

# Effect of pH and Phosphate on Calcium Carbonate Polymorphs Precipitated at near-Freezing Temperature

Yu-Bin Hu,<sup>\*,†</sup> Mariëtte Wolthers,<sup>‡,§</sup> Dieter A. Wolf-Gladrow,<sup>†,||</sup> and Gernot Nehrke<sup>†</sup>

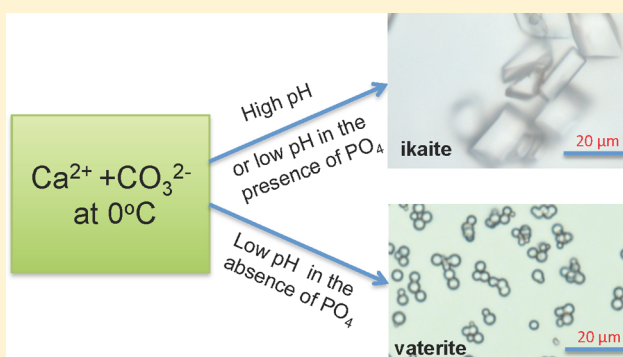
<sup>†</sup>Alfred-Wegener-Institut Helmholtz-Zentrum für Polar- und Meeresforschung, Bremerhaven, Germany, Postfach 12 01 61, D-27515 Bremerhaven, Germany

<sup>‡</sup>Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

<sup>§</sup>Department of Earth Sciences-Geochemistry, Utrecht University, P.O. Box 80021, 3508 TA Utrecht, The Netherlands

<sup>||</sup>University of Bremen, 28359 Bremen, Germany

**ABSTRACT:** The effects of pH and phosphate on the precipitation of calcium carbonate polymorphs from aqueous solution were investigated. Experiments were carried out at near-freezing temperature and two different pH conditions (pH 13.4 and 9.0). At each pH condition, solutions having different concentrations of  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  were mixed to achieve  $\text{Ca}/\text{CO}_3$  ratios of 1:1 and 10:1 at different pumping rates with and without phosphate. Results showed that, at pH 13.4, only ikaite was formed, independent of pumping rate,  $\text{Ca}/\text{CO}_3$  ratio, and phosphate. At pH 9.0, the precipitate was predominantly vaterite in the absence of phosphate and ikaite in the presence of phosphate regardless of the ratio of  $\text{Ca}/\text{CO}_3$ . These results indicate that at low temperatures and moderate alkaline conditions (pH 9.0), phosphate can act as a switch between ikaite and vaterite polymorphs. Contrastingly, at higher alkaline conditions (pH 13.4) phosphate is not prerequisite and the high pH in itself is enough to trigger ikaite formation over vaterite.



## 1. INTRODUCTION

Different polymorphs of calcium carbonate ( $\text{CaCO}_3$ ) exist: various amorphous forms, amorphous calcium carbonate (ACC);<sup>1,2</sup> two hydrated forms, calcium carbonate monohydrate (MCC) and calcium carbonate hexahydrate (ikaite); and three anhydrous polymorphs, vaterite, aragonite, and calcite.

The formation of different polymorphs of  $\text{CaCO}_3$  is strongly affected by precipitation conditions. Among them, pH and additives (e.g., phosphate) are considered to be two dominating factors controlling polymorphism during calcium carbonate precipitation.<sup>3,4</sup> pH-dependent change of  $\text{Ca}-\text{CO}_3$  binding strength is postulated to play an important role in determining different forms of ACC, which later transform into the particular calcium carbonate polymorphs.<sup>5</sup> However, changes in solution pH will affect the equilibrium concentration of different carbon species (e.g.,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ). This will affect the  $\text{Ca}/\text{CO}_3$  ratio in solution, making it difficult to separate the effects of pH and solution stoichiometry. The effect of additives on calcium carbonate crystallization has been extensively studied,<sup>4</sup> however, the mechanism by which additives influence precipitation at near-freezing temperature is not well-known.

Ikaite is a metastable calcium carbonate phase for which the formation mechanisms are poorly understood. Synthetic ikaite,  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ , has been known from laboratory studies since the 19th century.<sup>6</sup> In nature it was first found at the bottom of the Ika Fjord in Greenland and later in deep-sea sediments.<sup>7,8</sup>

In general, ikaite can be found in environments characterized by near zero temperatures, high alkalinity and phosphate ( $\text{PO}_4$ ) concentrations.<sup>9–11</sup> More recently, ikaite has also been observed in sea ice with relatively low  $\text{PO}_4$  concentrations.<sup>12,13</sup>

In our previous study,<sup>14</sup> we scanned a wide range of experimental conditions (pH from 8.5 to 10.0 and phosphate concentrations from 0 to  $50 \mu\text{mol}\cdot\text{kg}^{-1}$ ) at low temperatures and salinities up to 105 to understand how these parameters affect ikaite precipitation under the condition representative for sea ice. It was shown that ikaite is very likely the only calcium carbonate polymorph precipitated in sea ice, even though ikaite is a metastable form of calcium carbonate. In the current study we focus on the mechanism of calcium carbonate polymorph selection controlled by experimental conditions. The objective is to investigate the role of pH and  $\text{PO}_4$  on the calcium carbonate polymorphism at near-freezing temperature in low ionic strength solutions.

