

Lawrence Berkeley National Laboratory

Chemical Sciences

Title

A hydrated crystalline calcium carbonate phase: Calcium carbonate hemihydrate

Permalink

<https://escholarship.org/uc/item/88x9937w>

Journal

Science, 363(6425)

ISSN

0036-8075

Authors

Zou, Zhaoyong
Habraken, Wouter JEM
Matveeva, Galina
[et al.](#)

Publication Date

2019-01-25

DOI

10.1126/science.aav0210

Peer reviewed

SOLID-STATE CHEMISTRY

A hydrated crystalline calcium carbonate phase: Calcium carbonate hemihydrate

Zhaoyong Zou^{1*}, Wouter J. E. M. Habraken¹, Galina Matveeva², Anders C. S. Jensen¹, Luca Bertinetti¹, Matthew A. Hood¹, Chang-yu Sun³, Pupa U. P. A. Gilbert^{3,4}, Iryna Polishchuk⁵, Boaz Pokroy⁵, Julia Mahamid^{6,7}, Yael Politi¹, Steve Weiner⁸, Peter Werner⁹, Sebastian Bette¹⁰, Robert Dinnebier¹⁰, Ute Kolb^{2,11}, Emil Zolotoyabko⁵, Peter Fratzl^{1†}

As one of the most abundant materials in the world, calcium carbonate, CaCO₃, is the main constituent of the skeletons and shells of various marine organisms. It is used in the cement industry and plays a crucial role in the global carbon cycle and formation of sedimentary rocks. For more than a century, only three polymorphs of pure CaCO₃—calcite, aragonite, and vaterite—were known to exist at ambient conditions, as well as two hydrated crystal phases, monohydrocalcite (CaCO₃·1H₂O) and ikaite (CaCO₃·6H₂O). While investigating the role of magnesium ions in crystallization pathways of amorphous calcium carbonate, we unexpectedly discovered an unknown crystalline phase, hemihydrate CaCO₃·½H₂O, with monoclinic structure. This discovery may have important implications in biomineralization, geology, and industrial processes based on hydration of CaCO₃.

Calcium carbonate (CaCO₃) makes up nearly 4% of Earth's crust and is produced mainly by the sedimentation of skeletal remains of marine organisms accumulated over millions of years in the form of, for example, chalk and limestone. Calcium carbonate minerals are involved in the global carbon cycle and have been intensively investigated because of their importance for paleoclimate reconstructions (1), ocean acidification (2–4), and biomineralization (5, 6). Calcium carbonate is often referenced as a model system for studying nucleation and crystallization mechanisms from ion solutions (7, 8). For more than a century, three anhydrous crystalline polymorphs of CaCO₃ were known to exist at ambient conditions—calcite, aragonite, and vaterite—as well as two hydrated crystalline phases, monohydrocalcite (MHC) (CaCO₃·1H₂O) and ikaite (CaCO₃·6H₂O)

(9). In addition to these crystalline phases, calcium carbonate also exists in various amorphous states, known as amorphous calcium carbonate (ACC), which, together with organic macromolecules and inorganic ions, play a crucial role in controlling the formation of crystalline calcium carbonate biominerals (10–13). Here, we report the discovery and comprehensive characterization of a hitherto unknown hydrated crystalline calcium carbonate compound with a composition of CaCO₃·½H₂O, i.e., calcium carbonate hemihydrate (CCHH). This phase forms from ACC in solution in the presence of Mg²⁺ ions with a Mg/Ca molar ratio of ~5/1. At the same time, the Mg concentration in CCHH crystallites stays below 2 atomic %. Compared with the same process for calcite, entering of Mg²⁺ ions into CCHH is hampered because of the differences in the cation coordination (14). As we show below, Ca is eightfold coordinated in CCHH but sixfold coordinated in calcite. It is proposed that Mg²⁺ ions in solution inhibit the dehydration of ACC and control the hydration level of the crystalline phases. The discovery of this hydrated crystalline calcium carbonate phase emphasizes the importance of amorphous precursors and Mg²⁺ in controlling the crystallization pathways of calcium carbonate.

We synthesized CCHH by adding a premixed solution of CaCl₂ and MgCl₂ to Na₂CO₃ solution (15). ACC precipitates immediately, whereas CCHH starts to form after 2000 s. The CCHH formation is completed in nearly 4200 s. We first determined the composition of CCHH by combining inductively coupled plasma optical emission spectrometry (ICP-OES) (table S1) and thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) analysis (fig. S1), giving the preliminary chemical formula of Ca_{0.98}Mg_{0.02}CO₃·*m*H₂O with

factor *m* = 0.48. Factor *m* ≈ 0.5 was obtained by removing the amount of physisorbed water (evaporated below 115°C) (fig. S1) from the total water loss measured by TGA.

Morphological analysis shows that CCHH appears as needlelike crystals with a diameter of ~200 nm and a length between 1 and 5 μm (Fig. 1A), which are further composed of well-aligned nanocrystals with a diameter of ~30 nm (Fig. 1B). The infrared (IR) and Raman spectra of CCHH (Fig. 1, C and D) differ substantially from the spectra of all known calcium carbonate phases. However, the spectral peaks we observed can be attributed to known vibrational modes for calcium carbonate-based structures (table S2) (16). The most prominent feature is the symmetric stretching mode, ν₁, of the carbonate group (CO₃), which appears as a single sharp peak at 1102 cm⁻¹ (full width at half maximum: 4 cm⁻¹) in the Raman spectrum and a weak band at 1096 cm⁻¹ in the IR spectrum. These wave numbers are substantially higher than those known for all other calcium carbonate phases; for example, in calcite, ν₁ = 1085 cm⁻¹ (17).

In addition, the single sharp peak without splitting suggests a solitary site symmetry of the carbonate within the structure (18). The asymmetric stretching mode, ν₃, in the IR spectrum splits into four peaks, suggesting that the carbonate groups in the CCHH crystal structure are somewhat distorted. Without any distortions, the ν₃ vibrational mode is only allowed to be doubly degenerated. Similar carbonate vibrational modes exist in huntite [Mg₃Ca(CO₃)₄], barytocalcite [BaCa(CO₃)₂], and shortite [Na₂Ca₂(CO₃)₃] (19, 20). The in-plane bending mode, ν₄, splits into two peaks at 700 and 731 cm⁻¹ in the Raman spectrum and appears as weak peaks at 692 and 723 cm⁻¹ in the IR spectrum, which also differs from the bending mode appearance in other calcium carbonate phases.

For structural analysis, we carried out high-resolution x-ray powder diffraction (HRXRPD) measurements at the dedicated beamline ID22 of the European Synchrotron Radiation Facility. Even a quick analysis of the collected diffraction pattern (Fig. 1E) allows us to conclude that it does not fit any known calcium carbonate phases. Unidentified diffraction peaks of highest intensity appear at Bragg spacings (*d*) of 5.31 Å (2θ = 5.36°), 5.22 Å (2θ = 5.45°), 3.03 Å (2θ = 9.39°), and 2.50 Å (2θ = 11.37°). Detailed analysis of powder diffraction data, based on the developed structural solution, is given below and strongly supports the appearance of the previously unknown phase. In addition, the extracted pair distribution function pattern (fig. S2A) and x-ray absorption near-edge structure (XANES) spectra collected at the Ca K-edge (fig. S2B) of CCHH show some similarities to those of ACC and MHC but are distinct from those known for anhydrous crystalline phases of CaCO₃. XANES spectra, taken at the O K-edge (fig. S2C) and Ca L-edge (fig. S2D) by using photoemission electron microscopy (PEEM), differ from those collected from anhydrous calcium carbonate phases or any other CaCO₃ phases.

¹Department of Biomaterials, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany. ²Johannes Gutenberg-Universität Mainz, Institut für Anorganische und Analytische Chemie, Mainz, Germany. ³Department of Physics, University of Wisconsin–Madison, Madison, WI, USA. ⁴Departments of Chemistry, Geoscience, and Materials Science, University of Wisconsin–Madison, Madison, WI, USA. ⁵Department of Materials Science and Engineering, Technion-Israel Institute of Technology, Haifa, Israel. ⁶Department of Molecular Structural Biology, Max Planck Institute of Biochemistry, Martinsried, Germany. ⁷Structural and Computational Biology Unit, European Molecular Biology Laboratory, Heidelberg, Germany. ⁸Department of Structural Biology, Weizmann Institute of Science, Rehovot, Israel. ⁹Max Planck Institute of Microstructure Physics, Halle, Germany. ¹⁰Max Planck Institute for Solid State Research, Stuttgart, Germany. ¹¹Institute of Applied Geosciences, TU Darmstadt, Darmstadt, Germany.

*Present address: State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, China.

†Corresponding author. Email: fratzl@mpikg.mpg.de

We monitored the time-dependent pH and Ca^{2+} activity in solution (Fig. 2, A and B) to determine the range of reaction parameters for CCHH formation and correlated them with the products formed at different time points (Fig. 2, C to F). We subdivided the reaction kinetics into three stages. At stage I, ACC with ~ 6.5 mol % of Mg is precipitated immediately and remains stable in the mother solution for ~ 20 min. According to our TGA data, it comprises nearly one molecule of water per one molecule of CaCO_3 . At stage II, this monohydrated amorphous phase transforms into CCHH, as indicated by a sharp decrease in the Ca^{2+} activity. Here, the Mg content in CCHH decreases to ~ 1.5 mol %, which, together with an abnormal increase in pH, suggests that at this point Mg ions are released back into solution owing to dissolution of magnesium carbonate molecules stored in ACC. At stage III, CCHH gradually transforms into MHC, which is manifested by a slow decrease in pH and Ca^{2+} activity lasting nearly 11 hours. The transformation between the three stages also includes release and reacquisition of water molecules. ACC and MHC are monohydrated, whereas CCHH contains roughly half the amount of water. The structural aspects of the time-dependent transformations were also tracked by laboratory x-ray powder diffraction (XRPD) measurements (Fig. 2D).

The Raman spectra (Fig. 2E) help us easily distinguish ACC, CCHH, and MHC by comparing the wave numbers of the ν_1 -mode positioned, respectively, at 1083, 1102, and 1069 cm^{-1} . In IR spectra (Fig. 2F), we recognized the characteristic splitting of the ν_3 mode for ACC, which elaborates into four peaks for CCHH and turns back to two peaks for MHC. We used scanning electron microscopy (SEM) images (fig. S3) to show that the initially precipitated ACC nanoparticles are attached to the needlelike CCHH crystals during the ACC-to-CCHH transformation and, subsequently, CCHH needles are attached to the surface of MHC crystals. We concluded that CCHH is thermodynamically a metastable phase formed from an amorphous precursor. We stress that, in solution, it gradually transforms into MHC, but is stable (at least for a few months) when stored in vacuum. Transformation of the needle-shaped CCHH crystals to MHC resembles that of needle-shaped hemihydrate bassanite crystals ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (21).

We performed experiments at different initial carbonate concentrations and Mg^{2+} contents to uncover optimal conditions for CCHH synthesis (figs. S4 to S6). We found that CCHH can only be synthesized in solutions containing intermediate concentrations of Mg^{2+} and carbonate (Fig. 3A). In addition, the Mg^{2+} content

in the ACC must be maintained between 5 and 9%. A substantially lower Mg^{2+} content in the ACC as compared with the initial Mg^{2+} content in solution also suggests that after ACC formation the solution is enriched in Mg^{2+} . Therefore, knowing the $\text{Mg}^{2+}/\text{Ca}^{2+}$ molar ratio in solution after ACC formation is important (Fig. 3B). For CCHH formation, this ratio is between 4.3 and 6.1 (i.e., ~ 5.2), which is characteristic for modern seawater. We assume that the dissolved Mg^{2+} inhibits the crystallization of calcite in our system and promotes the formation of CCHH. We validated our hypothesis with additional experiments, in which Mg^{2+} ions were added after precipitation of pure ACC (fig. S7). CCHH is also formed in this scenario, but only if the molar ratio of $\text{Mg}^{2+}/\text{Ca}^{2+}$ in solution is in the range of ~ 4 to 6 (table S3).

