Amorphous Calcium Carbonate (ACC)

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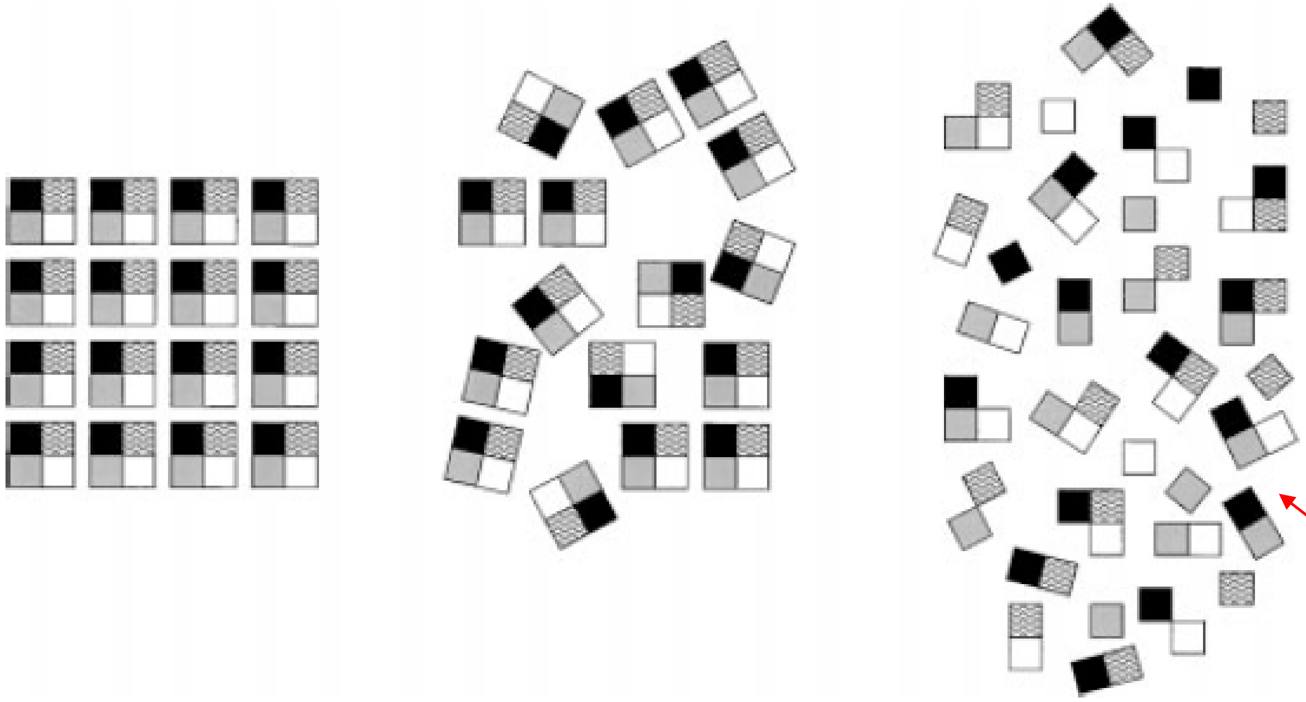
January 14, 2026

$CaCO_3$ comes in 5 crystalline forms, namely, vaterite, aragonite, calcite, monohydrocalcite and ikaite. $CaCO_3$ also mineralizes in an amorphous form (recognized as early as 1916) and it was named as "amorphous calcium carbonate," with the abbreviation of ACC. ACC is a metastable and high solubility phase and is known to act as a precursor to crystalline forms of $CaCO_3$. Its stability increases from seconds to minutes when the temperature is <4°C. This literature survey is intended to increase the knowledge base of researchers on ACC, who are focused on enforced or natural carbonation of solids, and liquids mineralizing solid phases.

ACC was detected in many marine organisms and can be readily synthesized without using any organic additives in a laboratory. This document provides numerous examples for the synthesis of ACC. Upon heating (*e.g.*, in TGA), ACC first loses its water (originally ≥15 wt%), then crystallizes into calcite. Further heating causes the decomposition of that calcite into CaO(s) and CO_2(g). The thermal decomposition of calcite crystallized out of ACC does not occur between 300° to 550°C. The mesopores (filled with water) in ACC makes it difficult to assess which gas is evaporating from it at temperatures lower than 550°C. TGA, TGA-DTA and TGA-DSC are not able to analyze the evolved gases. This document advises the researchers to use either a "combined TGA-FTIR" or a "combined TGA-MS" instrument for accurate CO_2 quantification when they suspect the presence of ACC (besides vaterite, aragonite and/or calcite) in their materials.

2D depiction of an amorphous substance



crystalline;
with *excellent*
ordering

amorphous

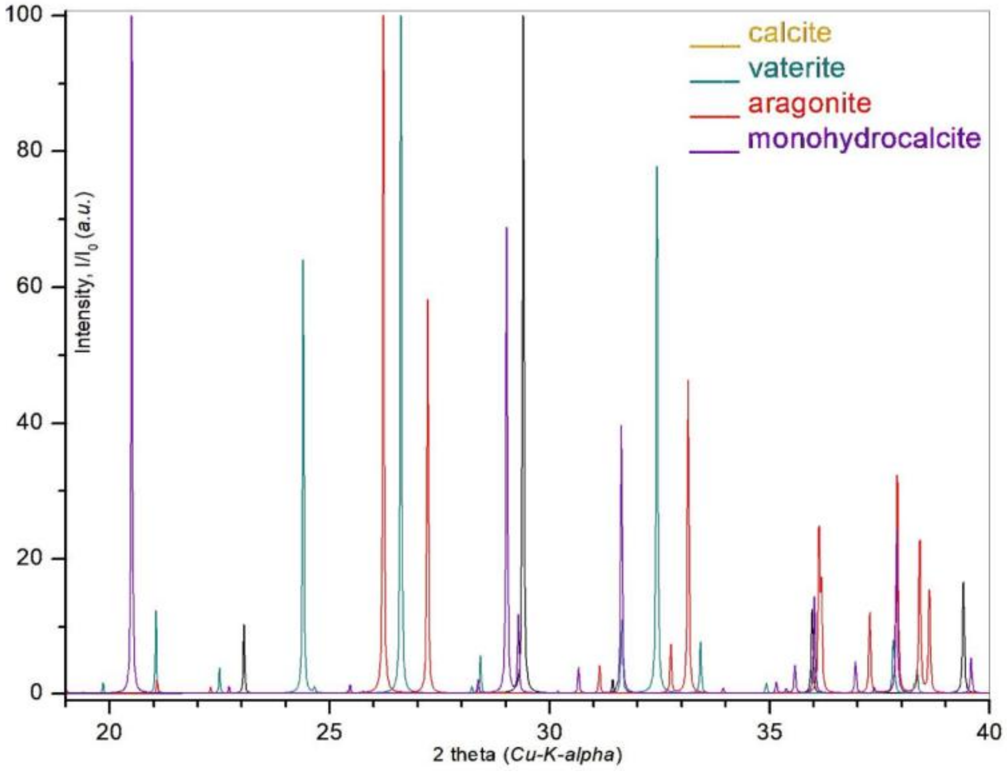
Figure 4. Schematic illustration of the concepts of long-range order (left), short-range order (middle) and a truly amorphous structure (right). Note that the same number of "molecules" is used in each illustration, showing how decreasing order correlates with increasing volume.

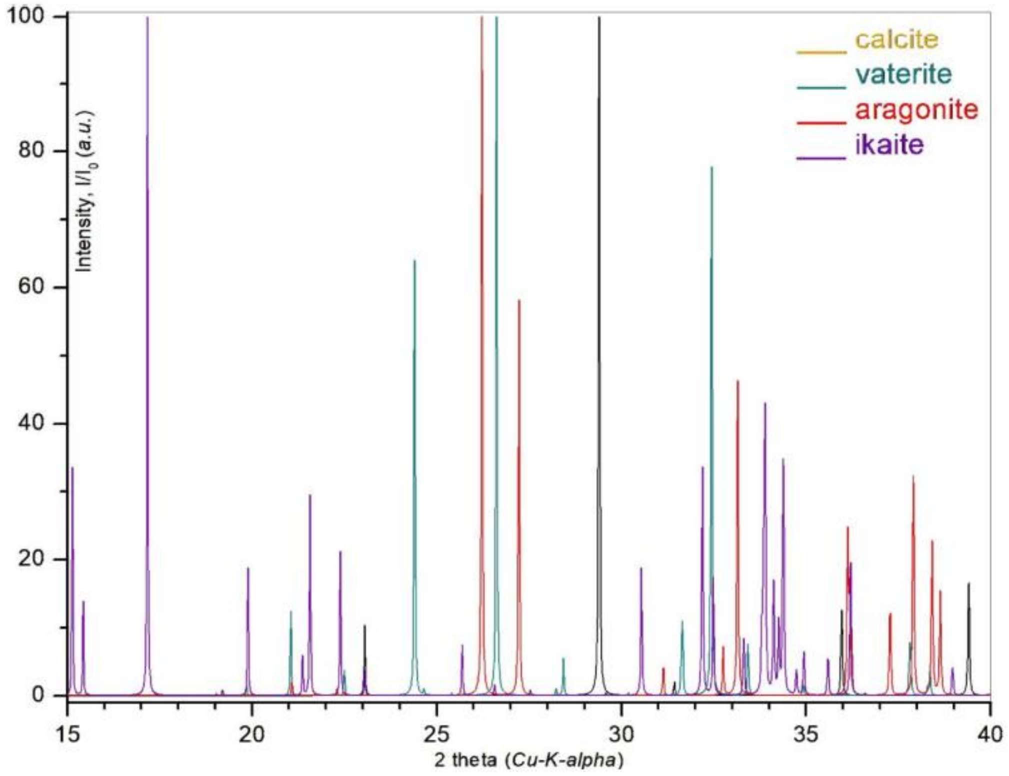
- Truly amorphous solids (such as amorphous calcium phosphate, amorphous calcium carbonate, amorphous magnesium carbonate, and glasses) do not generate any peaks in their X-ray diffraction patterns.

[1] S. Weiner, Y. Levi-Kalisman, S. Raz, L. Addadi, "*Biologically formed amorphous calcium carbonate*," *Connective Tissue Research*, 44 (Suppl. 1), 214-218 (2003).

Amorphous calcium carbonate, when examined by X-ray diffraction (XRD), does not generate any peaks at any 2θ value. A report by Johnston *et al*. (cited below) was "the first" to identify amorphous calcium carbonate in 1916.

Calcium carbonate exhibits 5 crystalline forms, namely, vaterite (CaCO3), aragonite (CaCO3), calcite (CaCO3), monohydrocalcite (CaCO3·H2O) and ikaite (CaCO3·6H2O). Vaterite, aragonite and calcite are the anhydrous crystalline forms of calcium carbonate. These 5 forms generate unique XRD patterns since they are crystalline, *i.e.*, not X-ray amorphous. (The below plots are from a previous work of mine, find its weblink here.)





[2] J. Johnston, H. E. Merwin, E. D. Williamson, "Various forms of calcium carbonate," *American Journal of Science*, 41, 473-512 (1916).

• When a substance can be prepared for TEM-SAED work (transmission electron microscope-selected area electron diffraction) “in the form of very thin (*i.e.*, 10 to 80 nm thickness) sample” (so that the incoming electrons can pass through the thin sample), then TEM-SAED can readily distinguish amorphous and crystalline regions of the said sample by generating diffraction patterns. See Fig. 6 of this article. ACC would not generate any diffraction (SAED) patterns.

• TEM-SAED and HRTEM (high resolution TEM) work typically generate satisfactory results on materials with high atomic numbers.

• However, TEM-SAED experiments are tedious (require expertise from a TEM user) and expensive, not comparable with today’s widely available X-ray diffractometers.

• Amorphous calcium carbonate is a hydrous (or hydrated) substance and is represented by this formula; $CaCO_3 \cdot H_2O$. This formula is identical with that of monohydrocalcite, where ACC is truly amorphous and monohydrocalcite is crystalline [3].

• ACC with the above formula contains 15.25 wt% water. Carefully synthesized phase-pure ACC samples exhibit water contents over the range of 13 to 15 wt% [3]. Due to this much of water present in ACC, its density (in its pure form) was measured to be 1.9 g/cm^3 [4]. Water content matters; more water in a sample of ACC could decrease its density to around 1.6-1.7 g/cm^3. The density of a truly amorphous ACC sample will increase upon its dehydration (*via* heat treatment). XRD and density measurements could be used simultaneously.

• To compare; the densities of vaterite, calcite, aragonite, monohydrocalcite and ikaite are 2.57, 2.71, 2.93, 2.42, and 1.83 g/cm^3, respectively [5].

• Revisit the sketch of p. 2 above to see how the volume of an amorphous substance would increase with respect to its crystalline counterpart, *i.e.*, the density of crystalline monohydrocalcite (even though it shares the same formula with ACC) is much higher.

[3] M. Neumann and M. Epple, "Monohydrocalcite and its relationship to hydrated amorphous calcium carbonate in biominerals," *European Journal of Inorganic Chemistry*, 14, 1953-1957 (2007).
[4] M. Faatz, G. Fytas, W. Cheng, R. S. Penciu, E. N. Economou, and G. Wegner, "Mechanical strength of amorphous $CaCO_3$ colloidal spheres," *Langmuir*, 21, 6666-6668 (2005).
[5] A. C. Tas, "Hydrous, crystalline forms of $CaCO_3$: Monohydrocalcite and Ikaite," July 2025, pp. 15 and 22

Can one find ACC in nature as a biogenic material? Yes! *(table from Ref. 6)*

Table 1. The known distribution of biogenic ACC.

Kingdom/ Phylum	Form of deposit and references	Presumed function	Mg/Mg+Ca [a] [atom-%]	P/Mg+Ca [a] [atom-%]	All forms of $CaCO_3$ deposited by these organisms [b]
Plantae	Cystoliths in leaves [21,71,72]	?	0–26		Calcite, aragonite, vaterite, ACC
Arthropoda/ Crustacea	Cuticle [10,21,73,74]	Stiffens exocuticle	0–20	5-49	**ACC**, Calcite
	Gastroliths [74]	Temporary storage			**ACC**
	Storage structure [68]	Temporary storage	–	6–14	**ACC**
Porifera	Spicule core [13,18]	?	6–17		**Calcite**, ACC
Ascidiacea	Spicule (body) [19,75]	Stiffens internal tissues and tunic	0–16	45–55	Calcite, aragonite, vaterite, ACC, monohydrocalcite
Echinodermata	Larval spicule [14]	Precursor phase	5		**Calcite**, ACC
Cnidaria/ Gorgonacea	Spicules [76]	Mechanical support	18	12–13	**Calcite**, aragonite, ACC
Mollusca/ Bivalvia	Granules [77]	Temporary storage	?		**ACC**, vaterite
Bivalvia	Larval shell [15]	Precursor phase	?		Aragonite, ACC
Gastropoda (Nudibranchia)	Spicules [78]	Stiffens tissue?			ACC
Platyhelminthes	Corpuscles [79]	?			ACC

[a] The atomic percentages of the magnesium and phosphorous were normalized according to the total cations in the sample. This normalization was mainly performed due to lack of information on light elements such as carbon in various analytical techniques (e.g., energy-dispersive X-ray spectroscopy). Data from the literature was therefore treated in a similar manner even when additional information was available to allow comparison between the different organisms. [b] The most commonly formed calcium carbonate deposits are shown in bold.

[6] L. Addadi, S. Raz, and S. Weiner, "Taking advantage of disorder: Amorphous calcium carbonate and its roles in biomineralization," *Advanced Materials*, 15, 959-970 (2003).

Organisms having biogenic ACC

Arthropods are invertebrates in the phylum Arthropoda. They possess an exoskeleton with a cuticle made of chitin, often mineralized with amorphous or crystalline calcium carbonate.

Crustaceans are invertebrate animals that constitute one group of arthropods; notable examples are crabs and lobsters.

Sponges or sea sponges are primarily marine invertebrates of the animal phylum Porifera. As their name implies, they are porous species still belonging to the Animalia kingdom.

