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## Solid-State Phase Transformation and Self-Assembly of Amorphous Nanoparticles into Higher-Order Mineral Structures

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1                   **Title: Solid-state phase transformation and self-assembly of**  
2                   **amorphous nanoparticles into higher-order mineral structures**

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24        **Abstract:**

25        Materials science has been informed by nonclassical pathways to crystallization based  
26 on biological processes to fabricate damage-tolerant composite materials. Various  
27 biomineralizing taxa, such as stony corals, deposit metastable, magnesium-rich, amorphous  
28 calcium carbonate nanoparticles that further assemble and transform into higher-order mineral  
29 structures. Here we examine a similar process in abiogenic conditions using synthetic,  
30 amorphous calcium magnesium carbonate nanoparticles. Applying a combination of high-  
31 resolution imaging and *in situ* solid-state nuclear magnetic resonance spectroscopy, we reveal  
32 the underlying mechanism of the solid-state phase transformation of these amorphous  
33 nanoparticles into crystals under aqueous conditions. These amorphous nanoparticles are  
34 covered by a hydration shell of bound water molecules. Fast chemical exchanges occur: the  
35 hydrogens present within the nanoparticles exchange with the hydrogens from the surface-  
36 bound H<sub>2</sub>O molecules which, in turn, exchange with the hydrogens of the free H<sub>2</sub>O molecule  
37 of the surrounding aqueous medium. This cascade of chemical exchanges is associated with  
38 an enhanced mobility of the ions/molecules that compose the nanoparticles which, in turn,  
39 allow for their rearrangement into crystalline domains via solid-state transformation.  
40 Concurrently, the starting amorphous nanoparticles aggregate, and form ordered mineral  
41 structures through crystal growth by particle attachment. Sphere-like aggregates and spindle-  
42 shaped structures were respectively formed from relatively high or low weights per volume of  
43 the same starting amorphous nanoparticles. These results offer promising prospects for  
44 exerting control over such a non-classical pathway to crystallization to design mineral  
45 structures that could not be achieved through classical ion-by-ion growth.

46 **Main text:**

47 Exerting control over non-classical pathways to crystallization to direct the growth,  
48 polymorphism, and self-assembly of inorganic nanoparticles into higher-order structures is an  
49 important goal of materials sciences, writ large <sup>1-9</sup>. To achieve this, the dominant strategy is to  
50 govern the initial nucleation stage in a multitude of precipitation reactions occurring far from  
51 thermodynamic equilibrium <sup>10</sup>. These reactions share the common purpose of converting  
52 solution precursors into solid mineral materials <sup>11</sup> and use various approaches to overcome the  
53 free-energy barrier to nucleation. In the case of calcium carbonate and calcium phosphate  
54 minerals, these approaches were initially implemented to uncover the biomineralization  
55 processes being used by marine calcifiers and vertebrates to allow support <sup>12</sup>, mastication <sup>13</sup>,  
56 defense <sup>14</sup>, attack <sup>15</sup>, or optical <sup>16</sup> functions. They span from the utilization of (i)  
57 supersaturated concentrations <sup>17-19</sup> sometimes combined with (ii) confinement effects <sup>20-23</sup>,  
58 the use of (iii) templates for epitaxial growth <sup>24</sup>, and of (iv) various types of mineralization-  
59 directing agents such as synthetic polyelectrolytes <sup>25-29</sup>, proteins <sup>30-34</sup> and amino acids <sup>35-37</sup>.  
60 The future exploitation of stable pre-nucleation clusters <sup>38-40</sup> may offer additional prospects  
61 for exerting some control over various non-classical crystallization processes <sup>41,42</sup>.

62 Some of the above mentioned approaches were successfully applied to design and  
63 manufacture different nature-inspired inorganic-organic composite materials <sup>43-48</sup>; however,  
64 they suffer from two main limitations. First, they often lead to final materials which are very  
65 limited in terms of size (generally not exceeding a few millimeters along one dimension).  
66 Second, the level of mineralization does not reach those of their natural analogues, principally  
67 bone and nacre. The latter is the main limitation that prevents the fabrication of high strength  
68 materials. Here we consider an alternative strategy that overcome these limitations and allow  
69 the manufacturing of novel materials. Future approaches likely will skip over the initial  
70 nucleation stage on which little control can be exercised, and focus on the conversion of solid,

71 metastable amorphous nanoparticles into their crystalline counterparts. Such metastable  
72 amorphous nanoparticles that assemble and transform into higher-order, hierarchical mineral  
73 structures have been observed across various biomineralizing taxa<sup>49–59</sup>, but their use in  
74 synthetic systems remains extremely limited<sup>60–64</sup>. Here we used Amorphous Calcium  
75 Magnesium Carbonate (ACMC) nanoparticles as models since most biogenic deposits of  
76 amorphous CaCO<sub>3</sub> contain Mg<sup>2+</sup> ions<sup>49,65,66</sup>. Especially, we monitored their pathway to  
77 crystallization in wet conditions to understand their potential use in the development of novel  
78 materials. To this end, we applied a combination of high-resolution imaging and *in situ* solid-  
79 state nuclear magnetic resonance (NMR) spectroscopy. In particular, the latter technique  
80 provides unprecedented atomic-scale insights into the mechanism of phase transformation of  
81 these amorphous nanoparticles over time.

## 82 **Chemical structure and composition**

83 A number of physical characterization techniques were applied to assess the structure  
84 and composition of a <sup>13</sup>C-labelled (98 atom% <sup>13</sup>C) Amorphous Calcium Magnesium  
85 Carbonate (ACMC) sample. This sample was first studied in dry conditions. Powder X-ray  
86 diffraction observations confirm that this is a non-crystalline solid given the absence of Bragg  
87 reflections (**Fig. S1**). According to TGA measurements (**Fig. S2**), the mass fraction of the  
88 hydrous species associated with the particles of ACMC is in the range of 22 to 26 wt. %. An  
89 average atomic Ca/Mg ratio  $\approx 4.0$  was estimated using energy-dispersive X-ray spectroscopy  
90 (EDS). As such, the atom% of Mg in ACMC [defined as  $\text{Mg}/(\text{Ca} + \text{Mg}) \times 100$ ] is about 20.0.  
91 This is similar to the value found in a number of biogenic deposits of amorphous calcium  
92 carbonate such as those in the cuticles and gastroliths in crustaceans, along with those in the  
93 spicules in cnidarians<sup>65</sup>. Scanning Helium Ion Microscopy (SHIM) observations show that  
94 ACMC is in the form of spherical nanosized particles with a diameter of about 60 to 90 nm

95 **(Fig. 1A)**. These features resemble those of biogenic, magnesium-rich, amorphous calcium  
96 carbonate particles present at early stages of coral biomineralization **(Fig. 1B)**.

97 Solid-state Nuclear Magnetic Resonance (ssNMR) spectroscopy was applied to  
98 investigate the carbon and hydrogen chemical environments of ACMC. One dimensional (1D)  
99  $\{^1\text{H}\}^{13}\text{C}$  cross polarization (CP) (solid lines), and  $^{13}\text{C}$  single-pulse (SP) (dotted lines) magic  
100 angle spinning (MAS) ssNMR spectra of ACMC are shown in **Fig. S3**. Both spectra are in the  
101 form of a single, symmetric resonance whose carbon chemical shift [ $\delta(^{13}\text{C}) = 168.2$  ppm], full  
102 width at half maximum (FWHM = 3.9 ppm) and Gaussian lineshape are characteristic of  
103 carbonate ions ( $\text{CO}_3^{2-}$ ) present in amorphous environments. This carbon chemical shift is  
104 similar with that of calcite<sup>67</sup> which suggests that the present sample may be considered as a  
105 proto-calcite amorphous calcium carbonate<sup>68</sup>. Further, the resonance in the  $^{13}\text{C}$  SP spectrum  
106 is identical with the one in the  $\{^1\text{H}\}^{13}\text{C}$  CP spectrum in terms of lineshape and linewidth:  
107  $\delta(^{13}\text{C}) = 168.2$  ppm and full FWHM = 3.9 ppm. This statement stands true regardless the CP  
108 contact time ( $t_{\text{CP}}$ ) as shown in **Fig. S4** where  $t_{\text{CP}}$  was varied from 0.2 to 10 ms. The  $\{^1\text{H}\}^{13}\text{C}$   
109 CP spectrum selectively exposes  $^{13}\text{C}$  nuclei nearby  $^1\text{H}$  nuclei that belong to different rigid  
110 hydrogen-bearing ions/molecules, whereas the  $^{13}\text{C}$  SP spectrum reveals all  $^{13}\text{C}$  nuclei since it  
111 was recorded in quantitative conditions. Indeed, a long relaxation delay (RD) of 600 seconds  
112 was chosen to allow for full relaxation of the longitudinal magnetization. According to their  
113 similarity in terms of lineshape and linewidth, the  $\{^1\text{H}\}^{13}\text{C}$  CP spectrum exposes similar  $^{13}\text{C}$   
114 nuclei as those observed upon direct excitation in the quantitative  $^{13}\text{C}$  SP spectrum. These  
115 observations provide important structural and chemical information. First, this is evidence that  
116 the rigid hydrogen-bearing ions/molecules are homogeneously distributed throughout the  
117 amorphous calcium carbonate nanoparticles; and a similar conclusion was previously reached  
118 by others<sup>68,69</sup>. Second, this also rules out the presence of bicarbonate ions ( $\text{HCO}_3^-$ ) given the

119 absence of a distinct upfield signal at short contact time (expected in the range of  $\delta(^{13}\text{C}) \approx$   
120 155-165 ppm<sup>67,70,71</sup>).

