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German Montes-Hernandez, Mamadou Bah, François Renard. Mechanism of formation of engineered magnesite: A useful mineral to mitigate CO₂ industrial emissions. *Journal of CO₂ Utilization*, 2020, 35, pp.272-276. 10.1016/j.jcou.2019.10.006 . hal-02896886

HAL Id: hal-02896886

<https://hal.science/hal-02896886>

Submitted on 5 Nov 2020

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1 **Mechanism of the formation of engineered magnesite: A useful**
2 **mineral to mitigate CO₂ industrial emissions**

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4 German Montes-Hernandez^{a*}, Mamadou Bah^a, François Renard^{a,b}

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6 ^a Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, IFSTTAR, ISTERre, 38000
7 Grenoble, France

8 ^b The Njord Centre, PGP, Department of Geosciences, University of Oslo, box 1048 Blindern, 0316
9 Oslo, Norway

10
11
12
13 *Corresponding author: G. Montes-Hernandez

14 E-mail address: german.montes-hernandez@univ-grenoble-alpes.fr

18 **Abstract**

19 Magnesium carbonate production at the industrial scale is a realistic option to reduce the industrial
20 emissions of CO₂. Ultrabasic rocks and/or alkaline mine waste provide magnesium sources and are
21 widely available in the Earth's crust. Here, we investigated the aqueous carbonation of magnesium
22 hydroxide under moderate temperature (25-90°C) and pressure (initial pressure of CO₂=50 bar)
23 using NaOH as the CO₂ sequestering agent. From time-resolved Raman measurements, we
24 demonstrate that the aqueous carbonation of magnesium hydroxide can be an effective engineered
25 method to trap CO₂ into a solid material and produce large amounts of magnesite MgCO₃ (6
26 kg/m³h), or hydromagnesite Mg₅(CO₃)₄(OH)₂·4H₂O (120 kg/m³h) at 90°C or nesquehonite
27 MgCO₃·3H₂O (40 kg/m³h) at 25°C. Higher production rates were measured for nesquehonite (at
28 25°C) and hydromagnesite (at 60 and 90°C). However, only the magnesite produced at 90°C
29 ensures a permanent CO₂ storage because this mineral is the most stable Mg carbonate under Earth
30 surface conditions, and it could be co-used as construction material in roadbeds, bricks with fire-
31 retarding property and granular fill. The use of specific organic additives can reduce the reaction
32 temperature to precipitate magnesite. For example, ferric EDTA (ethylenediaminetetraacetic acid)
33 reduces the temperature from 90 to 60°C. However, more time is required to complete magnesite
34 precipitation reaction at this lower temperature (15h at 90°C and 7 days at 60°C). These results
35 suggests that functionalized organic groups can reduce the energetic barriers during mineral
36 nucleation.

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39 **Keywords:** Engineered Magnesite Precipitation; Time-Resolved Raman Spectroscopy; Carbon
40 Dioxide Mineralization; CO₂ Mitigation; Mineral Nucleation and Growth

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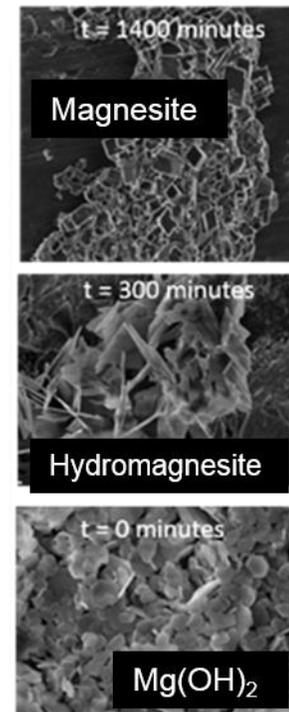
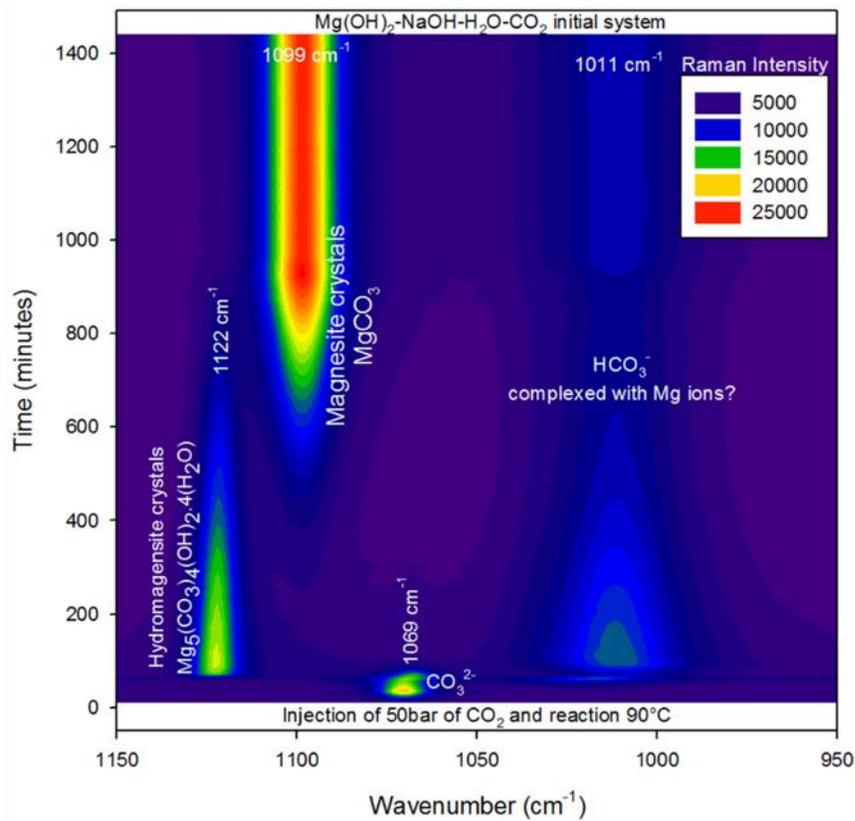
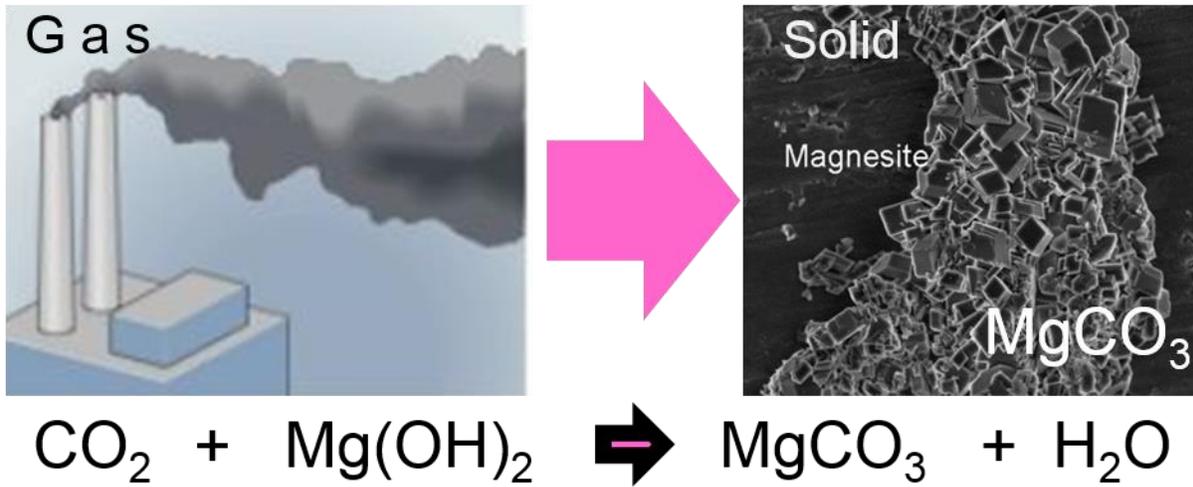
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60 **1. Introduction**

