Hydrous, crystalline forms of $CaCO_3$:
Monohydrocalcite ($CaCO_3 \cdot H_2O$) and *Ikaite* ($CaCO_3 \cdot 6H_2O$)

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Underlined blue texts throughout have hyperlinks.

Is it possible to hydrate a nano powder of calcite or vaterite or aragonite (*i.e.*, anhydrous crystalline $CaCO_3$ polymorphs) in water at RT and 1 atm without dissolving those?

Would calcite or vaterite or aragonite particles form (again at RT and 1 atm pressure) a thin hydrous $CaCO_3$ layer on their surfaces that escape the resolving power of the characterization tools currently available in typical materials science research labs?

Would amorphous calcium carbonate or amorphous magnesium carbonate ("the mother of all") with certain ions present in its aqueous environment/surroundings lead to the crystallization of hydrous calcium carbonate or hydrous magnesium carbonate phases under certain specific conditions?

What is the role of magnesium and pH on the crystallization of hydrous $CaCO_3$ free of Mg?

I am sure most of us whoever worked with calcite (or vaterite or aragonite) in their research programs came across such questions. This document will shed some light on the topic framed by the above questions.

"Calcium carbonate ($CaCO_3$) is an important material of marine and geological biomineralization processes. $CaCO_3$ powders are also widely used in pharmaceuticals (commonly as a calcium supplement or as an antacid), cosmetics, toothpaste, biomedical, rubber, plastic, paper-making, printing ink, and food industries.

Calcium carbonate has three naturally occurring anhydrous polymorphs; calcite, aragonite and vaterite. Amorphous calcium carbonate (ACC), calcium carbonate monohydrate ($CaCO_3 \cdot H_2O$; monohydrocalcite) and calcium carbonate hexahydrate ($CaCO_3 \cdot 6H_2O$; ikaite) may be regarded as the fourth, fifth and sixth polymorphs of calcium carbonate. At the ambient temperature and pressure, calcite is the most stable and abundant polymorph of calcium carbonate, while vaterite (μ-$CaCO_3$), named after Heinrich Vater, is known to be the least stable among the anhydrous polymorphs."

• The text in italics above is from the issued (on June 25, 2013) U.S. patent 8,470,280 B2 entitled ("Calcium carbonate microtablets and method for the preparation thereof") of the author which was written and initially filed with WIPO-PCT in August 2007.

• The hydrous forms of $CaCO_3$ are (1) monohydrocalcite, (2) ikaite and (3) amorphous calcium carbonate. Amorphous calcium carbonate (ACC) formula is $CaCO_3 \cdot nH_2O$. The conditions of the formation of ACC is similar to those of ACP (amorphous calcium phosphate; $Ca_3(PO_4)_2 \cdot nH_2O$).

ANHYDROUS: a substance that lacks water molecules in its structure

HYDROUS: a substance that has water molecules "within its structure"

• Such "structural water" excludes the adsorbed water that would be present on the external surfaces of any substance (if and when the %RH in the environment is not below 5-10%) and it is often named as "water of crystallization."

This pamphlet presents

(1) first the crystal structures of monohydrocalcite and ikaite,

(2) a literature survey (*non-exhaustive*) on the formation and transformation of these hydrous calcium carbonates,

(3) implications for the follow-up industrial/academic research.

Examples of **anhydrous** and **hydrous** phases/compounds

$CuSO_4$: anhydrous copper sulphate (mineral chalcocyanite)
$CuSO_4 \cdot 5H_2O$: hydrous copper sulphate (mineral chalcanthite)

$CaSO_4$: anhydrous calcium sulphate (mineral anhydrite)
$CaSO_4 \cdot 2H_2O$: hydrous calcium sulphate (mineral gypsum)

$CaHPO_4$: anhydrous dicalcium phosphate (mineral monetite)
$CaHPO_4 \cdot 2H_2O$: hydrous dicalcium phosphate (mineral brushite)

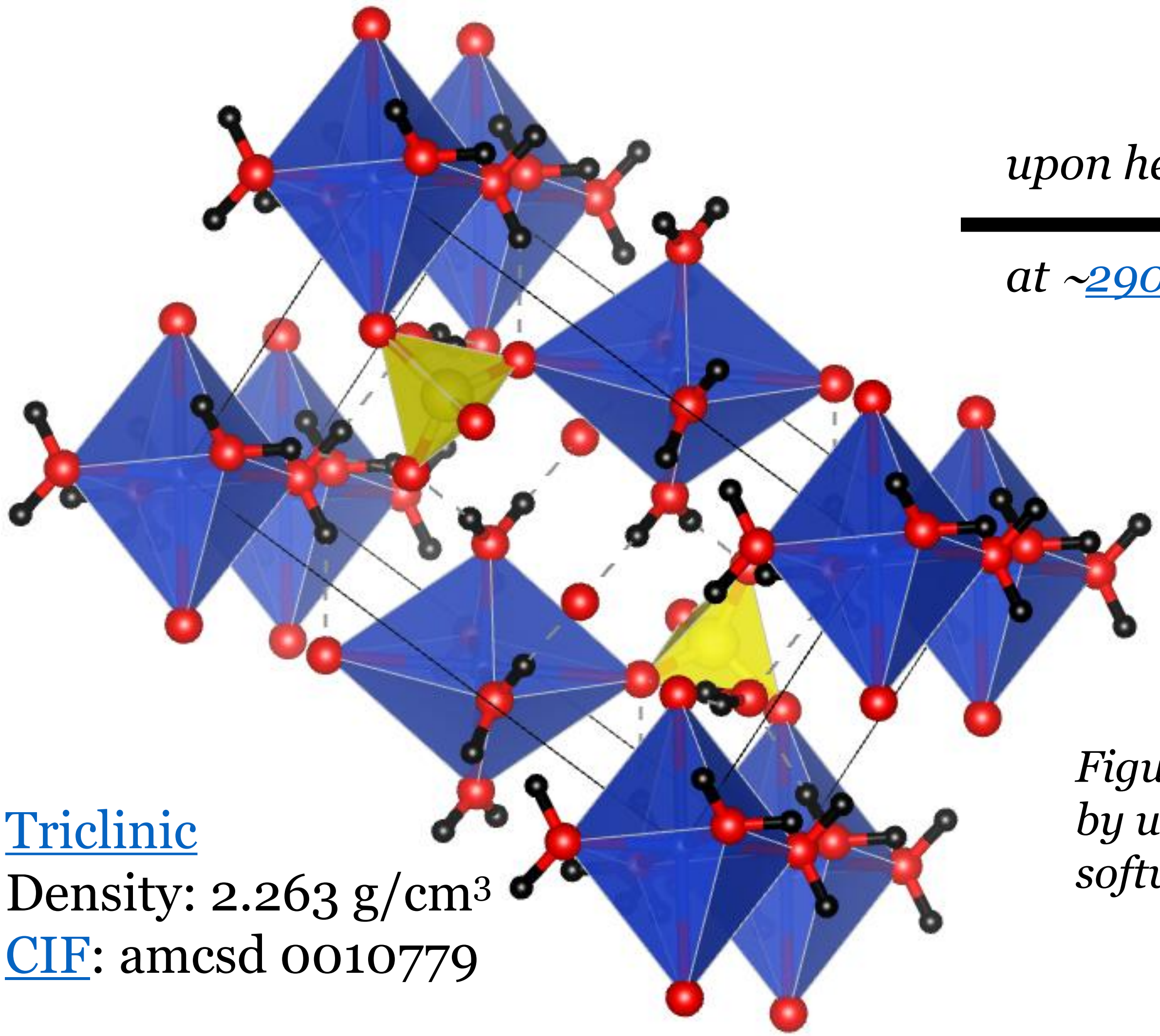
$CaCO_3$: (anhydrous) calcite, aragonite or vaterite
$CaCO_3 \cdot H_2O$: (hydrous) monohydrocalcite
$CaCO_3 \cdot nH_2O$: (hydrous) X-ray-amorphous calcium carbonate
$CaCO_3 \cdot 6H_2O$: (hydrous) ikaite

When all the hydrous compounds listed above are heated at temperatures up to 400°C, typically to ~300°C, they lose the structural waters indicated in their formula and transform into their anhydrous forms. These are "reconstructive" transformations that involve a change in crystal structure.

Those without some geochemistry background may sometimes call such hydrous phases/compounds as “hydrated” phases/compounds.

The formation of hydrous phases (such as monohydrocalcite and ikaite) involves the incorporation of water molecules inside the crystal structure and should not be confused with the chemical mechanisms such as those in the hydrating/moisturizing creams employ (which are surface-limited and adsorption-based hydration processes for porous membranes such as skin).

$CuSO_4 \cdot 5H_2O$ chalcanthite



[Triclinic](#)
Density: 2.263 g/cm³
[CIF](#): amcsd 0010779

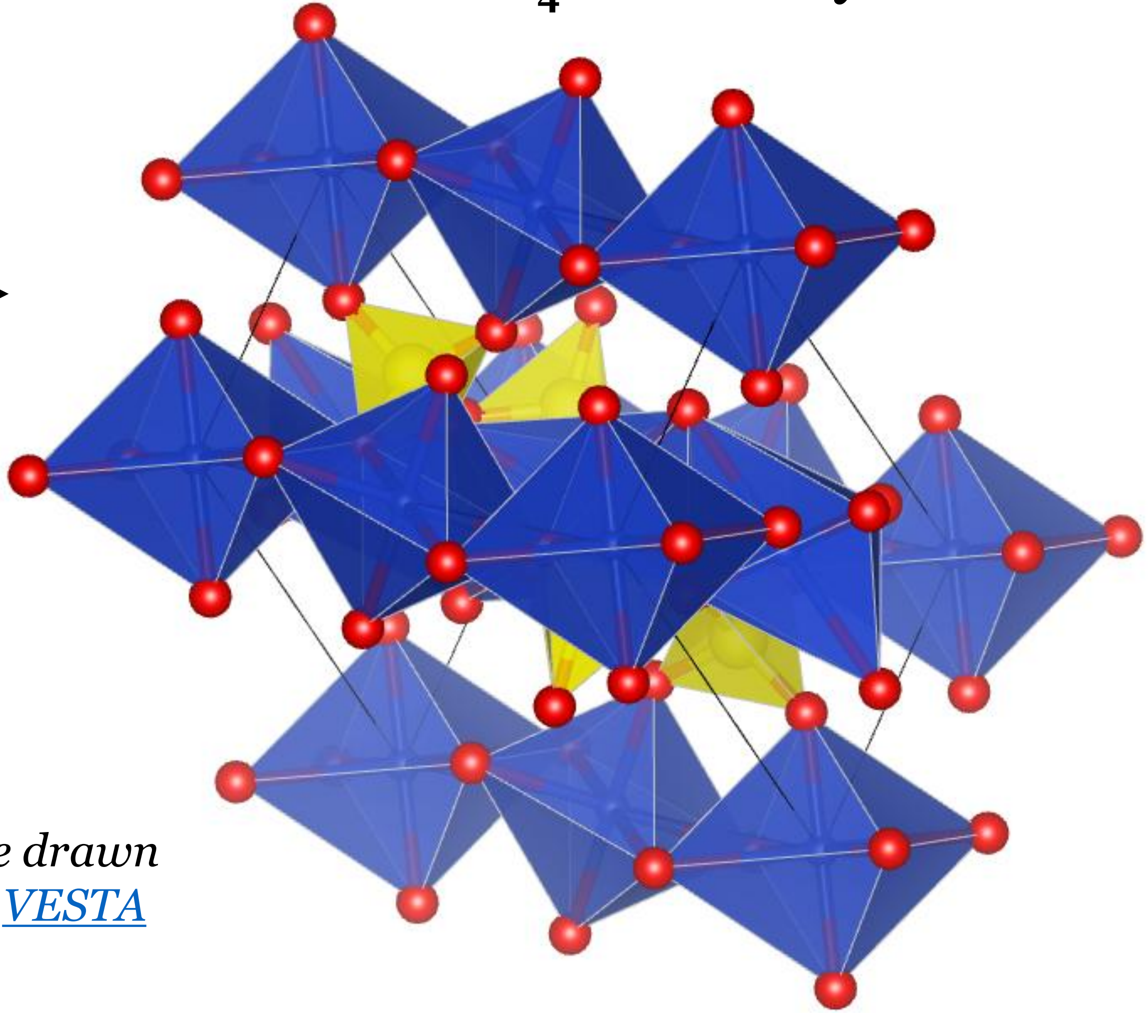
H_2O molecules are bound to the cupric octahedra.

upon heating

→

at ~290°C

$CuSO_4$ chalcocyanite



Orthorhombic
Density: 3.888 g/cm³
CIF: amcsd 0014619

Figures were drawn by using the VESTA software.

Location of S: centers of yellow tetrahedra
Location of Cu: centers of blue octahedra
Red: O, H: black

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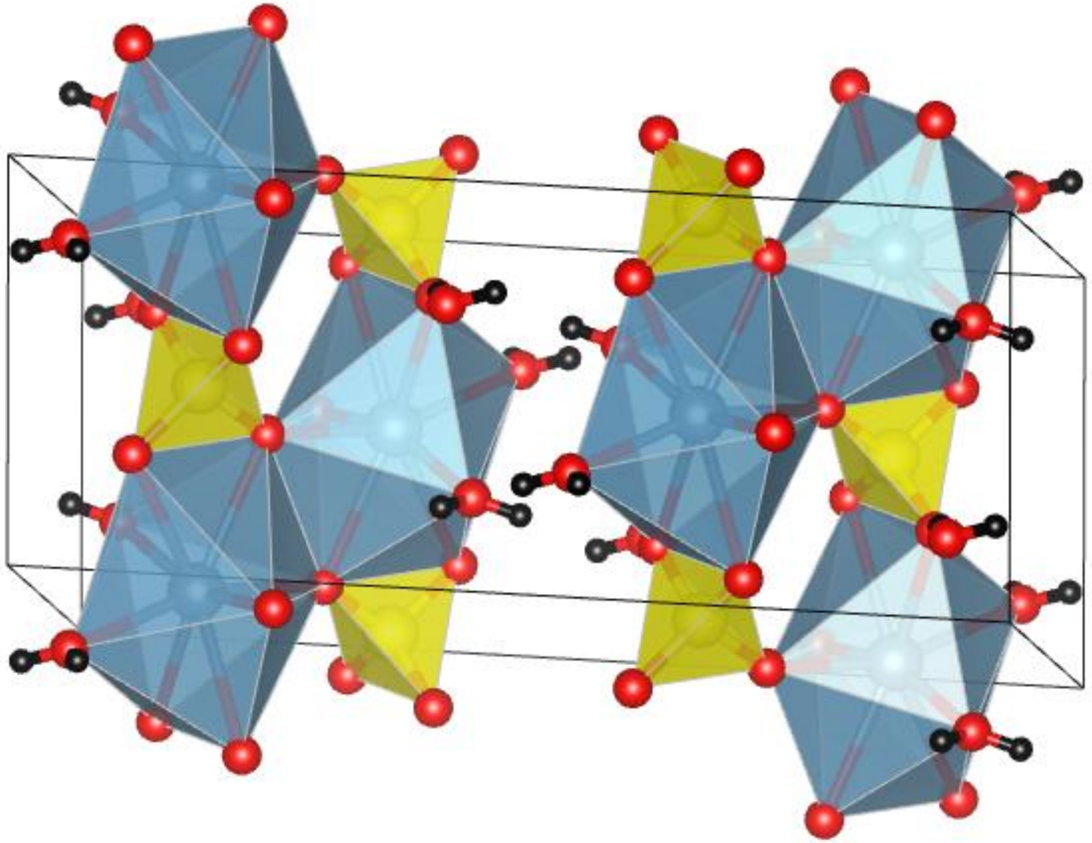
$CaSO_4 \cdot 2H_2O$ gypsum



[Monoclinic](#)
Density: 2.318 g/cm3
[CIF](#): amcsd 0004651

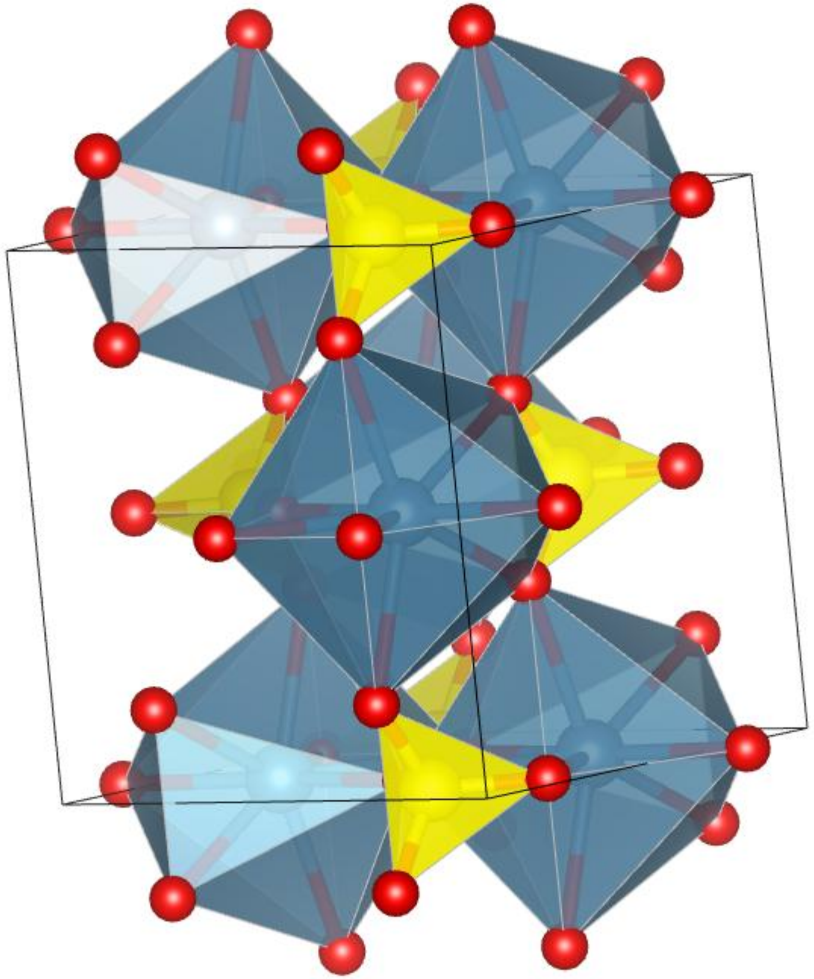
H_2O molecules are bound to the Ca-containing polyhedra.

upon heating

at ~[240°C](#)

Figures were drawn by using the [VESTA](#) software.