To determine the atomic structure of CCHH, we resorted to automated electron diffraction tomography (ADT) (22) and HRXRPD (Fig. 1E), as the crystals were too small for single-crystal XRD and not stable under the electron beam used in transmission electron microscopy (TEM). The HRXRPD pattern has both broad and sharp reflections, with some peaks having a characteristic triangular shape that indicates strong stacking-fault-like structural disorder (23, 24). Because ab initio crystal structure solution based

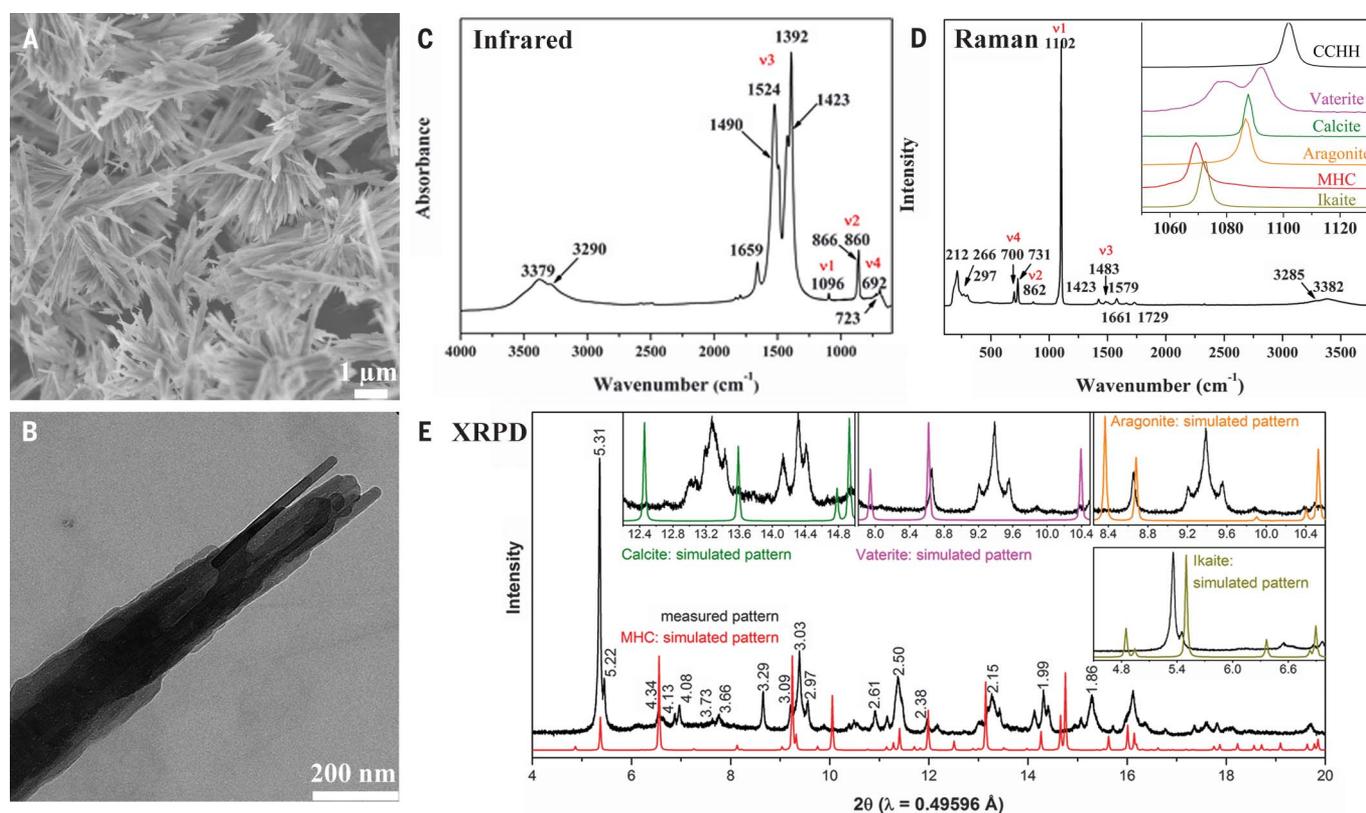


Fig. 1. Morphological and structural characterization of CCHH.

SEM (A) and TEM (B) images, IR (C) and Raman (D) spectra, and synchrotron HRXRPD pattern (E) of CCHH using a wavelength of 0.49596 Å. The inset in (D) shows a comparison of the Raman spectra

of CCHH with those of other calcium carbonate phases in the range of 1050 to 1115 cm^{-1} . The insets in (E) show comparisons of the measured HRXRPD pattern of CCHH with simulated patterns of other calcium carbonate phases.

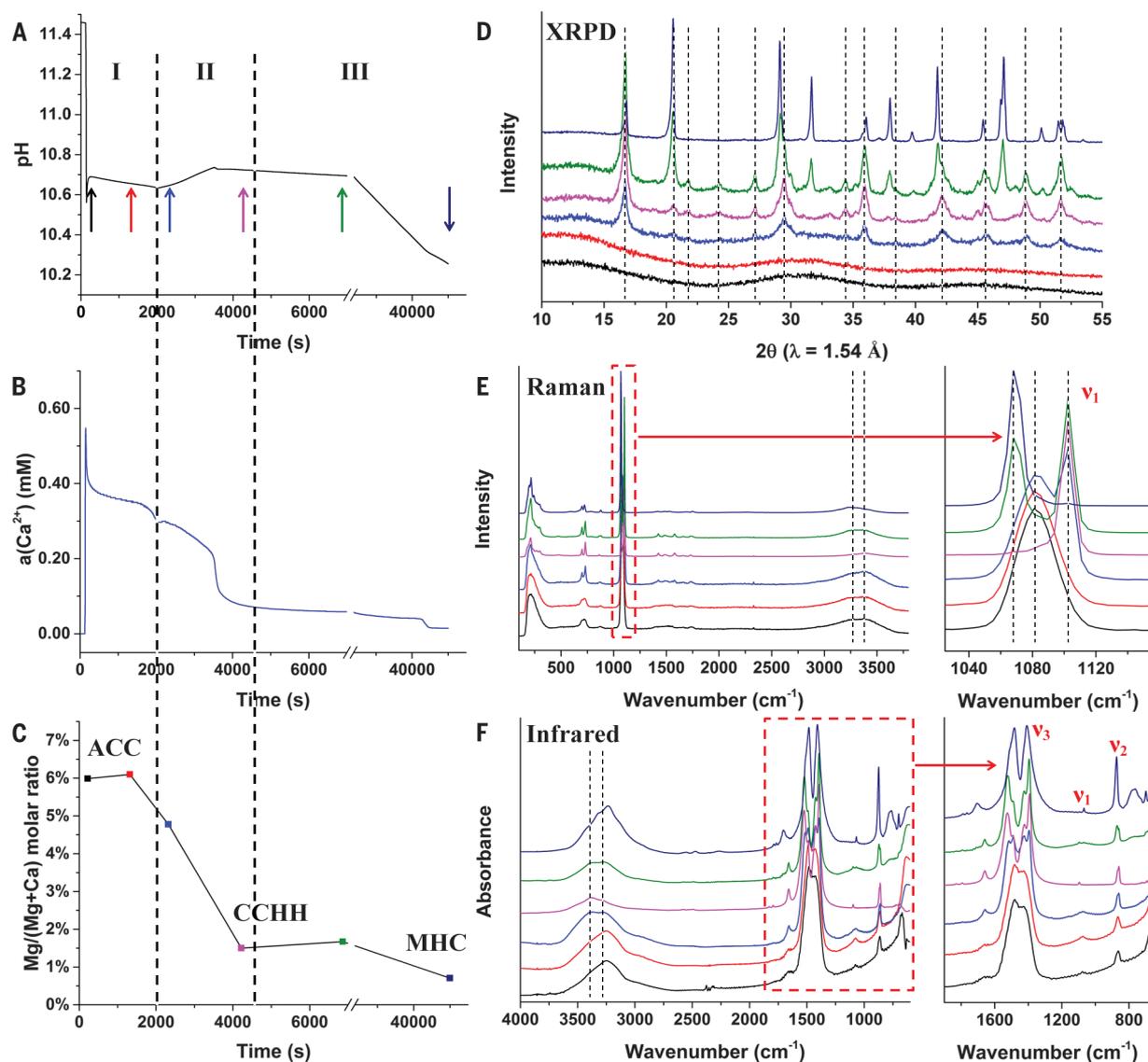


Fig. 2. Chemical and structural evolution during the formation and transformation of CCHH in solution. pH (A) and Ca^{2+} activity (B) changes in the reaction solution at a calcium carbonate concentration of 40 mM in the presence of 20% Mg. The $\text{Mg}/(\text{Mg}+\text{Ca})$ molar ratio (C),

laboratory XRPD pattern (D), and Raman (E) and IR (F) spectra of the samples extracted at several time points, marked by the differently colored arrows in (A). Dashed lines in (D) to (F) help with visualization of the difference in the peak positions. λ indicates x-ray wavelength.

on HRXRPD data was not possible, we applied the ADT method that allows for structural analysis of single nanocrystals. Our three-dimensional reconstruction of ADT data taken from needle-shaped crystals (fig. S8) led to a monoclinic unit cell for $\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ with space group $P2_1/c$ and lattice parameters $a = 9.33 \text{ \AA}$, $b = 10.44 \text{ \AA}$, $c = 6.16 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90.5^\circ$, and $\gamma = 90^\circ$ (table S4). The structure solution with a final residual R(F) of 0.219 (table S5), implemented using the direct method approach, yielded atomic positions of calcium and carbonate in a rational geometry, as well as the positions of the additional oxygen from water molecules (fig. S9 and data S1). The simulated HRXRPD pattern for this structure, in general, fits reasonably well the measured synchrotron diffraction pattern (fig. S10), though some extra reflections still

exist, which we attributed to a small amount of additional phases, structurally interrelated with CCHH. This situation in some ways resembles that of vaterite (25, 26).

Because of the slow transformation of CCHH into MHC in solution (Fig. 2), the presence of the latter phase is reasonable and we clearly see the 111 reflection of MHC at $2\theta = 6.55^\circ$ in the HRXRPD pattern (fig. S10). In addition, we found another solid phase, exhibiting a platelike morphology (fig. S8) by ADT analysis. On the basis of the unit cell dimensions (table S4), this phase most likely is another calcium carbonate hydrate $\text{CaCO}_3 \cdot n\text{H}_2\text{O}$ with $n = \frac{3}{4}$.

Therefore, the most probable origin of the structural disorder in CCHH samples is incorporation of additional water molecules into the crystal structure of CCHH. This leads to coexist-

ing coherent domains of CCHH, $\text{CaCO}_3 \cdot \frac{3}{4}\text{H}_2\text{O}$, and MHC within the crystals. The borders between domains appear as stacking faults. Such an intergrowth is likely only when the defects are commensurate. To confirm this, we transformed the unit cells of $\text{CaCO}_3 \cdot \frac{3}{4}\text{H}_2\text{O}$ and MHC into the metric of the cell of CCHH (table S4). After the transformation, we found only small mismatches ($\sim 2\%$) for the transformed a and b lattice parameters, whereas the c lattice parameter of MHC has a large mismatch of 22.56%, with respect to the CCHH lattice. Therefore, commensurate crystallographic intergrowth is possible only in the c direction of CCHH.

A comparison of the layered motifs in the crystal structures of CCHH and MHC perpendicular to the c axis (Fig. 4) shows that the packing in MHC is denser than in CCHH (see

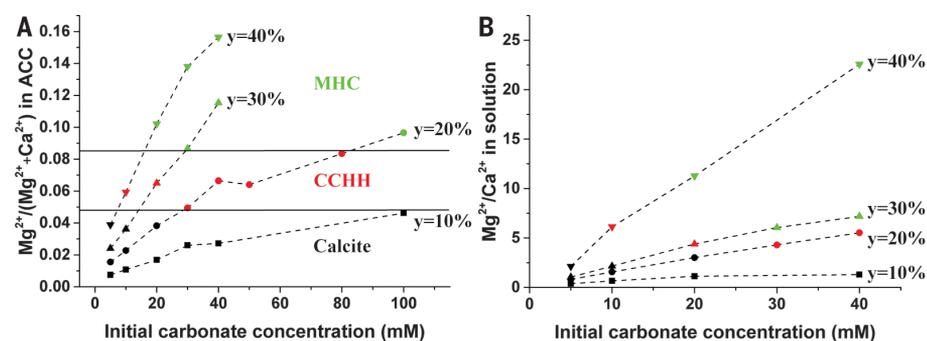
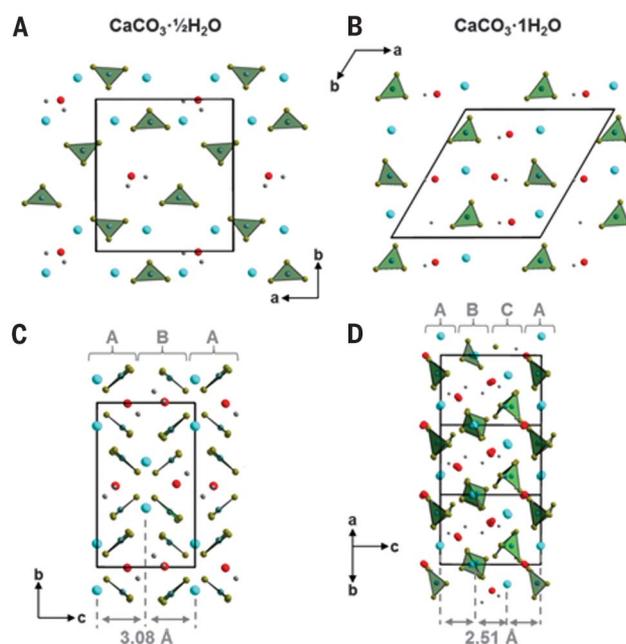


Fig. 3. Diagram for CCHH formation under various conditions. (A) The $\text{Mg}^{2+}/(\text{Mg}^{2+}+\text{Ca}^{2+})$ molar ratio in ACC, as a function of the initial carbonate concentration in solution (5 to 100 mM) and initial Mg^{2+} content [$y = \text{Mg}^{2+}/(\text{Mg}^{2+}+\text{Ca}^{2+})$ molar ratio] in solution upon mixing (10 to 40%). (B) The $\text{Mg}^{2+}/\text{Ca}^{2+}$ molar ratio in solution after ACC formation was estimated on the basis of Ca^{2+} activity of the solution and the $\text{Mg}^{2+}/(\text{Mg}^{2+}+\text{Ca}^{2+})$ ratio in the ACC. Differently colored points are associated with different crystalline phases (black, red, and green represent, respectively, calcite, CCHH, and MHC). The horizontal lines separate the diagram regions in which the three distinct mineral phases form.