61 CO₂ emissions have increased since the industrial revolution: about 36 Gt of CO₂ that
62 originate from fossil fuel are annually emitted into the atmosphere with 30% from industrial
63 activities and 70% from transport, agriculture and other sources [1]. These non-regulated emissions
64 have led to concerns about global warming as a progressive increase of CO₂ concentration into
65 atmosphere has been recorded in the last two centuries [1]. The energy transition (i.e., the use of
66 carbon-free energy sources such as hydrogen, solar, wind, marine, hydraulic, geothermal) could
67 significantly decrease CO₂ emissions. Some limitations, such as the supply of rare Earth elements,
68 large amounts of water requirements and natural risks, have raised some concerns about how fast
69 this transition will occur [2-3]. Moreover, conventional and unconventional fossil resources (gas,
70 carbon and oil) are still available in geological formations [4], and their exploitation and resulting
71 CO₂ emissions have been predicted to continue for 50-100 years [5]. Therefore, CO₂ capture from
72 industrial sources and its transformation into re-usable products (e.g. ethanol, syngas, etc.) and/or
73 non-energetic materials (e.g. calcite, magnesite, siderite, etc.) has been proposed to reduce CO₂
74 emissions into the atmosphere [6-9]. CO₂ capture from industrial sources does not represent a
75 technological or scientific obstacle, but the existing methods and technologies (including recovery
76 of high-purity of CO₂ and its liquefaction) remain highly expensive. In this way, the improvement
77 and optimization on the CO₂ capture units still represent important challenges. The goal of the
78 present experimental study is to demonstrate that engineered magnesite (MgCO₃) could be used as
79 an effective option to store carbon dioxide within magnesite-rich solids. The obtained magnesite-
80 rich solids could then be used as civil construction materials (e.g. roadbed materials, bricks,
81 granular fill) [10]. Magnesite is the most stable carbonate mineral under typical Earth surface

82 conditions, with the highest resistance to leaching and weathering [11]. The magnesite dissolution
83 rate is 100-1000 times lower than that of calcite in a wide range of conditions, from ambient
84 temperature to 150°C and pH from 1 to 14 [11]. For this reason, anhydrous magnesium carbonates
85 (magnesite and dolomite) have been considered as relevant minerals to store permanently
86 anthropogenic carbon dioxide. Magnesite and dolomite precipitation kinetics have been widely
87 studied because their abiotic precipitation at ambient temperature (~25°C) is virtually impossible
88 within typical experimental time scales [12-13]. The strong solvation shells of magnesium ions in
89 aqueous media produces this limitation [12]. However, the sole effect of Mg hydration might not
90 be the only factor of inhibition of magnesite and/or dolomite formation. Recent studies claim that
91 a more intrinsic crystallization barrier and the influence of fluid chemistry (e.g., relative size of the
92 constituting cations) prevent the formation of a long-range ordered crystallographic structures at
93 ambient conditions [14-15]. Conversely, a recent study has reported magnesite precipitation in
94 batch reactors at room temperature after 77 days of reaction with the aid of carboxylated
95 polystyrene microspheres [16]. Diluted ionic solutions (<0.1M) and microspheres coated with a
96 high density of carboxyl groups at their surface allowed the binding and dehydration of Mg²⁺ ions
97 in solution, thereby minimizing the kinetic barrier and facilitating magnesite formation [16].
98 However, the reaction mechanism and the nature of precipitating minerals between 1 and 77 days
99 remain to be identified, and whether precipitation occurred via the formation of transient phases or
100 by a direct nucleation event is unknown. Moreover, this method needs to be up-scaled to produce
101 high-amounts of magnesite in reasonable time (24 hours). In order to overcome these limitations,
102 the present study demonstrates magnesite precipitation at moderate temperature (60 and 90°C) by
103 aqueous carbonation of magnesium hydroxide (Mg(OH)₂) under anisobaric conditions (initial CO₂
104 pressure = 50 bar). These conditions allow the production of high amounts of magnesite in only

105 15h at 90°C or 7 days at 60°C. Herein, NaOH was used as a CO₂ sequestering agent and the ferric
106 EDTA as a dehydration agent of Mg²⁺ ions. Magnesium hydroxide was chosen because its
107 engineered production from olivine and serpentine-rich materials was actively investigated for CO₂
108 mineralization purpose [17-18]. Magnesium oxide (MgO) and magnesium hydroxide (Mg(OH)₂)
109 may be produced from serpentine and other Mg-rich silicates. Both synthesized minerals have
110 numerous industrial applications, and have been proposed as sinks to store anthropogenic carbon
111 dioxide by transforming it into magnesium carbonate minerals [17-18].

