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Amorphous calcium-magnesium carbonate (ACMC) accelerates dolomitization at room temperature under abiotic conditions

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Abstract

The challenge to produce dolomite $CaMg(CO_3)_2$ at low temperature (20-35°C) over laboratory time scales remains so far unsuccessful, which has led to long-lasting scientific debates in the last two centuries. This mineral exerts a major control on the natural carbon dioxide sequestration into various sedimentary, basaltic and mantellic rocks. The present study reports on specific abiotic conditions that allows the precipitation of disordered dolomite, high Mg-calcite and high Ca-magnesite at room temperature over time scales of hours to days. Here we show that an amorphous calcium magnesium carbonate (ACMC) phase accelerates dolomitization at room temperature. ACMC is initially precipitated by mixing a carbonate ($HCO_3^-/CO_3^{2-}=1$; $pH \sim 10.3 \sim pK_{a2}$) alkaline solution with a Mg-Ca ionic solution (Mg molar fraction between 0 and 1). Then, time-resolved in situ Raman spectroscopy monitored the transformation of ACMC into Mg-rich carbonate minerals. The initial Mg molar fraction controlled both the reaction mechanism (e.g. nature of transient crystalline phases) and the kinetics. Nanosized crystallites with short-range order, called disordered dolomite $CaMg(CO_3)_2$, precipitated following a complex reaction pathway. Firstly, nesquehonite ($MgCO_3.3H_2O$: nucleation time = 2.5h), then disordered dolomite ($CaMg(CO_3)_2$: nucleation time = 3.2h) and then monohydrocalcite ($CaCO_3.H_2O$: nucleation time = 3.4h) formed from ACMC transformation. Nesquehonite and monohydrocalcite are transient phases that nourish the slow precipitation of disordered dolomite, which reached a spectral equilibrium after 7 days of reaction. Direct transformation of ACMC into disordered dolomite was also measured. Our experimental results demonstrate that disordered dolomite precipitates at room temperature when ideal Mg/Ca ratio, high-carbonate alkalinity and high ionic-concentration are reached in abiotic systems. This result suggests the possibility of a physicochemical rather than to biotic control on the formation

of disordered dolomite at low temperature in several geosystems.

Keywords: Disordered dolomite, Mg-carbonate, Amorphous carbonate; Time-resolved Raman spectroscopy; Mineral nucleation and growth

1. Introduction

Dolomite, $CaMg(CO_3)_2$, precipitation kinetics and formation mechanism have been widely studied and controversial claims have been reported in the past two centuries (1). Abiotic precipitation of dolomite at ambient temperature (~25°C) is virtually impossible within typical laboratory experimental time scales (2-5). This difficulty is interpreted to originate from the strongly bonded solvation shells of magnesium ions into aqueous media (2). Dehydration of Mg ions is significantly facilitated by bacterial activity, including exopolymeric substances, and organic functionalized surfaces (6-7). Therefore, several studies have claimed that dolomite may precipitate in bio-assisted systems at ambient laboratory conditions (6-12). Therefore, both textural and crystallographic characterization, reaction mechanism, and kinetics studies of dolomite precipitation at ambient/low temperature remain exciting scientific challenges for geochemists and mineralogists (13-17).

In addition, the effect of Mg hydration might not be the only factor of inhibition of dolomite formation at room temperature. Recent studies claimed that a more intrinsic crystallization barrier and the influence of fluid chemistry (e.g., relative size of the cations in solution) may prevent the formation of long-range ordered crystallographic structures in dolomite at ambient conditions (3-5). Lippmann (18) described specific superstructures, called ordering-reflections, in the X-ray diffraction patterns of dolomite that were related to the regular alternation of monolayers of Ca and Mg oriented perpendicular to the c-axis of dolomite crystals. This organization indicates an equal Mg and Ca composition in the structure at the crystal scale. In natural dolomites, structural imperfections are frequently measured and, sometimes, nanometer sized crystallites with short-range order may be expected (1). In this last case, the term disordered dolomite (also called protodolomite) is used because the superstructures ordering reflections, corresponding to the peaks

(101), (015) and (021)) in X-ray diffraction patterns, are not detected (13, 19).

The present study demonstrates that an amorphous calcium-magnesium carbonate phase (ACMC) accelerates the dolomitization process at room temperature under abiotic conditions. Herein, an ACMC phase was instantaneously precipitated by using concentrated ionic solutions (HCO_3^-/CO_3^{2-} solution – Mg^{2+}/Ca^{2+} solution interactions). Then, the persistence time or lifetime (i.e. the duration until ACMC starts transforming) and transformation of ACMC into new minerals in the interacting solutions were monitored in real-time by using dynamic Raman spectroscopy (20). We also investigated the effect of the Mg molar fraction with respect to Ca in solution. This parameter controls the amount of Mg that can be incorporated into the carbonate crystal lattice and the nature of transient carbonate phases, allowing to the precipitation of calcite (Mg/(Mg+Ca) = 0), low Mg-calcite (Mg/(Mg+Ca)<10%), high Mg-calcite (10%<Mg/(Mg+Ca)<45%), disordered dolomite (45%<Mg/(Mg+Ca)≤55%) and high Ca-magnesite (Mg/(Mg+Ca)>60%), as reported in the literature (e.g. 21-25).

High Mg-calcite and disordered dolomite precipitation at room temperature is frequently related to bio-mineralization processes, as observed in corals, seashells and many other invertebrates or observed in laboratory experiments under biotic conditions (16, 21). The present experimental study demonstrates that disordered dolomite, $CaMg(CO_3)_2$, can precipitate at low temperature when ideal Mg/Ca ratio, high-carbonate alkalinity (HCO_3^-/CO_3^{2-} coexistence) and high ionic-concentration are reached in abiotic or biotic systems. Herein, the formation of an amorphous phase plays a significant role to produce disordered dolomite

2. Materials and Methods

2.1. Disordered dolomite $CaMg(CO_3)_2$ formation at room temperature

The conditions to precipitate disordered dolomite at room temperature (27-31°C) were the following: 100 mL of $NaHCO_3$ (1M) and 100 mL of Na_2CO_3 (1M) were placed into a Hastelloy C22 reactor (Parr, total internal volume of 600 mL) coupled with a Raman probe immerged into solution/suspension in order to monitor in real-time precipitating carbonate particles and aqueous carbonate species. This experimental setup was reported previously in Montes-Hernandez group (20). Raman spectra were collected with a Raman RXN1, Kaiser Optical Systems with an exposure time of three seconds and averaged over three scans.

