   change in activation energy from *intermediate* to *dry* condition, we are likely documenting here water-

559   content dependent diffusion mechanisms, where cation mobility is enhanced by the presence of

560   absorbed water at the grain surfaces (i.e., in the grain boundaries). However, it is possible that even

561   minor amounts of water, such as it is the case here, enhance diffusivity not by widening grain

562   boundaries – therefore increasing the structural grain boundary width – but by creating locally

563   connected porosity (most likely in the form of tubules at triple junctions). This would result in an

564   increased effective grain boundary width, which no longer relates to the actual structural grain

565   boundary width; and the term intergranular diffusion should be preferred over grain boundary diffusion.

566   We note, however, that so far, there has been no systematic measurement of the grain

567   boundary width or structure evolution with increasing pressure. There is, therefore, a clear need for in-

568   situ experiments which investigate, for instance, how confining pressure affects transport properties.

569

Water content and intergranular Ca-diffusion regimes

571   The effect of water content on calcium transport (reaction rim growth) derived here is very

572   consistent, at least from a qualitative point of view, with recent work on Mg and Al intergranular

573   transport (Milke et al., 2013; Gardés *et al.*, 2012; Carlson, 2010). In these studies, as in the present one,

574   the addition of small amounts of water, ≤ 1 wt.%, was reported to enhance intergranular diffusion by

575   several orders of magnitude, resulting in equal transport properties at temperatures lower by hundreds

576   of degrees. We note that in all cases the activation energies are reported to decrease significantly with

577   increasing water content. The present results are also in good agreement with the results of Gasc et al.

578   (2011), where, using a PC set-up that was open with respect to water, a drastic reduction of the

579   electrical conductivity of polycrystalline brucite was observed between samples dried in an oven at

580   393 K –possibly containing adsorbed water– and samples chemically dried by the addition of CaO. This

581   was also accompanied by an increase of the activation energy of the electrical conductivity from 84 to

582   106 kJ mol^{-1}. Similarly, the kinetics of the $Ca(OH)_2 + MgCO_3 \rightarrow CaCO_3 + Mg(OH)_2$ exchange reaction,

583   which is also controlled by intergranular transport under the investigated PT conditions, showed a

584   strong positive dependency with water content from *dry* to *saturated* conditions (Figure 4).

585   In the present study, *dry* conditions were achieved using chemical drying, i.e., by maintaining

586   low water fugacity in the sample with a $CaO/Ca(OH)_2$ solid buffer. The notion of *dry* conditions may

587   appear somehow contradictory since the *dry* sample contains hydroxide phases. It should rather be

588   understood in the frame of diffusivity regimes (Farver & Yund, 1995), which were recently redefined by

589   Gardés et al. (2012) on enstatite and enstatite + forsterite reaction rims. These authors suggested that

590   four different regimes can be distinguished as a function of water content; the first regime

591   corresponding to conditions where grain boundaries are essentially anhydrous. The exchange of water

592   between brucite inner grains and grain boundaries observed by Gasc et al. (2011) precludes the

593   occurrence of anhydrous grain boundaries in the presence of brucite, as in the present study. Indeed,

594   Milke et al. (2013) showed that water content at the 10th of ppm level is sufficient to switch from

595   anhydrous to hydrous-like reaction textures in OPX reaction rims at 850-900°C. Hence, the *dry*

596   conditions obtained here with the addition of CaO cannot correspond to Regime 1 defined by Gardés et

597   al. (2012). In addition, the fact that our diffusion data show the least scattering in the *dry* case (Figures 4

598   and 7a) suggests that they are relevant to Regime 3, corresponding to hydrous saturated grain

599   boundary, rather than Regime 2 where diffusivity is expected to be strongly dependent of water

600   content. Regarding our *intermediate* conditions, although our approach suffers from undetermined

601   water content, the absorbed water on grain surfaces is estimated to represent 1 wt.% of the starting

602   material at most, a value that is close to the 0.5 wt.% threshold proposed by Gardés et al. (2012) for the

603   transition between Regimes 3 and 4 for anhydrous magnesium silicates. Besides, according to Gardés et

604   al. (2012), diffusivity variations with water content are also expected to be encountered in Regime 4,

605   where interconnected fluid channels start occurring. This is consistent with the scattering of our

606   diffusivity data in *intermediate* conditions, since the water content in the sample likely varied from one

607   experiment to the other due to variable hygrometric conditions and to partial water draining during the

608   experiment. In fact, it might not be fortuitous that the lowest temperature datapoint at 573 K

609 performed under *intermediate* conditions led to a significantly higher diffusivity value than its

610 counterparts. For this reason, and despite the low uncertainty returned, the (apparent) activation

611 energy for the *intermediate* conditions should be considered with caution.

612 Helpa et al. (2014) studied experimentally Mg and Ca diffusion in dolomite reaction rims but

613 could not distinguish whether GB or volume diffusion was the dominant process. Both studies were

614 performed in anhydrous conditions and their results are compared to ours in Figure 7b. Extrapolation of

615 the Ca diffusion coefficients obtained in *dry* conditions to the 750-800°C temperature range indicates

616 that we found higher diffusivity by four and six orders of magnitude than Helpa et al. (2014) and Farver

617 and Jund (1996), respectively. This apparent discrepancy can be accounted for by different water

618 conditions investigated by these authors, which likely corresponded to Regime 1 (anhydrous) whereas

619 we interpreted our *dry* experiments as reflecting diffusional Regime 3 defined by Gardés et al. (2012).

620 For comparison, we also plotted on Figure 7b, the data on Mg diffusion in enstatite rims by Gardés et al.

621 (2012) and Gardés and Heinrich (2011) who respectively investigated Regime 3 and Regime 1. It can be

622 seen that differences of, at least, 6 orders of magnitude are encountered at 800°C between these two

623 diffusional regimes for $\overline{D}^{GB}_{MgO}\delta$. This comparison with Mg diffusivity in enstatite rims confirms that our

624 *dry* conditions are consistent with Regime 3.

625 Interestingly, a major difference between our results and the ones of Helpa et al. (2014) is the

626 unilateral aspect of the diffusion in our case, where Mg immobility is evidenced, whereas both species

627 (Mg and Ca) are found to diffuse at comparable rates in the experiments of Helpa et al (2014). The

628 difference is even more notable when comparing to the Mg-Ca-Si system, where it has been established

629 that Mg is the most mobile specie (Joachim *et al.*, 2011, Joachim *et al.*, 2012). Although these

630 differences are admittedly difficult to interpret in terms of diffusion mechanisms, it may well be related

631 to the fact that, in our particular case, Ca diffuses jointly with H_2O, associated to the breakdown of

632 portlandite upon reaction, which could, in turn, result in faster Ca mobility, relative to Mg.

633 Oxygen diffusivity in grain boundary of hot-pressed calcite aggregates was investigated by

634 Farver and Jund (1998) under hydrous conditions (Regime 3). As shown on Figure 7b, the corresponding

635 $D^{GB}\delta$ values for oxygen under these water conditions lie around our Ca diffusion data under *intermediate*

636 conditions.