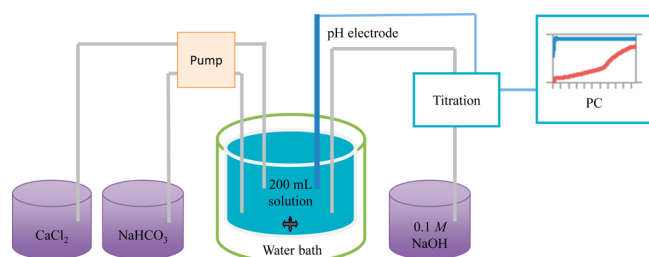
## 2. EXPERIMENTAL PROCEDURES

**2.1. Experiment Setup.** A pH-stat system was used for the precipitation experiments (Figure 1). This system consisted of a reaction vessel in which the precipitation experiment was conducted. This reaction vessel was placed in a double walled water jacket

Received: June 6, 2014

Revised: February 9, 2015

Published: February 20, 2015



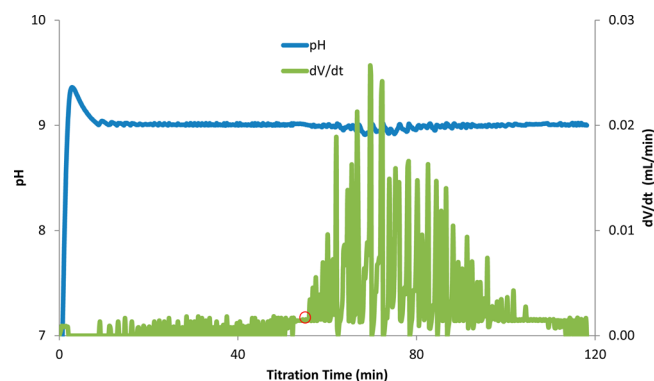
**Figure 1.** Experimental setup for calcium carbonate precipitation under varied experimental conditions at near-freezing temperature.

connected to a water-bath to keep the temperature between 0–0.5 °C. At the beginning of the experiment, 200 mL of deionized water was filled in the reaction vessel. Stock solutions of  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  were pumped separately to the reaction vessel using two channels of a high precision peristaltic pump (IPC-N, Ismatec). Solution pH was adjusted at either 13.4 or 9.0 over the course of experiment by means of NaOH addition. At pH 13.4, nearly all dissolved inorganic carbon (DIC) is present in the form of  $\text{CO}_3^{2-}$ ; while at pH 9.0, ~10% of DIC is  $\text{CO}_3^{2-}$ . At pH 13.4, two sets of stock solutions of  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  were used (0.3 : 0.3 mol·L<sup>-1</sup> and 0.3 : 0.03 mol·L<sup>-1</sup>) to achieve ratios of 1:1 and 10:1 for Ca/ $\text{CO}_3$  in the reaction vessel. At pH 9.0, 0.3 : 0.3 mol·L<sup>-1</sup> and 0.03 : 0.3 mol·L<sup>-1</sup> of  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  stock solutions were used to achieve ratios of 10:1 and 1:1 for Ca/ $\text{CO}_3$  in the reaction vessel. The effect of  $\text{PO}_4$  (0 versus 10  $\mu\text{mol}\cdot\text{L}^{-1}$ ) was tested under each experimental condition. At pH 13.4 and stock solutions of  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  0.3 : 0.3 mol·L<sup>-1</sup>, various pumping rates from 3.6 to 100  $\mu\text{L}\cdot\text{min}^{-1}$  were also applied in the absence of  $\text{PO}_4$ . The solution in the reaction vessel was stirred at a constant rate of 400 rpm by means of a Teflon-coated magnetic stirring bar. At pH 13.4, solution pH did not change throughout the experiment. At pH 9.0, 0.1 M NaOH solution was added by a titration system (TA20 plus, SI Analytics) to keep the solution pH constant. Duplicates for each experimental condition were carried out at 10 min interval.

**2.2. Determination of Onset Time.** Onset time in this study is defined as the time span between the moment when pumping starts (i.e.,  $\text{Ca}^{2+}$  and DIC are added to the reaction vessel) and the moment the first crystals are observed in the reaction vessel. At pH 13.4, the onset of precipitation was determined by the moment when the first precipitates were observed using a microscope (Zeiss, Axiovert 200M). Every 5 min, around 2 mL solutions from one experiment was taken and checked carefully under the microscope using an objective with 63× magnification. When crystals from the first experiment were observed under the microscope, solutions from the parallel experiment, which started 10 min after the first one, were checked at 2 min interval until crystals were observed. This procedure was used to narrow down the accuracy of the determined onset time to less than 2 min.

At pH 9.0, the onset of precipitation was determined by the titration curve. While calcium carbonate is precipitated from solution,  $\text{CO}_3^{2-}$  is consumed, resulting in the dissociation of  $\text{HCO}_3^-$  to restore the  $\text{CO}_3^{2-}/\text{HCO}_3^-$  equilibrium, which is accompanied by the release of  $\text{H}^+$  that in turn decreases solution pH. This rapid change in pH could have been used to determine the onset of precipitation. However, pH in solution was kept constant by the addition of NaOH during the experiment. Therefore, the sudden increase in the rate of NaOH addition ( $\text{dV}/\text{dt}$ ) to the reaction vessel was used to determine onset time (marked with a circle in Figure 2). When the consumption of NaOH solution increased drastically, the precipitate was also checked under microscope to make sure the precipitate was crystalline instead of powder-like ACC.

