


Article

# Influence of Selected Saccharides on the Precipitation of Calcium-Vaterite Mixtures by the CO<sub>2</sub> Bubbling Method

Donata Konopacka-Łyskawa <sup>1,\*</sup>, Natalia Czaplicka <sup>1</sup>, Barbara Kościelska <sup>2</sup>, Marcin Łapiński <sup>2</sup> and Jacek Gębicki <sup>1</sup>

<sup>1</sup> Department of Process Engineering and Chemical Technology, Faculty of Chemistry, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland; nat.czap1@student.pg.edu.pl (N.C.); jacek.gebicki@pg.edu.pl (J.G.)

<sup>2</sup> Department of Solid State Physics, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland; basia@mif.pg.gda.pl (B.K.); marcin.lapinski@pg.edu.pl (M.Ł.)

\* Correspondence: donata.konopacka-lyskawa@pg.edu.pl; Tel.: +48-58-347-2910

Received: 31 January 2019; Accepted: 20 February 2019; Published: 23 February 2019



**Abstract:** Calcium carbonate is a compound existing in living organisms and produced for many biomedical applications. In this work, calcium carbonate was synthesized by a CO<sub>2</sub> bubbling method using ammonia as a CO<sub>2</sub> absorption promotor. Glucose, fructose, sucrose, and trehalose were added into the reaction mixture to modify characteristics of precipitated calcium carbonate particles. To determine the polymorphic form of produced calcium carbonate particles, Fourier transform infrared spectroscopy (FTIR-ATR) and X-ray diffraction (XRD) analysis were performed. Scanning electron microscopy (SEM) was used to estimate the size and shape of produced particles. Mixtures of vaterite and calcite were synthesized in all experiments. The percentage content of the vaterite in the samples depended on used additive. The highest concentration of vaterite (90%) was produced from a solution containing sucrose, while the lowest concentration (2%) was when fructose was added. Saccharides affected the rate of CO<sub>2</sub> absorption, which resulted in a change in the precipitation rate and, therefore, the polymorphic composition of calcium carbonate obtained in the presence of saccharides was more varied.

**Keywords:** calcium carbonate; calcite; vaterite; precipitation; carbonation; additives; saccharides

## 1. Introduction

Calcium carbonate is one of the mostly used compounds in nature and industry. It exists naturally in limestone, marbles, and chalk. Calcium carbonate can be produced by living organisms in the biomineralization process to form shells, cell walls, spicules, or spines. However, synthetic calcium carbonate is manufactured in a precipitation process that allows the obtaining of the product of controlled quality [1]. Calcium carbonate precipitation depends on the factors affecting nucleation and subsequent crystal growth as well as its agglomeration and/or transformation. Parameters such as a supersaturation, temperature, pH, mixing intensity, seed crystals, solvent selection and additives should be controlled to obtain precipitated calcium carbonate (PCC) with defined characteristics [2], which is described, among others by polymorphic composition, morphology, crystal size distribution, surface area, and brightness.

Calcium carbonate can form three anhydrous polymorphs: calcite, aragonite, and vaterite in order of increasing solubility and decreasing thermodynamic stability. The values of solubility products ( $K_{SP}$ ) at temperature 20 °C expressed as  $\log(K_{SP})$  are  $-8.45$ ,  $-8.31$  and  $-7.87$  for calcite, aragonite,

and vaterite, respectively [3]. Calcite and aragonite usually are mono-crystalline and well-faceted particles, while the least stable vaterite crystallizes often as polycrystalline spherical particles that can easily transform into one of the other two polymorphic forms [4–6]. Relatively low density, high porosity, and specific surface area, as well as a greater hydrophilicity characterize vaterite particles. Specific properties of this polymorph, its biocompatibility, non-toxicity, easy degradation in solution of slightly acidic pH and low cost cause that calcium carbonate in vaterite form is proposed as a component of bone implants, abrasives, cleaners, absorbers and encapsulation or drug delivery in biomedicine [7]. Precipitation of vaterite particles has been intensively investigated using various methods and various scale of processes. There are two main methods used to  $\text{CaCO}_3$  synthesis: (i) a liquid-liquid method, when solutions containing calcium ions and carbonate ions are mixed [8–12] and (ii) a gas-liquid method, when carbon dioxide is bubbled into the solution of soluble calcium salt and a  $\text{CO}_2$  absorption promotor such as ammonia or amines [13–15]. Calcium carbonate has been also obtained by other methods such as a  $\text{CO}_2$  diffusion method [8,16,17], and precipitation with using carbonate ions precursors in an ambient [18] or solvothermal condition [19].

Organic soluble organic compounds such as alcohols [12,20,21], aminoacids [8,10,22,23], amines [23,24], saccharides and polysaccharides [16,25–29], as well as proteins [27,30] can influence on calcium carbonate precipitation. Different explanations of the role of additives during the formation of  $\text{CaCO}_3$  polymorphs are proposed. Most often, the action as a stabilizer of the unstable calcium carbonate form is attributed to organic substances that prevent transformation of vaterite particles to calcite [6,20,22,26]. Also, the interactions of additives with the faces of mineral particles are discussed [6,24–26]. Furthermore, the organic additives can decrease the free energy of nucleation [8] and affect the rate of calcium carbonate precipitation [20].

