



## RESEARCH ARTICLE

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## Key Points:

- Phosphate is strongly coprecipitated with ikaite
- Phosphate concentration and pH affect phosphate coprecipitation with ikaite
- Temperature and salinity do not affect phosphate coprecipitation with ikaite

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## Laboratory study on coprecipitation of phosphate with ikaite in sea ice

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**Abstract** Ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) has recently been discovered in sea ice, providing first direct evidence of  $\text{CaCO}_3$  precipitation in sea ice. However, the impact of ikaite precipitation on phosphate ( $\text{PO}_4$ ) concentration has not been considered so far. Experiments were set up at pH from 8.5 to 10.0, salinities from 0 to 105, temperatures from  $-4^\circ\text{C}$  to  $0^\circ\text{C}$ , and  $\text{PO}_4$  concentrations from 5 to  $50 \mu\text{mol kg}^{-1}$  in artificial sea ice brine so as to understand how ikaite precipitation affects the  $\text{PO}_4$  concentration in sea ice under different conditions. Our results show that  $\text{PO}_4$  is coprecipitated with ikaite under all experimental conditions. The amount of  $\text{PO}_4$  removed by ikaite precipitation increases with increasing pH. Changes in salinity ( $S \geq 35$ ) as well as temperature have little impact on  $\text{PO}_4$  removal by ikaite precipitation. The initial  $\text{PO}_4$  concentration affects the  $\text{PO}_4$  coprecipitation. These findings may shed some light on the observed variability of  $\text{PO}_4$  concentration in sea ice.

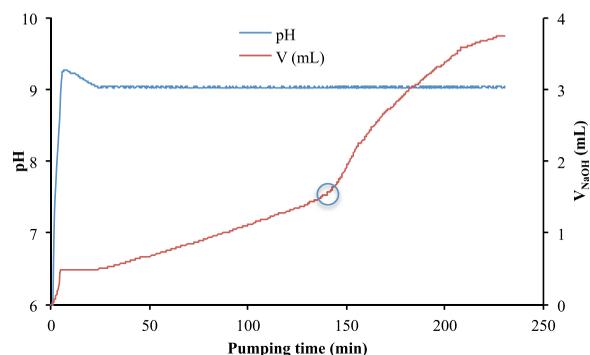
### 1. Introduction

When sea ice forms, a portion of the seawater is trapped in the sea ice matrix, where it becomes concentrated in brine pockets and channels. When the ice temperature further decreases, the brine salinity increases accordingly. As a result, the chemical compounds including the dissolved inorganic nutrients (e.g., total dissolved inorganic carbon ( $C_T$ ), dissolved inorganic phosphate) in the brine are also enriched.

During the formation and melting of sea ice, the nutrients in sea ice brine are expected to behave conservatively as a function of brine salinity [Gleitz *et al.*, 1995]. However, it is often found that the salinity-normalized nutrients in sea ice brine are depleted compared to those in surface seawater [Dieckmann *et al.*, 1991; Gleitz and Thomas, 1993], which is generally explained by the biological activity within sea ice [Günther *et al.*, 1999; Papadimitriou *et al.*, 2007]. According to the Redfield ratio for inorganic nutrient uptake during photosynthesis, the nutrient uptake follows the ratio C:N:P = 106:16:1 [Redfield *et al.*, 1963]. However, quite often there is no clear correlation between the salinity-normalized  $C_T$  and the rest of the inorganic nutrients in sea ice [Papadimitriou *et al.*, 2007]. Instead, the depletion of  $\text{PO}_4$  in sea ice is much stronger than that of  $C_T$  [Gleitz *et al.*, 1995; Papadimitriou *et al.*, 2007], which indicates that there might be another mechanism explaining the excess depletion of  $\text{PO}_4$  in sea ice.

Ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) in sea ice was only recently discovered [Dieckmann *et al.*, 2008, 2010] and for a long time  $\text{PO}_4$  has been considered to be crucial for ikaite formation as ikaite is very often found in  $\text{PO}_4$ -rich environments [Bischoff *et al.*, 1993; Buchardt *et al.*, 2001; Council and Bennett, 1993; Selleck *et al.*, 2007]. A recent study by Hu *et al.* [2014] showed that  $\text{PO}_4$  is only crucial for ikaite formation in freshwater and in NaCl medium, whereas in seawater-based solutions,  $\text{PO}_4$  is not required for the formation of ikaite. Therewith, in seawater-based solutions, other ions (such as  $\text{Mg}^{2+}$  and/or  $\text{SO}_4^{2-}$ ) might inhibit precipitation of other, more stable calcium carbonate polymorphs and hence favor ikaite formation at low temperatures. Besides, the presence of  $\text{PO}_4$  does not affect ikaite precipitation thermodynamically or kinetically [Hu *et al.*, 2014]. The effect of ikaite precipitation on  $\text{PO}_4$  concentration is studied here because  $\text{PO}_4$  is an important nutrient and the enrichment or depletion of  $\text{PO}_4$  in sea ice has a major effect on the biological activity in sea ice.

The removal of  $\text{PO}_4$  by calcium carbonate has long been known.  $\text{PO}_4$  can be removed by coprecipitation with calcium carbonate as well as through adsorption to suspended calcium carbonate [Kitano *et al.*, 1978]. Several studies describe the coprecipitation of  $\text{PO}_4$  with calcium carbonate observed in lakes [Danen-Louwerse *et al.*, 1995; House, 1990; Murphy *et al.*, 1983]. The study by Murphy *et al.* [1983] showed that the  $\text{PO}_4$  in the photic zone of a eutrophic lake could be completely removed by calcite precipitation. There is also considerable evidence regarding the adsorption of  $\text{PO}_4$  onto calcite, aragonite, vaterite, and



**Figure 1.** A typical NaOH titration profile obtained at pH = 9.0,  $S = 70$ ,  $T = 0^{\circ}\text{C}$ , and  $[\text{PO}_4] = 10 \mu\text{mol kg}^{-1}$ . The circle indicates the onset of calcium carbonate precipitation.

monohydrocalcite [Millero *et al.*, 2001; Sawada *et al.*, 1992; Yagi and Fukushi, 2011]. However, to the best of our knowledge, no studies have dealt with the effect of ikaite precipitation on  $\text{PO}_4$  removal.