$CaSO_4$ anhydrite



[Orthorhombic](#)
Density: 2.960 g/cm3
[CIF](#): amcsd 0005117

Location of S: centers of yellow tetrahedra
Location of Ca: centers of green Ca polyhedra
Red: O, H: black

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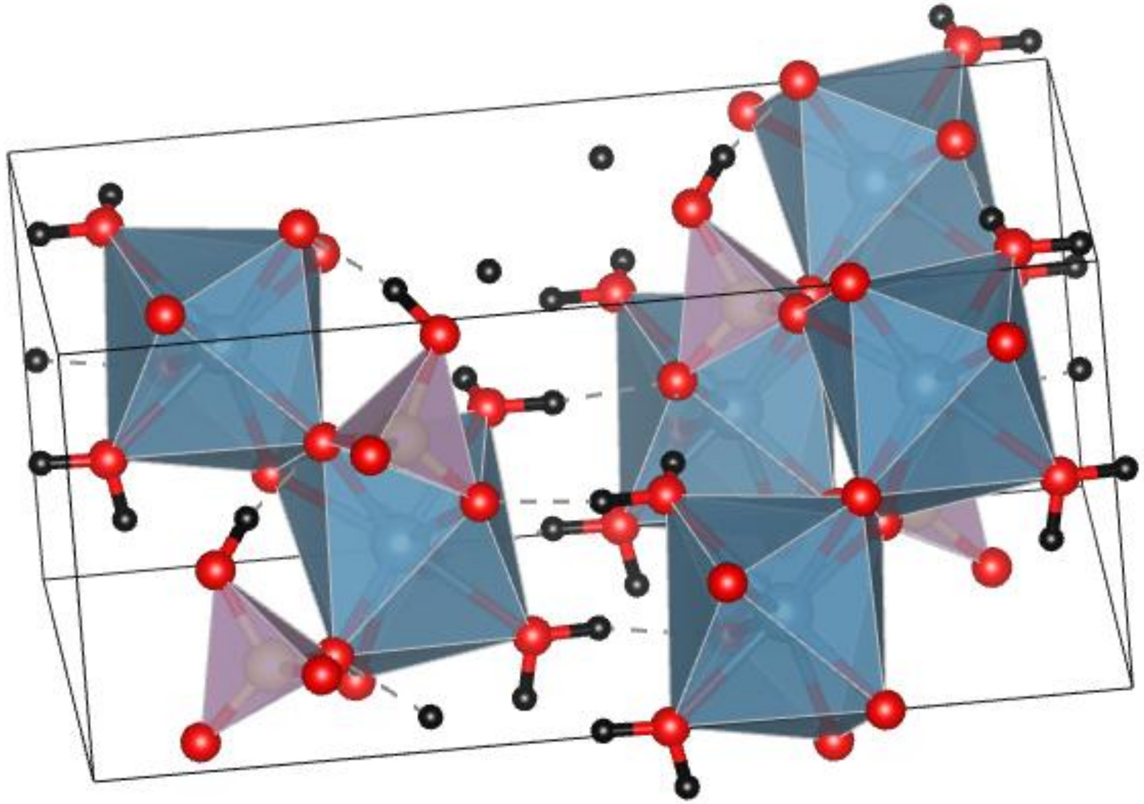
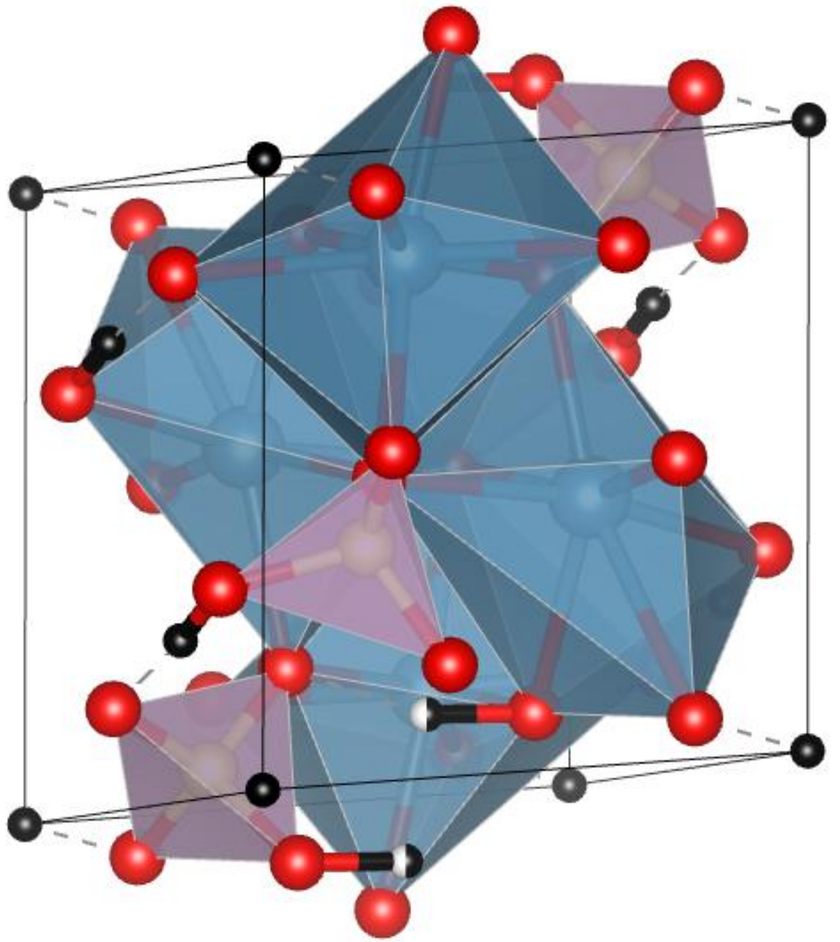
$CaHPO_4 \cdot 2H_2O$ brushite

$CaHPO_4$ monetite



upon heating

at ~200°C



Monoclinic
Density: 2.389 g/cm3
CIF: amcsd 0-08898

Figures are drawn by using the VESTA software.

Triclinic
Density: 2.922 g/cm3
CIF: amcsd 0009584

H_2O molecules are bound to the Ca-containing polyhedra.

Location of P: centers of pink tetrahedra
Location of Ca: centers of green Ca polyhedra
Red: O, H: black

Did you note that the loss of structural waters in all of the examples of the last three pages caused dramatic increases in the respective densities?

The scientific and patent work on monohydrocalcite and ikaite are rather limited (this pamphlet will present and discuss a part of that limited work).

The last 50 years have seen a significant increase in research efforts focusing on the synthesis of carbonated forms of alkaline earth elements, such as Ca and Mg, in unison with the sharp rise in the atmospheric CO_2 levels (from the 330 ppm of 1975 to 430 ppm of June 2025; a 30% increase).

• Ca- and/or Mg-silicates (either as natural minerals, such as wollastonite or olivine, or synthetic silicate clinkers), Ca-hydroxide or even Ca-oxide (*i.e.*, CaO used in Ca-looping) have now been the starting materials for transforming CO_2(g), of various sources, into solid $CaCO_3$ forms. Ordinary Portland cement (OPC) and Portland limestone cement (PLC) are also known to form $CaCO_3$(s) upon the exposure of their concrete to the ambient. In all of this type of work, the scientists seemed to encounter only the anhydrous forms of $CaCO_3$, namely, calcite, aragonite and/or vaterite. The question is: did these anhydrous forms of $CaCO_3$ first form the transient hydrous forms such as ACC, monohydrocalcite or ikaite?

• This pamphlet, by presenting the literature on monohydrocalcite and ikaite, the thermal and X-ray diffraction characterization tools for monohydrocalcite and ikaite (the two crystalline hydrous forms of $CaCO_3$), as well as amorphous calcium carbonate characterization by using sophisticated thermal analysis techniques, could be helpful to detect whether there might be some monohydrocalcite or ikaite present in synthetic, carbonated samples or not (besides anhydrous $CaCO_3$).

This is the only page of this document dedicated to "amorphous calcium carbonate (ACC)."

One cannot use XRD (powder X-ray diffraction) to identify ACC in any sample since ACC is amorphous, *i.e.*, amorphous materials do not have any long-range order and a unique crystal structure that can be detected by XRD. Therefore, the easiest way of detecting ACC in a sample is to run a rather "sophisticated thermal analysis technique." One should use either combined TG-FTIR or combined TG-MS or better combined TG-FTIR-MS equipment for ACC identification, where FTIR is Fourier-transform infrared spectroscopy and MS stands for mass spectroscopy. Unfortunately, ordinary labs around the world do only have TG (thermogravimetric analyzer). Simple TG runs can only show a mass loss that occurs at any given temperature or temperature range, but they will not be able to ascertain the chemistry of the evolved gas, in other words, regular TG cannot distinguish between $H_2O(g)$ or $CO_2(g)$ evolution. When one has a sample made out of ACC, a combined TG-FTIR or combined TG-MS run on it will show at what temperature its H_2O and CO_2 evolve. These two devices perform evolved gas analysis on top of generating quantitative mass loss data. We provide the below couple of articles [1, 2] as competent references which show that ACC does not decompose to CaO at temperatures less than 550-570°C, which is the typical T range for the $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ reaction to start. TG-FTIR or TG-MS need to be used for samples containing monohydrocalcite and/or ikaite as well.

[1] N. Koga, Y. Nakagoe, and H. Tanaka, "Crystallization of amorphous calcium carbonate," *Thermochim. Acta*, 318, 239-244 (1998).
[2] Y. Kojima, A. Kawanobe, T. Yasue, and Y. Arai, "Synthesis of amorphous calcium carbonate and its crystallization," *J. Ceram. Soc. Japan*, 10, 1145-1152 (1993).

Crystal structure of monohydrocalcite ($CaCO_3 \cdot H_2O$)

A. C. Tas

Link for a photo gallery of naturally-occurring **monohydrocalcite** ($CaCO_3 \cdot H_2O$) deposits

A. C. Tas

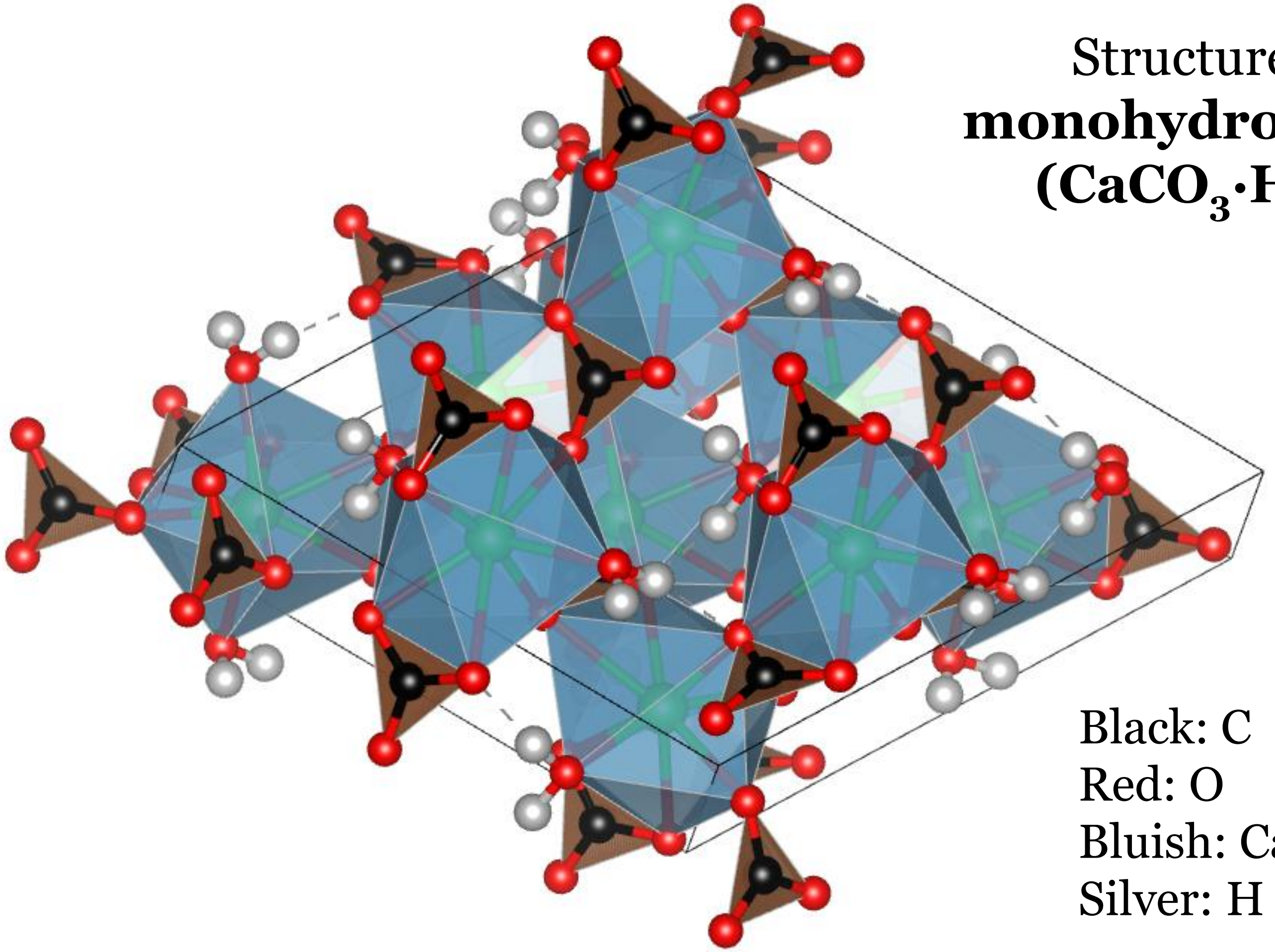
Structural info **Monohydrocalcite ($CaCO_3 \cdot H_2O$)**	Structural info **vaterite**	Structural info **aragonite**	Structural info **calcite**
a = 10.5547 Å b = 10.5547 Å c = 7.5644 Å α = 90° β = 90° γ = 120°	a = 7.290 Å b = 7.290 Å c = 25.302 Å α = 90° β = 90° γ = 120°	a = 4.9614 Å b = 7.9671 Å c = 5.7404 Å α = 90° β = 90° γ = 90°	a = 4.990 Å b = 4.990 Å c = 17.0615 Å α = 90° β = 90° γ = 120°
Density = 2.419 g/cm³ Space group = P 3 1 (H-M # 152)	Density = 2.569 g/cm³ Space group = P 6_5 2 2 (H-M # 179)	Density = 2.930 g/cm³ Space group = P m c n (H-M # 62)	Density = 2.710 g/cm³ Space group = R -3 c (H-M # 167)
Hexagonal crystal family / trigonal pyramidal	Hexagonal crystal family / hexagonal trapezohedral	Orthorhombic crystal family / dipyramidal	Trigonal crystal family / hexagonal scalenohedral
CIF: amcsd 0004611 [3]	CIF: amcsd 0004854	CIF: amcsd 0000233	CIF: amcsd 0000098