112

113 **2. Materials and Methods**

114 *2.1. Magnesite precipitation using NaOH as sequestering agent of CO₂*

115 As already demonstrated in our group (e.g. [8, 19]), the NaOH enhances the magnesite precipitation
116 at 90°C via aqueous carbonation process of magnesium hydroxide with compressed CO₂. An initial
117 CO₂ pressure of 50bar ensures an excess of CO₂ with respect to Mg(OH)₂ in the reactor and ideal
118 gas condition. In the present study, two new experiments were performed at 90 and 27°C,
119 respectively, and monitored by time-resolved in situ Raman spectroscopy as described in Montes-
120 Hernandez and Renard, 2016 [19]. Herein, carbonate speciation and precipitated particles were
121 monitored for 24h with a 1-minute spectral acquisition time. The Raman spectra were treated in
122 order to estimate the position, full wide half maximum (FWHM) and integrated surface area as a
123 function of time for specific stronger peaks in order to explain the reaction mechanism and kinetics
124 of Mg carbonates precipitation and particularly magnesite (MgCO₃).

125

126 *2.2. Magnesite precipitation using NaOH and organic additives*

127 Magnesite precipitation was also investigated at 60°C in the presence of three organic molecules
128 (Aspartame, ferric EDTA, and citric acid tri-sodium salt), expecting a dehydration effect of Mg²⁺
129 ions or a chelation effect. In these experiments, 15 g of Mg(OH)₂, provided by Sigma-Aldrich with
130 chemical purity of 99%, 20g of NaOH, 1 g of organic additive, and 500 mL of high-purity water
131 were mixed in the reactor (total internal volume of 960 mL). The slurry was immediately dispersed
132 by mechanical agitation (400 rpm) and gaseous CO₂, provided by Linde Gas S.A., was injected at
133 50 bar into the reactor. About 3 minutes at 25°C were required to reach the pre-defined pressure.
134 The agitation speed was kept to 400 rpm using a rotor with two blades (Parr reactor) that ensured
135 homogeneous dispersion of reacting and precipitating solids and fast dispersion of the injected CO₂
136 in the system. Following injection, the system was heated to 60°C, the pH of the solution and the
137 CO₂ consumption (pressure drop) were monitored in-situ during mineral formation for 24, 72 or
138 168 hours.

139 At the end of the experiment, the residual CO₂ was degassed from the reactor by opening the gas
140 line valve for five minutes. The solid product was recovered by centrifugation and washed twice
141 with ultrapure water and then was dried directly in the centrifugation flasks at 60 °C for 48 h. The
142 dry solid products were stored in plastic flasks for subsequent characterization by Raman
143 spectroscopy, Field Emission Gun Scanning Electron Microscopy (FESEM) and powder X-ray
144 diffraction (XRD). All ten performed experiments are summarized in Table 1.

145

146

147 *2.3. Ex situ characterization of precipitates*

148 XRD analyses were performed using a Siemens D5000 diffractometer in Bragg-Brentano
149 geometry, equipped with a theta-theta goniometer with a rotating sample holder. Diffraction
150 patterns were collected using Cu $k\alpha_1$ ($\lambda_{k\alpha_1}=1.5406 \text{ \AA}$) and $k\alpha_2$ ($\lambda_{k\alpha_2}=1.5444 \text{ \AA}$) radiation in the
151 range $2\theta = 10 - 70^\circ$, with a step size of 0.04° and a counting time of 6 seconds per step. For high-
152 resolution imaging, the solid products were dispersed by ultrasonic treatment in absolute ethanol
153 for five to ten minutes. One or two droplets of the suspension were then deposited directly on an
154 aluminum support and coated with platinum. The morphology of the crystals was imaged using a
155 Zeiss Ultra 55 FESEM with a maximum spatial resolution of approximately 1 nm at 15kV.

156 *2.4. Calculation of production rate*

157 The production rate of a given magnesium carbonate was calculated as follows:

158
$$P_{\text{rate}} = (\lambda * \text{Mol}_{\text{Mg(OH)}_2} * M_{\text{MgCarbonate}}) / (t_{\text{max}} * V_{\text{reactor}})$$

159 where λ is the chemical conversion factor for Mg carbonate phases determined from Raman
160 spectroscopy when peaks intensity is constant for a given time-interval. The value $\lambda=1$ is reached
161 when the peak intensity for a given Mg carbonate is constant and only a single mineral is detected.
162 $\text{Mol}_{\text{Mg(OH)}_2}$ is the initial amount (in mol) of Mg(OH)_2 (complete transformation was determined
163 from ex-situ XRD measurements in recovered solid products); $M_{\text{MgCarbonate}}$ is the molar mass of a
164 given Mg carbonate; t_{max} is the time where only one mineral phase exists and the peak intensity is
165 constant; V_{reactor} is the effective volume of the reactor which is equal to 0.6L (runs 1-2) or 1L (runs
166 3-10). This calculation using time-resolved experimental measurements could allow a realistic
167 extrapolation to pilot and/or industrial scale assuming roughly proportional dimensions and

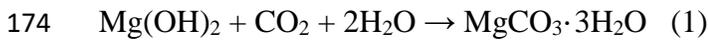
168 equivalent precipitation times.