Fig. 4. Comparison of layered motifs in the crystal structures of CCHH and MHC. (A and C) CCHH ($\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$) and (B and D) MHC ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$).



The layers of CCHH consist of $\text{Ca}(\mu_2\text{-CO}_3)_{2/5}(\mu_1\text{-CO}_3)_{3/5}(\text{H}_2\text{O})_{1/2}$ double zigzag chains running along the a axis (A); here, differently oriented (up and down) carbonate groups are indicated by indices μ_2 and μ_1 . Stacking in the c direction occurs in a conventional ABAB fashion (C) with an interlayer spacing (the distance between Ca planes) equal to 3.08 Å. The layers of MHC consist of a dense packing of $\text{Ca}(\mu_2\text{-CO}_3)_{2/4}(\mu_1\text{-CO}_3)_{2/4}(\text{H}_2\text{O})_{2/2}$ polyhedra (B). Along the c axis, condensed layers are stacked in an ABC fashion (D) with an interlayer distance of 2.51 Å. Different types of atoms are colored as follows: Ca, blue; carbonate groups, green; oxygen from water, red; and hydrogen, gray.

also table S4). Hence, the structural transition from CCHH to MHC does not occur by an intercalation of additional water molecules with shifts in the stacking order of the layers, but instead the transition causes a comprehensive change in the layers' constitution and stacking. An example of this effect is on the 002 reflection of CCHH ($d = 3.08$ Å, $2\theta = 9.23^\circ$), which has a very pronounced triangular shape broadening toward lower d spacing (fig. S11).

To check the suitability of the considered microstructure model that contains a commensurate crystallographic intergrowth, we performed

a Pawley fit (27) using three phases with transformed unit cells (table S4). This allowed us to successfully index and reproduce all reflections in the HRXRPD pattern (fig. S12). In particular, we can describe the sharp reflections at $2\theta = 6.5^\circ$ ($d = 4.37$ Å) and at $2\theta = 8.7^\circ$ ($d = 3.27$ Å) using the transformed cells of MHC and $\text{CaCO}_3 \cdot \frac{3}{4}\text{H}_2\text{O}$. Secondly, the preferred model provided an excellent fit (with a weighted profile R-factor of 7.55%) to the measured synchrotron HRXRPD pattern (fig. S12), allowing us to refine the lattice parameters (table S6). Moreover, the model also fits the spectroscopy data, indicating that inhomogeneous

distortion of the carbonate groups is caused by the abovementioned structural disorder.

Final proof of the microstructure model would require complex DIFFaX (28) simulations, including three stacking regimes with different layer constitutions, transitions among them, and specific faults within each individual regime; the structural characterization of $\text{CaCO}_3 \cdot \frac{3}{4}\text{H}_2\text{O}$; and a global optimization of the measured pattern by a Rietveld-compatible approach. Because the routines (29), which were successfully applied to faulted samples, were developed for less complex faulting models (24, 30), this is not currently possible. Besides, the addition of $\text{CaCO}_3 \cdot \frac{3}{4}\text{H}_2\text{O}$ and MHC phases is very minor. Because the water content, according to our TGA, is close to $\frac{1}{2}$ H_2O per CaCO_3 , we estimate that these phases comprise not more than a few percent. In fact, Rietveld refinement with CCHH and MHC yields less than 4% for the latter. Therefore, more than 90% in the reaction products is the CCHH phase.

The discovery of CCHH, its formation pathways, and its complete structure determination (data S1) substantially expand our knowledge of the CaCO_3 family. An essential step forward would be the search for CCHH crystals, via their diffraction and spectroscopic fingerprints, in nature (rocks, biomineralization outcomes) and within the products of relevant technological processes.

REFERENCES AND NOTES

1. J. W. Beck *et al.*, *Science* **257**, 644–647 (1992).
2. F. J. Millero, *Chem. Rev.* **107**, 308–341 (2007).
3. M. Cusack, A. Freer, *Chem. Rev.* **108**, 4433–4454 (2008).
4. S. Goffredo *et al.*, *Nat. Clim. Chang.* **4**, 593–597 (2014).
5. L. B. Gower, *Chem. Rev.* **108**, 4551–4627 (2008).
6. L. J. de Nooijer, H. J. Spero, J. Erez, J. Bijma, G. J. Reichart, *Earth Sci. Rev.* **135**, 48–58 (2014).
7. D. Gebauer, A. Völkel, H. Colfen, *Science* **322**, 1819–1822 (2008).
8. M. H. Nielsen, S. Aloni, J. J. De Yoreo, *Science* **345**, 1158–1162 (2014).
9. J. W. Morse, R. S. Arvidson, A. Lüttge, *Chem. Rev.* **107**, 342–381 (2007).
10. Y. Politi, T. Arad, E. Klein, S. Weiner, L. Addadi, *Science* **306**, 1161–1164 (2004).
11. L. Addadi, S. Raz, S. Weiner, *Adv. Mater.* **15**, 959–970 (2003).
12. L. Addadi, D. Joester, F. Nudelman, S. Weiner, *Chemistry* **12**, 980–987 (2006).
13. Y. U. T. Gong *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **109**, 6088–6093 (2012).
14. W. Sun, S. Jayaraman, W. Chen, K. A. Persson, G. Ceder, *Proc. Natl. Acad. Sci. U.S.A.* **112**, 3199–3204 (2015).
15. Z. Zou *et al.*, *Chem. Mater.* **27**, 4237–4246 (2015).
16. F. A. Andersen *et al.*, *Acta Chem. Scand.* **45**, 1018–1024 (1991).
17. W. D. Bischoff, S. K. Sharma, F. T. Mackenzie, *Am. Mineral.* **70**, 581–589 (1985).
18. G. Behrens, L. T. Kuhn, R. Ueb, A. H. Heuer, *Spectrosc. Lett.* **28**, 983–995 (1995).
19. H. H. Adler, P. F. Kerr, *Am. Mineral.* **48**, 839–853 (1963).
20. R. L. Frost, M. J. Dickfos, *Spectrochim. Acta A* **71**, 143–146 (2008).
21. A. E. S. Van Driessche *et al.*, *Science* **336**, 69–72 (2012).
22. U. Kolb, E. Mugnaioli, T. E. Gorelik, *Cryst. Res. Technol.* **46**, 542–554 (2011).
23. B. E. Warren, *Phys. Rev.* **59**, 693–698 (1941).
24. S. Bette *et al.*, *Dalton Trans.* **46**, 15216–15227 (2017).
25. L. Kabalala-Amitai *et al.*, *Science* **340**, 454–457 (2013).
26. E. Mugnaioli *et al.*, *Angew. Chem. Int. Ed.* **51**, 7041–7045 (2012).
27. G. Pawley, *J. Appl. Cryst.* **14**, 357–361 (1981).

28. M. M. J. Treacy, J. M. Newsam, M. W. Deem, *Proc. R. Soc. London Ser. A* **433**, 499–520 (1991).
29. S. Bette, R. E. Dinnebier, D. Freyer, *J. Appl. Cryst.* **48**, 1706–1718 (2015).
30. A. Kudielka *et al.*, *J. Mater. Chem. C Mater. Opt. Electron. Devices* **5**, 2899–2909 (2017).

ACKNOWLEDGMENTS

Funding: Z.Z. was supported by China Scholarship Council (CSC). P.U.P.A.G. acknowledges DOE grant DE-FG02-07ER15899 and NSF grant DMR-1603192. The XANES-PEEM spectra were acquired at the Advanced Light Source, supported by DOE grant DE-AC02-05CH11231. **Author contributions:** Z.Z., W.J.E.M.H., and P.F. conceived of and planned the experiments. Z.Z. synthesized all samples; performed and analyzed the titration experiments; and performed laboratory XRD, IR, and Raman spectroscopy, as well

as ICP-OES, TGA/DSC, and SEM measurements. S.W. helped to analyze the IR data. Y.P. and M.A.H. performed XANES spectroscopy at calcium K-edge and Y.P., M.A.H., and Z.Z. analyzed the data. Z.Z., C.-y.S., and P.U.P.A.G. performed XANES spectroscopy at oxygen K-edge and calcium L-edge and analyzed the data. L.B., A.C.S.J., Y.P., and W.J.E.M.H. performed the x-ray total scattering measurements. Z.Z. and L.B. analyzed the x-ray total scattering data. P.W. performed TEM measurements and J.M. acquired initial three-dimensional electron diffraction data. G.M. and U.K. performed ADT measurements and analyzed the ADT data. S.B. and R.D. created the microstructural model. I.P. and B.P. collected HRXRPD pattern. Z.Z., W.J.E.M.H., I.P., B.P., A.C.S.J., L.B., S.B., R.D., U.K., E.Z., and P.F. analyzed and interpreted the HRXRPD data. Z.Z., W.J.E.M.H., and E.Z. led the drafting of the manuscript and compiled the figures. All authors discussed the results and provided feedback on the manuscript. **Competing interests:** Authors declare

no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper or the supplementary materials.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/363/6425/396/suppl/DC1
Materials and Methods
Figs. S1 to S12
Tables S1 to S6
References (31–43)
Data S1

6 August 2018; accepted 3 December 2018
10.1126/science.aav0210



Supplementary Materials for
**A hydrated crystalline calcium carbonate phase:
Calcium carbonate hemihydrate**

Zhaoyong Zou, Wouter J. E. M. Habraken, Galina Matveeva, Anders C. S. Jensen, Luca Bertinetti, Matthew A. Hood, Chang-yu Sun, Pupa U. P. A. Gilbert, Iryna Polishchuk, Boaz Pokroy, Julia Mahamid, Yael Politi, Steve Weiner, Peter Werner, Sebastian Bette, Robert Dinnebier, Ute Kolb, Emil Zolotoyabko, Peter Fratzl†

†Corresponding author. Email: fratzl@mpikg.mpg.de

Published 25 January 2019, *Science* **363**, 396 (2019)
DOI: 10.1126/science.aav0210

This PDF file includes:

Materials and Methods
Figs. S1 to S12
Tables S1 to S6
Caption for Data S1
References

Other Supplementary Material for this manuscript includes the following:
(available at www.sciencemag.org/content/363/6425/396/suppl/DC1)

Data S1 (.cif)

Materials and Methods

Sample preparation

Analytical grade calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), sodium carbonate decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) were purchased from Sigma-Aldrich and used as received. 50 mL of a one molar Mg-Ca solution was prepared by dissolving 0.01 mol $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.04 mol $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in ultra-pure water. The carbonate solution was prepared by dissolving 2 mmol $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in 48 mL ultra-pure water. A computer controlled titration system (905 Titrand, Metrohm Ltd.) was utilized for these experiments.

In a typical experiment, 2 mL of calcium solution was dosed at a rate of 10 mL/min into a 100 mL reaction vessel filled with 48 mL of carbonate solution. The total volume of the solution after dosing was 50 mL and the theoretical concentrations of cations (Mg^{2+} and Ca^{2+}) and anions (CO_3^{2-} and HCO_3^-) were equal to 40 mM. The precipitates were extracted by fast vacuum filtering of the reaction solution and then rinsed with ethanol. The collected powders after filtration were further dried and stored in a vacuum desiccator for subsequent characterization.

