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LETTER

The glass transition temperature of anhydrous amorphous calcium carbonate

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25 **Abstract**

26 Amorphous calcium carbonate (ACC) is the least stable polymorph of calcium
27 carbonates. It has been identified to play an important role in nature (e.g.,
28 biomineralization and speleothem formation), where it acts as a precursor for the
29 transformation to more stable polymorphs such as calcite. Further, the use of ACC in
30 technical applications requires a robust understanding of the material's properties. We
31 present the first study that reveals the existence of a glass transition for synthetic and
32 anhydrous ACC. The glass transition occurs at 339 °C. Such measurements are
33 impossible with conventional differential scanning calorimetry (DSC) due to the high
34 tendency of ACC to crystallize. Fast scanning DSC with heating rates of 500 °C/s and
35 higher, however, can be used to separate the endothermic glass transition signature from
36 the exothermic crystallization event since crystallization is shifted to higher temperatures.
37 This allows the detection and quantification of the glass transition for ACC. These
38 observations indicate that ACC is a structural glass and is especially significant because
39 the synthesis of ACC, precipitation from a solution followed by lyophilization, contrasts
40 with the more conventional and well-known route of glass formation the rapid cooling of
41 a melt. Moreover, we prove that a structural glass can be produced from a simple single-
42 component carbonate system.

43

44 **Keywords:** glass transition temperature – amorphous calcium carbonate – flash
45 differential scanning calorimetry - lyophilization

46 **Introduction**

47

48 Amorphous calcium carbonate (ACC), $\text{CaCO}_3 \cdot n\text{H}_2\text{O}$, is a naturally occurring, although
49 unstable form of calcium carbonate and has been recognized as playing an important role
50 in biomineralization processes. Since its discovery (Sturcke 1898), it has been the subject
51 of particular interest since, aside from its role in biogenesis there are further technical
52 applications in, for example pharmaceuticals and in CO_2 sequestration, e.g., Politi et al.
53 (2004). Despite this, the characteristic properties of ACC and the formation process are
54 not well understood. ACC is the least stable form of calcium carbonate and has been
55 shown to exist in hydrous and anhydrous forms. Anhydrous ACC can be transformed to
56 more stable polymorphs of calcium carbonate such as vaterite, aragonite and ultimately
57 calcite by the progressive reduction of enthalpy (Radha et al. 2010).

58

59 Amorphous solids show no long-range order identified e.g., by the lack of Bragg
60 reflections in wide-angle X-ray or electron diffraction. Tammann (1903) proposed the
61 “classical” method to produce amorphous glassy materials to bypass the crystallization
62 by rapidly cooling a melt below the glass transition. Further techniques are used to make
63 a glass e.g., spray drying or lyophilization. For the definition of a glass we follow C.A.
64 Angell: “A (structural) glass is an amorphous solid, which is capable of passing
65 continuously into the viscous liquid state, usually, but not necessarily, accompanied by an
66 abrupt increase in heat capacity” (Angell 2004). Therefore, the observation of a glass
67 transition in ACC implies that it is a structural glass.

68

69 Usually, the glass transition (i.e., an abrupt change in heat capacity), can be identified by
70 differential scanning calorimetry (DSC). In the case of rapidly crystallizing materials like
71 ACC, the glass transition may be completely superimposed by the exothermal
72 crystallization peak. Such crystallization peak has been measured in ACC between 320
73 and 330 °C and no glass transition (i.e., endothermal peak) was observed (Koga et al.
74 1998; Koga and Yamane 2008; Wolf and Günther 2001; Radha et al. 2010). However,
75 the higher heating rate dependence of crystallization, compared to that of glass transition,
76 provides a way to separate the two processes at sufficiently high heating rates (Schawe
77 and Löffler 2019). Thus, we use the fast-scanning calorimetry to identify and quantify the
78 glass transition of ACC. A classification of ACC as a structural glass, although
79 synthesized in the laboratory under controlled conditions in this study, will further
80 deepen our understanding of its role in natural applications such as biomineralization and
81 carbonate melts.

82

83 **Materials and Methods**

84 *Synthesis*

85

86 Hydrous amorphous calcium carbonate (ACC: $\text{CaCO}_3 \cdot n\text{H}_2\text{O}$) was synthesized by mixing
87 the two solutions 0.25M CaCl_2 and 0.25M Na_2CO_3 produced from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, Na_2CO_3
88 (Carl Roth Chemicals) and ultrapure deionized water (DW: $18.2 \text{ M}\Omega \text{ cm}^{-1}$). The solutions
89 were kept in a refrigerator at 10 ± 1 °C for at least 4 hours prior to mixing. The
90 precipitated ACC was separated using a 0.2 μm cellulose filter and a suction filtration
91 device and rinsed twice with pre-cooled DW to remove Na^+ and Cl^- ions. Instantaneously

92 after filtration, the separated ACC was freeze-dried for 12 hours in a Virtis Benchtop 3L
93 and subsequently stored in a desiccator at ambient temperature using silica gel as drying
94 agent.