637 One of the most striking feature of Figure 7b is the location of the Mg intergranular high-

638 temperature diffusivity data (0.1-0.5 and 5 wt.% H_2O, i.e., Regime 3 and 4, respectively) derived by

639   Gardés et al. (2012). Despite the addition of water, these data lie on the very slow diffusion side of the

640   plot, relatively close to the data for Ca diffusion in anhydrous carbonates (Farver and Yund, 1996; Helpa

641   et al., 2014) and far from hydrous Ca and O diffusion data in carbonates (this study and Farver and Jund,

642   1996, respectively). We believe that this discrepancy does not rely on the element/oxide that is

643   considered (Mg vs. Ca/O) in these studies but rather on the mineralogical/chemical system that was

644   investigated: silicate on the one side and $CaCO_3$ (Farver and Yund, 1994, 1996), $CaMg(CO_3)_2$ (Helpa et al.,

645   2014) or $CaCO_3$-$Mg(OH)_2$ (this study) on the other side. In the case of volume diffusion, such differences

646   were already pointed out by Farver (1994), who showed that oxygen self-diffusion in non-silicates such

647   as magnetite, apatite and calcite, is more than two orders of magnitude larger than in silicates with the

648   same total ionic porosity. In the present case, it is very likely that the hydrated brucite surfaces provide a

649   faster diffusion medium than the silicate ones in Gardés et al. (2012), the hydrophobic surface of which

650   likely favors the formation of water pores even at the 10th of ppm water content level (e.g., Milke et al.,

651   2013). However, in this case, one would expect their experiments performed in Regime 4, with

652   saturated hydrous grain boundaries, to yield diffusion coefficients similar or close to ours, which is far

653   from true, as shown by the data point corresponding to 1 wt.% of water from Gardés et al. (2012) in

654   Figure 7b. One major aspect one has to keep in mind when comparing these results is that, unlike for

655   self-diffusion experiments, the diffusion mechanism, here, as well as in Gardés et al. (2012), is driven by

656   a chemical reaction, as shown by the presence of the ΔG term in our Equations (16) and (A5) or in

657   Equations (1), (2) and (3) of Gardés et al. (2012). Now, the GB diffusivity contrast between our

658   experiments and those of Gardés et al. (2012) implies a huge gap between the temperatures required to

659   achieve measurable reaction rims at laboratory timescale (400°C vs. 1000°C, respectively). We believe

660   that this highlights the generally well known difference between reaction kinetics in silicate and

661   carbonate systems, which is often expressed in terms of dissolution rates contrast between rather

662   soluble carbonates and less soluble silicates (Dolejs and Manning (2010) and references therein). In

663   nature, when intergranular fluids are present and transport is no longer limiting, these solubility

664   differences tend to control the kinetics of metamorphic equilibration (Carlson *et al.*, 2015). We show

665   here that the kinetic contrast between the silicate and carbonate systems seems to hold at very low

666   water contents and even under *dry* conditions. As a consequence, although the drastic effect of low

667   water content (< 1 wt.%) on intergranular diffusion in mineral aggregates can be understood in the

668   frame of water sensitive diffusional regimes (Rubie, 1986; Farver and Jund, 1995; Carlson, 2010, Gardés

669   et al., 2012), substantial intergranular diffusivity variations will depend on the chemical and physical

670   properties of intergranular media, which may drastically differ in laboratory experiments and in Nature.

671

Implications for metamorphism

673   The need for short run duration imposed by the synchrotron beam availability led us to focus on

674   a system characterized by relatively high reaction kinetics, even under *dry* conditions. Consequently, our

675   experiments significantly departed from nature-relevant kinetics, where slow diffusing species such as Al

676   control the reaction rate. Our conclusions on the effect of water content are, however, in line with those

677   from Carlson (2010) who, based on natural metamorphic reaction coronae, showed that large gaps exist

678   between aluminum grain boundary diffusivities under "nearly anhydrous" and "hydrous but fluid-

679   undersaturated" conditions. Carlson (2010) also suggested an increase of the activation energy of the

680   diffusion from fluid-saturated to anhydrous conditions. Furthermore, it seems that another large

681   diffusivity gap exists as the water content increases and the fluid phase becomes interconnected

682   (Brenan, 1993). Considering now the recent study by Gardés et al. (2012), which depicts the same type

683   of picture, it seems that a general scheme arises with a set of diffusivity regimes controlled by water

684   content.

685   A central question with respect to natural systems is whether water content will affect

686   metamorphic reactions in the temperature range at which they occur. Indeed, the decrease of the

687   activation energy of the diffusion with increasing water content, suggests that reaction kinetics are

688   unaffected by water content above a given temperature. In our case, the temperature corresponding to

689   the intersection between the Arrhenius laws determined under *dry* and *intermediate* conditions lies at

690   ~ 1600 K. For both the data reported by Carlson (2010) and Gardés et al. (2012), this intersection is

691   found at even higher temperature values. It is therefore likely that the strong effect of water activity

692   (even when < 1) on reaction kinetics reported here will be relevant to most metamorphic conditions.

693   In high-grade lower crustal rocks, water activity is mostly expected to be below unity (e.g.,

694   Yardley and Valley, 1997) and, therefore, aside from Regime 4, the various diffusivity regimes re-defined

695   by Gardés et al. (2012) can potentially operate. In dry lower-crustal rocks, when hydrous silicates are still

696   present, for example, water activity is close to 10^{-2} (Yardley and Valley, 1997), this corresponds to what

697   we called *dry* conditions here and tentatively interpreted as saturated (or partly saturated) grain

698   boundaries, although in the absence of free fluids. Even if our understanding of intergranular transport

699   in water undersaturated rock is still very poor, our experiments show that, in lower crustal rocks, grain

700   boundary diffusion rates are rendered much faster by the simple presence of hydrous phases such as

701 brucite. Furthermore, since the addition of minor amounts of water are sufficient to allow transition

702 from Regime 3 to 4, mineral reaction rates are prone to vary by several orders of magnitude with

703 relatively small changes in water activity. It can therefore be emphasized that, as much as temperature,

704 water activity is a first order parameter that will control reaction rates among minerals. In water-bearing

705 rocks – meaning here rocks which are not anhydrous – the effect of increasing temperature on grain

706 boundary diffusivity will be enhanced by structural water contained in hydrous minerals being

707 progressively transferred into grain boundaries, e.g., Gasc et al. (2011) for a laboratory case and Hetenyi

708 et al. (2007) for a natural case.

709

APPENDIX 1: Estimation of grain coarsening parameters and implementation in the analytical solution of Abart et al. (2009) for a spherical geometry.

Sample PC175 which was obtained under intermediate conditions exhibits the largest reaction front, which allows the most precise characterization of grain growth among our samples. Measurements of grain size across the reaction front showed that it is proportional to the distance from the Ara+Bru│Mag interface, where the products nucleate (Figure A1).

This implies that the grain size of the products is proportional to the reaction front width, i.e. $l \propto \Delta x$. Since PC175 is a 1-D diffusion experiment, we can consider the relation defined by Gardés and Heinrich (2011) where reaction front growth controlled by grain boundary diffusion obeys:

$$\Delta x = A\sqrt{t^{1-1/n}} \tag{A1}$$

and where A is a constant, and n is the grain growth exponent. At a given temperature, grain growth is known to have an exponential dependence with time of the form

$$l = (\rho t)^{1/n} \tag{A2}$$

where ρ is the growth rate constant. Proportionality between grain size and Δx whatever t implies that $\frac{1-1/n}{2} = 1/n$, i.e, $n = 3$. Note that this is the value of n that is used in Gardés and Heinrich (2011). Then, assuming a value of $n = 3$ for *intermediate* conditions, ρ could be retrieved for experiments where SEM images allowed measuring the maximum grain size, l, of the products; and using Equation (A2). This was done for six *intermediate* and two *dry* conditions experiments, respectively. However, under dry conditions, grain growth is limited, with final grain sizes that never exceed 150 nm. In addition, the nucleus size of the reaction products in the reaction rim is unknown. Grain growth in *dry* conditions was therefore neglected without inducing significant error on the retrieved diffusion values.

The temperature dependency of ρ is of Arrhenius type:

$$\rho = \rho_0 \times exp\left[-\frac{Q}{RT}\right] \tag{A3}$$

739 with Q = 274 kJ mol^{-1} and r_0 = 6.85 × 10^{-5} m$^{1/3}$ s^{-1} for the *intermediate* dataset (Fig. A2). Using relation

740 (A3), ρ could be calculated for all DIA experiments run under *intermediate* conditions and further used

741 to calculate the corresponding $\overline{D}_{CaO}^{GB}\delta$ product as described in the Results section.