The carbonate speciation in initial solution was verified by Raman spectroscopy before the injection of Ca-Mg solution (HCO_3^- peaking at 1016 cm^{-1} and CO_3^{-2} peaking at 1066 cm^{-1}; see Fig. S1-A). This carbonate alkaline solution was immediately dispersed by mechanical agitation (400 rpm) before 200 ml of a Ca-Mg solution (Mg molar fraction of 0.75 and Mg concentration of 0.375M) were injected for about 1-2 minutes with a syringe. Following this injection step, the carbonate speciation and precipitated particles (i.e. transformation of amorphous calcium-magnesium carbonate ACMC into carbonate crystalline phases) were monitored by Raman spectroscopy for three to seven days, with an acquisition frequency of one Raman spectra every minute during the first three hours and every five or ten minutes in the remaining time.

Selected Raman peaks corresponding to identified mineral phases (see Table S1) were fitted by using simple or combined Gaussian model in order to estimate both the full wide half maximum (FWHM) and integrated peak area as a function of time (Movie S1). This calculation provided the

112 peak decomposition necessary to propose relevant reaction mechanisms and to quantify the kinetics
113 of precipitation of disordered dolomite ($MgCa(CO_3)_2$).

114 *2.2. Role of Mg molar fraction*

115 The persistence time of amorphous calcium magnesium carbonate (ACMC) and its transformation
116 into crystalline carbonate phases in the interacting solutions were measured as a function of Mg
117 molar fraction (Mg molar fraction = $(V_{Mg}/(V_{Mg}+V_{Ca}))$ that was varied between 0 and 1
118 (experiments 5-11 in Table 1). Herein, the persistence time, also called lifetime, is defined as the
119 duration over which ACMC is the only precipitate phase present in the suspension before starting
120 to transform into crystalline carbonate phases. We define the nucleation time of each crystalline
121 phase as the time where this mineral is detected by Raman spectroscopy. These experiments were
122 performed following the same protocol described in section 2.1, except for the added volume of
123 Ca and Mg solutions that was adjusted for each investigated Mg molar fraction. Table 1
124 summarizes all precipitation experiments performed in this study; each experiment was repeated
125 at least twice to verify reproducibility of the results.

126 *2.3. Ex situ characterization of precipitates*

127 At the end of each experiment, the solid product was recovered by centrifugation and washed twice
128 with ultrapure water, and once with ethanol. Then, it was dried under a laminar flow of air at 20°C
129 for 48 h. The dry solid products were stored in plastic flasks for subsequent characterization of
130 selected samples by Field Emission Gun Scanning Electron Microscopy (FESEM), Transmission
131 Electron Microscopy (TEM) and powder X-ray diffraction (XRD).

132 Powder XRD spectra were acquired using a Siemens D5000 diffractometer in Bragg-Brentano

geometry, equipped with a theta-theta goniometer with a rotating sample holder. Diffraction patterns were collected using Cu kα_1 ($\lambda_{k\alpha1}$=1.5406 Å) and Cu kα_2 ($\lambda_{k\alpha2}$=1.5444 Å) radiations in the range 2θ = 10 - 70°, with a step size of 0.04° and a counting time of six seconds per step. For high-resolution imaging, the solid products were dispersed by ultrasonic treatment in absolute ethanol for five minutes. Two droplets of the suspension were then deposited directly on an aluminum support and coated with gold-platinum. The powder was imaged using a Zeiss Ultra 55 FESEM with a maximum spatial resolution of approximately 1 nm at 15kV. In addition, recovered solid products from experiments 1 and 2 (Table 1) were shaken in ethanol for a short time in order to separate the aggregates without any additional treatment. One droplet of the suspension was deposited on a perforated carbon foil and placed on a conventional copper micro-grid for further observations with a JEOL 2100F Transmission Electron Microscope (TEM) operating at 200 kV, equipped with a field emission gun and a high-resolution pole piece achieving a point-to-point resolution of 1.8 Å. Chemical analyses in selected points on the sample were performed by Electron Dispersive Spectroscopy (EDS).

3. Results

3.1. Precipitation of disordered dolomite at room temperature: Reaction mechanism and kinetics

Concentrated ionic solutions were chosen to produce an amorphous calcium-magnesium carbonate (ACMC) phase. Our in-situ Raman spectroscopy data confirmed the instantaneous formation of ACMC when alkaline carbonate solution (HCO_3^-/CO_3^{-2}=1) was mixed with Mg-Ca solution (Mg molar fraction = 0.75), as displayed for three experiments in Fig. S1-B. The precipitated ACMC ($Ca_{0.5}Mg_{0.5}CO_3.nH_2O$) is characterized by a broad Raman peak at 1085 cm^{-1}, shifted 6 cm^{-1} away

and broader with respect to the peak of amorphous calcium carbonate (ACC: $CaCO_3.nH_2O$) at 1079 cm^{-1} (this study), close to the value of 1080 cm^{-1} reported in other studies (e.g. 26-27). Time-resolved Raman spectroscopy shows that ACMC starts transforming into crystalline phases after about 2.5 h of reaction. Nesquehonite ($MgCO_3.3H_2O$) is the first detected phase, with a peak at 1099 cm^{-1} and a nucleation time of 2.5 h, followed by monohydrocalcite ($CaCO_3.H_2O$), with a peak at 1067 cm^{-1} and a nucleation time of 3.3 h (Fig. 1). All phases detected in the time-resolved Raman spectroscopy measurements are summarized in Table S1 and their Raman feature assignation is supported by previous studies that used systematically ex-situ Raman spectroscopy onto powdered samples. Nesquehonite and monohydrocalcite are transient phases, i.e. their slow concurrent dissolution allows the continuous precipitation of disordered dolomite with a Raman peak at 1094 cm^{-1} (Fig. 2). Broad feature of the main peak and low Raman signal in lattice mode at 300 cm^{-1} suggest the presence of nanosized crystals, as confirmed by FESEM images that reveal crystallites with size in the range 20 to 80 nm and forming irregular aggregates (Fig. S2). Herein, we suggest that this phase is a disordered dolomite, i.e. short-range order forming nanosized crystallites, because the superstructures ordering reflections ((101), (015) and (021)) are not detected in our laboratory X-ray powdered diffraction, despite an ideal atomic composition (Mg/Ca=1) (Fig. S3). The movie S1 displays the time evolution of the peaks of the main mineral phases during experiment 2 (Table 1), leading to the formation of disordered dolomite, including the evolution of ACMC, nesquehonite, and monohydrocalcite. The surface areas of the peaks corresponding to these four phases evolve as a function of time and are used here as proxies to measure the relative concentrations of these components in the suspension (Fig. S4).

