CALCIUM BICARBONATE SOLUTIONS

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Underlined blue texts throughout have hyperlinks.

This and the following four pages serve as a refresher for the reactions almost everyone exposed a bit to the chemical mineral (*e.g.*, alkaline earth cation-containing) weathering [1] processes is aware of.

$$CO_2\,(g) \rightarrow CO_2\,(aq) \qquad (1a)$$

This reaction takes CO_2 (g) molecules (431 ppm as of now) from the atmosphere into water and generates "dissolved CO_2," which is written as CO_2 (aq). This reaction spontaneously occurs if one leaves a glass of water on a desk and the reaction requires a "gas-liquid interface" to be present.

$$CO_2\,(aq) + H_2O\,(l) \rightarrow H_2CO_3\,(aq) \qquad (1b)$$

This reaction starts with dissolved CO_2 and generates "carbonic acid, H_2CO_3." Carbonated beverages have low pH (causing the erosion of the apatitic enamel layer of teeth [2]) and that low pH is due to the presence of carbonic acid in such. Reaction 1b occurs in the liquid phase. If one inserts a plastic tube connected to a CO_2 tank into water (at 1 atm pressure) and starts slowly bubbling CO_2 (g), reactions 1a and then 1b quickly take place and the pH of water decreases sharply (to around 4.4) in a short period of time. The pressure (above that of the atmospheric) inside such carbonated beverage containers serves to increase the concentration of CO_2(aq) and H_2CO_3(aq), therefore, the pH of those become less than 3.

Equation 1b reaches completion at pH values (of the liquid phase) less than 4.

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[1] C. Exley *et al.*, "Silicic acid: the omniscient molecule," *Sci. Tot. Environ.*, 665, 432-437 (2019). (← see its Fig. 2)
[2] E. Beniash *et al.*, "The hidden structure of human enamel," *Nature Comm.*, 10, Art. No: 4383 (2019).

$$H_2CO_3\ (aq) \rightarrow HCO_3^-\ (aq) + H^+\ (aq) \qquad (2)$$

If the pH of the carbonated liquid is higher than 4 and is further increased (*e.g.*, this increase could be provided by the presence of a solid or liquid source of alkalinity in the solution) to 6.36 this reaction will proceed without any difficulty and carbonic acid (*i.e.*, aqueous H_2CO_3) will transform into the aqueous bicarbonate (HCO_3^-) ion.

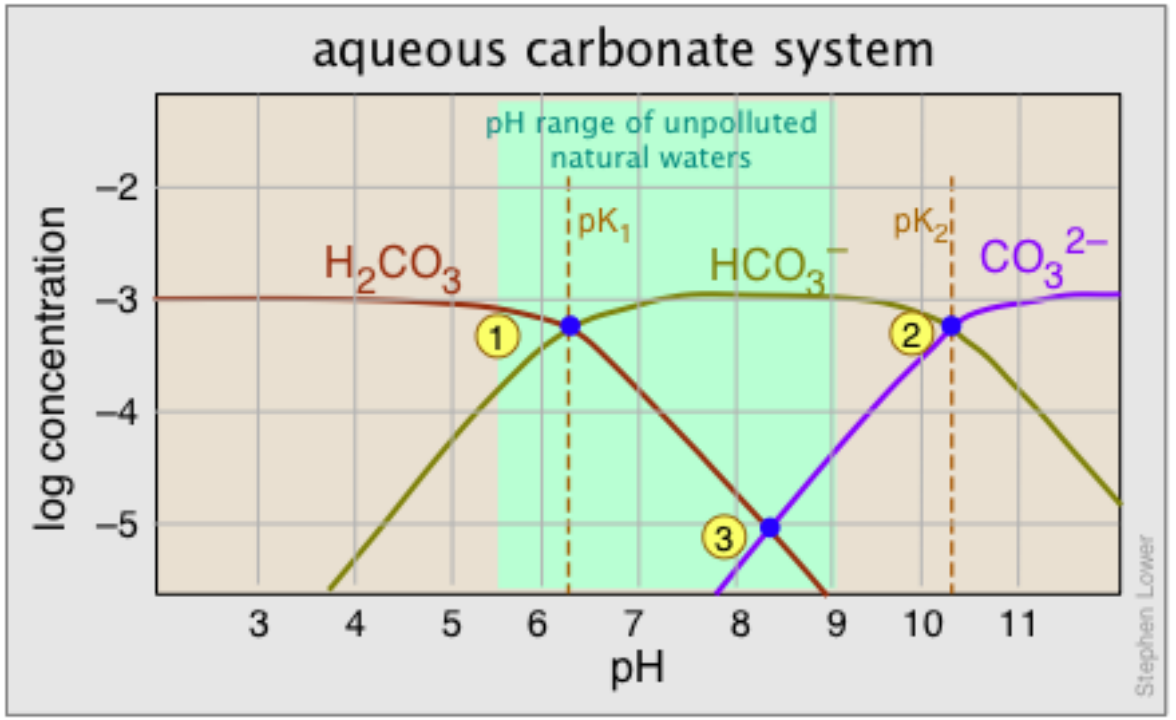
$$HCO_3^-\ (aq) \rightarrow CO_3^{2-}\ (aq) + H^+\ (aq) \qquad (3)$$

Bicarbonate is the major ion stable between pH of 6.37 and 10, however, at pH above 10 the carbonate (CO_3^{2-}) becomes the major ion. The below diagram summarizes the above.

One can use the below open access links to find out how the curves of the diagram at right were calculated.

Link-1 for potable water:
https://irp-cdn.multiscreensite.com/d34c7248/files/uploaded/Carbonate%20Chemistry.pdf

Link-2 for seawater:
https://www.pmel.noaa.gov/co2/files/dickson_thecarbondioxidesystem inseawater_equilibriumchemistryand measurementspp17-40.pdf



Source of the diagram:

(by Prof. S. Lower):

https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_Chem1_(Lower)/12%3A_Solubility_Equilibria

This page summarizes the contents of the previous pages to reach at the understanding that if one writes the below equation (which is an important reaction for transforming the abundant GHG (greenhouse gas) CO_2 into a solid and "persistent/durable" form)

Mineral (s) + CO_2 (g) + H_2O (l and/or vapor) → Carbonation product of the mineral (s) + unreacted mineral (s) + excess CO_2 (g and/or aq) + excess H_2O (aq and/or vapor) (4),

where the CO2 (g), that could, *e.g.*, be directly taken from a cement or coal-burning power plant's flue gas, shown as a reactant in that equation should go through the below chain reaction:

CO_2 (g) → CO_2 (aq) → H_2CO_3 (aq) → HCO_3^- (aq) and/or CO_3^{2-} (aq) (5).