In this study, we investigated how the precipitation of ikaite affects the  $\text{PO}_4$  concentration under conditions representative for natural sea ice. Experiments were set up at pH from 8.5 to 10.0, salinities from 0 to 105, temperatures from  $-4^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ , and  $\text{PO}_4$  concentrations from 5 to  $50 \mu\text{mol kg}^{-1}$  so as to understand how changes in these parameters affected  $\text{PO}_4$  removal during ikaite precipitation in sea ice.

## 2. Methods

### 2.1. Solution Preparation

Artificial seawater (ASW) of different salinities was prepared according to Millero [2006] with slight modifications.  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  were not added initially. The amount of salt missing from not adding  $\text{NaHCO}_3$  and  $\text{CaCl}_2$  was compensated for by adding  $\text{NaCl}$ . Ten kilograms of ASW of salinity 70 was prepared as a stock solution. In addition, 1 kg ASW of salinity 35 as well as salinity 105 was prepared separately. Stock solutions of  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  at concentrations of 2.5 and  $0.5 \text{ mol kg}^{-1}$ , respectively, were prepared by dissolving 183.775 g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and 21.002 g  $\text{NaHCO}_3$  into 500 g solutions using ultrapure water and subsequently stored in gas-tight Tedlar bags (SKC). All chemicals were obtained from Merck (EMSURE<sup>®</sup> ACS, ISO, Reag, Ph Eur) except  $\text{SrCl}_2$  and  $\text{H}_3\text{BO}_3$ , which were from Carl Roth (p.a., ACS, ISO). Different concentrations of  $\text{PO}_4$  were prepared from a phosphate stock solution (Merck, CertiPUR<sup>®</sup>) by diluting with ultrapure water.

### 2.2. Experimental Setup

Four parameters were varied: pH (8.5–10.0), salinity (0–105), temperature ( $-4$  to  $0^{\circ}\text{C}$ ), and  $\text{PO}_4$  concentration ( $5$ – $50 \mu\text{mol kg}^{-1}$ ). The standard values were pH = 9.0,  $S = 70$ ,  $T = 0^{\circ}\text{C}$ , and  $[\text{PO}_4] = 10 \mu\text{mol kg}^{-1}$ . Only one of these parameters was varied at a time.

Stock solutions of  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  ( $\text{Ca}^{2+}:\text{DIC} = 5:1$ , which is the typical concentration ratio in seawater) were pumped from the Tedlar bags into a Teflon reactor vessel with 250 g working solution using a high-precision peristaltic pump (IPC-N, Ismatec) at a constant pumping rate of  $20 \mu\text{L min}^{-1}$ . The solution was stirred at 400 rpm and the temperature was controlled by water bath using double-walled water jackets. pH electrodes (Metrohm 6.0253.100) were calibrated using NBS buffers at  $\text{pH } 7.000 \pm 0.010$  and  $10.012 \pm 0.010$  (Radiometer Analytical, IUPAC Standard). The pH of the solution was kept constant by adding  $\text{NaOH}$  ( $0.5 \text{ mol L}^{-1}$ ), which was controlled by a titration system (TA20 plus, SI Analytics). The value of pH and the volume of  $\text{NaOH}$  added to the solution were recorded every 10 s. Depending on the experimental conditions, the input of  $\text{CaCl}_2$ ,  $\text{NaHCO}_3$ , and  $\text{NaOH}$  into the working solution during the experiments is in the range of a few mL, which did not have a significant effect on solution volume. Duplicates for each experimental condition were run in parallel.

### 2.3. Determining the Onset of Precipitation

When calcium carbonate is precipitated from solution,  $\text{CO}_2$  is released, which leads to a large decrease in solution pH. This rapid change in pH was compensated for by adding  $\text{NaOH}$ . Therefore, the onset of precipitation was determined by the sudden change of  $\text{NaOH}$  volume ( $V_{\text{NaOH}}$ ) added into the solution, as marked with a circle in Figure 1. The uncertainty in determining the onset of precipitation by this method is within 1 min.

### 2.4. Crystal Identification

Immediately after the crystals were precipitated, indicated by a sudden increase in the volume of  $\text{NaOH}$  addition (section 2.3), around 2 mL of the well-stirred solution together with the crystals was sampled by means of a pipette and quickly transferred to a glass Petri dish. The morphology of the crystals was characterized using a microscope (Zeiss, Axiovert 200M) with an objective of 63X magnification. The phase

identification of the crystals was done by means of Raman microscopy. This method can be used to reliably distinguish between the various polymorphs of calcium carbonate [Nehrke et al., 2012; Tlili et al., 2001]. The confocal Raman microscope (WITec®, Ulm, Germany) was equipped with a diode laser (532 nm) and an Olympus® 20X Teflon-coated water submersible objective. During the Raman measurements, crystals were maintained in the original solution and placed in a glass Petri dish, which was kept cold using an ice-water bath.

### 2.5. Determination of Solution Supersaturation at Onset of Precipitation

The logarithm of the ion activity product of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  (log (IAP)) and the solution supersaturation with respect to ikaite ( $\Omega = \text{IAP}/K_{\text{sp,ikaite}}$ ) under different experimental conditions was calculated by using the chemical equilibrium model Visual-Minteq 3.0 [Gustafsson, 2011] which was modified by the implementation of the solubility constant of ikaite ( $K_{\text{sp,ikaite}}$ ) derived from  $\log K_{\text{sp,ikaite}} = 0.15981 - 2011.1/T$ , where  $T$  (K) is the absolute temperature [Bischoff et al., 1993]. The activities were calculated using the Davies equation. Although the calculation of ionic activities is not very accurate at high salinities, especially the calculation of  $\text{CO}_3^{2-}$  activity, the trend of  $\Omega$  under different experimental conditions should be still adequate.

### 2.6. Quantification of Ikaite and $\text{PO}_4$

In order to avoid further precipitation of calcium carbonate after sampling, the samples were diluted with 0.01 M HCl. Before precipitation started, at the pumping time of 10 min, 1 mL solution was withdrawn and diluted with 0.01 M HCl to a final volume of 10 mL (for  $\text{PO}_4$  analysis). For calcium analysis, 1 mL diluted solution was further diluted by a factor of 10. After the onset of ikaite precipitation, approximately 7 mL solution together with ikaite crystals was sampled every 10 min for 1 h. The samples were collected with a syringe and filtered through 0.45  $\mu\text{m}$  syringe filter (Thermo Scientific Nalgene); 5 mL filtrate was collected and diluted with 0.01 M HCl to 10 mL. Thereafter, 0.2 mL of the diluted solution was further diluted with 0.01 M HCl to a final volume of 10 mL. The first and second diluted solutions were used for  $\text{PO}_4$  and  $\text{Ca}^{2+}$  measurements, respectively.

