

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 CaCO_3 precipitation in sea ice. However, the impact of ikaite precipitation on phosphate (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°C to 0°C , and 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 PO_4 concentration in sea ice under different conditions. Our results show that PO_4 is coprecipitated with ikaite under all experimental conditions. The amount of PO_4 removed by ikaite precipitation increases with increasing pH. Changes in salinity ($S \geq 35$) as well as temperature have little impact on PO_4 removal by ikaite precipitation. The initial PO_4 concentration affects the PO_4 coprecipitation. These findings may shed some light on the observed variability of 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 $\text{C:N:P} = 106:16:1$ [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 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 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 PO_4 has been considered to be crucial for ikaite formation as ikaite is very often found in 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 PO_4 is only crucial for ikaite formation in freshwater and in NaCl medium, whereas in seawater-based solutions, PO_4 is not required for the formation of ikaite. Therewith, in seawater-based solutions, other ions (such as Mg^{2+} and/or 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 PO_4 does not affect ikaite precipitation thermodynamically or kinetically [Hu *et al.*, 2014]. The effect of ikaite precipitation on PO_4 concentration is studied here because PO_4 is an important nutrient and the enrichment or depletion of PO_4 in sea ice has a major effect on the biological activity in sea ice.

The removal of PO_4 by calcium carbonate has long been known. 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 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 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 PO_4 onto calcite, aragonite, vaterite, and

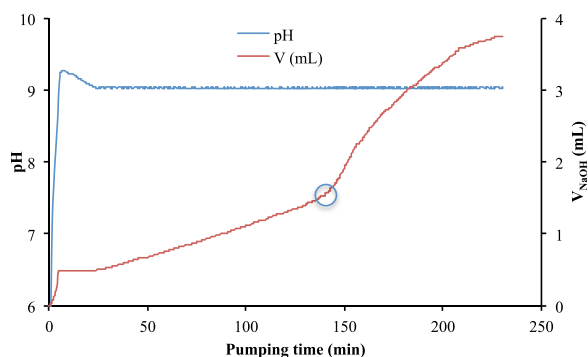


Figure 1. A typical NaOH titration profile obtained at pH = 9.0, $S = 70$, $T = 0^{\circ}\text{C}$, and $[\text{PO}_4] = 10 \mu\text{mol kg}^{-1}$. The circle indicates the onset of calcium carbonate precipitation.

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 PO_4 removal.

In this study, we investigated how the precipitation of ikaite affects the 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°C to 0°C , and PO_4 concentrations from 5 to $50 \mu\text{mol kg}^{-1}$ so as to understand how changes in these parameters affected 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. Ca^{2+} and HCO_3^- were not added initially. The amount of salt missing from not adding NaHCO_3 and CaCl_2 was compensated for by adding 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 CaCl_2 and NaHCO_3 at concentrations of 2.5 and 0.5 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 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[®] ACS, ISO, Reag, Ph Eur) except SrCl_2 and H_3BO_3 , which were from Carl Roth (p.a., ACS, ISO). Different concentrations of PO_4 were prepared from a phosphate stock solution (Merck, CertiPUR[®]) 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°C), and 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 CaCl_2 and 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 ± 0.010 (Radiometer Analytical, IUPAC Standard). The pH of the solution was kept constant by adding NaOH (0.5 mol L^{-1}), which was controlled by a titration system (TA20 plus, SI Analytics). The value of pH and the volume of NaOH added to the solution were recorded every 10 s. Depending on the experimental conditions, the input of CaCl_2 , NaHCO_3 , and 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, CO_2 is released, which leads to a large decrease in solution pH. This rapid change in pH was compensated for by adding NaOH . Therefore, the onset of precipitation was determined by the sudden change of NaOH volume (V_{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 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 Ca^{2+} and 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 CO_3^{2-} activity, the trend of Ω under different experimental conditions should be still adequate.

2.6. Quantification of Ikaite and 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 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 μm 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 PO_4 and Ca^{2+} measurements, respectively.

Ca^{2+} concentrations were determined using Inductively-Coupled Plasma Optical Emission Spectrometry (IRIS Intrepid Optical Emission Spectrometer Duo HR, Thermo Fisher Scientific). 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 Ca^{2+} pumped into the reaction vessel minus the moles of Ca^{2+} remaining in solution. The change in solution mass and the loss of 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 (g kg^{-1}) in solution at the i^{th} sampling, $i = 1$ to 5; C_0 Ca^{2+} concentration (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^{th} sampling; C_i Ca^{2+} concentration (mol kg^{-1}) measured at the i^{th} sampling time after precipitation; m_i mass (g) of solution at the i^{th} sampling; $\sum_{k=0}^{i-1} n_k$ total moles of 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 ν_1 (1071 cm^{-1}) and ν_4 (718 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°C to 0°C , and 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 μm (Figure 2b).