121 To reveal the nature of the hydrogen-bearing ions/molecules present in the amorphous  
122 nanoparticles, further  $^1\text{H}$ -based ssNMR experiments were applied. The 1D  $^1\text{H}$  direct  
123 excitation (DE) MAS ssNMR spectrum of ACMC is shown in **Fig. S5A**. However, this  
124 spectrum exposes a broad signal centered around  $\delta(^1\text{H}) = 4.9$  ppm along with two narrow  
125 resonances at  $\delta(^1\text{H}) = 1.2$  and 3.6 ppm respectively, respectively due to the presence of water  
126 and mobile ethanol molecules weakly adsorbed onto the surface of the particles. The latter  
127 originate from anhydrous ethanol that was used post-precipitation to allow preservation of the  
128 solid as an amorphous phase upon storage. As an alternative, we recorded a 1D  $\{^1\text{H}-^{13}\text{C}\}^1\text{H}$   
129 double cross polarization (CP) MAS ssNMR experiment (**Fig. S5B**). It gives rise to a  $^{13}\text{C}$ -  
130 filtered  $^1\text{H}$  spectrum whose signals correspond to structural hydrogen-bearing ions/molecules  
131 present within the amorphous nanoparticles. This approach was successfully used to  
132 investigate the hydrogen-bearing ions/molecules present in bone mineral in intact bone tissue  
133<sup>72</sup>. Here two main resonances are clearly observable. According to their respective chemical  
134 shift, they reflect the presence of hydroxyl ions ( $\text{OH}^-$ ) [observable at  $\delta(^1\text{H}) = 1.0$  ppm<sup>73,74</sup>]  
135 and structural water molecules [observable at  $\delta(^1\text{H}) = 5.6$  ppm]. In addition, the apparent  
136 dissymmetry of the main water resonance suggests the presence of a broad downfield signal  
137 that spreads up to  $\delta(^1\text{H}) \approx 13$  ppm (black arrow). Further, the fact that the  $^{13}\text{C}$ -filtered  $^1\text{H}$   
138 spectrum cannot be satisfactorily fitted with only two peaks at  $\delta(^1\text{H}) = 1.0$  ppm ( $\text{OH}^-$ ) and 5.6  
139 ppm ( $\text{H}_2\text{O}$ ) confirms the presence of this additional broad signal (**Fig. S6A**). In contrast, the  
140 same  $^{13}\text{C}$ -filtered  $^1\text{H}$  spectrum can be properly fitted with three peaks at  $\delta(^1\text{H}) = 1.0$  ppm ( $\text{OH}^-$ )  
141 ), 5.6 ppm ( $\text{H}_2\text{O}$ ) and 7.0 ppm (**Fig. S6B**). The use of a single peak centered at  $\delta(^1\text{H}) = 7.0$   
142 ppm to materialize the additional broad signal is somewhat arbitrary. Indeed, this broad signal  
143 is probably composed of heterogeneous hydrogen environments leading to a wide distribution

144 of NMR chemical shifts. However, the fact that this broad signal is centered at  $\delta(^1\text{H}) = 7.0$   
145 ppm suggests the presence of structural water molecules engaged in stronger hydrogen bonds  
146 than those observed at  $\delta(^1\text{H}) = 5.6$  ppm <sup>75</sup>.

### 147 **Kinetics of crystallization**

148 Time resolved, *in situ* ssNMR experiments were undertaken to investigate the kinetics  
149 of crystallization of ACMC under aqueous conditions. To this end, the amorphous powder  
150 was soaked in deionized water. Following this, 1D <sup>13</sup>C single-pulse (SP) MAS ssNMR spectra  
151 were recorded consecutively. After a period of approximately 1 h, a second carbon resonance  
152 appears, and its intensity increases over time (**Fig. 2A**). This second carbon resonance is  
153 narrow (FWHM = 0.70 ppm) and centered at  $\delta(^{13}\text{C}) = 171.7$  ppm, and, hence, reflects the  
154 growth of monohydrocalcite (MHC, calcium carbonate monohydrate:  $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ ) <sup>67</sup>.  
155 Monohydrocalcite is one of the six crystalline forms of calcium carbonate. It is deposited in a  
156 variety of sedimentary environments (*e.g.*, lakes <sup>76</sup> and speleothems <sup>77</sup>). Monohydrocalcite is  
157 also the result of a number of biomineralization processes including otoliths of vertebrates <sup>78</sup>,  
158 calcareous corpuscles of certain flatworms <sup>79</sup> and guinea pig bladder stones <sup>80</sup>. Further,  
159 monohydrocalcite could also be a metastable intermediate phase in the formation of both  
160 aragonite and calcite <sup>81,82</sup>. It is well documented that amorphous calcium carbonates are  
161 metastable and spontaneously crystallize in water. Especially if crystallization occurs via  
162 solid-state transformation (which is discussed in the next section), one could expect here the  
163 formation of calcite since ACMC may be considered as a proto-calcite amorphous calcium  
164 carbonate (**Fig. S3**). However, it is also well documented that magnesium regulates the  
165 crystallization of amorphous calcium carbonates <sup>83,84</sup> and, in certain conditions, favors the  
166 formation of monohydrocalcite <sup>81,82,85–87</sup>. Here the consecutive <sup>13</sup>C SP MAS ssNMR spectra  
167 were recorded under quantitative conditions (recycling delay, RD = 600s). As such, they  
168 allow for determining the conversion rate of the starting amorphous environments into

169 monohydrocalcite as a function of time (**Fig. 2B**). This conversion rate is here expressed in  
170 terms of the molar percentage of carbonate ions present in monohydrocalcite environments.  
171 To achieve this, the consecutive  $^{13}\text{C}$  SP MAS ssNMR spectra were all fitted with two peaks as  
172 shown in **Fig. S7**. The area under each peak was integrated to obtain the molar ratio of  
173 carbonate ions present in crystalline and amorphous environments. As a result, here we show  
174 that nearly 40% of the carbonate ions of ACMC were converted into monohydrocalcite after a  
175 period of about 20 h.

### 176 **Solid-state phase transformation versus dissolution-precipitation?**

177 To shed light on the phase transformation process of ACMC into monohydrocalcite, a  
178 two-dimensional (2D)  $^{13}\text{C}$ - $^{13}\text{C}$  Dipolar Assisted Rotational Resonance (DARR) MAS ssNMR  
179 experiment was performed (**Fig. 3A**). To this end, the amorphous powder was soaked in water  
180 until its conversion rate into monohydrocalcite reached about 30%, which took approximately  
181 12 h (**Fig. 2B**). The 2D  $^{13}\text{C}$ - $^{13}\text{C}$  DARR MAS ssNMR spectrum is in the form of a  $^{13}\text{C}$ - $^{13}\text{C}$   
182 correlation map in which off-diagonal signals are due to magnetization exchange between  
183 nearby  $^{13}\text{C}$  nuclei. Here a strong off-diagonal signal (red dotted lines) connects the carbonate  
184 ions present in monohydrocalcite [observable at  $\delta(^{13}\text{C}) = 171.7$  ppm] with those present in the  
185 amorphous environments [observable at  $\delta(^{13}\text{C}) = 168.2$  ppm]. As a consequence, these results  
186 clearly suggest that the nascent crystalline environments together with the starting amorphous  
187 environments belong to the same particles. This is strong evidence that the starting amorphous  
188 nanoparticles transform into monohydrocalcite via a mechanism of solid-state phase  
189 transformation.

190 An alternative scenario would see first the dissolution of the starting amorphous  
191 nanoparticles followed by their reprecipitation into monohydrocalcite. Indeed, using various  
192 methods [including isotopic labelling <sup>88</sup>, in situ liquid cell transmission electron microscopy  
193 (TEM) <sup>89</sup> and Raman spectroscopy <sup>82</sup>, time resolved scanning electron microscopy (SEM) <sup>86</sup>,

194 pH and supersaturation measurements <sup>90</sup>, Energy Dispersive X-ray Diffraction (ED-XRD) <sup>91</sup>,  
195 small and wide angle X-ray scattering (SAXS/WAXS) <sup>81,92</sup>, or the combination of several of  
196 these techniques], various mechanisms including steps of dissolution-reprecipitation were  
197 pointed out in the pathway to crystallization of different nanoparticles of synthetic amorphous  
198 calcium carbonates into calcite, magnesian calcite, aragonite, vaterite and even  
199 monohydrocalcite. Why under certain conditions some types of nanoparticles of amorphous  
200 calcium carbonate crystalize via solid-state transformation while some others first dissolve  
201 and then reprecipitate is still unclear. This major discrepancy is certainly multifactorial,  
202 depending on the polymorph and the chemical composition of the starting amorphous  
203 particles together the chemistry of the reaction solution. In this direction, a recent study  
204 suggests that the presence of Mg<sup>2+</sup> ions incorporated in the solid phase brings excess  
205 structural water which, in turn, “weakens the ionic binding network” and favors a solid-state  
206 transformation <sup>89</sup>. In addition, it was also reported that an increased water content accelerates  
207 the mechanism of solid-state transformation in the case of a temperature-induced  
208 crystallization <sup>93,94</sup>. As such, it is important to rule out the eventuality of a mechanism of  
209 dissolution-reprecipitation during the crystallization of ACMC in the present study. To this  
210 end, we simulated a mechanism of dissolution-reprecipitation using a physical mixture  
211 containing 40 wt. % monohydrocalcite particles and 60 wt. % amorphous particles soaked in  
212 water. The former particles originate from a new <sup>13</sup>C-labelled (99 atom% <sup>13</sup>C)  
213 monohydrocalcite sample (MHC) (whose powder X-ray diffraction pattern is shown in **Fig.**  
214 **S8**) that was prepared by a direct precipitation method <sup>85</sup>, whereas the latter particles are those  
215 of the amorphous ACMC sample. The <sup>13</sup>C-<sup>13</sup>C DARR MAS ssNMR spectrum of this physical  
216 mixture soaked in water is shown in **Fig. 3B**. This spectrum was recorded within 90 minutes  
217 following the wetting step so that the conversion rate of ACMC into monohydrocalcite  
218 remains very low (must be below  $\approx 2\%$  - **Fig. 2B**). As expected, here the absence of off-

219 diagonal signal confirms that the carbonate ions present in the monohydrocalcite  
220 environments of MHC are not in proximity with those present in the amorphous environments  
221 of ACMC. As such, the observation of an off-diagonal signal in the  $^{13}\text{C}$ - $^{13}\text{C}$  DARR MAS  
222 ssNMR spectrum of the ACMC sample partially converted into monohydrocalcite excludes a  
223 mechanism of dissolution-reprecipitation (**Fig. 3A**).