95

96 ***Transmission Electron Microscopy***

97

98 A probe-corrected FEI Themis microscope operated at an acceleration voltage of 300 kV
99 and equipped with a SuperXG1 EDX detector was used to obtain high-angle annular
100 dark-field scanning transmission electron microscopy (HAADF-STEM) images, electron
101 diffraction patterns, energy-dispersive X-ray (EDX) spectra and elemental mappings of
102 powder sample of freeze-dried ACC which was deposited onto 2 nm carbon-coated TEM
103 grid (QUANTIFOIL®). The data were analyzed with the software DigitalMicrograph®
104 (Gatan) and Velox (ThermoFisher Scientific).

105

106 ***Thermal gravimetry and conventional DSC***

107

108 Thermal gravimetry combined with conventional DSC was performed at heating rates of
109 10 °C/min using a Netzsch STA 449 F1. Samples of 3 to 5 mg of freeze-dried ACC and
110 ACC further dried at 250 °C (anhydrous ACC) were heated in Pt-crucibles with a lid up
111 to 350 °C. These measurements were performed in a high purity argon atmosphere with
112 flow rates of 100 ml/min.

113

114 ***Fast scanning differential scanning calorimetry (FDSC)***

115

116 The Flash DSC 2+ (Mettler-Toledo), which was used with a UFS1 calorimeter chip (van
117 Herwaarden et al. 2011). This sensor provides typical maximum heating and cooling rates
118 of 40,000 °C/s and 4,000 °C/s, respectively. Due to the low heat conductivity of ACC we
119 use heating and cooling rates up to 2000 °C/s to minimize effects of thermal inertia. The
120 sample side of the sensors were coated with a thin layer of silicon oil (AK 500.000
121 Wacker) to improve the thermal contact between sensor and samples with irregular shape
122 (Koulialias et al. 2021). The temperature program consisted of an initial isothermal
123 segment at 250 °C of 10 min followed by four heating-cooling cycles with matching
124 heating and cooling rates. ACC crystallized upon cooling after the first heating, even
125 though heating was terminated right after the glass transition was observed and before
126 crystallization during heating occurred. The three heating curves of the crystallized
127 material were used as baseline. All FDSC measurements were performed in a CO₂ flow
128 of 30 mL/min. The glass transition temperature is defined as thermodynamic glass
129 transition temperature (Richardson and Savill 1975) or the limiting fictive temperature
130 (Moynihan et al. 1976). Both definitions equally quantify T_g by the integral technique.

131

132 **Results**

133 The morphology and size of freeze-dried ACC was characterized by HAADF-STEM.
134 The acquired images reveal that ACC exists as polydisperse spheres with diameters
135 between 10 and 150 nm, which form random aggregates (Figure 1A). Compositional

136 homogeneity was verified by EDXS. High resolution HAADF-STEM images lack any
137 signs of crystallinity, thus confirming the amorphous structure of ACC (Figure 1B).
138 Weight loss curves obtained by heating from ambient temperature to 350 °C using STA
139 (a combination of thermal gravimetry (TGA) and conventional differential scanning
140 calorimetry (DSC)) indicate that the original ACC material (freeze-dried) contains $6.89 \pm$
141 0.1 wt% water (0.411 mole H_2O per mole ACC) (Figure 2). No further weight loss is
142 observed for material that has been dried at 250 °C (anhydrous ACC).

143

144 We performed calorimetric measurements to determine the glass transition temperature,
145 T_g , of anhydrous ACC using FDSC. ACC is hydrous after synthesis, see above. To obtain
146 anhydrous ACC, samples were further dried at 250 °C for 10 min in CO_2 directly in the
147 FDSC device. At these conditions no crystallization and further mass loss was observed,
148 as proven by STA. FDSC measurements were performed during heating with 500, 1000,
149 1500, and 2000 °C/s (Figure 3A). Glass transition and crystallization separate clearly at
150 these rates. The glass transition temperature, T_g , seems to increase with increasing
151 heating rate (Figure 3B). The reason is the influence of thermal inertia on the
152 measurement curves. This behavior is described by equation 1 (Schawe 2007).

153
$$T_g = T_{g0} + \beta\tau(1 - \exp(-\frac{\Delta T}{2\beta\tau})) \quad (1)$$

154 where T_g is the measured glass transition temperature at a specific heating rate, T_{g0} is the
155 glass transition temperature corrected by the thermal inertia, β is the heating rate, τ is the
156 effective thermal lag of sensor and sample, and ΔT is the width of the glass transition.