From these time-resolved Raman measurements and spectra analyses (Figs. 1, 2 and S4), the following reactions are proposed, which summarize the mechanism for disordered dolomite

178 formation:

179 **Nesquehonite formation**

180 $2Ca_{0.5}Mg_{0.5}CO_3.nH_2O + 3H_2O \rightarrow MgCO_3.3H_2O + CaCO_3.nH_2O + nH_2O$ (1)

181 **Monohydrocalcite formation**

182 $CaCO_3.nH_2O + H_2O \rightarrow CaCO_3.H_2O + nH_2O$ (2)

183 **Formation of disordered dolomite via concurrent dissolution of transient phases**

184 $MgCO_3.3H_2O + CaCO_3.H_2O \rightarrow CaMg(CO_3)_2 + 4H_2O$ (3)

185 Data show that the concurrent slow dissolution of nesquehonite and monohydrocalcite nourish the
186 precipitation of disordered dolomite. However, disordered dolomite nucleation formed during the
187 first hours (nucleation time = 3.2h), as detected by fitting the Raman spectra (see Movie S1 and
188 Fig. S4). These results imply that nesquehonite and monohydrocalcite play a critical retarding
189 effect on the formation of disordered dolomite as discussed below.

190 The precipitation of disordered dolomite from direct transformation of ACMC could also occur as:

191 $2Ca_{0.5}Mg_{0.5}CO_3.nH_2O \rightarrow CaMg(CO_3)_2 + 2nH_2O$ (4)

192 This more simple reaction mechanism was detected by time-resolved Raman spectroscopy (Fig. 3,
193 experiment 1 in Table 1), but with a low experimental reproducibility (once over four total
194 experiments performed under identical conditions, experiments 1 to 4 in Table 1). In this particular
195 case, the lifetime of ACMC was larger and equal to 10 hours, as shown on Fig. 3. Herein, the
196 particle size distribution of disordered dolomite was more homogeneous with an average size of
197 20 nm (see FESEM images in Fig. S2 for experiment 1). We assumed that, in this particular case,
198 ACMC reached an ideal Mg/Ca ~ 1 ratio and then its direct transformation into disordered dolomite
199 could take place, as demonstrated by the Raman data (Fig. 3). However, this chemical event might
200 be strongly sensitive to small fluctuations of room temperature, fluid chemistry, mechanical

agitation and time of mixture of ionic solutions because it happened only once over the four experiments performed under the same conditions (experiments 1-4 in Table 1).

In natural open systems oversaturated with respect to dolomite, fluid chemistry and temperature fluctuations could inhibit dolomite formation and the precipitated transient phases could remain persistent and stable for long durations (e.g. 28-29). Such observations may provide an explanation why dolomite is absent in natural systems presently oversaturated with respect to dolomite.

3.2. Role of Mg molar fraction

At the investigated carbonate alkaline conditions (HCO_3^-/CO_3^{2-} = 1, 0.5 M for each specie, and pH~pK_{a2}~10.3), both the concentration of Mg and its molar fraction with respect to Ca play a critical role on the lifetime of ACMC. When the Mg molar fraction is larger than 0.5, the ACMC lifetime increases substantially (Fig. 4). The reaction mechanism, i.e. the nature of transient crystalline phases and final recovered products, is also strongly dependent on the concentration of Mg (see Table 1). For example, when the Mg molar fraction is less or equal than 0.2, vaterite polymorph is the main transient phase before the formation of low Mg-calcite ($Mg_xCa_{1-x}CO_3$ with $x<0.1$) (Fig. S5). Here, three reaction steps are clearly identified: (1) ACC formation with a lifetime of 3 minutes; (2) concurrent transformation of ACC into vaterite and Mg-calcite; and (3) slow transformation of vaterite into low Mg-calcite via coupled dissolution-crystallization process. This reaction mechanism is in agreement with results obtained from in-situ time-resolved synchrotron-based wide-angle X-ray scattering (WAXS) and energy dispersive X-ray diffraction (ED-XRD), despite the difference in pH and Mg concentration (30). At higher Mg molar fraction (e.g. 0.5 and 0.6), high Mg-calcite mesocrystals ($Mg_xCa_{1-x}CO_3$ with $0.1<x<0.45$) form and the vaterite phase is not detected (see Table 1). Mg-calcite mesocrystals are micrometric porous aggregates constituted

of oriented nano-crystals and that form cauliflower and peanut-like morphologies (Fig. S6). These peculiar morphologies and the process of aggregation of nanocrystals have been reported in previous studies (e.g. 22-23). In some studies, high-Mg calcite with peculiar morphologies and with Mg content into crystal lattice (<45%) was misinterpreted as disordered dolomite (e.g. 15-16). Therefore, Mg-calcite mesocrystals are not necessary made of disordered dolomite, except when the Mg/Ca ratio of the crystal lattice is close to 1.

At a Mg molar fraction of 0.75 and under abiotic conditions, we observed the formation of disordered dolomite ($CaMg(CO_3)_2$), as discussed in section 3.1. In complement, X-ray data (Fig. 5) show the (104) reflection in the solid products recovered at the end of experiments that used different initial Mg molar fraction (see also Table 1. In addition, from Rietveld refinements of XRD patterns, the Table 2 summarizes the mineral composition and Mg content into calcite crystal lattice. In general, our results are in agreement with studies that have investigated the influence of Mg molar fraction on the lifetime of ACC and ACMC phases and their transformation into crystalline phases (e.g. 28-30). In addition to already published studies, our study reports specific experimental conditions that allow the synthesis of disordered dolomite by controlling exclusively the Mg molar content (0.75) and the carbonate alkalinity (HCO_3^-/CO_3^{2-}=1, pH~pK_{a2}~10.3) at room temperature (experiments 1-4 in Table 1).

Finally, for Mg molar fraction of 0.9 (experiment 10 in Table 1), the lifetime of ACMC was prolonged to about 4.5 hours and a more complex reaction mechanism was monitored by time-resolved Raman spectroscopy (Fig. 6). In this experiment, monohydrocalcite ($CaCO_3 \cdot H_2O$) was detected as a transient phase before the formation of disordered dolomite and high Ca-Magnesite was measured by X-ray diffraction in the product recovered after the experiment (Fig. 5 and Table

2). Dypingite ($Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$) was also detected, and this hydrated carbonate co-existed with disordered dolomite and Ca-magnesite until the end of experiment (Fig. 6). These results demonstrate that the Mg molar fraction controlled the lifetime of ACMC in the interacting solutions, the reaction mechanism, the kinetics, and the amount of Mg incorporated into the carbonate.