The effect of mono- and disaccharides on the calcite and vaterite synthesis was studied in the  $\text{CO}_2$  diffusion system [16] and during  $\text{CaCO}_3$  precipitation on polyelectrolyte film by providing continuously two solutions of reactants [28]. The enhancement nucleation of calcite was reported for all tested saccharides in the diffusion method [16]. Also, an increase in the concentration of calcite in PCC on the surface of used polyelectrolyte films was observed [28]. However, almost no effect of fructose and sucrose on calcite characteristics was observed when precipitation was carried out in the gas-liquid system by the ethanolamine process [31] or in the gas-slurry system using calcium hydroxide as a substrate [32], but a higher degree of particles agglomeration in both studies was observed.

Therefore, in this work the influence of glucose, fructose, sucrose, and trehalose on the precipitation of calcium carbonate was investigated. The used saccharides are non-toxic and calcium carbonate prepared in their presence can be used as an additive to cosmetic and pharmaceutical preparations. The  $\text{CO}_2$  bubbling method was used to obtain mixture of vaterite and calcite particles. The applied procedure allowed comparison of the effect of tested additives on the characteristics of the obtained calcium carbonate particles in the gas-liquid systems. As discussed earlier, no studies have been carried out to assess the effect of saccharides on the transformation of less stable vaterite in calcite during the precipitation of calcium carbonate in the gas-liquid system. It is known that the reaction carried out with the use of  $\text{CO}_2$  gas is controlled by its absorption into the reaction mixture. We assume that the addition of saccharides affecting the  $\text{CO}_2$  absorption may result in a change in the precipitated  $\text{CaCO}_3$  particles.

## 2. Materials and Methods

### 2.1. Reagents

Calcium chloride, anhydr. (STANLAB), ammonium carbonate (POCH), ammonium hydroxide solution 25% in water (POCH), sucrose, glucose, fructose (Sigma-Aldrich) were of analytical reagent grade and were used in this study without further purification. Trehalose was synthesized in the Department of Chemistry, Technology, and Biotechnology of Food, Faculty of Chemistry, Gdansk



University of Technology and its purity was minimum 98%. Water purified by a reverse osmosis method was used to prepare all solutions. Carbon dioxide was purchase from Oxygen s.c.

## 2.2. Preparation

Synthesis of calcium carbonate was carried out at room temperature (22 °C) in a 250 mL beaker equipped with a gas distributor made of sintered glass, a pH electrode, and a magnetic stirrer. 150 mL of the solution containing 400 mM calcium chloride and 600 mM ammonium hydroxide were used in all experiments. Glucose, fructose, sucrose, or trehalose was used in experiments with saccharides. The concentration of additives was equal to 90 mM.

The CO<sub>2</sub> flow rate was adjusted to 10 dm<sup>3</sup>/h and a stirrer speed was controlled to be around 200 rpm. pH values of a reactive mixture were measured every 1 s with a pH electrode and recorded in a computer. Precipitation of calcium carbonate was carried out until the reaction mixture reached a pH value of 9.

All produced CaCO<sub>3</sub> precipitates were filtered, washed with methanol and dried at 100 °C.

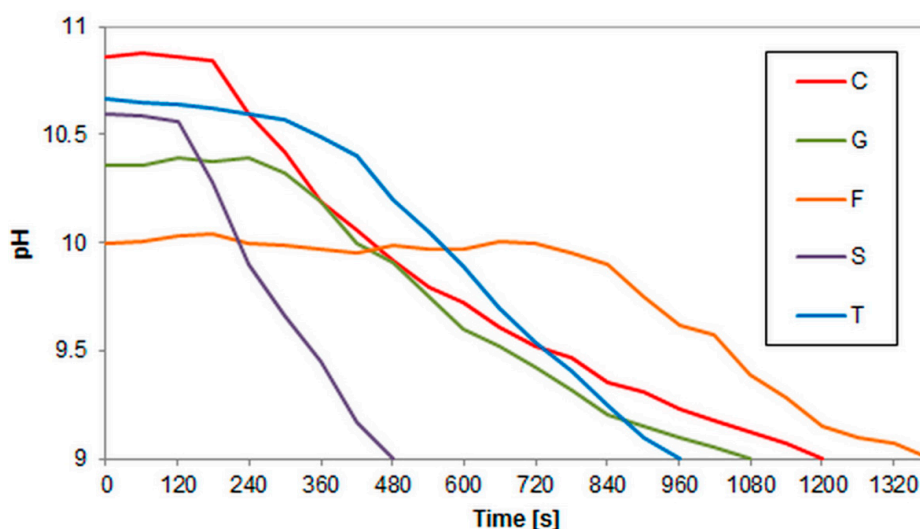
The dynamic viscosity of initial solutions was measured by a rotational viscometer (Brookfield DV-II+) at a shear rate of 200 s<sup>-1</sup>.

## 2.3. Characterization of CaCO<sub>3</sub> Particles

Crystalline structure of calcium carbonate particles and its polymorph composition was determined using the conventional X-ray diffraction analysis (XRD) (Philips X'Pert diffractometer system, PANanalytical, Almelo, The Netherlands) with Cu-K $\alpha$  radiation. The XRD spectra were collected at a scan rate 0.2° and 2 theta range 10–80° at room temperature. To identify the types of chemical bonds in the structural units present in the samples FTIR spectra were recorded on a Nicolet 8700 FTIR spectrometer from Thermo Scientific, (Waltham, MA, USA). The method of suppressed total reflection (ATR) was applied. The infrared spectra were registered from 4500 to 524 cm<sup>-1</sup> at 2 cm<sup>-1</sup> resolution. For the particle characterization scanning electron microscope (SEM) FEI Quanta FEG 250 with an Everhart-Thornley (ET) secondary electron detector (FEI, Hillsboro, OR, US) was used.