In order to chemically erode the mineral (under the action of carbonic acid, H_2CO_3 (aq)) "ion-by-ion" (which preferably contains Ca and/or Mg) and then makes bicarbonate (HCO_3-) and/or carbonate (CO_3^2) ions (depending on pH) available to the mineral's leached out alkaline earth Ca^{2+} and/or Mg^{2+}. (The starting mineral may contain Na and K (alkali elements) at significant quantities, they may carbonate to form $NaHCO_3$, $KHCO_3$, Na_2CO_3 or K_2CO_3, but all four are water-soluble carbonates, therefore, even if the carbonated mineral product captured CO_2 (according to equation 4) to form one or more of these alkali carbonates, they are not persistent and durable solid products. They will wash away under rain and emit CO_2 throughout their lifetimes. One rather wants to form compounds of the CaO-CO_2 and/or MgO-CO_2-H_2O and/or CaO-SiO_2-CO_2-H_2O (Ca-carbosilicates) binary, ternary or quaternary systems.

When and if the aim is to nucleate $CaCO_3$ (vaterite, aragonite or calcite), then one needs Ca^{2+} (aq) ions to be present in the liquid phase so that the Ca^{2+} ions (from the mineral of reaction 4) can react with either HCO_3^- (*i.e.*, $CaCO_3$ crystallization events taking place at medium pH) or CO_3^{2-} (*i.e.*, $CaCO_3$ crystallization occurs at high pH) according to the below reactions. Crystallization occurs at the solid-liquid interface and carbonate(s) will form, where the surfaces of those solids will also present a liquid-solid interface. That liquid-solid interface is important since reactions 6 and 7 are both reversible, meaning that if the pH of the liquid phase decreases to 4.4 for any reason, $CaCO_3$ particles will dissolve.

$$Ca^{2+}\,(aq) + HCO_3^-\,(aq) \rightarrow CaCO_3\,(s) + H^+\,(aq) \qquad (6)\ \textit{medium pH}$$

$$Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \rightarrow CaCO_3\,(s) \qquad (7)\ \textit{high pH}$$

What could be the source of Ca^{2+} ions in the liquid phase?

1.) dissolved water-soluble salts of calcium, namely, Ca-chloride, Ca-nitrate, Ca-acetate, *etc.*,

2.) expensive Ca metal [3],

3.) any inexpensive solid that has the ability to "leach out" (*a hydrometallurgical term*) Ca^{2+} into the liquid phase in the presence of CO2 (g) (and *via* carbonic acid), such as an industrial waste gas that contains CO_2 in it. This third possibility is what the chemical mineral weathering industry practices [4] in the name of transforming an undesired source of GHG (greenhouse gas) CO_2 gas into a solid $CaCO_3$ form. One now works with a three-phase equilibrium established at the liquid-gas-solid interface.

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[3] A. C. Tas, "Synthesis of amorphous calcium phosphate or poorly crystalline calcium phosphate powders by using calcium metal," U.S. Patent No: 9,108,860, August 18, 2015.

[4] A. C. Tas *et al.*, "Production of Supplementary Cementitious Materials through Wet Carbonation Method," U. S. Patent Application No: 2023/0382792 A1, November 30, 2023.

The significance of the three-phase liquid-gas-solid interface:

(*i*) liquid is essential since one cannot otherwise have Ca^{2+} (aq) ions in the system,
(*ii*) CO_2 gas is essential to the extent that the rate of uninterrupted CO_2 supply (as micro-bubbles) to the system should be high enough so that all Ca^{2+} (aq) present in the system must be converted to $CaCO_3$ in real time, otherwise the efficiency of the process in generating $CaCO_3$ (or Mg-carbonates or hydroxycarbonates of the MgO-CO_2-H_2O ternary) will be unacceptably low and that will adversely affect the economics of the chemical weathering process,
(*iii*) the solid, which is comprised of fine particulates of a chosen mineral or industrial waste that will serve as the Ca^{2+} source, must possess sufficient surface reactivity. That surface reactivity is typically governed by the combination of the particle size distribution, BET surface area and surface chemistry of the particulate material used.

The rate of agitation of the liquid and the size of the micro-bubbles of the CO_2-containing gas introduced into it are extremely important, as well as the temperature and pressure of the reaction system.

The fine particles used as the source of calcium (and/or magnesium) should not have hydrophobic surfaces, meaning that some organic residues that may be originally covering (partially or completely) the surfaces of such particles may decrease their hydrophobic character and that needs to be avoided. The surface composition/chemistry of the particulate material must be carefully investigated with analytical tools.

$$Ca^{2+}\,(aq) + 2HCO_3^{-}\,(aq) \rightarrow Ca(HCO_3)_2\,(aq) \qquad (8a)$$

Calcium bicarbonate forms according to this simplified reaction.

The generation of aqueous Ca-bicarbonate by equation 8 can occur through a few different routes as shown below, but there will always be one requirement, *i.e.*, the prevalence of the "2:1 molar ratio of bicarbonate ions to the Ca^{2+} ions" (and this is how equation 8 differs from equation-6).

Ca^{2+} (aq) + $2HCO_3^-$ (aq) → $Ca(HCO_3)_2$ (aq) (8a),

"1 mole of Ca^{2+} (aq) originating from $CaCO_3$ (s)" + $2HCO_3^-$ (aq) → $Ca(HCO_3)_2$ (aq) (8b),

"1 mole of Ca^{2+} (aq) originating from a Ca-ctg mineral (s) + $2HCO_3^-$ (aq) → $Ca(HCO_3)_2$ (aq) (8c).

In equation **8a**, where one has Ca^{2+} ions coming from (into the water) one of the dissolved water-soluble salts of Ca (such as Ca-chloride, -nitrate or -acetate), the source of HCO_3- could either be CO_2 (aq) or dissolved $(NH_4)HCO_3$ or $NaHCO_3$ or $KHCO_3$ salts. Using any ammonium carbonate salt at the industrial scales is quite difficult since the ammonia gas to evolve is highly hazardous and toxic [5], no need to mention the high cost of ammonium bicarbonate salt. Therefore, in these equations one should consider CO_2 (aq) as the HCO_3^- source which is obtained by introducing CO_2 (g) into water. Equation **8b** is for the easiest way of generating aqueous Ca-bicarbonate by starting with CO_2 (aq). There were some excellent applications of this approach in the literature, we will discuss those. Equation **8c**, on the other hand, depicts what an industrialist would observe (if the HCO_3^- concentration was high) who initially wanted to transform any GHG-CO_2 (g) to a solid form by using an aqueous carbonation process and using an inexpensive solid industrial waste to extract the Ca^{2+} ions from.

The first route of generating aqueous Ca-bicarbonate by equation **8a**, shown below, uses, *e.g.*, 0.2 mole of Ca-nitrate tetrahydrate pre-dissolved in the system water (deionized or triply-distilled water), is the least efficient way of forming Ca-bicarbonate (aq).

$$Ca^{2+}\,(aq) + 2HCO_3^-\,(aq) \rightarrow Ca(HCO_3)_2\,(aq) \qquad (8a)$$

When one then adds, let's say, 0.4 mole of $NaHCO_3$, most of the Ca^{2+} (aq) will react with the HCO_3^- ions to precipitate a mixture of solid vaterite and calcite at room temperature and the atmospheric pressure. The clear, transparent mother solution (*a.k.a.* the mother liquor or supernatant) remaining over the precipitates, upon filtering it using a Millipore 0.2 μm filter membrane, will have an extremely low concentration of Ca (which is typically quantified by, *e.g.*, using ICP-OES analysis) while having a high carbonate concentration. In this case, the concentration of the $Ca(HCO_3)_2$ (aq) present in that mother solution will be very low.