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170 **3. Results and discussion**

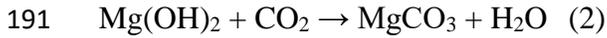
171 *3.1. Magnesite precipitation at 90°C: Reaction mechanism and kinetics*

172 Carbonation of Mg(OH)₂ at 25°C leads the precipitation of nesquehonite, with the following global
173 reaction:

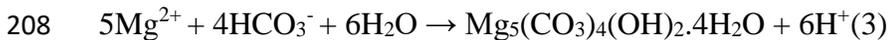


175 The successive events involved during magnesium hydroxide carbonation are displayed in Fig. 1.
176 Dissolved NaOH enhanced the rate and amount of sequestration of injected CO₂ (initial P_{CO2} =50
177 bar). The carbon dioxide dissolved into interacting alkaline solution (CO_{2(gas)} ↔ CO_{2(aq)}) was
178 rapidly dissociated into CO₃²⁻ (CO_{2(aq)} + 2NaOH → CO₃²⁻ + H₂O + 2Na⁺). A fraction of the
179 carbonate ions was protonated after about 60 minutes (CO₃²⁻ + H⁺ → HCO₃⁻) producing a pH change
180 in the interacting solution, and simultaneously enhancing the dissolution of magnesium hydroxide
181 (Mg(OH)₂ → Mg²⁺ + 2OH⁻). All these combined reactions led to the precipitation of nesquehonite
182 (Mg²⁺ + HCO₃⁻ + 3H₂O → MgCO₃·3H₂O + H⁺) with a nucleation induction time of 105 minutes.
183 This mineral grew by continuous dissolution of magnesium hydroxide until complete consumption
184 in the reactor. Nesquehonite remained stable in the interacting solution until the end of experiment
185 (72 h). Ex-situ FESEM images revealed micrometric crystals of prismatic elongated morphology
186 (Fig. SI-1). Time-resolved Raman measurements and ex-situ characterization of solid confirm that
187 magnesite precipitation was inhibited by nesquehonite precipitation at 25°C. Conversely,
188 magnesite formation was rapidly obtained at 90°C and only 15 h were required to produce high-
189 purity magnesite (~6 kg/m³h) as monitored by Raman spectroscopy (Fig. 2). The global reaction

190 summarizes the process:



192 A complete aqueous carbonation reaction was obtained at 90°C exclusively when NaOH was used
193 as the CO₂ sequestering agent, in agreement with previous results [8]. In the present study, a more
194 detailed reaction mechanism and kinetics are demonstrated from the time-resolved in-situ Raman
195 spectroscopy measurements and all temporal reaction events are shown in Fig. 2 and Fig. SI-2.
196 Similar to the nesquehonite case, the aqueous carbon dioxide ($\text{CO}_{2(\text{gas})} \leftrightarrow \text{CO}_{2(\text{aq})}$) was rapidly
197 dissociated into CO_3^{2-} ($\text{CO}_{2(\text{aq})} + 2\text{NaOH} \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} + 2\text{Na}^+$), but this reaction remained active
198 only during the first 100 minutes. Then, carbonate ions were rapidly protonated, forming
199 bicarbonate ions ($\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$) that may complex with Mg^{2+} , leading to a shift of the
200 maximum of the Raman peak of HCO_3^- from 1020 cm^{-1} (Fig.1) to 1011 cm^{-1} (Fig. 2). After 150
201 minutes, aqueous carbon dioxide and bicarbonate ions were the dominant species in the reactor,
202 which induced a significant pH change in the interacting solution as suggested from carbonate
203 speciation in relation with pH (inorganic carbonate fraction vs pH diagram). Under these
204 conditions, the dissolution of magnesium hydroxide ($\text{Mg}(\text{OH})_2 \rightarrow \text{Mg}^{2+} + 2\text{OH}^-$) was enhanced,
205 and the release of magnesium ions generated oversaturation states with respect to several
206 magnesium carbonates. Consequently, the nucleation of hydromagnesite was detected in-situ after
207 60 minutes of reaction (first nucleation-event).



209 Hydromagnesite formed as a transient mineral phase that reached a maximum spectral intensity
210 after 120 minutes. Then, this mineral dissolved in a destabilization processes through a decrease of
211 spectral peak surface area (i.e., Fig. 3) progressively before the nucleation of magnesite that was
212 detected after 240 minutes of reaction (second nucleation-event).



214 After this magnesite nucleation event, the growth of magnesite was mainly nourished by
215 progressive dissolution of hydromagnesite. The temporal evolution of peak surface areas and Full
216 Width Half Maximum (FWHM) for hydromagnesite and magnesite minerals (Figs. 3 and 4)
217 suggest that this reaction included coupled dissolution-reprecipitation. Hydromagnesite was
218 completely consumed after 13 h. An Ostwald ripening process could explain the growth in the
219 following two hours. Equilibrium was reached after 15 h of reaction, as demonstrated by the
220 constant FWHM of magnesite after this time (Fig. 4). FESEM images revealed rhombohedral
221 single crystals with sizes $<5 \mu\text{m}$ (Fig. SI-3), in agreement with previous work [8].

222

223 *3.2. Role of temperature and organic additives*

224 Several complementary experiments were performed in order to assess the evolution of pH in-situ,
225 the dehydration effect of organic additives around Mg ions, and the role of reaction temperature
226 (Table 1, Fig. 5). For all of these experiments, the pH decreased from 12.4 to 9 in the first 10
227 minutes and then continued to decrease at a slower rate until stabilization to a value in the range
228 5.5-6 after 1 h of reaction. This result indicates that the pH was mainly controlled by inorganic
229 carbonate speciation and CO_2 pressure (Figs. SI-4 and 5), and that organic additives had a little or
230 undetected influence. This result is in agreement with time-lapse Raman measurements where a
231 protonation process of carbonate ions was also detected, indicating a pH change in the interacting
232 solution (Figs. 1, 2). Conversely, organic additive has significant effect on the texture (crystal size)
233 and structural water content of the mineral produced, as identified in recovered suspensions by
234 Raman ex-situ measurements (Fig. 5). Hydromagnesite was the main mineral phase precipitated at
235 60°C for 24 h in the absence or presence of organic additive. However, both the mineral texture,
12

236 measured by the Full Width Half Maximum (FWHM) of the largest Raman peak, and the structural
237 water content, measured by the position of largest Raman peak, were slightly different with respect
238 to the reference of the hydromagnesite precipitated in a solution free of additive. In addition, some
239 traces of magnesite were detected after 24 h of reaction when ferric EDTA or citric acid tri-sodium
240 salt were used. For the EDTA additive, slow hydromagnesite-to-magnesite transformation was
241 detected and about 7 days were required to obtain high-purity magnesite at 60°C. Only
242 nesquehonite was detected at 25°C in the presence of EDTA (Fig. 5). This result confirms that
243 magnesite precipitation from the aqueous carbonation of magnesium hydroxide at room
244 temperature was inhibited, or strongly retarded, by the precipitation of nesquehonite.