**2.3. Polymorph Identification.** The phase identification of the crystals was done by means of combined optical imaging and Raman spectroscopy. Raman spectroscopy can be used to reliably distinguish between the various polymorphs of calcium carbonate.<sup>15,16</sup> Here, we assumed that crystals with similar morphology are of the same phase. This was confirmed by XRD method in a previous study.<sup>17</sup> Crystals



**Figure 2.** pH curve and rate of NaOH addition over the course of an example experiment. The circle indicates the onset of calcium carbonate precipitation.

with different morphologies were checked using Raman spectroscopy for phase identification. Over the course of the experiment, the morphology of the crystals was used for quick phase identification using an optical microscope. The reliability of this optical method was verified by random crosschecks using Raman spectroscopy.

**2.4. Evolution of the Ion Activity Product of Calcium and Carbonate.** The evolution of the ion activity product of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  (IAP) in the solution until the onset of calcium carbonate precipitation under different experimental conditions was calculated by using the chemical equilibrium program Visual-Minteq 3.0.<sup>18</sup> Since the solubility constant of ikaite ( $K_{\text{sp,ikaite}}$ ) is not in the standard database of Visual-Minteq,  $K_{\text{sp,ikaite}}$  from the study of Bischoff et al.<sup>9</sup> was added to the Visual-Minteq database. For our experimental conditions, log  $K_{\text{sp,ikaite}}$  was  $-7.20$  at 0 °C.

### 3. RESULTS

On the basis of the optical images and Raman spectra (Figure 3a–d), two types of polymorphs could be identified in this study. After a comparison with the available references,<sup>16,19</sup> and in house reference standards the precipitates were identified as ikaite and vaterite. It is possible to distinguish between both polymorphs unambiguously, based on the two internal vibrational modes (in-plane deformation  $\nu_4$ , and symmetric stretching  $\nu_1$ ). For ikaite the peak position of  $\nu_4$  is 718  $\text{cm}^{-1}$  whereas for vaterite a doublet at 745 and 752  $\text{cm}^{-1}$  can be observed. The peak position of  $\nu_1$  is 1072  $\text{cm}^{-1}$  for ikaite and a doublet with 1075 and 1090  $\text{cm}^{-1}$  for vaterite.

At high pH (pH 13.4), only ikaite was formed, independent of  $\text{PO}_4$  or the ratio of Ca/ $\text{CO}_3$ . At low pH (pH 9.0), the precipitate was predominantly vaterite and a few ikaite crystals in the absence of  $\text{PO}_4$  and only ikaite in the presence of  $\text{PO}_4$  regardless of the ratio of Ca/ $\text{CO}_3$ . At constant pumping rate of 100  $\mu\text{L}\cdot\text{min}^{-1}$ , the shortest onset time of about 17 min was observed at pH 13.4 and Ca/ $\text{CO}_3$  = 1:1 regardless of  $\text{PO}_4$ . The onset time (~44 min) was similar between pH 13.4, Ca/ $\text{CO}_3$  = 10:1 and pH 9.0, Ca/ $\text{CO}_3$  = 10:1. The longest onset time (~100 min) was observed at pH 9.0 and Ca/ $\text{CO}_3$  = 1:1. No significant difference in onset time was found regardless of  $\text{PO}_4$  concentrations (0 versus 10  $\mu\text{mol}\cdot\text{L}^{-1}$ ) under the otherwise same conditions.

At pH 13.4 and in the absence of  $\text{PO}_4$ , ikaite was the only calcium carbonate phase observed at pumping rates from 3.6 to 100  $\mu\text{L}\cdot\text{min}^{-1}$ . The corresponding onset time decreased from 180 to 17 min.