157 The resulting effective thermal lag is 16 ms, ΔT is 54 °C, and the glass transition
158 temperature of synthetic anhydrous ACC is $T_{g0} = 339$ °C.

159

160 **Discussion**

161

162 Synthetic anhydrous ACC undergoes a stepwise increase in heat capacity while crossing
163 the glass transition. This is a clear indication for a structural glass, although it was
164 produced by precipitation from a solution followed by lyophilization. Recently, Hess et
165 al. (2023) have demonstrated the glass-forming abilities for a binary carbonatitic system
166 (amorphous calcium-magnesium carbonate, APMC). Here, we have shown for the first
167 time that a single component carbonate system (calcium carbonate), can form glass
168 following the same synthesis procedure. Compared to ACC with a T_g of 339 °C, APMC
169 exhibits “higher“ glass transition temperatures at all heating rates with a heating-rate-
170 independent glass transition temperature of 376 °C. This suggests that the substitution of
171 Ca by Mg in ACC increases the glass transition temperature. Since APMC is more stable
172 than ACC, it was previously possible to study the amorphous two-component carbonate.

173 **Implications**

174

175 Our study shows that a material that was thought to be an amorphous solid is a structural
176 glass. The observation of a glass transition for anhydrous ACC was only possible by
177 applying very fast heating rates. It is therefore reasonable to assume that the same is true
178 for other amorphous materials. For such materials, then, the separation between

179 amorphous solids and glasses is meaningless and the limiting fictive temperature could be
180 used as a general order parameter to describe the solid amorphous state in the sense of
181 Gupta and Moynihan (1976). However, to characterize the kinetics of the glass transition,
182 it is necessary to determine its cooling rate dependence. This has not been achieved so
183 far. Our study expands the still very limited knowledge about glass transitions of
184 carbonate systems that are of petrological relevance (cf. Weidendorfer et al. (2023) and
185 Hess et al. (2023)). This may provide important implications for carbonate phases in
186 subsurface environments (e.g., biomineralization or magmatic processes). The fact that an
187 amorphous solid that is formed through lyophilization can be a structural glass, i.e., it is
188 formed by crossing a glass transition, implies that the materials properties change
189 drastically while crossing this boundary, which will finally affect the material's
190 macroscopic behavior in natural and anthropogenic applications.

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197

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200 investigation, writing; MD, DBD: writing.

201

202 **Competing Interest Statement:** The authors declare no competing interest.

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261 **Figure captions:**

262 **Figure 1:** **A** – HAADF-STEM image of an aggregate of freeze-dried ACC. **B** –
263 Magnification of a single ACC spherule of the aggregate shown in A. Signs of
264 crystallinity are absent.

265

266 **Figure 2:** Results from TGA (black) and conventional DSC (blue) measurements for
267 freeze-dried (dotted lines) ACC and ACC that has been dried at 250 °C (i.e., anhydrous).
268 Heating rates were 10 °C/min.

269

270 **Figure 3: A** - Heat flow curves obtained during heating at rates of 500, 1000, 1500, and
271 2000 °C/s using FDSC. All curves exhibit the glass transition (T_g indicated by arrows)
272 before crystallization (intense exothermic peak). **B** - The glass transition temperatures
273 determined at different heating rates for ACC (black symbols). A correction for thermal
274 lag (equation 1, red line) provides the glass transition temperature of 339 °C, which is
275 independent of the heating rate. The glass transition temperature of synthetic anhydrous
276 ACC is lower than that of synthetic anhydrous ACMC (Hess et al. 2023), which is 376
277 °C (grey symbol and line). Note, only one datapoint for ACMC is shown, since the other
278 measurements of ACMC were performed at higher heating rates of up to 6000 °C/s.