742 In order to use the grain coarsening model above to retrieve $\overline{D}_{CaO}^{GB}\delta$ in the spherical geometry,

743 differential equation (32) *in* Abart et al. (2009) has been modified to yield the following integral form:

744

$$\int_1^y y \left(\frac{y}{(1+u(y^3-1))^{1/3}} - 1 \right) dy = -\overline{D}_{CaO}^{GB}\delta \frac{\Delta_r G}{RT}\frac{V_m}{V_r}\frac{\pi}{2r_0^2\rho^{1/n}} \int_0^t t^{-\frac{1}{n}}dt \tag{A4}$$

746

747 Noting that y = 1 for t = 0, we obtain the relation between grain boundary diffusivity, time and rim

748 dimensions for a spherical geometry:

749

$$\frac{1-y^2}{2} - \frac{1}{2u}\left\{ 1 - [1+u(y^3-1)]^{2/3} \right\} = -\overline{D}_{CaO}^{GB}\delta \frac{\Delta_r G}{RT}\frac{V_m}{V_r}\frac{\pi}{2r_0^2\rho^{1/n}}\frac{n}{n-1}t^{\frac{n-1}{n}} \tag{A5}$$

751 where $y = \frac{r_B}{r_0}$.

752 Equation (A5) was used to calculate grain boundary diffusion coefficients based on

753 measurements of r_A and r_B (Figure 6b). However, using this solution implies calculating first the position

754 of the initial interface r_0. The position of r_0 relative to r_A and r_B can be found assuming that one mole of

755 portlandite (i.e., CaO + H$_2$O) entering the rim, yields one mole of reaction products, $n_M = n_r$, where,

756 again, the brucite + aragonite assemblage is considered as a single phase with a molar volume V_r that is

757 the sum of brucite and aragonite individual molar volumes. We note that, at any time, the volume of a

758 magnesite grain having reacted corresponds to $n_M V_M = \frac{4}{3}\pi(r_0^3 - r_B^3)$. Similarly, we can write that the

759 volume of the reaction products corresponds to the volume of the rim, $n_p V_r = \frac{4}{3}\pi(r_A^3 - r_B^3)$. As stated

760 above, the equality between the number of moles on each side, leads to the relation:

$$\frac{V_M}{V_r} = \frac{r_0^3 - r_B^3}{r_A^3 - r_B^3} \tag{A6}$$

762 The r_0 values were therefore calculated using Equation (A6) and then used to retrieve $\overline{D}_{CaO}^{GB}\delta$

763 values with Equation (A5).

764

APPENDIX 2: Dependency of diffusivity data on the input grain size distribution

766   The distribution of the initial magnesite grain size in our model impacts the diffusion coefficient retrieved, simply because finer grains tend to react faster than their coarser counterparts. Although the initial grain size distribution was partly characterized by SEM images, the consistency between the two parameters that control the grain size distribution, γ_0 and σ, and the actual magnesite grains dimensions was tested by a series of simulations. This also allowed us to estimate the errors resulting from approximations made on the aforementioned grain size distribution.

772   In the log-normal distribution, γ_0 represents the natural logarithm of the median value, which, based on SEM characterization, was set to 2 μm. The impact of γ_0 on diffusivity was tested for values varying from $\exp(\gamma_0) = 1–5$ μm. In the investigated range, the retrieved $\overline{D}_{CaO}^{GB}\delta$ values vary almost linearly with γ_0 (from 1.66×10^{-24} to 4.94×10^{-23} m^{3}s^{-1} for experiment X11, for example). The parameter σ is also critical since it impacts the proportion of large grains present in the sample; it was estimated based on SEM images, which show that large grains, coarser than 20 μm, represent ~30% of the whole magnesite initial volume. This is best modeled with $\sigma = \ln(2.5)$. However, we considered here that the uncertainty resulting from the error on σ corresponds to $2.2 < \exp(\sigma) < 2.9$, which translates into a volume percentage of large grains comprised between ~10 to 50 %. We remind that this error does not represent an actual variation of grain size distribution in the starting material but rather the amount of large grains sampled by the X-ray beam –therefore contributing to the overall kinetic. This may vary due to poor statistics, i.e. a handful of large grains only could result in an apparently slower kinetic, and, in the contrary, if little to no large grains are present, kinetic will appear faster, as it will be mainly controlled by the reaction of small grains. The results of these tests show that, for experiment X11 for example, when $\exp(\sigma)$ varies from 2.2 to 2.9, the obtained values of $\overline{D}_{CaO}^{GB}\delta$ vary from 2.80×10^{-24} to 2.25×10^{-23} m^{3}s^{-1}. It should be noted here, that we expect the grain size distribution in the starting material to be similar in all experiments and, therefore, errors discussed above should not affect the variations of $\overline{D}_{CaO}^{GB}\delta$ observed upon water content and temperature.

790

791 **ACKNOWLEDGEMENTS**

796   **FIGURE CAPTIONS**

797

798   **Figure 1**: XRPD patterns collected on sample Y13 showing the early water activity buffering of the lime
799   (LIM) – portlandite (POR) pair upon heating at 1.8 GPa. MAG, BRU, CAL and ARA stand for
800   magnesite, brucite, calcite and aragonite, respectively. The grey and black patterns correspond to data
801   collected at room temperature and shortly before the target temperature of 833 K was reached,
802   respectively. Note that most peaks are shifted towards lower energies upon heating due to thermal
803   expansion. At ca. 833 K upon heating, small amounts of reaction products, i.e., brucite and aragonite, are
804   present along with minor transient calcite. The persistence of CaO is evidenced by its (200) reflection at
805   33.85 keV (black pattern), the intensity of which drastically decreased upon heating, as shown by the
806   comparison between the grey and black diffraction patterns, then remained constant during the rest of the
807   experiment. The partial consumption of CaO is interpreted as resulting from the reaction with the
808   sample/assembly water to form $Ca(OH)_2$. Numbers in parentheses are Miller indices of the diffracting
809   planes.

810

811   **Figure 2**: In-situ XRPD data for Reaction (1) under *intermediate* conditions at 573 K and 1.8 GPa (run
812   X15). The spectra were collected with a step time of 45 s. The main diffraction peaks are indexed,
813   including reflections used for the calculation of reaction progress and the BN reflection used for intensity
814   normalization. Note that the corresponding diffraction energies differ from Figure 1 due to a different
815   angle of the detector relative to the incident beam.

816

817   **Figure 3**: Bulk kinetic data (reaction progress) and simulated kinetic curves. (a) *Dry* conditions (DIA);
818   (b) *Intermediate* conditions (DIA); (c) *Saturated* conditions (PC). Reaction progress data were obtained
819   from diffraction reflections relative intensities for (a) and (b) (see text for details) and from Equation (4)
820   for (c).

821

822   **Figure 4**: Half-reaction times obtained from all 16 DIA experiments as well as from the two sets of PC
823   experiments, at 393 K and 423 K. Values are plotted on a logarithmic scale vs. reciprocal temperature.
824   Usual time measures are given as a guide to apprehend the tremendous effect of temperature on the
825   kinetics, which range from seconds to weeks within less than a 200-degree span. Triangles, diamonds and
826   circles stand for *dry*, *intermediate* and water *saturated* conditions, respectively.

827

828   **Figure 5**: FE-SEM images in back-scattered electrons (BSE) mode of recovered samples. Abbreviations
829   Por, Mag, Bru and Ara stand for portlandite, magnesite, brucite and aragonite respectively. (a) 1D-PC
830   sample PC180. The reaction front between Portlandite (lower, bright phase) and $MgCO_3$ (upper dark
831   phase) is visible. The Pt chip (white color) is at the Port│Ara+Bru interface. The fracture network formed
832   upon sample decompression and was not present when the sample reacted. (b) and (c) DIA samples Y10
833   and Y11, respectively. After collection of the kinetic data (shown in Figure 3) the temperature was
834   increased for both samples to ~1073 K (see experimental section for details). (b) As a result these samples

835 show large reaction rims around the coarsest residual magnesite grains. (c) Also thanks to higher
836 temperatures, nicely defined palisade-type rims with brucite and aragonite (darker and brighter phases,
837 respectively) intergrowths are observed. The edge of a residual magnesite grain is visible in the lower left
838 corner. (d) and (e) Detailed views of a reaction rim in samples AA13 and AA10, respectively. The
839 reacting magnesite grain is visible in the bottom lower corner in both cases. Note the finer grain size of
840 the reaction products in (e), due to a lower temperature.