4. Discussion and concluding remarks

Dolomite is a critical mineral that incorporates large volumes of carbon dioxide into a solid form in many geological environments (1). Primary dolomite formation ($Mg^{2+} + Ca^{2+} + 2CO_3^{2-} \rightarrow CaMg(CO_3)_2$) at low temperature (20-35°C) and secondary dolomite formation ($2CaCO_3 + Mg^{2+} \rightarrow CaMg(CO_3)_2 + Ca^{2+}$) at higher temperature (diagenetic or hydrothermal, 60-300°C) have been proposed to explain dolomitization processes in natural environments (1). Primary dolomite formation has led to controversial claims because ordered dolomite could not be synthesized in laboratory under abiotic conditions and only disordered dolomite and high Mg-calcite are generally observed in environments oversaturated with respect to dolomite (2, 15-17). Bio-assisted primary dolomite formation, and/or formation mediated by living organisms, have been proposed. In such cases, cellular and intracellular surfaces and exopolymeric substances can overcome the kinetic barrier to nucleate dolomite (e.g. 6-12). Functionalized organic molecules/surfaces can also decrease the Mg hydration barrier and catalyze dolomite formation at low temperature (e.g. 31). However, the reaction mechanism responsible for dolomite formation (e.g., role of transient amorphous or crystalline phases) and clear proofs or explanations concerning the dolomite superstructures ordering reflections in the X-ray diffraction patterns have been ambiguously provided (6, 12). Based on the present study and on recent mechanisms proposed to explain mineral

nucleation (e.g. 32-36), we infer that primary dolomite, as initially defined ($Mg^{2+} + Ca^{2+} + 2CO_3^{2-} \rightarrow CaMg(CO_3)_2$), has a very low probability to form at room temperature in abiotic or biotic systems, i.e. through heterogeneous nucleation (pre-existence of reactive surfaces) and a non-classical nucleation mechanism is therefore expected. The present study demonstrates that transient amorphous or crystalline phases play a significant role in the formation of disordered dolomite. Such transient phases can decrease the energy barrier under ideal fluid chemistry conditions (e.g. direct transformation of ACMC into disordered dolomite), but, they can also retard dolomite precipitation (e.g. via concurrent dissolution of nesquehonite and monohydrocalcite) as demonstrated in the present study (Figs. 1, 2, 3 and movie S1). Crystalline phases (e.g. dypingite, monohydrocalcite, aragonite) can produce an inhibiting effect in laboratory experiments or in some natural dolomitic environments (1). From the present experimental study, we conclude that ACMC accelerates dolomitization in a short interval of Mg molar content (0.6-0.75) at low temperature and the revealed reaction mechanism could exist in natural dolomitic environments such as lagoons, evaporitic settings, or caves.

Another critical point concerning the so-called primary dolomite is the existence of superstructures ordering reflections in X-ray diffraction patterns (e.g. (101), (015) and (021), Fig. S3). Herein, some factors can perturb their unambiguous detection. For example, when dolomite crystal size is larger than 100 nm and coexisting crystalline phases have a low concentration, X-ray powder diffraction or electron diffraction in TEM allow a clear identification of superstructure ordering reflections. Conversely, if dolomite crystal size is of the order or smaller than 20 nm (Fig. S7), the detection of superstructure ordering reflections is more challenging in X-ray diffraction patterns and by electron diffraction in TEM when nanoparticles are aggregated, despite the ideal Mg content (Ca/Mg ~1) in the structure lattice (Fig. S3). In such case, disordered dolomite, i.e. short-range

ordered crystallographic structures, is assumed and in general, longer range ordering is reached with an increase of temperature (corresponding to an increase of average size of dolomite crystals) as already demonstrated in a previous study (13). We claim that the detection limit of laboratory X-ray diffraction data when nanoparticles exist (the peaks are broader and have lower intensity and the low intensity of superstructure ordering reflections) and the difficulty to synthesize dolomite in laboratory experiments have led to contradictory interpretations on the formation of dolomite at low temperature. In this perspective, the formation of disordered dolomite at low temperature in abiotic systems can be achieved at room temperature. A future challenge would be to determine whether a regular alternation of monolayers of Ca and Mg (perpendicular to the c-axis) may exist in nanosized dolomitic crystals, that would require to develop specific analytical and imaging methods, such as energy filtered transmission electron microscopy combined with electron energy loss spectroscopy.

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Appendix A. Supplementary data

Supplementary material (1 Table, 7 additional figures and a spectral movie) related to this article can be found, in the online version, at

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Table 1. List of experiments with time-lapse Raman spectroscopy for precipitation of disordered dolomite at room temperature and influence of Mg molar ratio. A constant carbonate alkalinity of HCO_3^-/CO_3^{2-}=1 (0.5M) and a total cationic (Mg-Ca) concentration of 0.5M were imposed.

Exp.	**Temperature (°C)**	**Mg molar fraction**	**Exp. duration (days)**	**Lifetime of ACMC** (min. / h)	**Mineral transient phase(s)**	**Final mineral phase(s)**
1	27	0.75	3	10 h	none	disordered dolomite*
2	31	0.75	7	2.5 h	nesquehonite monohydrocalcite	disordered dolomite*
3	31	0.75	7	2.3 h	nesquehonite monohydrocalcite	disordered dolomite
4	30	0.75	10	1.9 h	nesquehonite monohydrocalcite	disordered dolomite
5	28	0	1	0.75 min.	vaterite	calcite*
6	28	0.05	1	1.75 min.	vaterite	calcite*
7	29	0.20	2	3 min.	vaterite	low Mg-calcite*
8	27	0.5	2	3 min.	none	high Mg-calcite*
9	28	0.6	2	30 min.	none	high Mg-Calcite*
10	29	0.9	2	4.5 h	monohydrocalcite	disordered dolomite* dypingite*
11	28	1	3	2 h	none	Dypingite

* these phases were also characterized by powder X-ray diffraction

435 Table 2. Mineral carbonate composition and Mg content in lattice structure identified from Rietveld
436 refinement of X-ray diffraction patterns. In experiment 10, aragonite, dypingite and eteilite were
437 also detected.