An echinoderm is any animal of the phylum Echinodermata, which includes starfish, brittle stars, sea urchins, sand dollars and sea cucumbers. (See one of my previous experiment-based reports here.)

A group within the cnidarian subclass Octocorallia (class Anthozoa), comprising organisms known as gorgonians. common name for the members of Gorgonacea include sea rods and sea fans. Gorgonians are animals of the soft coral variety.

Mollusca is a phylum of protostomic invertebrate animals, whose members are known as molluscs or mollusks. Molluscs are the largest marine phylum, comprising about 23% of all the named marine organisms.

Gastropods are a vast and diverse group of invertebrates within the phylum Mollusca, comprising the animals commonly known as snails and slugs. With an estimated 65,000 to 80,000 living species, they form the second-largest animal class after the insects.

• $CaCO_3$ biomineralization in marine organisms proceeds *via* the crystallization of initially amorphous precursor (submicron) particles [7].

• ACC is also known to act as a precursor to the formation of calcite and aragonite of stalactites and stalagmites of caves [8, 9].

[7] T. Mass, A. J. Giuffre, C. Y. Sun, C. A. Stifler, M. J. Frazier, M. Neder, N. Tamura, C. V. Stan, M. A. Marcus, and P. U. P. A. Gilbert, "Amorphous calcium carbonate particles from coral skeletons." *Proceedings of the National Academy of Sciences*, 114, E7670-E7678 (2017).
[8] N. T. Enyedi, J. Makk, L. Kotai, B. Berenyi, S. Klebert, Z. Sebestyen, Z. Molnar, A. K. Borsodi, S. Leel-Ossy, A. Demeny, and P. Nemeth, "Cave bacteria-induced amorphous calcium carbonate formation," *Scientific Reports*, 10, 8696 (2020).
[9] " Stalactites, stalagmites and cave formations," https://www.nps.gov/maca/learn/nature/stalactites-stalagmites-and-cave-formations.htm

How does the solubility of ACC compare with that of vaterite, aragonite and calcite?

Temperature (°C)	**ACC** (*log* K_{SP}) [10]	**vaterite** (*log* K_{SP}) [11]	**aragonite** (*log* K_{SP}) [11]	**calcite** (*log* K_{SP}) [11]
10	-6.27			
25	-6.39			
40	-6.59			
55	-6.82			
25		-7.91	-8.33	-8.48
37		-8.05	-8.40	-8.56

- *log* K_{SP} value of -6.39 for **ACC** at 25°C means that its solubility product (K_{SP}) is equal to 4.07×10^{-7} M^2

- *log* K_{SP} value of -7.91 for **vaterite** at 25°C means that its solubility product (K_{SP}) is equal to 1.23×10^{-8} M^2

- *log* K_{SP} value of -8.33 for **aragonite** at 25°C means that its solubility product (K_{SP}) is equal to 4.68×10^{-9} M^2

- *log* K_{SP} value of -8.48 for **calcite** at 25°C means that its solubility product (K_{SP}) is equal to 3.31×10^{-9} M^2

- ACC has a high solubility that is not comparable to those of the anhydrous crystalline CaCO3 polymorphs. ACC is metastable, it forms at the very early stages of nucleation, it dissolves and causes the precipitation of one or more of the anhydrous polymorphs of CaCO3. (Materials scientists name such phenomena as dissolution-reprecipitation" processes.)

[10] L. Brecevic and A. E. Nielsen, "Solubility of amorphous calcium carbonate," *Journal of Crystal Growth*, 98, 504-510 (1989).
[11] L. N. Plummer and E. Busenberg, "The solubilities of calcite, aragonite and vaterite in CO2-H2O solutions between 0° and 90°C, and an evaluation of the aqueous model for the system CaCO3-CO2-H2O," *Geochimica et Cosmochimica Acta*, 46, 1011–1040 (1982).

Is ACC a stable phase like aragonite and calcite?

No!

Is it possible to synthesize ACC in a laboratory then characterize it by using XRD, SEM, FTIR, TGA and/or DSC?

Yes!

However, pure ACC (when not stabilized by magnesium ions, phosphate ions or organic macromolecules) has quite a short lifetime before its *in situ/autogenic* transformation to vaterite or aragonite or Mg-calcite (*a.k.a.*, magnesian calcite) or calcite. It may also transform into monohydrocalcite and ikaite under the right conditions [5].

Lab-based aqueous syntheses (those without using any organics) of ACC requires

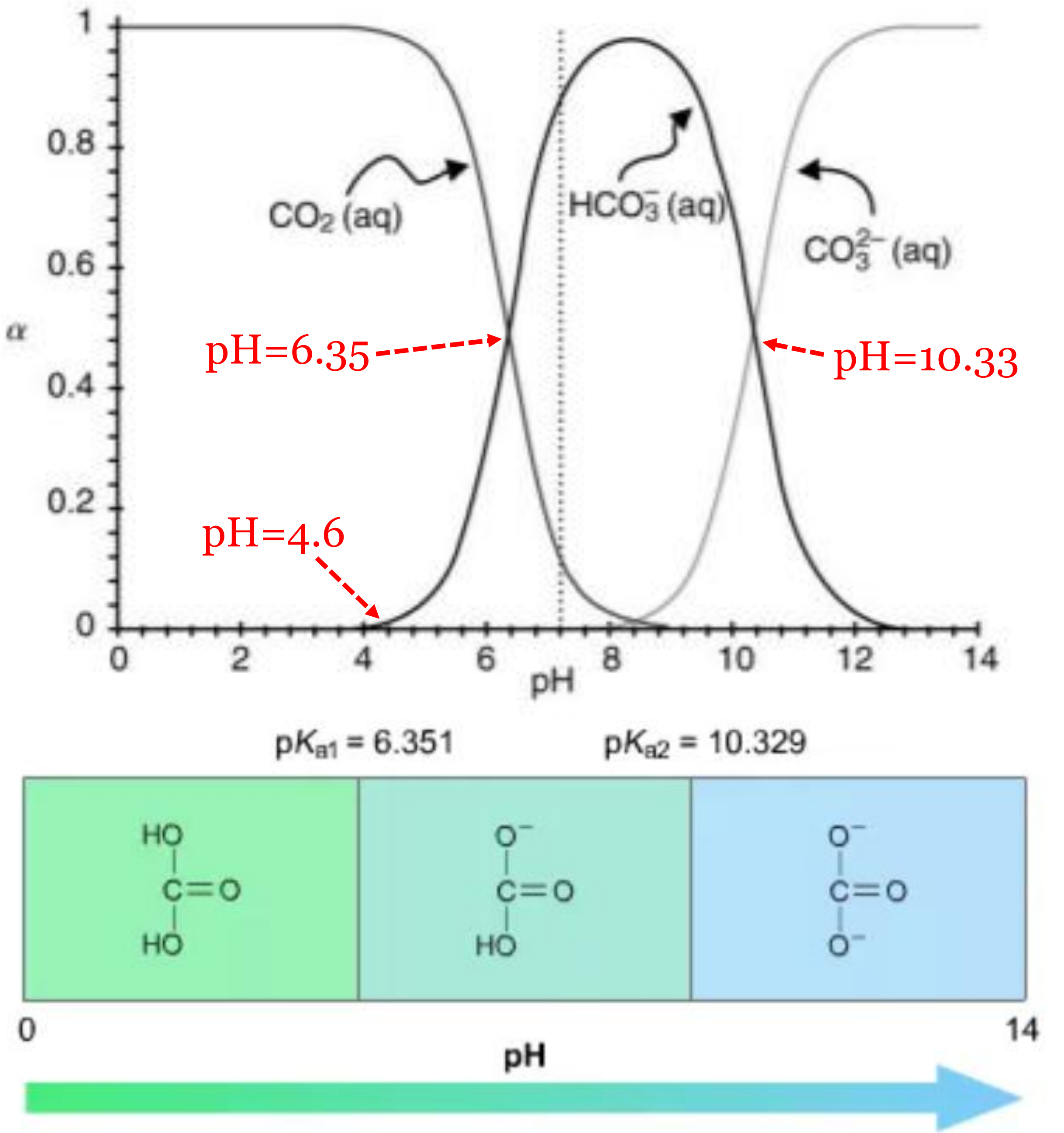
(i) very high pH (*11.5 to 13.5*),

(ii) low synthesis temperature (*typically 1° to 6°C*),

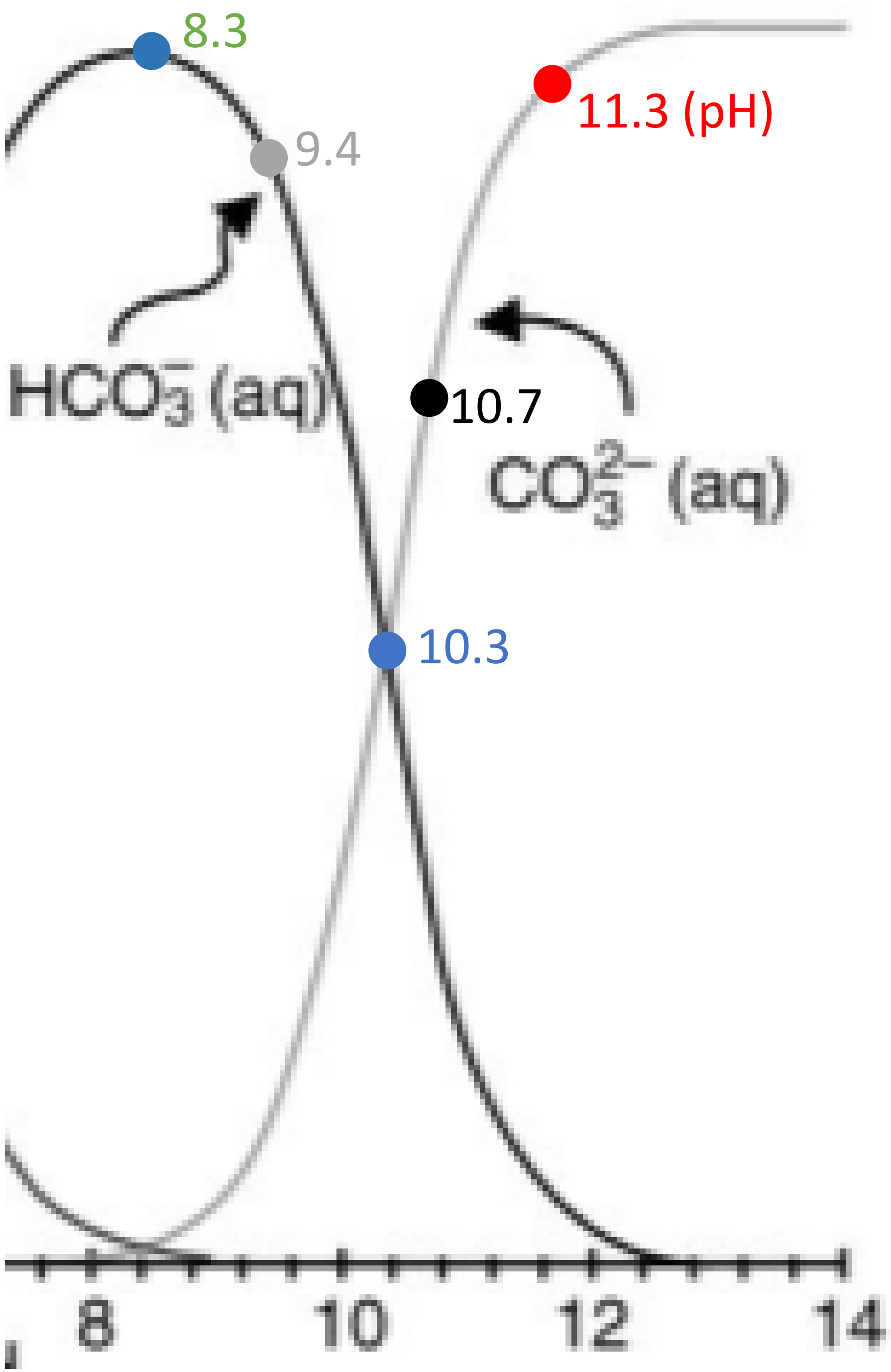
(iii) CO_3^{2-} (*aq*),

(iv) Ca^{2+} (*aq*) and/or Mg^{2+} (*aq*).

Although the co-presence of Ca^{2+} and Mg^{2+} is not strictly required to form ACC, Mg^{2+} presence in solution exerts a minor stabilizing effect. The biogenic ACC occurrences observed in marine organisms (see p. 7 above) benefit from the high magnesium content of seawater having an ionic strength of 0.772 M [12]. The plot on the right is the well-known CO2-containing aqueous species chemistry in water, where α denotes the molar ratio of a given species to the next, such as CO2 (*aq*), HCO_3^- (*aq*) and CO_3^{2-}(*aq*). It is obvious from this plot that when the ACC synthesis medium has a pH between 11.5 and 13.5, the dominant carbonate species will be CO_3^{2-} (*aq*) but not HCO_3^- (*aq*). The employment of a low synthesis temperature ensures slowing down the rate of "ACC to vaterite/aragonite/calcite" transformation(s).



[12] A. C. Tas, "Aragonite coating solutions (ACS) based on artificial seawater," *Applied Surface Science*, 330, 262-269 (2015).



This is a “*zoom in*” to the plot of the previous page.

It shows the significance of having a pH of at least 11.5 in synthesizing ACC having a thermodynamic stability for more than several seconds.

When pH is 11.5, one will have CO_3^{2-} ions as the major species.

A. C. Tas

• The previous literature has two seminal articles on the synthesis of ACC without using any organics [13, 14]. Such synthesis studies were needed to understand what ACC is or is not.

• Both of these studies [13, 14] employed solutions (of high pH) having dissolved Ca-chloride, Na_2CO_3 and NaOH.

• While the Kojima *et al*. [13] study synthesized ACC at 0°C, the Koga *et al*. [14] study synthesized ACC at 5°C.

• Owing to the metastable nature of ACC, the precipitates formed in solutions (upon mixing the pre-refrigerated Ca-chloride solution with that of Na_2CO_3 and NaOH) of both studies were immediately filtered out of their mother liquors, followed by washing the solids with acetone or ethanol and drying the recovered precipitates in vacuum desiccators kept at the ambient lab temperature. Kojima [13] and Koga [14] recipes are quite simple (to reproduce); this is their beauty.

• Although we will reproduce some of their data in the following pages, we strongly recommend the readers to first study these seminal ACC synthesis articles before forming any strong opinions about ACC. It is a bit awkward that today's Journals push the authors of new manuscripts to limit their list of references to articles published in the last decade or two. Authors who would blindly obey (without questioning and any resistance) such a "publication date limitation" in their submitted manuscripts will certainly miss the Kojima and Koga work.

[13] Y. Kojima, A. Kawanobe, T. Yasue, and Y. Arai, "Synthesis of amorphous calcium carbonate and its crystallization," *Journal of The Ceramic Society of Japan*, 101, 1145-1152 (1993).
[14] N. Koga, Y .Nakagoe, and H. Tanaka, "Crystallization of amorphous calcium carbonate," *Thermochimica Acta*, 318, 239-244 (1998).