For the experiments on the effects of $\text{Mg}^{2+}/(\text{Mg}^{2+} + \text{Ca}^{2+})$ ratio on the formation and crystallization of ACC in solution, the initial $\text{Mg}^{2+}/(\text{Mg}^{2+} + \text{Ca}^{2+})$ ratio was varied from 10% to 40%, whereas the carbonate concentration was raised from 5 to 40 mM. The calculated concentration of $(\text{Mg}^{2+} + \text{Ca}^{2+})$ is equal to the carbonate concentration after mixing. The reaction was indexed, as $\text{N}_1(\text{MgACC}) - \text{N}_2(\text{mM})$, where N_1 corresponds to the initial $\text{Mg}^{2+}/(\text{Mg}^{2+} + \text{Ca}^{2+})$ ratio multiplied by 100, and N_2 corresponds to the carbonate concentration (as shown in legends in Fig. S4).

Monitoring pH and calcium concentration in solution

The pH and calcium concentration of the solution during reaction were monitored using a pH electrode and a calcium-sensitive electrode (Ca-ISE, Metrohm Ltd.) connected to the titration system. Electrodes, vessel, and burette tips were cleaned with dilute hydrochloric acid and carefully rinsed with distilled water after each experiment. The Ca-ISE was calibrated before every experiment by dosing the 1 M calcium solution to 50 ml water at room temperature at a rate of 0.1 mL/min, and measuring the signal (in mV), as a function of calcium concentration. During the calibration of calcium concentration, the pH of the solution was kept at 10.5 by titrating 0.01M NaOH. The pH-electrode was calibrated every day using standard buffers at pH 4.00, pH 7.00 and pH 9.00 (Metrohm Ltd.).

Scanning electron microscopy and transmission electron microscopy

The sample morphology was imaged using a field emission scanning electron microscope (JEOL, JSM-7500F) working at 5 kV. Samples were not coated prior investigation. Transmission electron microscopy was performed using a ZEISS, EM 912 transmission electron microscope operating at 120 kV.

X-ray powder diffraction

The laboratory X-ray diffraction (XRD) measurements were carried out in the Bragg-Brentano scattering geometry, using a Bruker D8-Advance X-ray powder diffractometer ($\text{Cu K}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$) in the 2θ -range of $10\text{--}80^\circ$ and scan speed of $0.36^\circ/\text{min}$. High-resolution X-ray powder diffraction (HRXRPD) measurements were performed at the dedicated beamline

ID22 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) using a wavelength of 0.49596 Å. Total X-ray scattering patterns were acquired continuously at ID11 beamline of ESRF using a beam-size of $1 \times 1 \text{ mm}^2$ in cross-section. X-ray energy was set to 87 keV (wavelength, $\lambda = 0.142511 \text{ Å}$). Data was acquired using a Frelon2K or Frelon4M detector with a 10–30 s integration time and processed with Fit2D software (31). Pair distribution functions (PDF) were produced using the PDFgetX3 software (32).

X-ray absorption near-edge structure (XANES) spectroscopy

The XANES spectra for oxygen K-edge and calcium L-edge were acquired by photoemission electron microscopy (PEEM) at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (CA, USA) on beamline 11.0.1. The Ca spectrum in Fig. S2 is averaged over 237 single-pixel spectra and the O spectrum is averaged over 105 single-pixel spectra, acquired between 340–360 eV and 525–555 eV, respectively. The energy step between PEEM images was 0.1 eV in the central peak-containing region and 0.5 eV in the featureless pre- and post-edge energy regions. Both Ca and O spectra were extracted from two separate movies acquired on different areas and in repeated acquisitions. The O spectrum is normalized to a background intensity acquired on the pure platinum coating. Both O and Ca spectra are presented in comparison with those collected with other calcium carbonate minerals (33). All spectra were first aligned, so the O spectra had their peak (marked as 1 in Fig. S2) at 534 eV, and the Ca spectra had the L_2 main peak at 352.6 eV. These two alignment energy positions are indicated in Fig. S2 by two black vertical lines that run across the plots. All spectra, taken from CCHH ($\text{CaCO}_3 \cdot 0.5\text{H}_2\text{O}$) and other minerals, were peak-fitted again using the GG Macros (<https://home.physics.wisc.edu/gilbert/software/>), because several fine details of the spectra were discovered after the publication (33), e.g. the small pre-edge peaks at approximately 347 eV in calcite and vaterite, which also exist in CCHH. The energy positions obtained from accurate peak fitting are displayed as black vertical lines in O spectra (Fig. S2C) and as black vertical segments in Ca spectra (Fig. S2D).

The XANES spectra at the Ca K-edge were acquired at the LUCIA beamline at the SOLEIL Synchrotron Light Source (Saint-Aubin, France). The X-ray beam energy was varied from 4000 to 4080 eV in 1.0 eV steps before the pre-edge and in 0.2 eV steps thereafter. The electron energy in the synchrotron storage ring was 2.75 GeV and the current was up to 400 mA. The X-ray energy was selected by a double-crystal Si(111) monochromator, which was calibrated using Ti foil and setting the edge at 4966 eV. The beam size of the sample was ca. $1.5 \times 1.5 \text{ mm}^2$. Powder samples of CCHH, ACC, vaterite, aragonite and calcite were mounted with a sticky tape. To improve the signal-to-noise ratio, all spectra were averaged over three to five scans. Baseline subtraction and normalization were performed using the ATHENA of the IFEFFIT software package (34). The edge energy was determined at the maximum of the third peak of the first derivative of the XANES data. Normalization was performed using a linear pre-edge function and a quadratic polynomial for the post-edge.

Automated electron diffraction tomography (ADT)

Three-dimensional electron diffraction data acquisitions were performed in the Johannes Gutenberg-Universität, Mainz with a FISCHIONE tomography sample holder cooled with liquid N_2 , using the ADT acquisition module (35) developed for FEI TECNAI F30 TEM. A condenser aperture of 10 μm and mild illumination setting (gun lens 8 and spot size 6) were used in order to

produce a quasi-parallel beam of 50 nm in diameter on the sample and reduce the electron irradiation dose. Sample image tracking was performed in the microprobe HAADF-STEM mode, whereas electron diffraction was acquired with nano-electron diffraction (NED) setting. ADT tilt series were collected both with and without precession of the beam. Precession electron diffraction (PED) was used in order to improve the reflection intensity integration quality (36) and only ADT/PED data were used for structure solution. PED was performed using the SpinningStar unit developed by NanoMEGAS Company, Belgium. The precession angle was kept at 1.2°. For data processing and extraction, a ADT software (developed in the group of Dr. Kolb, Johannes Gutenberg-University Mainz, Germany and distributed by the NanoMegas Company, Belgium) was used, including three-dimensional diffraction reconstruction and visualization, cell determination based on clustering routines (37), and reflection intensity integration (36, 38, 22).

Structure solution based on ADT data

STEM imaging revealed crystals with two different morphologies, as presented in Fig. S8. Type-1 crystals (left panel) are thin and elongated needles which produce single crystal diffraction only at the tip. Crystals of the second type (middle panel) are thin needle-like platelets. Four ADT data sets were taken from crystals exhibiting type-1 morphology, which can be accounted to the majority of the detected crystals. The cell parameters, as shown in Table S4, and used for data extraction, were found in all these data sets to be similar within the expected error bars. Extinctions follow the rule ($h0l$) with $l = 2n$, indicating the c -glide plane perpendicular to the b -axis (see Fig. S8, right panel). Due to preferred orientation for all data sets the b -axis was situated inside the missing cone.

Two data sets (indicated as Cr-1 and Cr-2 in Table S5) provided a reasonable coverage of the reciprocal space (>50%) for structure solution in space group $P2_1/c$. *Ab initio* structure solution was performed in kinematic approximation ($I \sim F^2(hkl)$) by direct methods, as implemented in the program SIR2014 (39). Scattering factors for electrons were taken from Doyle and Turner (40). The remaining two data sets were successfully used for structure solution with comparable results applying a resolution limit of 1 Å. In order to increase the coverage of the reciprocal space data set Cr-2 (tilt approximately around (1-11)) and Cr-3 (tilt approximately around (-101)) were merged ($R_{\text{int}}=0.169$), see Table S5. The *ab initio* structure solution using SIR2014 converged to a final residual $R(F)$ of 0.219. The potential map shows two strongest maxima (3.01, 3.51 eÅ³) corresponding to two Ca atoms. The next nine maxima resemble the carbonate groups (1.18 to 0.75 eÅ³) and one maximum at 0.48 eÅ³ indicates the water oxygen. The residual potential has a height of 0.39 eÅ³ and is situated in the vicinity (approx. 1.5 Å) of Ca and O_{CO3}. Isotropic temperature factors, U_{iso} , were found independently for each atom of the carbonate group to be between 0.03 to 0.09 Å².

Subsequent SHELXL (41) refinement converged to a residual $R(F)$ of 28% for a two sigma threshold, which is common for beam sensitive material solved by electron diffraction tomography (42). The coverage of independent reflections of 62% leads to an elongation of scattering potentials in direct space causing some errors in temperature factor and C-O distances. Thus, an overall U_{iso} for carbonate atoms and the SADI extraction was used leading to C-O distances of 1.22, 1.24, 1.41 and 1.29, 1.35, 1.38 Å. Nevertheless, as is seen in Fig. S9, the carbonate groups are nearly planar. Both types of Ca positions are eightfold coordinated (Fig. S9, right panel).

Additionally, ADT diffraction data were collected from crystals showing morphology of type 2. From the reconstructed volumes, the cell parameters were extracted and given in Table S4. Only reflections with $k = 2n$ along the b^* -axis of reciprocal space could be detected. A structure solution has not been undertaken since the coverage of the reciprocal space was too low.

Raman and infrared (IR) spectroscopy

Raman spectra were collected using a confocal Raman microscope ($\alpha 300$; WITec) equipped with a Nikon objective (10 \times) and a 532 nm laser. Spectra were acquired with a CCD camera (DV401-BV; Andor) behind a spectrometer (UHTS 300; WITec) (40 accumulations, integration time 1 s). The ACC powders were dropped on a microscope slide just before individual measurement. IR spectra were recorded on a pellet with KBr and the sample using a Fourier transform infrared spectrometer (Bruker Optik GmbH) equipped with a MCT-detector (32 scans, resolution 4 cm^{-1}).

Thermogravimetric analysis/differential scanning calorimetry

Weight loss and heat flow were simultaneously measured during programmed heating (25-500 $^{\circ}\text{C}$, at the rate of 1.5 $^{\circ}\text{C}/\text{min}$) using thermogravimetric analysis coupled with differential scanning calorimetry (SENSYS evo TGA-DSC, SETARAM Instrumentation, Caluire, France). For these measurements, nearly 15 mg of the dried powders were placed in an alumina crucible. Dry nitrogen was used as the purge gas.

ICP-OES analysis

Element analysis was performed by inductively coupled plasma-optical emission spectrometry (PerkinElmer, Optima 8000 ICP-OES Spectrometer). Sample solutions were prepared by dissolving certain amounts of as-prepared powders in the diluted HNO_3 solution.

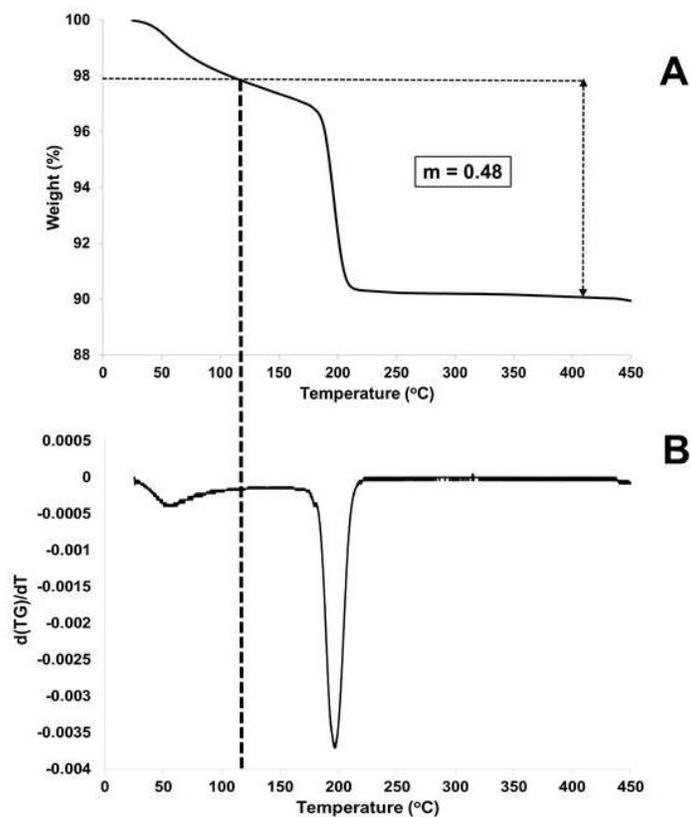


Fig. S1.