#### 224 **Surface hydration shell and Hydrogen-Hydrogen chemical exchanges**

225 The possible interactions of the amorphous nanoparticles of ACMC with water  
226 molecules were examined. To this end, 2D  $\{^1\text{H}\}^{13}\text{C}$  HetCor MAS ssNMR experiments of  
227 ACMC were performed both in dry and wet conditions (**Fig. 4**). In wet conditions, the sample  
228 was soaked in water and the 2D  $\{^1\text{H}\}^{13}\text{C}$  HetCor MAS ssNMR experiment was performed  
229 within one hour following the wetting step. In these conditions, monohydrocalcite has yet not  
230 been formed, or rather remains below the detection threshold of ssNMR (**Fig. 2B**). These 2D  
231  $\{^1\text{H}\}^{13}\text{C}$  HetCor MAS ssNMR spectra are in the form of  $^1\text{H}$ - $^{13}\text{C}$  correlation maps in which the  
232 different signals, named “correlation peaks”, reveal atomic-scale spatial proximities among  
233 rigid hydrogen-bearing ions/molecules (displayed along the vertical, indirect  $^1\text{H}$  dimension)  
234 and carbon-bearing ions (displayed along the horizontal, direct  $^{13}\text{C}$  dimension). In dry  
235 conditions, a broad signal associated with two intense spinning sidebands are observable. This  
236 signal results from the juxtaposition of two different correlation peaks which, similarly to the  
237  $\{^1\text{H}$ - $^{13}\text{C}\}^1\text{H}$  double cross polarization (CP) MAS ssNMR experiment, are due to the presence  
238 of  $\text{OH}^-$  ions [observable at  $\delta(^1\text{H}) \approx 1.0$  ppm] and structural water molecules [observable in the  
239 range of  $\delta(^1\text{H}) \approx 5$ -13 ppm]. In contrast, in wet conditions, only a single and sharp correlation  
240 peak is observable while the two intense spinning sidebands are no longer observable. This  
241 sharp correlation peak is at  $\delta(^1\text{H}) = 4.7$  ppm (FWHM = 0.6 ppm) in the indirect  $^1\text{H}$  dimension,  
242 and, hence, reflects the presence of water molecules. Since Brownian motion averages dipolar  
243 couplings to zero, these water molecules must be adsorbed onto the particles’ surface to allow

244 CP magnetization transfer. We can infer from this that a hydration shell of bound water forms  
245 around the particles of ACMC under aqueous conditions.

246 Further, the fact that the broad isotropic signal seen in dry conditions is no longer  
247 observed in wet conditions where only a sharp water correlation peak is present (**Fig. 4**), is  
248 diagnostic of a fast hydrogen exchange regime on the NMR time scale. Indeed, this is  
249 evidence that fast chemical exchanges occur between hydrogens from the free water  
250 molecules and those from the rigid hydrogen-bearing ions/molecules (i.e., OH<sup>-</sup> and H<sub>2</sub>O)  
251 present in the amorphous solid. Due to the presence of the hydration shell of bound water,  
252 these chemical exchanges are likely to occur in two steps: the hydrogens present in the  
253 amorphous solid phase exchange with the hydrogens from the surface-bound H<sub>2</sub>O molecules  
254 which, in turn, exchange with the hydrogens of the free H<sub>2</sub>O molecule of the surrounding  
255 aqueous medium. Our TGA measurements (**Fig. S2**) show that, in dry conditions, the mass  
256 fraction of the different populations of hydrogen-bearing ions/molecules (OH<sup>-</sup> and H<sub>2</sub>O)  
257 associated with the particles of ACMC is in the range of 22 to 26 wt. %. As a result, we could  
258 calculate the proportion of hydrogens originating from the particles over the total number of  
259 hydrogens present in the MAS rotor following the wetting step: i.e., from about 5 to 10%. The  
260 number of hydrogens from the free water molecules is therefore in large excess over the  
261 number of hydrogens present in the particles and, hence, the latter are not detected in wet  
262 conditions (fast exchange regime) and solely the excess water signal is observed at  $\delta(^1\text{H}) =$   
263 4.7 ppm. In addition, the fact that the two intense spinning sidebands observed in dry  
264 conditions are no longer observable when the particles are soaked in water also advocate for  
265 chemical exchanges. This is evidence that the hydrogens from the particles were mobilized in  
266 wet conditions due to their exchanges with the hydrogens from the free water molecules.  
267 Further, similar hydrogen-hydrogen exchanges were also pointed out not only for synthetic

268 particles of amorphous calcium phosphate (ACP) soaked in water, but also for the ACP-like  
269 surface of bone mineral particles from a fresh and intact bone tissue sample <sup>95</sup>.

270 For further evidence of the presence of a hydration shell of bound water, cryogenic  
271 transmission electron microscopy (cryo-TEM) observations were obtained from the  
272 amorphous nanoparticles of ACMC dispersed in water (**Fig. S9**). This dispersion was  
273 cryofixed in liquid ethane within 10 min after its preparation and, hence, crystallization has  
274 not yet started. A low magnification micrograph shows aggregates of nanoparticles that were  
275 highlighted by yellow circles in **Fig. S9A**. Regions immediately around these aggregates  
276 appear darker, indicating that the amorphous ice is thicker. This is evidence that the  
277 nanoparticles (shown at higher magnification in **Fig. S9B**) retain water. Further, when these  
278 nanoparticles are not “piled up” on top of each other as those pointed out with yellow arrows  
279 in **Fig. S9B**, tiny lighter zones are visible and are certainly due to the presence of pores.  
280 These pores are almost certainly not artifacts caused by electron beam irradiation since they  
281 do not evolve upon prolonged observation. As a result, we suggest that the pores facilitate the  
282 fast hydrogen-hydrogen exchanges that we observed in the 2D  $\{^1\text{H}\}^{13}\text{C}$  MAS HetCor ssNMR  
283 experiments performed in wet conditions.

284 To better understand the origin of the hydrophilic properties of ACMC, we examined  
285 whether a surface hydration shell can also form around the particles of a hydrated calcium  
286 carbonate mineral soaked in water. To this end, the MHC sample was used since  
287 monohydrocalcite ( $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ , with one water molecule per calcium carbonate group) is a  
288 suitable model mineral for amorphous calcium carbonates in terms of chemical composition  
289 <sup>96</sup>. The  $^{13}\text{C}$  single-pulse (SP) MAS ssNMR spectrum of MHC is shown in **Fig. S10A**. This  
290 sample is mainly composed of monohydrocalcite environments, but also contains residual  
291 amorphous environments that were not converted into monohydrocalcite (**Fig. S10B**). Further,  
292 the 1D  $\{^1\text{H}-^{13}\text{C}\}^1\text{H}$  double cross polarization (CP) MAS ssNMR spectrum of MHC is shown

293 in **Fig. S10C**. This spectrum exposes a single, symmetric resonance [centered at  $\delta(^1\text{H}) = 6.0$   
294 ppm; FWHM = 8.9 ppm] attributed to structural water molecules in monohydrocalcite  
295 environments. As for the possible interactions of the particles of MHC with water molecules,  
296 they were investigated in a similar manner as for ACMC. Two-dimensional  $\{^1\text{H}\}^{13}\text{C}$  HetCor  
297 MAS ssNMR experiments of MHC were performed both in dry and wet conditions and are  
298 shown in **Fig S11**. The signal due to the presence of the residual amorphous environments  
299 differs in dry and wet conditions. While this signal is broad and barely visible in dry  
300 conditions (grey arrow), it is clearly detected in wet conditions where a sharp correlation peak  
301 at  $\delta(^1\text{H}) = 4.7$  ppm in the indirect  $^1\text{H}$  dimension shows the presence of surface-bound water  
302 molecules. In contrast, the signal due to the presence of the monohydrocalcite environments  
303 was unchanged after hydration. In both dry and wet conditions, this signal is in the form of a  
304 broad correlation peak due to the presence of  $\text{CO}_3^{2-}$  ions [observable at  $\delta(^{13}\text{C}) = 171.7$  ppm in  
305 the direct  $^{13}\text{C}$  dimension] near structural  $\text{H}_2\text{O}$  molecules [centered at  $\delta(^1\text{H}) = 6.0$  ppm in the  
306 indirect  $^1\text{H}$  dimension]. As such, contrary to the amorphous environments of MHC but also  
307 those of ACMC, the presence of an excess of free water in the MAS rotor does not cause the  
308 formation of a hydration shell of bound water associated with the monohydrocalcite  
309 environments. These results suggest that the hydrophilic properties of ACMC are not due to a  
310 specific chemical composition including  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions along with structural  $\text{H}_2\text{O}$   
311 molecules, but are rather the result of a definite amorphous structure.

### 312 **Evolution of the hydrogen chemical environments as crystallization progresses**

313 The evolution of the hydrogen chemical environments during the conversion of the  
314 starting amorphous nanoparticles into monohydrocalcite was also scrutinized. To this end,  
315 additional 2D  $\{^1\text{H}\}^{13}\text{C}$  HetCor MAS ssNMR experiments of ACMC soaked in water were  
316 therefore undertaken consecutively following the initial wetting step (**Fig. 5**). The previously  
317 mentioned, quantitative 1D  $^{13}\text{C}$  SP MAS ssNMR spectra, were recorded between each of

318 these 2D  $\{^1\text{H}\}^{13}\text{C}$  HetCor experiments so that the molar percentage of monohydrocalcite is  
319 known. Here the growth of monohydrocalcite appears in the form of a broad, composite  
320 signal along the vertical, indirect  $^1\text{H}$  dimension whose intensity progressively increases  
321 [observable at  $\delta(^{13}\text{C}) = 171.7$  ppm in the horizontal, direct  $^{13}\text{C}$  dimension]. This broad,  
322 composite signal is also observable in the  $^1\text{H}$  slices taken at the monohydrocalcite position  
323 (**Fig. S12A**). The signal arises from hydrogen-bearing ions/molecules present within the  
324 nascent crystalline environments and spreads from  $\delta(^1\text{H}) \approx -5$  to 15 ppm; this is in agreement  
325 with the  $^{13}\text{C}$ -filtered  $^1\text{H}$  MAS NMR spectrum of the reference sample of monohydrocalcite  
326 shown in **Fig. S10C**. Moreover, intense spinning sidebands, signature of hydrogen-bearing  
327 ions/molecules with restricted mobility, are also observed in agreement with the crystalline  
328 nature of these nascent environments (**Fig. S12A**).