Exp.	Mg molar fraction	Calcite	Low Mg-Calcite	High Mg-Calcite	Disordered Dolomite	High Ca-Magnesite
5	0	$CaCO_3$	none	none	none	None
6	0.05	$CaCO_3$	none	none	none	none
7	0.20	$CaCO_3$	$Mg_{0.05}Ca_{0.95}CO_3$	none	none	none
8	0.50	none	none	$Mg_{0.15}Ca_{0.85}CO_3$ $Mg_{0.23}Ca_{0.77}CO_3$	none	none
9	0.6	none	none	$Mg_{0.35}Ca_{0.65}CO_3$	none	none
1	0.75	none	none	none	$Mg_{0.49}Ca_{0.51}CO_3$	none
10	0.9^x	none	$Mg_{0.07}Ca_{0.93}CO_3$	none	$Mg_{0.45}Ca_{0.55}CO_3$	$Mg_{0.68}Ca_{0.32}CO_3$

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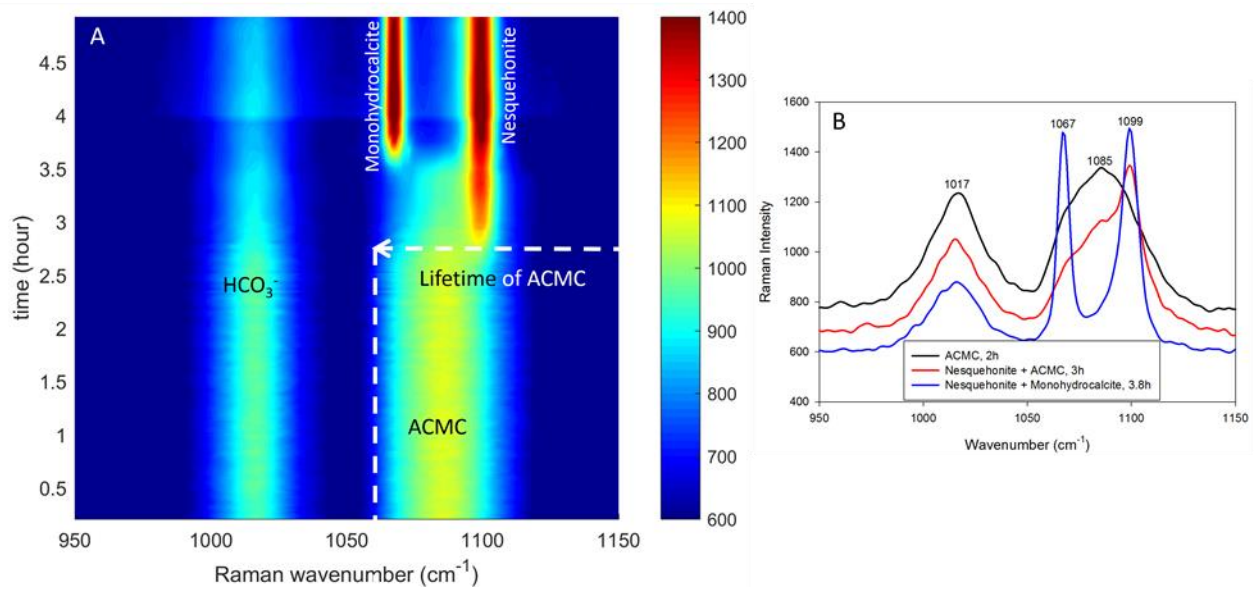
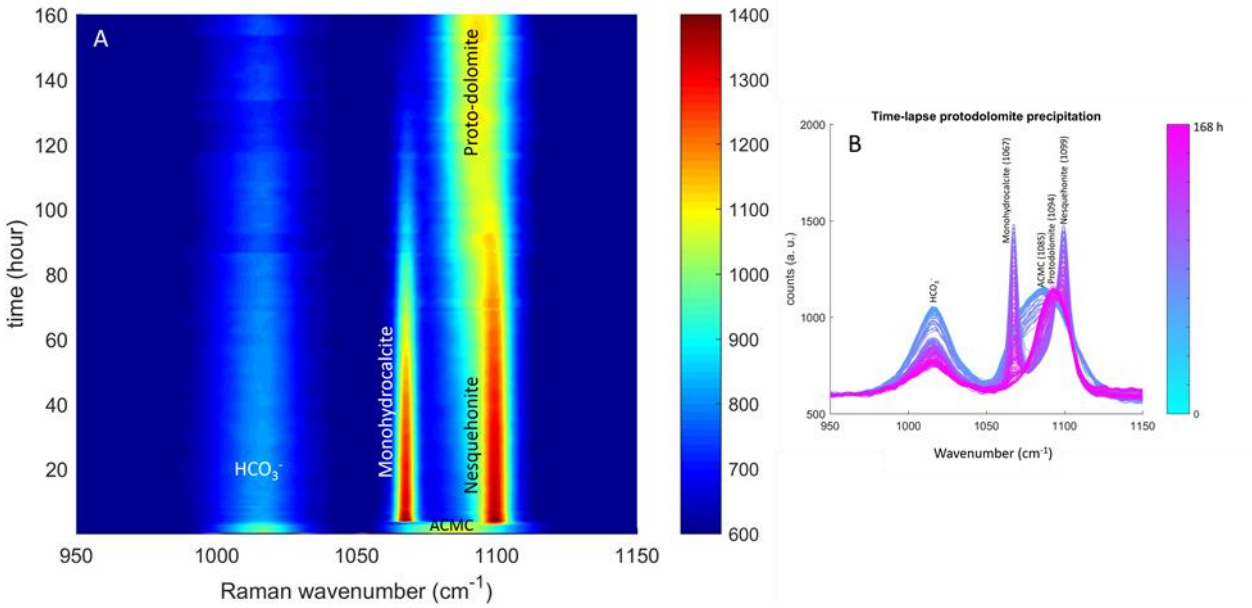


Figure 1. Time-lapse Raman spectroscopy monitoring of amorphous calcium-magnesium carbonate (ACMC) transformation into crystalline phases during the first four hours of experiment 2 (Table 1). The lifetime of ACMC and positions of crystalline phases are indicated.