$CaCO_3 \cdot H_2O$ (*s*) → $CaCO_3$ (*s*) + H_2O (*l or g*) ← a mass loss (due to the removal of H_2O) of **15.254** wt%

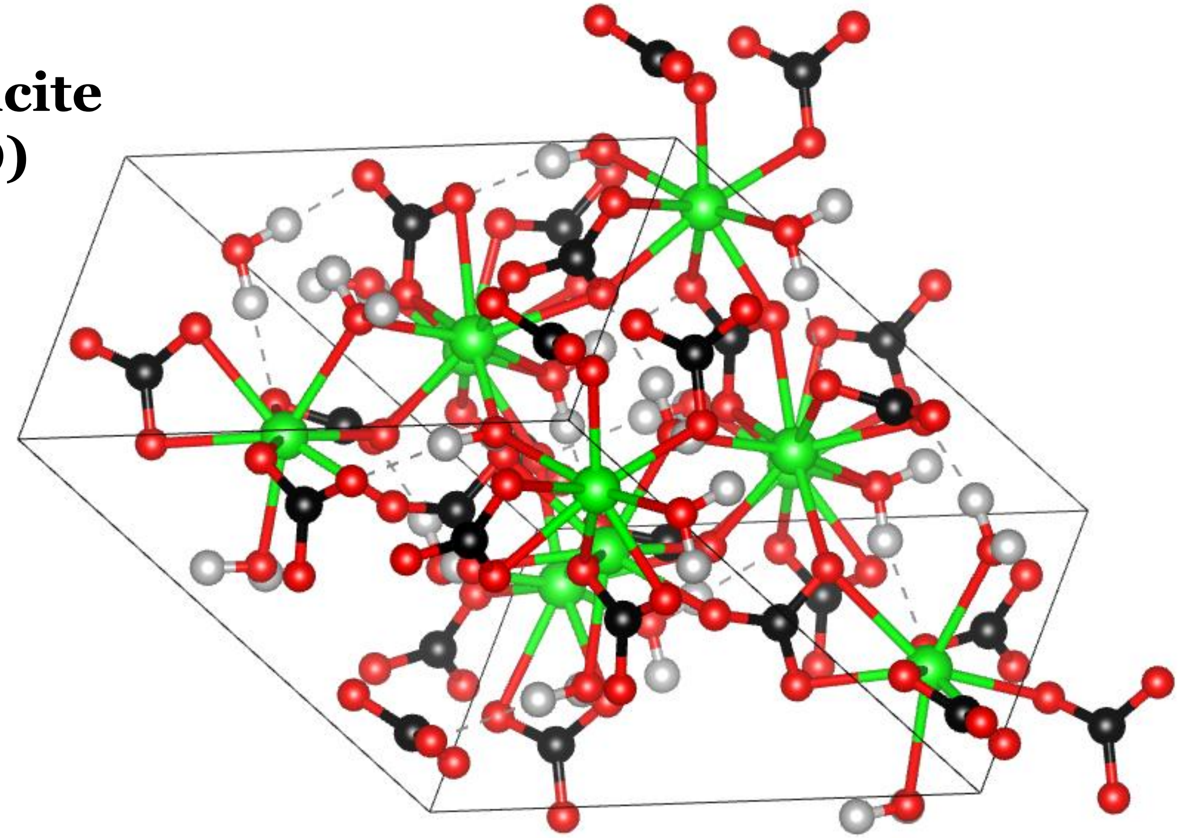
When the above reaction occurs, to form either vaterite, aragonite or calcite, it will be accompanied by a significant degree of physical "shrinkage" (see the increases in densities).

[3] I. P. Swainson, *American Mineralogist*, 93, 1014-1018 (2008).

Structure of
monohydrocalcite
($CaCO_3 \cdot H_2O$)

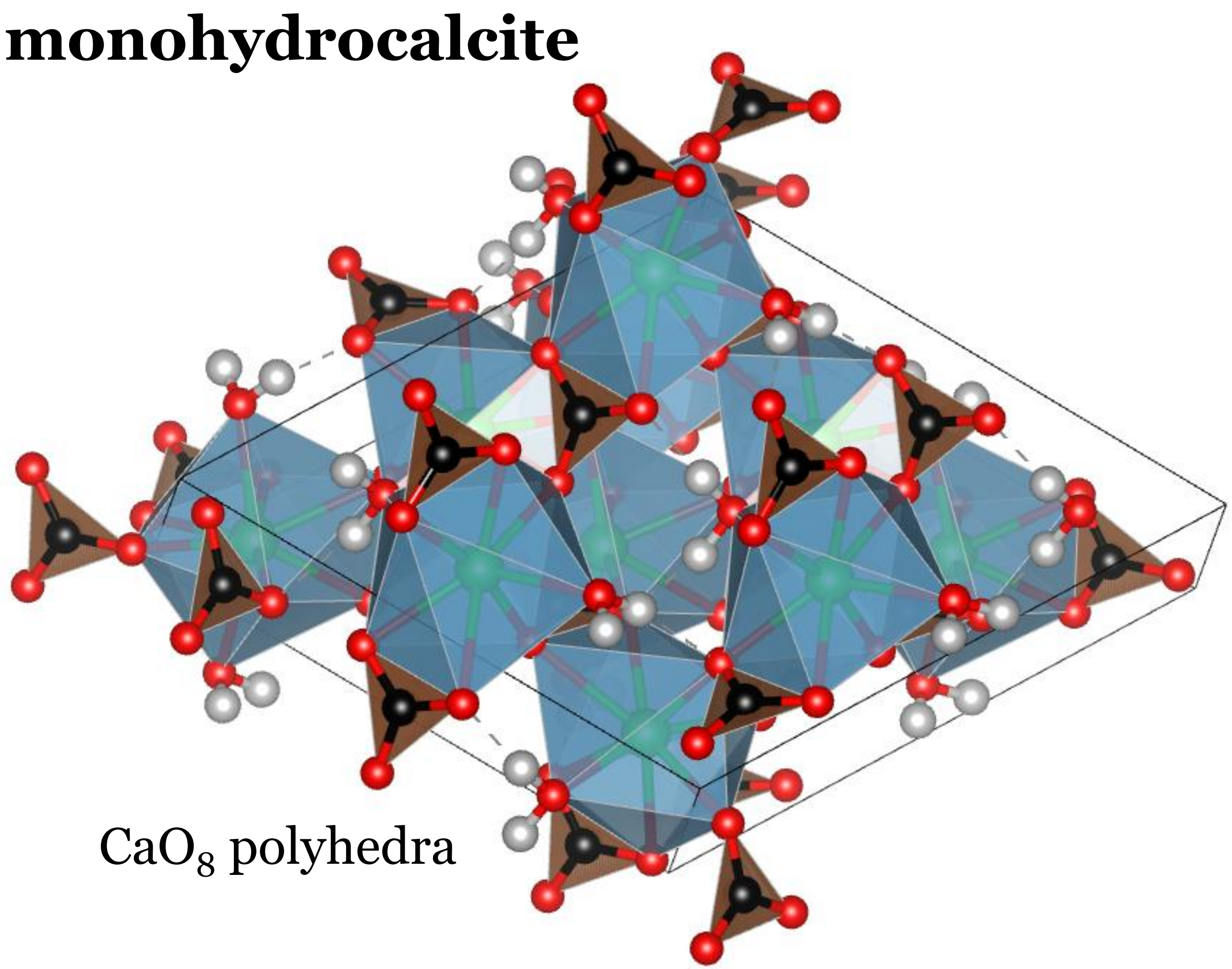


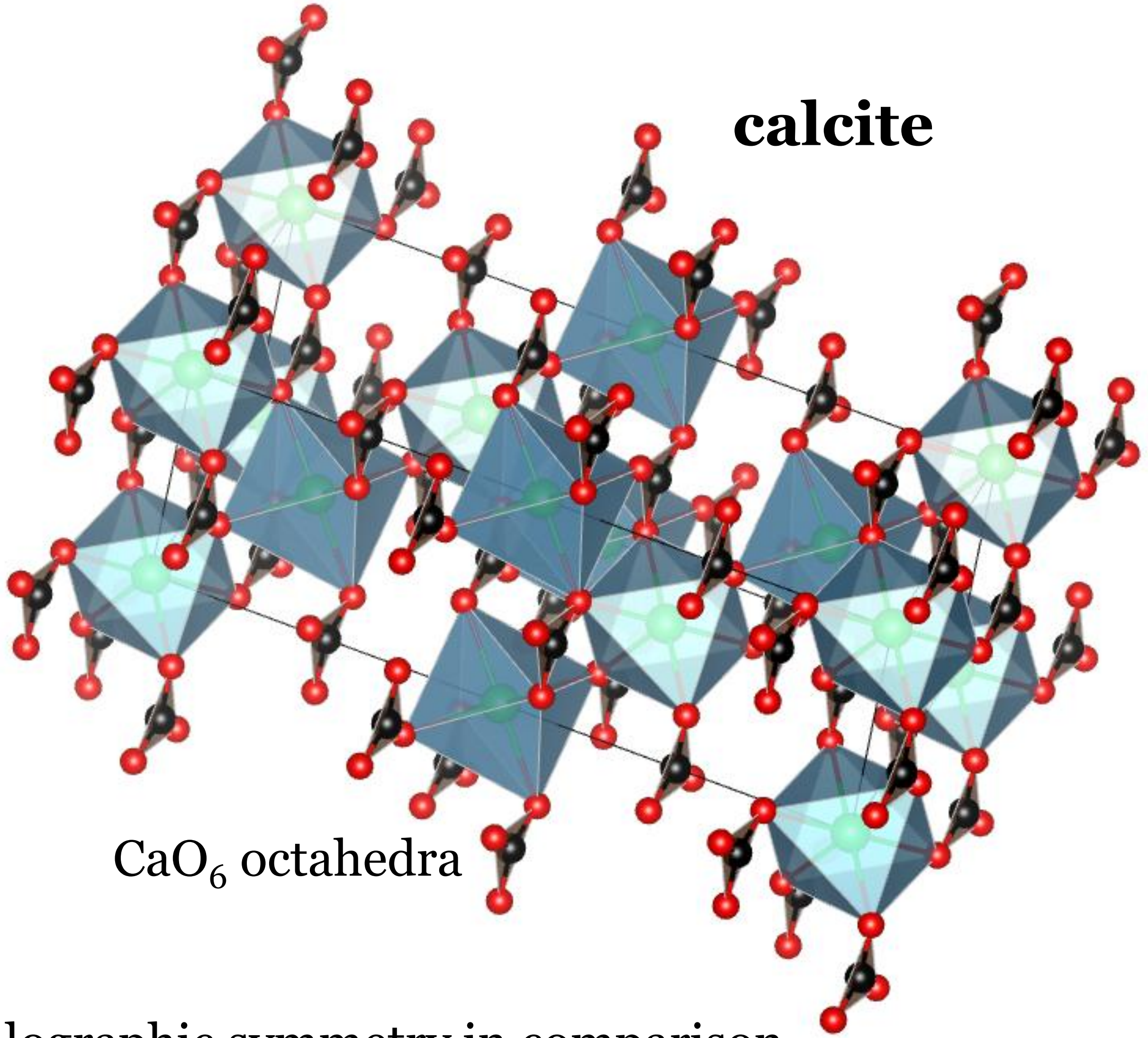
Black: C
Red: O
Bluish: Ca
Silver: H



Each Ca is surrounded by 8 oxygens; trigonal planar CO_3 molecules connect CaO_8 polyhedra with one another; two oxygens of each CaO_8 polyhedron are provided by two separate H_2O molecules; each CaO_8 polyhedron is surrounded by four CO_3 molecules

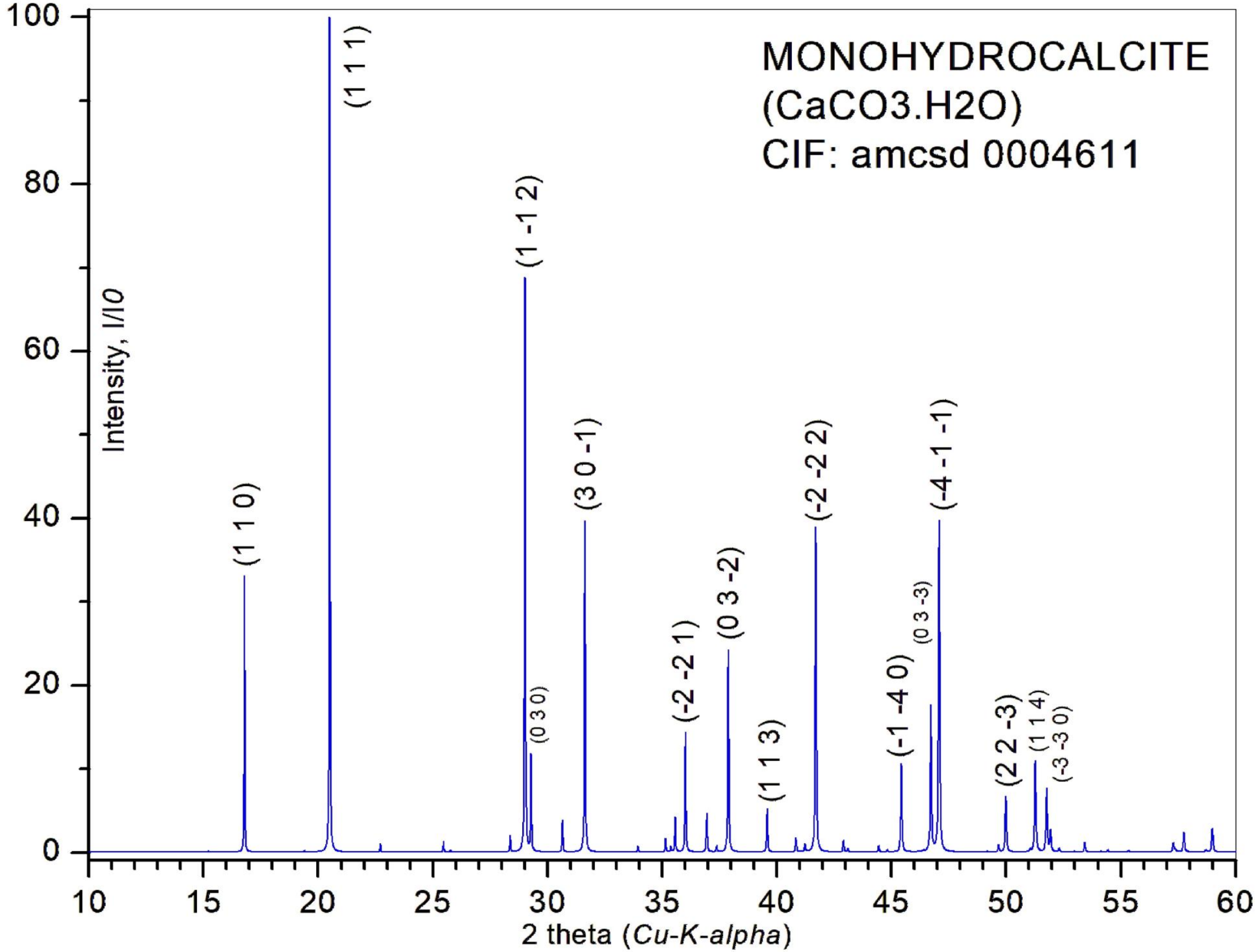
To compare, while calcite has its Ca^{2+} ions located in perfect octahedra (*i.e.*, CaO_6) with a radius of 1.00 Å (in 6-coordination), the ionic radius of Ca^{2+} ions of monohydrocalcite increases to 1.12 Å (in 8-coordination).