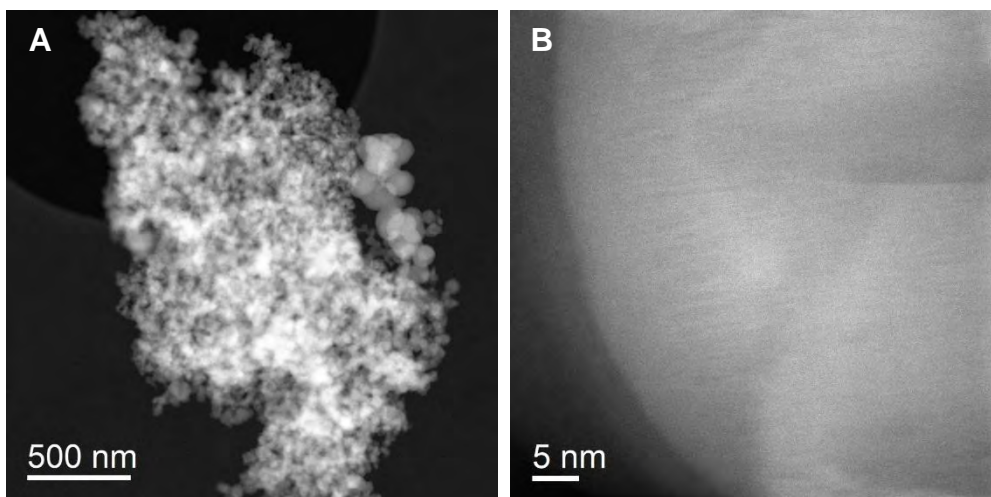


Figure 1

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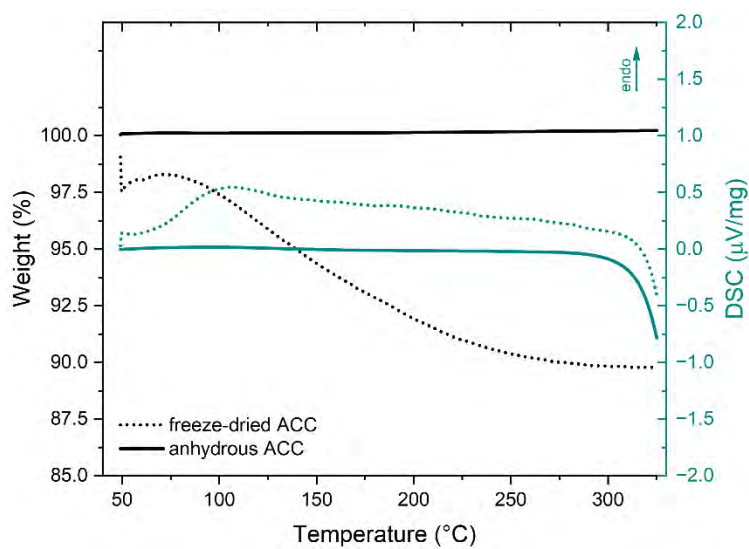


Figure 2

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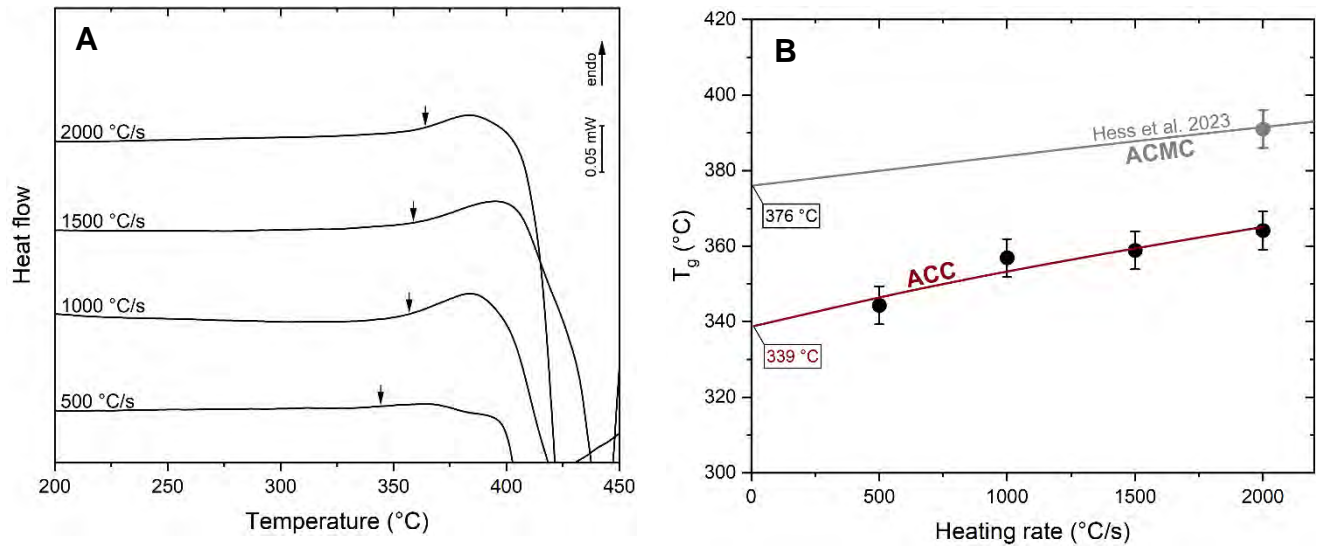


Figure 3

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