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LETTER

The glass transition temperature of anhydrous amorphous calcium carbonate

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Abstract

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

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

Introduction

Amorphous calcium carbonate (ACC), $CaCO_3 \cdot nH_2O$, is a naturally occurring, although unstable form of calcium carbonate and has been recognized as playing an important role in biomineralization processes. Since its discovery (Sturcke 1898), it has been the subject of particular interest since, aside from its role in biogenesis there are further technical applications in, for example pharmaceuticals and in CO_2 sequestration, e.g., Politi et al. (2004). Despite this, the characteristic properties of ACC and the formation process are not well understood. ACC is the least stable form of calcium carbonate and has been shown to exist in hydrous and anhydrous forms. Anhydrous ACC can be transformed to more stable polymorphs of calcium carbonate such as vaterite, aragonite and ultimately calcite by the progressive reduction of enthalpy (Radha et al. 2010).

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

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

Materials and Methods

Synthesis

Hydrous amorphous calcium carbonate (ACC: $CaCO_3 \cdot nH_2O$) was synthesized by mixing the two solutions 0.25M $CaCl_2$ and 0.25M Na_2CO_3 produced from $CaCl_2$ $2H_2O$, Na_2CO_3 (Carl Roth Chemicals) and ultrapure deionized water (DW: 18.2 MΩ cm^{-1}). The solutions were kept in a refrigerator at 10±1 °C for at least 4 hours prior to mixing. The precipitated ACC was separated using a 0.2 μm cellulose filter and a suction filtration device and rinsed twice with pre-cooled DW to remove Na^+ and Cl^- ions. Instantaneously

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

Transmission Electron Microscopy

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

Thermal gravimetry and conventional DSC

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

Fast scanning differential scanning calorimetry (FDSC)

The Flash DSC 2+ (Mettler-Toledo), which was used with a UFS1 calorimeter chip (van Herwaarden et al. 2011). This sensor provides typical maximum heating and cooling rates of 40,000 °C/s and 4,000 °C/s, respectively. Due to the low heat conductivity of ACC we use heating and cooling rates up to 2000 °C/s to minimize effects of thermal inertia. The sample side of the sensors were coated with a thin layer of silicon oil (AK 500.000 Wacker) to improve the thermal contact between senor and samples with irregular shape (Koulialias et al. 2021). The temperature program consisted of an initial isothermal segment at 250 °C of 10 min followed by four heating-cooling cycles with matching heating and cooling rates. ACC crystallized upon cooling after the first heating, even though heating was terminated right after the glass transition was observed and before crystallization during heating occurred. The three heating curves of the crystallized material were used as baseline. All FSDC measurements were performed in a CO_2 flow of 30 mL/min. The glass transition temperature is defined as thermodynamic glass transition temperature (Richardson and Savill 1975) or the limiting fictive temperature (Moynihan et al. 1976). Both definitions equally quantify T_g by the integral technique.

Results

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

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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 ±
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 FSDC 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 $$T_g = T_{g0} + \beta\tau\left(1 - \exp\left(-\frac{\Delta T}{2\beta\tau}\right)\right) \qquad (1)$$

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, ACMC). 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, ACMC
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 ACMC 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

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

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

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205 **REFERENCES CITED**

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Figure captions:

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

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

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

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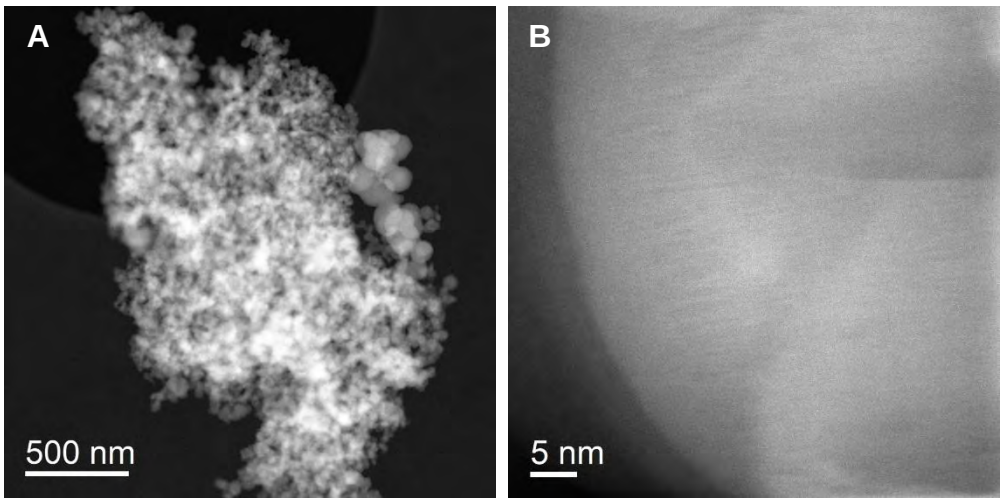