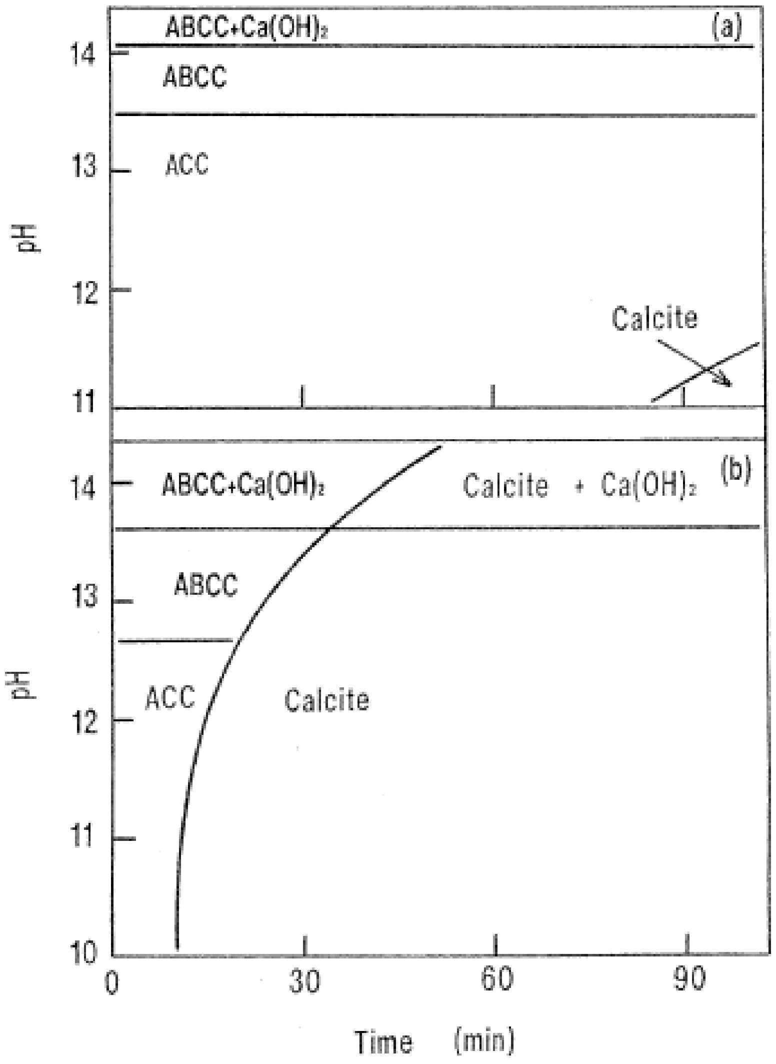


Fig. 2. Formation region of amorphous calcium carbonate in mother liquor.
Concentration of $CaCl_2$ and Na_2CO_3 soln. ($mol \cdot dm^{-3}$): 0.1
Concentration of NaOH soln. ($mol \cdot dm^{-3}$): 0–3.0
$CaCl_2/Na_2CO_3/NaOH$ soln. volume ratio: 1/1/1
Temperature (℃): (a) 0, (b) 20
ACC: Amorphous calcium carbonate
ABCC: Amorphous basic calcium carbonate

This plot [13] is like a "user's manual" for the benefit of the follow-up ACC researchers.

• It shows the effect of synthesis temperature (for both 0°C and 20°C) on the resultant ACC's stability.

• It presents the effect of the pH of ACC synthesis media (*a.k.a.* solutions).

• It shows the lifetime (*i.e.*, the x-axes of both Fig. 2a and Fig. 2b) of ACC before it transforms into calcite, as a function of the pH of the ACC synthesis medium.

[13] Y. Kojima, A. Kawanobe, T. Yasue, and Y. Arai, "Synthesis of amorphous calcium carbonate and its crystallization," *Journal of The Ceramic Society of Japan*, 101, 1145-1152 (1993).

This plot teaches the follow-up researchers how much NaOH they should add to the synthesis medium when the temperature is to be set at 0°C and the same medium had 0.1 M Ca-chloride and Na2CO3.

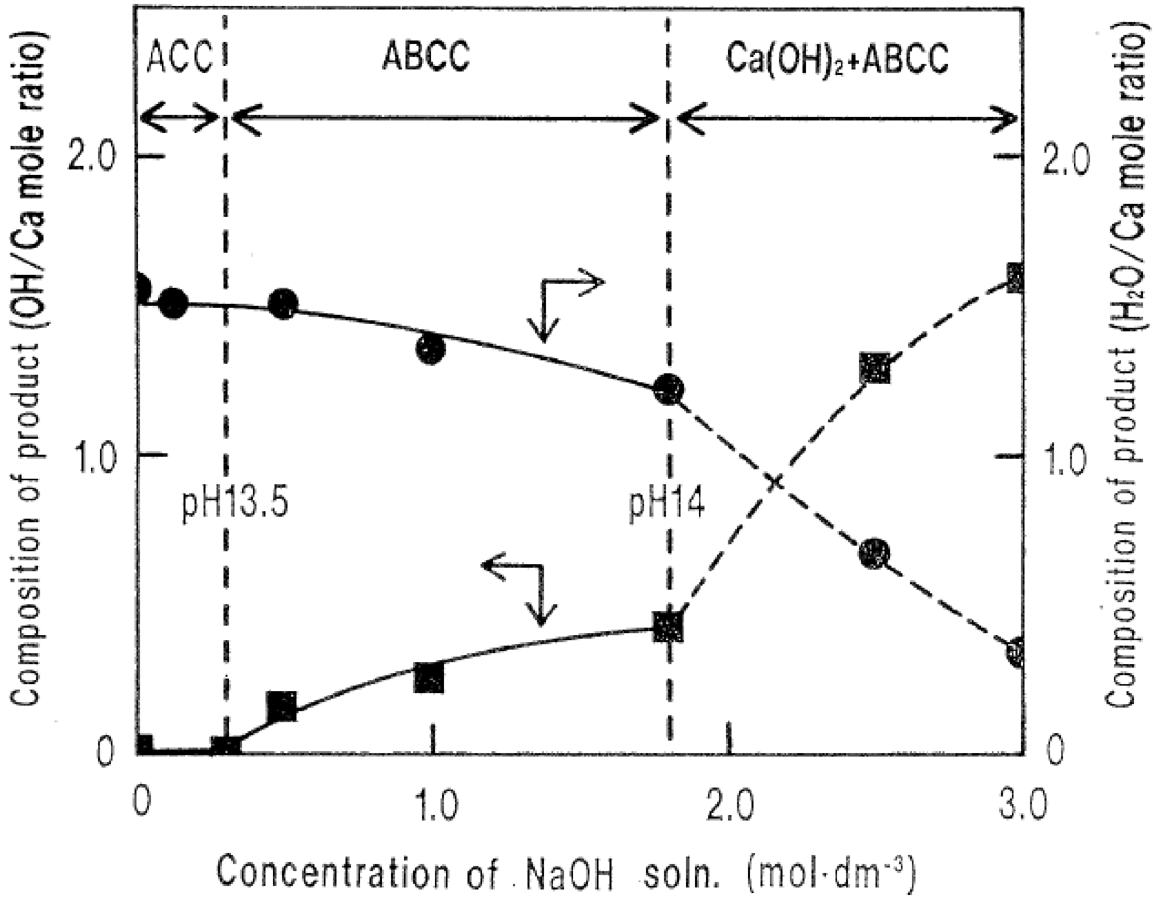
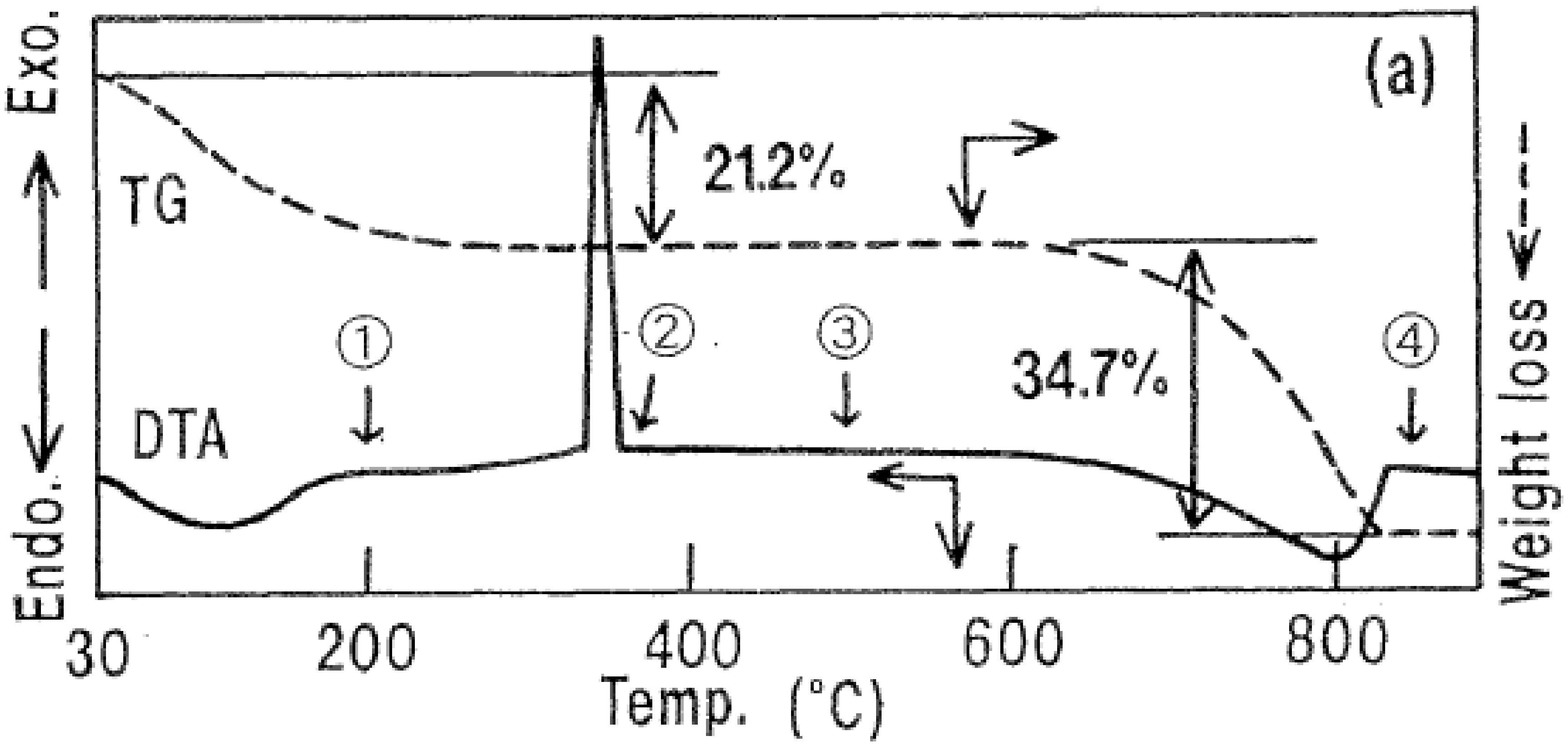


Fig. 3. Effect of pH on composition of amorphous calcium carbonate and amorphous basic calcium carbonate.
Concentration of $CaCl_2$ and Na_2CO_3 soln. ($mol \cdot dm^{-3}$): 0.1
Concentration of NaOH soln. ($mol \cdot dm^{-3}$): 0–3.0
$CaCl_2/Na_2CO_3/NaOH$ soln. volume ratio: 1/1/1
Temperature (℃): 0

[13] Y. Kojima, A. Kawanobe, T. Yasue, and Y. Arai, "Synthesis of amorphous calcium carbonate and its crystallization," *Journal of The Ceramic Society of Japan*, 101, 1145-1152 (1993).



- This is the simultaneous TG/DTA (thermogravimetry/ differential thermal analysis) plot of the ACC synthesized by Kojima *et al.* [13]. Their ACC had a formula similar to $CaCO_3 \cdot 1.5H_2O$ and 21.2% water loss was observed up to the temperature of around 260°C.

- Calcite crystallization (the sharp exothermic peak of the DTA trace) took place at around 330-350°C. ACC thus completely transformed at <400°C into calcite, then this calcite started its thermal decomposition at the usual 580-590°C.

<u>A key fact to be remembered</u>:
• ACC does not decompose (into CaO and CO_2) at a temperature lower than 520-550°C.

We will elaborate more on this later in this document, since it is a very important piece of knowledge.

[13] Y. Kojima, A. Kawanobe, T. Yasue, and Y. Arai, "Synthesis of amorphous calcium carbonate and its crystallization," *Journal of The Ceramic Society of Japan*, 101, 1145-1152 (1993).

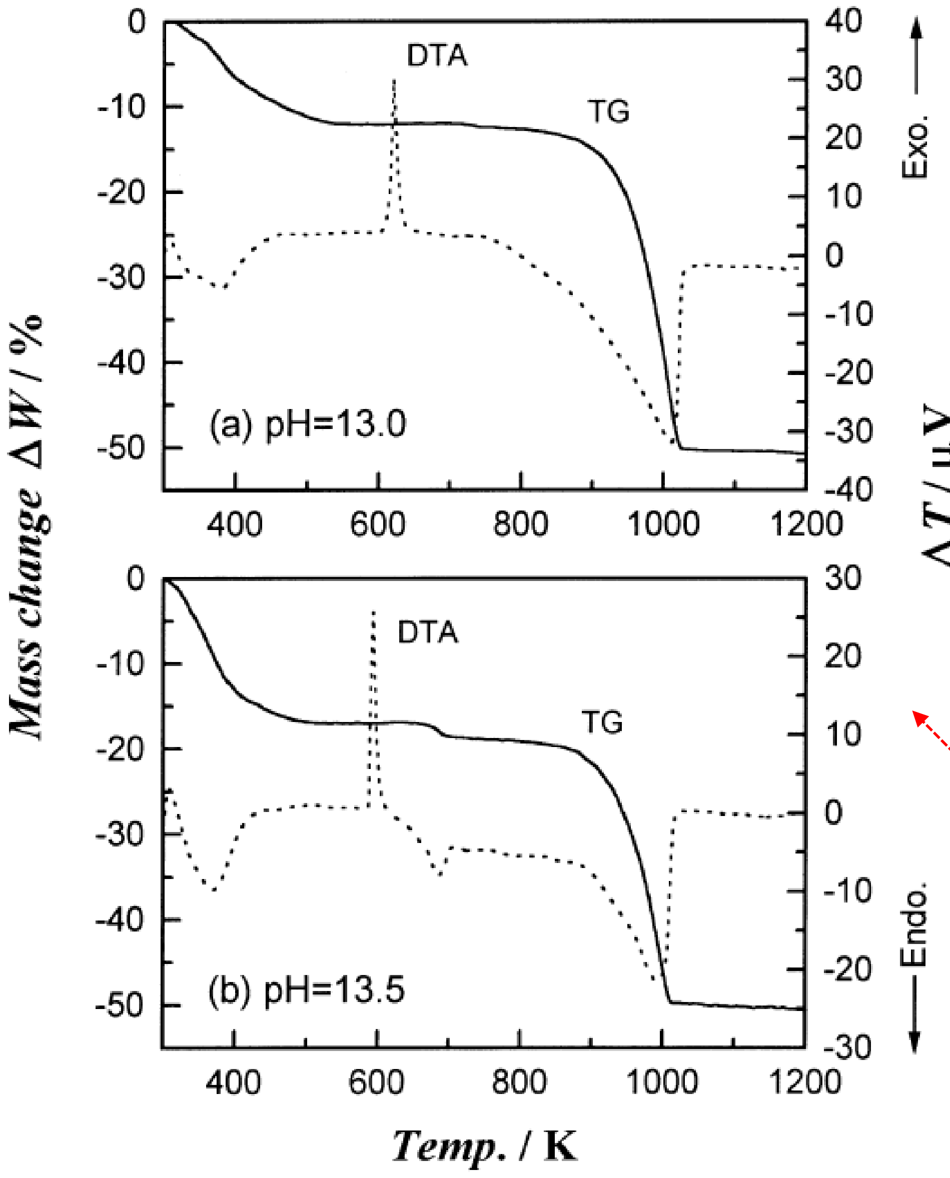


Fig. 1. Typical TG–DTA curves for ACC prepared at pH 13.0 and 13.5.