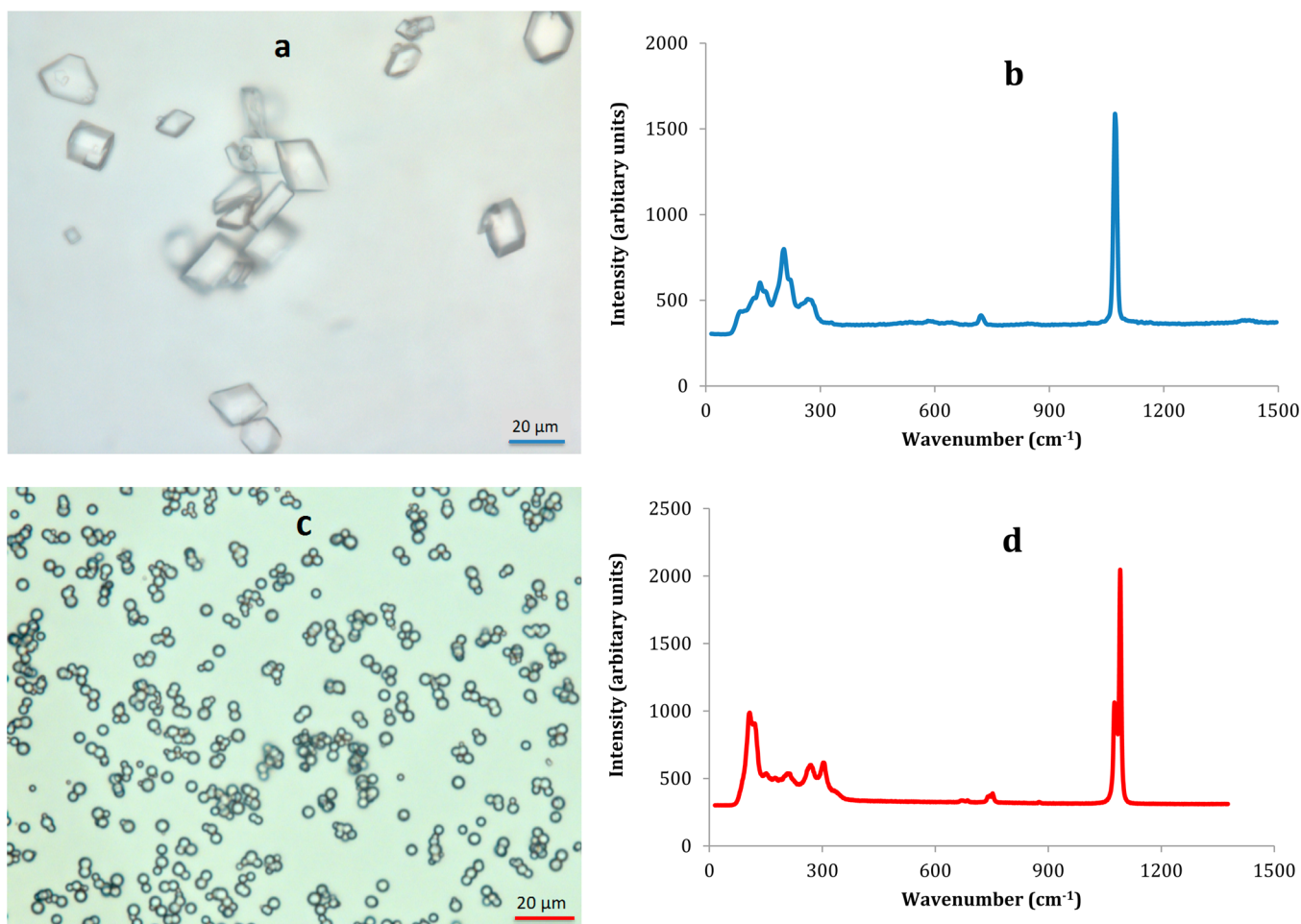


Figure 3. Typical ikaite morphology (a) and Raman spectrum (b); vaterite morphology (c) and Raman spectrum (d) obtained in this study.

## 4. DISCUSSION

**4.1. Calcium Carbonate Polymorphs Precipitated in the Absence of  $\text{PO}_4$ .** The different polymorphs of calcium carbonate (ikaite or vaterite) precipitated under two pH conditions in the absence of  $\text{PO}_4$  might result from the differences in solution saturation state, pH,  $\text{Ca}/\text{CO}_3$  ratio and induction time of vaterite  $\tau_v$ , which is the time span from the moment that the ion activity product of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  (IAP) passes through the vaterite solubility until the onset of any calcium carbonate precipitation (in this study, the precipitate is either vaterite or ikaite). Next, we discuss which of these conditions might be the controlling factor(s) on the different polymorphs precipitated.

**4.1.1. Effect of Solution Saturation State.** The ion activity product of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  at the onset of calcium carbonate precipitation is shown in Table 1. In the absence of  $\text{PO}_4$ , at pH 9.0 and  $\text{Ca}/\text{CO}_3 = 10:1$ , the log (IAP) is nearly identical to the one at pH 13.4 and  $\text{Ca}/\text{CO}_3 = 1:1$ , but the precipitates are

different, namely vaterite at pH 9.0 and ikaite at pH 13.4. Similar results are found at pH 9.0,  $\text{Ca}/\text{CO}_3 = 1:1$  and pH 13.4,  $\text{Ca}/\text{CO}_3 = 10:1$ . This suggests that the different precipitates at two pH conditions are not determined by the saturation state of the solution.

**4.1.2. Effect of Induction Time.** The log (IAP) of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  evolution with time is shown in Figure 4a. Under all conditions, the log (IAP) passes through both vaterite and ikaite solubilities. In the absence of  $\text{PO}_4$ , at pH 13.4, regardless of the ratio of  $\text{Ca}/\text{CO}_3$ , the precipitates are ikaite; at pH 9.0, the precipitates are vaterite regardless of the ratio of  $\text{Ca}/\text{CO}_3$ .

