Introduction

Amorphous calcium carbonate (ACC) is a highly soluble solid phase that commonly occurs as a precursor of crystalline CaCO₃ (e.g. calcite, aragonite) in modern biotic and abiotic precipitation environments. Its (trans)formation has been observed in calcifying organisms, microbial ferments from alkaline lakes, biofilms from hot springs and speleothems. ACC can include significant amounts of MgCO₃, which is known to play a significant role in its temporal stabilization. In this context, the transformation of amorphous magnesium carbonates (AMC) into crystalline Ca–Mg carbonate minerals is of particular interest as it represents an energetically favorable pathway for high magnesium-calcite (Mg-calcite) and disordered dolomite formation. However, the impact of Mg on the temporal stability and transformation behavior of AMC is not fully elucidated and a systematic study on the solubility of the AMC system is still missing.

The earlier experimental work of Brečević and Nielsen showed that Mg-free ACC is significantly more soluble than calcite. These authors also documented an ion activity product of ACC (log(IAPACC); “solubility” of ACC) of -6.39 ± 0.02 at 25 °C. More recently, Gebauer et al. found the solubility of ACC to be lower and reported log(IAPACC) values of -7.51 and -7.42 for ACC phases with “calcite-like” and “vaterite-like” short range order, respectively. To our knowledge the only published values so far for ACC are those obtained in our previous study (Purgstaller et al.), where we documented log(IAPACC) values ranging from -6.14 to -7.01 for ACC with ≤10 mol% Mg.

In the scope of an energetically oriented study on synthetic ACMCs, Radha et al. observed that ACC with low Mg content transforms faster into crystalline carbonates than ACC with high Mg content under atmospheric conditions. The longer stability of ACC with elevated Mg content has been attributed to the strong bond between structural water and Mg ions which retards the process of dehydration and subsequent phase transformation. However, inconsistent data are available for the water contents of ACC at distinct Mg concentrations. For example, the moles of water per unit formula Ca₄Mg₃₋ₓCO₃ are reported to vary from 0.81 to 1.75 for ACC with 45 ± 2 mol% Mg.

New findings indicate that the stability of Mg-free ACC under atmospheric conditions is significantly controlled by the availability of H₂O in the transformation environment. In this regard, Konrad et al. proposed that H₂O molecules are adsorbed by ACC promoting its transformation into calcite/vaterite via a dissolution and reprecipitation mechanism.
More recently, experimental studies on ACMC (trans)formation in an aqueous solution suggested that the chemical composition of the reactive solution (e.g. Mg/Ca ratio) significantly affects the temporal stability of ACMC and its subsequent transformation into the final product (Mg-calcite, monohydrocalcite etc.).\(^{24-27}\) However, the exact mechanisms controlling ACMC stability and transformation behavior is still under debate and further experimental work is needed to describe the interaction between solutions and ACMC phases.

The aim of the present work is to provide an advanced understanding about the “solubility product” of ACMC as a function of its Mg content in terms of an ion activity product at chemical steady-state conditions. Therefore, distinct function of its Mg content in terms of an ion activity product “understanding about the phases.

### Experimental section

#### Synthesis of amorphous calcium magnesium carbonates

Amorphous calcium magnesium carbonates with Mg contents ranging from 0 to 100 mol% Mg (hereafter referred to as ACMCs) were synthesized by a previously described method.\(^{23}\) Briefly, 80 mL of a 250 mM (Ca,Mg)Cl\(_2\) solution was poured into a beaker containing 80 mL of a 250 mM NaHCO\(_3\) solution. The reaction products were immediately separated from solution by a 0.2 μm cellulose filter using a suction filtration unit. Subsequently, the separated precipitate was washed with ultrapure water (Millipore Integral 3: 18.2 MΩ cm\(^{-1}\)) and transferred into a freeze dryer (Virtis Benchtop 3L). The freeze-dried ACMCs were stored in closed vials in a desiccator with silica gel (relative humidity = 3%). In total, 9 synthesis experiments were carried out, where the Mg content of the (Ca,Mg)Cl\(_2\) stock solution, \([\text{Mg}]_{\text{stock}} = ([\text{Mg}]/([\text{Ca}] + [\text{Mg}])) \times 100\), was systematically varied between 0 and 100 mol% (see Table 1). All solutions were prepared by analytical grade chemicals (CaCl\(_2\)-2H\(_2\)O, MgCl\(_2\)-6H\(_2\)O and Na\(_2\)CO\(_3\) from Roth) mixed with ultrapure water.