$\text{Ca}^{2+}$  concentrations were determined using Inductively-Coupled Plasma Optical Emission Spectrometry (IRIS Intrepid Optical Emission Spectrometer Duo HR, Thermo Fisher Scientific).  $\text{PO}_4$  concentrations were measured using a Nutrient Autoanalyzer (ALLIANCE). Each sample was measured twice.

The amount of ikaite precipitated at each sampling time was determined by the moles of  $\text{Ca}^{2+}$  pumped into the reaction vessel minus the moles of  $\text{Ca}^{2+}$  remaining in solution. The change in solution mass and the loss of  $\text{Ca}^{2+}$  during sampling was considered. The amount of ikaite precipitated at each sampling time was thus calculated using the equation below:

$$C_{\text{ikaite}, i} = \frac{\left( \frac{C_0 * m_0 * t_i}{t_0} - C_i * m_i - \sum_{k=0}^{i-1} n_k \right) * M}{m_i}$$

$C_{\text{ikaite}, i}$  ikaite concentration ( $\text{g kg}^{-1}$ ) in solution at the  $i^{\text{th}}$  sampling,  $i = 1$  to 5;  $C_0$   $\text{Ca}^{2+}$  concentration ( $\text{mol kg}^{-1}$ ) measured at pumping time 10 min;  $m_0$  mass (g) of solution at pumping time 10 min;  $t_0$  pumping time (= 10 min);  $t_i$  pumping time at the  $i^{\text{th}}$  sampling;  $C_i$   $\text{Ca}^{2+}$  concentration ( $\text{mol kg}^{-1}$ ) measured at the  $i^{\text{th}}$  sampling time after precipitation;  $m_i$  mass (g) of solution at the  $i^{\text{th}}$  sampling;  $\sum_{k=0}^{i-1} n_k$  total moles of  $\text{Ca}^{2+}$  removed from solution due to samplings;  $M$  ikaite molecular weight ( $= 208 \text{ g mol}^{-1}$ ).

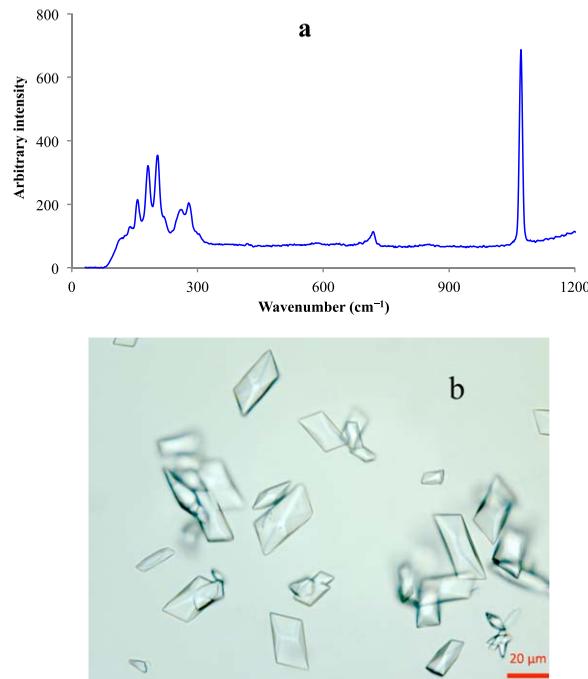
## 3. Results

### 3.1. The Precipitate Under Different Experimental Conditions

According to the typical vibration modes seen in the Raman spectra  $\nu_1$  ( $1071 \text{ cm}^{-1}$ ) and  $\nu_4$  ( $718 \text{ cm}^{-1}$ ) (Figure 2a), ikaite was the only calcium carbonate polymorph identified at pH from 8.5 to 10.0, salinities from 0 to 105, temperatures from  $-4^\circ\text{C}$  to  $0^\circ\text{C}$ , and  $\text{PO}_4$  concentrations from 5 to 50  $\mu\text{mol kg}^{-1}$ . The morphology of ikaite crystals precipitated was similar under all conditions, with an average crystal size of approximately 20  $\mu\text{m}$  (Figure 2b).

### 3.2. Removal of $\text{PO}_4$ by Ikaite Precipitation

Results of the ikaite precipitation experiments conducted at different pH values (8.5–10), salinities (0–105), temperatures ( $-4$  to  $0^\circ\text{C}$ ), and initial  $\text{PO}_4$  concentrations (5–50  $\mu\text{mol kg}^{-1}$ ) are shown in Figures 3–6. The duplicate experiments (exp. 1 and exp. 2) show a good reproducibility. All experiments reveal the same pattern of  $\text{PO}_4$  removal by ikaite precipitation. The concentration of  $\text{PO}_4$  in solution decreases with the amount of ikaite precipitated. The concentration of  $\text{PO}_4$  drops steeply during the early stage of ikaite precipitation,



**Figure 2.** (a) Ikaite Raman spectra and (b) ikaite morphology obtained under the experimental condition of pH = 9.0, S = 70, T = 0°C, [PO<sub>4</sub>] = 10 μmol kg<sup>-1</sup>, and representative of all precipitates in this study.

followed by a much slower decrease, and then the PO<sub>4</sub> concentration in solution reaches an equilibrium (within 1 h) even though ikaite crystals continue to grow. The pattern of PO<sub>4</sub> removal by ikaite precipitation under all experimental conditions presented in this study is similar to that observed in studies on PO<sub>4</sub> coprecipitation with calcite and aragonite [House and Donaldson, 1986; Kitano et al., 1978]. The total amount of PO<sub>4</sub> in solution removed by ikaite precipitation is independent of the amount of ikaite precipitated.