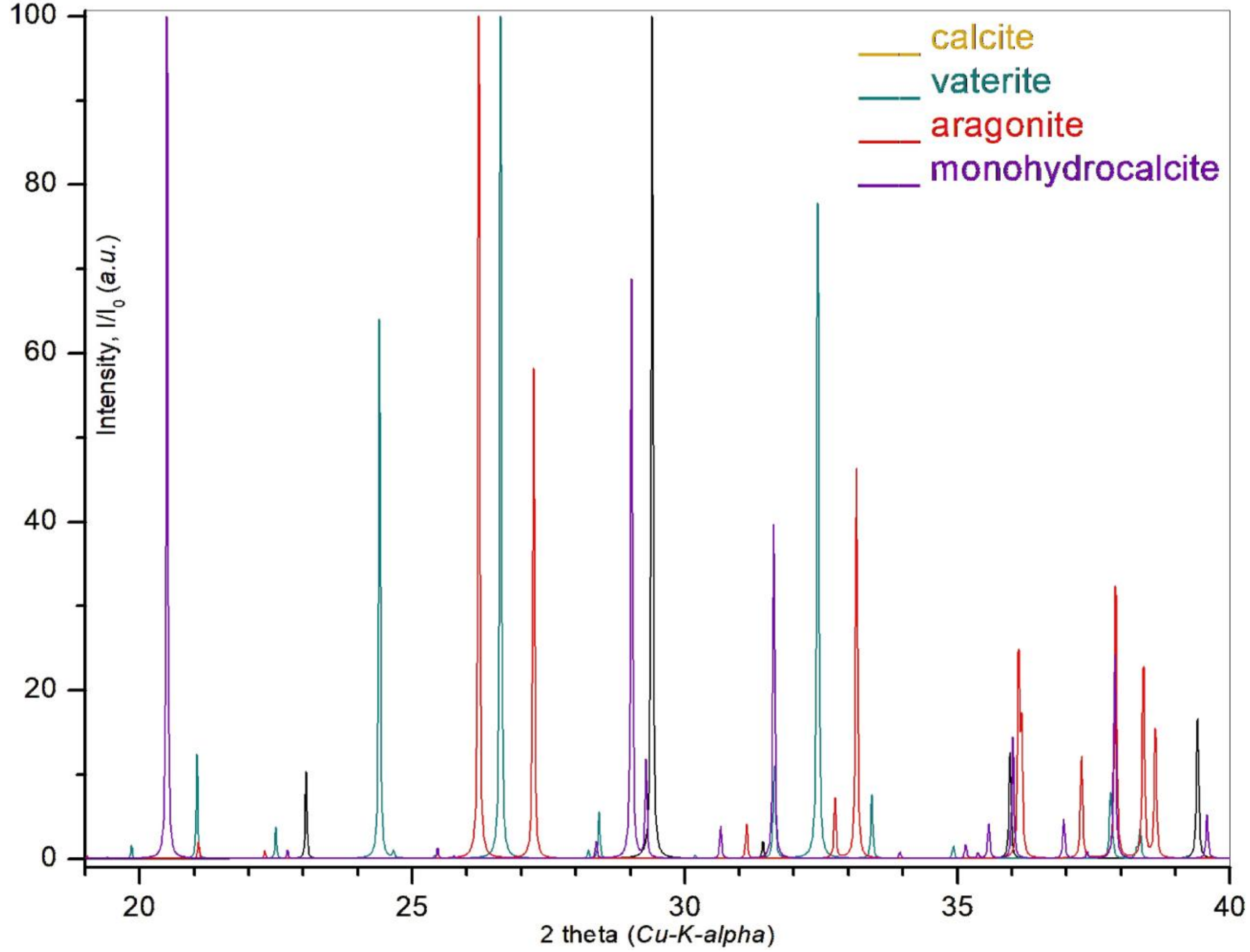
The structure of monohydrocalcite has a lower crystallographic symmetry in comparison to that of calcite.

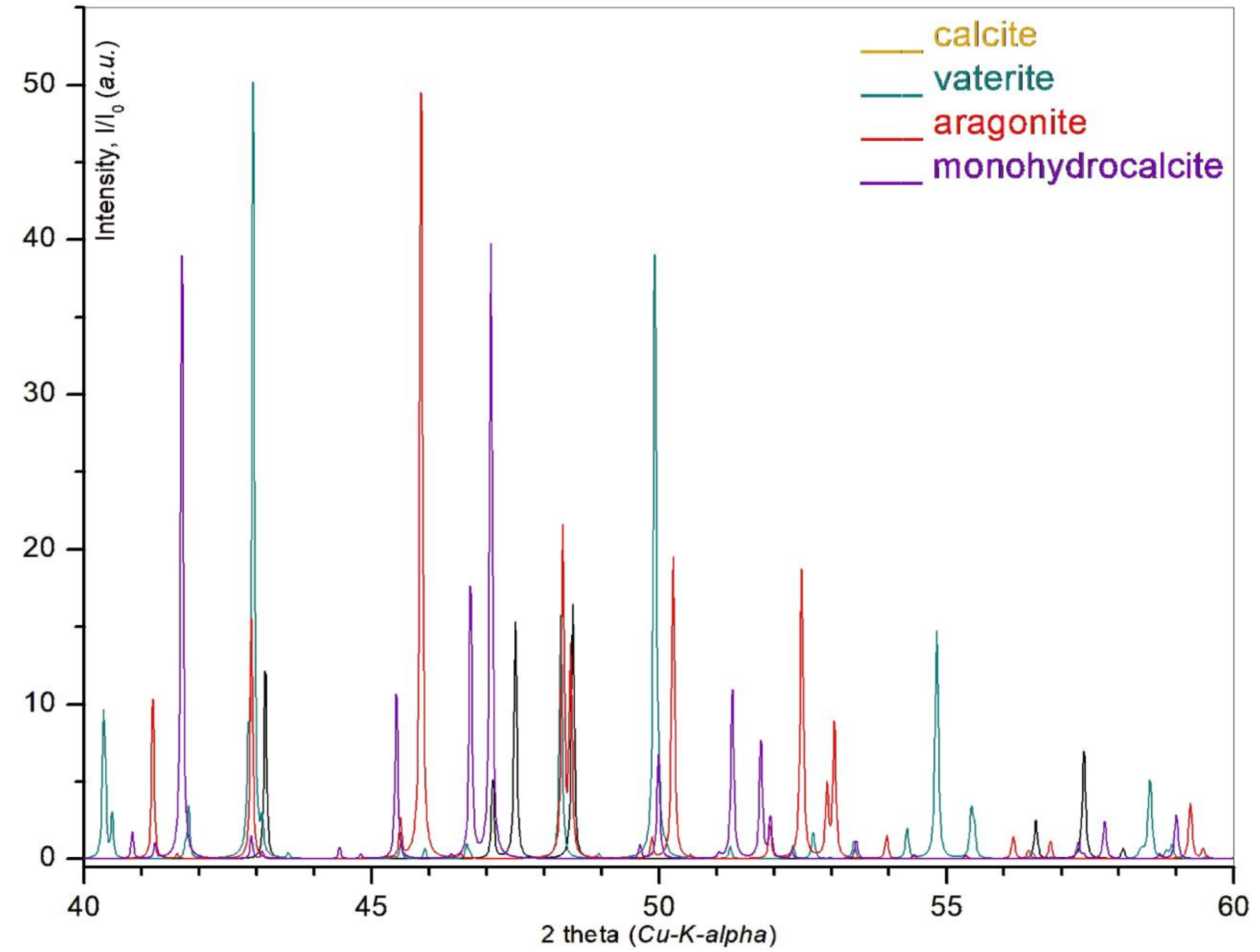
Geometrically perfect octahedra (each hosting a Ca^{2+} ion at its center) of calcite are no longer present in monohydrocalcite.



This will be the XRD diffractogram to be obtained from a sample of single-phase **monohydrocalcite** of high crystallinity.

The raw XRD data and the *hkl* indices of this plot was obtained by opening the indicated CIF file in VESTA.





These plots show that even when monohydrocalcite partially transforms into vaterite, aragonite and/or calcite, X-ray diffraction will still be useful to quantify (*via* Rietveld analysis and amorphous content estimation) the amount of each phase in a given phase mixture. If there were severe peak overlaps between the phases, then using Rietveld analysis would have been unfruitful. The above plots indicate that there are no such severe peak overlaps between monohydrocalcite, vaterite, aragonite and calcite.

Crystal structure of ikaite ($CaCO_3 \cdot 6H_2O$)

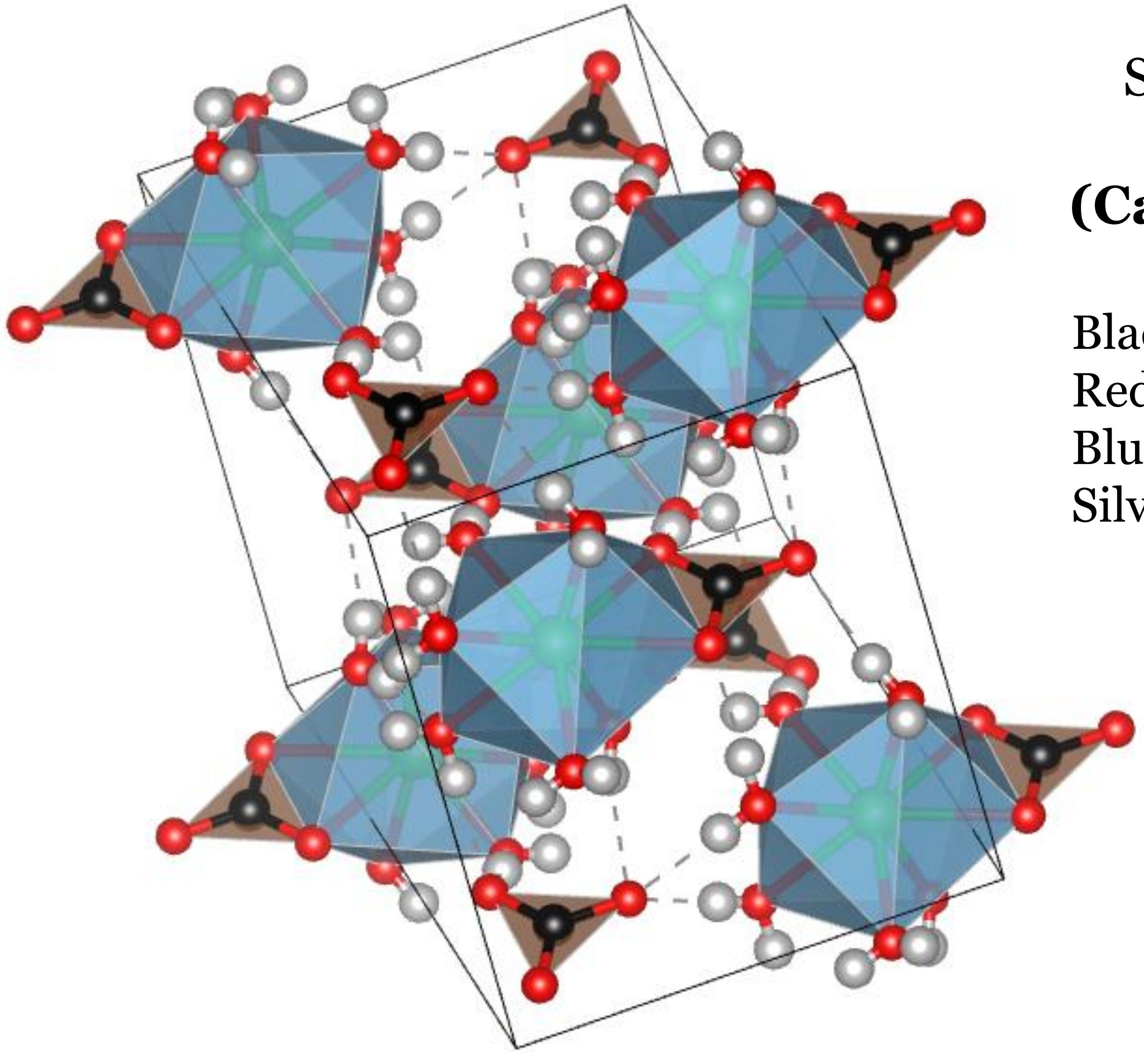
Link for a photo gallery of naturally-occurring **ikaite** ($CaCO_3 \cdot 6H_2O$) deposits

Structural info **ikaite ($CaCO_3 \cdot 6H_2O$)**	Structural info **vaterite**	Structural info **aragonite**	Structural info **calcite**
a = 8.792 Å	a = 7.290 Å	a = 4.9614 Å	a = 4.990 Å
b = 8.310 Å	b = 7.290 Å	b = 7.9671 Å	b = 4.990 Å
c = 11.021 Å	c = 25.302 Å	c = 5.7404 Å	c = 17.0615 Å
α = 90°	α = 90°	α = 90°	α = 90°
β = 110.53°	β = 90°	β = 90°	β = 90°
γ = 90°	γ = 120°	γ = 90°	γ = 120°
Density = 1.834 g/cm³	Density = 2.569 g/cm³	Density = 2.930 g/cm³	Density = 2.710 g/cm³
Space group = C 1 2/*c* 1	Space group = P 6_5 2 2	Space group = P m c n	Space group = R -3 c
(H-M # 15)	(H-M # 179)	(H-M # 62)	(H-M # 167)
Monoclinic crystal family / prismatic	Hexagonal crystal family / hexagonal trapezohedral	Orthorhombic crystal family / dipyramidal	Trigonal crystal family / hexagonal scalenohedral
CIF: amcsd 0010853 [4]	CIF: amcsd 0004854	CIF: amcsd 0000233	CIF: amcsd 0000098

$CaCO_3 \cdot 6H_2O$ (*s*) → $CaCO_3$ (*s*) + $6H_2O$ (*l or g*) ← a mass loss (due to H_2O shedding) of **51.923** wt%

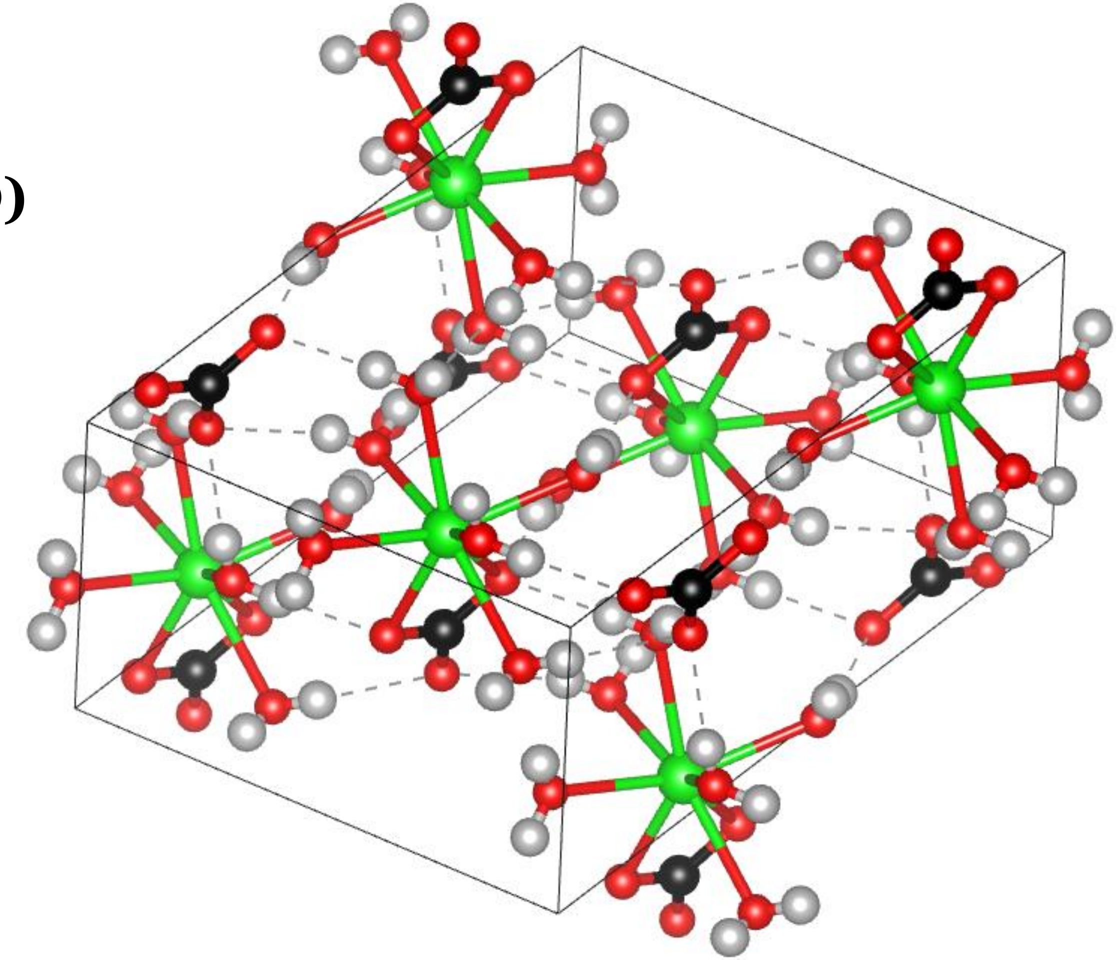
When the above reaction occurs, to form either vaterite, aragonite or calcite, it will be accompanied by a significant degree of physical "shrinkage" (see the increases in densities).

