

Liquid pressure-transmitting media inhibit pressure-induced dehydration and subsequent crystallisation of amorphous calcium carbonate

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Calcium carbonate (CaCO_3) has a complex phase diagram involving many high-pressure variants of calcite and aragonite. Amorphous calcium carbonate (ACC) is a non-crystalline form of hydrated calcium carbonate ($\text{CaCO}_3 \cdot n \text{H}_2\text{O}$; typically $n < 1.5$). It has been reported that ACC can be crystallised into anhydrous polymorphs by applying pressures of 0.2–0.64 GPa [1–3]. However, more recent studies reported no crystallisation even at ~20 GPa [4,5]. In this study, we investigated the role of pressure-transmitting media (PTM) on the pressure-induced crystallisation of ACC by *in-situ* x-ray diffraction experiments.

Fig. 1a summarises the structural changes of ACC ($\text{CaCO}_3 \cdot 1.3 \text{H}_2\text{O}$) compressed in a diamond anvil cell (DAC) without any PTM. ACC first crystallised into a mixture of calcite and vaterite, followed by vaterite-to-calcite transition, the formation of ikaite ($\text{CaCO}_3 \cdot 6 \text{H}_2\text{O}$), and the phase transition of calcite into a high-pressure phase called calcite-II. On the other hand, no pressure-induced crystallisation was observed when ACC was dehydrated in advance by heating (yielding $\text{CaCO}_3 \cdot 0.0 \text{H}_2\text{O}$). These results revealed that the crystallisation of ACC is triggered by water released from ACC under pressure.

Next, ACC was compressed in a liquid PTM, namely Daphne 7373. Daphne 7373 is a mixture of several olefines and can be used as a liquid PTM up to 2.2 GPa at room temperature [6]. X-ray diffraction patterns (**Fig. 1b**) indicate no pressure-induced crystallisation. This suggests that the dehydration of ACC, which occurred without PTM, was somehow inhibited by the liquid PTM. To further corroborate the absence of pressure-induced dehydration, ACC was compressed up to 1.0 GPa with Daphne 7373 using a piston-cylinder apparatus and then recovered to ambient pressure for further characterisation. Thermogravimetric analysis showed that the recovered ACC retained the same amount of water as the initial state, and infrared absorption spectroscopy showed no changes in the vibration structures, particularly the broad O-H stretching bands.

This study revealed that PTM inhibits the dehydration of ACC, and therefore its crystallisation into anhydrous polymorphs. As far as we know, this is a novel type of pressure-induced behaviour which can be controlled by changing the surrounding environment.

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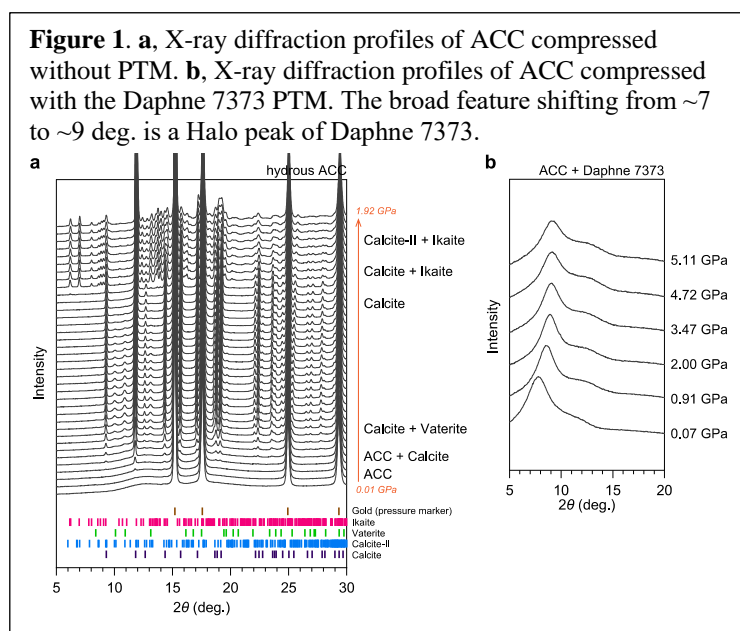


Figure 1. a, X-ray diffraction profiles of ACC compressed without PTM. b, X-ray diffraction profiles of ACC compressed with the Daphne 7373 PTM. The broad feature shifting from ~7 to ~9 deg. is a Halo peak of Daphne 7373.