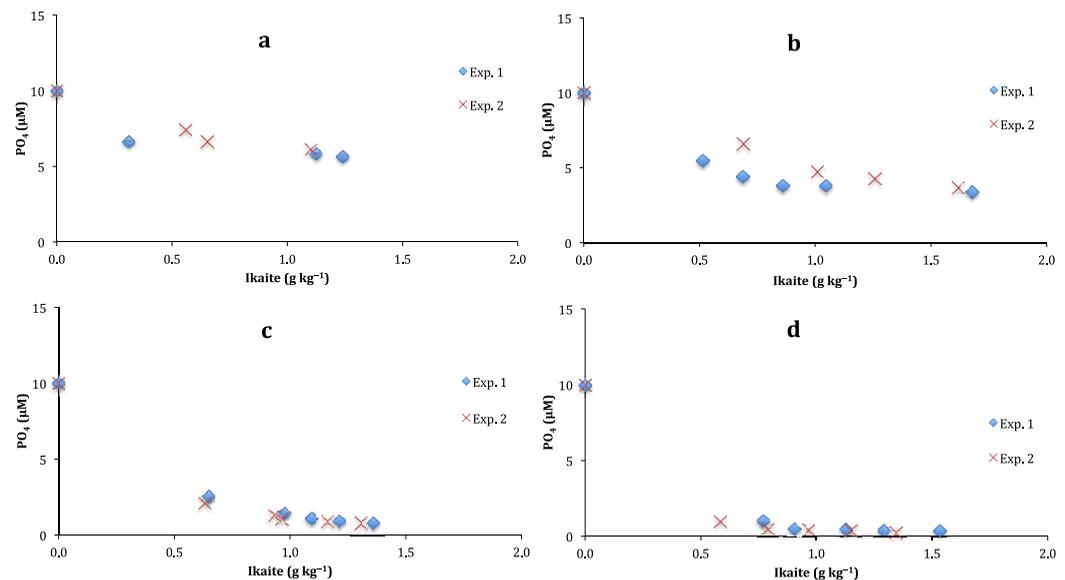
### 3.3. Solution Supersaturation at the Onset of Ikaite Precipitation

The solution supersaturation with respect to ikaite ( $\Omega$ ) under different pH values, salinities, temperatures, and PO<sub>4</sub> concentrations at the onset of ikaite precipitation is shown in Table 1. An increase in pH from 8.5 to 10 leads to an increase in  $\Omega$  from 3.0 to 5.4. There is no significant difference in  $\Omega$  at different salinities as well as at different temperatures and PO<sub>4</sub> concentrations.

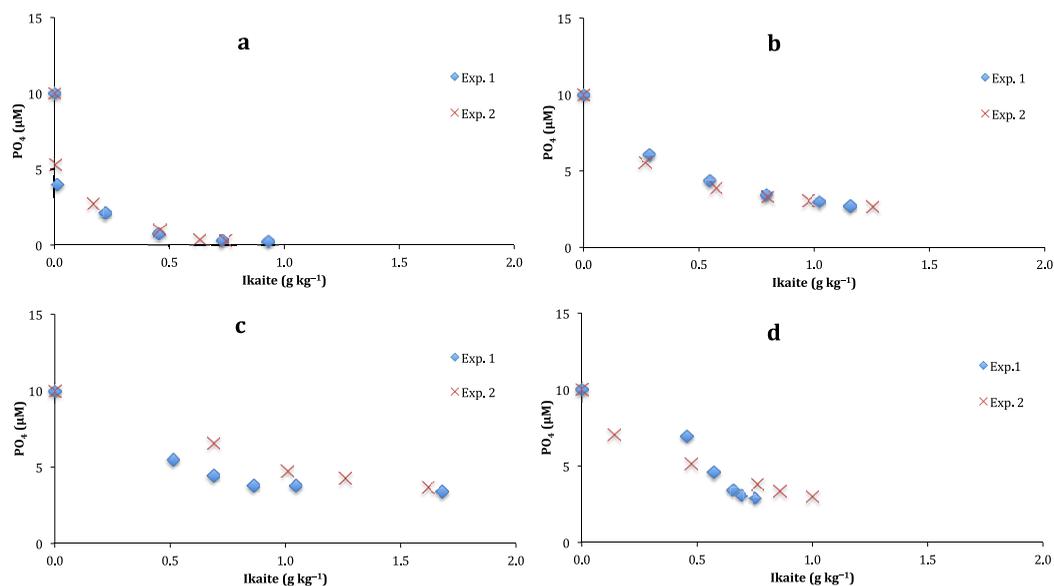
## 4. Discussion

### 4.1. General Pattern of PO<sub>4</sub> Coprecipitation With Ikaite

In this study, the concentrations of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> in solution increase with pumping time until the onset of ikaite precipitation when the solution reaches the highest  $\Omega$ . After ikaite precipitation starts,  $\Omega$  decreases until it reaches  $\Omega = 1$  (ikaite solubility). As the nucleation rate depends on solution supersaturation [Boistelle and Astier, 1988], a high nucleation rate will be expected at the initial stage of precipitation. Immediately after nucleation, the solution saturation level drops rapidly, and so does the nucleation rate, while growth



**Figure 3.** Coprecipitation of PO<sub>4</sub> with ikaite at different pH values and an initial PO<sub>4</sub> concentration of 10 μmol kg<sup>-1</sup>, S = 70, T = 0°C: (a) pH = 8.5, (b) pH = 9.0, (c) pH = 9.5, and (d) pH = 10.0.



**Figure 4.** Coprecipitation of  $\text{PO}_4$  with ikaite at different salinities and an initial  $\text{PO}_4$  concentration of  $10 \mu\text{mol kg}^{-1}$ ,  $\text{pH} = 9.0$ ,  $T = 0^\circ\text{C}$ : (a)  $S = 0$ , (b)  $S = 35$ , (c)  $S = 70$ , and (d)  $S = 105$ .

of crystals continues [Vekilov, 2010]. The removal behavior of  $\text{PO}_4$  by ikaite precipitation indicates that coprecipitation of  $\text{PO}_4$  with ikaite mainly occurs during the ikaite nucleation stage and that the subsequent growth of ikaite crystals has little effect on the removal of  $\text{PO}_4$ , and thus the  $\text{PO}_4$  concentration in solution does not change with the subsequent growth of ikaite. However, the final  $\text{PO}_4$  equilibrium concentration differs under different experimental conditions.