#### Experimental setup for solubility study

The chemical composition of the synthesized ACMC solids used for solubility investigations is shown in Table 1. Experiments were performed at 24.5 ± 0.5 °C in a 100 mL glass reactor containing 50 mL of a 100 mM NaHCO\(_3\) and 30 mM MgCl\(_2\) solution, stirred at 350 rpm. The pH of the solution was adjusted to 8.33 ± 0.03 by the addition of a 500 mM NaOH solution. At the onset of the experiment, 1.5 g of the synthetic ACMC sample was introduced into the reactor. The temporal evolution of the mineralogy was monitored using an in situ Raman probe immersed in the suspension. In order to follow the chemical composition of the solution and the solid phase, homogeneous sub-samples of the experimental solution/suspension (1.5 mL) were collected with a pipette at certain reaction times (Table S1†). The solids were separated from the solution by a 0.2 μm cellulose acetate filter using a suction filtration unit, washed with ethanol and dried in an oven at 40 °C.

#### Solid phase characterization

X-ray diffraction (XRD) patterns of the synthesized ACMCs (Fig. S1†) and of the ACMCs separated from the experimental solutions during the solubility study (not shown) were acquired using a PANalytical X’Pert Pro diffractometer (Co-K\(_{\alpha}\) radiation) at a 2θ range from 4 to 85° and a scan speed of 0.03° s\(^{-1}\). Thermogravimetric analyses (TGA) of freeze-dried ACMCs (Fig. S2†) were realized using a PerkinElmer STA8000. The samples were heated from 25 °C to 800 °C at 10 °C min\(^{-1}\) in the presence of 99.999% N\(_2\) atmosphere. Selected synthesized ACMCs were gold coated and imaged (Fig. S3†) using a scanning electron microscope (SEM, ZEISS DSM 982 Gemini). Time-resolved in situ Raman spectroscopy of the experimental solution/suspension was realized using a Raman RXN2™ analyzer from Kaiser Optical Systems with a Kaiser MR Probe head (quarter-inch immersion optic) and a 785 nm laser beam. In situ Raman spectra were collected every 60 s in the 100–1890 cm\(^{-1}\) region with a resolution of 1 cm\(^{-1}\).

### Table 1  Chemical composition of synthesized ACMCs

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Mg](_{\text{stock}})(^{a}) (mol%)</th>
<th>[Mg](_{\text{ACMC}})(^{b}) (mol%)</th>
<th>nH(<em>2)O(</em>{\text{f.d.}})(^{c}) (mol)</th>
<th>Sample composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACC</td>
<td>0</td>
<td>0</td>
<td>0.44</td>
<td>CaCO(_3)-0.44H(_2)O</td>
</tr>
<tr>
<td>ACMC_9</td>
<td>20.1</td>
<td>9.0</td>
<td>0.49</td>
<td>Ca(<em>{0.21})Mg(</em>{0.79})CO(_3)-0.49H(_2)O</td>
</tr>
<tr>
<td>ACMC_15</td>
<td>30.3</td>
<td>14.9</td>
<td>0.51</td>
<td>Ca(<em>{0.28})Mg(</em>{0.52})CO(_3)-0.51H(_2)O</td>
</tr>
<tr>
<td>ACMC_22</td>
<td>40.1</td>
<td>21.9</td>
<td>0.53</td>
<td>Ca(<em>{0.28})Mg(</em>{0.52})CO(_3)-0.53H(_2)O</td>
</tr>
<tr>
<td>ACMC_31</td>
<td>50.1</td>
<td>30.8</td>
<td>0.56</td>
<td>Ca(<em>{0.28})Mg(</em>{0.52})CO(_3)-0.56H(_2)O</td>
</tr>
<tr>
<td>ACMC_39</td>
<td>60.7</td>
<td>39.4</td>
<td>0.59</td>
<td>Ca(<em>{0.28})Mg(</em>{0.52})CO(_3)-0.59H(_2)O</td>
</tr>
<tr>
<td>ACMC_53</td>
<td>72.1</td>
<td>53.4</td>
<td>0.66</td>
<td>Ca(<em>{0.28})Mg(</em>{0.72})CO(_3)-0.66H(_2)O</td>
</tr>
<tr>
<td>ACMC_80</td>
<td>89.1</td>
<td>80.0</td>
<td>0.71</td>
<td>Ca(<em>{0.28})Mg(</em>{0.80})CO(_3)-0.71H(_2)O</td>
</tr>
<tr>
<td>AMC</td>
<td>100</td>
<td>100</td>
<td>0.79</td>
<td>MgCO(_3)-0.79H(_2)O</td>
</tr>
</tbody>
</table>