3.2. Removal of 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°C), and initial 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 PO_4 removal by ikaite precipitation. The concentration of PO_4 in solution decreases with the amount of ikaite precipitated. The concentration of PO_4 drops steeply during the early stage of ikaite precipitation,

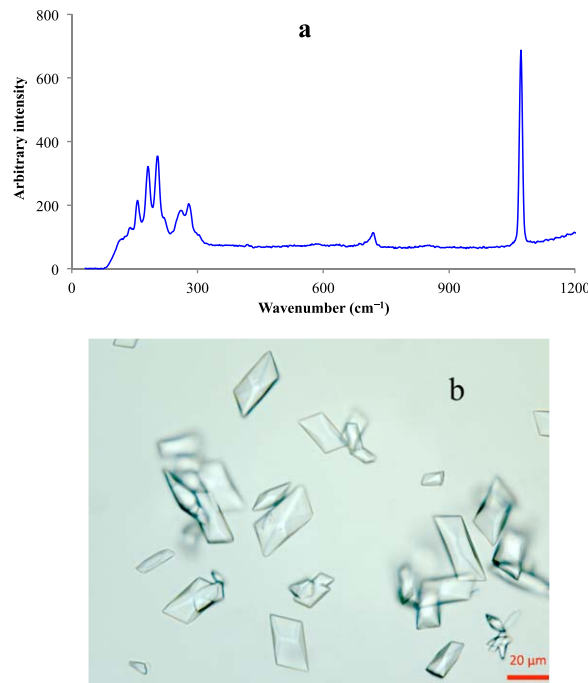


Figure 2. (a) Ikaite Raman spectra and (b) ikaite morphology obtained under the experimental condition of pH = 9.0, S = 70, T = 0°C, [PO₄] = 10 μmol kg⁻¹, and representative of all precipitates in this study.

followed by a much slower decrease, and then the PO₄ concentration in solution reaches an equilibrium (within 1 h) even though ikaite crystals continue to grow. The pattern of PO₄ removal by ikaite precipitation under all experimental conditions presented in this study is similar to that observed in studies on PO₄ coprecipitation with calcite and aragonite [House and Donaldson, 1986; Kitano et al., 1978]. The total amount of PO₄ 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 (Ω) under different pH values, salinities, temperatures, and PO₄ 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 Ω from 3.0 to 5.4. There is no significant difference in Ω at different salinities as well as at different temperatures and PO₄ concentrations.

4. Discussion

4.1. General Pattern of PO₄ Coprecipitation With Ikaite

In this study, the concentrations of Ca²⁺ and CO₃²⁻ in solution increase with pumping time until the onset of ikaite precipitation when the solution reaches the highest Ω . After ikaite precipitation starts, Ω 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

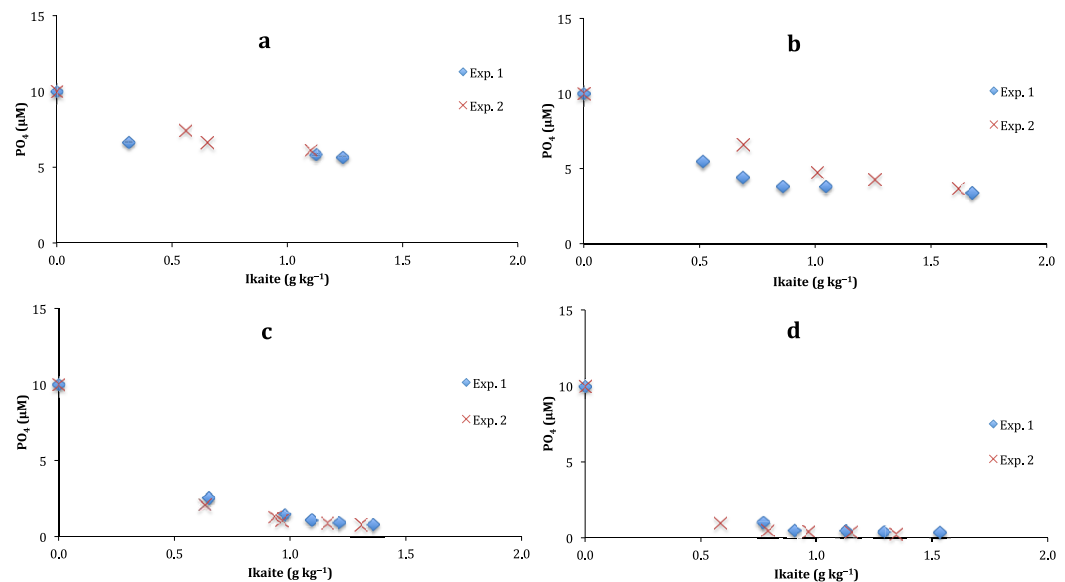


Figure 3. Coprecipitation of PO₄ with ikaite at different pH values and an initial PO₄ concentration of 10 μmol kg⁻¹, S = 70, T = 0°C: (a) pH = 8.5, (b) pH = 9.0, (c) pH = 9.5, and (d) pH = 10.0.