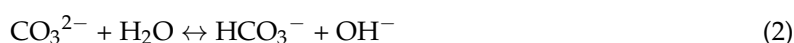
## 3. Results and Discussion

The evolution of the pH during calcium carbonate precipitation with and without saccharides is shown in Figure 1.



**Figure 1.** Evolution of the pH in the reaction mixture without additives (C), with addition of glucose (G), fructose (F), sucrose (S), and trehalose (T).

Changes of the pH values depended on the CO<sub>2</sub> absorption. The region of constant pH was observed at the beginning of all experiments. Significantly lower initial pH value was for a solution containing fructose, while reduction of initial pH values of solutions prepared using other saccharides was smaller. The pK<sub>a</sub> value for fructose is lower than for glucose and sucrose [33,34] (no data on trehalose was found), which means that solutions of fructose have lower pH than other sugars. Our results confirm more acidic properties of fructose and therefore the lower pH of the initial solution during carbonation causes the absorption of CO<sub>2</sub> in the solution to be slower. Extended periods of constant initial pH were for precipitation carried out in the presence of glucose, fructose, and trehalose. The addition of sucrose to the medium resulted in the reduction of the constant pH period compared to the process without the addition of saccharides. Presence of ammonia in investigated systems facilitates CO<sub>2</sub> absorption and causes that pH is, in part, controlled by the ammonia-ammonium and carbonate-bicarbonate buffers [35]:



And therefore, the constant pH period at the beginning of the CO<sub>2</sub> bubbling process is observed as a result of a mild basic buffer formation after entering CO<sub>2</sub> to the system.

When precipitation was carried out by bubbling the time needed to reach the pH assumed value was shorter in the presence of glucose, sucrose, and trehalose. Only the addition of fructose resulted in the longer process time. Values of the initial pH, the time of constant pH periods and the end time of precipitation for performed experiments are summarized in Table 1. Usually a basic pH of a reactive mixture with ammonia enables formation of calcite-vaterite mixture [13,14] and thus the reaction in the bubbling system was conducted until pH 9. The time needed to reach this pH value in these processes depends on the CO<sub>2</sub> transfer from a gas phase to a liquid phase. When saccharides are components of solutions, the shortening of reaction time is most probably caused by the increase of the CO<sub>2</sub> absorption rate. Vasquez et al. [36] reported the enhancement of CO<sub>2</sub> adsorption rate in alkaline buffers when fructose, glucose, or sucrose was added to the solutions. The increase in CO<sub>2</sub> mass transfer from the gas phase to the liquid phase was related to the number of hydroxyl groups in the solute molecules and for the solution containing sucrose was higher than for solutions with glucose or fructose. Our results are consistent with the above-described principle for glucose and sucrose, while the reaction time in fructose solutions was slightly longer than for the control process.

**Table 1.** Summary of precipitation conditions: the viscosity of initial solution ( $\mu$ ), the initial pH ( $\text{pH}_i$ ), the time period of constant pH ( $\tau_{\text{pH const}}$ ), the time of reaction ( $\tau_r$ ).

Saccharide	$\mu$ , mPas <sup>1</sup>	$\text{pH}_i$	$\tau_{\text{pH const}}$ , min	$\tau_r$ , min
- *(C)	1.11	10.9	3	20
Glucose (G)	1.27	10.4	5	18
Fructose (F)	1.41	9.8	13	21
Sucrose (S)	1.51	10.6	2	8
Trehalose (T)	1.45	10.6	6	16

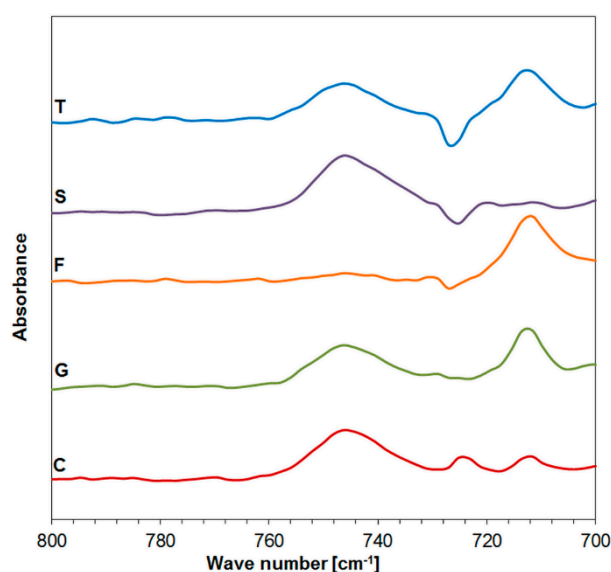
\* experiment without saccharides.

These results corresponds to those reported by Rao et al. [37] who observed a longer nucleation time determined for early stage of precipitation in the presence of fructose and a reduction in a nucleation time when glucose, sucrose, and trehalose were added to the reaction mixture. The concentration of saccharides used in the described studies was lower (20 mM) than that used in our experiments (90 mM), hence probably differences with respect to the control sample.