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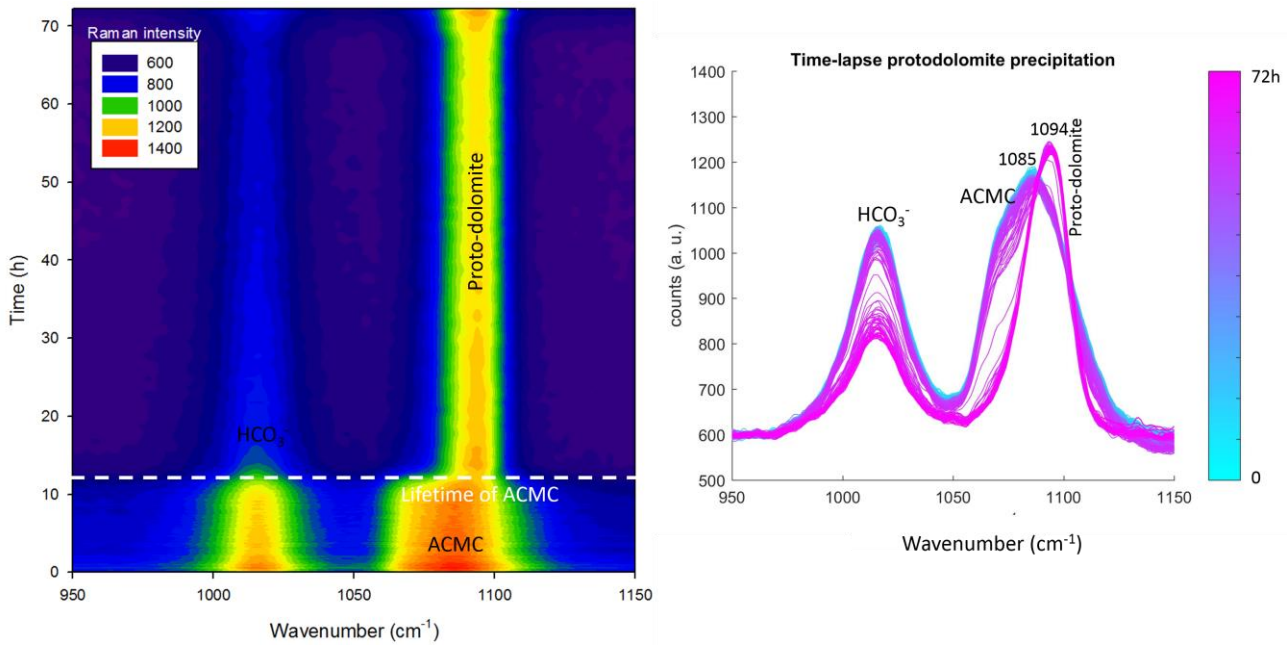
454 Figure 2. Time-lapse Raman spectroscopy monitoring of the formation of disordered dolomite from
455 ACMC in experiment 2 (Table 1). Left: evolution of the two transient phases, nesquehonite and
456 monohydrocalcite. Right: time-lapse evolution of the main peaks.



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458 Figure 3. Left: Time-lapse Raman spectroscopy monitoring of the formation of disordered dolomite
459 from direct transformation of ACMC in experiment 1 (Table 1). Right: time-lapse evolution of the
460 main peaks.