[4] K. F. Hesse, H. Küppers and E. Suess, *Zeitschrift für Kristallographie*, 163, 227-231 (1983).



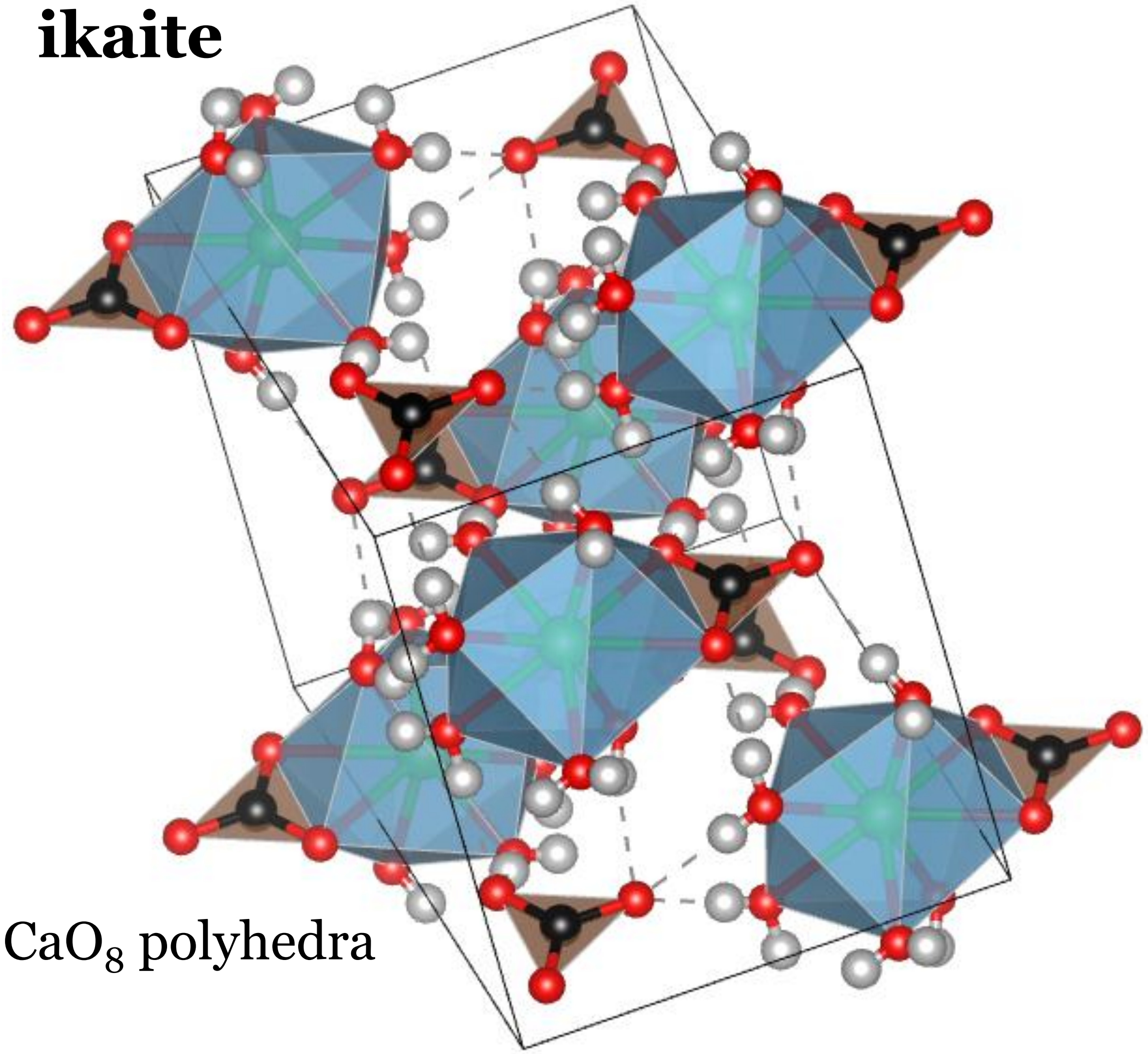
Structure of
ikaite
($CaCO_3 \cdot 6H_2O$)

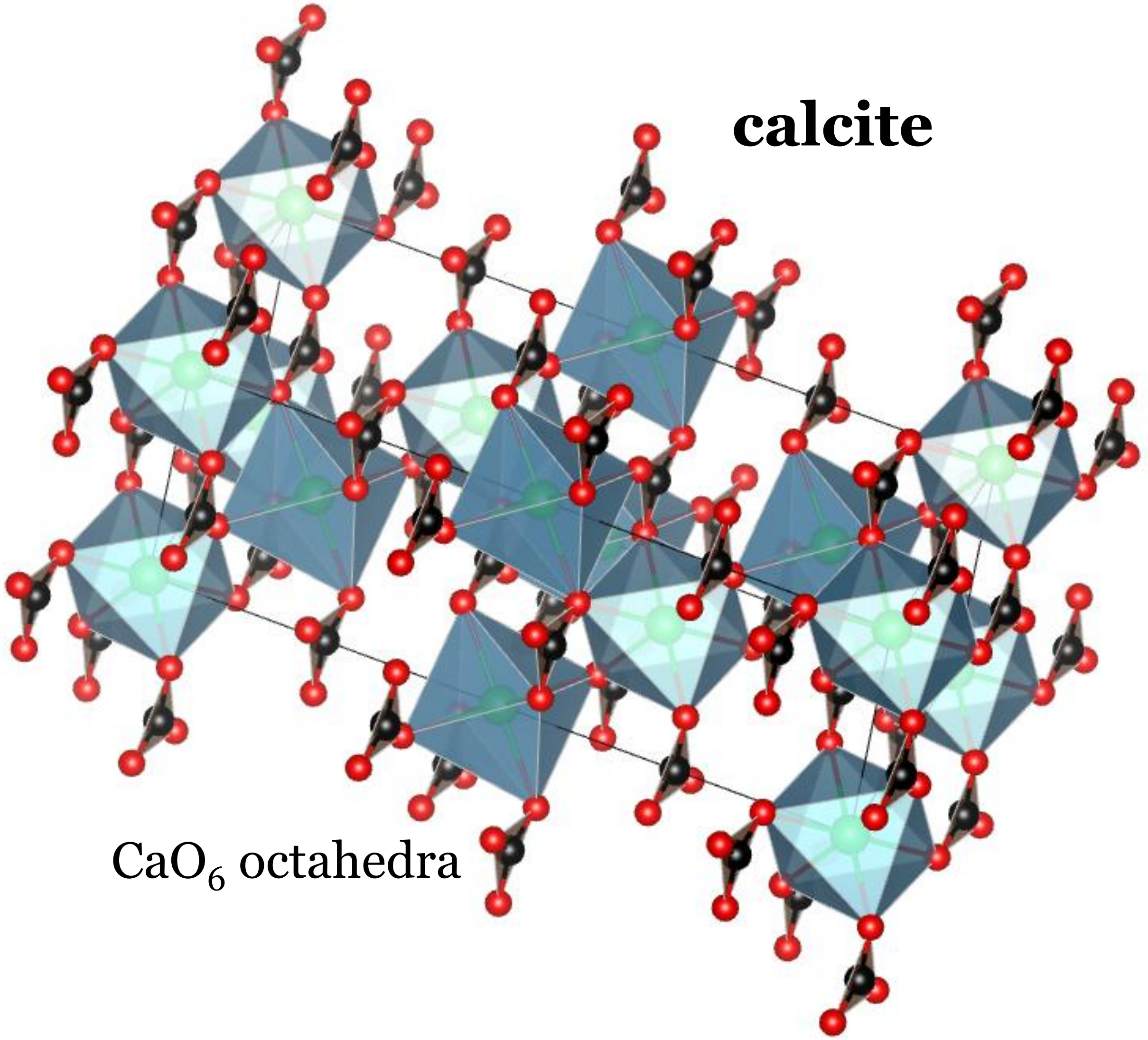
Black: C
Red: O
Bluish/green: Ca
Silver: H



In comparison to monohydrocalcite, there are more H_2O molecules in the structure of ikaite (as dictated by its formula) and, now, every CaO_8 polyhedron binds only one CO_3 triangular planar molecule (while borrowing two of its oxygens) to itself. Some CO_3 molecules remain in the bulk of the structure without bonding to the CaO_8 polyhedra.

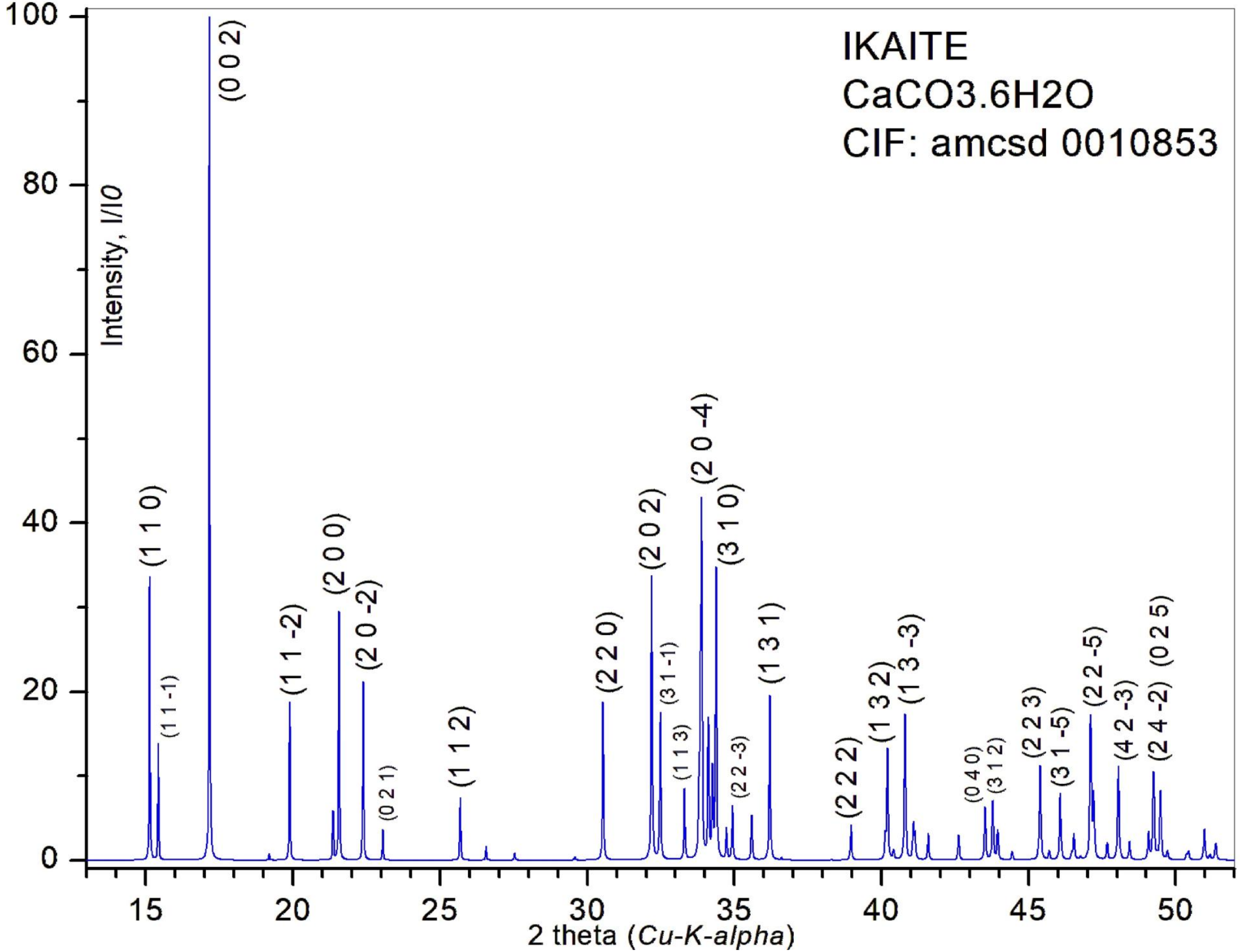
A. C. Tas





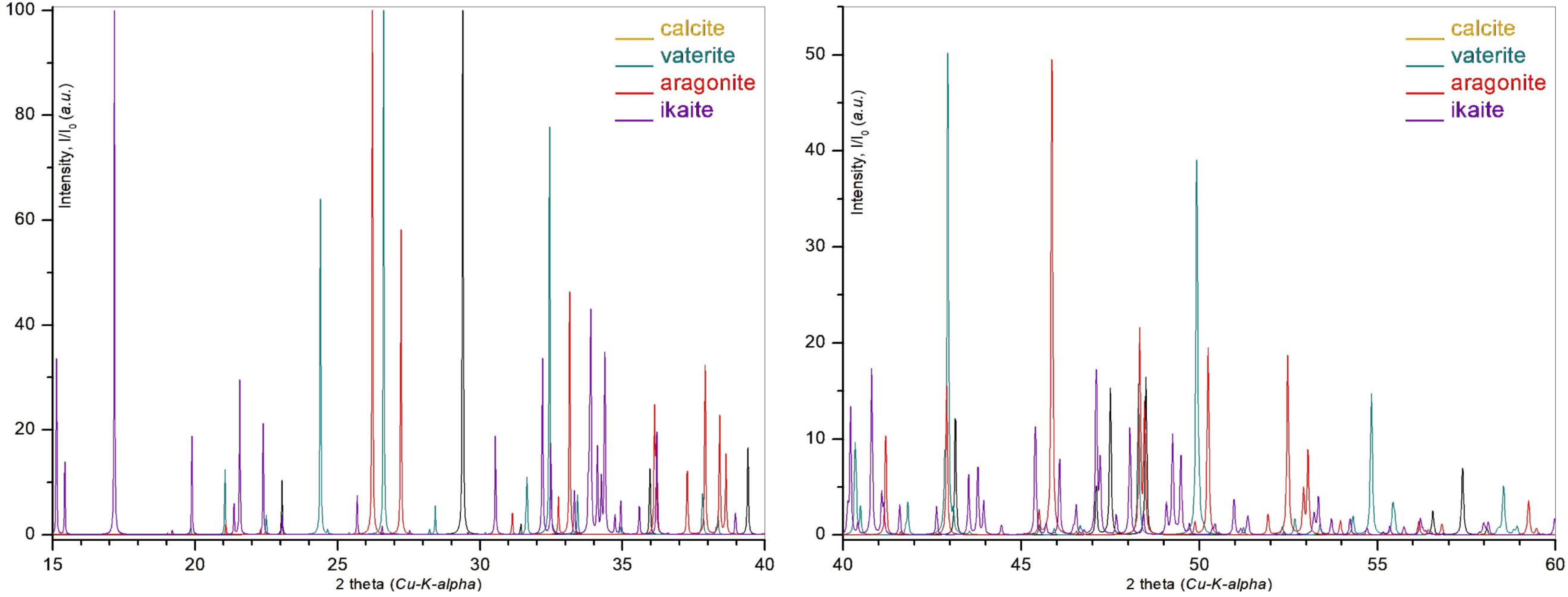
The ikaite structure has a lower crystallographic symmetry in comparison to that of calcite.

Geometrically perfect octahedra (each hosting a Ca^{2+} ion at its center) of calcite are no longer present in monohydrocalcite.