\(^{a}\)Mg content of the stock solution in mol%. \(^{b}\)Mg content of the ACMC solid in mol%. \(^{c}\)Moles of water per formula unit Ca\(_{x}\)Mg\(_{1-x}\)CO\(_3\), where \((1-x) = [\text{Mg}]_{\text{ACMC}}/100\).
Chemical composition of the experimental solutions and solids

During the experimental run, the pH of the experimental solution was measured with a SI Analytics Silamid® gel electrode, which was calibrated against NIST buffer standard solutions at pH 4.01 and 7.00. The total alkalinity of the experimental solutions was measured by a Schott TitroLine alpha plus titrator using a 10 mM HCl solution with a precision of ±2%. The aqueous Ca, Mg and Na concentrations of the (Ca,Mg)Cl₂ stock solutions, of the experimental solutions and of the solids (digested in 6% HNO₃) were determined using inductively coupled plasma optical emission spectrometry (Perkin Elmer Optima 8300 DV). The analytical error was <±3% for Ca and Mg analyses and <±5% for Na analyses.

Aqueous speciation and ion activity product calculation

The aqueous speciation of the experimental solutions was calculated at 25 °C using the PHREEQC software together with its minteq.v4 database. For the ionic strength of our experiments (i.e. 0.17 ± 0.02 M; Table S2†), the calculation of individual ion activity coefficients for the solute species is based on the Davis equation.²⁸,²⁹ The activities (a) of Ca²⁺, Mg²⁺ and CO₃²⁻ ions in solution and the stoichiometry of the digested CaMg₅+₄CO₃-nH₂O solids (where (1−x) = [Mg]ACMC/100) were used to calculate ion activity products for the amorphous calcium magnesium carbonates (IAPACMC) as a function of experimental time according to equation

\[
\text{IAP}_{\text{ACMC}} = (a\text{Ca}^2+)^{(a\text{Mg}^2+)\frac{1}{x}}(a\text{CO}_3^2-)^{(a\text{H}_2\text{O})}^n \quad (1)
\]

In the present solubility experiments, the aH₂O values of the experimental solutions remained constant at 0.955 ± 0.004. Thus, for the calculation of the IAP_{ACMC}, the aH₂O was assumed to be unity.

Results and discussion

Characterization of synthesized ACMC material

The measured Mg contents of the stock solutions, [Mg]_{stock}, and of the synthesized ACMC, [Mg]_{ACMC}, are reported in Table 1 and displayed in Fig. 1. The results reveal a preferential enrichment of the amorphous solid in Ca and are in good agreement with those of Radha et al.,²⁰ who synthesized a set of amorphous CaMg₅+₄CO₃-nH₂O solids by batch method using (Ca,Mg)Cl₂ and Na₂CO₃ solutions (Fig. 1). The preferential enrichment of the amorphous phase in Ca likely stems from the strong free energy of hydration of the Mg²⁺ ion compared to Ca²⁺.²⁰,²⁰,²⁰ The strongly hydrated aqueous Mg²⁺ is a well-known limitation in the formation of anhydrous crystalline Ca–Mg-carbonates, such as Mg-calcite, dolomite and magnesite, at ambient temperatures.³¹ Instead, hydrous crystalline Mg-carbonates (e.g. hydromagnesite)³² and hydrous ACMC phases³³,³⁴ tend to precipitate.