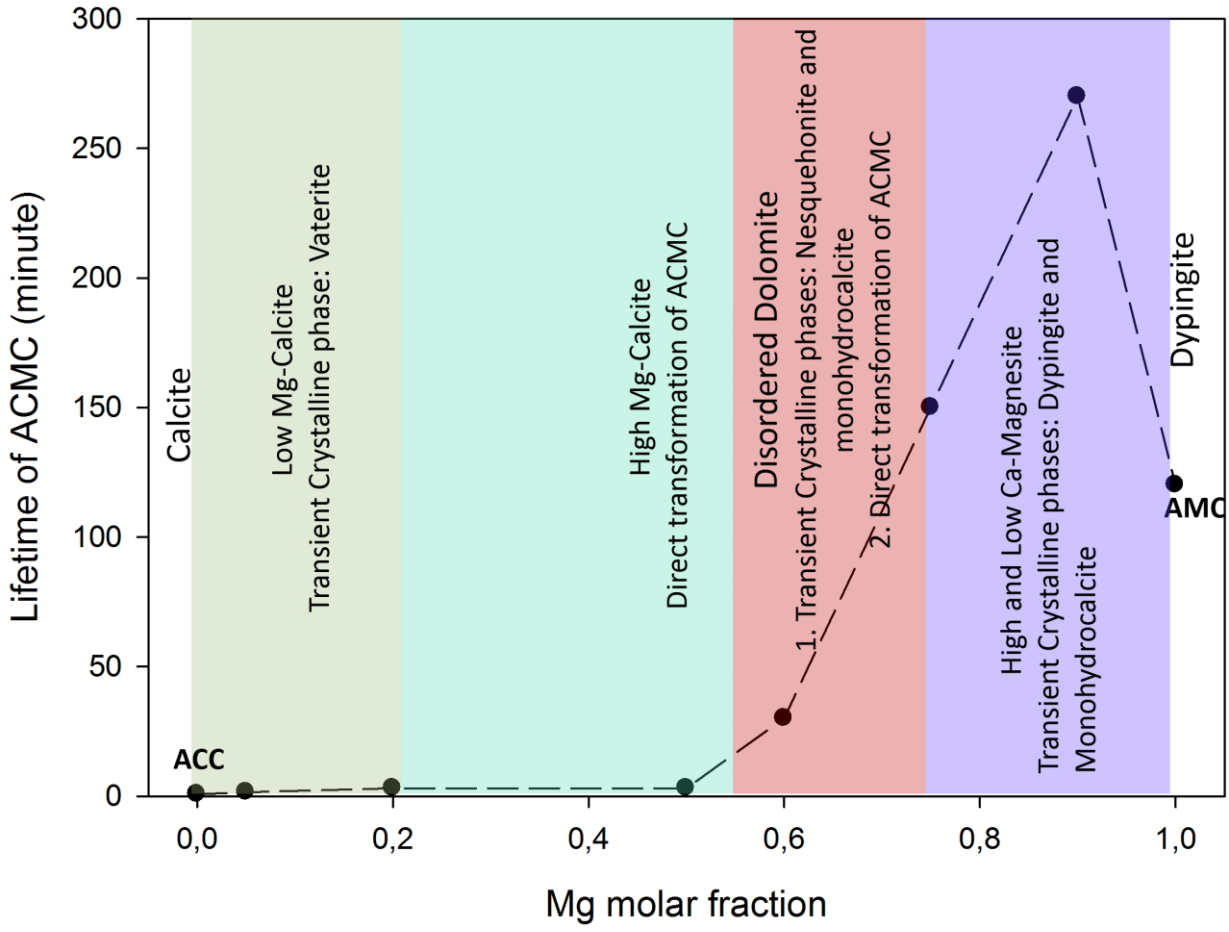
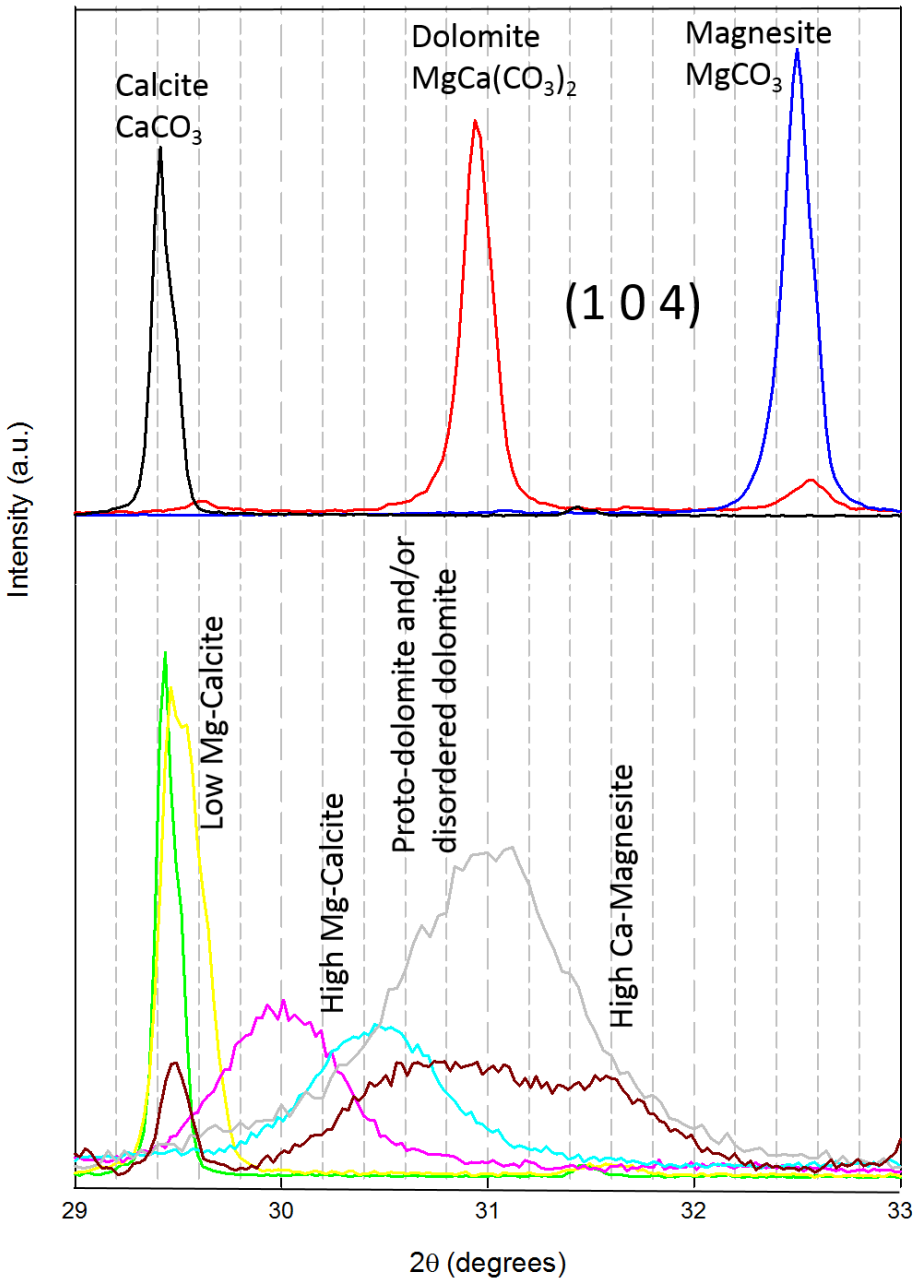


Figure 4. Lifetime of ACMC determined from time-resolved Raman measurements as a function of Mg molar fraction. Eight precipitation experiments were performed with initial alkaline solution (HCO_3^-/CO_3^{2-} molar ratio =1, and 0.5 M) at room temperature. ACC: amorphous calcium carbonate; ACMC: amorphous calcium-magnesium carbonate; AMC: amorphous magnesium carbonate.



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468 Figure 5. X-ray diffraction data showing the (104) reflection for calcite, dolomite and magnesite
469 references (13) and solids obtained for different initial Mg molar fraction in the solution: 0.05:
470 green; 0.2: yellow; 0.5: pink; 0.6: cyan; 0.75: gray; 0.9: dark red, corresponding to experiments 6-
471 10 in Table 1, respectively.