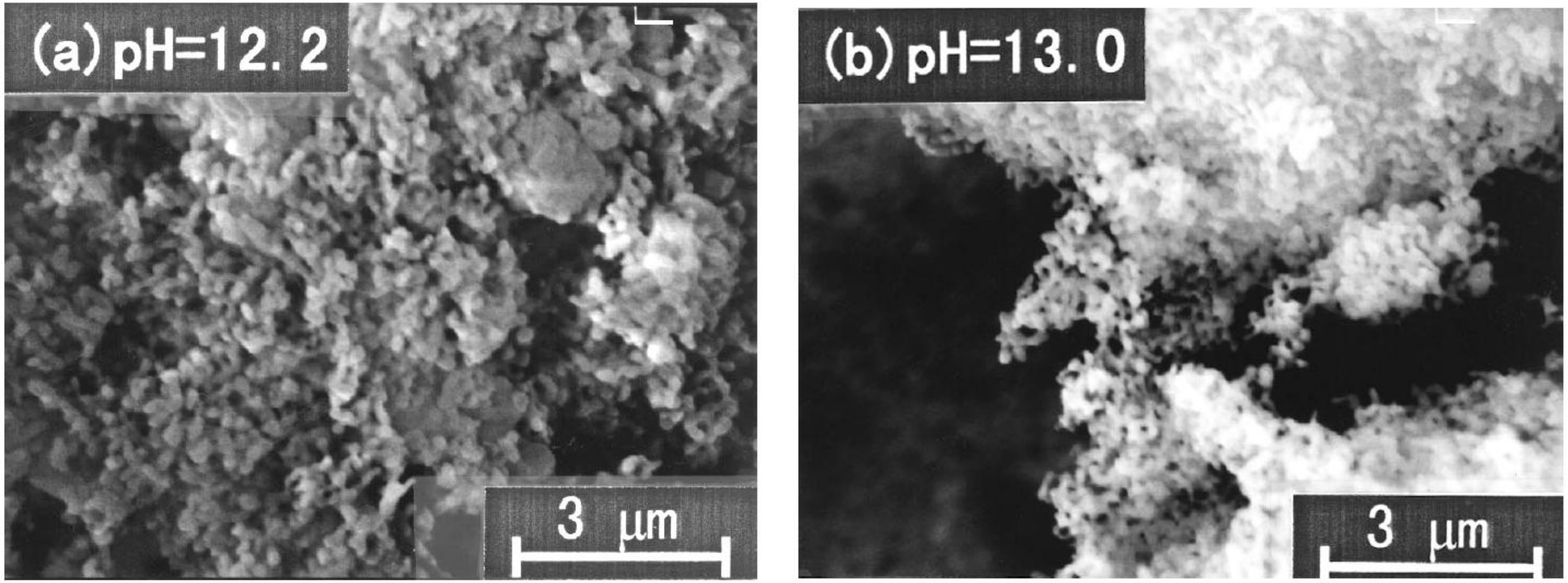
Table 1
The enthalpy change ΔH and apparent activation energy E for the crystallization of ACC prepared at various pH

pH	Range of ϕ/K min^{-1}	$-\Delta H$/ (kJ (mol $CaCO_3$)$^{-1}$)	E[a]/ (kJ mol^{-1})
13.0	2.0–10.0	12.26±0.22	304.1±23.6
12.7	3.0–15.0	50.7±2.9	261.8±19.9
12.5	3.0–15.0	50.2±2.1	199.9±10.3
12.2	5.0–30.0	39.9±2.1	151.6±13.7

[a] Averaged over 0.2≤a≤0.8.

• Koga *et al.* [14] again used Ca-chloride, Na2CO3 and NaOH solutions to synthesize ACC, however, their temperature of synthesis was 5°C. TG/DTA: after the loss of ACC-water, calcite crystallized and it started its avalanche-type decomposition at around 570°C. The ACC prepared at a solution pH of 13.5 also showed the thermal decomposition of Ca(OH)2 at around 400°C.

[14] N. Koga, Y .Nakagoe, and H. Tanaka, "Crystallization of amorphous calcium carbonate," *Thermochimica Acta*, 318, 239-244 (1998).



These are two of the SEM (scanning electron microscope) images from the Koga *et al.* [14] article. They noted that they first heated the ACC samples at 150°C prior to SEM imaging. According to their TG/DTA data, at 150°C (=425 K), only a portion of the water of ACC (*i.e.*, ACC = CaCO3·*n*H2O) would be lost but calcite would not crystallize yet at this low temperature. I can understand why Koga *et al.* [14] decided to image (*via* SEM) their samples after drying them first at 150°C. In SEM (especially by using an ordinary SEM of the 90's) studies, if a sample contains water, then it becomes difficult to eliminate sample charging to obtain sharp images.

[14] N. Koga, Y .Nakagoe, and H. Tanaka, "Crystallization of amorphous calcium carbonate," *Thermochimica Acta*, 318, 239-244 (1998).

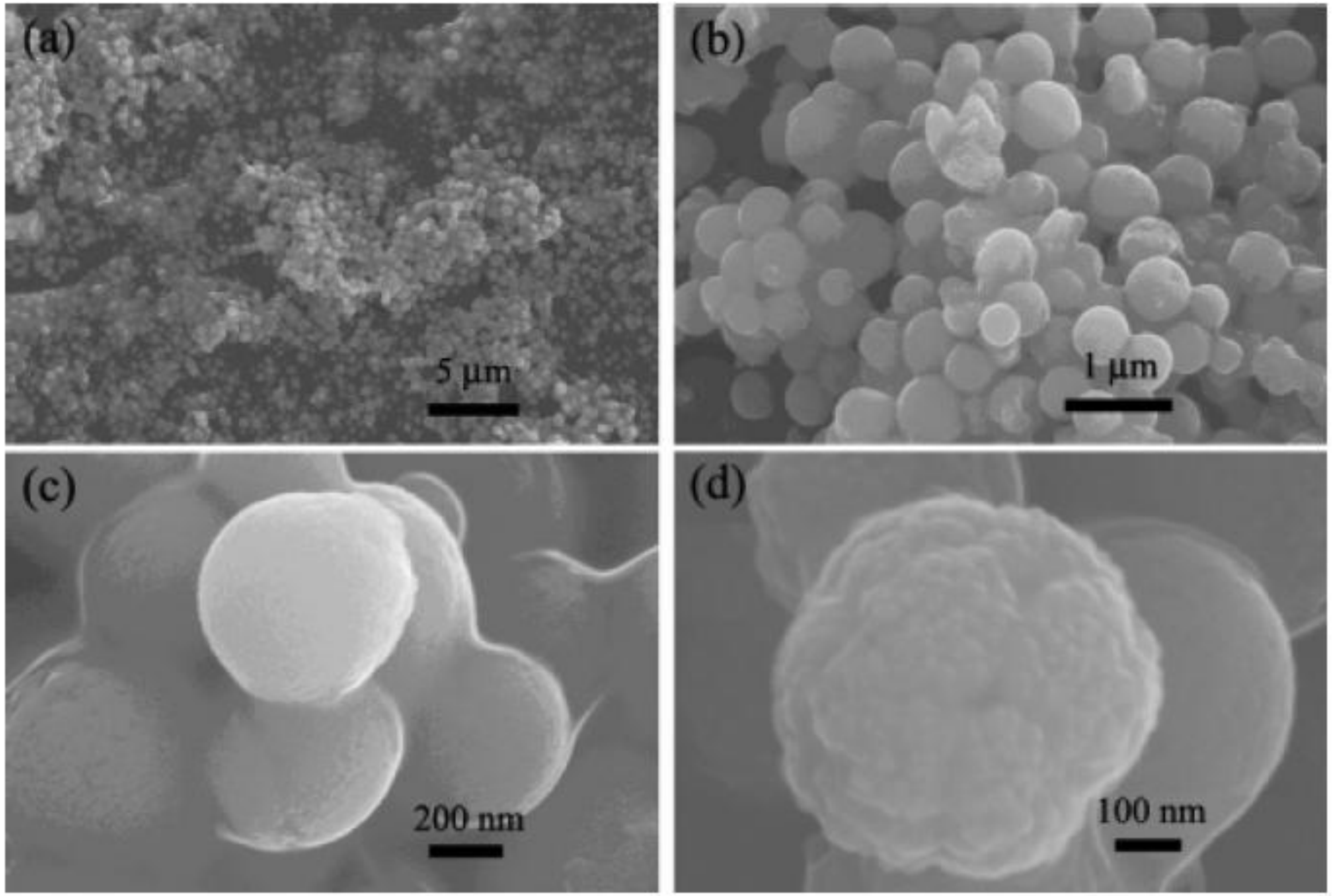


Figure 1. SEM images of the precipitated $CaCO_3$ particles sampled at 10 s after the rapid mixing of equal volumes of 100.0 mM $CaCl_2$ and 100.0 mM Na_2CO_3 solutions. Panels a−d are the gradually magnified picture.

- Shen *et al.* [15] studied the ACC formation by also using Ca-chloride, Na2CO3 and NaOH-containing solutions, however, their synthesis temperature was 26°C.

- The authors captured these images of ACC at 10 seconds after mixing the two solutions of CaCl2 (pH 6.35) and Na2CO3 (pH 12, achieved by increasing the pH of the original Na2CO3 solutions by adding NaOH). ACC spheres were thus formed at a pH lower than 11 and at a temperature of 26°C. That was most probably the reason why their ACC particles did not possess the stability of the ACC of the Kojima *et al.* [13] study.

- Figure (c) shows an "ACC gel" glueing individual spherules together.

[15] Q. Shen, H. Wei, Y. Zhou, Y. Huang, H. Yang, D. Wang, and D. Xu, "Properties of amorphous calcium carbonate and the template action of vaterite spheres," *Journal of Physical Chemistry B*, 110, 2994-3000 (2006).

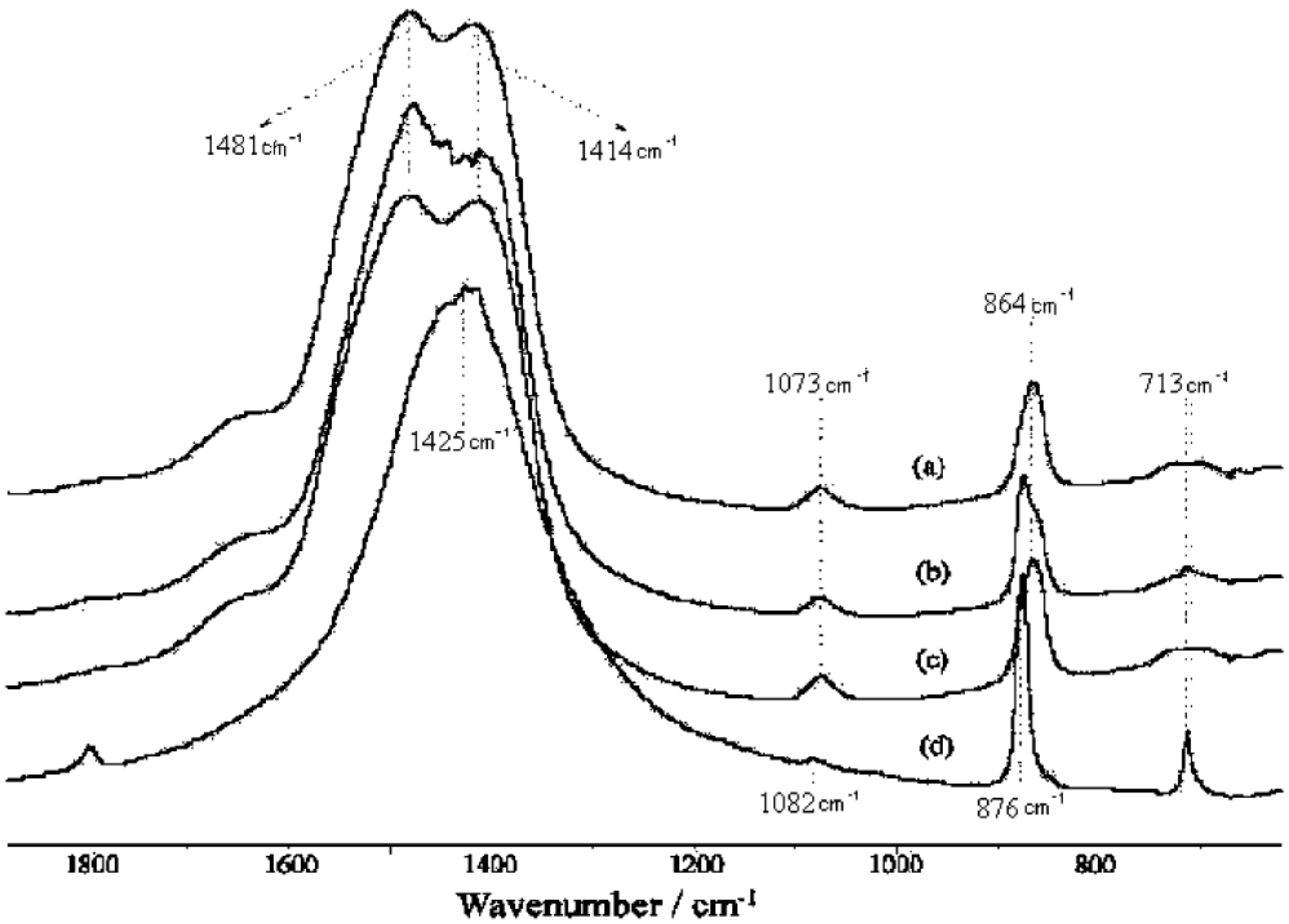


Figure 6. FT IR spectra of the $CaCO_3$ precipitates sampled at different incubation times of 5 (a), 10 (b), 30 (b), and 60 s (d), respectively, after the rapid mixing of 50.0 mM reactant solutions.

- These FTIR (Fourier-transform infrared) traces [15] teach that when the solids recovered were pure ACC (after 5 s), the ν_2 band is observed at 864 cm^{-1} and the broad ν_3 band depicts a notable split to 1481 and 1414 cm^{-1}. Calcite's ν_3 band does not show such a distinct split.

- After 60 seconds of mixing the synthesis solution, the solids Shen *et al.* [15] recovered (by rapid filtering and washing) were of pure calcite, the ν_2 band shifted to 876 cm^{-1}, the split in the broad ν_3 band disappeared and the $\nu_1+\nu_4$ band of calcite became visible at 1790 cm^{-1}.

- This is quite a useful article [15] for the ACC researchers since it provided an excellent FTIR-based characterization of the transformation of ACC to calcite. They did not analyze their samples by TG/DTA or TG/DSC (differential scanning calorimetry).

[15] Q. Shen, H. Wei, Y. Zhou, Y. Huang, H. Yang, D. Wang, and D. Xu, "Properties of amorphous calcium carbonate and the template action of vaterite spheres," *Journal of Physical Chemistry B*, 110, 2994-3000 (2006).