#### 4.2. Effect of pH on $\text{PO}_4$ Coprecipitation With Ikaite

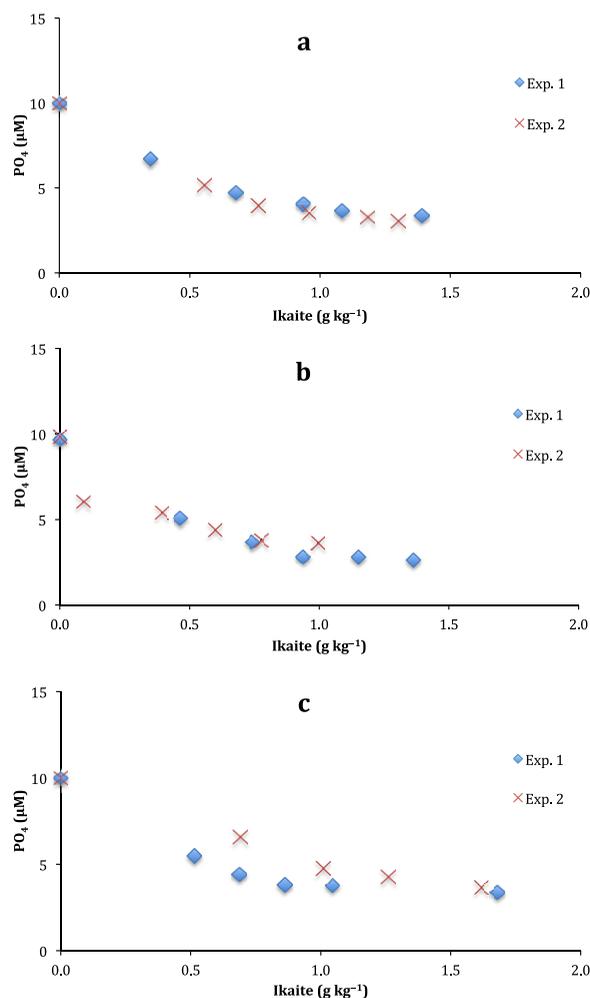
The pH value has a significant effect on  $\text{PO}_4$  removal by ikaite precipitation (Table 1). The coprecipitation of  $\text{PO}_4$  with ikaite increases with increasing pH. At  $\text{pH} = 8.5$ , 42% of  $\text{PO}_4$  is removed from solution by ikaite precipitation; above  $\text{pH} = 9.5$ , >90% of  $\text{PO}_4$  is coprecipitated with ikaite. This might be due to the high ikaite nucleation rate resulting from the higher  $\Omega$  at higher pH (Table 1), which leads to more  $\text{PO}_4$  being removed as discussed in section 4.1.

It is necessary to point out that in our experimental design, the solution pH was kept constant during the course of the experiment. However, in natural sea ice, the precipitation of ikaite will lead to a decrease in brine pH, resulting in a decrease in brine supersaturation with respect to ikaite. Therefore, the precipitation of ikaite will cease until an appropriate level of oversaturation is reached again by further concentration of brine solution and/or pH change [Hu *et al.*, 2014]. Nevertheless, as discussed in section 4.1,  $\text{PO}_4$  removal mainly occurs at the ikaite nucleation stage; further growth of ikaite does not have a significant impact on  $\text{PO}_4$  removal. From this perspective, there should be no difference in  $\text{PO}_4$  removal between pH variable conditions and our pH-constant condition. However, if ikaite in natural sea ice is precipitated very slowly, i.e., ikaite precipitation occurs when brine  $\Omega$  is only slightly above 1, independent of brine pH, then, unlike the results shown in this study, there may be no difference in  $\text{PO}_4$  removal under different pH conditions.

In sea ice brine, pH can vary from 8 to 10 [Gleitz *et al.*, 1995; Papadimitriou *et al.*, 2007]. The elevated pH is attributed to photosynthetic activity [Gleitz *et al.*, 1996]. It is reasonable to speculate that the initial enrichment of nutrients would enhance photosynthetic activity in sea ice [Gleitz and Thomas, 1993], resulting in an increase of pH in brine. The increase in pH and thus the increase in brine  $\Omega$  in turn might promote ikaite precipitation [Hu *et al.*, 2014], which is again likely to limit biological activity due to the removal of  $\text{PO}_4$  by ikaite precipitation.

#### 4.3. Effect of Salinity on $\text{PO}_4$ Coprecipitation With Ikaite

Salinity affects the  $\text{PO}_4$  removal by ikaite precipitation (Table 1).  $\text{PO}_4$  is nearly completely coprecipitated with ikaite in freshwater ( $S = 0$ ). However, at salinity 35 or higher, there is no significant difference in  $\text{PO}_4$  removal at varied salinities, and up to 70% of  $\text{PO}_4$  can be removed from solution by ikaite precipitation. As discussed in



**Figure 5.** Coprecipitation of  $\text{PO}_4$  with ikaite at different temperatures and an initial  $\text{PO}_4$  concentration of  $10 \mu\text{mol kg}^{-1}$ ,  $\text{pH} = 9.0$ ,  $S = 70$ : (a)  $T = -4^\circ\text{C}$ , (b)  $T = -2^\circ\text{C}$ , and (c)  $T = 0^\circ\text{C}$ .

also shows that the amount of  $\text{PO}_4$  coprecipitated with calcite is independent of temperature in the temperature range from  $12^\circ\text{C}$  to  $32^\circ\text{C}$  [Rodriguez *et al.*, 2008]. Thus, one might expect that at lower brine temperatures, the removal of  $\text{PO}_4$  by ikaite precipitation does not differ substantially from that observed in the temperature range used in this study.

#### 4.5. Effect of Initial $\text{PO}_4$ Concentration on $\text{PO}_4$ Coprecipitation With Ikaite

Initial  $\text{PO}_4$  concentration greatly affects the amount of  $\text{PO}_4$  coprecipitated with ikaite (Table 1). The percentage of  $\text{PO}_4$  removal by ikaite precipitation decreases slightly with increasing initial  $\text{PO}_4$  concentration. This result indicates that the distribution coefficient of  $\text{PO}_4$  in solution and  $\text{PO}_4$  coprecipitated with ikaite ( $k = C_{\text{in ikaite}}/C_{\text{in solution}}$ ) depends on the initial  $\text{PO}_4$  concentration; the distribution coefficient  $k$  decreases with increasing initial  $\text{PO}_4$  concentration. Nevertheless, the absolute amount of  $\text{PO}_4$  removed by ikaite precipitation is still larger at higher initial  $\text{PO}_4$  concentrations. For example,  $3.6 \mu\text{mol kg}^{-1}$   $\text{PO}_4$  was removed at an initial  $\text{PO}_4$  concentration of  $5 \mu\text{mol kg}^{-1}$ ; while about  $30 \mu\text{mol kg}^{-1}$  can be removed at an initial  $\text{PO}_4$  concentration of  $50 \mu\text{mol kg}^{-1}$ . From this result, we can infer that if the  $\text{PO}_4$  concentration in sea ice brine is low, the precipitation of ikaite can remove  $\text{PO}_4$  more efficiently, while if ikaite precipitation occurs at high  $\text{PO}_4$  concentrations, more  $\text{PO}_4$  can be removed from sea ice.