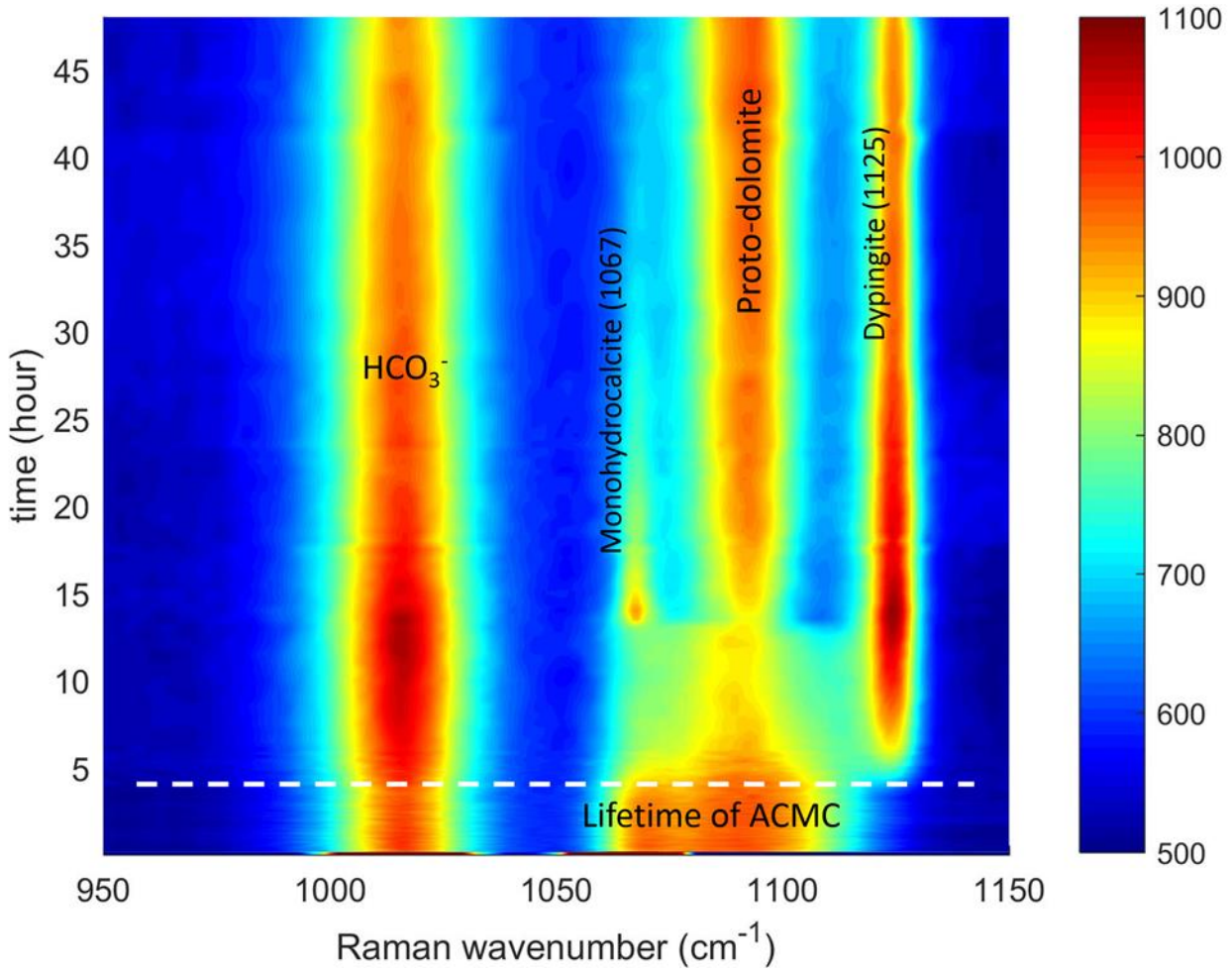
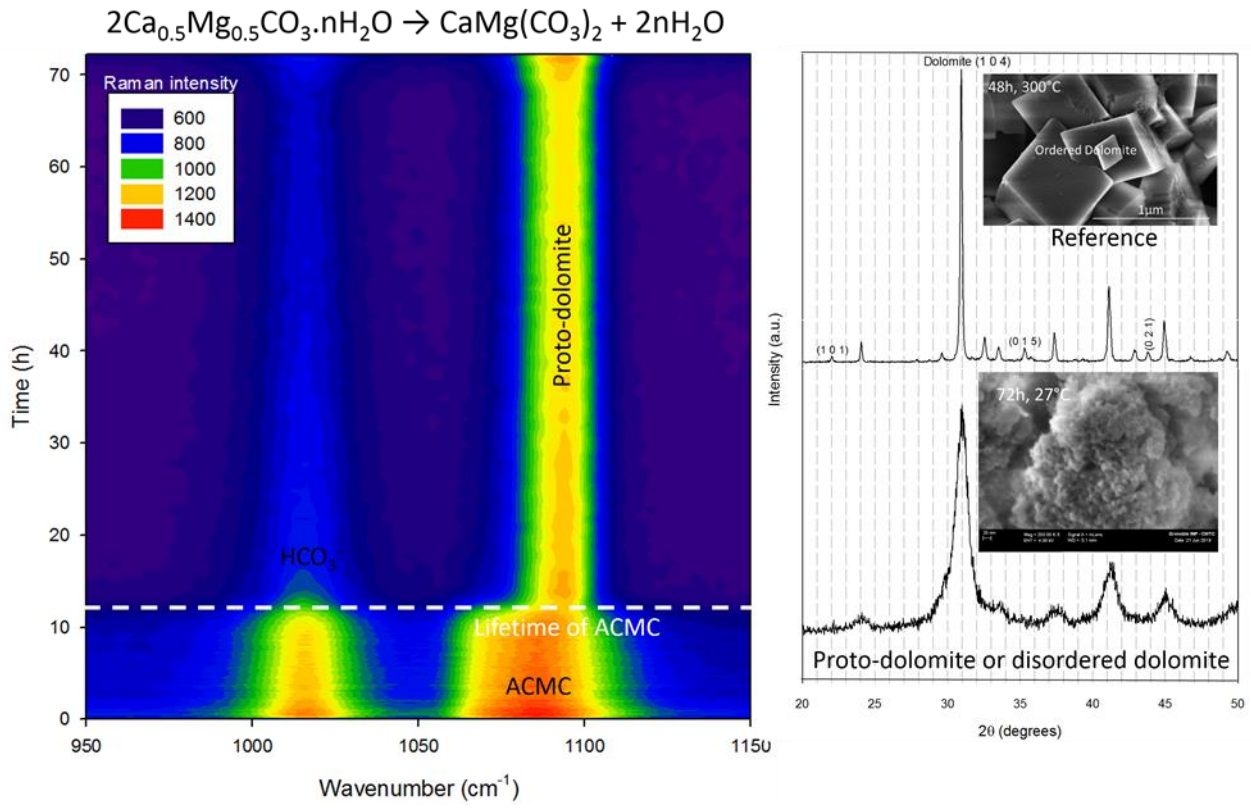


Figure 6. Time-lapse Raman spectroscopy monitoring of the formation of disordered dolomite from ACMC in experiment 10 (Table 1). Monohydrocalcite is a transient phase (Mg molar fraction of 0.9) and dypingite (hydrated Mg carbonate mineral: $Mg_5(CO_3)_4(OH)_2.5H_2O$) coexist with disordered dolomite until the end of experiment.

Amorphous calcium-magnesium carbonate (ACMC) accelerates dolomitization at room temperature under abiotic conditions

By German Montes-Hernandez, François Renard, Anne-Line Auzende, Nathaniel Findling

Table of Contents Graphic



Synopsis: The present study reports on specific abiotic conditions that allows the precipitation of disordered dolomite, high Mg-calcite and high Ca-magnesite at room temperature over time scales of hours to days. Here we show that an amorphous calcium magnesium carbonate (ACMC) phase accelerates dolomitization at room temperature.