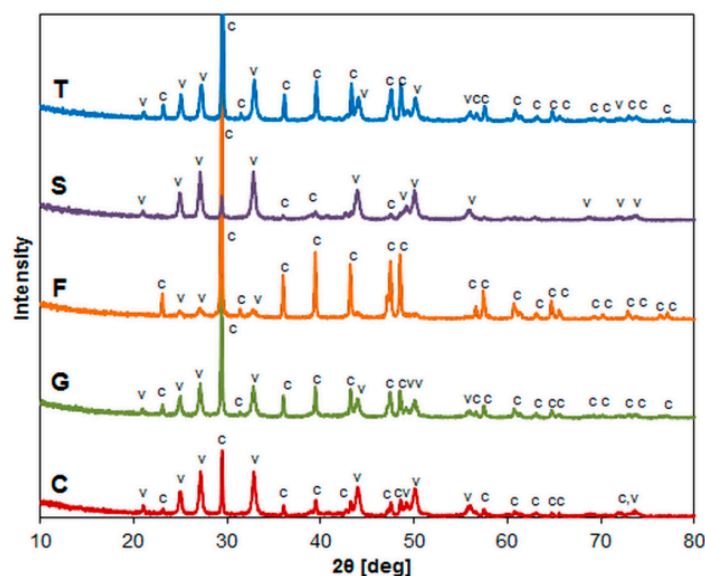
Identification of calcium carbonate polymorphs was based on the FTIR-ATR and the XRD. The fingerprint range of FTIR spectra are in Figure 2 and XRD pattern are in Figure 3. The FTIR



spectra recorded throughout the entire range of wave numbers can be found in Supplementary Materials in Figure S1.



**Figure 2.** FTIR spectra of calcium carbonate particles precipitated without additives (C), with glucose (G), fructose (F), sucrose (S) and trehalose (T).



**Figure 3.** XRD patterns of calcium carbonate particles precipitated without additives (C), with glucose (G), fructose (F), sucrose (S) and trehalose (T).

A peak with the maximum absorption at  $745\text{ cm}^{-1}$  corresponding to vaterite is observed for calcium carbonate samples precipitated without saccharides, with glucose, sucrose, and trehalose. Also, peaks attributed to calcite are in FTIR spectra of calcium carbonate synthesized with addition of glucose or trehalose. However, a characteristic peak for vaterite is not observed in the FTIR-ATR spectrum of calcium carbonate produced with fructose as an additive while a calcite peak is much more intense. The strong absorption in the  $1500\text{--}1400\text{ cm}^{-1}$  region with a characteristic split is observed for calcium carbonate samples composed mainly with vaterite (Figure S1). No bands were observed in the range  $3450\text{--}2900\text{ cm}^{-1}$  assigned to CH and OH vibrations groups characteristic for the spectra of saccharides.

Both calcite and vaterite are detected in all samples by XRD analysis. The percentage content of vaterite in calcite-vaterite mixtures can be calculated using the equation [38]:

$$X_v = \frac{7.691(I_v^{110})}{I_C^{104} + 7.691(I_v^{110})} \quad (3)$$

where  $X_v$  is a fraction of vaterite in a calcite-vaterite precipitate,  $I_v^{110}$  is the intensity of the reflection peak at (110) for vaterite and  $I_C^{104}$  at (104) for calcite. The concentrations of vaterite in the calcium carbonate samples are in Table 2. According to these results, vaterite is present in all produced calcium carbonate, also in that sample obtained with the addition of fructose, in which the peak of vaterite in the FTIR spectrum was not observed. FTIR analysis is less sensitive than XRD. Using the standard FTIR procedure, the polymorphic composition can be determined when concentration of one component in the mixture is higher than 5% [39]. The addition of sucrose caused an increase of the percentage content of vaterite, while the presence of glucose, fructose, and trehalose contributed to a decrease of the content of this crystalline form, the most in the case of fructose (2% of vaterite).

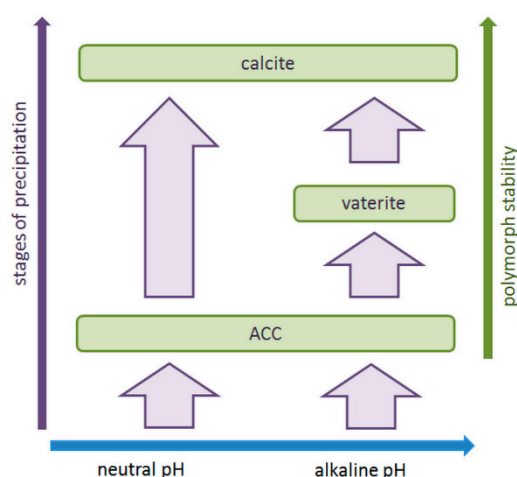
**Table 2.** Percentage content of vaterite and the mean size of calcite and vaterite crystallites in produced calcium carbonate particles.