Representative thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves of the synthesized ACMCs are presented in Fig. S2 (ESI†). The DSC curve of ACC (Ca endmember of ACMC) shows an endothermic peak at 120 °C, a sharp exothermic peak at 340 °C and a second endothermic peak at 731 °C (Fig. S2A†). These DSC features have been earlier shown to be associated with the enthalpies of dehydration, crystallization and decomposition of ACC.²⁰,³⁴ In contrast to ACC, AMC (Mg endmember of ACMC) decomposes without crystallization, as it is indicated by the absence of the sharp exothermic peak in the DSC curve (Fig. S2F†). The weight loss curves of ACC and AMC show two weight loss steps (Fig. S2A and F†), where the first step is due to the loss of structural water and the second step due to the decomposition of CaCO₃ and MgCO₃ to CaO, MgO and CO₂.²⁰,³⁵ After ACC dehydration, the TGA curve achieves a plateau in heating before CaCO₃ decomposes to CaO and CO₂ at near 600 °C (Fig. S2A†). In contrast, AMC shows a continuous drop of the TGA curve (without a plateau) for the same temperature range, which indicates that AMC dehydration and decomposition may overlap (Fig. S2F†). Based on our TGA data we suggest that AMC decomposition occurs at around 275 °C, as it is indicated by the inflection point of the weight loss curve (Fig. S2F†). In contrast to the pure endmembers, the ACMCs show multistep weight loss curves (Fig. S2B–E†). These trends are in accordance with the findings of Radha et al.,²⁰ who associated these features with multistep carbonate decomposition caused by (i) an initial heterogeneous amorphous material or (ii) thermally induced phase segregation during the heating process.

The water contents of the synthetic ACMCs were calculated from the weight losses between 25 and 275 °C. Above this temperature, mass loss might occur due to the decomposition of MgCO₃ to MgO, as it is suggested by the TGA curve.
of AMC (Fig. S2f†). The moles of water per unit formula \( \text{Ca}_x\text{Mg}_{1-x}\text{CO}_3 \) \((n_{H_2O,p.f.})\) determined by thermal analyses vary between 0.4 for ACC and 0.8 for AMC (Table 1, Fig. 2). As it can be seen in Fig. 2, the water content determined for ACC is in excellent agreement with those reported by Schmidt et al.\textsuperscript{35} and Konrad et al.\textsuperscript{23} Overall, thermal analyses revealed a linear correlation between the \( n_{H_2O,p.f.} \) and the \([\text{Mg}]_{\text{ACMC}}\) according to the equation

\[
n_{H_2O,p.f.} = 0.0034 \pm 0.0002[\text{Mg}]_{\text{ACMC}} + 0.4574 \pm 0.0124 \quad (2)
\]

where \( R^2 = 0.99 \). Previous experimental work documented significantly higher \( n_{H_2O,p.f.} \) values for ACMCs (Fig. 2).\textsuperscript{20} These differences probably originate from different drying methods (freeze-dryer \textit{versus} vacuum oven). In the study of Radha et al.,\textsuperscript{20} the loosely bound physisorbed \( H_2O \) on the ACMC particles were probably not completely removed by the vacuum oven prior to thermogravimetric analyses. However, our findings are in good agreement with the results of Lin et al.,\textsuperscript{21} who reported \( n_{H_2O,p.f.} \) values of 0.6, 0.8 and 0.9 for ACMC with 17, 44 and 100 mol% Mg (Fig. 2). In the latter case, the synthesized ACMC samples were washed with ethanol and lyophilized prior to TGA-analysis.