The results of TGA in CCHH. Temperature-dependent weight loss (A) and its derivative (B) measured upon heating at a rate of 1.5 °C/min. Weight loss below 115 °C (vertical dashed line) occurs due to evaporation of the absorbed water (first dip in (B)), while above this temperature and up to nearly 450 °C, the discharge of structural water is observed with the maximum release rate at about 200 °C (second dip in (B)). Counting the weight loss of structural water between 115 and 400 - 450 °C (dotted arrow in (A)) yields chemical formula of CCHH, $\text{CaCO}_3 \cdot m\text{H}_2\text{O}$, with $m = 0.48$.

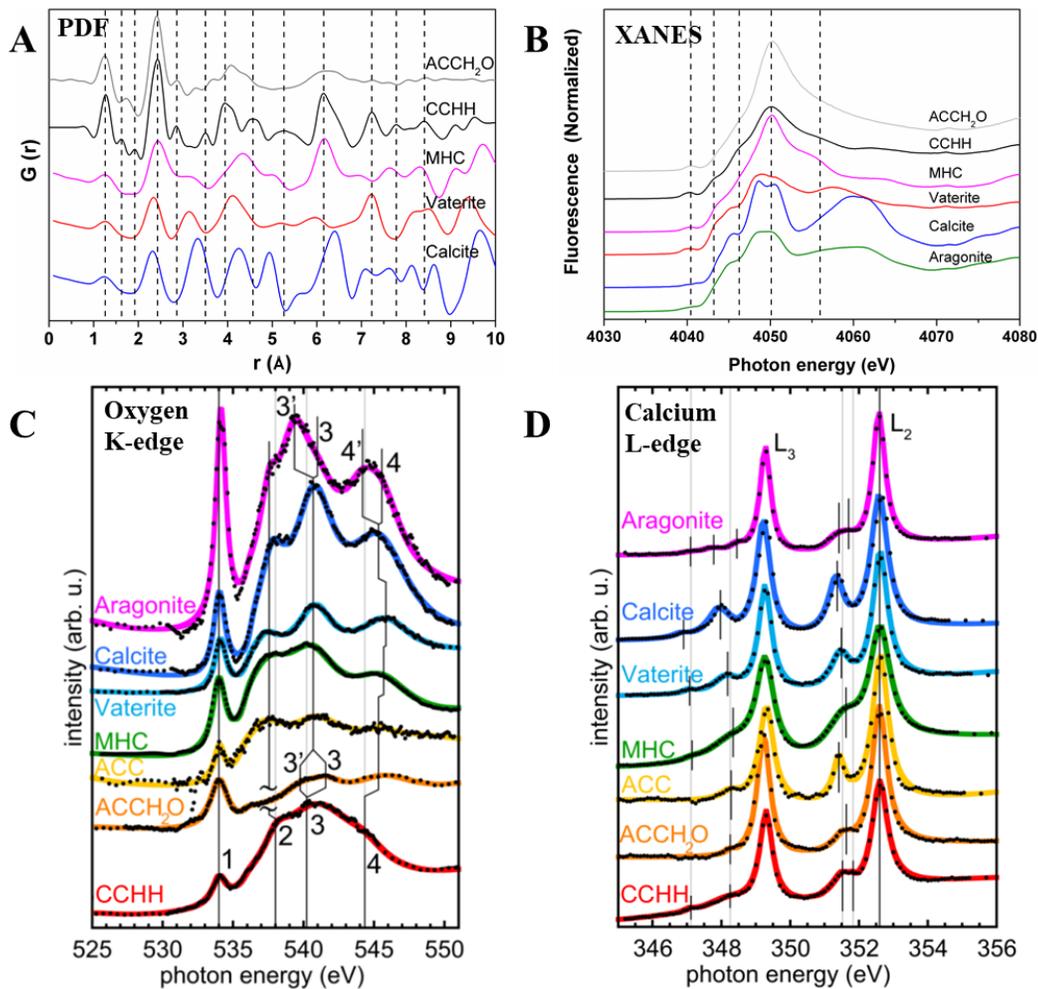


Fig. S2.

PDF patterns (A), Ca K-edge XANES spectra (B), oxygen K-edge XANES spectra (C) and Ca L-edge XANES spectra (D) of CCHH and other known calcium carbonate phases. The PDF pattern of CCHH shows some similarities to hydrated ACC (ACC·1H₂O) and MHC, but differs from those of vaterite and calcite. For example, the most intense PDF peak of CCHH occurs at ~2.44 Å (attributed to the average Ca-O bond distance), which is similar to that of ACC and MHC, but its relative intensity is much higher than that in MHC. Moreover, while ACC shows only short range order up to 6 - 7 Å, the order in CCHH extends above 10 Å, similarly to other crystalline phases. The Ca K-edge XANES spectrum of CCHH also differs from those known for other calcium carbonate phases. The pre-edge feature at ~4040.4 eV (attributed to 1s→3d transition, indicative of a non-centrosymmetric coordination) is similar to both ACC and MHC, but the general shape of the spectrum is more similar to that of MHC. The multiple-scattering peak at 4046 eV is indicative of increased order relative to ACC and the edge shape including intra-atomic transitions (shoulders at 4044 – 4046 eV) are similar to those observed in MHC. In (C) and (D), the experimental data are represented by black dots, whereas the peak-fitted spectra - by colored solid lines. Black vertical lines indicate the position of each peak found by peak fitting, the light gray vertical lines indicate the peak positions for CCHH, thus making it easier to see the difference between CCHH and all other calcium carbonate phases. The oxygen

K-edge spectrum of CCHH differs from those known for all other calcium carbonate crystalline or amorphous mineral phases. In particular, the peak, marked as 4, appears at 544 eV in CCHH and at 545 - 546 eV in all other phases. The calcium L-edge spectrum of CCHH resembles in shape that of ACC·1H₂O, but shows an additional small peak in the pre-L₃-edge at 347.1 eV, which appears at similar energies only in crystalline calcite, vaterite, MHC, and aragonite. Moreover, only CCHH and aragonite have two peaks in the pre-L₂-edge region, but in CCHH these are at 351.5 and 351.8 eV, while in aragonite they appear at lower energies. The collected XANES spectra, therefore, demonstrate that CCHH is distinct from all other calcium carbonate phases.

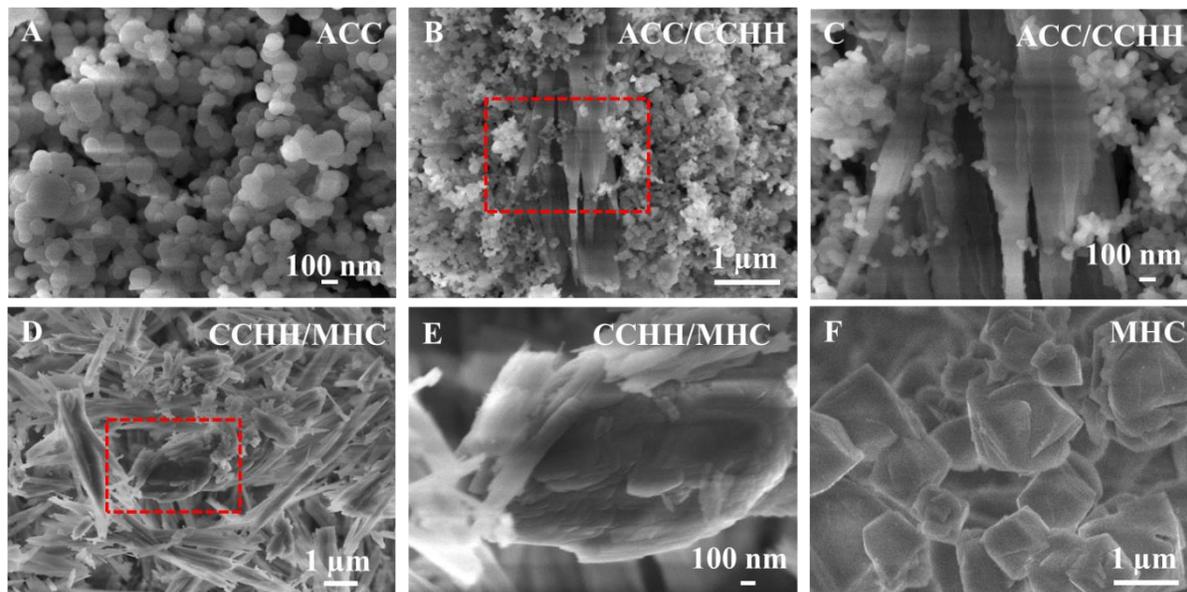


Fig. S3.

SEM images of ACC nanoparticles (A), coexistence of ACC nanoparticles and CCHH crystals (B, C), coexistence of CCHH and MHC crystals (D, E) and MHC crystals (F). The initially precipitated Mg-containing ACC nanoparticles have spherical shapes with an average diameter of 71 ± 28 nm, which is similar to the pure ACC, synthesized at a calcium carbonate concentration of 40 mM. During growth of CCHH crystals, some of these nanoparticles are attached to the needle-like crystals (within red rectangle in (B) and in image (C)), suggesting a possibility of local dissolution/re-precipitation. During the CCHH/MHC transformation, the CCHH needles are attaching to the surface of MHC crystals (within red rectangle in (D) and in image (E)), resulting in the micrometer-sized MHC crystals with well-developed facets, visible in image (F).

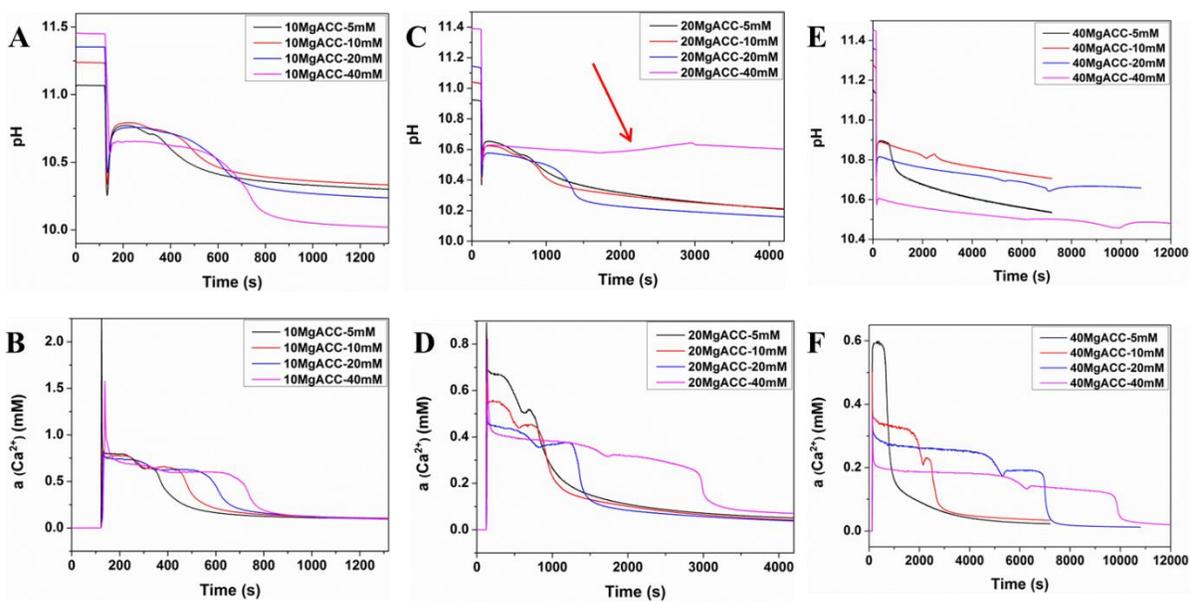


Fig. S4.

The pH (A, C, E) and Ca^{2+} activity (B, D, F) change in the solution for all investigated reactions. For 10% Mg^{2+} reactions (A, B), similar to the pure system, both pH and Ca^{2+} activity decrease rapidly within 10 min, indicating fast crystallization of crystalline calcium carbonate polymorphs with lower solubility. For 20% Mg^{2+} in the range of 5 – 20 mM (C, D) and 40% Mg^{2+} at 5 mM (E, F), the curves are similar to the 10% Mg^{2+} reactions. However, for 20% Mg^{2+} at 40 mM (C, D) and 40% Mg^{2+} at 10 mM (E, F), the pH shows an abnormal increase for about 20 min (marked by red arrow in C), followed by the gradual decrease. For 40% Mg^{2+} at 20 and 40 mM, the pH curves reveal two sudden drops in pH after which the pH stabilizes, in accordance with the step-wise decrease in Ca^{2+} activity. Line colors are indicated in the respective inserts.