245

246 *3.3 Environmental implications*

247 Magnesite formation at room temperature (<30°C) from the aqueous carbonation of magnesium
248 hydroxide remains a scientific challenge. This formation could make the magnesite precipitation
249 an economical issue to store permanently the CO₂ with important environmental advantages:

250 (1) reduce CO₂ emissions from the industrial sector (e.g. steel and cement industry, coal-fired
251 power),

252 (2) obtain magnesite-rich or high-purity magnesite materials with an aggregate value (e.g.
253 fabrication of roadbed materials, bricks, granular fill, fire-retardant building material) at low or
254 moderate temperature and reduced time (<24 h) and,

255 (3) use of mine solid wastes (e.g., mines in ultrabasic rocks) or widely available Mg-silicates as a
256 magnesium source to capture CO₂.

257 In practice, the residual alkaline-solution used during magnesite production could be recycled for
258 future carbonation experiments or re-used in other chemical processes, but these options were not

259 assessed in the present study.

260 In this context, the production of magnesite material as an effective solution to reduce the industrial
261 CO₂ emission may be a serious option at industrial scale as now proposed by Cambridge Carbon
262 Capture (<http://www.cacaca.co.uk/#news>).

263

264 **4. Conclusion**

265 In the present study, we demonstrated that high-purity magnesite can be produced from the
266 carbonation of magnesium hydroxide at a rate of about 6 kg/m³h, and thus a mineralization rate of
267 CO₂ into magnesite of about 3kg/m³h. Higher productions were estimated for hydromagnesite (120
268 kg/m³h) and nesquehonite (40 kg/m³h), but these minerals are thermodynamically less stable at
269 Earth surface conditions than magnesite.

270 Our time-resolved Raman measurements allowed a detailed description of reaction mechanism and
271 kinetics of carbonation of magnesium hydroxide in batch reactor conditions. This experimental
272 setup offers new possibilities for investigating mineral condensation from ionic solutions and
273 slurries, and for investigating other chemical reactions at the solid-fluid interfaces.

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282 **Acknowledgements**

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284 The authors acknowledge funding from the French National Centre for Scientific Research
285 (CNRS). We thank Nathaniel Findling for technical assistance.

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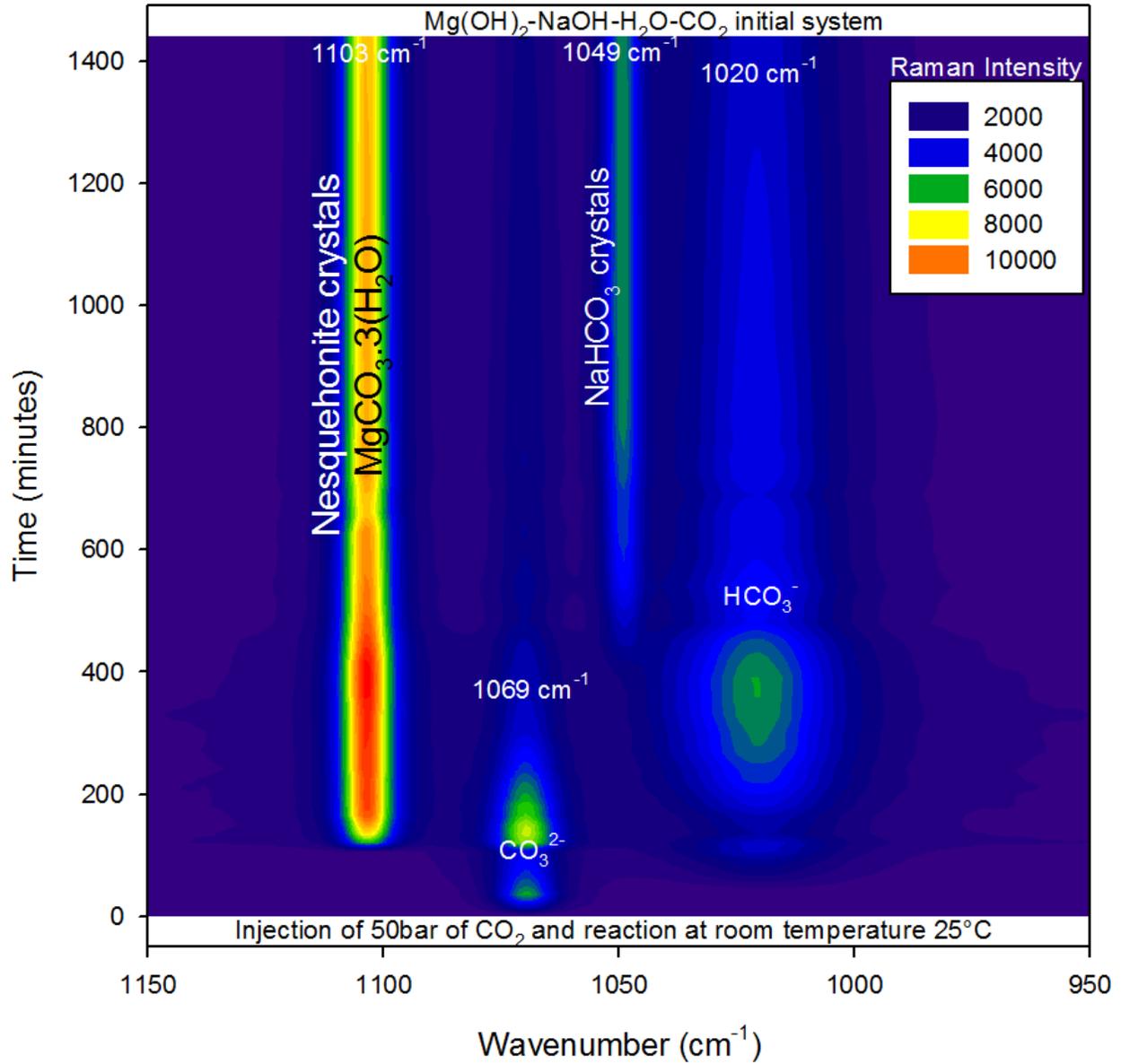
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354 Table 1. Experiments of magnesium carbonates precipitation from Mg(OH)₂-NaOH-H₂O-CO₂
 355 slurry under anisobaric conditions (initial CO₂ pressure of 50bar).