841

842 **Figure 6**: Idealized geometries taken for the calculation of $\bar{D}_{CaO}^{GB}\delta$. (a) Planar geometry used for
843 calculations of diffusion coefficients from reaction front thickness (1D-PC experiments). (b) Spherical
844 geometry used for the calculation of $\bar{D}_{CaO}^{GB}\delta$ from reaction rim dimensions (DIA experiments, microscopic
845 approach) and using the analytical solution derived from Abart et al. (2009) to fit the kinetic curves (DIA
846 experiments, macroscopic approach).

847

848 **Figure 7**: Summary of the $\bar{D}_{CaO}^{GB}\delta$ values obtained in this study and comparison with literature data. (a)
849 Triangles and squares correspond to *intermediate* and *dry* data, respectively. Empty symbols represent
850 values retrieved from SEM measurements of reaction rim widths for both *intermediate* and *dry* conditions
851 (microscopic approach) with down-pointing triangles representing the 1D-PC data obtained under
852 *intermediate* conditions. Diffusion data extracted from reaction progress vs. time curves are reported with
853 filled symbols (bulk approach). The dashed lines represent Arrhenius laws obtained by least square fitting
854 of the *dry* and *intermediate* data; the activation energies and their respective uncertainties obtained are
855 also labelled. (b) The Arrhenius laws corresponding to our data and shown on (a) are also reported here
856 (same dashed lines) along with grain boundary diffusion data from the literature regarding carbonates:
857 Farver and Yund (1996), Ca diffusion in calcite (empty diamonds); Farver and Yund (1998), O diffusion
858 in calcite (filled diamonds); Helpa et al. (2014), Ca diffusion during dolomite rim growth (empty stars).
859 Additional data were added to illustrate previously demonstrated effect of water content: the black and
860 grey curves and the circle represent diffusion regimes 1, 3 and 4 of Mg in enstatite grain boundaries, as
861 defined in Gardés and Heinrich (2011) and Gardés et al. (2012); these correspond to dry conditions and
862 0.1-0.5 wt.% and 2.1 wt.% water, respectively.

863

864 **Figure A1**: Grain size of the reaction products across the reaction front in sample PC175. Grain sizes
865 correspond to the average measurement of the five largest identified grains in each location. An SEM
866 backscattered electron image of the reaction front is superimposed to illustrate the grain size gradient.

867

868 **Figure A2**: Arrhenius plot showing the values of ρ obtained from grain size measurements at various
869 temperatures for *intermediate* and *dry* experiments (circles and squares, respectively). The linear
870 regression shown by the dashed line returned the values indicated in the adjacent box, according to
871 equation (A3), with Q in J mol^{-1}.

872

873

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Table 1: List of symbols used and their significance

Symbol	Significance	Unit
T	Temperature	K
P	Pressure	Pa
t	Time	s
$\xi(t)$	Reaction progress (comprised between 0 and 1)	no unit
I_i	XRPD peak intensity. Subscripts P and B refer to portlandite and brucite respectively	Counts
χ_i	Weight proportion of phase i. Subscripts P and B refer to portlandite and brucite respectively	no unit
Φ	Calibration factor which relates phase proportion and selected Bragg's reflection intensity ratio	no unit
M_i	Molar weight of phase i, where subscripts P and B refer to portlandite and brucite respectively	g mol^{-1}
J_i	Flux of species i	mol m^{-2} s^{-1}
D_{CaO}	CaO diffusion coefficient	m^2 s^{-1}
$\overline{D}_{CaO}$	Mean effective CaO diffusion coefficient across the reaction front or rim	m^2 s^{-1}
C_{CaO}	Concentration of CaO species	mol m^{-3}
R	Ideal gas constant	J mol^{-1} K^{-1}
μ^0_{CaO}	Chemical potential of CaO at the interface between portlandite and the reaction products (i.e., brucite and aragonite)	J mol^{-1}
μ'_{CaO}	Chemical potential of CaO at the interface between the reaction products (i.e., brucite and aragonite) and magnesite	J mol^{-1}
$\Delta\mu_{CaO}$	CaO chemical potential difference across the reaction front or rim	J mol^{-1}
Δx	Reaction front (or rim) thickness	m
$\Delta_r G$	Free Gibbs energy of the reaction	J mol^{-1}
$\overline{D}^{GB}_{CaO}$	Mean grain boundary diffusion coefficient of CaO across the reaction front or rim	m^2 s^{-1}
l	Grain size of the reaction products, brucite and aragonite, in the reaction front or rim	m
δ	Grain boundary width	m
V_i	Molar volume of phase i with subscripts r, m and p corresponding to the reaction products (i.e., equimolar mix of aragonite and brucite), magnesite and portlandite, respectively	m^3 mol^{-1}
r_i	Radii used in the spherical geometry. Subscripts A and B refer to the outer and inner radii of the reaction rim respectively and 0 corresponds to the initial magnesite grain radius	m
V_r	Volume of the reaction rim. Can be expressed as the difference between the volumes of the spheres having r_A and r_B for radii	m^3
n_i	Molar amount with subscripts p and m corresponding to portlandite and magnesite, respectively	mol
ν	Ratio between molar volumes of magnesite and portlandite, V_m/V_p	no unit
$X(t)$	Reaction progress for a single coarse magnesite grain, comprised between 0 and 1	no unit
Port │ Ara+Bru	Reaction interface with portlandite on one side and aragonite + brucite on the other	
n	Grain coarsening time exponent, equals to 3 in our case.	no unit
ρ	Grain coarsening constant. Unit depends on n	m^3 s^{-1}
γ_0	Mean of the natural logarithm of the initial magnesite grain size (with radii log-normally distributed)	no unit
σ	Standard deviation of the natural logarithm of the initial magnesite grain size	no unit

Table 2: Experimental conditions, bulk kinetics and reaction rim growth data, and corresponding diffusivity parameters.

Experiment type	Hydration level	Dataset[a]	Peaks used (Bulk)	T, K	t, s	$t(\xi = 0.5)$, s	$\Delta_r G$, kJ mol^{-1}	ρ, m^3 s^{-1}	$D^{GB} \times \delta \pm 1\sigma$, m^3 s^{-1} (Bulk)	Δx[b], μm	r_A, μm	r_B, μm	$D^{GB} \times \delta \pm 1\sigma$, m^3 s^{-1} (Micro)[d]
		X07	Por Bru	873	1,499	4.50E+01	-41.3	-	2.28E-21 ± 4.3E-20	-	-	-	-
		X08	Mag Bru Ara	843	6,759	1.90E+02	-41.6	-	4.81E-22 ± 9.2E-21	-	-	-	-
		X09	Mag Bru Ara	823	9,911	5.10E+03	-42.0	-	9.77E-24 ± 1.9E-22	-	3.6	1.9 ± 0.1	9.72E-24 ± 1.5E-24
	Dry	Y11	Por Bru	833	10,160	4.20E+02	-41.9	-	2.10E-22 ± 4.0E-21	-	-	-	-
		Y13	Por Bru	833	9,927	1.90E+03	-41.9	-	2.57E-23 ± 4.9E-22	-	-	-	-
		AA12	Mag Bru Ara	853	279	6.00E+00	-41.6	-	9.49E-21 ± 1.8E-19	-	5.1	2.3 ± 0.1	4.44E-22 ± 5.6E-23
		AA13[c]	-	823	1,064	-	-42.0	-	-	-	6.8	2.3 ± 0.1	2.50E-22 ± 3.1E-23
DIA		X10	Por Bru	823	816	2.00E+00	-42.0	2.72E-22	1.54E-20 ± 2.2E-19	-	-	-	-
		X11	Por Bru	673	8,739	4.80E+02	-43.2	3.60E-26	7.94E-24 ± 1.1E-22	-	5.0	2.4 ± 0.2	6.76E-25 ± 1.0E-25
		X12	Por Bru	743	408	1.40E+00	-42.8	3.64E-24	2.47E-21 ± 3.5E-20	-	-	-	-
		X15	Por Bru	573	14,866	2.80E+03	-43.6	6.97E-30	3.31E-26 ± 4.7E-25	-	-	-	-
		Y09	Por Bru	623	6,267	1.24E+06	-43.5	7.06E-28	1.17E-26 ± 1.7E-25	-	-	-	-
		Y10	Por Bru	598	8,918	2.16E+06	-43.5	7.72E-29	4.11E-27 ± 5.8E-26	-	-	-	-
	Intermediate	Y14	Por Bru	673	3,131	9.10E+02	-43.2	3.60E-26	1.28E-24 ± 1.8E-23	-	-	-	-
		AA9	Mag Bru Ara	648	5,730	1.60E+05	-43.3	5.44E-27	3.98E-26 ± 5.6E-25	-	10.0	9.0 ± 0.3	7.04E-26 ± 6.7E-27
		AA10	Mag Bru Ara	723	4,184	1.40E+04	-42.9	1.07E-24	1.28E-24 ± 1.8E-23	-	15.0	12.3 ± 0.1	4.07E-24 ± 9.0E-26
		AA11	Mag Bru Ara	648	5,218	9.80E+03	-43.3	5.44E-27	2.51E-25 ± 3.5E-24	-	5.0	4.4 ± 0.1	2.64E-26 ± 1.7E-27
		PC182	-	823	234,000	-	-42.0	2.72E-22	-	850 ± 75	-	-	4.26E-19 ± 1.2E-19
1D-PC		PC180	-	773	1,897,200	-	-42.5	2.04E-23	-	280 ± 62	-	-	4.48E-21 ± 3.9E-21
		PC175	-	873	259,200	-	-41.3	2.70E-21	-	1,380 ± 125	-	-	2.43E-18 ± 6.9E-19
PC	*Saturated*	PC_120	Por Bru	393	-	2.16E+04	-	-	-	-	-	-	-
		PC_150	Por Bru	423	-	6.00E+03	-	-	-	-	-	-	-