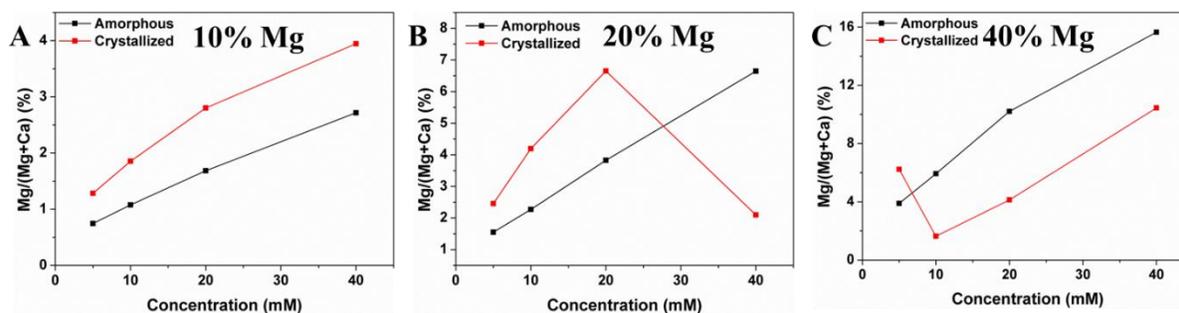


Fig. S5.

$\text{Mg}^{2+}/(\text{Mg}^{2+}+\text{Ca}^{2+})$ ratio in the amorphous and crystallized samples prepared with different amounts of Mg^{2+} and overall carbonate concentrations (A-C). As the particle size of ACC decreases with increasing concentrations, the Mg^{2+} content in ACC increases slightly with decreasing particle size. After crystallization, lower Mg^{2+} incorporation in ACC ($< 5\%$) resulted in the increased Mg^{2+} content in the crystallized products (i.e. calcite), while higher Mg^{2+} incorporation in ACC ($> 5\%$) resulted in the significantly lower Mg^{2+} content in the crystallized products (i.e. MHC or CCHH).

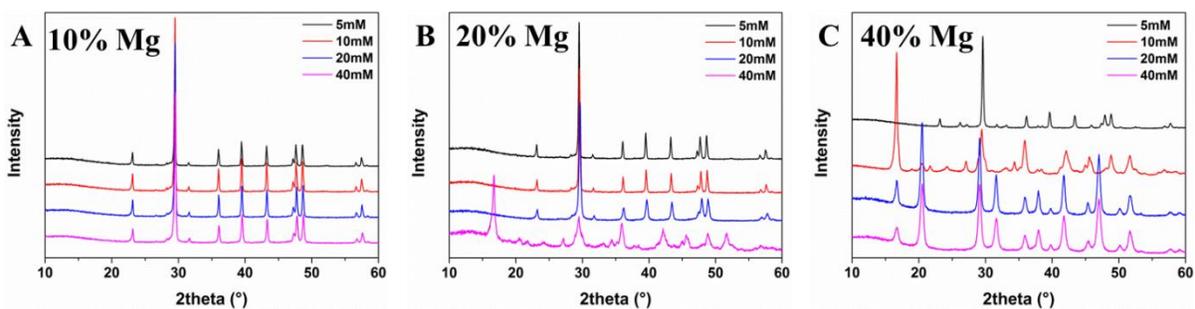


Fig. S6.

Laboratory XRD patterns taken after sample crystallization. For 10% Mg^{2+} at all concentrations (A), as well as for 20% Mg^{2+} at 5 – 20 mM (B) and 40% Mg^{2+} at 5 mM (C), all crystallized samples show Mg^{2+} -calcite. For 20% Mg^{2+} at 40 mM (B) and 40% Mg^{2+} at 10 mM (C), CCHH is obtained. For 40% at 20 and 40 mM (C), pure MHC is formed. Line colors are indicated in the respective inserts.

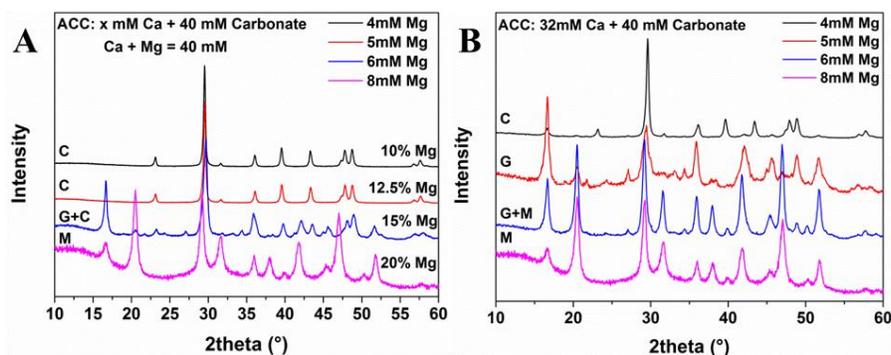


Fig. S7.

Laboratory XRD patterns of crystallized samples prepared by adding first a 1M CaCl_2 solution to 40 mM Na_2CO_3 solution and then adding a 1M MgCl_2 solution. In (A), variable amounts of Ca^{2+} and Mg^{2+} are used, while keeping the total concentration of Ca^{2+} and Mg^{2+} equal to the concentration of carbonate. In (B), fixed amount of Ca^{2+} (32 mM) was added to 40 mM carbonate solution to produce ACC and then variable amounts of Mg^{2+} were added to the solution with the final concentrations of Mg^{2+} to be 4, 5, 6, and 8 mM. These data demonstrate that the solution concentration of Mg^{2+} indeed determines the polymorph selection, since CCHH can also be obtained when Mg^{2+} is not incorporated in ACC at all. Line colors are indicated in the respective inserts.

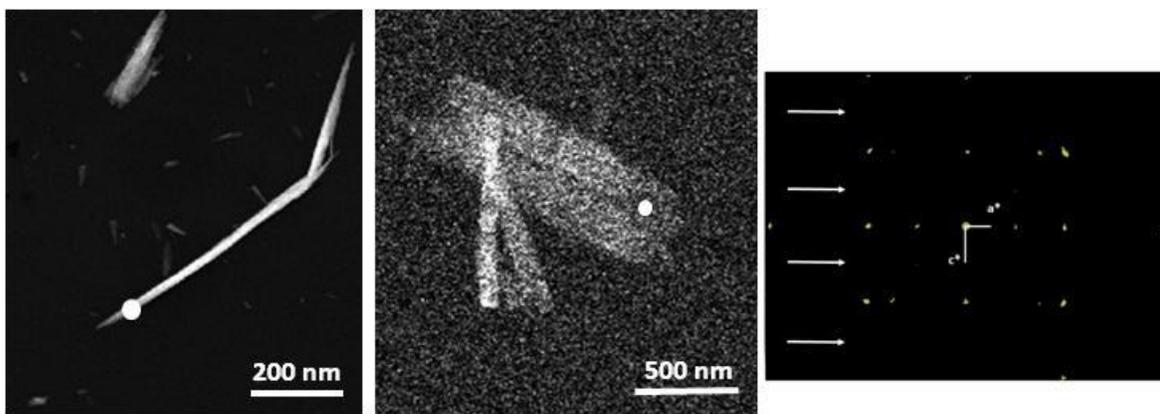


Fig. S8.

STEM images of the detected crystal morphologies. Thin needles of CCHH ($\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$) crystals (left panel) and thin needle-like platelets (middle panel). Electron beam sizes and positions used for ADT data acquisition are indicated as white spots in the left and middle panels. In right panel, a slice of the [010] zone cut from 3D reconstruction of ADT data set is shown. Extinctions due to the c -glide plane are indicated as white arrows (right panel).

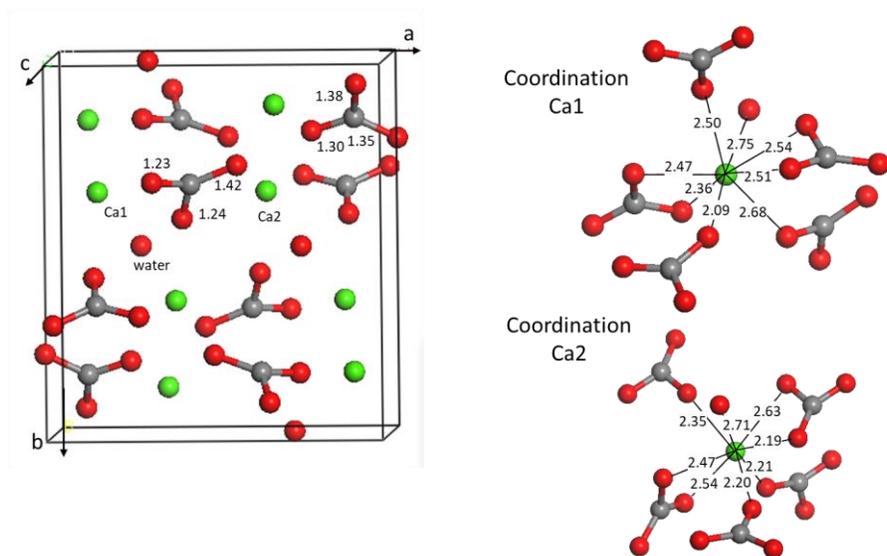


Fig. S9.

Crystal structure of CCHH ($\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$), including C-O distances (left panel) and coordination spheres for both types of Ca atomic positions (right panel).

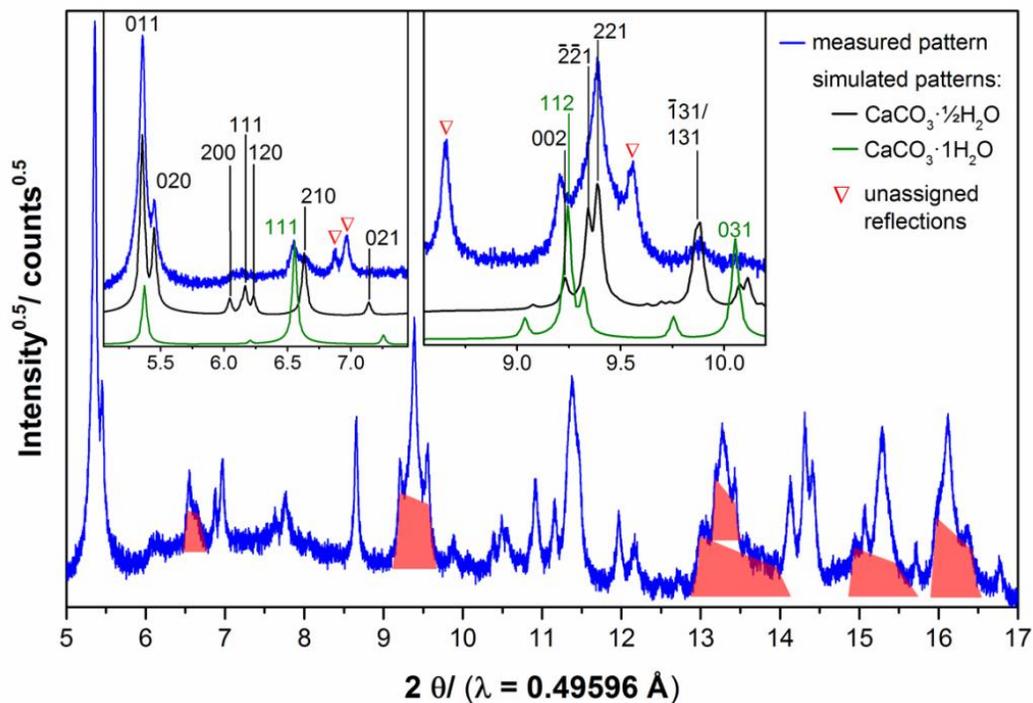


Fig. S10.

Synchrotron HRXRPD pattern of CCHH ($\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$) with several peaks of characteristic triangular shape (highlighted in red). These peaks indicate stacking fault-type lattice disorder in CCHH. Selected sections of the measured diffraction profile (see inserts) are compared to simulated patterns of CCHH and $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ (MHC). While the (011), (020) and (221) reflections originated from CCHH are rather sharp, the (200), (111), (120), (210), (021), ($\bar{1}31$) and (131) reflections are vastly broadened; they almost merge with the background. In addition, there are extra reflections (marked by red triangles in inserts) that cannot be assigned to CCHH or MHC. These reflections are originated from $\text{CaCO}_3 \cdot \frac{3}{4}\text{H}_2\text{O}$.