If an industrial application is focused on the production of precipitated $CaCO_3$ at bulk/industrial volumes, the processing route shown in equation 8a may be used with the recycling of the mother solution. Nevertheless, when the industrial application is the production of precipitated $CaCO_3$, they typically do not start with so much of an excess of HCO_3^- concentration given by equation 8a. (We are not going to discuss in this note the industrial production of precipitated $CaCO_3$ by slurry carbonation (bubbling of CO_2(g) into an agitated $Ca(OH)_2$ slurry) of finely particulated $Ca(OH)_2$ since such processes [6] push the $Ca(OH)_2$-CO_2-H_2O water reaction to near completion.)

[6] S. M. Shih, C. S. Ho, Y. S. Song, and J. P. Lin, "Kinetics of the reaction of $Ca(OH)_2$ with CO_2 at low temperature," *Ind. Eng. Chem. Res.*, 38, 316-1322 (1999).

We had previously written equation 8b as shown below.

"1 mole of Ca^{2+} (*aq*) originating from $CaCO_3$ (*s*)" + 2(HCO_3^-) (*aq*) → $Ca(HCO_3)_2$ (*aq*) (8b)

One can write its reactants as

$CaCO_3$ (s) in water + 2CO_2 (g) → $CaCO_3$ (s) in water + 2CO_2 (aq) → $CaCO_3$ (s) in water + 2H_2CO_3 (aq) → $CaCO_3$ (s) in water + 2(HCO_3^-) (aq).

Above is a four-step reaction for the reactants of equation 8b and it occurs readily when one bubbles CO_2 (g) through a stirred dispersion of a fine powder of $CaCO_3$ (1 -2 g of $CaCO_3$ in 1 L of water).

$CaCO_3$ (*e.g.*, Fisher Scientific C63 calcite) powder stirred in water yields a pH of 8.3 to 8.5. The carbonic acid generated by the CO_2 bubbling is not enough to dissolve all of the $CaCO_3$ powder. The aim here is not to dissolve all of the starting $CaCO_3$ but rather to form the aqueous species $Ca(HCO_3)_2$, by leaching out of a certain limited quantity of Ca^{2+} from calcite, as a "transparent, precipitate-free solution."

The $Ca(HCO_3)_2$ aqueous species is known since a long time [7] and thus our interest in it since the times of our academic studies on the physiological solution/media development [8].

[7] W. F. Neuman *et al.*, "Evidence for complex ion formation in the calcium bicarbonate system," *J. Biol. Chem.*, 219, 551-555 (1956).
[8] A. C. Tas, "The use of physiological solutions or media in calcium phosphate synthesis and processing," *Acta Biomater.*, 10, 1771-1792 (2014).

A (*non-exhaustive*) literature survey yields the below peer-reviewed/refereed Journal articles which all synthesized the aqueous $Ca(HCO_3)_2$ solutions. This list of articles will be more than sufficient to serve as an introduction to the topic of this note.

[9] D. F. Zhao *et al.*, "Novel method of generation of $Ca(HCO_3)_2$ and $CaCO_3$ aerosols and first determination of hygroscopic and cloud condensation nuclei activation properties," *Atmos. Chem. Phys.*, 10, 8601-8616 (2010).

[10] J. Jiang *et al.*, "Polymorph and morphology control of $CaCO_3$ via temperature and PEG during the decomposition of $Ca(HCO_3)_2$," *J. Am. Ceram. Soc.*, 95, 3735-3738 (2012).

[11] V. Ivanov *et al.*, "Ecofriendly calcium phosphate and calcium bicarbonate biogrouts," *J. Clean. Produc.*, 218, 328-334 (2019).

[12] Y. Wang *et al.*, "Effect of calcium bicarbonate on the properties of ordinary Portland cement paste," *Constr. Build. Mater.*, 225, 591-600 (2019).

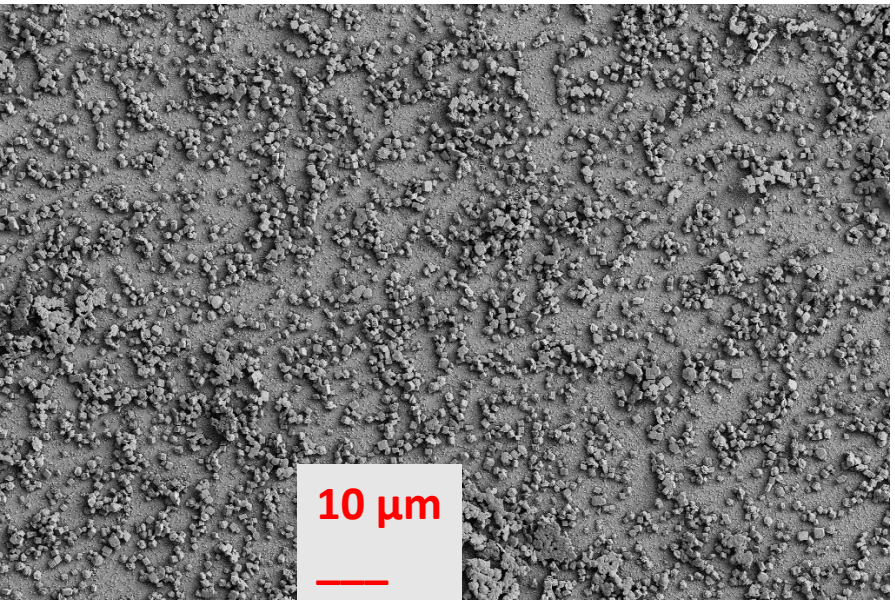
[13] I. Maruyama *et al.*, "A new concept of calcium carbonate concrete using demolished concrete and CO_2," *J. Adv. Concr. Technol.*, 19, 1052-1060 (2021).

Reference [7] was the inspiration point of the below experiment. (I was a Professor at that time at the Department of Biomedical Engineering of Yeditepe University (Istanbul, Turkey) and the formation of $CaCO_3$ (vaterite) on the heart valves (*i.e.*, calcification) was one of my research / interest areas.)