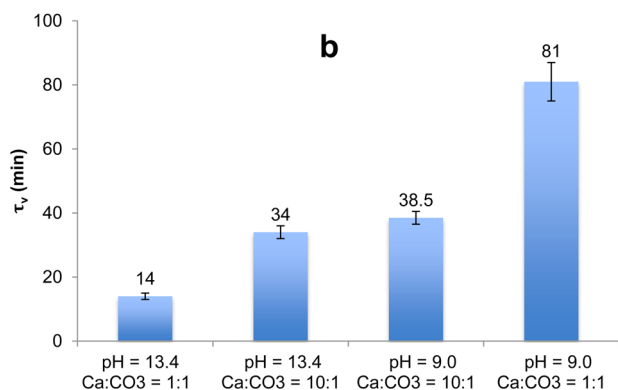
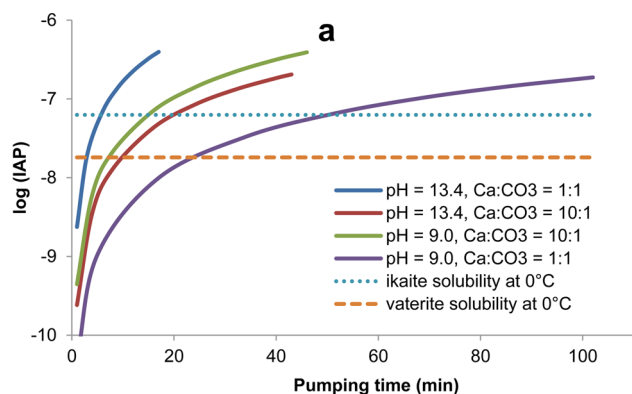
We noticed that  $\tau_v$  is longer at low pH than at high pH regardless of  $\text{Ca}/\text{CO}_3$  ratio (Figure 4b). At pH 9.0 and  $\text{Ca}/\text{CO}_3$  ratio of 1:1,  $\tau_v$  is 81 min. Such a long  $\tau_v$  might favor the precipitation of the more stable anhydrous form of calcium carbonate, namely, vaterite in this experiment, which might be an explanation for the precipitation of vaterite at low pH.

Nevertheless, the effect of  $\tau_v$  can be excluded based on another experiment. The evolution of the log (IAP) of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  with time as well as vaterite induction time carried out at pH 13.4 and different pumping rates (from 100 to  $3.6 \mu\text{L} \cdot \text{min}^{-1}$ ) is shown in Figure 5a and 5b.  $\tau_v$  varies from 14 to 100 min, which covers the induction time apparently sufficient for vaterite formation at low pH (Figure 4b). If the long  $\tau_v$  is the reason for vaterite precipitation, the precipitates at high pH and low pumping rates should be vaterite as well. In fact, no vaterite was observed even at  $\tau_v = 100$  min at pH 13.4. At these

Table 1. log (IAP) of Calcium and Carbonate and Precipitates at Varied pH and  $\text{Ca}/\text{CO}_3$  Ratios in the Absence of  $\text{PO}_4$

pH	13.4		9.0	
$\text{Ca}/\text{CO}_3$	1:1	10:1	10:1	1:1
log (IAP)	−6.403	−6.690	−6.408	−6.727
precipitate	ikaite	ikaite	vaterite	vaterite





**Figure 4.** Evolution of the log (IAP) of calcium and carbonate with pumping time until the onset of precipitation (a) and induction time of vaterite  $\tau_v$  (b) at varied pH and Ca/CO<sub>3</sub> ratios in the absence of PO<sub>4</sub>. The precipitates are ikaite at pH 13.4 and predominantly vaterite at pH 9.0 regardless of the ratio of Ca/CO<sub>3</sub>.

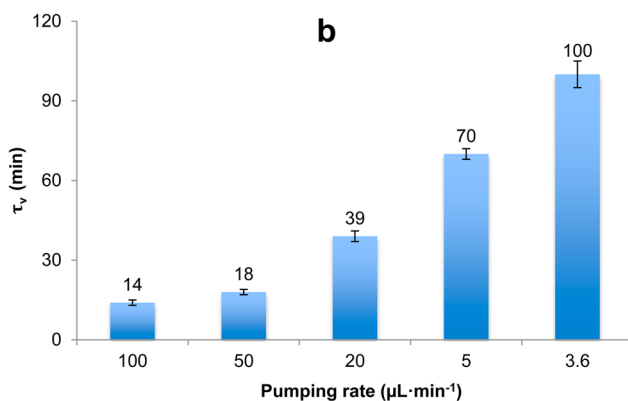
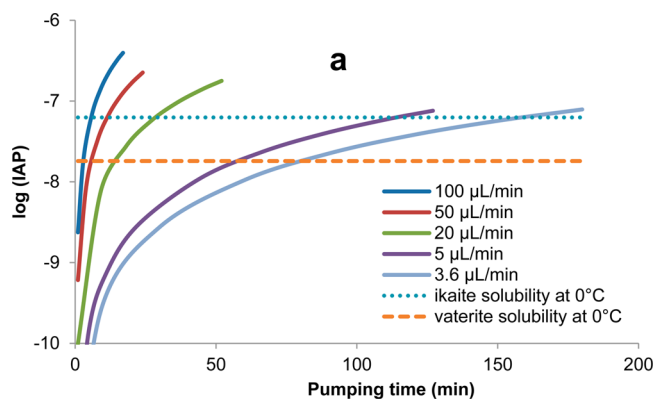
pumping rates and pH 13.4, ikaite was the only calcium carbonate polymorph precipitated. This indicates that the precipitation of vaterite at pH 9.0 is not caused by the longer period the system is supersaturated with respect to vaterite.