329 As for the starting amorphous environments, a sharp water correlation peak not  
330 associated with any spinning sidebands (which is diagnostic of a fast hydrogen exchange  
331 regime on the NMR time scale) is visible at the ACMC position [i.e.,  $\delta(^{13}\text{C}) = 168.2$  ppm in  
332 the horizontal, direct  $^{13}\text{C}$  dimension] (**Fig. 5**). As a result, the  $^1\text{H}$  slices taken at the ACMC  
333 position only expose a single and narrow resonance [centered at  $\delta(^1\text{H}) = 4.7$  ppm; FWHM in  
334 the range of 0.6 to 1.3 ppm] attributed to water molecules bound to the particles' surface (**Fig.**  
335 **S12B**). These observations are similar to what is observed for ACMC in wet conditions before  
336 crystallization (**Fig. 4B**), and highlight that the starting amorphous environments remain  
337 hydrated while crystallization progresses. They also imply that the hydrogen-bearing  
338 ions/molecules remaining in the starting amorphous environments keep undergoing chemical  
339 exchanges with the free water molecules as crystallization progresses.

#### 340 **Hydrogen-deuterium chemical exchanges**

341 For further evidence of these chemical exchanges, 2D  $\{^1\text{H}\}^{13}\text{C}$  HetCor MAS ssNMR  
342 experiments of ACMC soaked in heavy water ( $\text{D}_2\text{O}$  - 99.99 atom% D) were undertaken

343 sequentially (**Fig. 6**). Quantitative 1D  $^{13}\text{C}$  SP MAS ssNMR spectra were recorded between  
344 each of the 2D  $\{^1\text{H}\}^{13}\text{C}$  HetCor experiments so that the conversion rate of ACMC into  
345 monohydrocalcite is known. Here this conversion rate reaches up 26% after 1130 minutes  
346 which is therefore about 40% lower than in the case of ACMC soaked in  $\text{H}_2\text{O}$  at the same  
347 stage (conversion rate, 36%) (**Fig. 2B**); and this discrepancy is likely related to a kinetic  
348 isotope effect. In contrast to the successive 2D  $\{^1\text{H}\}^{13}\text{C}$  HetCor MAS ssNMR spectra of  
349 ACMC soaked in  $\text{H}_2\text{O}$  where a broad, composite signal was observed along the indirect  $^1\text{H}$   
350 dimension, here the growth of monohydrocalcite appears in the form of a single, narrow  
351 correlation peak [observable at  $\delta(^{13}\text{C}) = 171.7$  ppm in the horizontal, direct  $^{13}\text{C}$  dimension].  
352 The  $^1\text{H}$  slices taken at the monohydrocalcite position reveal a single, symmetric resonance  
353 [centered at  $\delta(^1\text{H}) = 6.0$  ppm; FWHM = 2.2 ppm] (**Fig. S13A**); this chemical shift is  
354 characteristic of structural water molecules in monohydrocalcite environments (**Fig. S10C**).  
355 However, the associated linewidth is much smaller due to a reduction of the  $^1\text{H}$  dipolar  
356 couplings induced by a partial deuteration. Indeed, here  $^1\text{H}/^2\text{H}$  chemical exchanges led to the  
357 deuteration of the hydrogen-bearing ions/molecules present in the starting amorphous  
358 nanoparticles before crystallization occurs (after about 1 h - **Fig. 2B**). As a result, the protium  
359 isotopes, originating from ACMC, were diluted following the addition of the large excess of  
360 deuterium isotopes originating from the  $\text{D}_2\text{O}$  solution [ $^2\text{H}/(^2\text{H} + ^1\text{H}) \geq 90$  atom% in the MAS  
361 rotor]. This “isotopic dilution” has largely lowered the magnitude of the homonuclear  $^1\text{H}$ - $^1\text{H}$   
362 dipolar couplings within the particles which, in turn, gave rise to  $^1\text{H}$  spectra of the  
363 monohydrocalcite environments with higher resolution (compared with  $\text{H}_2\text{O}$ ). The same  
364 phenomenon also explains the presence of weaker spinning sidebands associated with the  
365 nascent crystalline environments growing in  $\text{D}_2\text{O}$  compared to  $\text{H}_2\text{O}$  (**Fig. S13A**).

366 As for the starting amorphous environments, the sharp water correlation peak that was  
367 previously seen at  $\delta(^1\text{H}) = 4.7$  ppm (FWHM in the range of 0.6 to 1.3 ppm) along the indirect

368  $^1\text{H}$  dimension of the successive 2D  $\{^1\text{H}\}^{13}\text{C}$  HetCor MAS ssNMR spectra of ACMC soaked  
369 in  $\text{H}_2\text{O}$  was not observed. Instead, two narrow correlation peaks due to the presence of  
370 structural  $\text{OH}^-$  ions [ $\delta(^1\text{H}) = 1.0$  ppm - no longer observed after 330 min] and structural water  
371 molecules [ $\delta(^1\text{H}) = 5.6$  ppm; FWHM  $\approx 2.9$  ppm] arise from the starting amorphous  
372 environments (**Fig. 6**). The intensity of the water correlation peak progressively declines up to  
373 970 minutes, after which the peak becomes almost no longer visible; this is also observable in  
374 the  $^1\text{H}$  slices taken at the ACMC position [i.e.,  $\delta(^{13}\text{C}) = 168.2$  ppm in the direct  $^{13}\text{C}$   
375 dimension] (**Fig. S13B**). The number of hydrogens originating from the particles initially  
376 represents almost 100% of the total number of hydrogens present in the MAS rotor following  
377 the wetting step with  $\text{D}_2\text{O}$ . The surface-bound water molecules (mostly in the form of  $\text{D}_2\text{O}$ ,  
378 and in a less extent  $\text{H}_2\text{O}$  but also HDO that were formed following the chemical exchanges)  
379 are not detected in the 2D  $\{^1\text{H}\}^{13}\text{C}$  HetCor spectra due to the fast exchange regime where  
380 solely the excess  $\text{OH}^- / \text{H}_2\text{O}$  and HDO signals arising from the particles are observed. Further,  
381 the disappearance of these  $\text{OH}^- / \text{H}_2\text{O}$  and HDO signals is due to the rearrangement of these  
382 populations of hydrogen-bearing ions/molecules present in the starting amorphous  
383 environments to form of monohydrocalcite via a solid-state phase transformation (**Fig. 3A**).

#### 384 **Crystal growth by accretion of amorphous nanoparticles**

385 The mineral structures resulting from the crystallization of ACMC soaking in water in  
386 the MAS rotor were scrutinized by Scanning Helium Ion Microscopy (SHIM). To this end,  
387 the previously mentioned, consecutive  $^{13}\text{C}$  SP MAS ssNMR experiments of ACMC soaked in  
388 water, have been run until the signal arising from the starting amorphous environments stops  
389 evolving (after a period of approximately 2500 min). Hence, at this stage, the conversion rate  
390 of ACMC into monohydrocalcite has reached its maximum (**Fig. S14**). Following this, the  
391 wet powder was simply collected from the MAS rotor, washed with deionized water, and then  
392 dried at ambient temperature. The resulting dry powder was analyzed by X-ray diffraction

393 that has confirmed the presence of monohydrocalcite (**Fig S15**). From the same powder, an  
394 average atomic Ca/Mg ratio  $\approx 5.0$  was estimated using energy-dispersive X-ray spectroscopy  
395 (EDS). It corresponds to an atom% of Mg in ACMC converted into monohydrocalcite  
396 [defined as  $\text{Mg}/(\text{Ca} + \text{Mg}) \times 100$ ] of about 16.6 (against 20.0 for ACMC before  
397 crystallization). It shows that a small proportion of  $\text{Mg}^{2+}$  have been expelled out of the  
398 particles following crystallization. This suggests that the leading process of solid-state  
399 transformation of ACMC into monohydrocalcite is here associated with a small loss of  
400 magnesium that possibly occurs via a mechanism of Ostwald ripening <sup>81</sup>. As for the SHIM  
401 observations, a low magnification micrograph clearly shows that the crystallization process of  
402 ACMC occurs via a spherulitic growth mechanism (**Fig. 7A**). Successive magnification  
403 micrographs on an open spherulite reveal the presence of crystals that greatly differ from the  
404 classical view of inorganic crystals with faceted surfaces (**Fig. 7, B to D**). Instead, acicular  
405 crystals displaying a highly textured surface due to the apparent presence of spherical  
406 nanoparticles “building-blocks” are here observed. Similar acicular crystals are also  
407 observable at the surface of a spherulite (double yellow arrows in **Fig. 7E**), where the  
408 spherical nanoparticles “building-blocks” match with the starting amorphous nanoparticles of  
409 ACMC in terms of size (**Fig. 7F**). Such “nano-particulate” texture was initially observed for  
410 biological aragonite in nacre <sup>53,97</sup> and more recently for biological aragonite in coral (**Fig. 7G**)  
411 <sup>49</sup> and across a broad range of biomineralizing taxa <sup>98</sup>. This “nano-particulate” texture is  
412 another evidence for a mechanism of solid-state transformation; this is also signature of  
413 crystal growth by accretion of amorphous nanoparticles <sup>99,100</sup> which is one variety of  
414 crystallization by particle attachment <sup>101</sup>.