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[a]Each *intermediate* and *dry* conditions DIA dataset corresponds to a single experiment, whereas each of the two PC *saturated* datasets corresponds to a series of quench experiments. 1D-PC data in *intermediate* conditions also correspond to single experiments (see experimental section for details).

[b] Uncertainties on measurements of reaction front length and rim radii are given as ± 1 σ. Error on r_A is the same as for r_B.

[c] AA13 was run offline (without synchrotron XRPD) and was therefore not used in the bulk approach. Note that l = 120 nm.

[d] Most experiments were terminated by increasing the temperature until full reaction completion was observed, which does not allow those samples to be used for the microscopic approach.
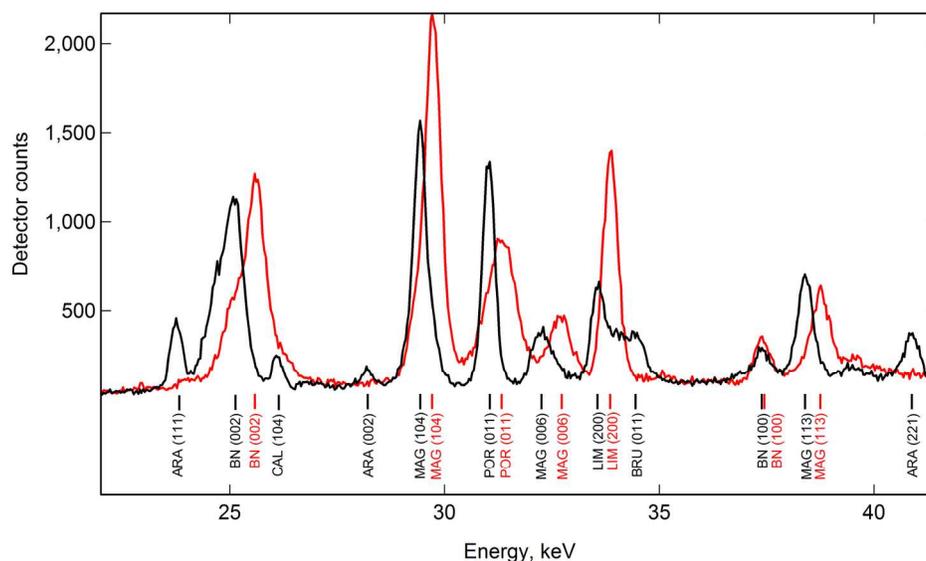
Fig. 1 : XRPD patterns collected on sample Y13 showing the early water activity buffering of the lime (LIM) – portlandite (POR) pair upon heating at 1.8 GPa. MAG, BRU, CAL and ARA stand for magnesite, brucite, calcite and aragonite, respectively. The grey and black patterns correspond to data collected at room temperature and shortly before the target temperature of 833 K was reached, respectively. Note that most peaks are shifted towards lower energies upon heating due to thermal expansion. At ca. 833 K upon heating, small amounts of reaction products, i.e., brucite and aragonite, are present along with minor transient calcite. The persistence of CaO is evidenced by its (200) reflection at 33.85 keV (black pattern), the intensity of which drastically decreased upon heating, as shown by the comparison between the grey and black diffraction patterns, then remained constant during the rest of the experiment. The partial consumption of CaO is interpreted as resulting from the reaction with the sample/assembly water to form Ca(OH)2. Numbers in parentheses are Miller indices of the diffracting planes.
175x101mm (300 x 300 DPI)
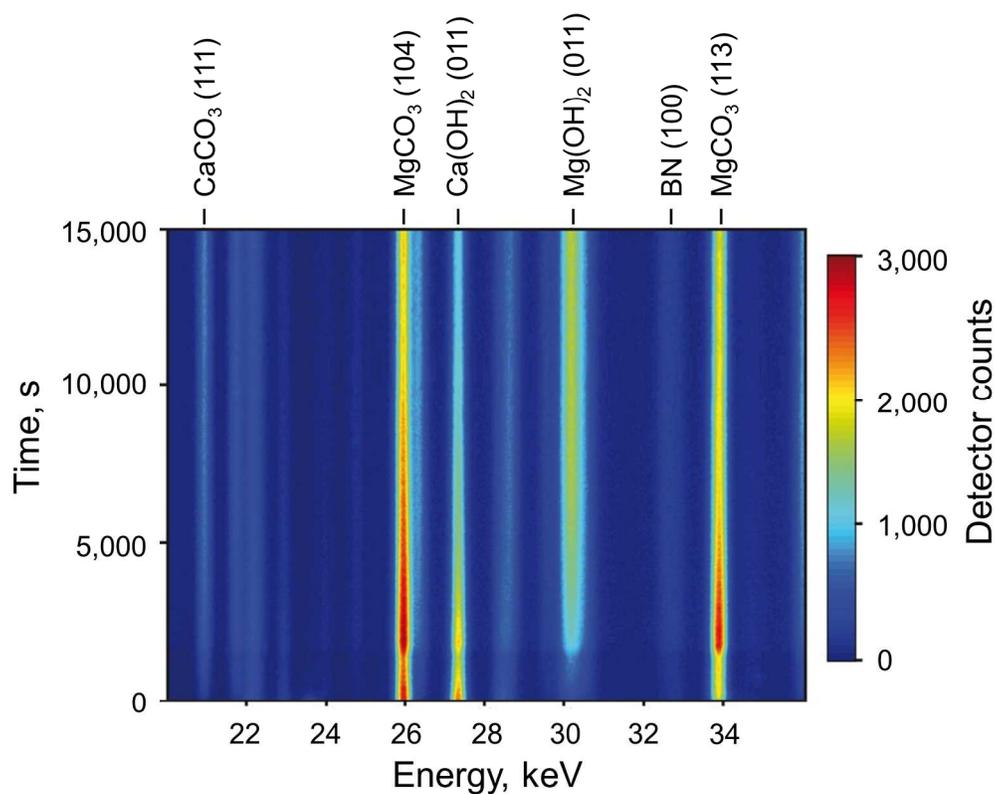
Fig 2 : In-situ XRPD data for Reaction (1) under intermediate conditions at 573 K and 1.8 GPa (run X15). The spectra were collected with a step time of 45 s. The main diffraction peaks are indexed, including reflections used for the calculation of reaction progress and the BN reflection used for intensity normalization. Note that the corresponding diffraction energies differ from Figure 1 due to a different angle of the detector relative to the incident beam.
198x159mm (300 x 300 DPI)
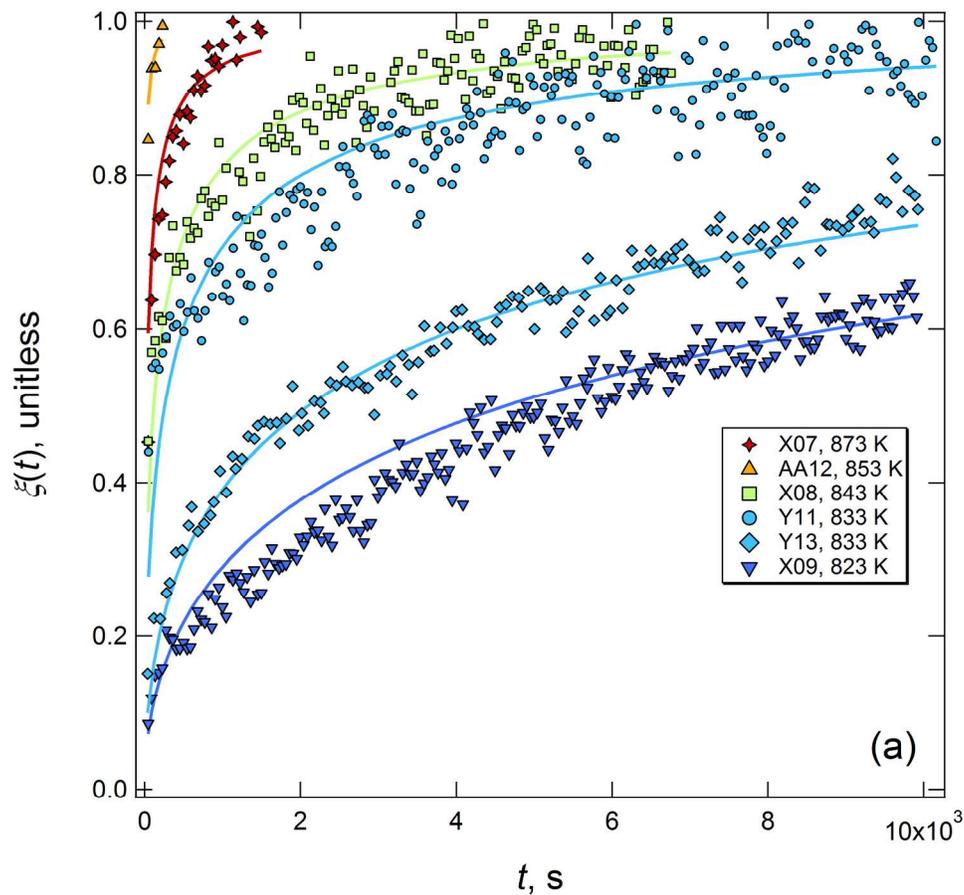
Fig 3a : Bulk kinetic data (reaction progress) and simulated kinetic curves. (a) Dry conditions (DIA); (b) Intermediate conditions (DIA); (c) Saturated conditions (PC). Reaction progress data were obtained from diffraction reflections relative intensities for (a) and (b) (see text for details) and from Equation (4) for (c).