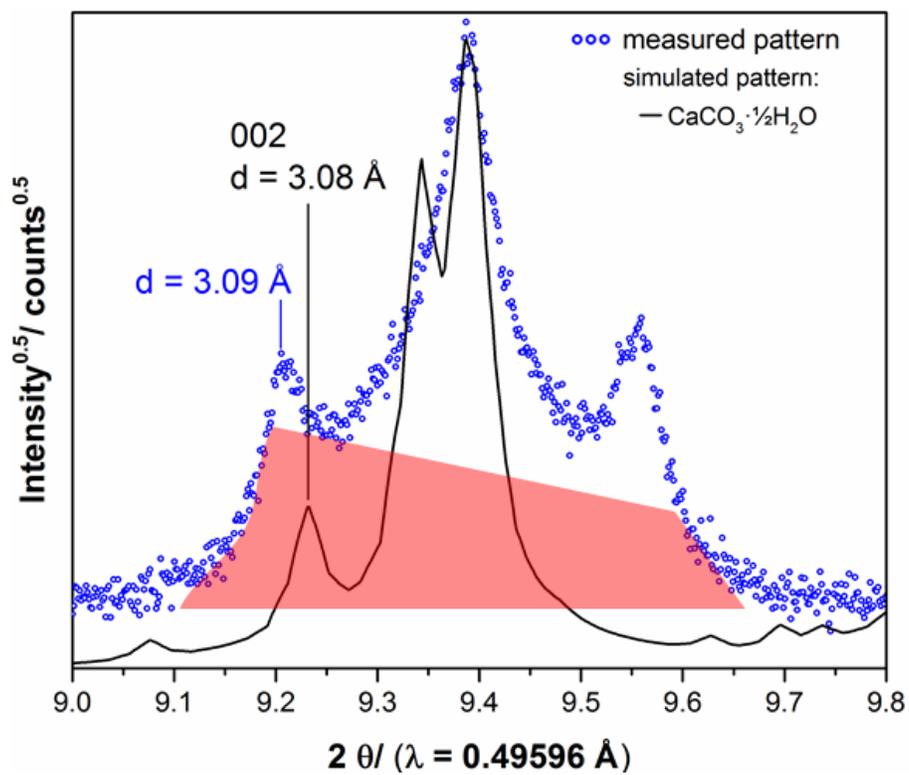


Fig. S11.

Excerpt of the measured synchrotron HRXRPD pattern of CCHH ($\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$), magnifying the characteristic triangular peak shape of the (002)-reflection (highlighted by a red area).

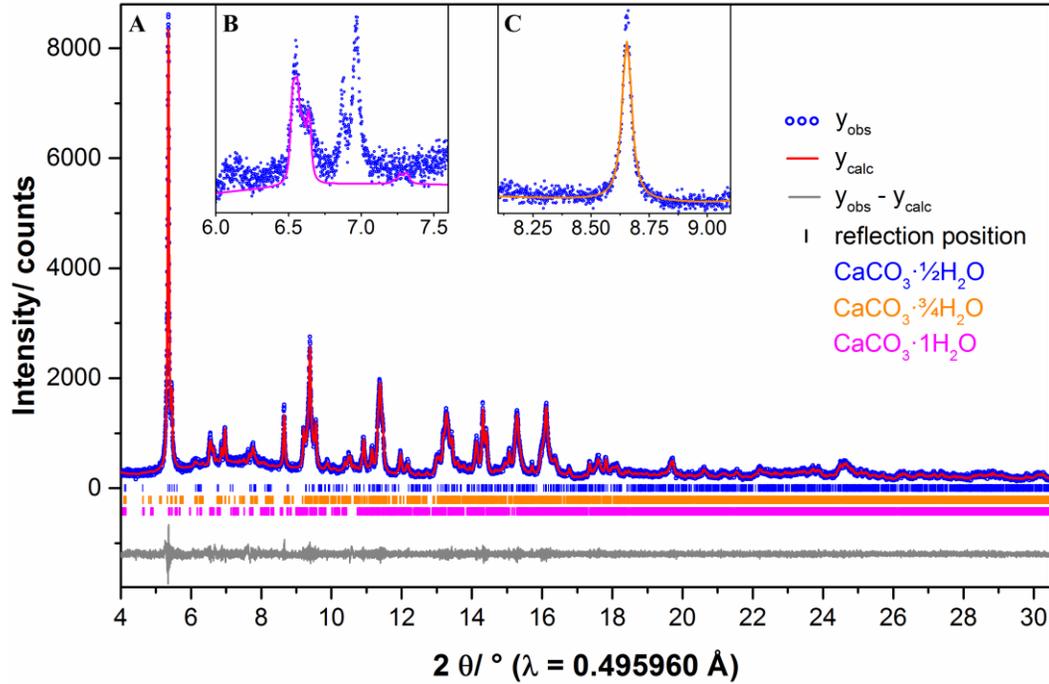


Fig. S12.

(A) Graphical results of the final fit to the measured synchrotron diffraction pattern ($R_{wp} = 7.55\%$) using the unit cells of CCHH ($\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$), $\text{CaCO}_3 \cdot \frac{3}{4}\text{H}_2\text{O}$, and MHC ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$). Constraints on the lattice parameters were applied to simulate commensurate faulting in the c -direction referring to CCHH. Inserts (B) and (C) show magnified fits near specific diffraction peaks located, respectively, at $2\theta = 6.5^\circ$ ($d = 4.37 \text{ \AA}$) and $2\theta = 8.7^\circ$ ($d = 3.27 \text{ \AA}$).

Table S1.

Chemical composition of CCHH. The Ca^{2+} , Mg^{2+} and Na^+ contents were measured using ICP, whereas the full water amount - by TGA, as weight loss between room temperature and 300 °C. Each measurement was repeated five times to obtain the most reliable data.

Composition	Ca^{2+} (wt%)	Mg^{2+} (wt%)	Na^+ (wt%)	H_2O (wt%)	CO_3^{2-} (wt%)
	$34.92 \pm$ 0.24	$0.41 \pm$ 0.08	$0.06 \pm$ 0.03	$10.05 \pm$ 0.53	$54.50 \pm$ 0.23

Table S2.

Peak positions in the Raman and IR spectra of CCHH and peak assignment to different vibration modes.

Raman (cm^{-1})	Infrared (cm^{-1})	Assignment
3382 3285	3379 3290	Anti- and symmetric OH stretch $\nu_{\text{OH}}(\text{B}_2)$
1661	1659	HOH bending $\nu_{\text{HOH}}(\text{A}_1)$
1579 1483 1423	1524 1490 1392 1423	Asymmetric CO stretching $\nu_{\text{CO}}^{\text{as}}(\text{E}', \nu_3)$
1102	1096	Symmetric CO stretching $\nu_{\text{CO}}^{\text{s}}(\text{A}1', \nu_1)$
862	866 860	Out-of-plane bending $\pi_{\text{CO}}^{\text{as}}(\text{A}2'', \nu_2)$
731 700	723 692	In-plane bending $\delta_{\text{CO}}^{\text{as}}(\text{E}', \nu_4)$
212 266 297		Lattice vibrations

Table S3.

The $\text{Mg}^{2+}/(\text{Mg}^{2+}+\text{Ca}^{2+})$ in ACC and the $\text{Mg}^{2+}/\text{Ca}^{2+}$ in solution at different reaction conditions. Mg^{2+} ions were added into the reaction solution immediately after the precipitation of ACC.

Carbonate (mM)	Mg^{2+} (mM)	$\text{Mg}^{2+}+\text{Ca}^{2+}$ (mM)	Initial $\text{Mg}^{2+}/(\text{Mg}^{2+}+\text{Ca}^{2+})$	$\text{Mg}^{2+}/(\text{Mg}^{2+}+\text{Ca}^{2+})$ in ACC	$\text{Mg}^{2+}/\text{Ca}^{2+}$ in solution	Crystalline phase
40mM	4	36	0.111	0.007614	3.5460	Calcite
40mM	5	37	0.135	0.00897	4.6764	CCHH
40mM	6	38	0.158	0.010035	4.9313	MHC
40mM	8	40	0.2	0.013706	5.8047	MHC
40mM	4	40	0.125	0.006361	2.6865	Calcite
40mM	5	40	0.15	0.008348	3.9544	CCHH
40mM	6	40	0.15	0.047261	2.4268	Calcite

Table S4.

Lattice parameters of the original unit cells of CCHH ($\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$), $\text{CaCO}_3 \cdot \frac{3}{4}\text{H}_2\text{O}$, and MHC ($\text{CaCO}_3 \cdot 1\text{H}_2\text{O}$), as well as the transformed unit cells (metric of CCHH).

original unit cells							
		$\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$		$\text{CaCO}_3 \cdot \frac{3}{4}\text{H}_2\text{O}$		$\text{CaCO}_3 \cdot 1\text{H}_2\text{O}$ (43)	
space group		$P2_1/c$		$P2_1$		$P3_1$	
Z		8		8		9	
$V/\text{\AA}^3$		600.17		610.55		727.73	
$a/\text{\AA}$		9.33		9.51		10.55	
$b/\text{\AA}$		10.44		6.16		10.55	
$c/\text{\AA}$		6.16		11.26		7.55	
$\alpha/^\circ$		90		90		90	
$\beta/^\circ$		90.5		112.3		90	
$\gamma/^\circ$		90		90		120	
transformed unit cells for commensurate defects							
$\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$		$\text{CaCO}_3 \cdot \frac{3}{4}\text{H}_2\text{O}$			$\text{CaCO}_3 \cdot 1\text{H}_2\text{O}$ (43)		
		trans- formation	mismatch		trans- formation	mismatch	
Z	8		16	-		18	-
$V/\text{\AA}^3$	600.17	$V' = 2 \cdot V$	1221.20	-	$V' = 2 \cdot V$	1455.46	-
$a/\text{\AA}$	9.33	$a' = a$	9.51	1.93 %	$a' = 2 \cdot b^*$	18.28	2.04 %
$b/\text{\AA}$	10.44	$b' = 2 \cdot c^*$	20.86	0.01 %	$b' = a$	10.55	1.05 %
$c/\text{\AA}$	6.16	$c' = b$	6.16	0.00 %	$c' = c$	7.55	22.56 %
$\alpha/^\circ$	90	$\alpha' = \alpha$	90	-	$\alpha' = \beta$	90	-
$\beta/^\circ$	90.5	$\beta' = \gamma$	90	-	$\beta' = \alpha$	90	-
$\gamma/^\circ$	90	$\gamma' = \beta^*$	90	-	$\gamma' = \gamma^*$	90	-

Table S5.

Quality parameters of ADT data sets for four measured CCHH crystals.

Crystal	R _{int} /%	Coverage of independent reflections, %	Overall B _{iso} , Å ²	Independent reflections	R(F)
Cr-1	17.7	55	2.55	314	0.271
Cr-2	17.1	59	2.63	376	0.293
Cr-3	13.9	37	1.25	232	-
Cr-4	15.3	40	2.08	252	-
Cr-2/Cr-3	16.9	62	2.35	392	0.219

Table S6.

Refined lattice parameters of the unit cells of CCHH ($\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$), $\text{CaCO}_3 \cdot \frac{3}{4}\text{H}_2\text{O}$, and MHC ($\text{CaCO}_3 \cdot 1\text{H}_2\text{O}$) used to simulate commensurate faulting in the c -direction, referring to the structure of CCHH.

	$\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	$\text{CaCO}_3 \cdot \frac{3}{4}\text{H}_2\text{O}$	$\text{CaCO}_3 \cdot 1\text{H}_2\text{O}$
space group	$P1$	$P1$	$P1$
Z	8	16	18
$V/\text{\AA}^3$	588.46(4)	1175.50(4)	1448.78(4)
$a/\text{\AA}$	9.1922(1)	9.1922(1)	18.3843(2)
$b/\text{\AA}$	10.4180(2)	20.8360(4)	10.4180(2)
$c/\text{\AA}$	6.1461(4)	6.1393(1)	7.5647(1)
$\alpha/^\circ$	90.57(1)	87.70(1)	89.64(1)
$\beta/^\circ$	90.87(1)	89.67(1)	89.88(1)
$\gamma/^\circ$	89.56(1)	89.56(1)	89.56(1)

Data S1.