Figure 1

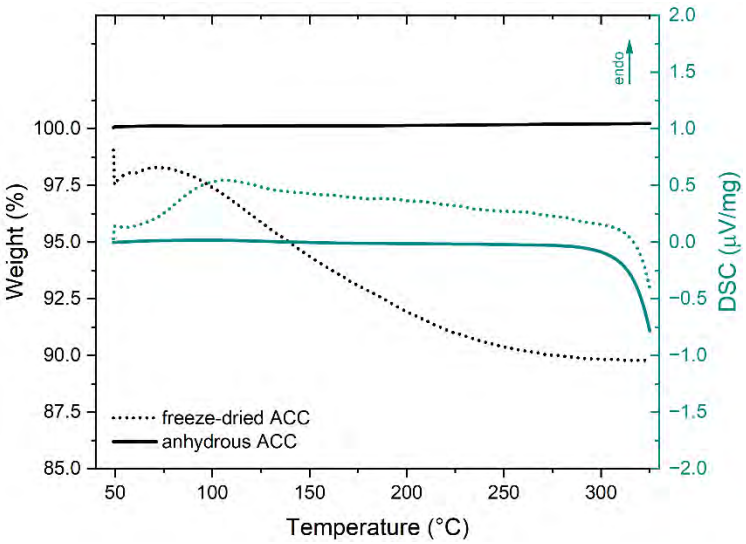

Figure 2

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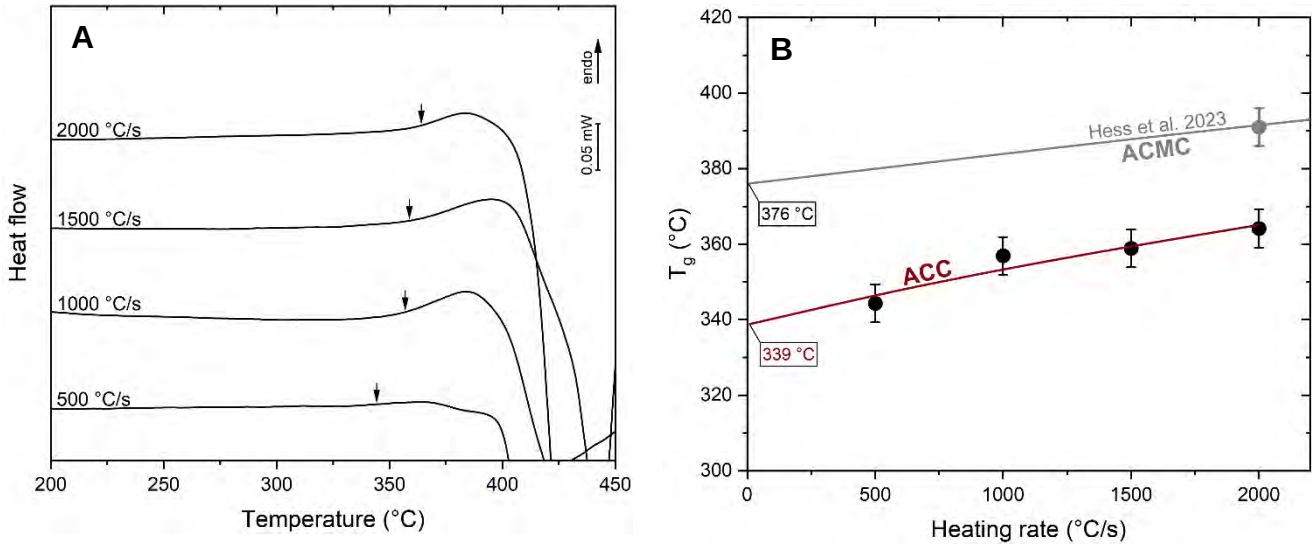

Figure 3

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