415 In addition, in order to assess the behavior of ACMC within in a higher volume of  
416 water, the mineral structures resulting from the crystallization of ACMC soaking in a reaction  
417 vial instead of in an NMR rotor were also scrutinized. To this end, the amorphous

418 nanoparticles of APMC were dispersed in deionized water in a 10ml vial (mass concentration  
419  $\approx 2\%$  w/v against about  $30\%$  w/v in the MAS rotor) and the resulting suspension was aged for  
420 a period of 24 hours to allow crystallization. This dispersion was then cryofixed in liquid  
421 ethane and imaged using cryogenic transmission electron microscopy (cryo-TEM). In the  
422 present conditions, sphere-like aggregates were not observed but a low magnification  
423 micrograph instead shows the presence of spindle-shaped, higher-order mineral structures  
424 (**Fig. S9C**). These mineral structures have a length from 800 to 1700 nm and a thickness from  
425 200 to 500 nm. At high magnification, it is clear that they are not monolithic but are rather in  
426 the form of bundles of smaller parallel units (**Figs. 7H and S9D**). Selected-area electron-  
427 diffraction (SAED) shows that these bundles of smaller parallel units are composed of  
428 monohydrocalcite (inset in **Fig. 7H**). Similar spindle-shaped mineral structures were also  
429 observed following the crystallization of amorphous calcium carbonate nanoparticles into  
430 aragonite<sup>102</sup>. In this study, nanoscale crystals formed within an “amorphous framework”  
431 composed of aggregated amorphous nanoparticles. Our results support an analogous  
432 mechanism for the crystallization of APMC into monohydrocalcite: the amorphous  
433 nanoparticles first aggregate (**Fig. S9A**) and then crystallize via solid-state transformation  
434 (**Figs. 3A, 7H and S9B**).

### 435 **Chemical and structural model of the surface region**

436 The results presented in the present study allowed us to design a two-dimensional  
437 chemical and structural model of the surface region of an amorphous particle of APMC  
438 soaked in water (**Fig. 8B**). The amorphous solid phase (grey area) is composed of  
439 homogeneously distributed, structural  $\text{OH}^-$  ions and  $\text{H}_2\text{O}$  molecules close to  $\text{CO}_3^{2-}$  ions. Here  
440 the coordination number of the cations is arbitrary. But a  $^{25}\text{Mg}$ -based solid-state NMR study  
441 suggests that, in Mg-stabilized amorphous calcium carbonates, each  $\text{Mg}^{2+}$  are surrounded by  
442 4-4.5  $\text{CO}_3^{2-}$  ions in average along with at least one  $\text{H}_2\text{O}$  molecule<sup>103</sup>. The surface of the

443 nanoparticle is hydrophilic and, hence, they are covered by a hydration shell of bound water.  
444 The assumption was made that the water molecules of the hydration shell form a second  
445 sphere of coordination around the surface ions. Fast chemical exchanges continuously occur:  
446 the hydrogens present in the amorphous solid phase exchange with the hydrogens from the  
447 surface-bound H<sub>2</sub>O molecules which, in turn, exchange with the hydrogens of the free H<sub>2</sub>O  
448 molecule of the surrounding aqueous medium. These exchanges may be facilitated due to the  
449 presence of pores (size, 1 to 3 nm) seen in the cryo-TEM micrograph shown in **Fig. 8A**.

## 450 **Conclusions**

451 Our results reveal the underlying mechanism of the solid-state phase transformation of  
452 Amorphous Calcium Magnesium Carbonate (ACMC) nanoparticles into crystals under  
453 aqueous conditions. First, we showed that the <sup>13</sup>C-<sup>13</sup>C Dipolar Assisted Rotational Resonance  
454 (DARR) ssNMR technique can be used to assess whether crystallization occurs via  
455 dissolution-precipitation or whether it occurs via solid-state transformation. Using this  
456 technique, we show that the nascent crystalline environments in the form of monohydrocalcite  
457 (MHC), together with the starting amorphous environments, belong to the same particles. This  
458 is clear evidence of a solid-state phase transformation of the starting amorphous nanoparticles  
459 into crystals. Second, we show that the surface of these amorphous nanoparticle is  
460 hydrophilic. Indeed, when soaked in aqueous medium, these nanoparticles are covered by a  
461 hydration shell of bound water (**Fig. 8**). As a result, when the particles come into contact  
462 following aggregation or simple sedimentation, this hydration shell drives particle-particle  
463 interactions. In a bigger picture, it is now acknowledged that “the role of hydration layers in  
464 biogenic systems needs to be considered and may be responsible for phenomena seen in  
465 biomineralization”<sup>104</sup>. Our results also show that fast chemical exchanges continuously occur:  
466 the hydrogens present in the particles exchange with the hydrogens from the hydration shell  
467 of bound water which, in turn, exchange with the hydrogens of the free H<sub>2</sub>O molecule of the

468 surrounding aqueous medium. We also revealed that the starting amorphous nanoparticles  
469 remain hydrated while crystallization progresses. And while the nanoparticles are partially  
470 converted into monohydrocalcite, the domains part of the nanoparticles that remain  
471 amorphous keep undergoing fast hydrogen-hydrogen chemical exchanges with the free H<sub>2</sub>O  
472 molecules of the surrounding aqueous medium. Hence, our results question the role played by  
473 these unceasing chemical exchanges towards crystallization. While hydrogens from the  
474 amorphous nanoparticles are relocated into the surrounding aqueous medium, hydrogens from  
475 the aqueous medium travel the reverse path. As a result, H-bonds, that presumably stabilizes  
476 amorphous solids against crystallization<sup>105</sup>, are being constantly broken and reformed  
477 throughout the amorphous solid. Our results suggest that this process is associated with an  
478 enhanced mobility of the ions/molecules that compose the amorphous nanoparticles which, in  
479 turn, could allow for rearrangement of these ions/molecules into crystalline domains via solid-  
480 state transformation. Further, we can hypothesize what sometimes triggers the total  
481 dissolution of certain amorphous nanoparticles under aqueous conditions<sup>81,86</sup> (not observed in  
482 the present study). We presume that an increased content of structural hydrous species will  
483 escalate the hydrogen-hydrogen exchanges and, concomitantly, rise the mobility of the  
484 ions/molecules that compose the amorphous nanoparticles. This mobility could reach a certain  
485 level where the amorphous nanoparticles breaks down into solubilized ions that are now  
486 available to reprecipitate into a new solid phase. From a wider perspective, our results shed  
487 light on the means available to living organisms for directing crystallization into a process of  
488 solid-state transformation rather than one of dissolution-precipitation and, as such, could help  
489 to reconstruct the puzzle of various biomineralization processes.

490 Last, the results presented here and elsewhere<sup>89,102,106,107</sup> reveal the capability of  
491 synthetic, amorphous inorganic nanoparticles to form higher-order mineral structures through  
492 pathways to crystallization that combine solid-state phase transformation and particle

493 attachment. As a such, taking advantage of these pathways to crystallization opens new  
494 avenues in materials science based on future strategies that will no longer be limited by the  
495 initial nucleation stage. In addition, since these pathways to crystallization also offers the  
496 opportunity to shape the resulting higher-order mineral structures into different morphologies  
497 <sup>63</sup> (such as the spherulitic aggregates and the spindle-shaped mineral structures shown in the  
498 present study), they also pave the way for future strategies that will no longer be “restricted by  
499 the constraints of the crystal unit cell” <sup>4</sup>.

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509

510           **Supporting Information:** X-ray diffraction analysis of ACMC (Figure S1); Weight  
511 loss and heat flow measurements of ACMC (Figure S2); Carbon environments of ACMC  
512 (Figure S3); Cross-polarization dynamics between  $^1\text{H}$  and  $^{13}\text{C}$  nuclei in ACMC (Figure S4);  
513 Hydrogen environments of ACMC (Figure S5); Rigid hydrogen-bearing ions/molecules  
514 present in ACMC (Figure S6); Evaluation of the conversion rate of ACMC into  
515 monohydrocalcite (Figure S7); X-ray diffraction analysis of the monohydrocalcite sample  
516 (Figure S8); Observations of the starting amorphous nanoparticles of ACMC and their  
517 resulting higher-order mineral structures following crystallization (Figure S9); Carbon and  
518 Hydrogen environments of the monohydrocalcite sample (Figure S10); Spatial proximities  
519 among carbon-bearing ions and hydrogen-bearing ions/molecules in the particles of the  
520 monohydrocalcite sample (Figure S11); Evolution of the hydrogen environments while the  
521 amorphous nanoparticles of ACMC are crystallizing in water (Figure S12); Evolution of the  
522 hydrogen environments while the amorphous nanoparticles of ACMC are crystallizing in  
523 heavy water (Figure S13); Carbon environments of ACMC before and after crystallization  
524 (Figure S14); X-ray diffraction analysis of ACMC following crystallization (Figure S15).