The CIF-file (CCHH.cif) for calcium carbonate hemihydrate

References and Notes

1. J. W. Beck, R. L. Edwards, E. Ito, F. W. Taylor, J. Recy, F. Rougerie, P. Joannot, C. Henin, Sea-surface temperature from coral skeletal strontium/calcium ratios. *Science* **257**, 644–647 (1992). [doi:10.1126/science.257.5070.644](https://doi.org/10.1126/science.257.5070.644) [Medline](#)
2. F. J. Millero, The marine inorganic carbon cycle. *Chem. Rev.* **107**, 308–341 (2007). [doi:10.1021/cr0503557](https://doi.org/10.1021/cr0503557) [Medline](#)
3. M. Cusack, A. Freer, Biomineralization: Elemental and organic influence in carbonate systems. *Chem. Rev.* **108**, 4433–4454 (2008). [doi:10.1021/cr078270o](https://doi.org/10.1021/cr078270o) [Medline](#)
4. S. Goffredo, F. Prada, E. Caroselli, B. Capaccioni, F. Zaccanti, L. Pasquini, P. Fantazzini, S. Fermani, M. Reggi, O. Levy, K. E. Fabricius, Z. Dubinsky, G. Falini, Biomineralization control related to population density under ocean acidification. *Nat. Clim. Chang.* **4**, 593–597 (2014). [doi:10.1038/nclimate2241](https://doi.org/10.1038/nclimate2241) [Medline](#)
5. L. B. Gower, Biomimetic model systems for investigating the amorphous precursor pathway and its role in biomineralization. *Chem. Rev.* **108**, 4551–4627 (2008). [doi:10.1021/cr800443h](https://doi.org/10.1021/cr800443h) [Medline](#)
6. L. J. de Nooijer, H. J. Spero, J. Erez, J. Bijma, G. J. Reichart, Biomineralization in perforate foraminifera. *Earth Sci. Rev.* **135**, 48–58 (2014). [doi:10.1016/j.earscirev.2014.03.013](https://doi.org/10.1016/j.earscirev.2014.03.013)
7. D. Gebauer, A. Völkel, H. Cölfen, Stable prenucleation calcium carbonate clusters. *Science* **322**, 1819–1822 (2008). [doi:10.1126/science.1164271](https://doi.org/10.1126/science.1164271) [Medline](#)
8. M. H. Nielsen, S. Aloni, J. J. De Yoreo, In situ TEM imaging of CaCO₃ nucleation reveals coexistence of direct and indirect pathways. *Science* **345**, 1158–1162 (2014). [doi:10.1126/science.1254051](https://doi.org/10.1126/science.1254051) [Medline](#)
9. J. W. Morse, R. S. Arvidson, A. Lüttge, Calcium carbonate formation and dissolution. *Chem. Rev.* **107**, 342–381 (2007). [doi:10.1021/cr050358j](https://doi.org/10.1021/cr050358j) [Medline](#)
10. Y. Politi, T. Arad, E. Klein, S. Weiner, L. Addadi, Sea urchin spine calcite forms via a transient amorphous calcium carbonate phase. *Science* **306**, 1161–1164 (2004). [doi:10.1126/science.1102289](https://doi.org/10.1126/science.1102289) [Medline](#)
11. L. Addadi, S. Raz, S. Weiner, Taking advantage of disorder: Amorphous calcium carbonate and its roles in biomineralization. *Adv. Mater.* **15**, 959–970 (2003). [doi:10.1002/adma.200300381](https://doi.org/10.1002/adma.200300381)
12. L. Addadi, D. Joester, F. Nudelman, S. Weiner, Mollusk shell formation: A source of new concepts for understanding biomineralization processes. *Chemistry* **12**, 980–987 (2006). [doi:10.1002/chem.200500980](https://doi.org/10.1002/chem.200500980) [Medline](#)
13. Y. U. T. Gong, C. E. Killian, I. C. Olson, N. P. Appathurai, A. L. Amasino, M. C. Martin, L. J. Holt, F. H. Wilt, P. U. P. A. Gilbert, Phase transitions in biogenic amorphous calcium carbonate. *Proc. Natl. Acad. Sci. U.S.A.* **109**, 6088–6093 (2012). [doi:10.1073/pnas.1118085109](https://doi.org/10.1073/pnas.1118085109) [Medline](#)
14. W. Sun, S. Jayaraman, W. Chen, K. A. Persson, G. Ceder, Nucleation of metastable aragonite CaCO₃ in seawater. *Proc. Natl. Acad. Sci. U.S.A.* **112**, 3199–3204 (2015). [doi:10.1073/pnas.1423898112](https://doi.org/10.1073/pnas.1423898112) [Medline](#)
15. Z. Zou, L. Bertinetti, Y. Politi, A. C. S. Jensen, S. Weiner, L. Addadi, P. Fratzl, W. J. E. M. Habraken, Opposite particle size effect on amorphous calcium carbonate

- crystallization in water and during heating in air. *Chem. Mater.* **27**, 4237–4246 (2015). [doi:10.1021/acs.chemmater.5b00145](https://doi.org/10.1021/acs.chemmater.5b00145)
16. F. A. Andersen, L. Brecevic, G. Beuter, D. B. Dell'Amico, F. Calderazzo, N. J. Bjerrum, A. E. Underhill, Infrared spectra of amorphous and crystalline calcium carbonate. *Acta Chem. Scand.* **45**, 1018–1024 (1991). [doi:10.3891/acta.chem.scand.45-1018](https://doi.org/10.3891/acta.chem.scand.45-1018)
 17. W. D. Bischoff, S. K. Sharma, F. T. Mackenzie, Carbonate ion disorder in synthetic and biogenic magnesium calcites: A Raman spectral study. *Am. Mineral.* **70**, 581–589 (1985).
 18. G. Behrens, L. T. Kuhn, R. Uvic, A. H. Heuer, Raman spectra of vateritic calcium carbonate. *Spectrosc. Lett.* **28**, 983–995 (1995). [doi:10.1080/00387019508009934](https://doi.org/10.1080/00387019508009934)
 19. H. H. Adler, P. F. Kerr, Infrared spectra, symmetry and structure relations of some carbonate minerals. *Am. Mineral.* **48**, 839–853 (1963).
 20. R. L. Frost, M. J. Dickfos, Raman and infrared spectroscopic study of the anhydrous carbonate minerals shortite and barytocalcite. *Spectrochim. Acta A* **71**, 143–146 (2008). [doi:10.1016/j.saa.2007.11.021](https://doi.org/10.1016/j.saa.2007.11.021) [Medline](#)
 21. A. E. S. Van Driessche, L. G. Benning, J. D. Rodriguez-Blanco, M. Ossorio, P. Bots, J. M. García-Ruiz, The role and implications of bassanite as a stable precursor phase to gypsum precipitation. *Science* **336**, 69–72 (2012). [doi:10.1126/science.1215648](https://doi.org/10.1126/science.1215648) [Medline](#)
 22. U. Kolb, E. Mugnaioli, T. E. Gorelik, Automated electron diffraction tomography - a new tool for nano crystal structure analysis. *Cryst. Res. Technol.* **46**, 542–554 (2011). [doi:10.1002/crat.201100036](https://doi.org/10.1002/crat.201100036)
 23. B. E. Warren, X-ray diffraction in random layer lattices. *Phys. Rev.* **59**, 693–698 (1941). [doi:10.1103/PhysRev.59.693](https://doi.org/10.1103/PhysRev.59.693)
 24. S. Bette, T. Takayama, K. Kitagawa, R. Takano, H. Takagi, R. E. Dinnebier, Solution of the heavily stacking faulted crystal structure of the honeycomb iridate $H_3LiIr_2O_6$. *Dalton Trans.* **46**, 15216–15227 (2017). [doi:10.1039/C7DT02978K](https://doi.org/10.1039/C7DT02978K) [Medline](#)
 25. L. Kabalah-Amitai, B. Mayzel, Y. Kauffmann, A. N. Fitch, L. Bloch, P. U. P. A. Gilbert, B. Pokroy, Vaterite crystals contain two interspersed crystal structures. *Science* **340**, 454–457 (2013). [doi:10.1126/science.1232139](https://doi.org/10.1126/science.1232139) [Medline](#)
 26. E. Mugnaioli, I. Andrusenko, T. Schüler, N. Loges, R. E. Dinnebier, M. Panthöfer, W. Tremel, U. Kolb, Ab Initio structure determination of vaterite by automated electron diffraction. *Angew. Chem. Int. Ed.* **51**, 7041–7045 (2012). [doi:10.1002/anie.201200845](https://doi.org/10.1002/anie.201200845) [Medline](#)
 27. G. Pawley, Unit-cell refinement from powder diffraction scans. *J. Appl. Cryst.* **14**, 357–361 (1981). [doi:10.1107/S0021889881009618](https://doi.org/10.1107/S0021889881009618)
 28. M. M. J. Treacy, J. M. Newsam, M. W. Deem, A general recursion method for calculating diffracted intensities from crystals containing planar faults. *Proc. R. Soc. Lond. Ser. A* **433**, 499–520 (1991). [doi:10.1098/rspa.1991.0062](https://doi.org/10.1098/rspa.1991.0062)
 29. S. Bette, R. E. Dinnebier, D. Freyer, Structure solution and refinement of stacking-faulted $NiCl(OH)$. *J. Appl. Cryst.* **48**, 1706–1718 (2015). [doi:10.1107/S1600576715017719](https://doi.org/10.1107/S1600576715017719)
 30. A. Kudielka, S. Bette, R. E. Dinnebier, M. Abeykoon, C. Pietzonka, B. Harbrecht, Variability of composition and structural disorder of nanocrystalline $CoOOH$

- materials. *J. Mater. Chem. C Mater. Opt. Electron. Devices* **5**, 2899–2909 (2017). [doi:10.1039/C6TC04626F](https://doi.org/10.1039/C6TC04626F)
31. A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, D. Hausermann, Two-dimensional detector software: From real detector to idealised image or two-theta scan. *High Press. Res.* **14**, 235–248 (1996). [doi:10.1080/08957959608201408](https://doi.org/10.1080/08957959608201408)
 32. P. Juhás, T. Davis, C. L. Farrow, S. J. L. Billinge, PDFgetX3: A rapid and highly automatable program for processing powder diffraction data into total scattering pair distribution functions. *J. Appl. Cryst.* **46**, 560–566 (2013). [doi:10.1107/S0021889813005190](https://doi.org/10.1107/S0021889813005190)
 33. R. T. DeVol, R. A. Metzler, L. Kabalah-Amitai, B. Pokroy, Y. Politi, A. Gal, L. Addadi, S. Weiner, A. Fernandez-Martinez, R. Demichelis, J. D. Gale, J. Ihli, F. C. Meldrum, A. Z. Blonsky, C. E. Killian, C. B. Salling, A. T. Young, M. A. Marcus, A. Scholl, A. Doran, C. Jenkins, H. A. Bechtel, P. U. P. A. Gilbert, Oxygen spectroscopy and polarization-dependent imaging contrast (PIC)-mapping of calcium carbonate minerals and biominerals. *J. Phys. Chem. B* **118**, 8449–8457 (2014). [doi:10.1021/jp503700g](https://doi.org/10.1021/jp503700g) [Medline](#)
 34. B. Ravel, M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **12**, 537–541 (2005). [doi:10.1107/S0909049505012719](https://doi.org/10.1107/S0909049505012719) [Medline](#)
 35. U. Kolb, T. Gorelik, C. Kübel, M. T. Otten, D. Hubert, Towards automated diffraction tomography: Part I—data acquisition. *Ultramicroscopy* **107**, 507–513 (2007). [doi:10.1016/j.ultramic.2006.10.007](https://doi.org/10.1016/j.ultramic.2006.10.007) [Medline](#)
 36. E. Mugnaioli, T. Gorelik, U. Kolb, “Ab initio” structure solution from electron diffraction data obtained by a combination of automated diffraction tomography and precession technique. *Ultramicroscopy* **109**, 758–765 (2009). [doi:10.1016/j.ultramic.2009.01.011](https://doi.org/10.1016/j.ultramic.2009.01.011) [Medline](#)
 37. S. Schlitt, T. E. Gorelik, A. A. Stewart, E. Schömer, T. Raasch, U. Kolb, Application of clustering techniques to electron-diffraction data: Determination of unit-cell parameters. *Acta Crystallogr. A* **68**, 536–546 (2012). [doi:10.1107/S0108767312026438](https://doi.org/10.1107/S0108767312026438) [Medline](#)
 38. U. Kolb, T. Gorelik, M. T. Otten, Towards automated diffraction tomography. Part II—Cell parameter determination. *Ultramicroscopy* **108**, 763–772 (2008). [doi:10.1016/j.ultramic.2007.12.002](https://doi.org/10.1016/j.ultramic.2007.12.002) [Medline](#)
 39. M. C. Burla, R. Caliendo, B. Carrozzini, G. L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori, Crystal structure determination and refinement via SIR2014. *J. Appl. Cryst.* **48**, 306–309 (2015). [doi:10.1107/S1600576715001132](https://doi.org/10.1107/S1600576715001132)
 40. P. A. Doyle, P. S. Turner, Relativistic Hartree-Fock X-ray and electron scattering factors. *Acta Crystallogr. A* **24**, 390–397 (1968). [doi:10.1107/S0567739468000756](https://doi.org/10.1107/S0567739468000756)
 41. G. M. Sheldrick, A short history of SHELX. *Acta Crystallogr. A* **64**, 112–122 (2008). [doi:10.1107/S0108767307043930](https://doi.org/10.1107/S0108767307043930) [Medline](#)
 42. U. Kolb, T. E. Gorelik, E. Mugnaioli, A. Stewart, Structural Characterization of Organics Using Manual and Automated Electron Diffraction. *Polym. Rev. (Phila. Pa.)* **50**, 385–409 (2010). [doi:10.1080/15583724.2010.494238](https://doi.org/10.1080/15583724.2010.494238)

43. I. P. Swainson, The structure of monohydrocalcite and the phase composition of the beachrock deposits of Lake Butler and Lake Fellmongery, South Australia. *Am. Mineral.* **93**, 1014–1018 (2008). [doi:10.2138/am.2008.2825](https://doi.org/10.2138/am.2008.2825)