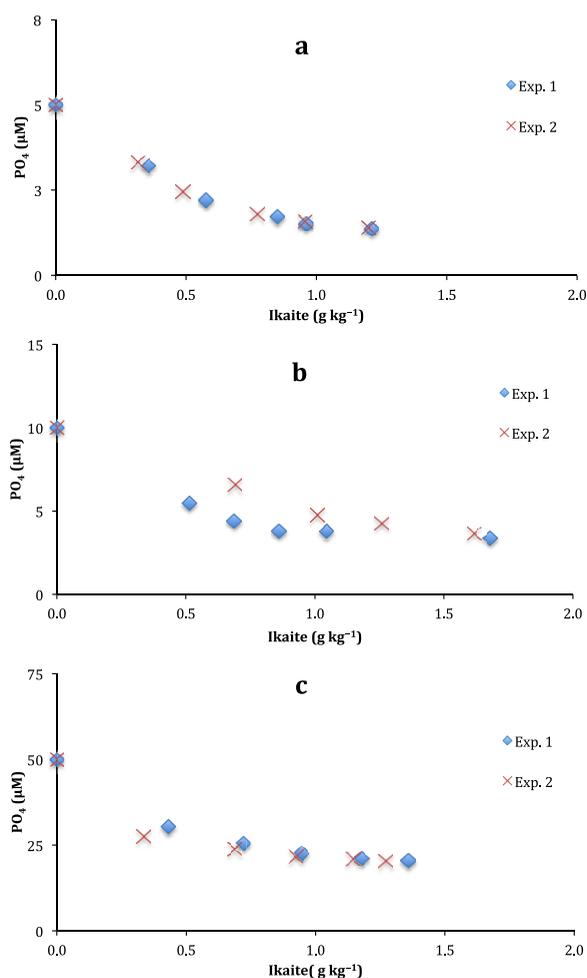
#### 4.6. Relevance of Experiments for Ikaite Precipitation in Natural Sea Ice

Ikaite has been reported to precipitate throughout sea ice with high concentrations usually found in the upper layers of sea ice. However, they have also been reported to occur in the lower layers of sea ice

section 4.1, the nucleation rate is driven by solution supersaturation. However, the nucleation rate can also be strongly affected by the presence of inhibitor ions, such as  $\text{Mg}^{2+}$  [Reddy and Wang, 1980]. As a result, although the solution  $\Omega$  at the onset of ikaite precipitation is similar between  $S = 0$  and  $S \geq 35$  (Table 1), the difference in  $\text{PO}_4$  removal by ikaite precipitation is probably due to the absence/presence of inhibitor ions in solution. The concentrations of inhibitor ions at different salinities do not seem to affect the coprecipitation of  $\text{PO}_4$  with ikaite in ASW. It is therefore reasonable to argue that the change in salinity in sea ice brine might not have a significant impact on the amount of  $\text{PO}_4$  removed by ikaite precipitation since the brine salinity would not drop to zero.

#### 4.4. Effect of Temperature on $\text{PO}_4$ Coprecipitation With Ikaite

The change in temperature in the studied range from  $-4^\circ\text{C}$  to  $0^\circ\text{C}$  has no effect on the amount of  $\text{PO}_4$  coprecipitated with ikaite (Table 1). The removal of  $\text{PO}_4$  by ikaite precipitation is nearly the same in this small temperature range. This could probably be explained by the equal ikaite nucleation rate indicated by the similar  $\Omega$  in this temperature range (Table 1). The temperature range studied here was limited because ASW at  $S = 70$  would have frozen at temperatures below  $-4^\circ\text{C}$  [Feistel, 2008]. Nevertheless, a laboratory study on the coprecipitation of  $\text{PO}_4$  with calcite



**Figure 6.** Coprecipitation of  $\text{PO}_4$  with ikaite at different initial  $\text{PO}_4$  concentrations and  $\text{pH} = 9.0$ ,  $T = 0^\circ\text{C}$ ,  $S = 70$ : (a)  $[\text{PO}_4] = 5 \mu\text{mol kg}^{-1}$ , (b)  $[\text{PO}_4] = 10 \mu\text{mol kg}^{-1}$ , and (c)  $[\text{PO}_4] = 50 \mu\text{mol kg}^{-1}$ .

note that with the precipitation of gypsum at lower temperatures,  $\text{PO}_4$  might be further removed from sea ice due to the coprecipitation with gypsum [Witkamp, 1989].

[Geilfus et al., 2013a; Rysgaard et al., 2014]. According to our experimental results, it is reasonable to speculate that the depletion of  $\text{PO}_4$  in natural sea ice can also be caused by the coprecipitation with ikaite in addition to the removal by biological activity. It is commonly believed that nitrate is the limiting nutrient for ice algal growth in sea ice, while an excess  $\text{PO}_4$  relative to nitrate is reported based on the Redfield ratio [Gleitz et al., 1995; Papadimitriou et al., 2007]. However, elevated  $\text{PO}_4$  concentrations observed might be due to the faster remineralization of organically bound phosphorus than organically bound nitrogen [Papadimitriou et al., 2007], which does not represent the nutrient conditions when biological activity takes place. Our study might suggest that during the early stage of sea ice formation, when ikaite is precipitated, ice algal growth is also likely to be limited by  $\text{PO}_4$  due to the competition resulting from ikaite precipitation.