Earlier models on the structure of Mg-free ACC suggested the presence of partially mobile water in the amorphous phase.\textsuperscript{36,37} In this context, ACC has been described to consist of a porous Ca-framework with interconnected channels formed by water molecules and carbonate ions, allowing water mobility to a certain extent.\textsuperscript{38} More recently, Jensen et al.\textsuperscript{39} has shown that water molecules are mainly coordinated to Ca and carbonate ions and less frequently to other water molecules, ruling out the scenario of hydrogen-bonded networks. This is consistent with the NMR-results of Lin et al.\textsuperscript{21} who concluded that the coordination shell of Mg in ACMC contains at least one water molecule. Indeed, in the present study, the \( n_{H_2O,p.f.} \) increases as a function of the Mg content (Fig. 2), indicating that partially hydrated Mg is incorporated into the amorphous solid. Our obtained results however suggest that the \( n_{H_2O,p.f.} \) values for ACMC are significantly lower than previously reported.\textsuperscript{20,22}
Exchange of ions between ACMC and aqueous solution

After the synthesized ACMCs were dispersed in the MgCl2–NaHCO3 buffered solutions, the collected in situ Raman spectra of the suspensions revealed the presence of a broad CO3\(^{2-}\) symmetric stretch (\(v_1\) band) of ACMC at 1080–1098 cm\(^{-1}\) (e.g. experiments ACMC\(_9\) and ACMC\(_{53}\) in Fig. 3). The \(v_1\) band shows systematic shifts in peak position (Table 2) and peak broadening due to different Mg contents of the ACMCs. These features arise from changes in the metal–oxygen bond length due to the presence of shorter Mg–O bonds compared to those of Ca–O in the amorphous solid.\(^\text{15,40}\) The intensities of the \(v_1\) bands of the ACMC phases remained constant for experimental times ranging from 5 to 85 min (referred to as Time\(_{ACMC}\) in Table 2). After this time interval, the \(v_1\) bands of the ACMCs decreased in intensity, while the \(v_1\) bands of crystalline hydrous and/or anhydrous Ca–Mg carbonates (Mg-calciite, monohydrocalcite and/or nesquehonite) evolved (not shown here). Thus, Time\(_{ACMC}\) denotes the time interval in which the ACMC was stable in the experimental solution (Table 2). Note that, the in situ Raman observations were confirmed by ex situ XRD analyses of the collected solid samples.

Although, Time\(_{ACMC}\) increased as a function of the Mg content in experiments conducted with ACMCs containing \(\leq \)22 mol% Mg, a reverse trend was obtained in experiments with ACMCs containing >22 mol% (Table 2). These observations imply that the temporal stability of ACMC in a solution is not strictly controlled by its primary Mg content. In contrast, the obtained data revealed changes in the chemical composition of the reacting ACMC and the experimental solution which might play a crucial role in the temporal stabilization of the precursor phase and its subsequent transformation into distinct crystalline calcium magnesium carbonates.

The chemical composition of the experimental solutions and solids collected during Time\(_{ACMC}\) can be found in Table S1.\(^\dagger\) Exemplarily, the temporal evolution of the chemical composition of the solutions and solids in experiments conducted with ACMC\(_{53}\) (53 mol% Mg) and with ACMC\(_9\) (9 mol% Mg) is illustrated in Fig. 4A–C. The obtained results documented a significant change in the chemical composition of the solids and experimental solutions within about 10 s after the ACMCs were dispersed into the MgCl2–NaHCO3 solutions. In each experiment, chemical steady state conditions were attained at a reaction time of about 2 min (Fig. 4A–C; Table S1\(^\dagger\)). The fast reaction between the amorphous solid and the solution can be explained by the nano-porous structured ACMC material consisting of large and highly reactive surface areas (Fig. S3\(^\dagger\)). The shifts in pH and alkalinity of the MgCl2–NaHCO3 buffered solution increase with increasing Mg content of the synthesized ACMCs (Fig. 4D). For example, dispersion of ACMC with 9 mol% Mg (ACMC\(_9\)) yields a slight shift in pH and alkalinity from 8.3 to 8.5 and 104 to 107 mM, respectively, whereas for ACMC with 53 mol% Mg (ACMC\(_{53}\)) a significant shift in pH to 9.1 and alkalinity to 143 mM was observed (Fig. 4A and B). This indicates that for attainment of chemical equilibrium between solid and solution, larger amounts of ACMC are required to dissolve in the experiment with ACMC\(_{53}\) (53 mol% Mg) compared to the experiment conducted with ACMC\(_9\) (9 mol% Mg).