199x181mm (300 x 300 DPI)
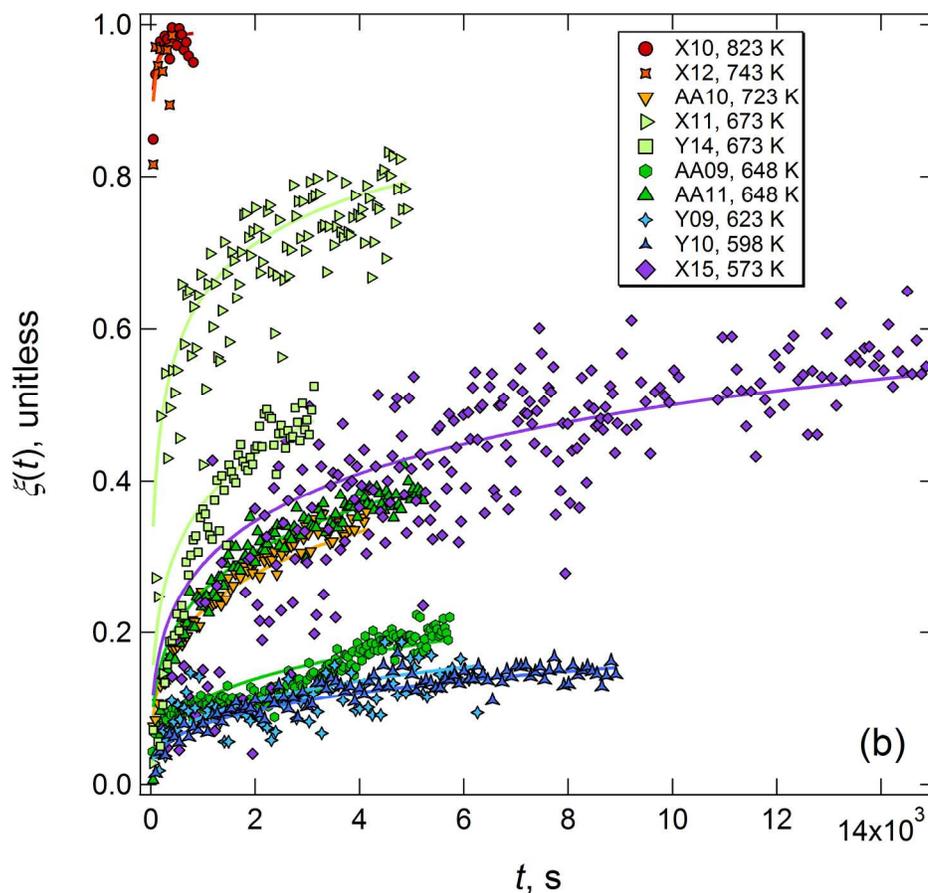
Fig 3b : Bulk kinetic data (reaction progress) and simulated kinetic curves. (a) Dry conditions (DIA); (b) Intermediate conditions (DIA); (c) Saturated conditions (PC). Reaction progress data were obtained from diffraction reflections relative intensities for (a) and (b) (see text for details) and from Equation (4) for (c).

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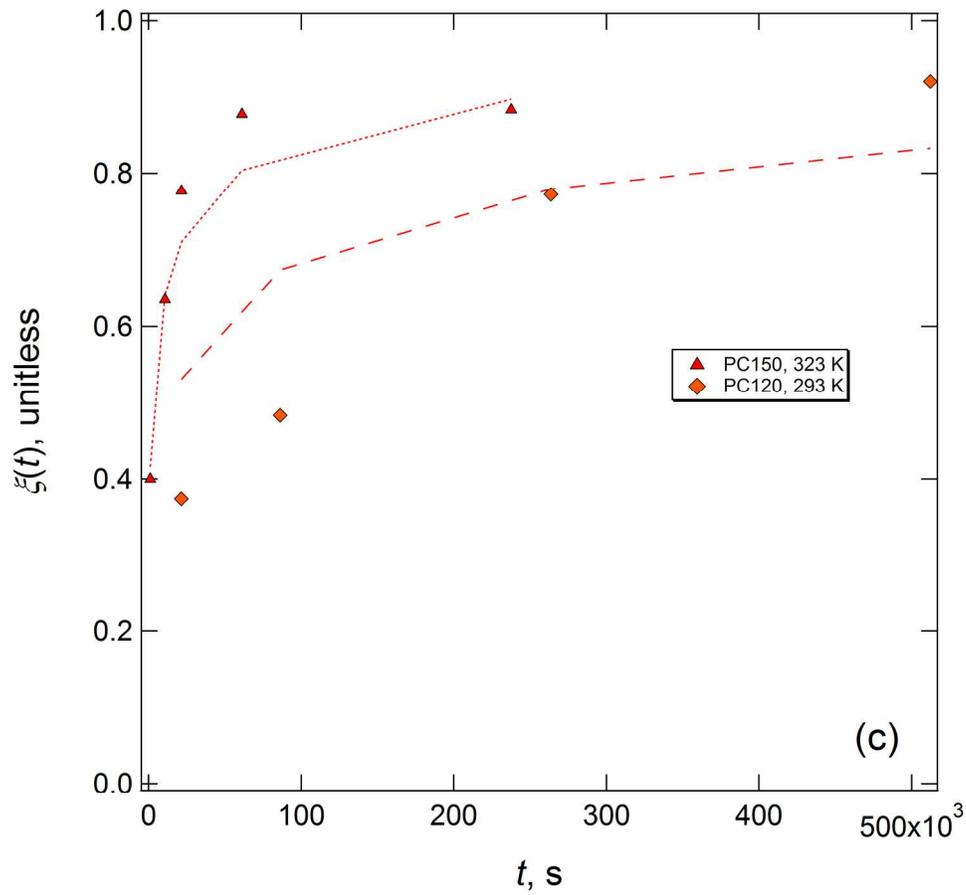
Fig 3c : Bulk kinetic data (reaction progress) and simulated kinetic curves. (a) Dry conditions (DIA); (b) Intermediate conditions (DIA); (c) Saturated conditions (PC). Reaction progress data were obtained from diffraction reflections relative intensities for (a) and (b) (see text for details) and from Equation (4) for (c).