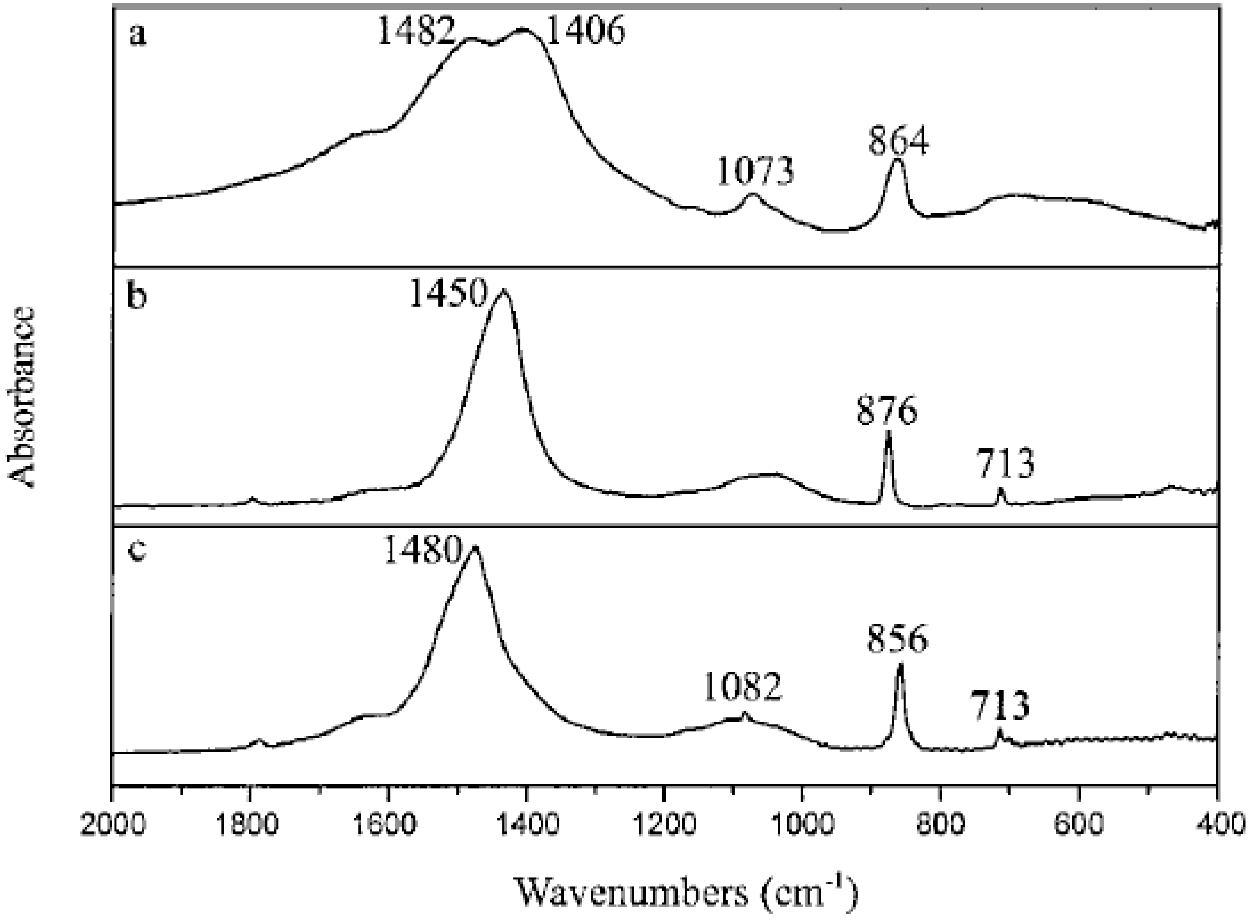


Figure 2. Infrared spectra of (a) ACC, (b) calcite, and (c) aragonite show that they are all different. The ACC spectrum is mainly characterized by a split in the asymmetric stretch of the carbonate ions at about 1420 and 1470 cm^{-1}. This split appears in all hydrated phases of calcium carbonate and is probably related to the local symmetry around the carbonate ions.

- This excellent FTIR plot, for the wavenumber range of 2000 to 400 cm^{-1}, was given by Weiner *et al.* [1] and provides a quick comparison between ACC, calcite and aragonite.

- Prof. Steve Weiner (*Google Scholar h-index: 136*) and Prof Addadi (*Google Scholar h-index: 109*) of Weizmann Institute of Science are just two of the world's most prominent scientists in this field.

[1] S. Weiner, Y. Levi-Kalisman, S. Raz, L. Addadi, "*Biologically formed amorphous calcium carbonate,*" *Connective Tissue Research*, 44 (Suppl. 1), 214-218 (2003).

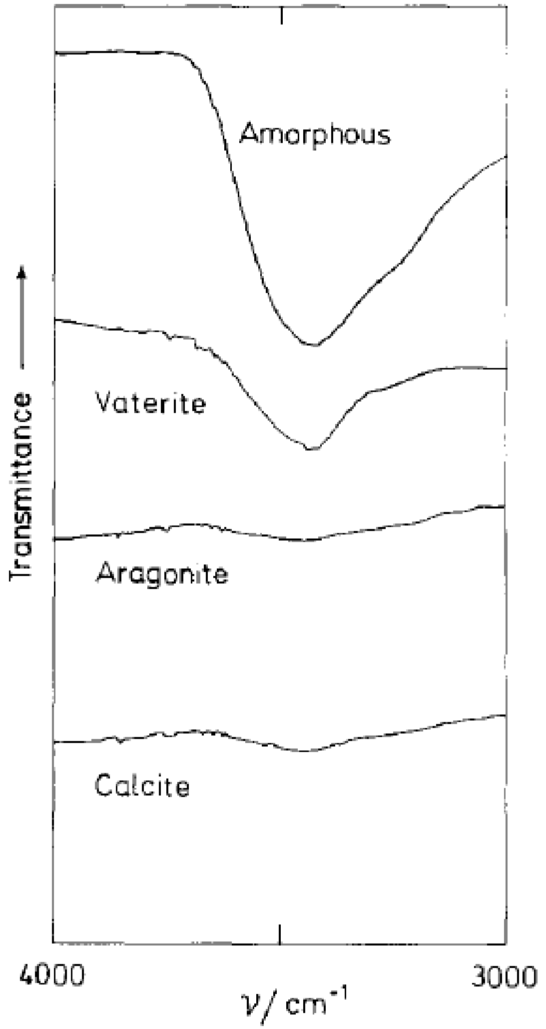


Fig. 8. IR absorption bands in the region from 3000 to 4000 cm^{-1} for amorphous calcium carbonate, vaterite, aragonite, and calcite. In contrast to the well-known anhydrous modifications, amorphous calcium carbonate shows strong absorption bands of $\nu_{a(O-H)}$ at 3430 cm^{-1} and $\nu_{s(O-H)}$ at 3220 cm-1.

• FTIR analysis (performed either by using the KBr pellet method or by using ATR (attenuated total reflection)-FTIR) is a competent tool of characterization, especially when working with hydrous materials that may contain ≥15 wt% water just like ACC.

• Dr. Ljerka Brecevic (https://hrcak.srce.hr/file/282983) was one of the prominent scientists of the world, who contributed a lot to the understanding of water-based nucleation and crystallization processes in various material systems.

• This article of Brecevic and Nielsen [10] showed that FTIR is able to quickly see (high quality FTIR scans typically take around 15-20 minutes) the water content of calcium carbonate forms by looking at the water region (4000 to 3000 cm^{-1}) of an FTIR scan. ACC and vaterite contain water, ACC has more water.

• The Shen *et al.* [15] study of the previous page did not report the 4000 to 3000 cm^{-1} region, although any FTIR scan automatically records that region as well.

[10] L. Brecevic and A. E. Nielsen, “Solubility of amorphous calcium carbonate,” *Journal of Crystal Growth*, 98, 504-510 (1989).

Bolze *et al*. [16] prepared ACC, at 25°C, by rapidly mixing equimolar (9 mM) solutions of $CaCl_2 \cdot 2H_2O$ and Na_2CO_3, after adjusting the pH of each solution to 10.5 by using NaOH additions.

The Bolze *et al*. [16] study had quite a unique experimental approach though; they did not need to remove the solids formed in the synthesis solutions/media by filtering and washing and they ran synchrotron small angle X-ray scattering (SAXS) experiments. Their SAXS data were collected after 9.5 s of mixing the Ca-chloride and Na_2CO_3 solutions and their exposure time for each SAXS measurement was only 50 to 100 ms (milliseconds).

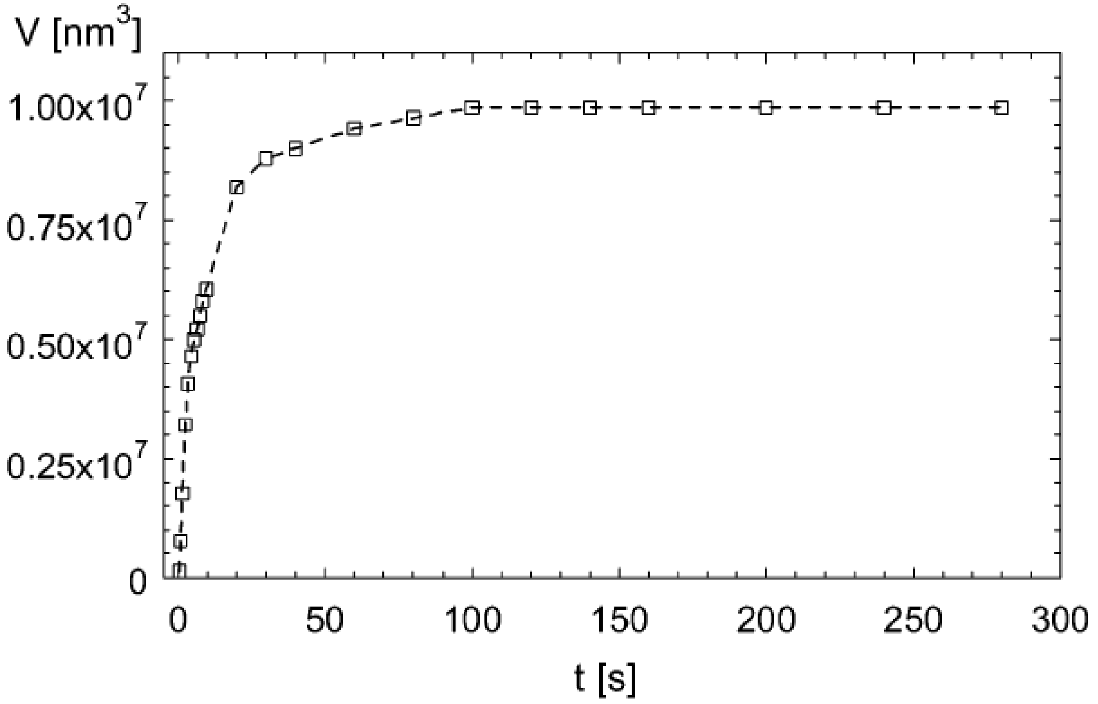


Figure 4. Increase of the volume *V* per particle as a function of time (initial salt concentrations, 9 mM).

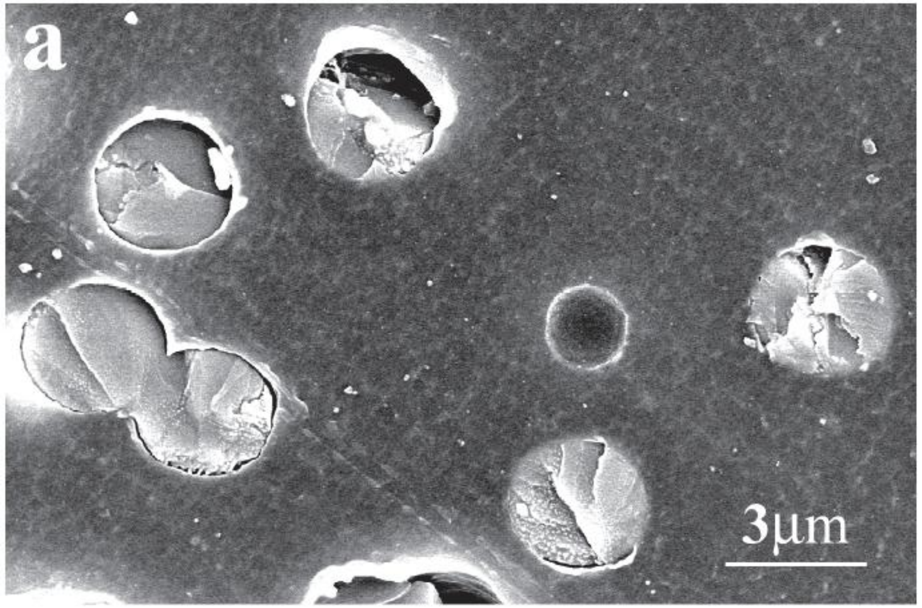
• Bolze *et al*. [16] efficiently observed the *in situ* volumetric growth of ACC particles. This plot depicts the growth of particles as a function of time they remained in the mother solution/liqour.

• This study [16] did not have an interest in determining the "kinetics" of the ACC-to-calcite transformation since that was already reported (as we provided in the articles of the literature) by the previous researchers. See Fig. 4 and Table 2 of the article by Koga *et al*. [14]

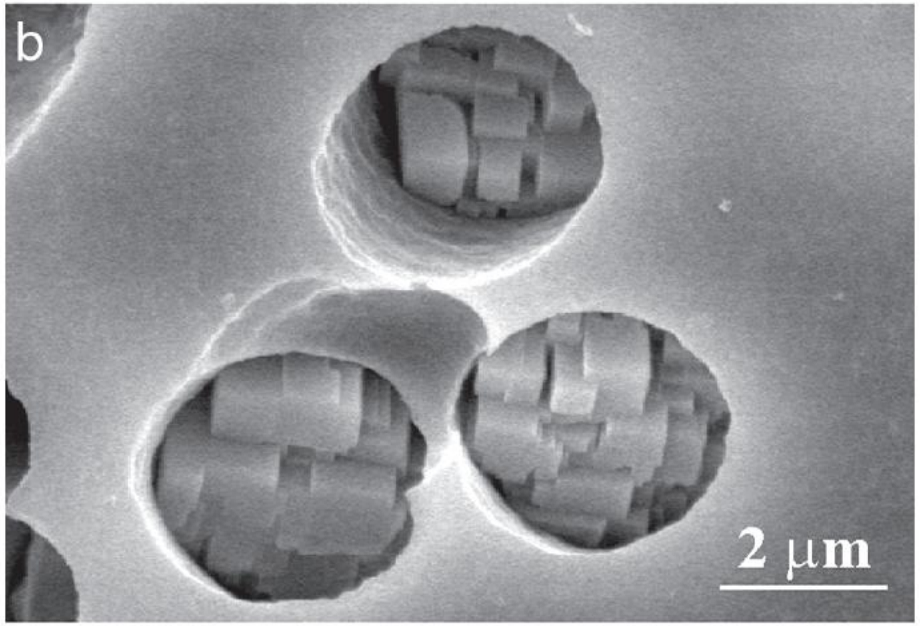
[16] J. Bolze, B. Peng, N. Dingenouts, P. Panine, T. Narayanan, and M. Ballauff, "Formation and growth of amorphous colloidal $CaCO_3$ precursor particles as detected by time-resolved SAXS," *Langmuir*, 18, 8364-8369 (2002).

An excerpt from the Loste & Meldrum article [17]

"As a simple model system, 10 mm thick polycarbonate [track-etch membranes](#) were used as the crystallization environment. These membranes possess cylindrical channels of diameter 3 μm, which are similar to the dimensions of [sea urchin](#) embryo spicules. ACC was precipitated in the membrane pores by placing a membrane between two half U-tube arms, and filling one tube with CaCl2 solution and the other with Na2CO3 solution. The experiments were carried out at 4–6°C in order to stabilize ACC, by reducing the rate of transformation to calcite."



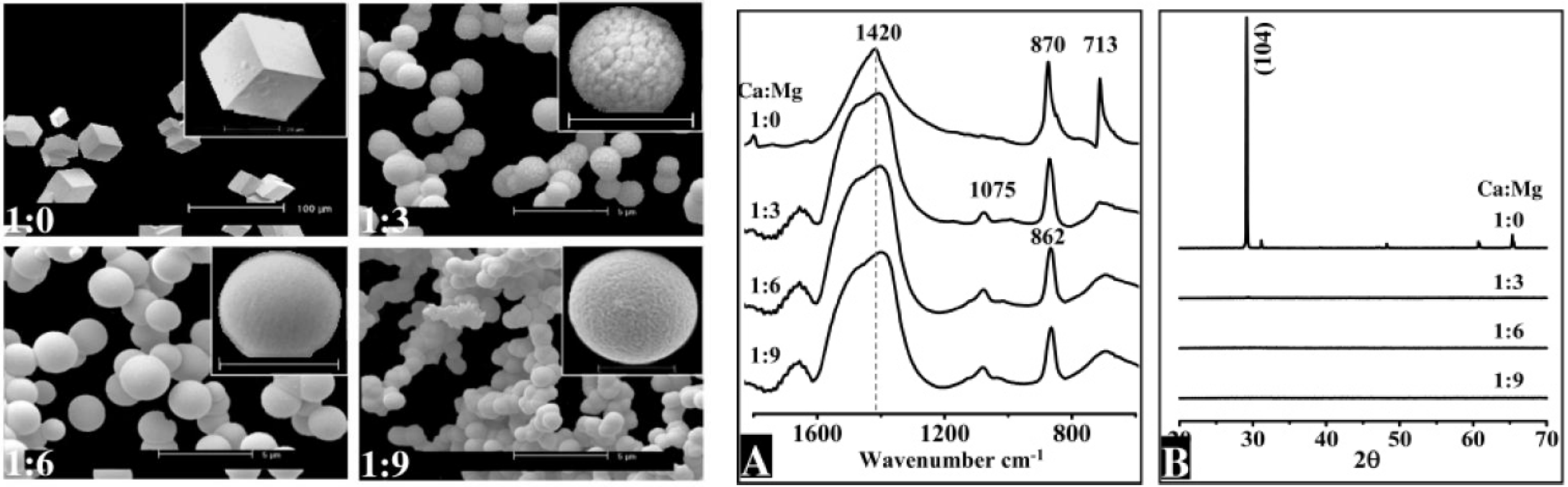
- Channels of the polycarbonate membrane initially filled with ACC



- Channels of the polycarbonate membrane after 24 h; calcite cubes crystallized within the channels as a result of the "ACC → calcite Transformation"

[17] E. Loste and F. C. Meldrum, "Control of calcium carbonate morphology by transformation of an amorphous precursor in a constrained volume," *Chemical Communications*, 10, 901-902 (2001).