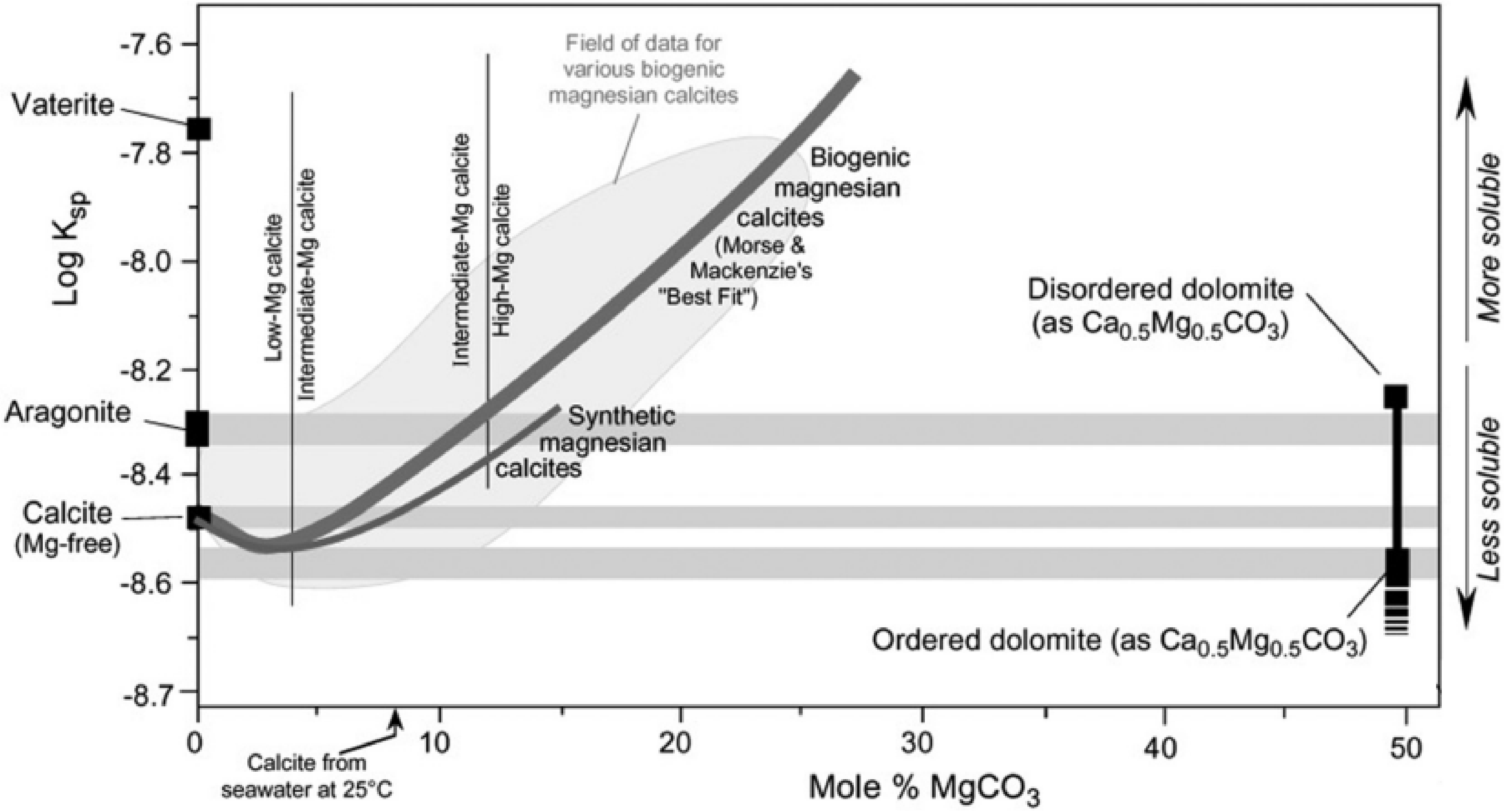


This will be the XRD diffractogram to be obtained from a sample of single-phase **ikaite** of high crystallinity.

The raw XRD data and the *hkl* indices of this plot was obtained by opening the indicated CIF file in VESTA.



These plots show that even when ikaite partially transforms into vaterite, aragonite and/or calcite, X-ray diffraction will still be useful to quantify (*via* Rietveld analysis and amorphous content estimation) the amount of each phase in a given phase mixture. If there were severe peak overlaps between the phases, then using Rietveld analysis would have been unfruitful. The above plots indicate that there are no such severe peak overlaps between ikaite, vaterite, aragonite and calcite.



Source (only the Figure): *Emeritus* Prof. L. Bruce Railsback, Department of Geology, University of Georgia, **https://railsback.org**/Fundamentals/820HMC-LMCSolubilities05LS.pdf

The left-hand side y-axis of this plot has the solubility products (*log* K_{sp}) of the anhydrous $CaCO_3$ phases of calcite, aragonite and vaterite.

The solubility products (*i.e.*, *log* K_{sp} values) of anhydrous $CaCO_3$ polymorphs:

calcite (-8.48 at 25°C / -8.56 at 37°C), aragonite (-8.33 at 25°C / -8.40 at 37°C) and vaterite (-7.91 at 25°C / -8.05 at 37°C) [5]

[5] J. H. Lee, A. S. Madden, W. M. Kriven and A. C. Tas, "Synthetic aragonite ($CaCO_3$) as a potential additive in calcium phosphate cements: Evaluation in Tris-free SBF at 37°C," Journal of The American Ceramic Society, 97, 3052-3061 (2014).

MONOHYDROCALCITE ($CaCO_3 \cdot H_2O$)

Monohydrocalcite was first synthesized by Brooks *et al.* [6] and later by Van Tassel [7] by reacting calcium chloride with sodium carbonate (in water at RT) in the presence of dissolved magnesium chloride or sodium polyphosphate ($Na_5P_3O_{10}$ is extensively used in detergents and by the food industry). (Mg^{2+} or phosphate ions, in synthesis solutions are well-known to inhibit calcite nucleation.) Bodily pathological calcification produces calcite and inorganic pyrophosphate (P_2O_7) has long been known as a by-product of many intracellular biosynthetic reactions which inhibits calcification [8]. Monohydrocalcite can form in air conditioner systems [9]. Hull and Turnbull [10] determined the solubility product of a natural crystal (recovered from the Fellmongery lake of South Australia) of monohydrocalcite as -7.60 at 25°C in water and at 1 atm; this value makes the monohydrocalcite a bit more soluble than vaterite (see the previous page). Swainson [11] determined the crystal structure of monohydrocalcite *via* neutron and X-ray diffraction (using natural samples collected from the Lake Fellmongery and the Lake Butler of Australia) and that work resulted in the CIF file (0004611) of AMCSD which we used in the previous pages.

- One learns from the above that very low temperatures are not needed for the formation of monohydrocalcite.

[6] R. Brooks, *et al.*, "Calcium carbonate and its hydrates," *Phil. Trans. Roy. Soc. London Ser. A*, 243, 145-167 (1950).
[7] von R. Van Tassel, "Carbonatniederschläge aus gemischten calcium-magnesiumchloridlösungen," *Z. Anorg. Allgem. Chem.*, 319, 107-112 (1962).
[8] I. R. Orriss *et al.*, "Pyrophosphate: A key inhibitor of mineralization," *Curr. Opin. Pharmocol.*, 28, 57-68 (2016).
[9] H. Marschner, "Hydrocalcite ($CaCO_3 \cdot H_2O$) and nesquehonite ($MgCO_3 \cdot 3H_2O$) in carbonate scales," *Science*, 165, 1119–1121 (1969).
[10] H. Hull and A. G. Turnbull, "A thermochemical study of monohydrocalcite," *Geochim. Cosmochim. Acta*, 37, 685-694 (1973).
[11] I. A. Swainson, "The structure of monohydrocalcite ....," *Am. Mineral.*, 93, 1014-1018 (2008).

MONOHYDROCALCITE ($CaCO_3 \cdot H_2O$)

"Our results show that the formation of monohydrocalcite takes place *via* a 4-stage process that starts with the formation of an Mg-rich ACC precursor. This amorphous precursor crystallized to monohydrocalcite through a dissolution-reprecipitation reaction, with monohydrocalcite forming *via* a constant nucleation process. The so formed monohydrocalcite further ages through Ostwald-ripening. The kinetics of these reaction stages are essentially driven by the Mg/Ca ratio and the initial supersaturation of the aqueous solution. These parameters also control the chemical composition of monohydrocalcite (*i.e.*, the Mg/Ca ratio, hydration), its crystallite size, unit-cell dimensions, particle size and shape. Furthermore, the transformation pathways into more stable Ca(Mg) carbonates (calcite or aragonite) is also dependent on the Mg/Ca ratio in the solids and the Mg (aq) in the supernatant solution. Interestingly, our data reveal that monohydrocalcite forms at conditions (Mg/Ca ratio in solution, supersaturations) that are equivalent to many other biogenic carbonates. Therefore, we hypothesize that some (Mg)-calcite and aragonite deposits in the geologic past that have formed through biomineralization could indeed be secondary in origin and may have been originally formed *via* a metastable monohydrocalcite intermediate."

The above, quoted text was taken directly from Ref. 12 below. We refer the reader, here, to our pamphlet entitled "Magnesian calcite globules of a sea star," which was focused on Mg-calcite (*aka* magnesian calcite).

• Kimura and Koga [13] observed that monohydrocalcite lost its crystal water (measured by using TG, *i.e.*, thermogravimetric analysis) at around 280°C and transformed into anhydrous $CaCO_3$, which then decomposed into CaO at around 600°C.

[12] J. D. Rodriguez-Blanco, S. Shaw , P. Bots, T. Roncal-Herrero, and L.G. Benning, "The mechanism of monohydrocalcite formation," *European Mineralogical Conference Vol 1*, EMC2012-397 (2012).

[13] T. Kimura and N. Koga, "Monohydrocalcite in comparison with hydrated amorphous calcium carbonate: Precipitation condition and thermal behavior," *Cryst. Growth Des.*, 11, 3877-3884 (2011).

MONOHYDROCALCITE ($CaCO_3 \cdot H_2O$)

The final stability of monohydrocalcite seems to be strongly dependent on the concentration of Mg^{2+} ions in its synthesis solution. By the way, Mg^{2+} ions are known to be potent aragonite stabilizers [5].

Munemoto and Fukushi [14] showed that in the presence of quite an excess of [Mg^{2+}] in the synthesis media, they were still able to initially produce single-phase monohydrocalcite but their precipitates started to transform into aragonite in less than a day at RT. Below is their synthesis procedure.

"0.06 M Ca-chloride and 0.06 M Mg-chloride were first dissolved in water at RT, followed by dissolving 0.08 M Na_2CO_3 in the solution. The resulting suspension of white precipitates were stirred at RT for 48 h, followed by filtering by using a 0.2 μm membrane and washing with water. The wet paste obtained was air-dried." [14]

Studies like the above should be interpreted with utmost caution before casting an opinion about the stability of monohydrocalcite since (*i*) it used a very high concentration of Mg^{2+}, *i.e.*, Ca^{2+} and Mg^{2+} being equimolar and (*ii*) the stirring time of 48 h was way too long. Both of these points serve to form aragonitic moieties in the initially-formed submicron precipitates (that cannot be detected by XRD). One does not need a high Mg concentration (to the extent that the Mg concentration being equal to that of Ca) in order to form monohydrocalcite. These authors continuously stirred the single-phase monohydrocalcite powders (80 mg) in 40 mL of 0.01 M NaCl solutions in order to assess the stability of powders. That continuous stirring in a saline solution is not the only appropriate method for stability studies, one should have also tested the stability at RT and at the %RH of ambient.

[14] T. Munemoto and K. Fukushi, "Transformation kinetics of monohydrocalcite to aragonite in aqueous solutions," *J. Mineral. Petrol. Sci.*, 103, 345-349 (2008).

MONOHYDROCALCITE ($CaCO_3 \cdot H_2O$)

The flatworms (*Mesocestoides corti*) which live in freshwaters like those of lakes, ponds, streams, ditches and temporary puddles, are known to contain a significant amount of inorganic material called as calcareous corpuscles. Calcareous corpuscles are mineral concretions, primarily composed of calcium carbonate, found in the tissues of worms. Flatworms can easily pass into dogs and cats. Senarole-Pose *et al.* [15] studied the *mesocestoides corti* flatworms by SEM, XRD and FTIR to report that their main inorganic phase was monohydrocalcite. The below data of Reference 11 belong to the calcareous corpuscles of those flatworms as reported by the authors [15].

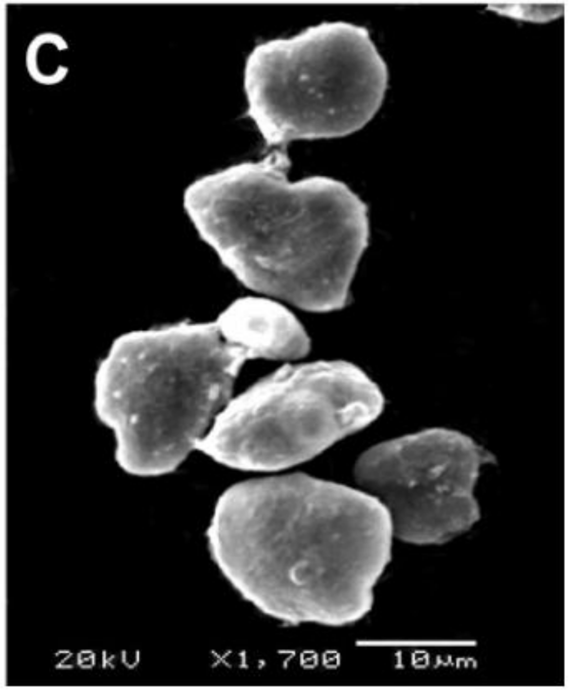


Fig. 1c of Ref. 15

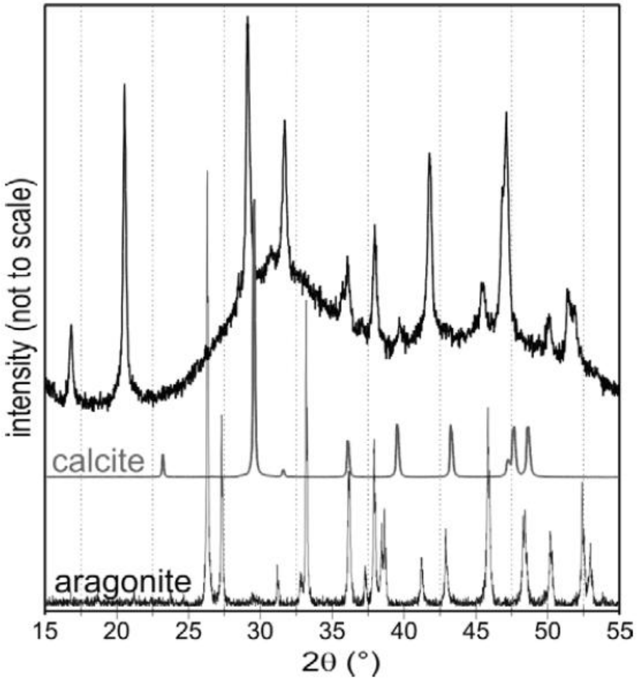


Fig. 2 of Ref. 15

FTIR band positions (in cm^{-1} units) of the monohydrocalcite phase of flatworms (band positions shown below were copied from Table 1 of Ref. 15):

3232, 1789, 1703, 1484, 1409, 1069, 873, 765 and 700

- The peaks of the XRD diffractogram shown here is in excellent agreement with the data we provided before and the structure resolved by Ref. 11. The significant background in the diffractogram of Ref. 15 means that the sample had some organic residue and/or amorphous calcium carbonate.

[15] M. Senarole-Pose, C. Chalar, Y. Dauphin, P. Massard, P. Pradel, and M. Marin, "Monohydrocalcite in calcareous corpuscles of *Mesocestoides corti*," *Exp. Parasitol.*, 118, 54-58 (2008).

MONOHYDROCALCITE ($CaCO_3 \cdot H_2O$)

Anyone who experimentally worked on the nucleation of $CaCO_3$ knows the monumental pioneering work of Kralj and Brecevic; they contributed a lot to this specific field, long before the CO_2-capturing efforts of today (*e.g.*, carbon dioxide removal, CDR) started. Kralj and Brecevic [16] prepared monohydrocalcite from an artificial seawater containing the ions of Na, Mg, Ca, Sr and Cl. A Na_2CO_3 solution was added to the artificial seawater resulting in the respective Mg/Ca and CO_3/Ca ratios of 5.3 and 1.2. The solution was agitated for 10 s in an ultrasonic bath and left overnight in a refrigerator. The suspension was filtered through a 0.45 μm membrane. The solids were washed several times with small amounts of water and a portion of absolute ethanol, and then dried in air for several hours. XRD patterns and FTIR spectra of the resulting solid showed it was single-phase (or phase-pure) monohydrocalcite (MHC) [17].