Experiment

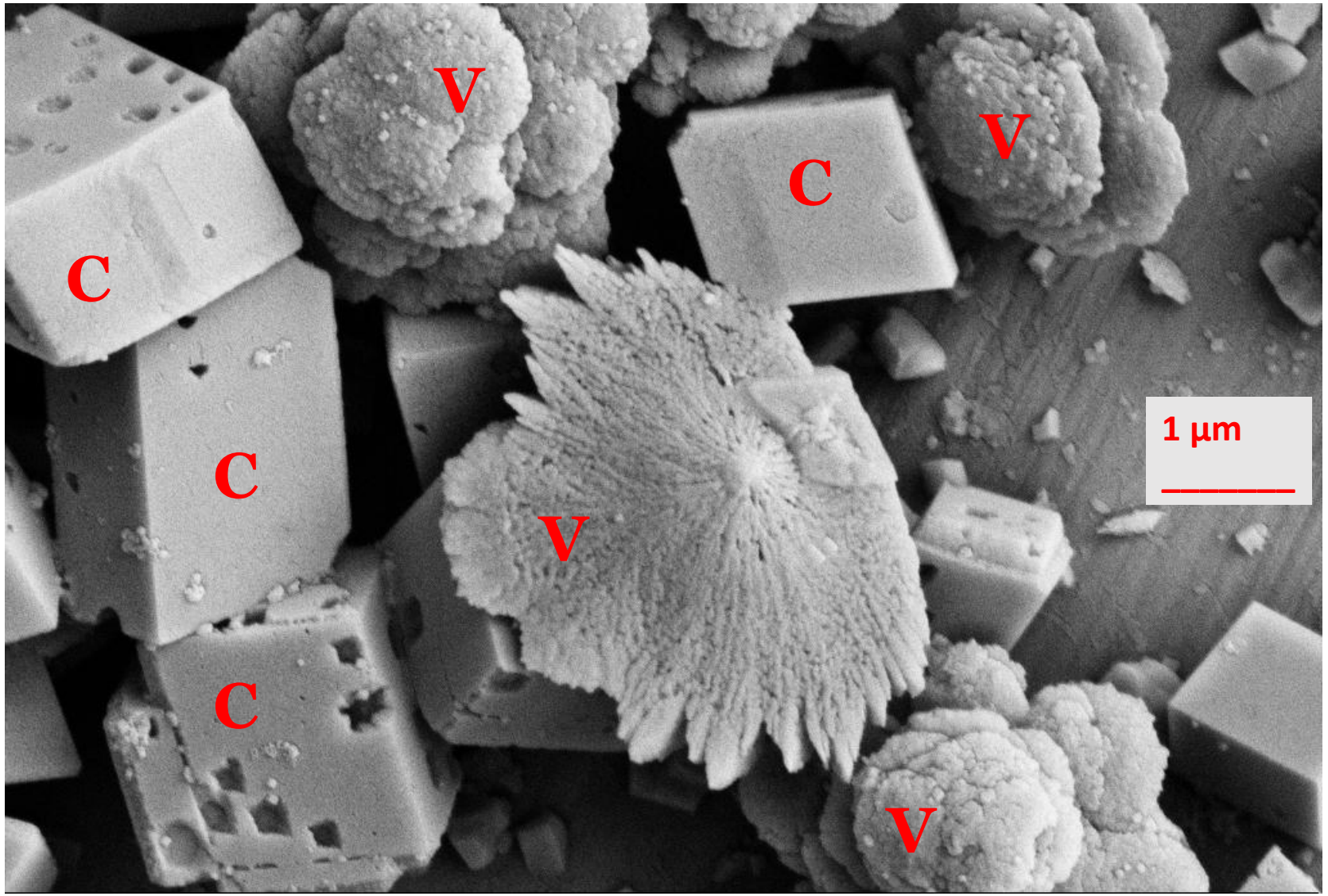
Place 5.0 g of Fisher Scientific C63 calcite powder into an uncovered beaker, followed by adding 1 liter of distilled water. The glass beaker has a Teflon-coated magnetic stir bar inside and the dispersion is stirred (at about 550-600 rpm) at room temperature (23°C) using an ordinary stir plate. A plastic tube (with an inner diameter of 3 mm) attached to a small CO_2 tank is inserted into the beaker (placed inside a fume hood) to bubble CO_2 at a modest rate. The tip of the CO_2 injection tube should reach the level of the stir bar and this ensures breaking of the incoming CO_2 gas into much smaller bubbles. The stirring and CO_2 injection lasts around 90 minutes (pH drops to 6, dependent on the CO_2 injection rate), followed by letting the calcite powder to settle for 20 minutes (without stirring) then filtering the supernatant (transparent mother solution) using 0.2 μm filter membranes in a typical Buechner funnel arrangement. This removes the unreacted calcite. A few SEM (scanning electron microscope) stubs, with conductive C tapes stuck on their flat surfaces, receives 5 drops of the transparent supernatant solution placed on those, followed by evaporating the liquid at 37°C in a drying oven (in a CO_2-free lab) together with the SEM stubs, overnight. Finally, the sample stubs having the "evaporites" are sputter-coated with 20 nm-thick gold prior to the SEM imaging.

[7] W. F. Neuman *et al.*, "Evidence for complex ion formation in the calcium bicarbonate system," *J. Biol. Chem.*, 219, 551-555 (1956).