Saccharide	$X_v$ , %	$d_v$ , nm	$d_C$ , nm
- (C)	75	220	240
Glucose (G)	56	33	120
Fructose (F)	2	-	120
Sucrose (S)	90	110	-
Trehalose (T)	54	60	72

The precipitation mechanisms of calcium carbonate via vaterite to calcite particles have been widely discussed. When pH of solution is high the mechanism proposed by Rodriguez-Blanco et al. [5,6] distinguishes two stages of calcium carbonate crystallization. At the first stage amorphous calcium carbonate (ACC) is formed and then its transformation to vaterite takes place due to the rapid ACC dehydration. Formation of individual vaterite particles is preceded by the ACC internal structural reorganization. In the second stage, vaterite transforms into calcite via the slow dissolution. Because solubility product for calcite is lower than for vaterite, after crystallization of vaterite particles, the solution remains supersaturated with respect to calcite. Thus, vaterite dissolves releasing calcium and carbonate ions into solution, which then crystallize forming calcite particles. However, when  $\text{CaCO}_3$  precipitation process is carried out at a neutral pH, ACC nanoparticles tend to transform directly to calcite. The diagram of precipitation stages carried out at a neutral and alkaline pH is shown in Figure 4.

When the system is intensively mixing, the local changing of pH appears and therefore precipitation with the mechanism proposed both for high pH and neutral pH can occur. Our experiments are consistent with mechanisms described above and vaterite dominated in calcium carbonate particles produced without additives. The presence of sucrose in the reactive mixture caused a greater share of vaterite in precipitated  $\text{CaCO}_3$ . Other products contain more calcite, and the highest concentration of this polymorph is for calcium carbonate obtained with the addition of fructose. The vaterite concentration in the product depends on the rate of calcium carbonate precipitation. When the  $\text{CaCO}_3$  synthesis is carried out via carbonation route, i.e.,  $\text{CO}_2$  gas is supplied into the reactive mixture as a reactant, the slowest stage of  $\text{CaCO}_3$  precipitation is a  $\text{CO}_2$  absorption. The addition of sucrose increases the  $\text{CO}_2$  absorption and therefore higher rate of precipitation is observed that resulted in the higher concentration of vaterite in the product. The opposite effect is observed when the reaction solution contains fructose. The longer initial time to create supersaturation resulted in the lowest vaterite concentration in the final product.



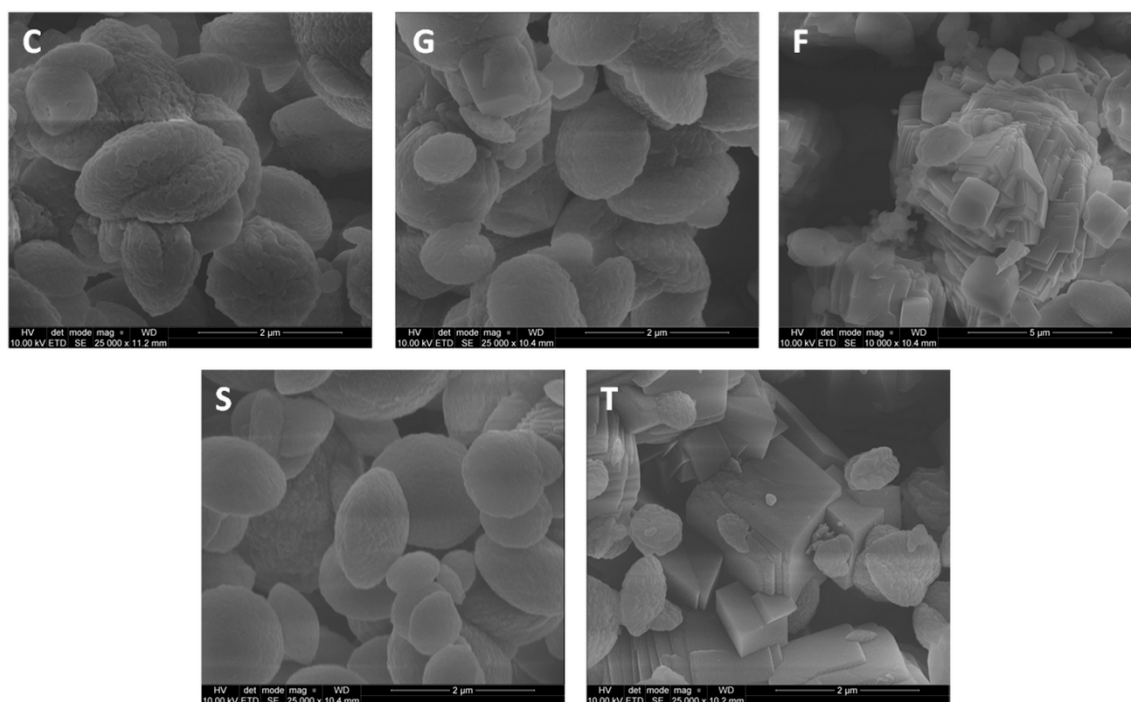


**Figure 4.** The diagram of  $\text{CaCO}_3$  precipitation stages for a neutral and alkaline pH (according mechanisms proposed by Rodriguez-Blanco et al. [5,6]).