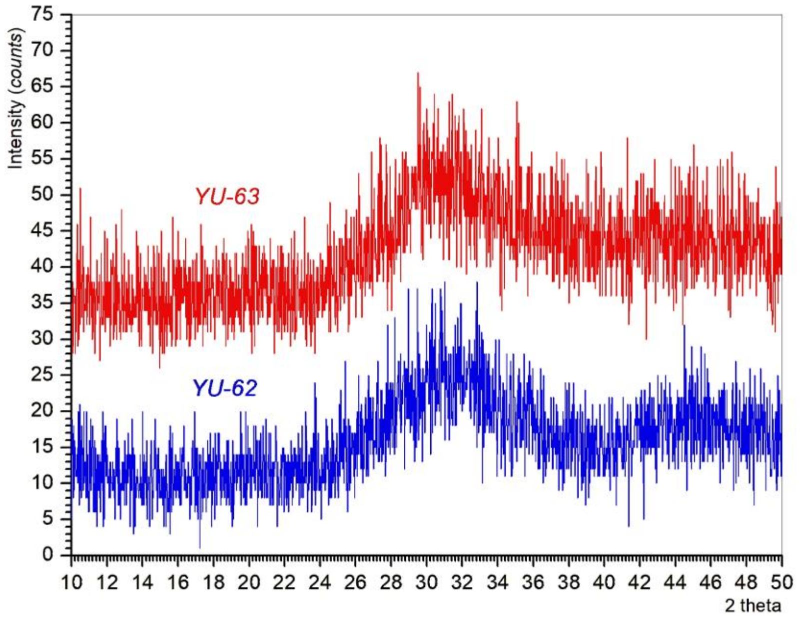
We advise the readers to study the articles of references [18] and [19] below, which examined the effect of adding Mg^{2+} (in the form of dissolved $MgCl_2$) to the ACC synthesis solutions. Mg^{2+} ions are expected to slow down the ACC → calcite transformation. The SEM, FTIR and XRD data below are from Fig. 1 of Reference 19.

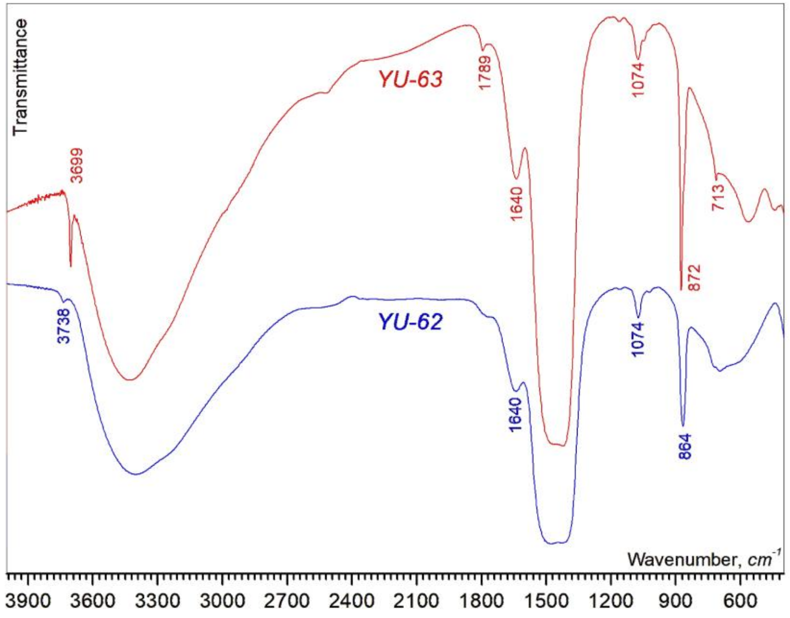


1:0, 1:3, 1:6, 1:9 refer to molar ratio of Ca/Mg.

[18] E. Loste, R. M. Wilson, R. Seshadri, and F. C. Meldrum, "The role of magnesium in stabilizing amorphous calcium carbonate and controlling calcite morphologies," *Journal of Crystal Growth*, 254, 206-218 (2003).
[19] P. K. Ajikumar, L. G. Wong, G. Subramanyam, R. Lakshminarayanan, and S. Valiyaveettil, "Synthesis and characterization of monodispersed spheres of amorphous calcium carbonate and calcite spherules," *Crystal Growth & Design*, 5, 1129-1134 (2005).

A. C. Tas





When I was a Professor at Yeditepe University (Istanbul, Turkey) back in 2009, I synthesized my version of ACC powders. These plots show the XRD and FTIR data of two of my ACC samples. This still remains as an unpublished work, therefore, I will not share here all the synthesis details.

I prepared two solutions to synthesize the YU-62 and YU-63 samples; solution A had Na2CO3 and NaOH, solution B had CaCl2·2H2O. Glass beakers having sol A and sol B were placed in ice baths for 90 min, then sol B was very rapidly added to sol A under vigorous stirring. I stirred the mixture for 60 s and filtered the solids by using a Whatman No. 42 filter paper, then washed them with EtOH, and kept the samples on their filter papers in air in a 37°C oven for 18 h. I collected the FTIR patterns the next day, but I collected their XRD patterns 2 d after synthesis. While the YU-62 (blue) solution mixture had an ionic strength of 113.8 mM, I increased the ionic strength of the solution mixture for YU-63 (red) to 1138 mM (by adding certain amounts of NaCl, KCl and MgCl2·6H2O on top of CaCl2·2H2O, Na2CO3 and NaOH).

Outcome: both samples of YU-62 and YU-63 were comprised of X-ray amorphous calcium carbonate. The FTIR data of YU-62 showed the 864 cm^{1} band while that of YU-63 showed the 872 and 713 cm^{-1} bands. Moreover, the YU-63 sample's FTIR trace depicted the very sharp 3699 cm^{-1} band that is typically assigned to (OH) of brucite. While both samples were amorphous, their FTIR data were drastically different. This was what I designed to see, which was not reported before. ACC is an exciting phase to study.

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The presence of dissolved phytic acid (IP_6 = inositol hexaphosphate) at the concentration of 1 gpL (g L^{-1}) in CaCl2 solutions which were then reacted with the gas (consisting of NH3 and CO2) *in situ* generated from ground ammonium carbonate placed to the vicinity of the CaCl2 solution (in a closed system) resulted, after 5 days, in the formation of spheres of ACC, as described in Reference 20.

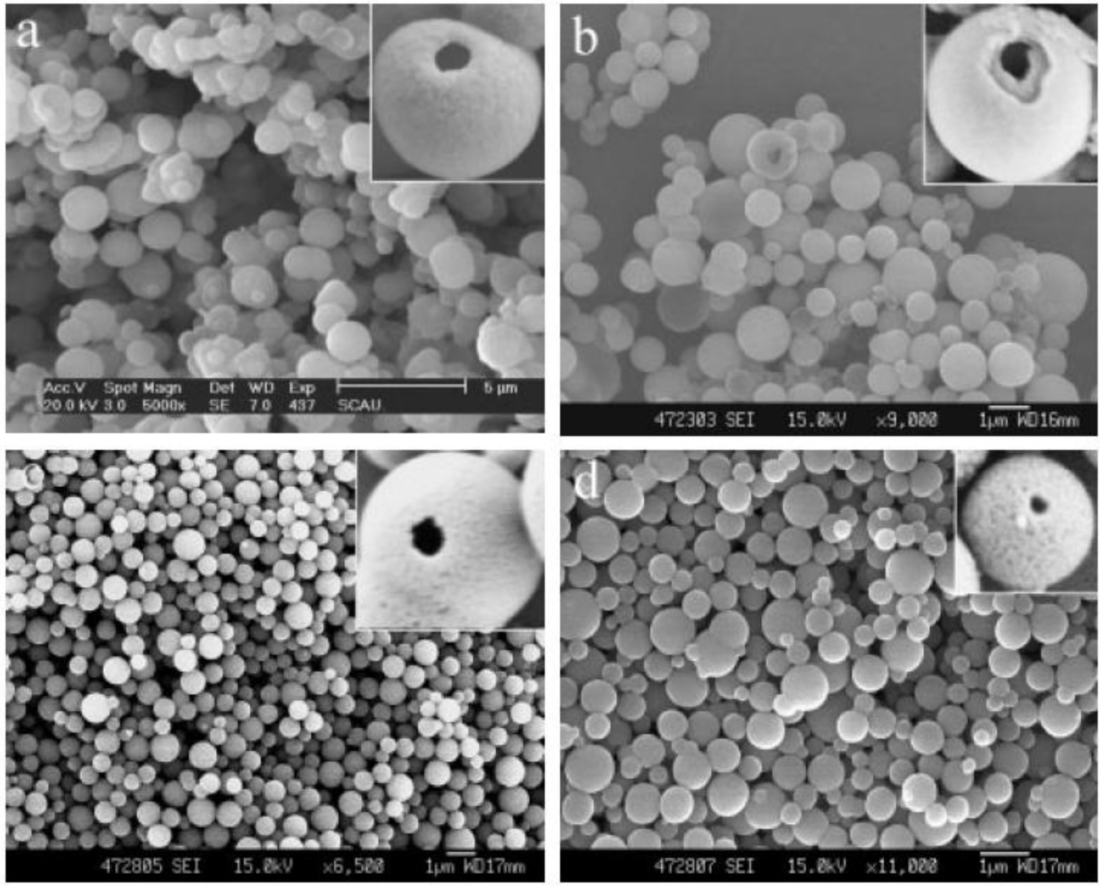
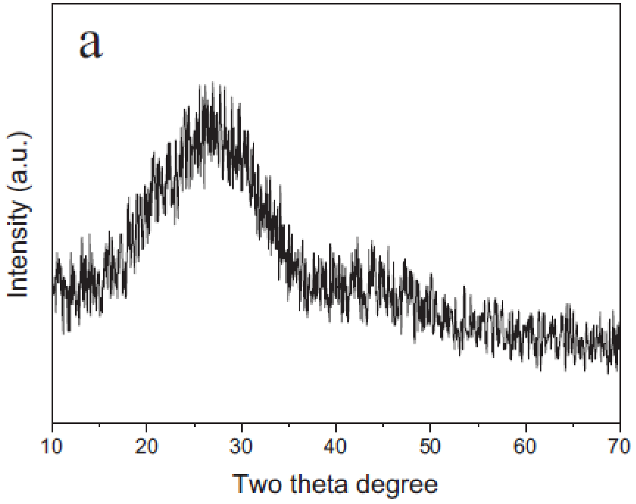
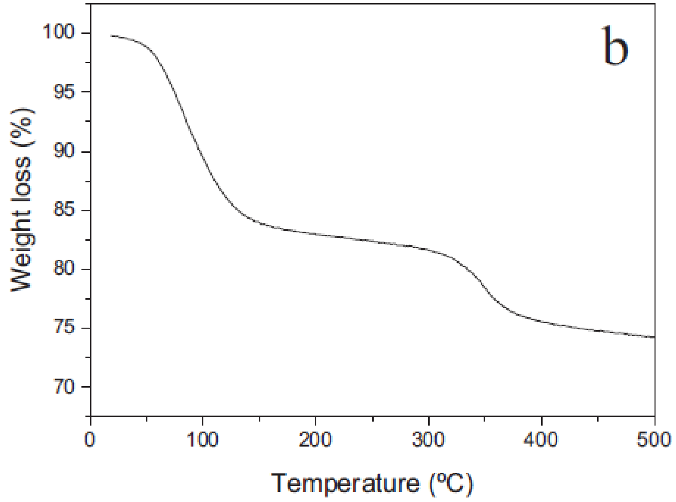


Figure 3. SEM images of the obtained ACC in the presence of IP_6 by the gas diffusion reaction for 5 days. IP_6: a) 0.5, b) 2, c) 5, d) 6 g L^{-1}.





- The XRD pattern showed that the hollow spheres were X-ray amorphous.

- Authors commented that the 2nd step weight loss of the above TGA trace was caused by the decomposition of the phytic acid additive (1 gpL).

[20] A. W. Xu, Q. Yu, W. F. Dong, M. Antonietti, and H. Colfen, "Stable amorphous CaCO3 microparticles with hollow spherical superstructures by phytic acid," *Advanced Materials*, 17, 2217-2221 (2005).

Faatz *et al.* [21] used, as the only carbonate source, dimethyl carbonate ($C_3H_6O_3 = CH_3OCOOCH_3$) initially added to the $CaCl_2$ solutions, followed by increasing the solution pH by NaOH additions. They did not use any Na_2CO_3, K_2CO_3 or ammonium carbonate as the carbonate source in synthesizing ACC. The authors removed the precipitates from the reaction mixture, after 2.5 minutes, by centrifugation for further analyses.

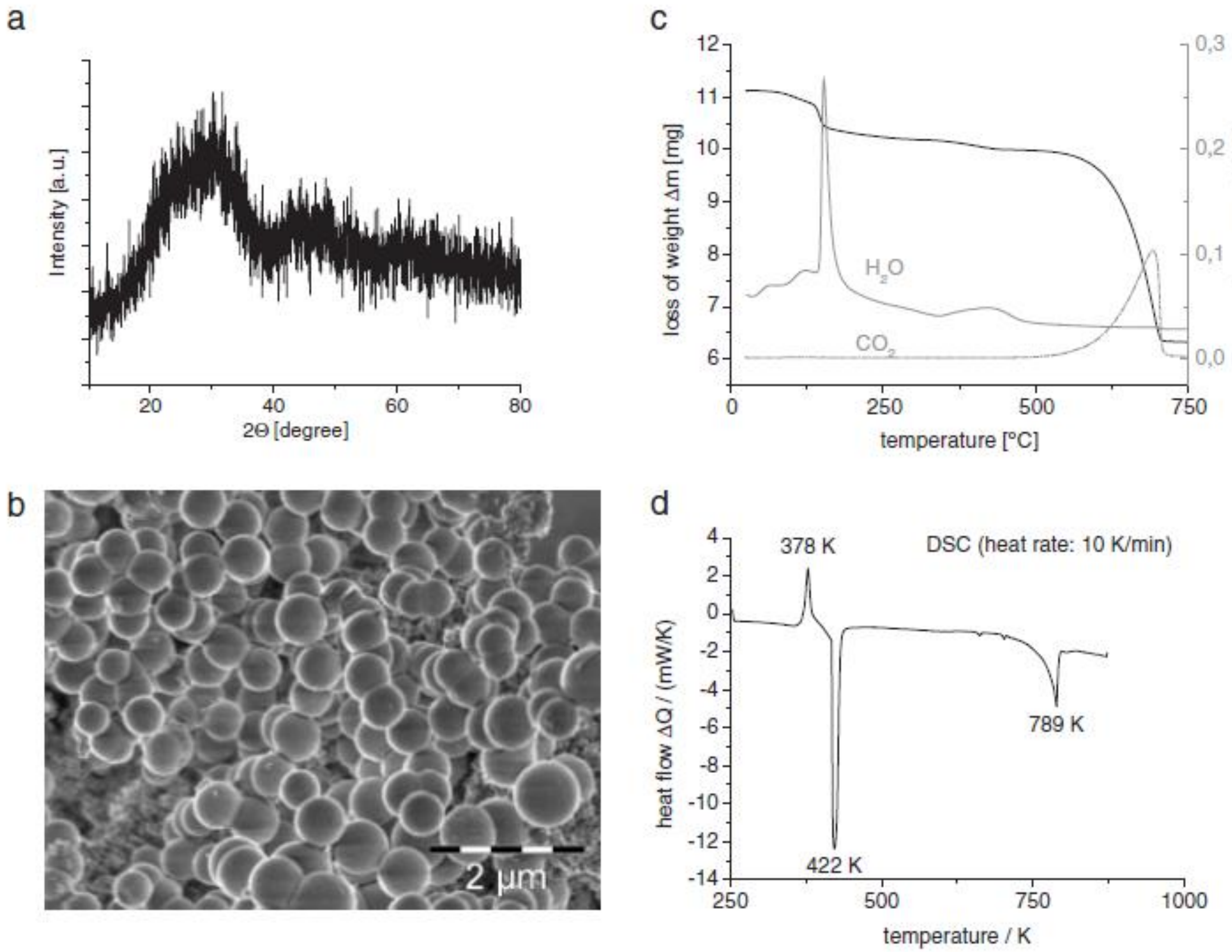


Figure 1. Amorphous calcium carbonate obtained by hydrolysis of dimethyl carbonate as source of CO_2 in an aqueous solution of $CaCl_2$. a) X-ray pattern; b) SEM image; c) TGA-MS curve; d) DSC trace.