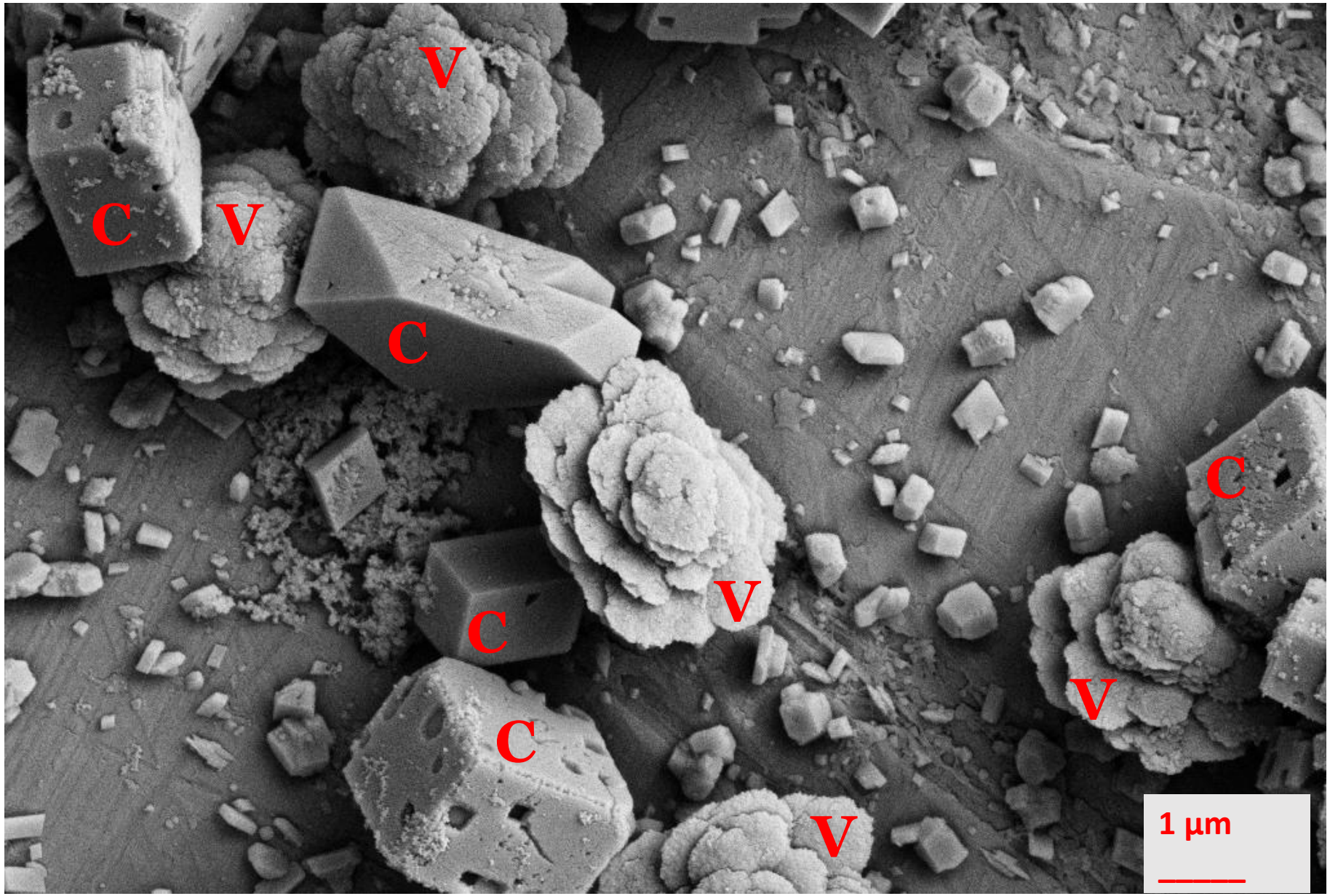
low magnification

C: calcite
V: vaterite



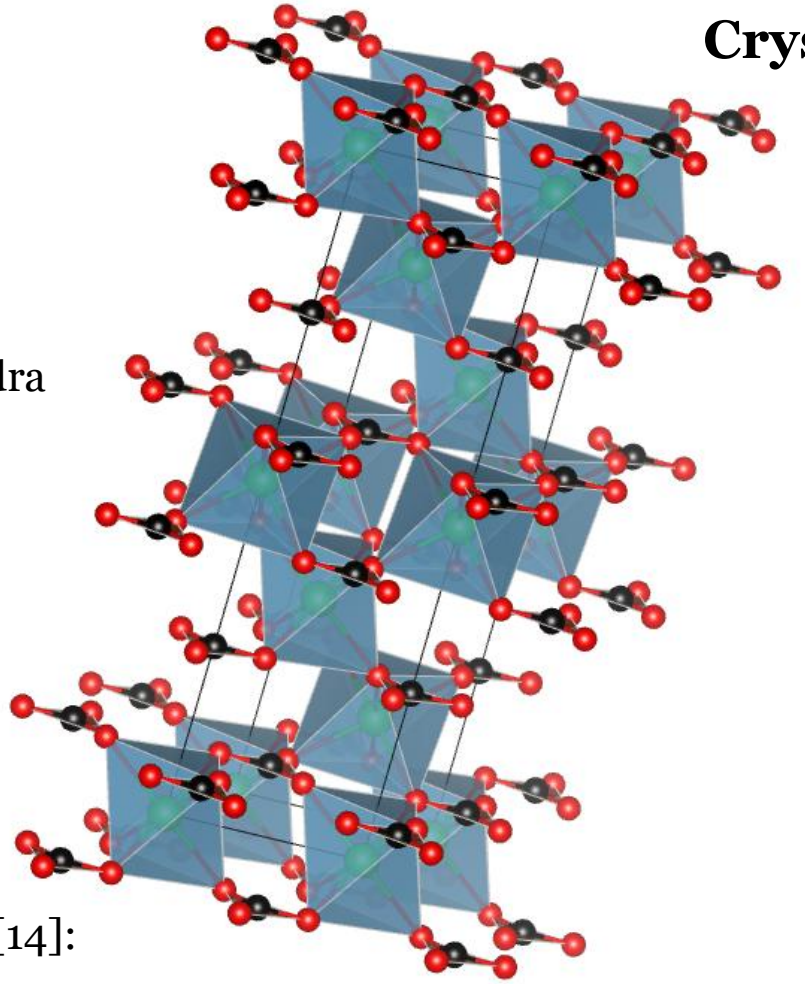
higher magnification

C: calcite
V: vaterite



Crystal structures (*unit cells*)

Red: oxygen
Black: carbon
Green: calcium,
in CaO_6 octahedra



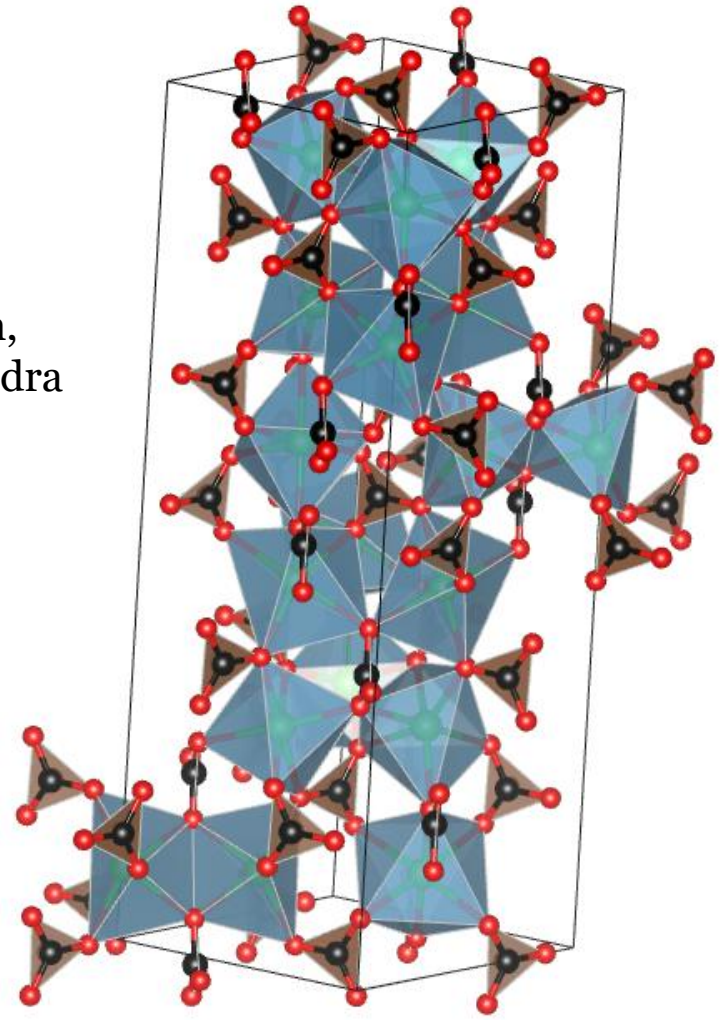
Calcite

log K_{SP} values [14]:
-8.48 at 25°C
-8.56 at 37°C

Rhombohedral/Trigonal
R -3 c (S.G. 167)
a=b=4.99 Å, c=17.0615 Å
α=β=90°, γ=120°
CIF: amcsd 0000098
Density: 2.710 g/cm³

[14] L.N. Plummer and E. Busenberg, *Geochim. Cosmochim. Acta*, 46, 1011–1040 (1982).