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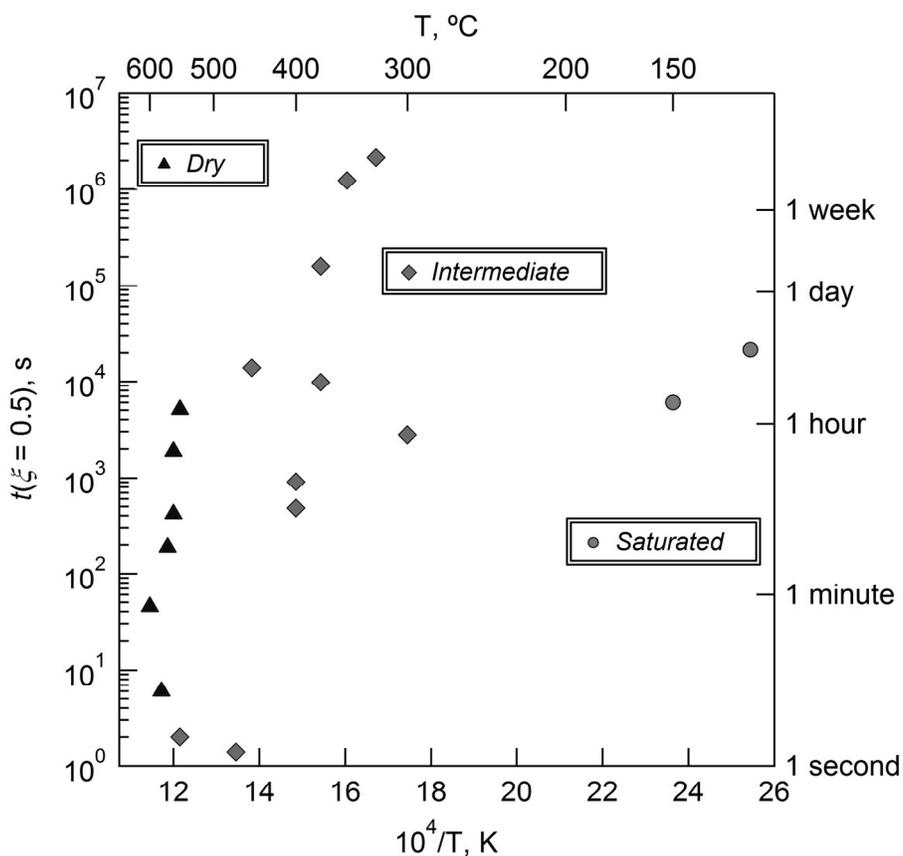
Fig. 4: Half-reaction times obtained from all 16 DIA experiments as well as from the two sets of PC experiments, at 393 K and 423 K.
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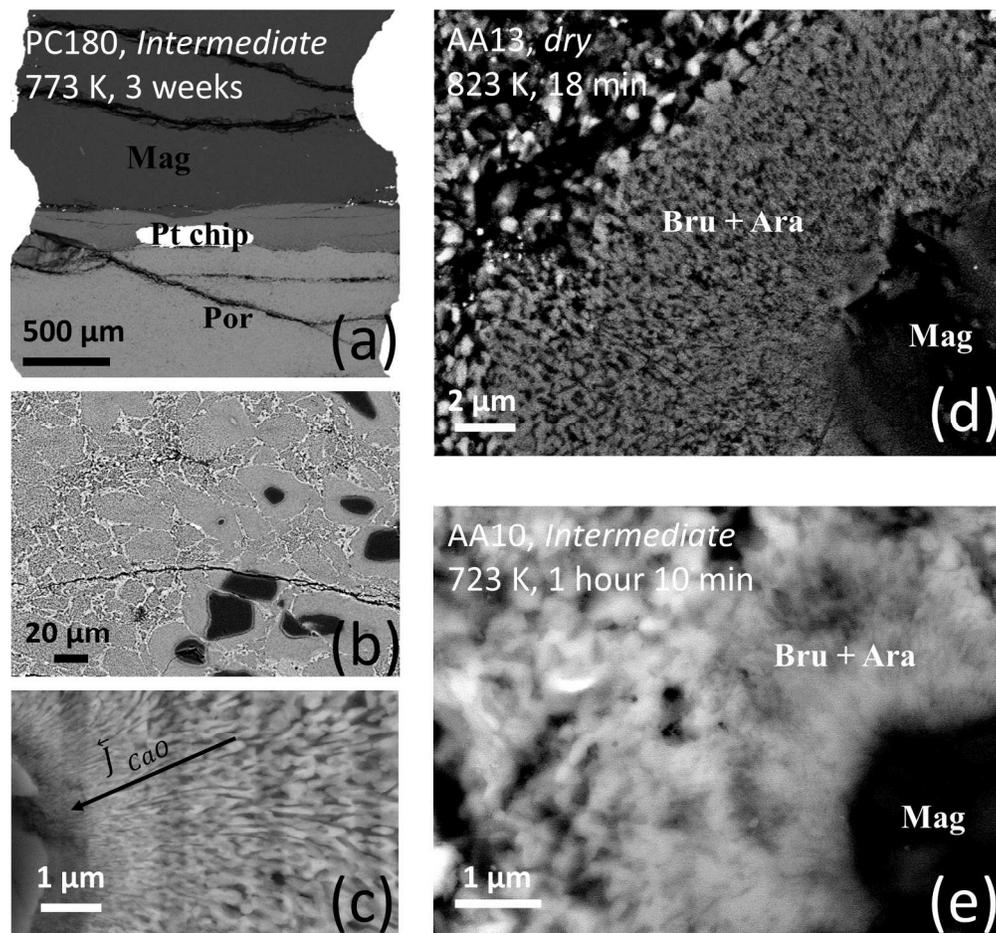
Fig. 5 : FE-SEM images in back-scattered electrons (BSE) mode of recovered samples. Abbreviations Por, Mag, Bru and Ara stand for portlandite, magnesite, brucite and aragonite respectively. (a) 1D-PC sample PC180. The reaction front between Portlandite (lower, bright phase) and MgCO3 (upper dark phase) is visible. The Pt chip (white color) is at the Port⎮Ara+Bru interface. The fracture network formed upon sample decompression and was not present when the sample reacted. (b) and (c) DIA samples Y10 and Y11, respectively. After collection of the kinetic data (shown in Figure 3) the temperature was increased for both samples to ~1073 K (see experimental section for details). (b) As a result these samples show large reaction rims around the coarsest residual magnesite grains. (c) Also thanks to higher temperatures, nicely defined palisade-type rims with brucite and aragonite (darker and brighter phases, respectively) intergrowths are observed. The edge of a residual magnesite grain is visible in the lower left corner. (d) and (e) Detailed views of a reaction rim in samples AA13 and AA10, respectively. The reacting magnesite grain is visible in the bottom lower corner in both cases. Note the finer grain size of the reaction products in (e), due to a lower temperature.
192x179mm (300 x 300 DPI)
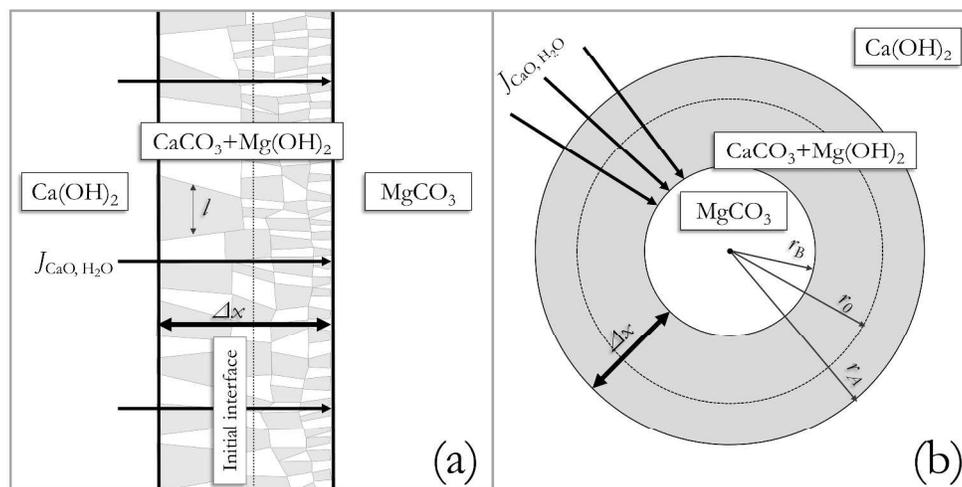
Fig. 6 : Idealized geometries taken for the calculation of . (a) Planar geometry used for calculations of diffusion coefficients from reaction front thickness (1D-PC experiments). (b) Spherical geometry used for the calculation of $\bar{D}_{CaO}^{GB}\delta$ from reaction rim dimensions (DIA experiments, microscopic approach) and using the analytical solution derived from Abart et al. (2009) to fit the kinetic curves (DIA experiments, macroscopic approach).
338x190mm (300 x 300 DPI)