Run	Temperature (°C)	Additive (1g)	Real-time monitoring	Exp. Duration (h)	Mineral transient phase(s)	Final mineral phase(s)
1	25	-	Raman spectroscopy	72	none	nesquehonite
2	90	-	Raman spectroscopy	24	hydromagnesite	magnesite
3	90	-	pH probe	24	N/A	Magnesite and residual hydromagnesite
4	60	-	pH probe	24	N/A	hydromagnesite
5	60	citric acid	pH probe	24	N/A	hydromagnesite
6	60	aspartame	pH probe	24	N/A	hydromagnesite
7	60	EDTA	pH probe	24	N/A	hydrogmagnesite
8	60	EDTA	pH probe	72	N/A	magnesite and hydromagnesite
9	60	EDTA	pH probe	168	N/A	magnesite
10	25	EDTA	pH probe	168	N/A	nesquehonite

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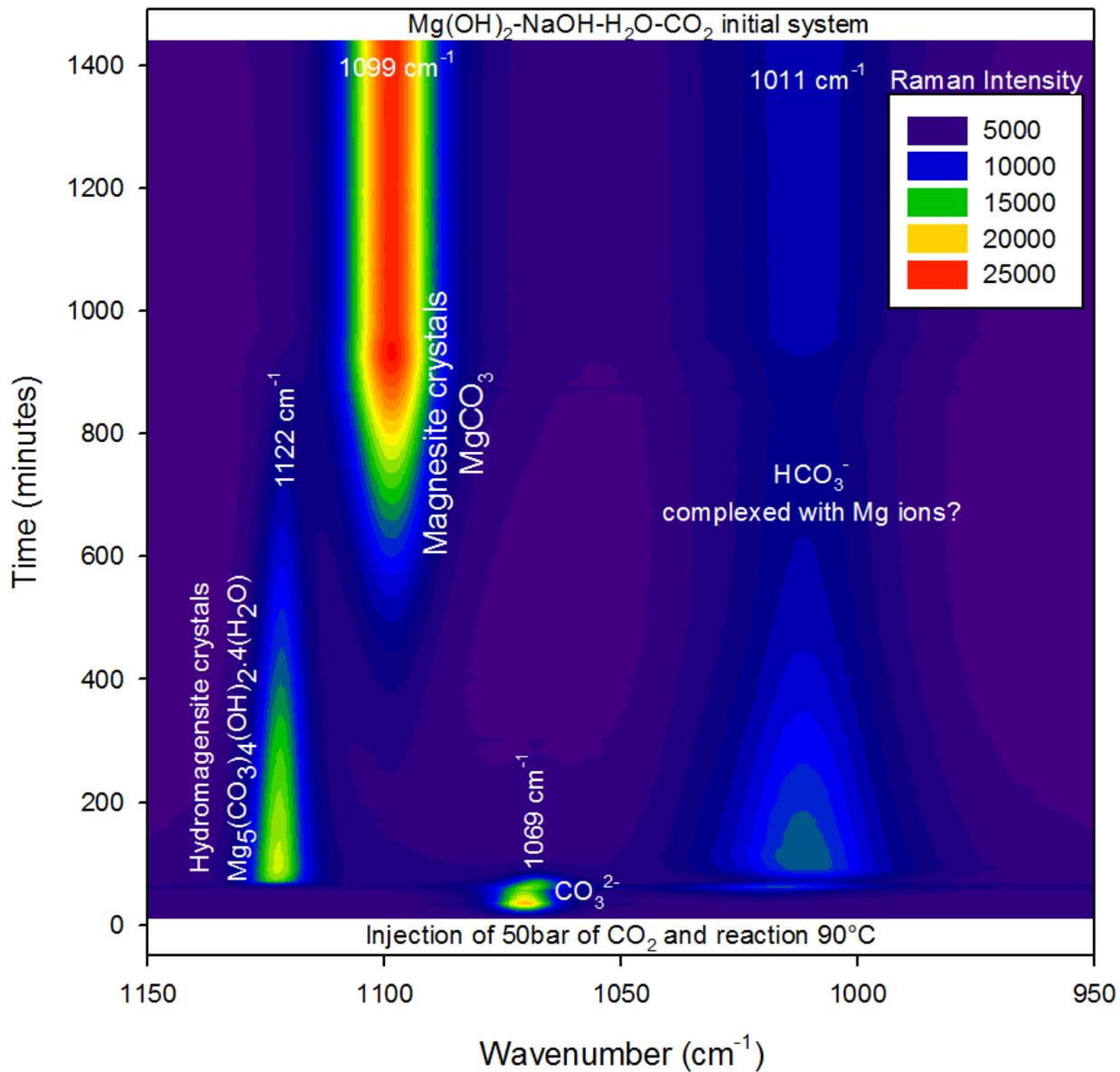
358 Figure 1. Time-lapse Raman spectroscopy monitoring of the aqueous carbonation of magnesium

359 hydroxide at 25 °C under anisobaric conditions. The positions of the Raman peaks and the

360 corresponding aqueous or mineral species are indicated on the figure.