A recent study revealed that another calcium compound, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) can also be precipitated in natural sea ice at temperatures between  $-3.2^\circ\text{C}$  and  $-10^\circ\text{C}$  [Geilfus et al., 2013b]. Although we did not observe this precipitate in our study, which can be easily distinguished by the different morphology from ikaite [Geilfus et al., 2013b], it is important to

**Table 1.** Common Logarithm of the Ion Activity Product of Calcium and Carbonate ( $\log(\text{IAP})$ ) and Solution Supersaturation ( $\Omega = \text{IAP}/K_{\text{sp,ikaite}}$ ) at the Onset of Ikaite Precipitation;  $\text{PO}_4$  Equilibrium Concentrations and Percentage of  $\text{PO}_4$  Removal by Ikaite Precipitation Under Different  $\text{pH}$ , Salinity, Temperature, and Phosphate Concentration Conditions<sup>a</sup>

Experimental Conditions	Experimental Variations	Log (IAP)	$\Omega$	$[\text{PO}_4]_{\text{Eq}}$ ( $\mu\text{M}$ )	$\text{PO}_4$ Removal %
pH effect: at S 70, T $0^\circ\text{C}$ , $\text{PO}_4$ 10 $\mu\text{M}$	8.5	$-6.73 \pm 0.025$	3.02	$5.8 \pm 0.19$	$42 \pm 1.9$
	9.0	$-6.67 \pm 0.011$	3.47	$3.3 \pm 0.04$	$67 \pm 0.4$
	9.5	$-6.53 \pm 0.005$	4.68	$0.8 \pm 0.00$	$92 \pm 0.0$
	10.0	$-6.48 \pm 0.020$	5.37	$0.2 \pm 0.11$	$97 \pm 1.1$
S effect: at pH 9.0, T $0^\circ\text{C}$ , $\text{PO}_4$ 10 $\mu\text{M}$	0	$-6.59 \pm 0.021$	4.17	$0.3 \pm 0.04$	$97 \pm 0.4$
	35	$-6.68 \pm 0.051$	3.47	$2.7 \pm 0.00$	$73 \pm 0.0$
	70	$-6.67 \pm 0.011$	3.47	$3.3 \pm 0.04$	$67 \pm 0.4$
	105	$-6.61 \pm 0.003$	3.98	$3.0 \pm 0.05$	$70 \pm 0.5$
T effect: at pH 9.0, S 70, $\text{PO}_4$ 10 $\mu\text{M}$	$0^\circ\text{C}$	$-6.67 \pm 0.011$	3.47	$3.2 \pm 0.22$	$68 \pm 2.2$
	$-2^\circ\text{C}$	$-6.73 \pm 0.023$	3.39	$3.1 \pm 0.73$	$69 \pm 7.3$
	$-4^\circ\text{C}$	$-6.74 \pm 0.017$	3.72	$3.3 \pm 0.04$	$67 \pm 0.4$
$[\text{PO}_4]$ effect: at pH 9.0, S 70, T $0^\circ\text{C}$	5 $\mu\text{M}$	$-6.71 \pm 0.024$	3.16	$1.4 \pm 0.03$	$72 \pm 0.6$
	10 $\mu\text{M}$	$-6.67 \pm 0.011$	3.47	$3.3 \pm 0.04$	$67 \pm 0.4$
	50 $\mu\text{M}$	$-6.66 \pm 0.022$	3.55	$20.4 \pm 0.06$	$59 \pm 0.1$

<sup>a</sup>The standard deviation is derived from duplicate experiments.

## 5. Conclusions

We investigated the effect of ikaite precipitation on phosphate ( $\text{PO}_4$ ) concentration under conditions representative for sea ice brine and shows that the concentration of  $\text{PO}_4$  in solution is strongly affected by ikaite precipitation.  $\text{PO}_4$  can be coprecipitated with ikaite. The coprecipitation of  $\text{PO}_4$  with ikaite mainly occurs at the early stage of ikaite formation (nucleation), and  $\text{PO}_4$  reaches a constant concentration in solution even when ikaite crystals continue to grow. The highly variable physicochemical conditions in sea ice are likely to have an impact on  $\text{PO}_4$  removal by ikaite precipitation. The amount of  $\text{PO}_4$  coprecipitated with ikaite increases with increasing pH and initial  $\text{PO}_4$  concentration. Salinity ( $S \geq 35$ ) and temperature have little effect on  $\text{PO}_4$  coprecipitation with ikaite in ASW. The fact that  $\text{PO}_4$  can be strongly coprecipitated with ikaite indicates that ikaite precipitation could deplete the phosphate concentration in sea ice and thus has an impact on biological activity.