Based on XRD measurements, the mean size of crystallites forming calcium carbonate particles was determined using the Scherrer's equation. The calculated mean sizes of crystallites are in Table 2. The crystallite size of both polymorphs was smaller for  $\text{CaCO}_3$  particles produced in the presence of saccharides. Different nanostructure of precipitated vaterite particles can be caused by variation of saturation, temperature or additives [40,41]. It has been shown that vaterite crystallization is promoted by kinetic effects [42], while highly oriented vaterite structures can be formed due to thermodynamic effects [41]. Additives may affect each stage of calcium carbonate crystallization and nine types of independent actions have been distinguished, among them influence on the soluble-cluster formation and equilibria, inhibition of nucleation of a precipitated nanoparticle phase, adsorption on nucleated particles and the face-specific adsorption [43]. It has been shown that the used additive may influence on calcium carbonate crystallization in several ways [37,43], e.g., citric acid affects both adsorption of calcium ions, formation of soluble-clusters, and local structures of nucleated particles. The early stage of calcium carbonate crystallization in the presence of selected monosaccharides, oligosaccharides, and polysaccharides was tested by Rao et al. [37], using the liquid-liquid method. Their experiments demonstrate that some saccharides, among them fructose, glucose, sucrose, and trehalose, influence on the stability of solute pre-nucleation clusters, shifting the equilibrium towards the bond state. Also, an increase in the nucleation potential was found when glucose and sucrose were components of reactive mixtures. This may confirm our results regarding the size of crystallites. In addition, saccharides such as fructose and sucrose have been found as components that induce the precipitation of calcium carbonate polymorphs with lower apparent solubility. In the case of our results, promotion of calcite precipitation, i.e., a form with lower solubility, is only observed in the presence of fructose. However, the complexity of the precipitation process should be taken into account, in which influence of saccharides on the  $\text{CO}_2$  absorption and the formation of supersaturation are very important.

SEM images of calcium carbonate particles are in Figure 5 and in Supplementary Materials in Figure S2.

When reaction was carried out without additives, with glucose or sucrose mainly spherical and spindle vaterite particles were observed as a product. Calcite particles with polyhedral shape characteristics for rhombohedral type were produced in a reaction mixture containing fructose and both rhombohedral calcite particles and spherical vaterite particles were precipitated in the presence of trehalose. The observed particle morphology is consistent with the main polymorphic forms determined with the FTIR and XRD methods. The more uniform particles were obtained in the presence of glucose, while both  $\text{CaCO}_3$  crystals produced in the reaction mixture without additives and with addition of the other saccharides show a greater variety in size (see Figure S2).



**Figure 5.** SEM images of calcium carbonate particles precipitated without additives **C** and with saccharides: **G**—glucose, **F**—fructose, **S**—sucrose, **T**—trehalose.

#### 4. Conclusions

Glucose, fructose, sucrose, and trehalose were used to control the synthesis of calcium carbonate particles via carbonation route. These selected saccharides affected carbon dioxide absorption into the reaction mixtures. The polymorph composition of precipitated particles was related to the rate of CO<sub>2</sub> absorption. Intensification of the mass transfer in the presence of sucrose resulted in the enhancement of vaterite in the final product. The opposite effect was observed in the presence of fructose, i.e., the precipitation was slower, and the main component of produced calcium carbonate was calcite.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4352/9/2/117/s1>, Figure S1: FTIR spectra of calcium carbonate precipitated without additives (C), with glucose (G), fructose (F), sucrose (S), and trehalose (T), Figure S2: SEM images of calcium carbonate precipitated without additives (C), with glucose (G), fructose (F), sucrose (S), and trehalose (T).

**Author Contributions:** Conceptualization, D.K.-Ł.; methodology, D.K.-Ł.; investigation, N.C., D.K.-Ł., B.K. and M.L.; writing—original draft D.K.-Ł.; writing—review and editing, D.K.-Ł. and J.G.

**Funding:** The research described in this paper was financially supported by Faculty of Chemistry, Gdansk University of Technology, grant number DS 033155.

**Acknowledgments:** The authors would like to thank Piotr Bruździak from the Department of Physical Chemistry (Faculty of Chemistry) for the opportunity to perform FT-IR spectra. Also, special thanks go to Paweł Filipkowski from the Department of Chemistry, Technology, and Biotechnology of Food (Faculty of Chemistry) for providing trehalose.

**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. Carr, F.P.; Frederick, D.K. Calcium Carbonate. *Kirk-Othmer Encycl. Chem. Technol.* **2012**, *4*, 551–556.
2. Kitamura, M. Strategy for control of crystallization of polymorphs. *Cryst. Eng. Comm.* **2009**, *11*, 949–964. [[CrossRef](#)]
3. Plummer, N.L.; Busenberg, E. The solubilities of calcite, aragonite and vaterite in CO<sub>2</sub>-H<sub>2</sub>O solutions between 0 and 90 °C, and an evaluation of the aqueous model for the system CaCO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O. *Geochim. Cosmochim. Acta* **1982**, *46*, 1011–1040. [[CrossRef](#)]