The results revealed two distinctive trends of Mg and Ca exchange between ACMCs and the solution, depending on the Mg concentrations of synthesized ACMCs: (i) in experiments conducted with ACMCs containing \(\leq 15\) mol% Mg a net release of Ca into the solution together with an uptake of Mg from the solution into the solid is observed, which results in ACMCs with slightly higher Mg contents compared to the synthesized ACMC (e.g. ACMC\(_{9}\) in Fig. 4B and C; Table S1\(^\dagger\)). (ii) In contrast, in experiments conducted with ACMCs containing >20 mol% Mg a net release of Mg into the experimental solution and lower [Mg]ACMC values compared to the synthesized ACMCs were observed (e.g. ACMC\(_{53}\) in Fig. 4B and C; Table S1\(^\dagger\)). These observations suggest a dynamic exchange of Me\(^{2+}\) (Ca\(^{2+}\) and Mg\(^{2+}\)) ions between the amorphous solid and the experimental solution. It is likely that the total availability of Me\(^{2+}\) (Ca\(^{2+}\) and Mg\(^{2+}\)) and CO3\(^{2-}\) ions in the prevailing solution affects the formation of distinct crystalline calcium magnesium carbonates and the temporal stability of the ACMC precursor in solution. Evidence for that also comes from a recent study on ACC transformation.
showing prolonged stability of Mg-free ACC of up to ~11 hours in high concentrated MgCl₂ solutions (up to 1000 mM). It was concluded that strong aquocomplex formation of the dissolved carbonate molecule with Mg²⁺ ions retarded mineral formation and increased the stability of ACC in solution.

**Solubility approach**

The experimental solution in all experimental runs achieved chemical steady state conditions after 2 min of reaction time. These conditions remained steady during the time interval in which solid analyses (Raman spectra and XRD pattern) documented the stability of ACMC in the aqueous phase (TimeACMC in Table 2). Thus, speciation calculations were performed at reaction times ≥2 min and ≤TimeACMC. The input data for speciation calculations using PHREEQC modeling and selected output data are summarized in Table S2.† The results showed that the experimental solutions exhibit internal partial pressures of CO₂ ranging from 10⁻¹.₈ to 10⁻².₉ atmospheres (see pCO₂,g in Table S2†). As such, the pCO₂ pressure of the experimental solutions is higher compared to the atmosphere and thus CO₂ is likely degassing from the experimental solutions. However, in context of the present study, samples of the suspensions were collected during a short time interval (<45 min) in which pCO₂,g, pH and alkalinity values were monitored to be constant within the analytical precision (Table S2†). The shifts in pH and alkalinity increase with increasing [Mg]ACMC.