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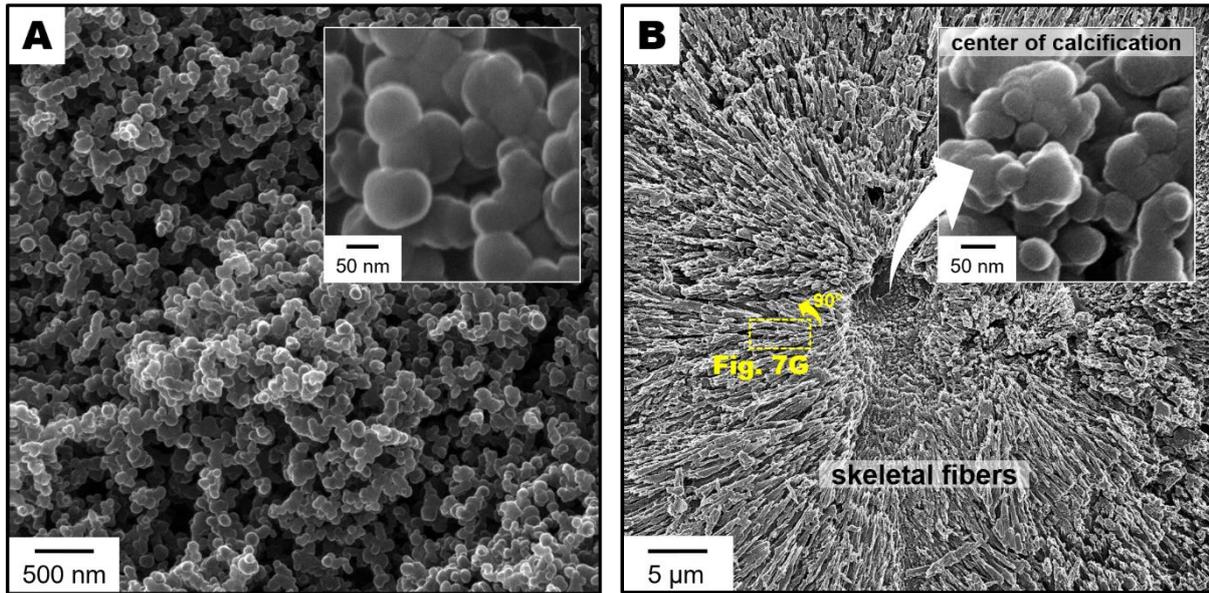
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- 905

906 **Figure 1.**



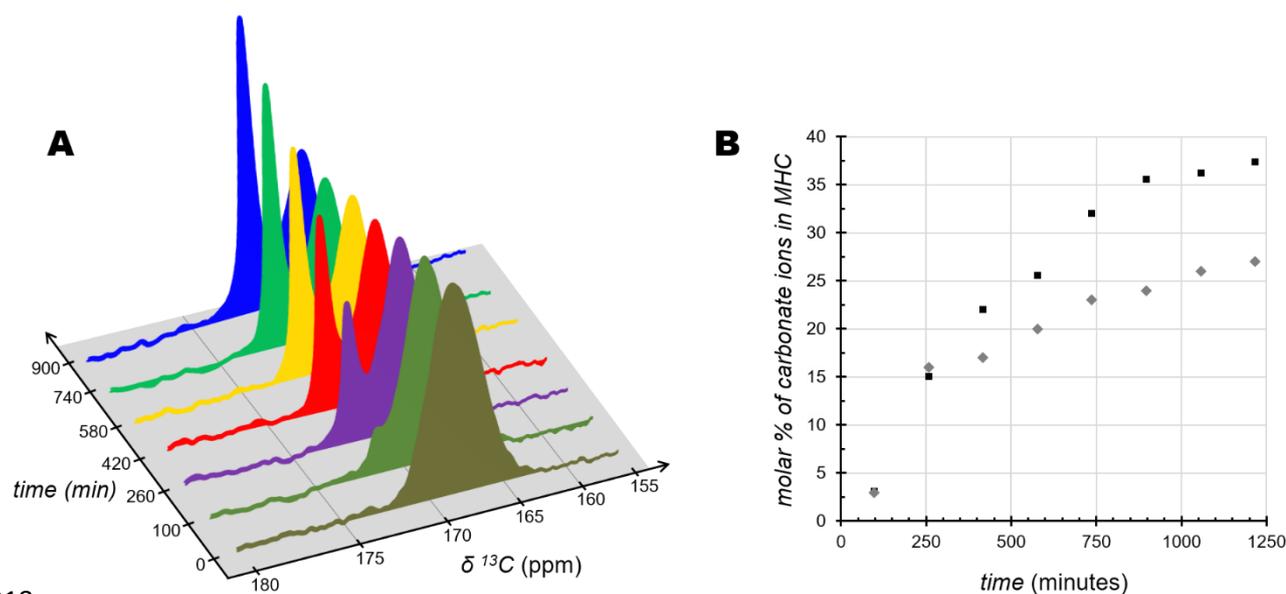
907

908 **Figure 1. Morphological features of synthetic and biogenic amorphous nanoparticles.**

909 Representative scanning helium ion microscopy (SHIM) micrographs of the synthetic,  
910 Amorphous Calcium Magnesium Carbonate (ACMC) sample (A). For the purpose of  
911 comparison with biogenic deposits of amorphous  $\text{CaCO}_3$ , also shown are representative  
912 SHIM micrographs obtained from the broken, unpolished, etched-surface of a coral skeletal  
913 branch that was transversely sectioned (B). Shown here is a trabecula composed of skeletal  
914 fibers in the form of acicular aragonite crystals, that radiate from a center of calcification  
915 (COC) composed of magnesium-rich, amorphous calcium carbonate nanoparticles <sup>108</sup>.

916

917 **Figure 2.**

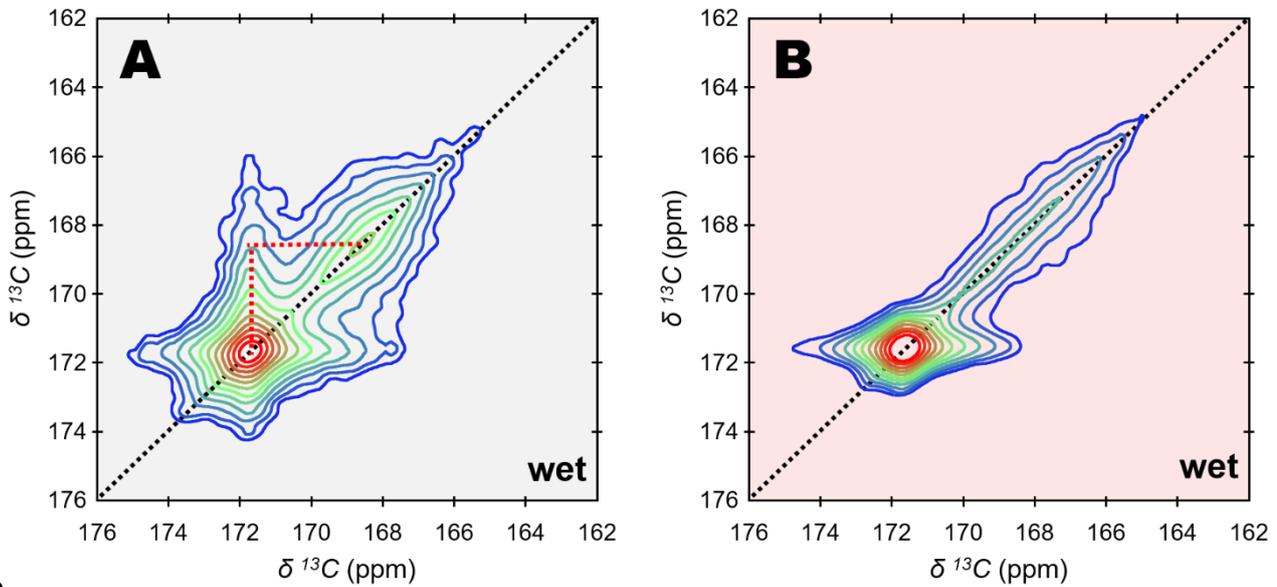


918

919 **Figure 2. Kinetics of crystallization of the synthetic amorphous nanoparticles. (A)** Non-  
920 normalized 1D  $^{13}\text{C}$  single-pulse (SP) MAS ssNMR spectra (recycling delay, RD = 600 s;  
921 number of scans, NS = 8; MAS frequency,  $\nu_{\text{MAS}} = 8$  kHz) of the synthetic, Amorphous  
922 Calcium Magnesium Carbonate (ACMC) sample soaked in deionized water as crystallization  
923 progresses. **(B)** Conversion rate of the starting amorphous environments into  
924 monohydrocalcite as a function of time for ACMC soaked in deionized water (**black squares**)  
925 or heavy water (**grey squares**). This conversion rate is here expressed in terms of the molar  
926 percentage of carbonate ions present in monohydrocalcite (MHC) environments.

927

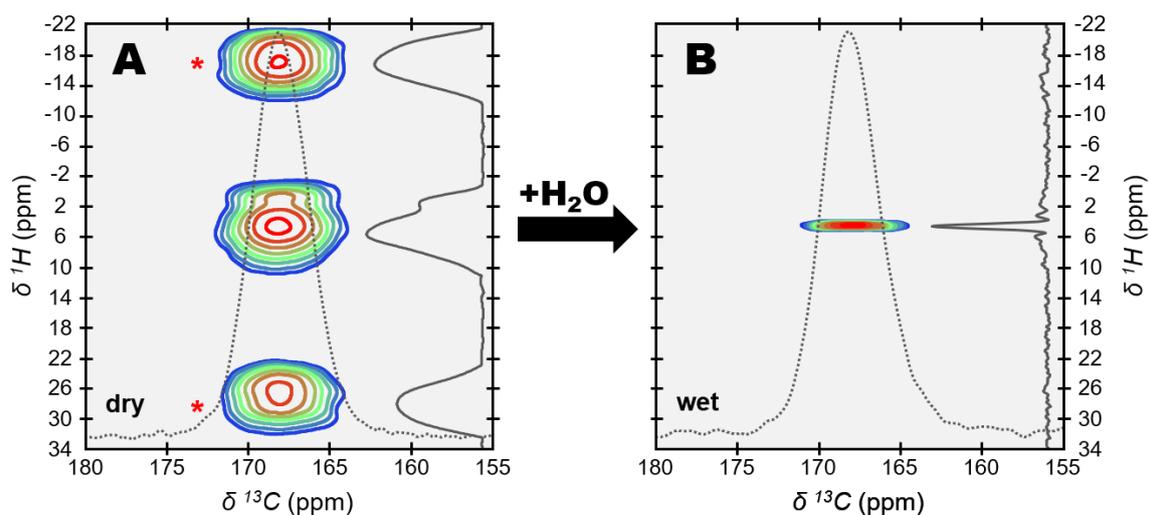
928 **Figure 3.**



929

930 **Figure 3. Spatial proximities among the carbon-bearing ions.** Contour plots of two-  
931 dimensional (2D)  $^{13}\text{C}$ - $^{13}\text{C}$  Dipolar Assisted Rotational Resonance (DARR) MAS ssNMR  
932 spectra (contact time,  $t_{\text{CP}} = 4$  ms; mixing time,  $\tau_{\text{mix}} = 500$  ms; 8 scans in each 384 t1  
933 increments; relaxation delay,  $\text{RD} = 1$  s; MAS frequency,  $\nu_{\text{MAS}} = 8$  kHz) of the synthetic,  
934 Amorphous Calcium Magnesium Carbonate (ACMC) sample soaked in deionized water, and  
935 partially converted into monohydrocalcite (conversion rate, 30%) (A); and of a physical  
936 mixture of two powders soaking in deionized water: the synthetic monohydrocalcite (MHC)  
937 sample and ACMC before crystallization (B). The signal intensity increases from blue to red.