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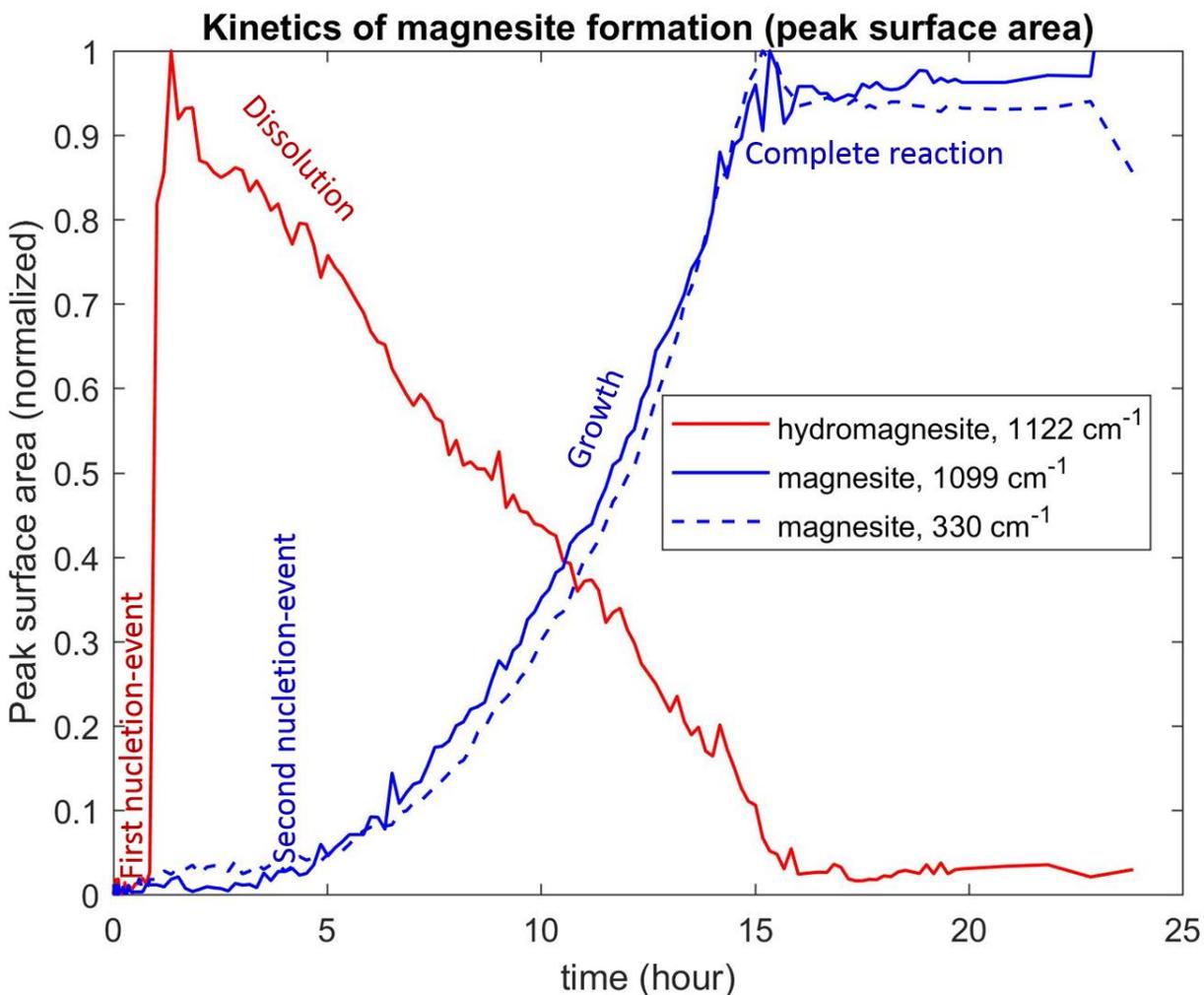
364 Figure 2. Time-lapse Raman spectroscopy monitoring of the aqueous carbonation of magnesium

365 hydroxide at 90°C under anisobaric conditions. The positions of the Raman peaks and the

366 corresponding aqueous or mineral species are indicated on the figure. The same data are shown on

367 Fig. SI-2 in the form of spectra.

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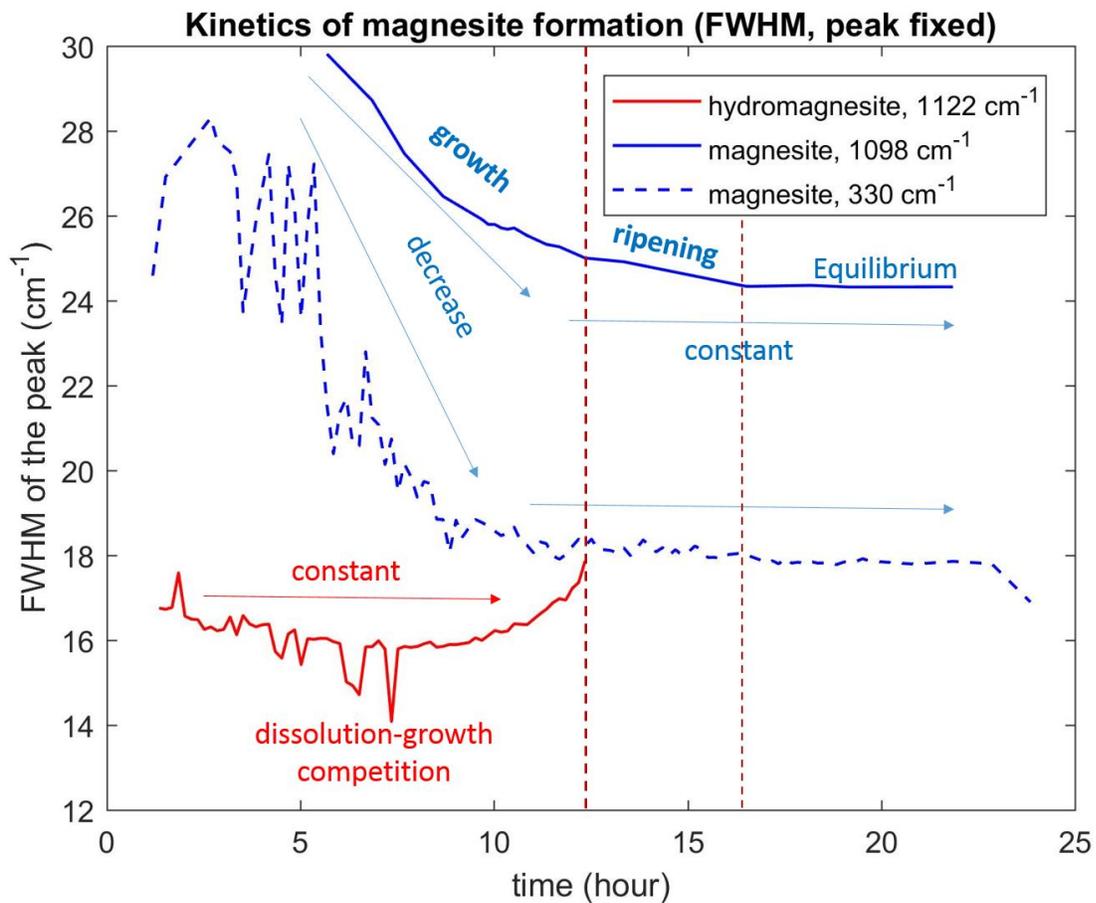
370 Figure 3. Kinetics of nucleation and growth of hydromagnesite and magnesite during aqueous