4. Beck, R.; Andreassen, J.P. The onset of spherulitic growth in crystallization of calcium carbonate. *J. Cryst. Growth* **2010**, *312*, 2226–2238. [[CrossRef](#)]
5. Rodriguez-Blanco, J.D.; Shaw, S.; Benning, L.G. The kinetics and mechanisms of amorphous calcium carbonate (ACC) crystallization to calcite, via vaterite. *Nanoscale* **2011**, *3*, 265–271. [[CrossRef](#)] [[PubMed](#)]
6. Rodriguez-Blanco, J.D.; Sand, K.K.; Benning, L.G. ACC and Vaterite as Intermediates in the Solution-Based Crystallization of CaCO<sub>3</sub>. In *New Perspectives on Mineral Nucleation and Growth*; Van Driessche, A.E., Kellermeier, M., Benning, L.G., Gebauer, D., Eds.; Springer International Publishing: Cham, Switzerland, 2017; pp. 93–111.
7. Trushina, D.B.; Bukreeva, T.V.; Kovalchuk, M.V.; Antipina, M.N. CaCO<sub>3</sub> vaterite microparticles for biomedical and personal care applications. *Mater. Sci. Eng. C* **2014**, *45*, 644–658. [[CrossRef](#)] [[PubMed](#)]
8. Hou, W.; Feng, Q. Morphology and formation mechanism of vaterite particles grown in glycine-containing aqueous solutions. *Mater. Sci. Eng. C* **2006**, *26*, 644–647. [[CrossRef](#)]
9. Andreassen, J.-P. Formation mechanism and morphology in precipitation of vaterite-nano-aggregation or crystal growth? *J. Cryst. Growth* **2005**, *274*, 256–264. [[CrossRef](#)]
10. Shivkumara, C.; Singh, P.; Gupta, A.; Hegde, M.S. Synthesis of vaterite CaCO<sub>3</sub> by direct precipitation using glycine and l-alanine as directing agents. *Mater. Res. Bull.* **2006**, *41*, 1455–1460. [[CrossRef](#)]
11. Mori, Y.; Enomae, T.; Isogai, A. Preparation of pure vaterite by simple mechanical mixing of two aqueous salt solutions. *Mater. Sci. Eng. C* **2009**, *29*, 1409–1414. [[CrossRef](#)]
12. Trushina, D.B.; Bukreeva, T.V.; Antipina, M.N. Size-Controlled Synthesis of Vaterite Calcium Carbonate by the Mixing Method: Aiming for Nanosized Particles. *Cryst. Growth Des.* **2016**, *16*, 1311–1319. [[CrossRef](#)]
13. Han, Y.S.; Hadiko, G.; Fuji, M.; Takahashi, M. Crystallization and transformation of vaterite at controlled pH. *J. Cryst. Growth* **2006**, *289*, 269–274. [[CrossRef](#)]
14. Konopacka-Lyskawa, D.; Kościelska, B.; Karczewski, J.; Gołabiewska, A. The influence of ammonia and selected amines on the characteristics of calcium carbonate precipitated from calcium chloride solutions via carbonation. *Mater. Chem. Phys.* **2017**, *193*, 13–18. [[CrossRef](#)]
15. Udrea, I.; Capat, C.; Olaru, E.A.; Isopescu, R.; Mihai, M.; Mateescu, C.D.; Bradu, C. Vaterite synthesis via gas-liquid route under controlled pH conditions. *Ind. Eng. Chem. Res.* **2012**, *51*, 8185–8193. [[CrossRef](#)]
16. Dickinson, S.R.; McGrath, K.M. Aqueous precipitation of calcium carbonate modified by hydroxyl-containing compounds. *Cryst. Growth Des.* **2004**, *4*, 1411–1418. [[CrossRef](#)]
17. Gómez-Morales, J.; Hernández-Hernández, Á.; Sazaki, G.; García-Ruiz, J.M. Nucleation and polymorphism of calcium carbonate by a vapor diffusion sitting drop crystallization technique. *Cryst. Growth Des.* **2010**, *10*, 963–969. [[CrossRef](#)]
18. Prah, J.; Maček, J.; Dražič, G. Precipitation of calcium carbonate from a calcium acetate and ammonium carbamate batch system. *J. Cryst. Growth* **2011**, *324*, 229–234. [[CrossRef](#)]
19. Li, Q.; Ding, Y.; Li, F.; Xie, B.; Qian, Y. Solvothermal growth of vaterite in the presence of ethylene glycol, 1,2-propanediol and glycerin. *J. Cryst. Growth* **2002**, *236*, 357–362. [[CrossRef](#)]
20. Manoli, F.; Dalas, E. Spontaneous precipitation of calcium carbonate in the presence of ethanol, isopropanol and diethylene glycol. *J. Cryst. Growth* **2000**, *218*, 359–364. [[CrossRef](#)]
21. Konopacka-Lyskawa, D.; Kościelska, B.; Karczewski, J. Effect of some organic solvent-water mixtures composition on precipitated calcium carbonate in carbonation process. *J. Cryst. Growth* **2015**, *418*. [[CrossRef](#)]
22. Manoli, F.; Kanakis, J.; Malkaj, P.; Dalas, E. The effect of aminoacids on the crystal growth of calcium carbonate. *J. Cryst. Growth* **2002**, *236*, 363–370. [[CrossRef](#)]
23. Chuajiw, W.; Takatori, K.; Igarashi, T.; Hara, H.; Fukushima, Y. The influence of aliphatic amines, diamines, and amino acids on the polymorph of calcium carbonate precipitated by the introduction of carbon dioxide gas into calcium hydroxide aqueous suspensions. *J. Cryst. Growth* **2014**, *386*, 119–127. [[CrossRef](#)]
24. Schenk, A.S.; Cantaert, B.; Kim, Y.-Y.; Li, Y.; Read, E.S.; Semsarilar, M.; Armes, S.P.; Meldrum, F.C. Systematic Study of the Effects of Polyamines on Calcium Carbonate Precipitation. *Chem. Mater.* **2014**, *26*, 2703–2711. [[CrossRef](#)]
25. Kontrec, J.; Kralj, D.; Brečević, L.; Falini, G. Influence of some polysaccharides on the production of calcium carbonate filler particles. *J. Cryst. Growth* **2008**, *210*, 4554–4560. [[CrossRef](#)]
26. Saraya, M.E.-S.I.; Rokbaa, H.H.A.E.-L. Formation and Stabilization of Vaterite Calcium Carbonate by Using Natural Polysaccharide. *Adv. Nanopart.* **2017**, *6*, 158–162. [[CrossRef](#)]