- This has been one of the rare articles which studied the thermal decomposition of ACC by using combined TGA-MS (mass spectroscopy), performed in pure N_2 atmosphere, instead of ordinary TGA. Excellent!!

- The TGA-MS data showed that the thermal decomposition of the ACC spheres of this study, through CO_2 (g) evolution, did not start below 500°C, it actually started at 516°C.

[21] M. Faatz, F. Grohn, and G. Wegner, "Amorphous calcium carbonate: synthesis and potential intermediate in biomineralization," *Advanced Materials*, 16, 996-1000 (2004).

Xu *et al.* [22] reproduced the ACC powder synthesis procedure of Ref. 21 (see the previous page) by using dimethyl carbonate.

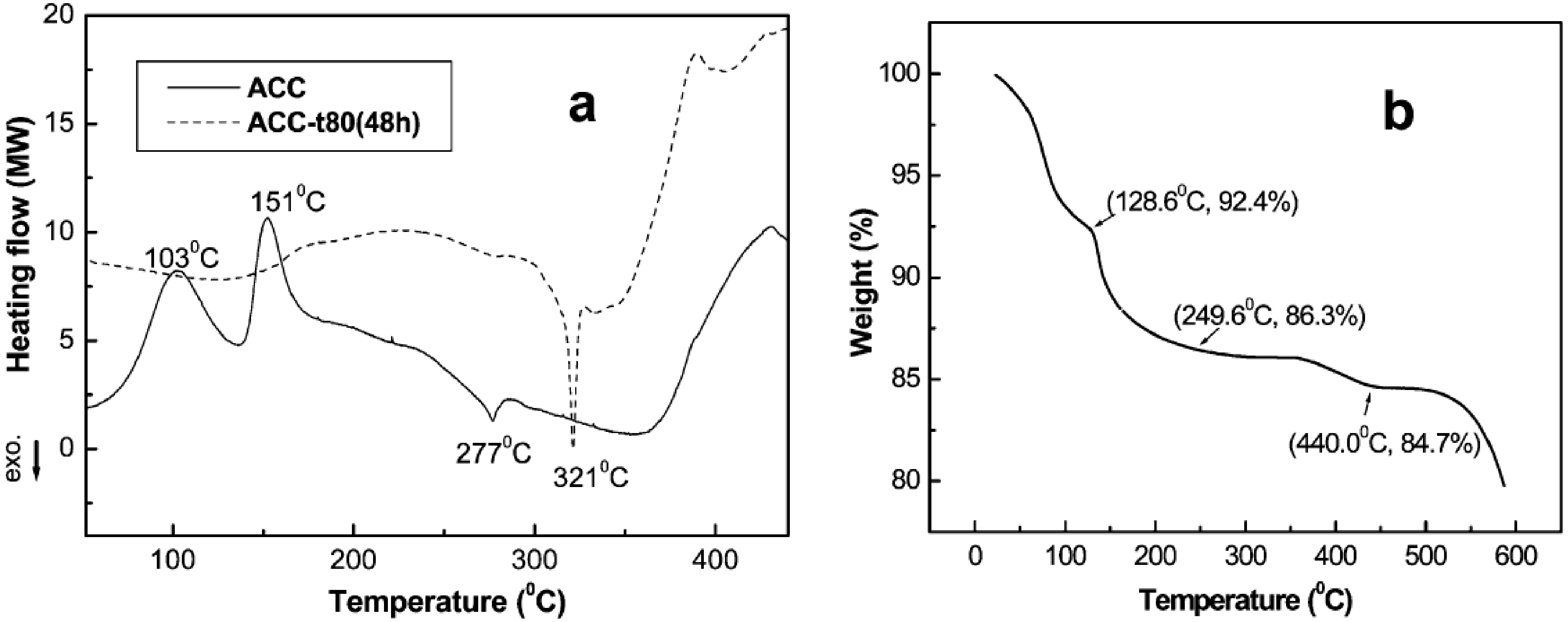


Figure 7. (a) DSC curves of ACC (solid line) and ACC heated at 80 °C for 48 h (dash line), heating rate 10K/min, N_2 atmosphere; (b) TGA curve of ACC at heating rate 10 K/min.

• The weight losses (TGA data plot at the right above) observed at around 129° and 440°C correspond to water loss (dehydration) taking place in two distinct steps. CO2 (g) evolution started at above 520°C.

[22] X. Xu, J. T. Han, D. H. Kim, and K. Cho, "Two modes of transformation of amorphous calcium carbonate films in air," *Journal of Physical Chemistry B*, 110, 2764-2770 (2006).

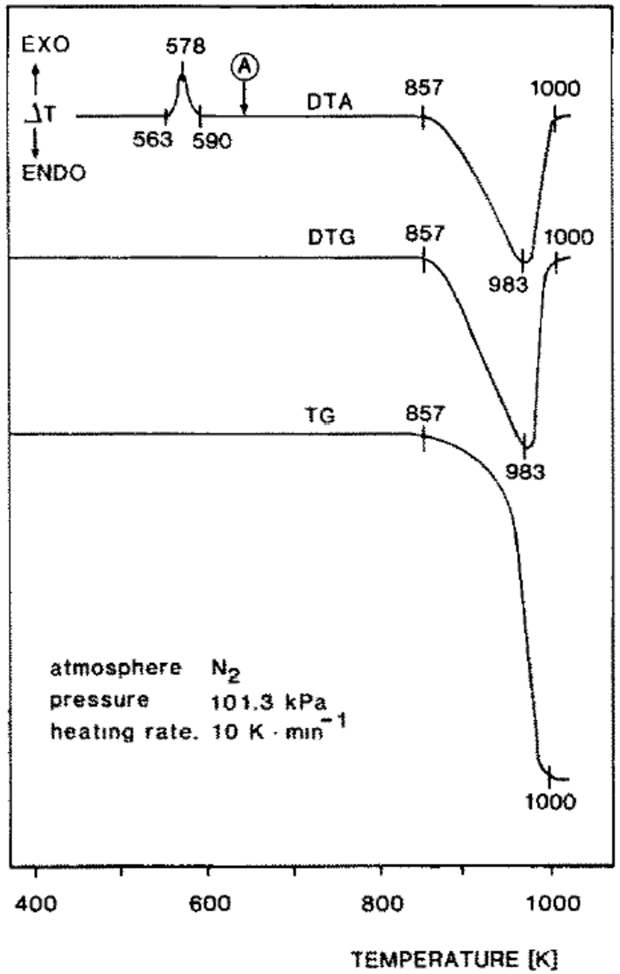
One should expect that any X-ray amorphous ACC powder synthesized without using any organic macromolecules and those synthesized in the presence of some organic macromolecules would not yield a literally "**identical**" response to controlled heating (recorded by instruments such as TGA, combined TGA-MS or combined TGA-FTIR).

The above statement was strongly supported by the TGA traces, as we demonstrated in this work, especially by those reproduced from References 13, 14 (without any organics in ACC synthesis) and Reference 22 (with dimethyl carbonate organic additive).

The pioneering work of Dr. Laurie Gower [23] in suppressing the rate of "ACC → crystalline $CaCO_3$ transformation" by using poly(acrylic acid) or poly(aspartic acid) provided good examples on the use of organic macromolecules. The decades long work of Prof. Stephen Mann on the effect of organic macromolecules on nucleation and crystallization of inorganic materials should be recognized in any work on ACC formation [24].

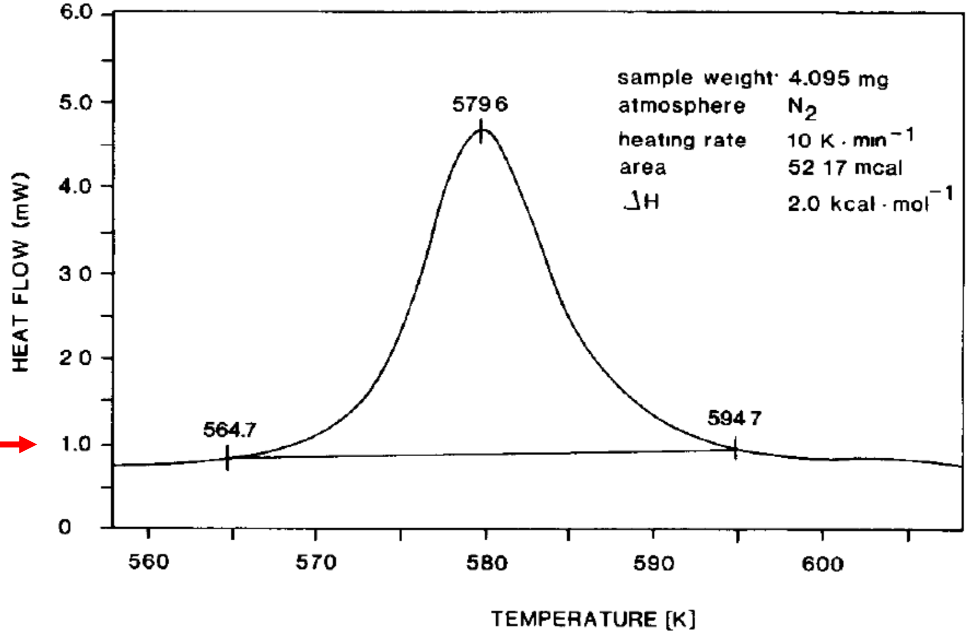
[23] E. DiMasi, S. Y. Kwak, F. F. Amos, M. J. Olszta, D. Lush, and L B. Gower, "Complementary control by additives of the kinetics of amorphous $CaCO_3$ mineralization at an organic interface: *In situ* synchrotron X-ray observations," *Physical Review Letters*, 97, 045503 (2006).
[24] S. Mann, "Molecular recognition in biomineralization," *Nature*, 332, 119-124 (1988).

ACC formation is, of course, not limited to aqueous solutions in which one has Ca^{2+} and CO_3^{2-} ions at high pH. The study of Maciejewski and Reller [25] showed, as early as 1989, that when one has a CaO powder of high enough reactivity, that reactive CaO powder can react with CO2(g) to form ACC (initially on the CaO particle surfaces, that surface-bound reaction zone proceeds towards the cores of the CaO particles with time) at temperatures as low as 47°C. Such an excellent work laid the foundation for today's "Ca-looping (CaL)" efforts.



The plot on the left [25] showed that ACC crystallizes to calcite between 290° and 317°C. The calcite crystallized from ACC then started its thermal decomposition at 584°C. Readers: do not jump into quick conclusions, when and if you see a weight loss in your TGA traces below 550°C, by believing that that was due to ACC decomposition and subsequent CO2 (g) evolution. It is due to H2O loss.

This was how the enthalpy of crystallization of ACC into calcite was estimated (*via* using DSC) by Maciejewski and Reller [25].



[25] M. Maciejewski and A. Reller, "Formation of amorphous CaCO3 during the reaction of CO2 with CaO," *Thermochimica Acta*, 142, 175-188 (1989).

Gunther *et al*. [26] provided an easy method to synthesize ACC (*scalable especially at the cold climate zones of earth*):

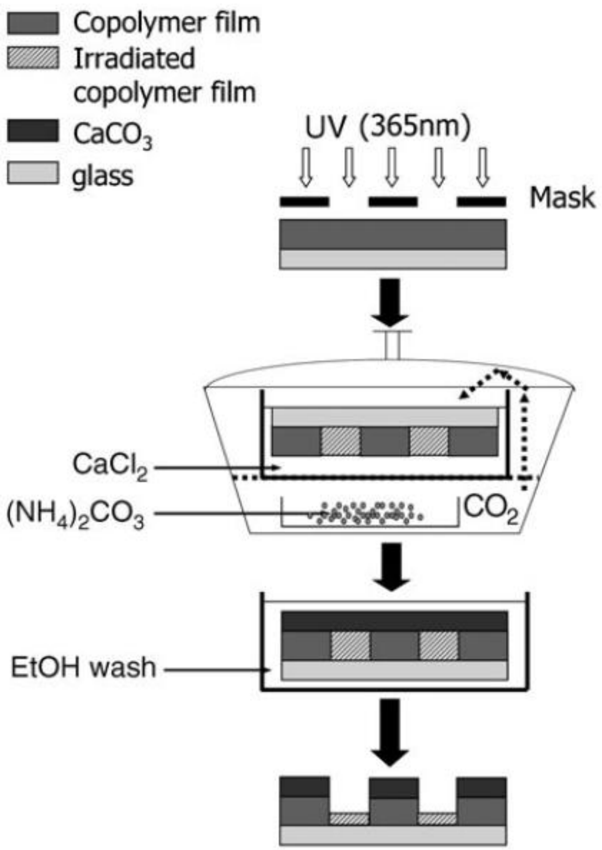
1.) prepare an aqueous slurry of Ca(OH)2,
2.) adjust the temperature of the slurry to **0°C**,
3.) bubble CO2 through the stirred slurry until the pH drops to 8,
4.) separate the solids from the slurry to obtain ACC particles with a small amount of yet unreacted Ca(OH)2 in their cores.

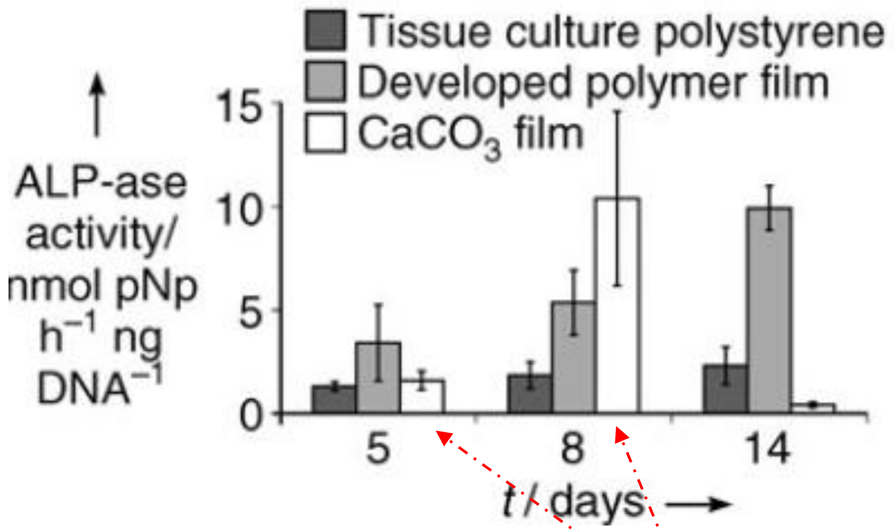
Note-1: If Gunther *et al*. [26] were using the starting powder of type S hydrated dolomitic lime, which has about 55:45 Ca(OH)2 to Mg(OH)2 composition) in their slurry, their ACC would be seeing the benefit of "stabilization of their ACC by magnesium;" they did not test this.