**4.1.3. Effect of pH and Ca/CO<sub>3</sub> Ratio.** Since the effect of solution saturation state and induction time are not the reason for the precipitation of different calcium carbonate polymorphs in the absence of PO<sub>4</sub>, there are only two variables left: pH and the ratio of Ca/CO<sub>3</sub>.

At the same pH (either 9.0 or 13.4) but different ratio of Ca/CO<sub>3</sub> and log (IAP), the precipitates are the same; at the same ratio of Ca/CO<sub>3</sub> but different pH and log (IAP), the precipitates are different (Table 1). As discussed in section 4.1.1, saturation states of the solution do not affect different polymorphs precipitated in this study. Therefore, this result indicates that the change in pH determines which polymorph is precipitated (ikaite or vaterite) rather than the Ca/CO<sub>3</sub> ratio.

**4.2. Calcium Carbonate Polymorphs Precipitated in the Presence of PO<sub>4</sub>.** At pH 9.0, different precipitates are observed with or without PO<sub>4</sub> at different ratios of Ca/CO<sub>3</sub>. The onset time is nearly identical at the same Ca/CO<sub>3</sub> ratio (Table 2) indicating that the degree of solution saturation and  $\tau_v$  are the same regardless of PO<sub>4</sub>. So the different precipitates are only caused by the presence or absence of PO<sub>4</sub>. This indicates that the addition of PO<sub>4</sub> triggers the formation of ikaite over vaterite at low pH.

**4.3. Mechanisms of the Ikaite/Vaterite Polymorph Switch.** From the discussion above, it is clear that pH and PO<sub>4</sub> can act as a switch between ikaite and vaterite polymorphs. In



**Figure 5.** Evolution of the log (IAP) of calcium and carbonate with pumping time until the onset of precipitation (a) and induction time of vaterite  $\tau_v$  (b) at varied pumping rates, pH 13.4, Ca/CO<sub>3</sub> = 1:1 and in the absence of PO<sub>4</sub>. Ikaite is the only precipitate under all the pumping rates.

**Table 2. Onset Time and Precipitates at pH 9, Varied Ca/CO<sub>3</sub> Ratios, and PO<sub>4</sub> Concentrations**

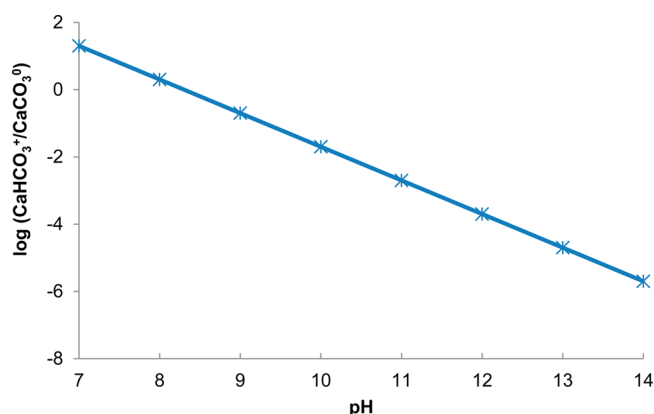
pH	9.0			
Ca/CO <sub>3</sub>	10:1	10:1	1:1	1:1
PO <sub>4</sub> ( $\mu\text{mol}\cdot\text{L}^{-1}$ )	0	10	0	10
onset time (min)	46 $\pm$ 2	49 $\pm$ 4	102 $\pm$ 6	101 $\pm$ 4
precipitate	vaterite	ikaite	vaterite	ikaite

the following subsections, we look into the mechanisms of pH and PO<sub>4</sub> in controlling the calcium carbonate polymorphs.

**4.3.1. Mechanism of pH Effect.** The effect of pH on calcium carbonate polymorphism might be related to the HCO<sub>3</sub><sup>−</sup>/CO<sub>3</sub><sup>2−</sup> ratio in solution. At pH 13.4, nearly all the dissolved inorganic carbon is in the form of CO<sub>3</sub><sup>2−</sup>, while at pH 9.0, HCO<sub>3</sub><sup>−</sup> becomes the dominant species with a ratio of HCO<sub>3</sub><sup>−</sup>/CO<sub>3</sub><sup>2−</sup> around 10:1. Now the question is how the change in HCO<sub>3</sub><sup>−</sup>/CO<sub>3</sub><sup>2−</sup> ratio affects the polymorphism of calcium carbonate.

It has long been reported that ion pairs of CaCO<sub>3</sub><sup>0</sup> and CaHCO<sub>3</sub><sup>+</sup> exist in calcium carbonate solution.<sup>20,21</sup> According to the calculation results from Visual-Minteq, at high pH, CaCO<sub>3</sub><sup>0</sup> is the dominant ion pair in solution while at pH 9.0, CaHCO<sub>3</sub><sup>+</sup> becomes a significant ion pair with an activity ratio {CaHCO<sub>3</sub><sup>+</sup>}/{CaCO<sub>3</sub><sup>0</sup>} = 0.2 (Figure 6).