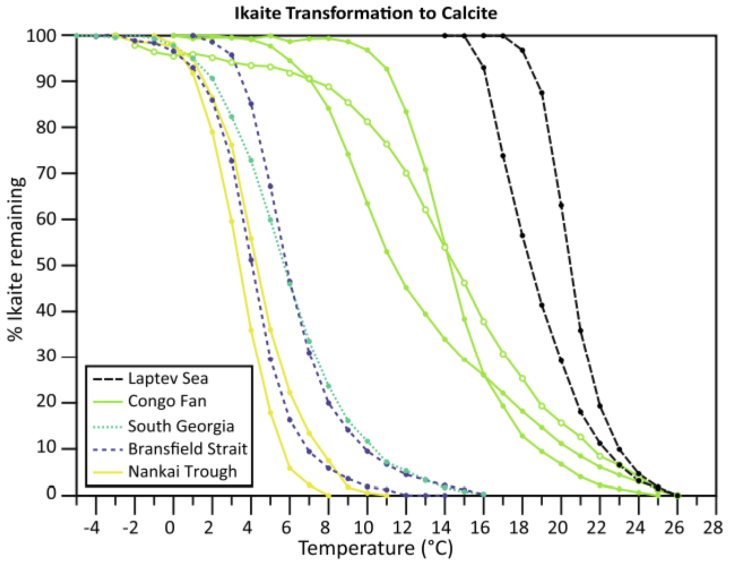
Artificial seawater nucleates aragonite when it is kept at elevated temperatures (such as 30°C and above). I had used artificial seawater and then developed its numerous variants [18] and since my aim was to coat aragonite on even inert substrates, I aged my precipitate-free solutions at 30°C to obtain “aragonite coating solutions, ACS.” The refrigeration of the artificial seawater at +4°C, by Kralj and Brecevic [16], suppressed the aragonite nucleation and their precipitates were single-phase monohydrocalcite (which did not eventually transform into aragonite). Therefore, references [16] and [18], when both were read simultaneously, would point to the transition point from monohydrocalcite to aragonite nucleation by using the same solution, *i.e.*, artificial seawater.

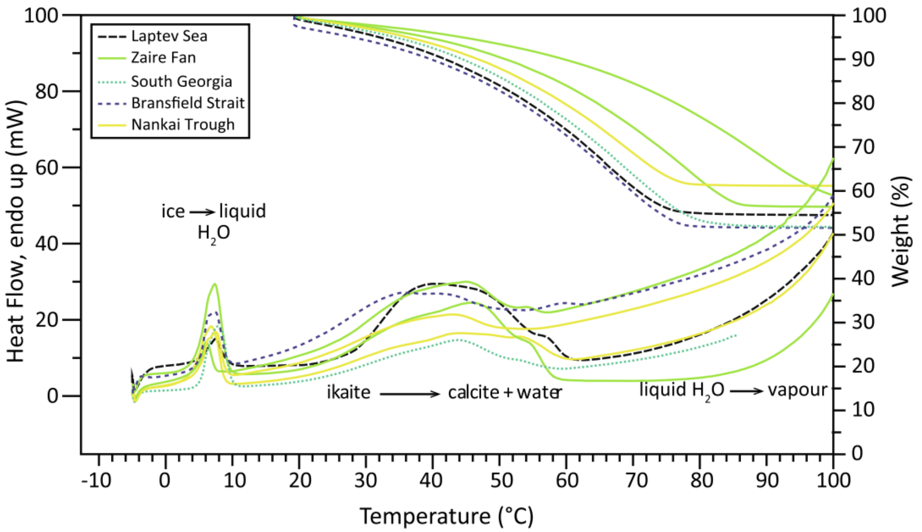
[16] D. Kralj and L. Brecevic, “Dissolution kinetics and solubility of calcium carbonate monohydrate,” *Colloid. Surface. A*, 96, 287-293 (1995).
[17] K. Fukushi, T, Munemoto, M. Sakai, and S. Yagi, “Monohdyrocalcite: a promising remediation for hazardous anions,” *Sci. Technol. Adv. Mater*., 12, 064702 (2011).
[18] A. C. Tas, “Aragonite coating solutions (ACS) based on artificial seawater,” *Appl. Surf. Sci*., 330, 262-269 (2015).

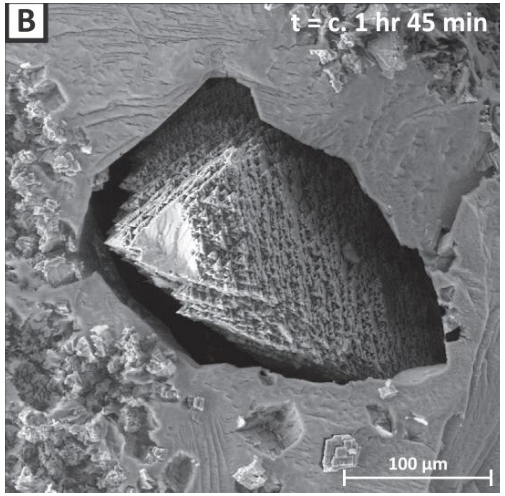
IKAITE ($CaCO_3 \cdot 6H_2O$)

The natural mineral ikaite takes its name from the Ikka Fjord of Greenland, where it was originally found. Ikka Fjord in southwest Greenland is the popularized locality for ikaite, a metastable (with respect to the anhydrous polymorphs of $CaCO_3$; namely, calcite, aragonite and vaterite) hexahydrate of calcium carbonate. Natural ikaite forms submarine tufa columns rising up to 18 m above the fjord bottom. The columns are spectacular examples of abiogenic carbonate precipitation in a **cold seawater** environment and represent the only known formation of ikaite in seawater [19].

In a milestone study, Vickers *et al.* [20] collected natural ikaite from a number of locations around the world, kept those under refrigeration until the time of analyses and then analyzed the natural ikaite samples by DSC, TGA, XRD (cryo), SEM and ICP-MS. They found that ikaite directly transformed to calcite during its thawing.



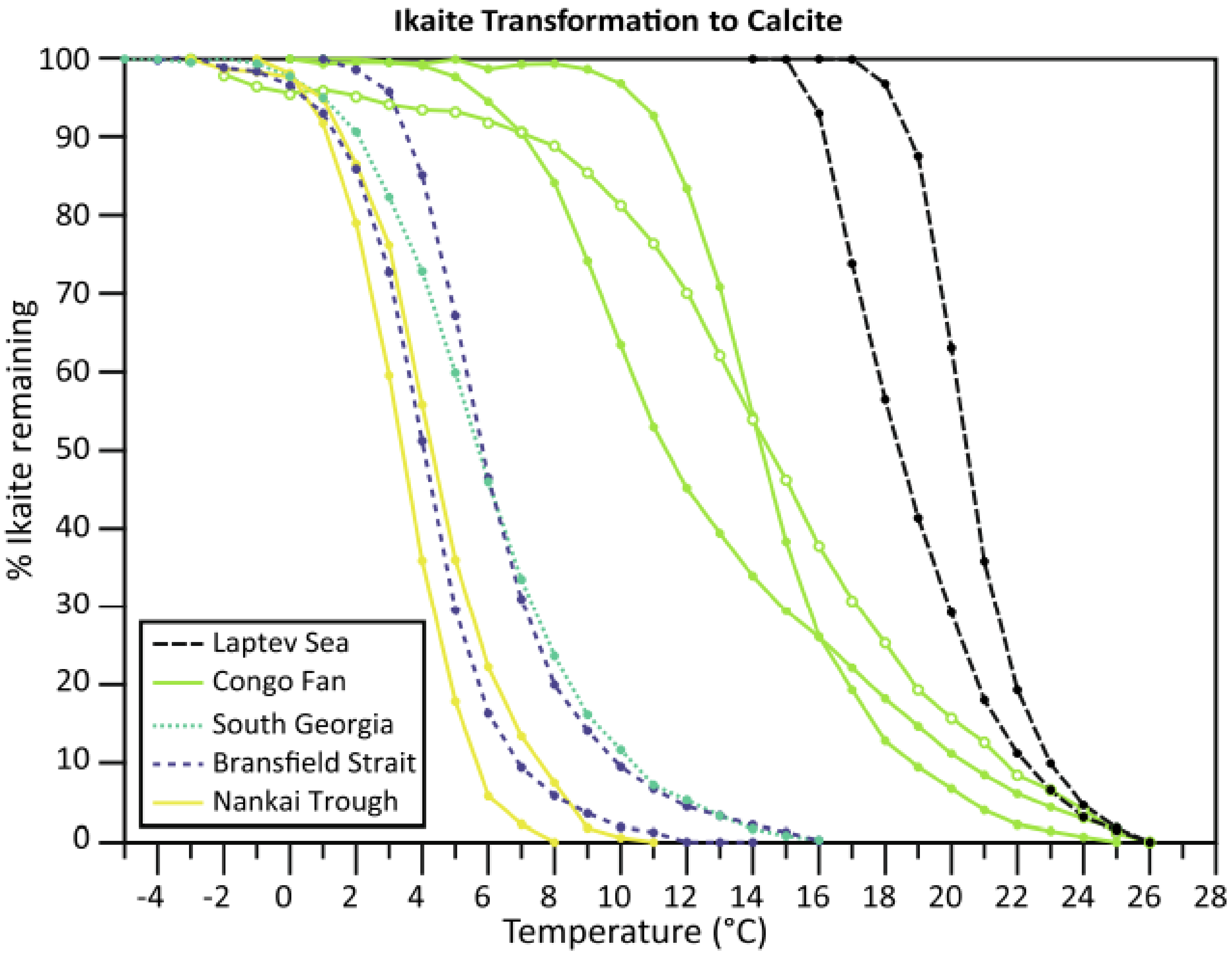




from left to right: Figures 3, 6 and 7b of Ref. 20

[19] B. Buchardt *et al.*, "Ikaite tufa towers in Ikka Fjord, Greenland," *J. Sediment, Res.*,71, 176-189 (2001).
[20] M. L. Vickers *et al.*, "The ikaite to calcite transformation: Implications for palaeoclimate studies," *Geochim. Cosmochim. Acta*, 334, 210-216 (2022).

IKAITE ($CaCO_3 \cdot 6H_2O$)



This figure of Vickers *et al.* [20] was created by running cryo-XRD on different natural ikaite samples. It is interesting to observe that "all ikaites were not created equal," for instance, the Laptev Sea sample did not start its decomposition to calcite even at 15°C.

There is a significant amount of literature, prior to the Ref. 20 study, which quickly asserted that ikaite "is not stable below +4°C." Differences in the chemical compositions of ikaites cause this thermal stability variations.

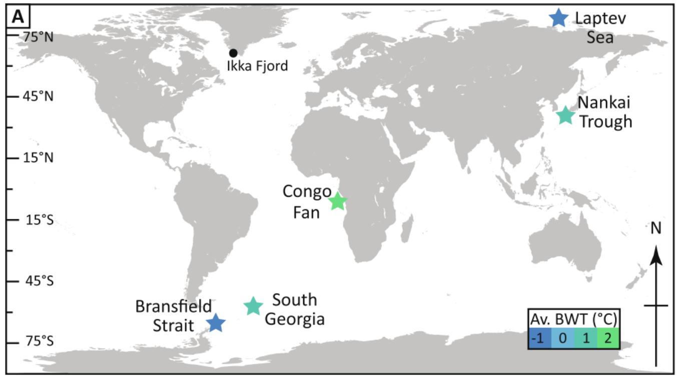
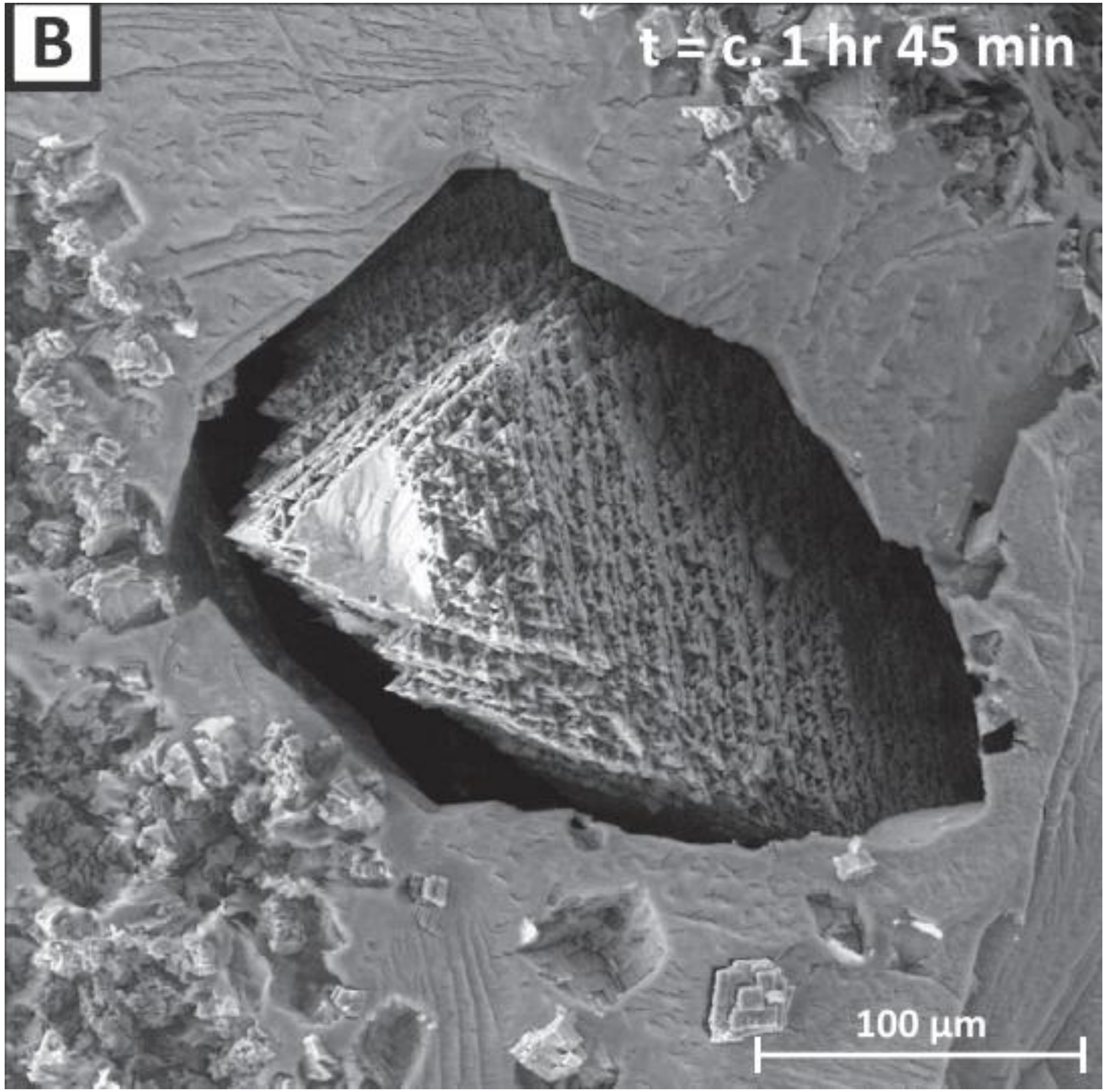


Fig. 1 of Ref. 20

[20] M. L. Vickers *et al.*, "The ikaite to calcite transformation: Implications for palaeoclimate studies," *Geochim. Cosmochim. Acta*, 334, 210-216 (2022).

IKAITE ($CaCO_3 \cdot 6H_2O$)



This SEM photomicrograph (of Fig. 7b of the Vickers *et al*. [20] article) is a tribute to why this pamphlet started by first giving the crystallographic information on ikaite (and monohydrocalcite) with respect to the anhydrous polymorphs of $CaCO_3$. The grey matrix in this photo denotes the ikaite not yet decomposed to calcite. The large prismatic aggregate (seen at the center of this image) is that of calcite comprised of numerous interwoven submicron calcite triangles. (See p. 40)

The important thing to note in this image is the gap that formed between the newly-formed calcite and the untransformed ikaite matrix. That drastic gap was formed because the crystallographic density of ikaite is 1.83 g/cm^3 while that of calcite is 2.71 g/cm^3 and this increase in density (from ikaite to calcite) causes "shrinkage." The authors of Ref. 20 very well documented this shrinkage by this photomicrograph.

[20] M. L. Vickers *et al.*, "The ikaite to calcite transformation: Implications for palaeoclimate studies," *Geochim. Cosmochim. Acta*, 334, 210-216 (2022).

IKAITE ($CaCO_3 \cdot 6H_2O$)

Pelouze [21] seems to be the first to produce synthetic ikaite, and this was followed by the article of Johnston *et al*. [22]. Bischoff *et al*. [23] used the method of Johnston *et al*. [22] and produced synthetic ikaite at 0°C to determine its solubility. Below is the recipe of ikaite synthesis at 0°C reproduced from the Bischoff *et al*. [23] article.