Red: oxygen
Black: carbon
Green: calcium,
in CaO_6 octahedra



Vaterite

log K_{SP} values [14]:
-7.91 at 25°C
-8.05 at 37°C

Hexagonal
vaterite is known to have some disorder
P 6_5 2 2 (S.G. 179)
a=b=7.29 Å, c=25.302 Å
α=β=90°, γ=120°
CIF: amcsd 0004854
Density: 2.645 g/cm³

The previous slides showed that one can easily prepare a transparent "calcium bicarbonate solution."

What happened in preparing such a calcium bicarbonate solution pregnant to produce $CaCO_3$, only upon its drying at a summertime temperature, can be explained by the below reaction taking place in water, if one ever needs an equation for it.

$$CaCO_3\,(s) + \{2CO_2(g) \rightarrow 2CO_2(aq) \rightarrow 2(HCO_3^-)\,(aq)\} \rightarrow Ca(HCO_3)_2\,(aq) + \text{unreacted } CaCO_3\,(s) \qquad (9)$$

The name vaterite originates from the work of Prof. Heinrich A. Vater and his meticulous contributions during the last years of the 19th century. It seems like he is the first one in the literature to prepare and name a "calcium bicarbonate solution."

I will now provide one of Vater's work dated back to 1897 [15]. It may be agonizing for some to see that nowadays we have some prominent Journal Editors who want, in writing, from their potential authors to limit the timespan of the list of references of the submitted manuscripts to the last two decades or so.

[15] H. Vater, "XXI. Ueber den Einfluss der Lösungsgenossen auf die Krystallisation des Calciumcarbonates," *Zeitschrift für die Krystallographie und Mineralogie*, 27, 477-512 (1897).

Zeitschrift für Krystallographie und Mineralogie
27 (1897) 477–512

XXI. Ueber den Einfluss der Lösungsgenossen auf die Krystallisation des Calciumcarbonates.

Theil V.

Die scheibenförmigen Krystalliten des Calciumcarbonates.

Von

Heinrich Vater in Tharandt [1]).

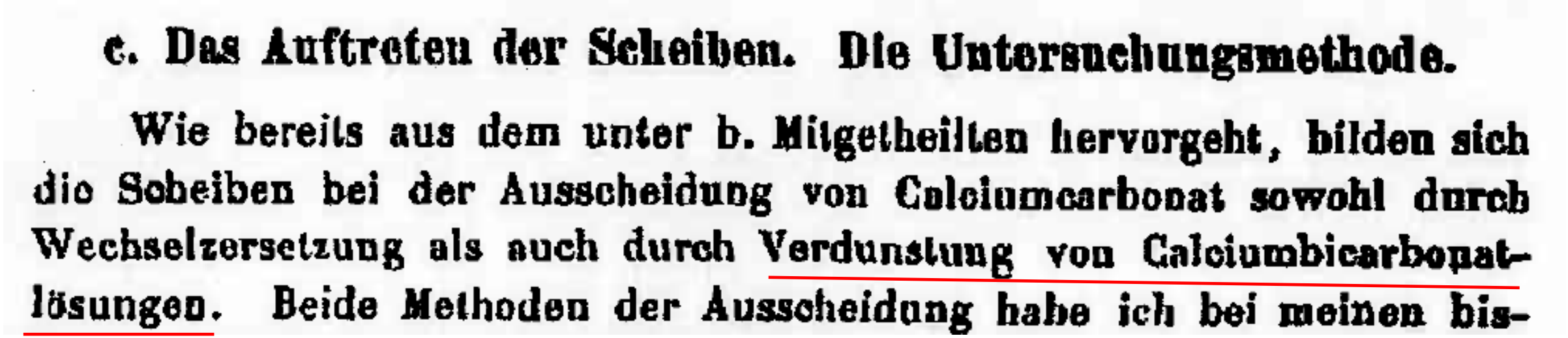
(Mit 8 Textfiguren.)

Inhalt: a. Einleitung. S. 477. — b. Die bisherigen Angaben über die Scheiben. S. 478. — c. Das Auftreten der Scheiben. Die Untersuchungsmethode. S. 482. — d. Entwickelung und Eigenschaften der farblosen Scheiben. Versuch 55. S. 485. — e. Gefärbte Scheiben. S. 494. — f. Die Abhängigkeit des Auftretens der Scheiben von dem Gehalte

This [paper] [15] in German, published by Heinrich A. Vater in 1897, is from my personal archive (from my years as an academician) like the original experimental work of the current note.

The address at the top of the 1st page of this article is in my hand-writing dated back to mid 90s, the time when I first received a paper copy of this significant article.

Below is the first sentence of Section C of Vater's 1897 article.



c. Das Auftreten der Scheiben. Die Untersuchungsmethode.

Wie bereits aus dem unter b. Mitgetheilten hervorgeht, bilden sich die Scheiben bei der Ausscheidung von Calciumcarbonat sowohl durch Wechselzersetzung als auch durch Verdunstung von Calciumbicarbonat-lösungen. Beide Methoden der Ausscheidung habe ich bei meinen bis-

Below is my attempt to translate it into English.

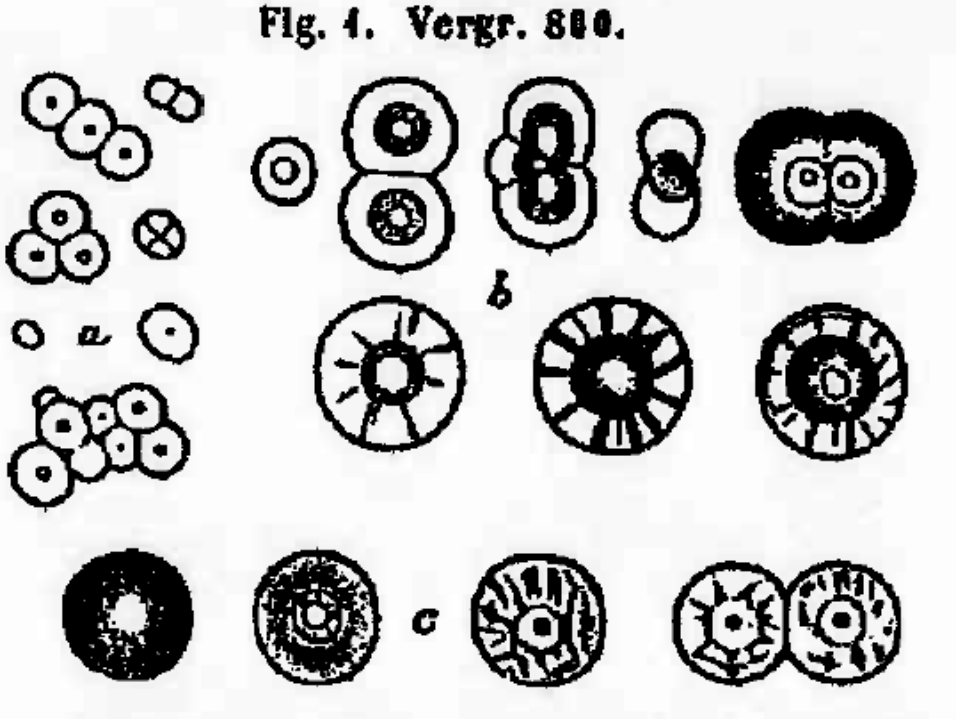
"c. The appearance of the discs. The investigation method.