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## References

- Bischoff, J. L., J. A. Fitzpatrick, and R. J. Rosenbauer (1993), The solubility and stabilization of ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) from  $0^\circ$  to  $25^\circ\text{C}$ : Environmental and paleoclimatic implications for thionite tufa, *J. Geol.*, *101*(1), 21–33.
- Boistelle, R., and J. P. Astier (1988), Crystallization mechanisms in solution, *J. Cryst. Growth*, *90*(1–3), 14–30, doi:10.1016/0022-0248(88)90294-1.
- Buchardt, B., C. Israelson, P. Seaman, and G. Stockmann (2001), Ikaite tufa towers in Ikka Fjord, southwest Greenland: Their formation by mixing of seawater and alkaline spring water, *J. Sediment. Res.*, *71*(1), 176–189, doi:10.1306/042800710176.
- Council, T. C., and P. C. Bennett (1993), Geochemistry of ikaite formation at Mono Lake, California: Implications for the origin of tufa mounds, *Geology*, *21*(11), 971–974, doi:10.1130/0091-7613(1993)021<0971:GOIFAM>2.3.CO;2.
- Danen-Louwerse, H. J., L. Lijklema, and M. Coenraats (1995), Coprecipitation of phosphate with calcium carbonate in Lake Veluwe, *Water Res.*, *29*(7), 1781–1785, doi:10.1016/0043-1354(94)00301-M.
- Dieckmann, G. S., M. A. Lange, S. F. Ackley, and J. C. Jennings Jr. (1991), The nutrient status in sea ice of the Weddell Sea during winter: Effects of sea ice texture and algae, *Polar Biol.*, *11*(7), 449–456, doi:10.1007/BF00233080.
- Dieckmann, G. S., G. Nehrke, S. Papadimitriou, J. Göttlicher, R. Steininger, H. Kennedy, D. Wolf-Gladrow, and D. N. Thomas (2008), Calcium carbonate as ikaite crystals in Antarctic sea ice, *Geophys. Res. Lett.*, *35*, L08501, doi:10.1029/2008GL033540.
- Dieckmann, G. S., G. Nehrke, C. Uhlig, J. Göttlicher, S. Gerland, M. A. Granskog, and D. N. Thomas (2010), Brief Communication: Ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) discovered in Arctic sea ice, *The Cryosphere*, *4*(2), 227–230, doi:10.5194/tc-4-227-2010.
- Feistel, R. (2008), A Gibbs function for seawater thermodynamics for  $-6$  to  $80^\circ\text{C}$  and salinity up to  $120\text{ g kg}^{-1}$ , *Deep Sea Res., Part I*, *55*(12), 1639–1671, doi:10.1016/j.dsr.2008.07.004.
- Geilfus, N. X., G. Carnat, G. S. Dieckmann, N. Halden, G. Nehrke, T. Papakyriakou, J. L. Tison, and B. Delille (2013a), 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. Oceans*, *118*, 244–255, doi:10.1029/2012JC007980.
- Geilfus, N. X., R. J. Galley, M. Cooper, N. Halden, A. Hare, F. Wang, D. H. Søgaard, and S. Rysgaard (2013b), Gypsum crystals observed in experimental and natural sea ice, *Geophys. Res. Lett.*, *40*, 6362–6367, doi:10.1002/2013GL058479.
- Gleitz, M., and D. N. Thomas (1993), Variation in phytoplankton standing stock, chemical composition and physiology during sea-ice formation in the southeastern Weddell Sea, Antarctica, *J. Exp. Mar. Biol. Ecol.*, *173*(2), 211–230, doi:10.1016/0022-0981(93)90054-R.
- Gleitz, M., M. R. v. d. Loeff, D. N. Thomas, G. S. Dieckmann, and F. J. Millero (1995), Comparison of summer and winter inorganic carbon, oxygen and nutrient concentrations in Antarctic sea ice brine, *Mar. Chem.*, *51*(2), 81–91, doi:10.1016/0304-4203(95)00053-T.
- Gleitz, M., H. Kukert, U. Riebesell, and G. S. Dieckmann (1996), Carbon acquisition and growth of Antarctic sea ice diatoms in closed bottle incubations, *Mar. Ecol. Prog. Ser.*, *135*, 169–177, doi:10.3354/meps135169.
- Günther, S., M. Gleitz, and G. S. Dieckmann (1999), Biogeochemistry of Antarctic sea ice: A case study on platelet ice layers at Drescher Inlet, Weddell Sea, *Mar. Ecol. Prog. Ser.*, *177*, 1–13, doi:10.3354/meps177001.
- Gustafsson, J. P. (2011), *Visual MINTEQ Ver. 3.0*. KTH, Dep. of Land and Water Resour. Eng., Stockholm.
- House, W. A. (1990), The prediction of phosphate coprecipitation with calcite in freshwaters, *Water Res.*, *24*(8), 1017–1023, doi:10.1016/0043-1354(90)90124-O.
- House, W. A., and L. Donaldson (1986), Adsorption and coprecipitation of phosphate on calcite, *J. Colloid Interface Sci.*, *112*(2), 309–324, doi:10.1016/0021-9797(86)90101-3.
- Hu, Y.-B., D. A. Wolf-Gladrow, G. S. Dieckmann, C. Völker, and G. Nehrke (2014), 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.*, *162*, 10–18, doi:10.1016/j.marchem.2014.02.003.
- Kitano, Y., M. Okumura, and M. Idogaki (1978), Uptake of phosphate ions by calcium carbonate, *Geochem. J.*, *12*, 29–37.
- Millero, F., F. Huang, X. R. Zhu, X. W. Liu, and J. Z. Zhang (2001), Adsorption and desorption of phosphate on calcite and aragonite in seawater, *Aquat. Geochem.*, *7*(1), 33–56, doi:10.1023/A:1011344117092.
- Millero, F. J. (2006), *Chemical Oceanography*, 3rd ed., CRC Press, Boca Raton, Fla.
- Murphy, T. P., K. J. Hall, and I. Yesaki (1983), Coprecipitation of phosphate with calcite in a naturally eutrophic lake, *Limnol. Oceanogr.*, *28*(1), 58–69, doi:10.4319/lo.1983.28.1.0058.
- Nehrke, G., H. Poigner, D. Wilhelms-Dick, T. Brey, and D. Abele (2012), Coexistence of three calcium carbonate polymorphs in the shell of the Antarctic clam *Laternula elliptica*, *Geochem. Geophys. Geosyst.*, *13*, Q05014, doi:10.1029/2011GC003996.
- Papadimitriou, S., D. N. Thomas, H. Kennedy, C. Haas, H. Kuosa, A. Krell, and G. S. Dieckmann (2007), Biogeochemical composition of natural sea ice brines from the Weddell Sea during early austral summer, *Limnol. Oceanogr. Methods*, *52*(5), 1809–1823.
- Reddy, M. M., and K. K. Wang (1980), Crystallization of calcium carbonate in the presence of metal ions: I. Inhibition by magnesium ion at pH 8.8 and  $25^\circ\text{C}$ , *J. Cryst. Growth*, *50*(2), 470–480, doi:10.1016/0022-0248(80)90095-0.
- Redfield, A. C., B. H. Ketchum, and F. A. Richards (1963), The influence of organisms on the composition of sea-water, in *The Sea*, edited by M. N. Hill, pp. 26–77, Interscience, N. Y.
- Rodriguez, I. R., C. Amrhein, and M. A. Anderson (2008), Laboratory studies on the coprecipitation of phosphate with calcium carbonate in the Salton Sea, California, *Hydrobiologia*, *604*, 45–55, doi:10.1007/s10750-008-9310-7.

- Rysgaard, S., et al. (2014), Temporal dynamics of ikaite in experimental sea ice, *The Cryosphere*, 8(4), 1469–1478, doi:10.5194/tc-8-1469-2014.
- Sawada, K., S. Yoshida, and T. Suzuki (1992), Adsorption of phosphate on vaterite, *J. Chem. Soc. Faraday Trans.*, 88(15), 2227–2231, doi: 10.1039/FT9928802227.
- Selleck, B., P. F. Carr, and B. G. Jones (2007), A review and synthesis of glendonites (pseudomorphs after ikaite) with new data: Assessing applicability as recorders of ancient coldwater conditions, *J. Sediment. Res.*, 77, 980–991, doi:10.2110/jsr.2007.087.
- Tlili, M. M., M. B. Amor, C. Gabrielli, S. Joiret, G. Maurin, and P. Rousseau (2001), Characterization of CaCO<sub>3</sub> hydrates by micro-Raman spectroscopy, *J. Raman Spectrosc.*, 33, 10–16.
- Vekilov, P. G. (2010), Nucleation, *Cryst. Growth Des.*, 10(12), 5007–5019, doi:10.1021/cg1011633.
- Witkamp, G. J. (1989), Crystallization of calcium sulfate and uptake of impurities, PhD thesis, Delft Univ. of Technol., Delft, Netherlands.
- Yagi, S., and K. Fukushi (2011), Phosphate sorption on monohydrocalcite, *J. Mineral. Petrol. Sci.*, 106(2), 109–113, doi:10.2465/jmps.101021a.