938 **Figure 4.**



939

940 **Figure 4. Spatial proximities among carbon-bearing ions and hydrogen-bearing**

941 **ions/molecules in the amorphous nanoparticles.** Contour plots of two-dimensional (2D)

942  $\{^1\text{H}\}^{13}\text{C}$  Heteronuclear Correlation (HetCor) MAS ssNMR spectra [contact time,  $t_{\text{CP}} = 4$  ms;

943 64 (dry conditions) or 16 (wet conditions) scans in each 120  $t_1$  increments; relaxation delay,

944  $\text{RD} = 2$  s; MAS frequency,  $\nu_{\text{MAS}} = 8$  kHz] of the synthetic, Amorphous Calcium Magnesium

945 Carbonate (ACMC) sample in dry conditions (A) and soaked in deionized water for 50

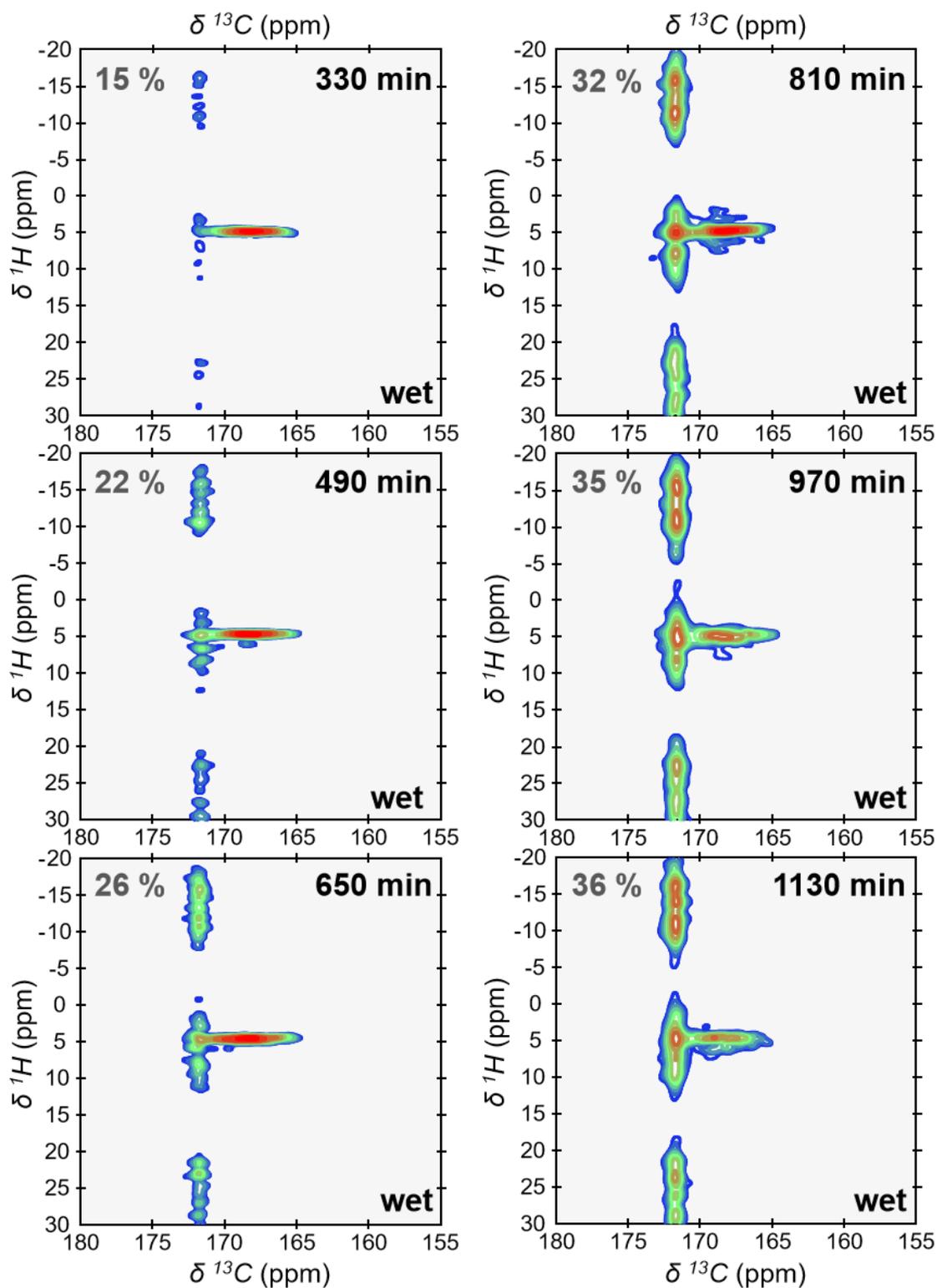
946 minutes (B). The signal intensity increases from blue to red. Also shown are the normalized,

947 projections of the vertical, indirect  $^1\text{H}$  dimensions (solid lines) and of the horizontal, direct

948  $^{13}\text{C}$  dimensions (dotted lines) of these two 2D  $\{^1\text{H}\}^{13}\text{C}$  HetCor MAS ssNMR spectra. The red

949 asterisks (\*) denote the intense spinning sidebands only seen in dry conditions.

950 **Figure 5.**

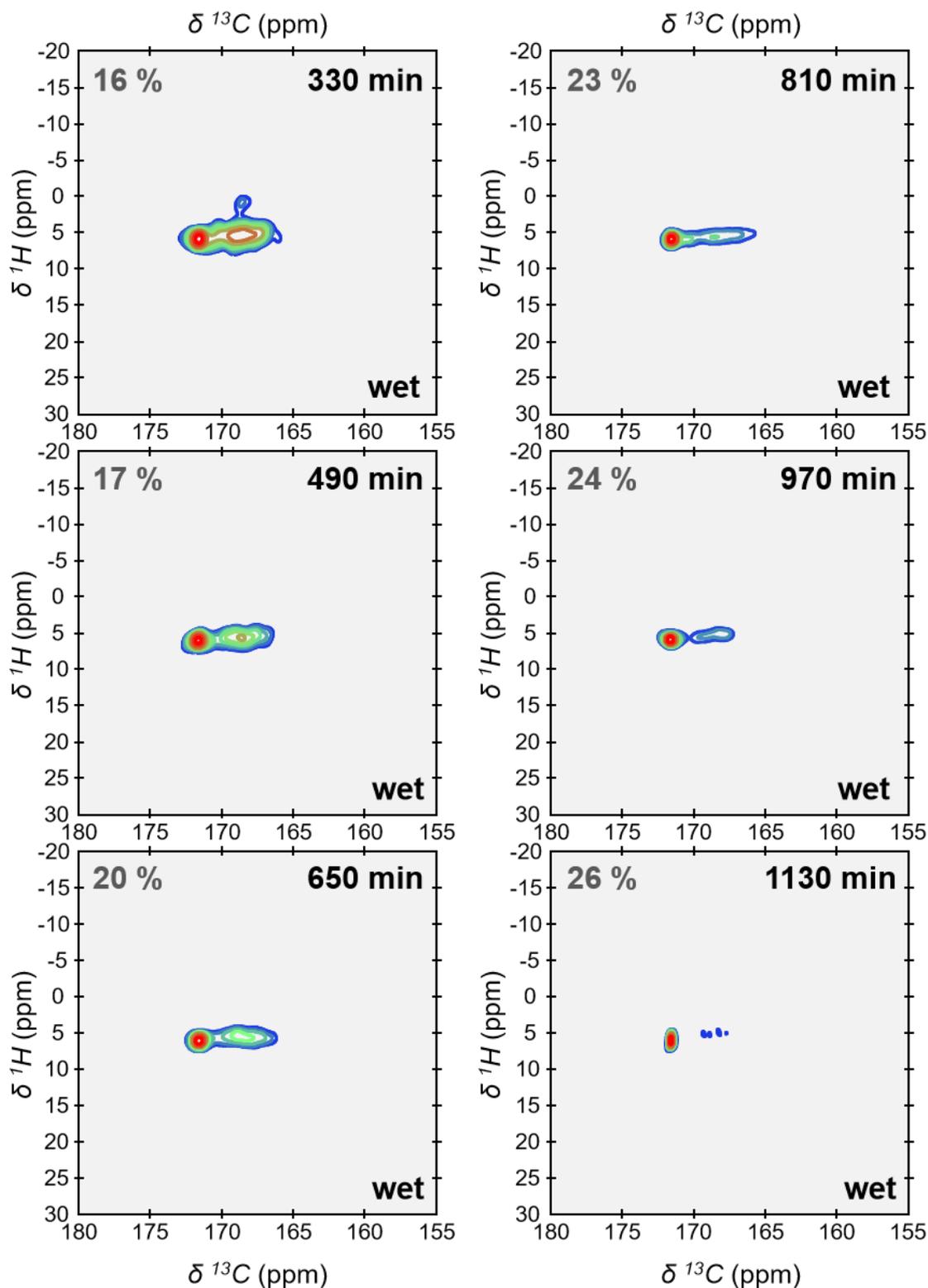


951

952 **Figure 5. Evolution of the hydrogen chemical environments during crystallization.**

953 Contour plots of 2D  $\{^1\text{H}\}^{13}\text{C}$  Heteronuclear Correlation (HetCor) MAS ssNMR spectra

954 (contact time,  $t_{CP} = 4$  ms; 16 scans in each 120 t1 increments; relaxation delay,  $RD = 2$  s;  
955 MAS frequency,  $\nu_{MAS} = 8$  kHz) of the synthetic, Amorphous Calcium Magnesium Carbonate  
956 (ACMC) sample soaked in deionized water while crystallization progresses. The signal  
957 intensity increases from blue to red. The percentages displayed in the upper left corner are the  
958 conversion rate of ACMC into monohydrocalcite, whereas the values shown in the upper right  
959 corner are the periods of time during which the sample has been soaking in water following  
960 the initial wetting step.