Fig. 7a : Summary of the D̄_CaO^GB δ values obtained in this study and comparison with literature data. (a) Triangles and squares correspond to intermediate and dry data, respectively. Empty symbols represent values retrieved from SEM measurements of reaction rim widths for both intermediate and dry conditions (microscopic approach) with down-pointing triangles representing the 1D-PC data obtained under intermediate conditions. Diffusion data extracted from reaction progress vs. time curves are reported with filled symbols (bulk approach). The dashed lines represent Arrhenius laws obtained by least square fitting of the dry and intermediate data; the activation energies and their respective uncertainties obtained are also labelled. (b) The Arrhenius laws corresponding to our data and shown on (a) are also reported here (same dashed lines) along with grain boundary diffusion data from the literature regarding carbonates: Farver and Yund (1996), Ca diffusion in calcite (empty diamonds); Farver and Yund (1998), O diffusion in calcite (filled diamonds); Helpa et al. (2014), Ca diffusion during dolomite rim growth (empty stars). Additional data were added to illustrate previously demonstrated effect of water content: the black and grey curves and the circle represent diffusion regimes 1, 3 and 4 of Mg in enstatite grain boundaries, as defined in Gardés and Heinrich (2011) and Gardés et al. (2012); these correspond to dry conditions and 0.1-0.5 wt.% and 2.1 wt.% water, respectively.
199x181mm (300 x 300 DPI)

Fig. 7b : Summary of the $\bar{D}\_CaO^GB$ δ values obtained in this study and comparison with literature data. (a) Triangles and squares correspond to intermediate and dry data, respectively. Empty symbols represent values retrieved from SEM measurements of reaction rim widths for both intermediate and dry conditions (microscopic approach) with down-pointing triangles representing the 1D-PC data obtained under intermediate conditions. Diffusion data extracted from reaction progress vs. time curves are reported with filled symbols (bulk approach). The dashed lines represent Arrhenius laws obtained by least square fitting of the dry and intermediate data; the activation energies and their respective uncertainties obtained are also labelled. (b) The Arrhenius laws corresponding to our data and shown on (a) are also reported here (same dashed lines) along with grain boundary diffusion data from the literature regarding carbonates: Farver and Yund (1996), Ca diffusion in calcite (empty diamonds); Farver and Yund (1998), O diffusion in calcite (filled diamonds); Helpa et al. (2014), Ca diffusion during dolomite rim growth (empty stars). Additional data were added to illustrate previously demonstrated effect of water content: the black and grey curves and the circle represent diffusion regimes 1, 3 and 4 of Mg in enstatite grain boundaries, as defined in Gardés and Heinrich (2011) and Gardés et al. (2012); these correspond to dry conditions and 0.1-0.5 wt.% and 2.1 wt.% water, respectively.
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Fig A1 : Grain size of the reaction products across the reaction front in sample PC175. Grain sizes correspond to the average measurement of the five largest identified grains in each location. An SEM backscattered electron image of the reaction front is superimposed to illustrate the grain size gradient.
237x155mm (300 x 300 DPI)
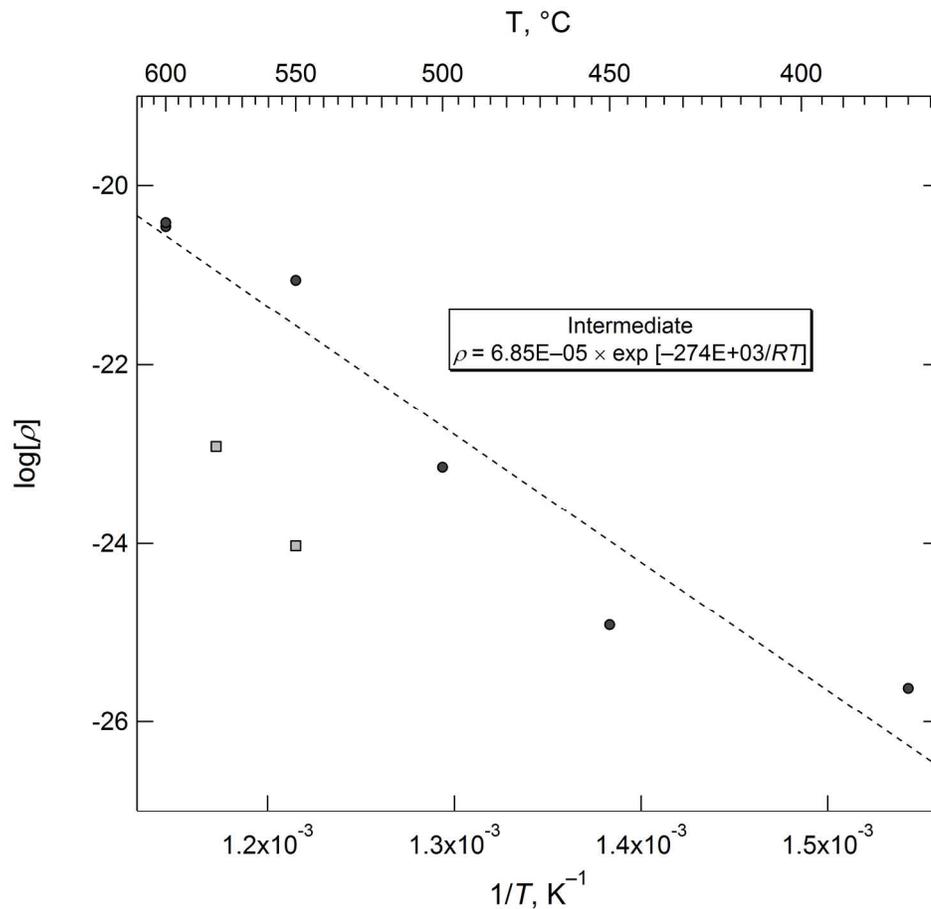
Fig A2 : Arrhenius plot showing the values of ρ obtained from grain size measurements at various temperatures for intermediate and dry experiments (circles and squares, respectively). The linear regression shown by the dashed line returned the values indicated in the adjacent box, according to equation (A3), with Q in J mol–1.
199x181mm (300 x 300 DPI)