Recent studies suggest that the nucleation of calcium carbonate occurs via stable prenucleation clusters and these calcium carbonate clusters display different structures related to



**Figure 6.** Logarithm of the activity ratio of  $\text{CaHCO}_3^+ / \text{CaCO}_3^0$  as a function of pH at 0 °C (Visual-Minteq).

different forms of ACC, which further transform into the particular crystalline polymorphs.<sup>5,22,23</sup> According to an atomistic simulation study, these stable prenucleation clusters might be liquid-like ionic polymers with units of  $\text{CaCO}_3^0$  and  $\text{CaHCO}_3^+$ , and their structures vary with pH; it was concluded that at low pH, the chain length is limited by competition between  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ , with the latter species generally acting as a chain terminator.<sup>24</sup> Since the ikaite/vaterite polymorph switch observed here occurs at a similar pH condition as the previously reported switch in prenucleation cluster size,<sup>24</sup> the formation of smaller prenucleation clusters at low pH due to the presence of “cluster-terminating”  $\text{HCO}_3^-$  may, in the present case, drive the switch. We therefore propose the presence of “cluster-terminating”  $\text{HCO}_3^-$  may be the driving force behind the ikaite/vaterite polymorph switch observed in this study.

**4.3.2. Mechanism of  $\text{PO}_4$  Effect.** A recent study showed that sodium-triphosphate can bind prenucleation clusters.<sup>25</sup> It was postulated that sodium-triphosphate might preferentially adsorb onto clusters with certain structures, which would lead to a change in the local structure of nucleated particles, simplifying the nucleation for particular polymorphs.<sup>25</sup> On the basis of our experimental results, the presence of  $\text{PO}_4$  might change the structure of the calcium carbonate clusters, which later favors the formation of ikaite. On the other hand, it has also been suggested, based on first-principles molecular dynamics simulations, that the hydration structure and water dynamics of the first and second hydration shell of calcium can even be influenced at the atomic level by simple anions such as halide ions.<sup>26</sup> Therefore, it is plausible to speculate that the presence of  $\text{PO}_4$  will play a similar or even more effective role in calcium carbonate crystallization processes. If the presence of  $\text{PO}_4$  in solution results in a decreasing dynamics of the solvation shell of  $\text{Ca}^{2+}$ , dehydration of  $\text{Ca}^{2+}$  will become slower, which might favor the formation of hydrated calcium carbonate polymorph,<sup>9</sup> thereby driving  $\text{CaCO}_3$  precipitation toward the hydrated polymorph, in our case, ikaite at pH 9.0.

## 5. CONCLUSIONS

At near-freezing temperature, precipitation of metastable forms of calcium carbonate from solution is favored (ikaite or vaterite). Both pH and phosphate contribute to the polymorph switch between vaterite and ikaite. At moderate alkaline conditions, formation of ikaite is favored over vaterite in the presence of phosphate; at high alkaline conditions, no

phosphate is needed to trigger ikaite formation. The effect of pH on different polymorphs of calcium carbonate is related to the ratio of  $\text{HCO}_3^- / \text{CO}_3^{2-}$ , which might affect the structure of prenucleation clusters. The presence of  $\text{PO}_4$  might change the structure of the calcium carbonate clusters and/or alter the hydration shell of calcium and thus affects the polymorph selection.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: Yubin.Hu@awi.de.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

Y.-B.H. is supported by AXA Research Fund, G.N. by the DFG by grant NE 1564/1-1 (SPP 1158), and M.W. by Natural Environment Research Council fellowship No. NE/J018856/1. We thank Karina Kaczmarek for assistance with the setup of the titration system.

## REFERENCES

- (1) Cartwright, J. H. E.; Checa, A. G.; Gale, J. D.; Gebauer, D.; Sainz-Díaz, C. I. Calcium carbonate polyamorphism and its role in biomineralization: How many amorphous calcium carbonates are there? *Angew. Chem., Int. Ed.* **2012**, *51*, 11960–11970.
- (2) Lam, R. S. K.; Charnock, J. M.; Lennie, A.; Meldrum, F. C. Synthesis-dependant structural variations in amorphous calcium carbonate. *CrystEngComm* **2007**, *9*, 1226–1236.
- (3) Han, Y. S.; Gunawan, H.; Masayoshi, F.; Minoru, T. Crystallization and transformation of vaterite at controlled pH. *J. Cryst. Growth* **2006**, *289*, 269–274.
- (4) Song, R.-Q.; Colfen, H. Additive controlled crystallization. *CrystEngComm* **2011**, *13*, 1249–1276.
- (5) Gebauer, D.; Völkel, A.; Colfen, H. Stable prenucleation calcium carbonate clusters. *Science* **2008**, *322*, 1819–1822.
- (6) Pelouze, M. J. Sur une combinaison nouvelle d'eau et de carbonate de chaux. *C. R. Acad. Sci.* **1865**, *60*, 429–431.
- (7) Pauly, H. Ikaite, A new mineral from Greenland. *Arctic* **1963**, *16*, 263–264.
- (8) Suess, E.; Balzer, W.; Hesse, K. F.; Muller, P. J.; Ungerer, C. A.; Wefer, G. Calcium carbonate hexahydrate from organic-rich sediments of the Antarctic Shelf: Precursors of glendonites. *Science* **1982**, *216*, 1128–1131.
- (9) Bischoff, J. L.; Fitzpatrick, J. A.; Rosenbauer, R. J. The solubility and stabilization of ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) from 0° to 25°C: Environmental and paleoclimatic implications for thénolite tufa. *J. Geol.* **1993**, *101*, 21–33.
- (10) Buchardt, B.; Seaman, P.; Stockmann, G.; Vous, M.; Wilken, U.; Duwel, L.; Kristiansen, A.; Jenner, C.; Whiticar, M. J.; Kristensen, R. M.; Petersen, G. H.; Thorbjørn, L. Submarine columns of ikaite tufa. *Nature* **1997**, *390*, 129–130.
- (11) Council, T. C.; Bennett, P. C. Geochemistry of ikaite formation at Mono Lake, California: Implications for the origin of tufa mounds. *Geology* **1993**, *21*, 971–974.
- (12) Dieckmann, G. S.; Nehrke, G.; Uhlig, C.; Göttlicher, J.; Gerland, S.; Granskog, M. A.; Thomas, D. N. Brief Communication: Ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) discovered in Arctic sea ice. *Cryosphere* **2010**, *4*, 227–230.
- (13) Geilfus, N. X.; Carnat, G.; Dieckmann, G. S.; Halden, N.; Nehrke, G.; Papakyriakou, T.; Tison, J. L.; Delille, B. First estimates of the contribution of  $\text{CaCO}_3$  precipitation to the release of  $\text{CO}_2$  to the atmosphere during young sea ice growth. *J. Geophys. Res.* **2013**, *118*, 244–255.
- (14) Hu, Y.-B.; Wolf-Gladrow, D. A.; Dieckmann, G. S.; Völker, C.; Nehrke, G. A laboratory study of ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) precipitation