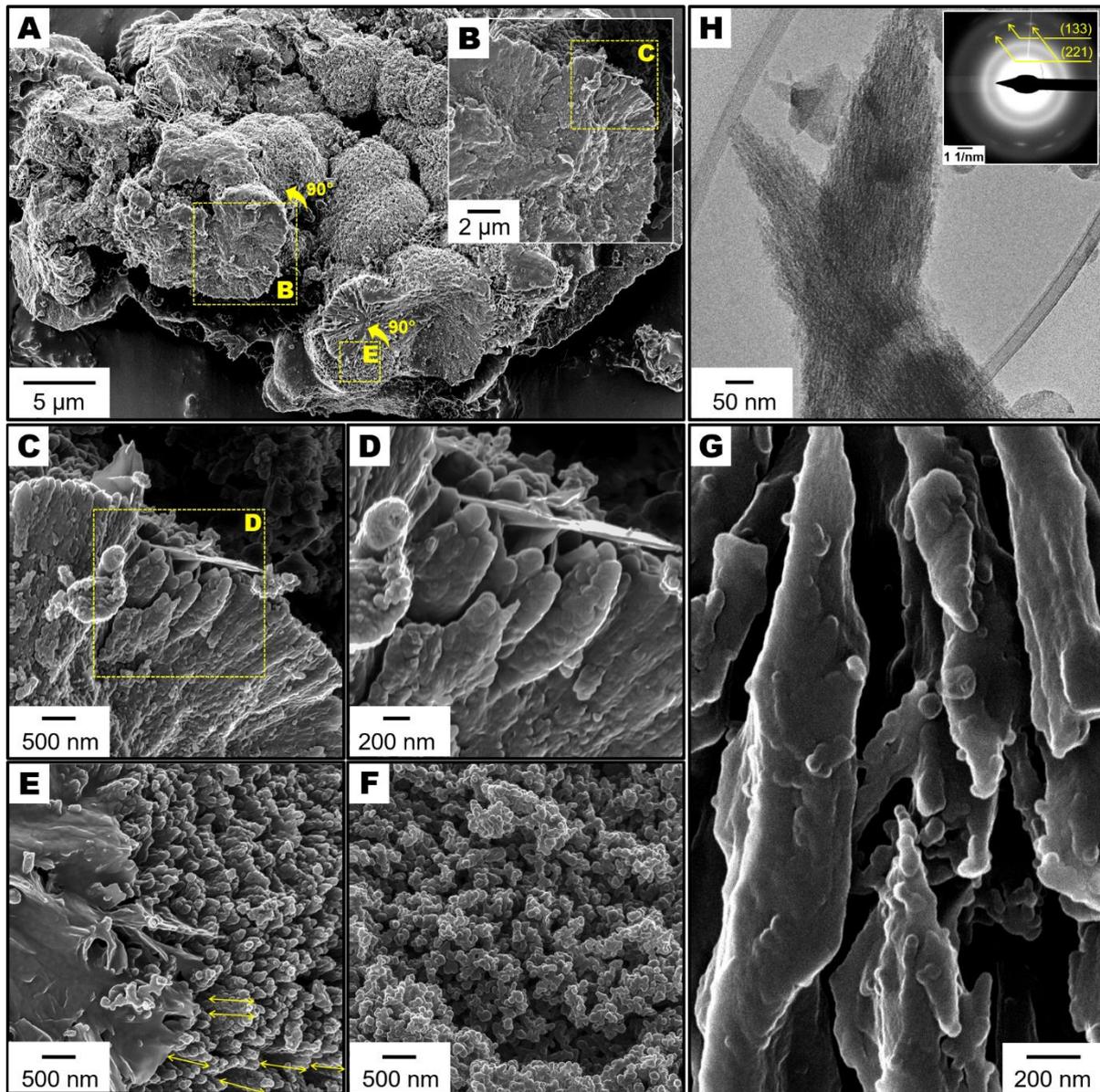


962

963 **Figure 6. Deuterium-hydrogen chemical exchanges during crystallization.** Contour plots

964 of 2D  $\{^1\text{H}\}^{13}\text{C}$  Heteronuclear Correlation (HetCor) MAS ssNMR spectra (contact time,  $t_{\text{CP}} =$

965 4 ms; 16 scans in each 120 t1 increments; relaxation delay, RD = 2 s; MAS frequency,  $\nu_{\text{MAS}} =$   
966 8 kHz) of the synthetic, Amorphous Calcium Magnesium Carbonate (ACMC) sample soaked  
967 in heavy water ( $\text{D}_2\text{O}$  - 99.99 atom% D) while crystallization progresses. The signal intensity  
968 increases from blue to red. The percentages displayed in the upper left corner are the  
969 conversion rate of ACMC into monohydrocalcite, whereas the values shown in the upper right  
970 corner are the periods of time during which the sample has been soaking in heavy water  
971 following the initial wetting step.

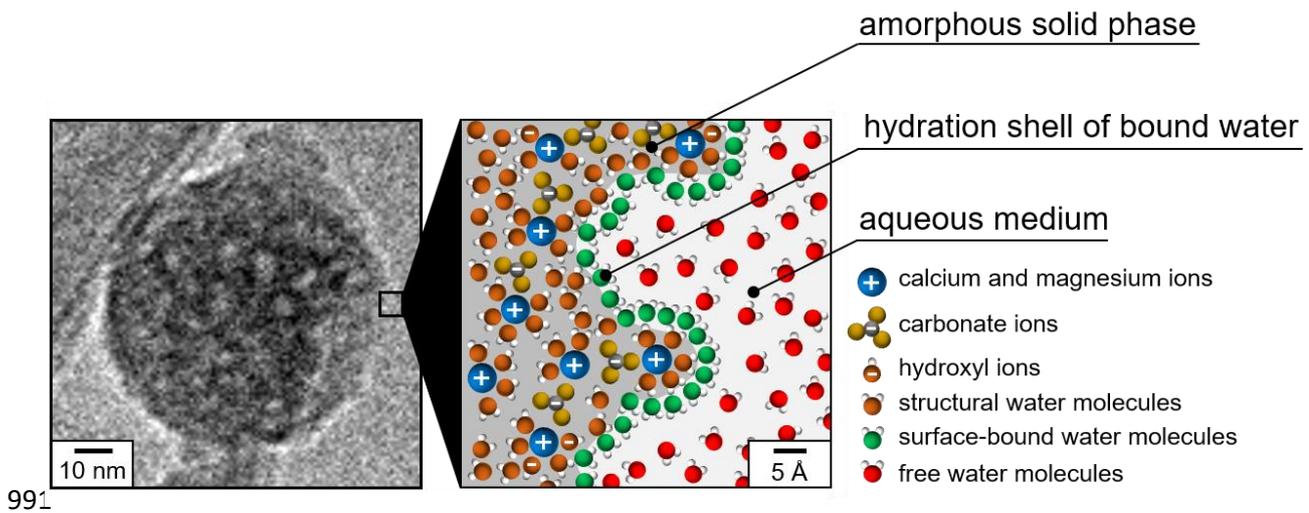


973

974 **Figure 7. Higher-order mineral structures following crystallization.** Representative  
 975 scanning helium ion microscopy (SHIM) micrographs of the higher-order mineral structures  
 976 resulting from the crystallization of the synthetic, Amorphous Calcium Magnesium Carbonate  
 977 (ACMC) sample soaked in deionized water in the MAS rotor (A to E); and of the ACMC  
 978 nanoparticles shown before crystallization (F). (A) is a low magnification micrograph that  
 979 displays the presence of spherulitic aggregates. (B to D) and (E) are different micrographs at  
 980 higher magnifications that reveal the features of the monohydrocalcite crystals that compose

981 the spherulitic aggregates shown in (A). For the purpose of comparison with biogenic crystals  
982 observed in coral skeleton, (G) shows a magnification of the square region marked by the  
983 yellow dashed line drawn in **Fig. 1B**. This high magnification micrograph exposes the skeletal  
984 fibers of a trabecula formed via a spherulitic growth mechanism <sup>109</sup>, and shows the “nano-  
985 particulate” texture of the acicular aragonite crystals. (H) Representative cryogenic  
986 transmission electron microscopy (cryo-TEM) micrograph of the higher-order mineral  
987 structures resulting from the crystallization of the synthetic ACMC sample soaked in  
988 deionized water in a 10ml vial. Inset shows a selected area electron diffraction (SAED)  
989 pattern of (H) labeled with monohydrocalcite crystal planes.

990 **Figure 8.**



992 **Figure 8. Chemical and structural model of the synthetic amorphous nanoparticles.**

993 Representative cryogenic transmission electron microscopy (cryo-TEM) micrograph of a

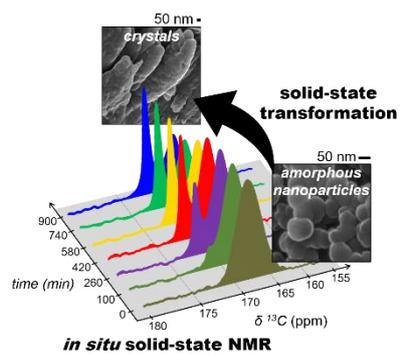
994 nanoparticle (diameter, about 80 nm) of the synthetic, Amorphous Calcium Magnesium

995 Carbonate (ACMC) sample dispersed in deionized water (**left**). Also shown is a two-

996 dimensional chemical and structural model of the surface region of an amorphous particle of

997 ACMC soaked in water (**right**).

998



999

1000

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