![Fig. 4 Temporal evolution of (A) pH and alkalinity concentration, (B) aqueous Ca and Mg concentration of the experimental solution, [Ca]aq and [Mg]aq, and (C) Mg content of ACMC solid, [Mg]ACMC, after synthesized ACMC solids were dispersed into the MgCl₂-NaHCO₃ solutions. Exemplarily the data for ACMC_53 and ACMC_9 are shown, where the experimental solution achieves constant chemical composition after 2 min of reaction time. Note that chemical data obtained at >2 min were used for estimating the ion activity products of the distinct ACMCs according to eqn (1) (Table 2). (D) Average alkalinity concentration versus pH values of the experimental solution at chemical steady state conditions (>2 min, see Table S2†). The shifts in pH and alkalinity increase with increasing [Mg]ACMC.](image-url)
log(IAPACMC) values of $-6.19 \pm 0.02$ and $-6.13 \pm 0.02$ for ACMCs with 2 and 10 mol% Mg, respectively, lay within the range of $-6.14 \pm 0.04$ for the low-Mg ACMC reported by Purgstaller et al.\textsuperscript{15} In this respect, it has to be noted that the solids collected in the present experiments were filtered through 0.2 μm membranes. Although the separation yields aggregated spherical nanoparticles (see Fig. S4†) and the solutions were visibly clear after filtration, the presence of ACMC individuals in the filtered solutions cannot be completely ruled out at this stage. Partially remaining ACMC in the solution would slightly increase the measured ion concentrations. However, the linear fit of the herein obtained log(IAPACMC) values is in good agreement with the log(IAPACC) value from Brečević and Nielsen,\textsuperscript{18} who determined the solubility of ACC by titration of water into the suspension without physical separation of the solid phase, indicating the effect of ACMC individuals in the filtered solutions to be negligibly small. The positive correlation between the log(IAPACMC) and [Mg]ACMC values obtained from this study, from Brečević and Nielsen\textsuperscript{18} and Purgstaller et al.\textsuperscript{15} can be described by the expression:

$$\log(\text{IAP}_{\text{ACMC}}) = 0.0174 \pm 0.0013 \times [\text{Mg}]_{\text{ACMC}} - 6.278 \pm 0.046 \quad (3)$$

where $R^2 = 0.98$.

Note here that the calculation of the IAPACMC values is based on the assumption that the ACMCs are amorphous Ca–Mg carbonate solid-solutions. However, a previous study on synthetic ACMCs by Radha et al.\textsuperscript{26} points towards a phase separation of ACMC solids with $\geq 47$ mol% Mg. It has been suggested that ACMC with $\geq 47$ mol% are composed by a mixture of a material nearly pure AMC with a material nearly 50 mol% Mg. However, such heterogeneity may also be introduced during the heating of the ACMC solids during thermogravimetric analyses (thermally driven MgCO$_3$ segregation).\textsuperscript{20} More recently, the $^{13}$C-NMR measurements on ACMCs by Yang et al.\textsuperscript{41} showed two types of carbonate ions in synthetic ACMC solids, whose short-range orders are identical to those of ACC and AMC. Based on these observations, Yang et al.\textsuperscript{41} suggested that the ACMC solids comprise a homogeneous mixture of the nano-clusters of ACC and AMC. In order to test the validity of the Ca–Mg carbonate solid-solution system, we calculated the IAP values of the experimental solutions at chemical steady state conditions with respect to the endmembers ACC and AMC according to the equations IAP$_{\text{ACC}} = (a\text{Ca}^{2+})(a\text{CO}_3^{2-})$ and IAP$_{\text{AMC}} = (a\text{Mg}^{2+})(a\text{CO}_3^{2-})$, respectively. As the Mg content of the solid increases from 2 to 78 mol% Mg, the log(IAP$_{\text{AMC}}$) and log(IAP$_{\text{ACC}}$) values change from $-5.4$ to $-4.5$ and $-6.2$ to $-6.5$, respectively. If the ACMCs consist of an ideal two phase mixture of ACC and AMC, we would expect constant log(IAP$_{\text{ACMC}}$) and log(IAP$_{\text{AMC}}$) in all experiments, irrespective of the Mg content of the solid initially introduced into the reactor. As such, the presence of discrete AMC and ACC phases in the ACMC solid can be excluded. In contrast, the obtained linear correlation between the average log(IAP$_{\text{ACMC}}$) and [Mg]ACMC values (see Fig. 5) points toward the presence of an homogeneous single phase in each experimental run.