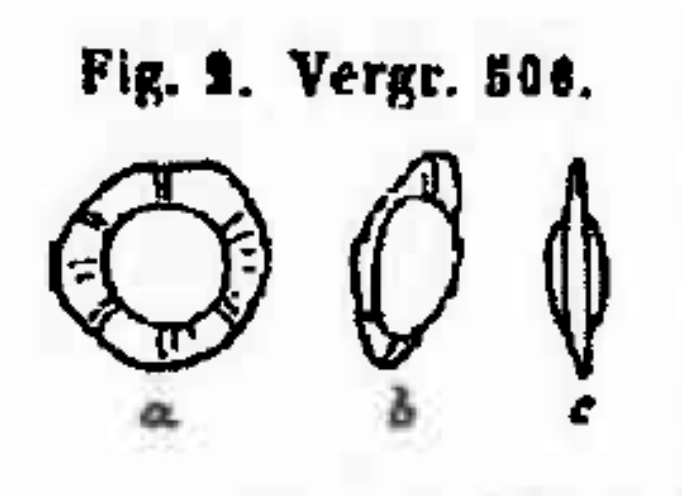
As already stated under b (Section b), the discs form during the precipitation of calcium carbonate both by alternating decomposition and by evaporation of calcium bicarbonate solutions."

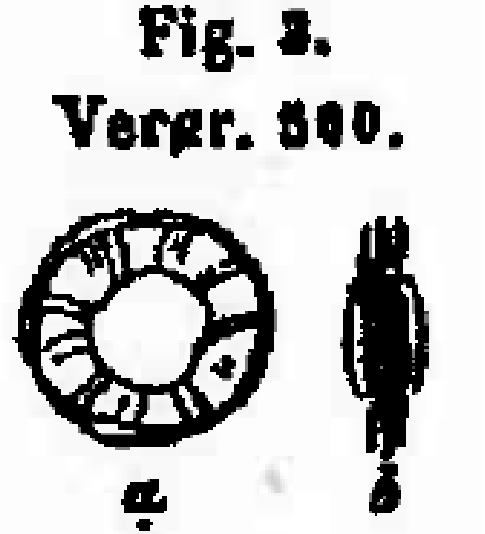
I was not able to find, yet, any literature evidence on the mention "calcium bicarbonate solutions" prior to the year 1897. Heinrich Vater was apparently the pioneer.

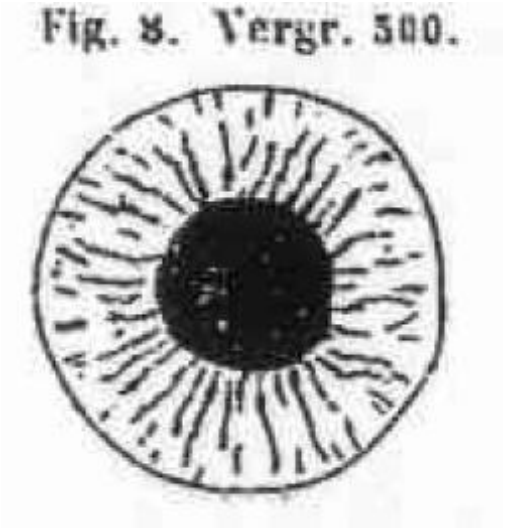
I will now provide some of his hand-drawings of the precipitates he observed by using an optical microscope that can readily reach magnifications of 500 to 800 times. All images come from Heinrich Vater's 1897 article [15].

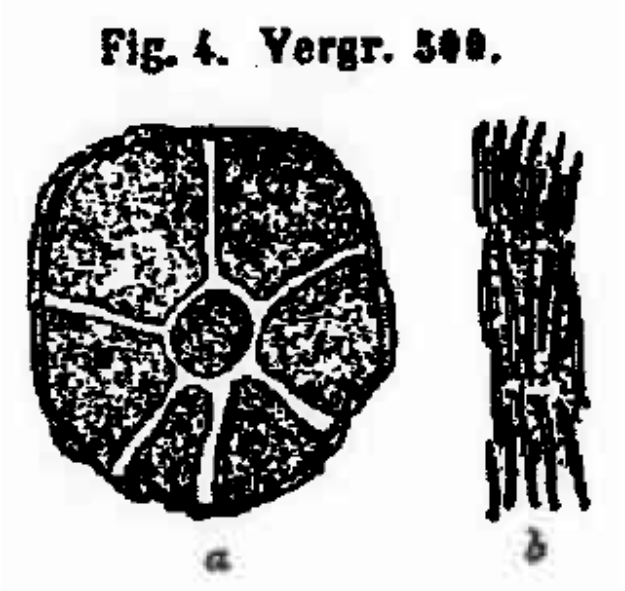
Vater prepared the calcium bicarbonate solutions by using the water-soluble salts of Ca-chloride and ammonium carbonate (prior to evaporation); it is indeed possible to obtain precipitate-free solutions even when using and aqueous mixture of these two salts. However, since Vater did not inject CO_2, the pH of his solutions cannot be as low as 6.

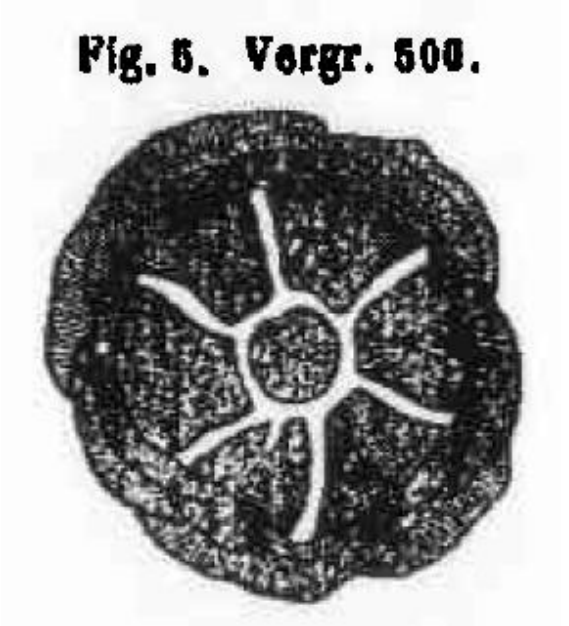












H. Vater indicated the microscope magnifications at the top of each figure [15].

There are five recent studies involving the Ca-bicarbonate solutions, which we cited before in p. 11. The highly interested parties are advised to take a look at those.