27. Liu, Y.; Chen, Y.; Huang, X.; Wu, G. Biomimetic synthesis of calcium carbonate with different morphologies and polymorphs in the presence of bovine serum albumin and soluble starch. *Mater. Sci. Eng. C* **2017**, *79*, 457–464. [[CrossRef](#)] [[PubMed](#)]
28. Lopez-Berganza, J.A.; Espinosa-Marzal, R.M. Mechanistic Approach to Predict the Combined Effects of Additives and Surface Templates on Calcium Carbonate Mineralization. *Cryst. Growth Des.* **2016**, *16*, 6186–6198. [[CrossRef](#)]
29. Yao, C.-L.; Ding, A.-M. Saccharides with Different Molecular Weight Affects Crystallization of Calcium Carbonate. *Asian J. Chem.* **2013**, *25*, 2939–2940. [[CrossRef](#)]
30. Polowczyk, I.; Bastrzyk, A.; Fiedot, M. Protein-mediated precipitation of calcium carbonate. *Materials* **2016**, *9*, 944. [[CrossRef](#)] [[PubMed](#)]
31. Vucak, M.; Peric, J.; Pons, M.-N. The Influence of Various Admixtures on the Calcium Carbonate Precipitation from a Calcium Nitrate and Monoethanolamine Solution. *Chem. Eng. Technol.* **1998**, *21*, 71–75. [[CrossRef](#)]
32. García-Carmona, J.; Gómez-Morales, J.; Fraile-Sainz, J.; Rodríguez-Clemente, R. Morphological characteristics and aggregation of calcite crystals obtained by bubbling CO<sub>2</sub> through a Ca(OH)<sub>2</sub> suspension in the presence of additives. *Powder Technol.* **2003**, *130*, 307–315. [[CrossRef](#)]
33. Feng, S.; Bagia, C.; Mpourmpakis, G. Determination of proton affinities and acidity constants of sugars. *J. Phys. Chem. A* **2013**, *112*, 5211–5219. [[CrossRef](#)] [[PubMed](#)]
34. Urban, F.; Shaffer, P.A. The acidic property of sugars. *J. Biol. Chem.* **1932**, *94*, 697–715.
35. Mani, F.; Peruzzini, M.; Stoppioni, P. CO<sub>2</sub> absorption by aqueous NH<sub>3</sub> solutions: Speciation of ammonium carbamate, bicarbonate and carbonate by a <sup>13</sup>C NMR study. *Green Chem.* **2006**, *8*, 995–1000. [[CrossRef](#)]
36. Vázquez, G.; Chenlo, F.; Pereira, G. Enhancement of the Absorption of CO<sub>2</sub> in Alkaline Buffers by Organic Solutes: Relation with Degree of Dissociation and Molecular OH Density. *Ind. Eng. Chem. Res.* **1997**, *36*, 2353–2358. [[CrossRef](#)]
37. Rao, A.; Berg, J.K.; Kellermeier, M.; Gebauer, D. Sweet on biomineralization: Effects of carbohydrates on the early stages of calcium carbonate crystallization. *Eur. J. Mineral.* **2014**, *26*, 537–552. [[CrossRef](#)]
38. Kontoyannis, C.G.; Vagenas, N.V. Calcium carbonate phase analysis using XRD and FT-Raman spectroscopy. *Analyst* **2000**, *125*, 251–255. [[CrossRef](#)]
39. Vagenas, N.V.; Gatsouli, A.; Kontoyannis, C.G. Quantitative analysis of synthetic calcium carbonate polymorphs using FT-IR spectroscopy. *Talanta* **2003**, *59*, 831–836. [[CrossRef](#)]
40. Kluge, T.; John, C.M. Technical Note: A simple method for vaterite precipitation for isotopic studies: Implications for bulk and clumped isotope analysis. *Biogeosciences* **2015**, *12*, 3289–3299. [[CrossRef](#)]
41. Rodríguez-Navarro, C.; Jiménez-Lopez, C.; Rodríguez-Navarro, A.; González-Muñoz, M.T.; Rodríguez-Gallego, M. Bacterially mediated mineralization of vaterite. *Geochim. Cosmochim. Acta* **2007**, *71*, 1197–1213. [[CrossRef](#)]
42. Kralj, D.; Brečević, L.; Nielsen, A.E. Vaterite growth and dissolution in aqueous solution II. Kinetics of dissolution. *J. Cryst. Growth* **1994**, *143*, 269–276. [[CrossRef](#)]
43. Gebauer, D.; Cölfen, H.; Verch, A.; Antonietti, M. The multiple roles of additives in CaCO<sub>3</sub> crystallization: A quantitative case study. *Adv. Mater.* **2009**, *21*, 435–439. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).