"*Ikaite was prepared by mixing 0.1 M solutions of $CaCl_2$ and K_2CO_3 dropwise from separate burettes into a 0.04 M KOH solution stirred and maintained at 0°C. Over a 6-8 h period, about 10 grams of ikaite, confirmed by X-ray diffraction, were produced consisting of well-formed prismatic crystals with average dimensions of about 30 by 35 by 15 microns with a calculated specific surface area of about 0.15 m²/g. The ikaite was filtered and stored frozen. The crystal size, quality, and the solubility of the ikaite produced is remarkably uniform from batch to batch, showing that the crystals are sufficiently large that surface effects are negligible.*"

Bischoff *et al*. [23] determined the solubility (log K_{sp}) of ikaite to be -7.20 at 0°C and -6.60 at 24.5°C, according to their experimentally-determined equation: $\log K_{sp} = 0.15981 - 2011.1/T$

We recommend the interested readers to inspect the stability (of ikaite) data of Table 3 of Ref. 23 showing that the synthetic ikaite crystals did not decompose when the crystals were kept in contact with the phosphate-rich Mono Lake water for about a year at 6°C.

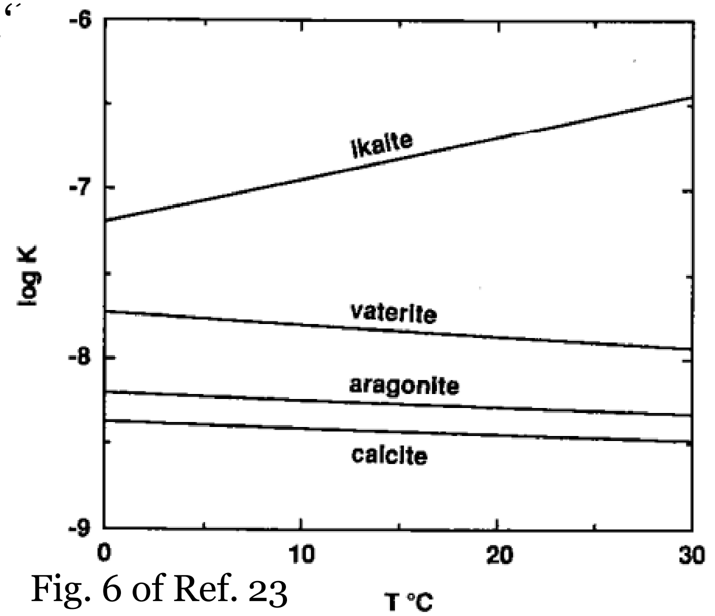


Fig. 6 of Ref. 23

[21] M. J. Pelouze, "Sur une combinaison nouvelle d'eau et de carbonate de chaux," *Chem. Rev*., 60, 429-431 (1865).
[22] J. Johnston, H. E. Merwin and E. D. Williamson, "The several forms of calcium carbonate," *Am. J. Sci*., 41, 473-512 (1916).
[23] J. L. Bischoff *et al*., "The solubility and stabilization of ikaite ($CaCO_3 \cdot 6H_2O$) from 0° to 25°C: Environmental and paleoclimatic implications for Thinolite tufa," *J. Geol*., 101, 21-33 (1993).

A. C. Tas

IKAITE ($CaCO_3{\cdot}6H_2O$)

- A more recent study by Y-B. Hu *et al.* [24] used artificial seawater to synthesize ikaite over the narrow temperature range of 0° to -4°C. (Seawater would not solidify at -4°C.)
- Boch *et al.* [25] observed the rapid ikaite crystallization in a man-made river bed (located between Vienna and Graz, Austria) over the temperature range of +3° to +6°C.
- Tollefsen *et al.* [26] used natural seawater and mixed solutions of Na_2CO_3+$NaHCO_3$ (to adjust the pH over a range, pure Na_2CO_3 solutions would give higher solution pH values) to synthesize pure ikaite and reported that they were able to form single-phase ikaite even at 35°C when the solution pH was between 9.5 and 9.8.

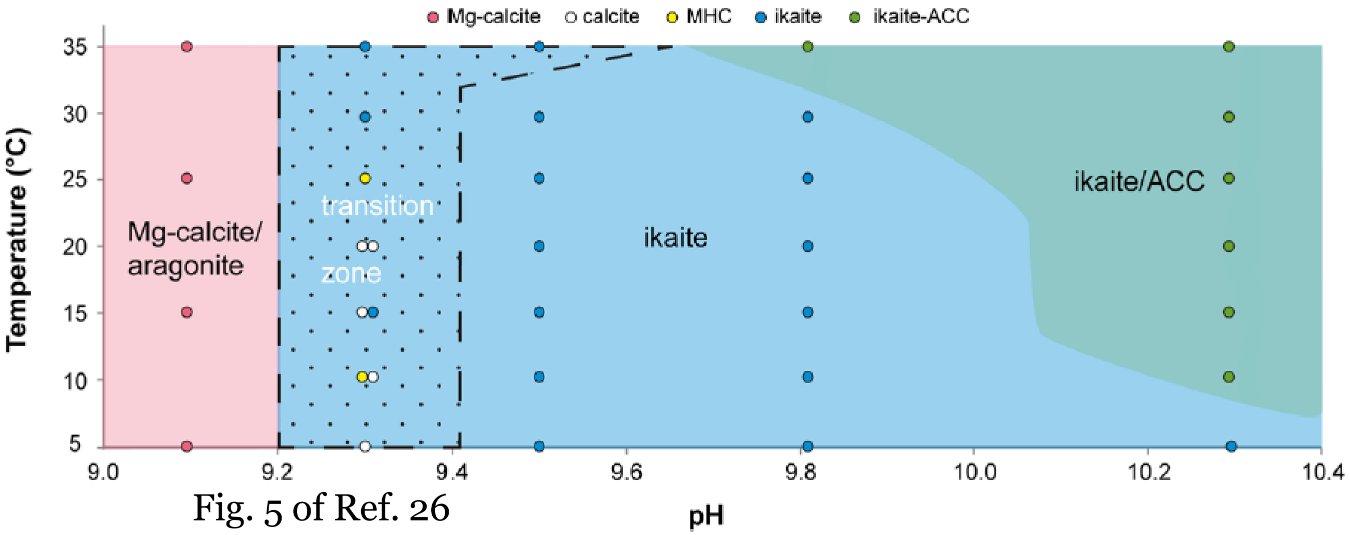


Fig. 5 of Ref. 26

- A recent patent ([27] E. Trampe, "Permanent storage of carbon dioxide," U.S. patent No. 12,209,029 B2, Jan. 28, 2025) is based on reacting artificial seawater with pre-mixed alkaline solutions of Na_2CO_3+$NaHCO_3$ to rapidly crystallize ikaite over the temperature range of +7° to +15°C.

[24] Y-B. Hu *et al.*, "A laboratory study of ikaite ($CaCO_3{\cdot}6H_2O$) precipitation as a function of pH, salinity, temperature and phosphate concentration," *Marine Chem.*, 162, 10-18 (2014).
[25] R. Boch *et al.*, "Rapid ikaite ($CaCO_3{\cdot}6H_2O$) crystallization in a man-made river bed: Hydrogeochemical monitoring of a rarely documented mineral formation," *Appl. Geochem.*, 63, 366-379 (2015).
[26] E. Tollefsen *et al.*, "Ikaite nucleation at 35°C challenges the use of glendonite as a paleotemperature indicator," *Scientific Reports*, 10(1), 8141 (2020).

Summary

p. 12: described the "appropriate" way to study the thermal decomposition of amorphous calcium carbonate (ACC), which is of utmost importance in the CO_2 quantification work of the industry segment of "CO2-capturing materials," if ACC is present in any sample (whatever we said in p. 12 is also applicable to amorphous magnesium carbonate);
-- aqueous olivine carbonation would first form AMC before crystallizing the phases of the MgO-CO_2-H_2O system

pp. 13 to 19: provided the crystallographic data of monohydrocalcite (in comparison to the anhydrous $CaCO_3$ polymorphs)

pp. 20 to 26: provided the crystallographic data of ikaite (in comparison to the anhydrous $CaCO_3$ polymorphs)

p. 27: provided the solubility of the anhydrous $CaCO_3$ polymorphs (calcite, aragonite, vaterite) and that of magnesian calcite

pp. 28 to 32: reviewed the literature of monohydrocalcite ($CaCO_3 \cdot H_2O$)

p. 32: underlined the fact that when the artificial seawater is heated to 30°C (Ref. 5) it would nucleate aragonite, while storing it at +4°C it will be prone to nucleate monohydrocalcite (Ref. 16) having a solubility higher than that of vaterite and aragonite

pp. 33 to 37: reviewed the literature of ikaite ($CaCO_3 \cdot 6H_2O$)

p. 37: showed the evolution of the ikaite synthesis literature from -4°C to +35°C (especially when researches started using artificial or natural seawater)

A couple of implications

As we have seen through the literature-based examples of this pamphlet, the high Mg/Ca ratio of seawater is able to favor the nucleation of ikaite *in lieu of magnesian calcite" (see our recent document on the "magnesian calcite of sea stars" here) at temperatures higher than 4°C, even at 35°C, only when its pH is increased to around 9.5 to 9.8 range or even higher. The concrete pore solution has a very high pH (*ca* 13). If the concrete has a constituent that is able to leach out Mg^{2+} over time and if the T of the poured concrete (*i.e.*, concrete in its service life) becomes less than the range of 7° to 15°C, then the formation of ikaite could be expected. Moreover, the solubility of CO_2(g) in aqueous solutions follows an inverse relation to the temperature, meaning that the solubility of CO_2(g) in water rapidly increases as the T drops. As a side note, since ikaite has quite a low density (*i.e.*, 1.83 g/cm^3) in comparison to that of concrete, the formation of such low-density crystals could mean "expansion" at micro-localities, such expansion phenomena may further contribute to the losses in strength. Anyhow, when concrete has Mg^{2+} ions in its pore solution, the formation of ikaite crystals cannot be ignored as a possibility.

If any (geological or biological) calcareous deposits contain monohydrocalcite and/or ikaite and when these two phases start their decomposition under a diverse set of geological or biological conditions or stimuli (since they have solubilities less than calcite), they may generate quite significant amounts of water while forming calcite as a decomposition product. If such a generation of water takes place at a time and place it was not expected at all, and such water may turn to be rich in the organic molecules (that are able to solubilize in water) which are present in and around those calcareous deposits.

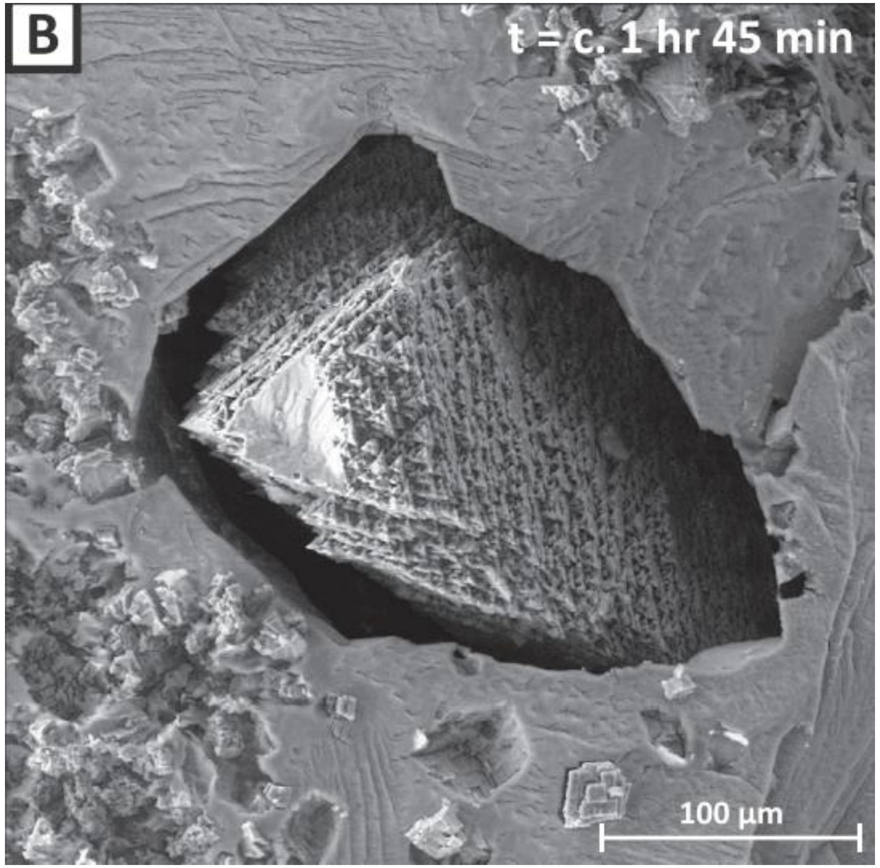
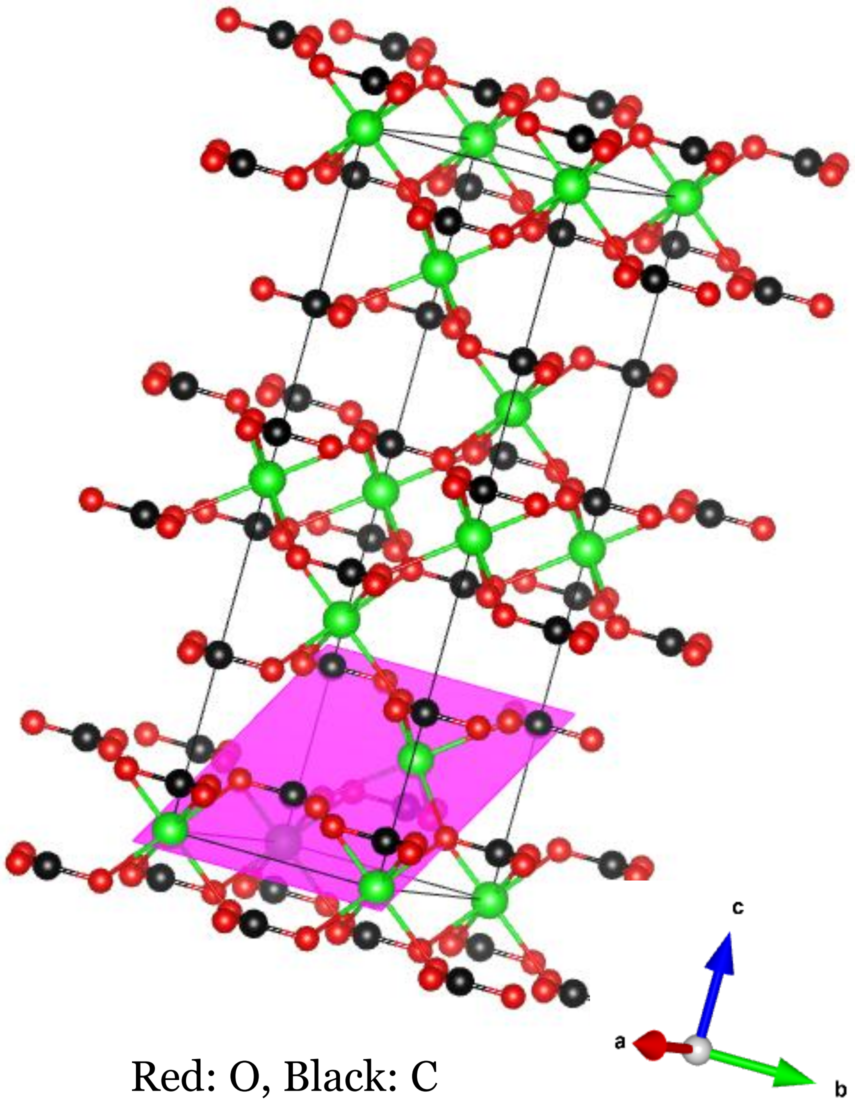


Fig. 7b of Ref. 20

What are those tiny triangles seen at the center of the above SEM photo?

In any XRD diffractogram generated from a pure calcite sample, the peak with the strongest intensity will have the *hkl* indices of (104), which refers to the plane shown in pink in the *rhs* figure. The distance of that plane to the origin of the unit cell shown here is 3.0357 Å, which is the d-spacing for this plane. This plane cuts through three Ca^{2+} and three carbons, therefore, it is a densely-packed plane. Do you see the triangles formed between the three calcium ions and three carbons on that plane? The tiny triangles of the SEM photo show us the (104) planes of the unit cell. Some call those as "[calcite's 104 surface]."



Red: O, Black: C
Green: Ca
Pink: (104) plane of calcite

[20] M. L. Vickers *et al.*, "The ikaite to calcite transformation: Implications for palaeoclimate studies," *Geochim. Cosmochim. Acta*, 334, 210-216 (2022).