(a) Ref [9], publication year 2010; 2 g of calcite in 1 L deionized water, stirred by pure CO_2 bubbling at 22°C, obtained clear $Ca(HCO_3)_2$ solution
(b) Ref [10], publication year 2012; 0.6 g of **$Ca(OH)_2$** in 1 L of water with CO_2 injection for 1 h, then removed $CaCO_3$ precipitates ($Ca(OH)_2$ particles are rapidly converted to $CaCO_3$ under these conditions) by filtration, finally heated the clear solutions at 70, 80 or 90°C; obtained well-crystallized rhombohedral (cuboids) $CaCO_3$ from the initially clear $Ca(HCO_3)_2$ solutions (their SEM photos did not show much of vaterite, which is normal, vaterite will not be stable at such high temperatures; note that my study was performing the solution evaporation on the SEM stubs and at 37°C (to observe vaterite particles as previously depicted by Heinrich Vater)
(c) Ref [11], publication year 2019; 1 g of calcite placed in 1 L of tap water, injected 0.5 L of CO_2 to the dispersion to obtain $Ca(HCO_3)_2$ solution with a pH of 6 to 6.3 (after decanting the clear solution)
(d) Ref [12], publication year 2019; used calcium bicarbonate in powder form
(e) Ref [13], publication year 2021; injected CO_2 to a reservoir containing limestone powder at its bottom (limestone having both Ca and Mg, most natural limestones have both of these alkaline earth elements and the presence of Mg is known to promote aragonite formation) whose temperature was kept at around 4°C (note that H. Vater also studied 4°C in his 1897 work [15])

The precipitate-free Ca-bicarbonate solutions can be used as solutions in numerous applications, that are not only limited to the cement and concrete industry, and such clear solutions will nucleate small $CaCO_3$ crystals upon heating above the ambient temperature.

Currently, when engineers of a wide spectrum of industrial applications need to add micron-size calcium carbonate particles in rather limited quantities (such as a few tons per week) into their process, the first thing they can think of is grinding natural limestone to a top particle size of 1 μm to quickly find out that such a grinding step is quite expensive.

Ref. [13] found out that in order to produce what is named as a calcium carbonate concrete (CCC), by using the Ca-bicarbonate solution, one would need 100 times larger volume of Ca-bicarbonate solution for a CCC comprised of calcium carbonate as the binder while the aggregate is recycled concrete, *i.e.*, mimicking the $CaCO_3$-concretion as observed in the seabed.

One does not need to use pure CO_2 to obtain the Ca-bicarbonate solution from inexpensive high purity limestone, what is needed, most probably, could be to intelligently design a water reactor (to operate at the ambient temperature) in which one can increase the air in and out rates (air contains 431 ppm CO_2 today, indoor air may have 600-800 ppm CO_2, if not one may enrich the air with a bit of CO_2 to reach at a final concentration of 5,000 ppm CO_2).

• In cement hydration, which can be translated to concrete, the $Ca(HCO_3)_2$ solution will react with the hydration product $Ca(OH)_2$ of the hydrating cement according to the below reaction.

$$Ca(HCO_3)_2\ (aq) + Ca(OH)_2\ (s) \rightarrow 2CaCO_3\ (s) + 2H_2O\ (l) \qquad (10)$$

This reaction generating liquid H_2O could help the *in situ*, internal curing of concrete that may lead to an increased strength, as previously reported by Wang *et al.* [12] (see p. 11 for its citation).

• Suppose that an engineer carbonated a concrete form by keeping it in a humidified CO_2-chamber for a certain time. One could observe the following situation. Over-curing (timewise) may cause a decrease in the "out-of-the-chamber" strength of the concrete form. However, our engineer may find that when he/she dried the CO_2-cured concrete form at above 100°C for long times, the desired strength is again observed, but the engineer cannot add the extra cost of that drying to the cost analysis he was given. Then, the below equation will explain what happened. The $CaCO_3$ shown in the reactants denotes the $CaCO_3$ formed during the "optimal" curing time and the sample was kept in the CO_2 chamber being exposed to more CO_2 (g) and H_2O (g), while both forming carbonic acid on the surfaces of the $CaCO_3$.

$$CaCO_3\ (s) + CO_2\ (g) + H_2O\ (g) \rightarrow Ca(HCO_3)_2\ (aq) \qquad (11)$$

The strength responsible from the optimally formed $CaCO_3$ decreased due to the chemical erosion by carbonic acid and some of the already incorporated CO_2 went into the liquid state (forming Ca-bicarbonate); only upon drying at above 100°C, the water of Ca-bicarbonate evaporated and the new $CaCO_3$ crystals formed as shown in this note, thus the strength bounced back only upon drying.

• One may "directly" collect the FTIR data (by using a proper liquid IR cell) of the transparent, clear, precipitate-free $Ca(HCO_3)_2$ solution as a characterization tool. The $Ca(HCO_3)_2$ solution would, most probably, exhibit its characteristic bands at 1032 and 1052 cm^{-1}.

On the other hand, the liquid IR bands of HCO_3^- (*i.e.*, bicarbonate) are observed at 1007, 1337 and 1360 cm^{-1}. (*Only for the HCO_3^- work: one may dissolve a small amount of $NaHCO_3$ powder in deionized water before collecting the liquid IR spectrum of the resultant solution.*)

• Is it feasible to inject CO_2 into the wash water (that is generated during the production of concrete and includes cement and/or SCM particulates) and then reuse that carbonated wash water as the mix water of concrete? Yes, this was already detailed in the U.S. Patent No. 11,958,212 B2 (G. S. Monkman *et al.* "Methods and compositions for treatment of concrete wash water," April 16, 2024).

Supplementary literature on $CaCO_3$ (available here)

[16] A. C. Tas, "Aragonite coating solutions (ACS) based on artificial seawater," *Appl. Surf. Sci.*, 330, 262-269 (2015).

[17] 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," *J. Am. Ceram. Soc.*, 97, 3052-3061 (2014).

[18] A. C. Tas, "The use of physiological solutions or media in calcium phosphate synthesis and processing," *Acta Biomaterialia*, 10, 1771-1792 (2014).

[19] P. R. Larson, A. S. Madden, and A. C. Tas, "Non-stirred synthesis of Na- and Mg-doped, carbonated apatitic calcium phosphate," *Ceramics International*, 39, 1485- 1493 (2013).

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[22] A. C. Tas, "Monodisperse $CaCO_3$ microtablets forming at 70°C in prerefrigerated $CaCl_2$-Gelatin-Urea solutions," *International Journal of Applied Ceramic Technology*, 6, 53-59 (2009).

[23] A. C. Tas, "Use of vaterite and calcite in forming calcium phosphate cement scaffolds," *Ceramic Engineering and Science Proceedings*, 28(9), 135-150 (2008).

[24] A. C. Tas, "Porous, biphasic $CaCO_3$-calcium phosphate biomedical cement scaffolds from calcite ($CaCO_3$) powder," *International Journal of Applied Ceramic Technology*, 4, 152-163 (2007).

[25] A. C. Tas and F. Aldinger, "Formation of apatitic calcium phosphates in a Na-K-phosphate solution of pH 7.4," *Journal of Materials Science: Materials in Medicine*, 16, 167-174 (2005).

[26] A. C. Tas, "Calcium carbonate microtablets and method for the preparation thereof," U.S. Patent No. 8,470,280, June 25, 2013.