Note-2: The CaCO3-calcite bulk powder industry (*e.g*., Omya) uses the above procedure [26] since a very long time, but at elevated (<100°C) temperatures, not at 0°C.

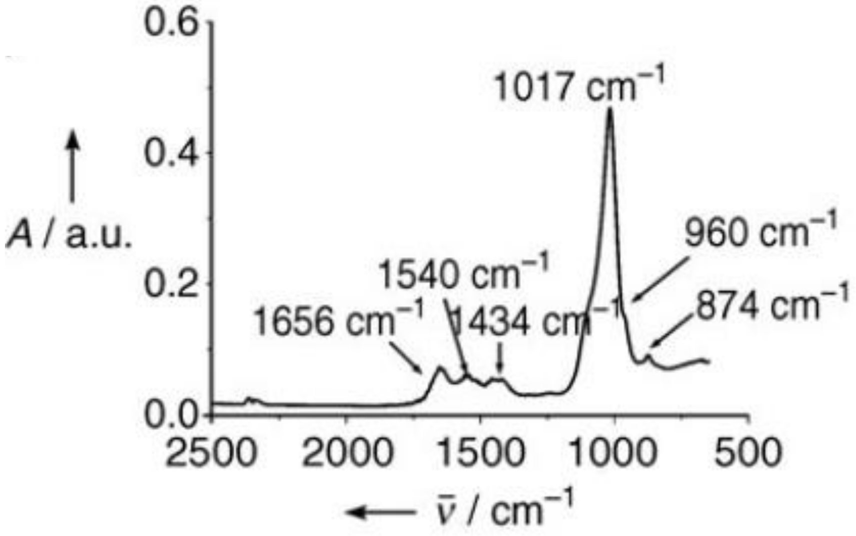
[26] G. Gunther, A. Becker, G. Wolf, and M. Epple, "*In vitro* synthesis and structural characterization of amorphous calcium carbonate," *Zeitschrift fur Anorganische und Allgemeine Chemie (ZAAC)*, 631, 2830-2835 (2005).

ACC can also find a place in the field of **synthetic bone substitute materials** (in which I enjoyed my time as a research-oriented academician from July 1993 to July 2015). Sommerdijk *et al.* [27] prepared ACC films as shown below and reported their superior response (up to 8 d of cell culture) to osteoblast-like cells by quantifying the ALP (alkaline phosphatase) activity. Osteoblast-like cells formed carbonated calcium phosphate on ACC films; super!





good ALP activity on ACC films



FTIR spectrum of the calcium phosphate mineral formed by osteoblast-like cells cultured on ACC films

[27] D. C. Popescu, E. N. M. van Leeuwen, N. A. A. Rossi, S. J. Holder, J. A. Jansen, and N. A. J. M. Sommerdijk, "Shaping amorphous calcium carbonate films into 2D model substrates for bone cell culture," *Angewandte Chemie International Edition*, 45, 1762-1767 (2006).

The well-organized efforts on providing industrial solutions to decrease CO_2 (g) emissions from cement kilns were started in 2008 by Solidia Technologies, *Inc.* CarbonCure Technologies then came in 2012. Moreover, the IPs generated by Calera (founded in 2007) were immensely helpful to the people working in this field of enforced carbonation of alternative cements or natural materials. As of today, there are many newcomer companies across the globe, this document is not the place to count them.

Solidia: produced its very own low carbon (Ca:Si molar ratio of 1 to 1.2), non-hydraulic cement in ordinary cement kiln runs (at temperatures much lower than those of Portland cement production) at large tonnages by using the same feedstock materials the cement plant has; Solidia clinker that came out from the cement kiln was ground similar to the particle size distribution of Portland cement; Solidia cement was not cured by water, it was cured by CO_2 (g). Solidia concrete in various forms (including aerated concrete and carbonated SCM with amorphous silica by-product) were successfully produced and scaled up to the industrial scales

CarbonCure: introduced CO_2 into wet concrete (while it was still in a concrete mixer) to *in situ* form $CaCO_3$ nanoparticles at limited amounts

A fraction of the intellectual property generated by both of the above companies can be reached at, *e.g.*, USPTO's patent search webpage.

Today many in the business of bringing any source of $CO_2(g)$ (cement kiln flue gas, coal-burning power plant flue gas, food-grade CO_2, *etc.*) in contact with any economically available, abundant and feasible alkali (potassium and sodium) and alkaline earth (calcium and magnesium) elements-containing powders using a professionally-designed reactor or chamber with the purpose of mineralizing $CaCO_3$ or $MgCO_3$ in the end product face a common problem: how will we accurately quantify the mass of CO_2 mineralized into a solid and durable form in our end product?

For CO_2 quantification in their end product, the scientists have been using (for decades) numerous techniques, such as acid digestion (*a.k.a.* calcimetry), quantitative X-ray diffraction, multi-step loss-on-ignition, quantitative FTIR, ordinary TGA, TGA-DTA, TGA-DSC, evolved gas analyzers that use a special TGA-IR combination for C and S quantifications, SEM-BSE imaging coupled with EDXS-based elemental X-ray mapping, *etc*. And, the scientists would want to perform their CO_2 quantification work by strictly observing what is written in the ASTM standards (or EN, JIS, *etc.*) which were not originally penned for what the scientists are supposed to do today.

Under the influence and mandate of, for instance, the ASTM standards, the scientists started using ordinary TGA as their main tool of CO_2 quantification. The ASTM C1910/C1910M-23 standard [28], for instance, recommends them to use an ordinary TGA (which does not have the ability to analyze the evolved gases) and start their CO_2 quantification by looking at the weight loss that took place at temperatures beyond 550°C. Until this point, everything seemed so-so.

[28] ASTM Standard C1910/C1910M-23, "Standard test methods for cements that require carbonation curing," ASTM International, West Conshohocken, Pennsylvania, U.S.A.

Something "not OK" started happening. The scientists were using an ordinary TGA and taking the cutoff temperature of 550°C (for $CaCO_3$) by observing the ASTM standards and running their TGA from room temperature until the end temperature of either 950° or 1000°C. The 550° to 950/1000°C range is where calcite would thermally decompose into CaO(s) and CO_2(g). Calcite will not decompose at 400°C, 450°C, and 500°C. (By the way, that 550°C does not apply to magnesium carbonate ($MgCO_3$); see Ref. 29.)

Our scientists started to name any TGA-weight loss observed below 550°C in a TGA trace, *i.e.*, at 500, 450 or even at 400°C, as "decomposition of amorphous calcium carbonate." By doing this, they were also mistakenly or intentionally increasing the total mass of CO_2 mineralized in their end product. This is not good! Those were the people who knew almost nothing about ACC.

• This was why I prepared this document with so many references contributed by competent research groups, hopefully, many can now see that ACC will form as a metastable precursor (transient) to vaterite, aragonite or calcite and ACC will come with around 15 wt% water in it, but upon heating, it will first lose its structural water up to a temperature like 330-340°C, and when it loses that water, it will instantly crystallize into calcite (or vaterite or aragonite) accompanied with an exothermic reaction. Then, this crystalline $CaCO_3$ will start its thermal decomposition at or above 550°C.

[29] D. Mahon, G. Claudio, and P. Eames, "An experimental study of the decomposition and carbonation of magnesium carbonate for medium temperature thermochemical energy storage," *Energies*, 14, 1316 (2021).

When one is working with non-crystalline materials, there may be different kinds of "combined (or retained or structural) water." Each of those kinds will start their evaporation at different temperatures, each kind having a different dehydration enthalpy.

1st kind of combined water: evaporates over 100° to 150°C, liquid water physically present in the small pores/capillaries of the amorphous material,

2nd kind of combined water: evaporates over 150° to 350°C, water molecules attached by hydrogen bonds,

3rd kind of combined water: evaporates over the range of 350° to 600°C, water molecules entrapped (during its synthesis) in the mesopores of the substance. If the material's synthesis water contained carbonate ions, then this mesopore water will also release small amounts of $CO_2(g)$ during this heating.

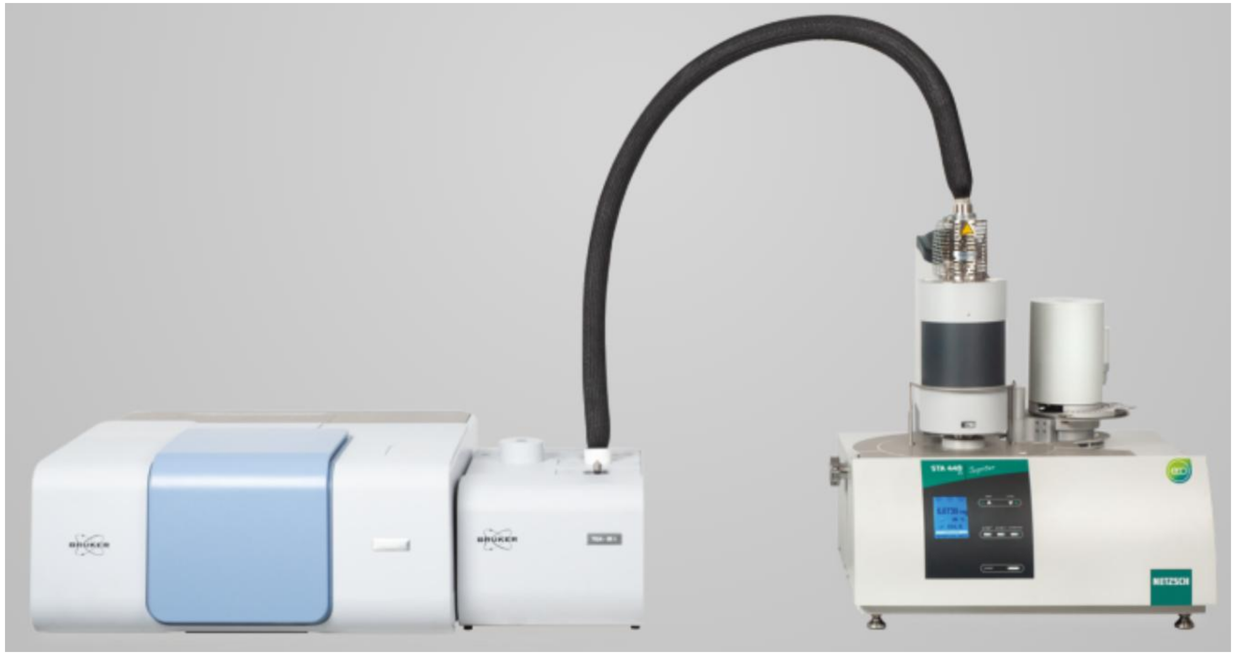
- The 3rd kind of water is the trickiest one since the evaporation temperature range of "water held in the mesopores" simply dives into the 550-950°C range at which the ASTM-specified CO_2 quantification work is performed (by using an ordinary TGA).

- The 3rd kind of water would especially be present in carbonated calcium (or magnesium) silicate-based substances (including basalt and slags), the "by-product amorphous silica" in such has lots of those mesopores and they will not easily let that water to go out at temperatures below 350°C.

The scientists, who started practicing what we described in the previous pages, were "not given the right tool" for CO2 quantification, they only have an ordinary and relatively inexpensive TGA.

There are two instruments out there, available since a long time, but more expensive than an ordinary TGA: (1) **combined TGA-MS** (MS: mass spectrometer) and (2) **combined TGA-FTIR**. Our scientists are not given these capable instruments.

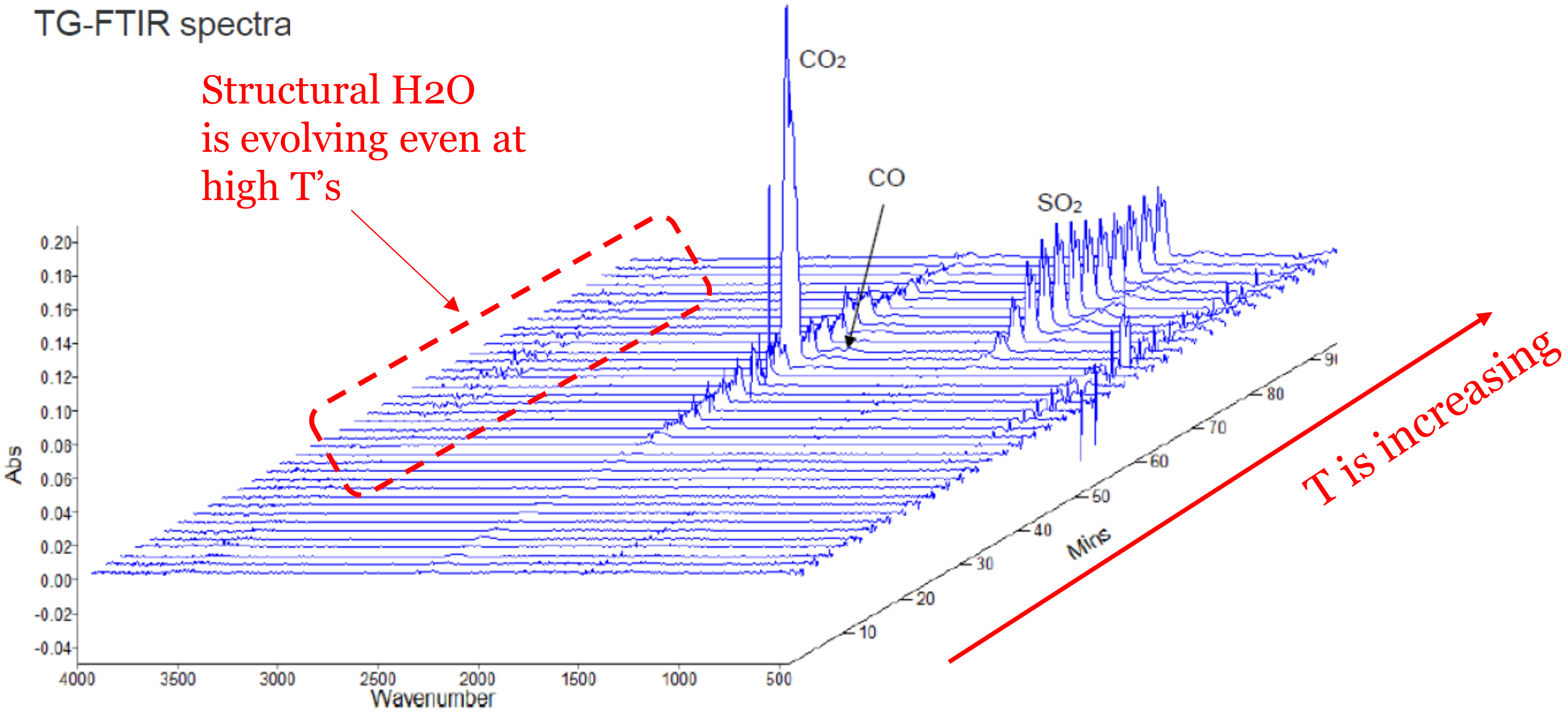
combined TGA-MS (link)



combined TGA-FTIR (link)

Note: Certain commercial instrument vendors are only identified here to foster understanding. Such identifications do not imply recommendation or endorsement by A. C. Tas, nor do they imply that the instruments identified are necessarily the best available for the purpose.

This is the outcome of a "combined TGA+FTIR analysis" performed on a carbonated (*i.e.*, enforced carbonation), industrial-scale calcium silicate-based material. It shows the user at what temperature H_2O, CO_2, SO_2, and other gases (depending on the material studied) will evolve. The CO_2 quantification in an ordinary TGA must then be based on the initial "convincing" information obtained from such a combined TGA-FTIR analysis. (This plot is not that of a typical evolved gas analyzer.)



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Final Words

• be extremely cautious in claiming the presence of "metastable" ACC in a carbonated material (synthetic or natural) studied "only by an ordinary TGA or TGA-DTA or TGA-DSC" just by trying to account for small weight losses observed below 550°C (this T being valid only for CaCO3 formation-based mineralization work); your claim of ACC presence will most probably be dubious

• try to get your hands on a "combined TGA-FTIR" or "combined TGA-MS" instrument if you are in the business of CO2 quantification (you can also use the TGA portion of the above instruments as a stand-alone unit, when needed)