as a function of pH, salinity, temperature and phosphate concentration. *Mar. Chem.* **2014**, *162*, 10–18.

(15) Nehrke, G.; Poigner, H.; Wilhelms-Dick, D.; Brey, T.; Abele, D. Coexistence of three calcium carbonate polymorphs in the shell of the Antarctic clam *Laternula elliptica*. *Geochem. Geophys. Geosyst.* **2012**, *13*, Q05014.

(16) Tlili, M. M.; Amor, M. B.; Gabrielli, C.; Joiret, S.; Maurin, G.; Rousseau, P. Characterization of  $\text{CaCO}_3$  hydrates by micro-Raman spectroscopy. *J. Raman Spectrosc.* **2001**, *33*, 10–16.

(17) Dieckmann, G. S.; Nehrke, G.; Papadimitriou, S.; Göttlicher, J.; Steininger, R.; Kennedy, H.; Wolf-Gladrow, D.; Thomas, D. N. Calcium carbonate as ikaite crystals in Antarctic sea ice. *Geophys. Res. Lett.* **2008**, *35*, L08501.

(18) Gustafsson, J. P. *Visual MINTeq*, version 3.0.; KTH, Department of Land and Water Resources Engineering; Stockholm, Sweden, 2011.

(19) Behrens, G.; Kuhn, L. T.; Ubric, R.; Heuer, A. H. Raman spectra of vateritic calcium carbonate. *Spectrosc. Lett.* **1995**, *28*, 983–995.

(20) Greenwald, I. The dissociation of calcium and magnesium carbonates and bicarbonates. *J. Biol. Chem.* **1941**, *141*, 789–796.

(21) Plummer, L. N.; Busenberg, E. The solubilities of calcite, aragonite and vaterite in  $\text{CO}_2$ – $\text{H}_2\text{O}$  solutions between 0 and 90 °C, and an evaluation of the aqueous model for the system  $\text{CaCO}_3$ – $\text{CO}_2$ – $\text{H}_2\text{O}$ . *Geochim. Cosmochim. Acta* **1982**, *46*, 1011–1040.

(22) Gebauer, D.; Kellermeier, M.; Gale, J. D.; Bergstrom, L.; Colfen, H. Pre-nucleation clusters as solute precursors in crystallisation. *Chem. Soc. Rev.* **2014**, *43*, 2348–2371.

(23) Gebauer, D.; Gunawidjaja, P. N.; Ko, J. Y. P.; Bacsik, Z.; Aziz, B.; Liu, L.; Hu, Y.; Bergström, L.; Tai, C.-W.; Sham, T.-K.; Edén, M.; Hedin, N. Proto-calcite and proto-vaterite in amorphous calcium carbonates. *Angew. Chem.* **2010**, *49*, 8889–8891.

(24) Demichelis, R.; Raiteri, P.; Gale, J. D.; Quigley, D.; Gebauer, D. Stable prenucleation mineral clusters are liquid-like ionic polymers. *Nat. Commun.* **2011**, *2*, 590.

(25) Gebauer, D.; Cölfen, H.; Verch, A.; Antonietti, M. The multiple roles of additives in  $\text{CaCO}_3$  crystallization: A quantitative case study. *Adv. Mater.* **2009**, *21*, 435–439.

(26) Di Tommaso, D.; de Leeuw, N. H. First principles simulations of the structural and dynamical properties of hydrated metal ions  $\text{Me}^{2+}$  and solvated metal carbonates ( $\text{Me} = \text{Ca}$ ,  $\text{Mg}$ , and  $\text{Sr}$ ). *Cryst. Growth Des.* **2010**, *10*, 4292–4302.