It is also worth pointing out that the $^{13}$C-NMR measurements on ACMCs by Yang et al.\textsuperscript{41} indicated the existence of bicarbonate species embedded in the matrix formed by ACC and AMC. Moreover, based on the Mg isotope composition of Mg-ACCs, Mavromatis et al.\textsuperscript{42} suggested that during the very fast precipitation of the amorphous phase from a highly supersaturated solution, MgHCO$_3^-$ and MgCO$_3^{0}$ species might be directly incorporated into the precipitating solid together with Mg(H$_2$O)$_6^{2+}$. If this holds true, the activities of Ca and Mg carbonate species have to be considered in the calculation of the IAP$_{\text{ACMC}}$ values. For this purpose, however, a more detailed characterization of the structure of ACMC is required, which should be in the focus of future studies.

Although the solubility of ACC is about two orders of magnitude higher than that of calcite, the dependence of IAP$_{\text{AMC}}$ on the Mg content of the solid (Fig. 5) is somehow similar to that observed for the Mg-calcite system.\textsuperscript{43} Indeed experimental work conducted during the last 3 decades documents an overall increase in solubility of Mg-bearing calcites with increasing Mg content.\textsuperscript{13–45} Note, that significant discrepancies exist between reported solubility values of Mg-calcites, which were attributed to differences in mineral source and structure (biogenic or synthetic solids) as well as different experimental setups.\textsuperscript{43–45} The change in calcite solubility as Mg is incorporated in its structure can likely be attributed to the distortion of the octahedral site in calcite. The substitution of Ca by Mg in the calcite structure results in a decrease of interatomic metal–O distances and shortening of the c-axis.\textsuperscript{46,47} Consequently, Ca, C and O atoms exhibit large thermal motions which cause periodic stretching and weakening of the bonds in the structure.\textsuperscript{46}
In contrast to the crystalline Ca-Mg carbonate system, amorphous carbonates exhibit no order beyond 1.5 nm. In situ Raman results from the present work and from previous studies however showed that the substitution of Ca$^{2+}$ by Mg$^{2+}$ changes the average metal-oxygen bond lengths in the amorphous phase, which might change its short-range order and solubility. Moreover, the linear relationship between the IAP$_{ACMC}$ and [Mg]$_{ACMC}$ values (Fig. 1) as well as of the [Mg]$_{ACMC}$ and $\delta$H$_2$O$_{ref}$ values (Fig. 2) suggests that the increase in solubility of ACMC as a function of the Mg content is attributed to the increasing water content in the structure of ACMC. A similar behavior has been observed for the hydrated crystalline Mg-carbonate system, where the more hydrated lansfordite (MgCO$_3$·5H$_2$O) exhibits a higher solubility than the less hydrated nesquehonite (MgCO$_3$·3H$_2$O) at 25 °C.

Conclusions

The experimental results indicated a fast exchange of ions between the synthesized amorphous ACMC solids and the aqueous solutions, which is likely stimulated by the large surface area of the nano-porous ACMC solid. Chemical steady state conditions between ACMC and corresponding solution were reached within 2 min of reaction time. The calculated ion activity products documented that the solubility of ACMC increases as a function of the Mg content. This feature is probably linked to the increasing water content and changes in short-range order, as Ca is substituted by Mg in the ACMC structure. Overall, the results reveal a high sensitivity of the ACMC phase in respect to the chemical composition (e.g. magnesium concentration) of the aqueous environment. The exchange of ions between the amorphous solid and the solution causes changes in the chemical composition of the solution (e.g. pH and alkalinity) and that of the solid (e.g. Mg content). This ion exchange probably affects the temporal stability of the amorphous precursor in solution and its subsequent transformation into distinct crystalline calcium magnesium carbonates. Essentially, our findings suggest that the Mg content of ACMC is not the governing parameter for its temporal stability in solution. In contrast, the chemical composition of both the solution and the amorphous solid, have to be taken into account as a potential parameter controlling ACMC stability and transformation behavior. For example, in a closed system the chemistry of the fluid (e.g. calcifying fluid in the biomineralisation space) would influence the temporal stability of the amorphous precursor and its transformation pathway to the final crystalline carbonate mineral.

Conflicts of interest

There are no conflicts to declare.

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