371 carbonation of magnesium hydroxide at 90°C measured by Raman spectroscopy. The peak surface

372 area is calculated as a function of time for one Raman peak of hydromagnesite and two Raman

373 peaks for magnesite, from the data shown in Figs. 2 and SI-2.

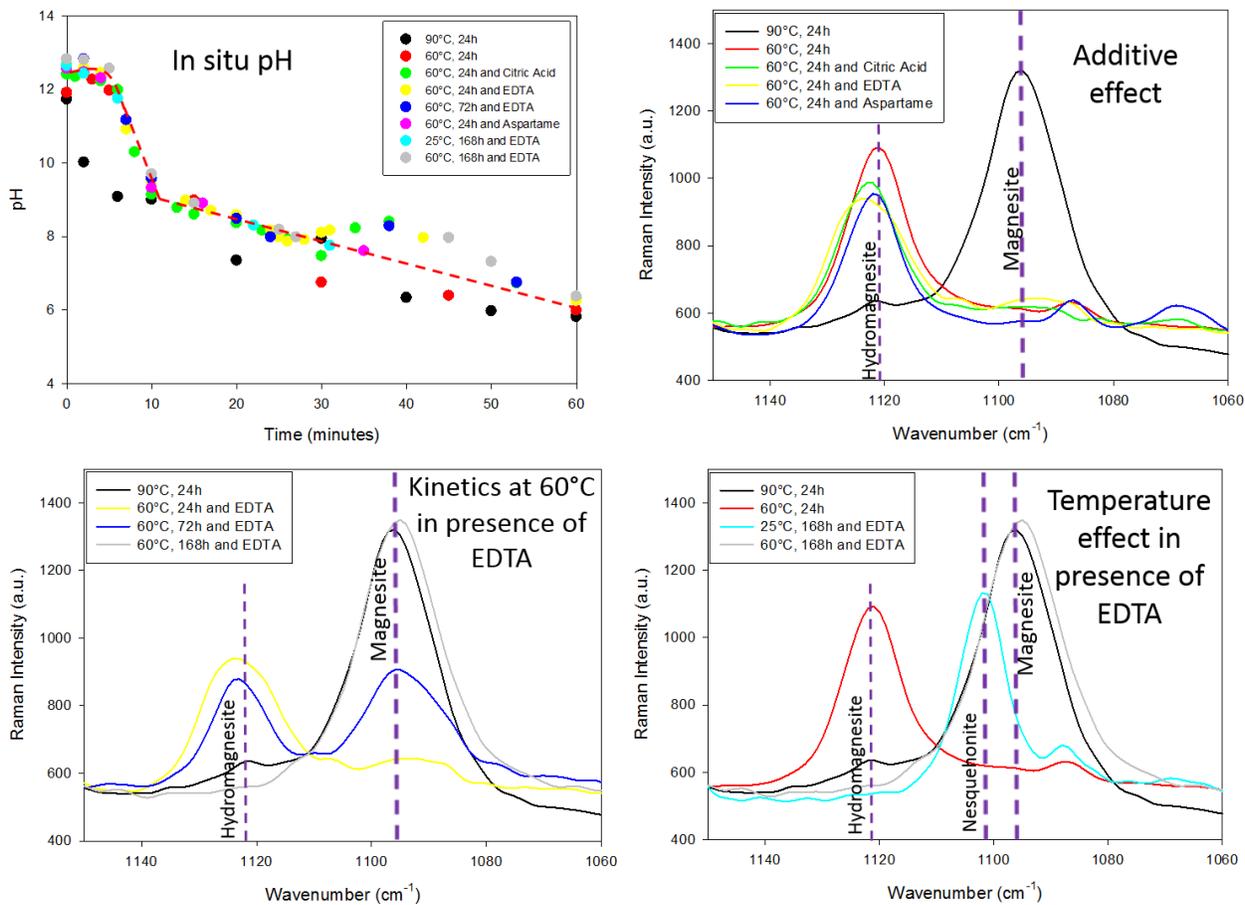
374



375

376 Figure 4. Crystal growth mechanism of magnesite (blue) at 90°C, nourished by hydromagnesite
 377 dissolution (red) and measured by the Full Width at Half Maximum (FWHM) of the Raman peaks
 378 shown in Figs. 2 and SI-2.

379



380

381 Figure 5. pH measured in-situ during aqueous carbonation of magnesium hydroxide in eight
 382 experiments (Table 1), with or without additive. Influence of organic additives and temperature on
 383 the aqueous carbonation of magnesium hydroxide (Mg(OH)₂-NaOH-H₂O-CO₂ slurry) under
 384 anisobaric conditions.

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