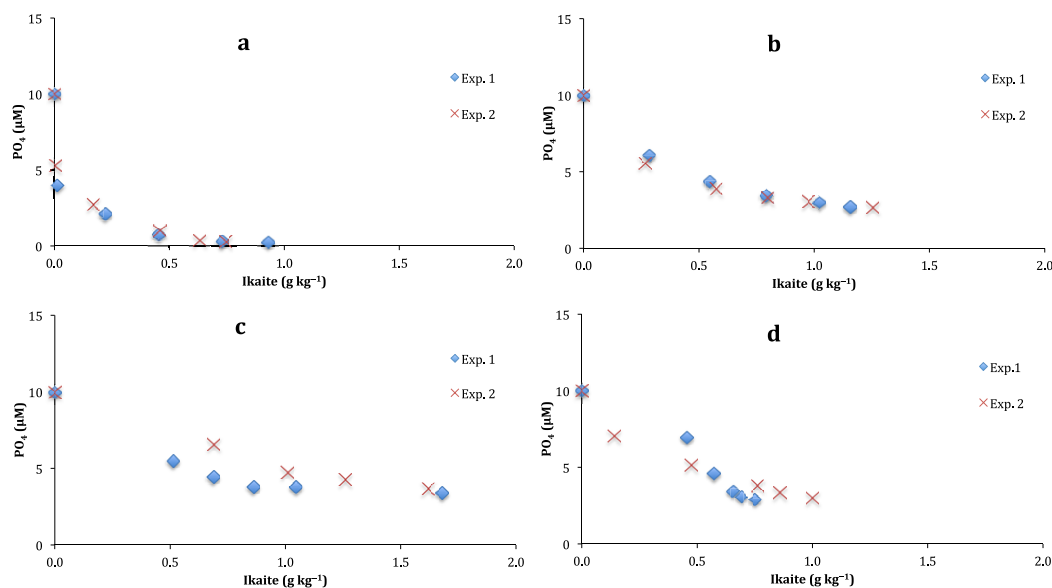


Figure 4. Coprecipitation of PO_4 with ikaite at different salinities and an initial PO_4 concentration of $10 \mu\text{mol kg}^{-1}$, $\text{pH} = 9.0$, $T = 0^\circ\text{C}$: (a) $S = 0$, (b) $S = 35$, (c) $S = 70$, and (d) $S = 105$.

of crystals continues [Vekilov, 2010]. The removal behavior of PO_4 by ikaite precipitation indicates that coprecipitation of 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 PO_4 , and thus the PO_4 concentration in solution does not change with the subsequent growth of ikaite. However, the final PO_4 equilibrium concentration differs under different experimental conditions.

4.2. Effect of pH on PO_4 Coprecipitation With Ikaite

The pH value has a significant effect on PO_4 removal by ikaite precipitation (Table 1). The coprecipitation of PO_4 with ikaite increases with increasing pH. At $\text{pH} = 8.5$, 42% of PO_4 is removed from solution by ikaite precipitation; above $\text{pH} = 9.5$, >90% of PO_4 is coprecipitated with ikaite. This might be due to the high ikaite nucleation rate resulting from the higher Ω at higher pH (Table 1), which leads to more 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, PO_4 removal mainly occurs at the ikaite nucleation stage; further growth of ikaite does not have a significant impact on PO_4 removal. From this perspective, there should be no difference in 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 Ω is only slightly above 1, independent of brine pH, then, unlike the results shown in this study, there may be no difference in 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 Ω in turn might promote ikaite precipitation [Hu *et al.*, 2014], which is again likely to limit biological activity due to the removal of PO_4 by ikaite precipitation.

4.3. Effect of Salinity on PO_4 Coprecipitation With Ikaite

Salinity affects the PO_4 removal by ikaite precipitation (Table 1). PO_4 is nearly completely coprecipitated with ikaite in freshwater ($S = 0$). However, at salinity 35 or higher, there is no significant difference in PO_4 removal at varied salinities, and up to 70% of PO_4 can be removed from solution by ikaite precipitation. As discussed in

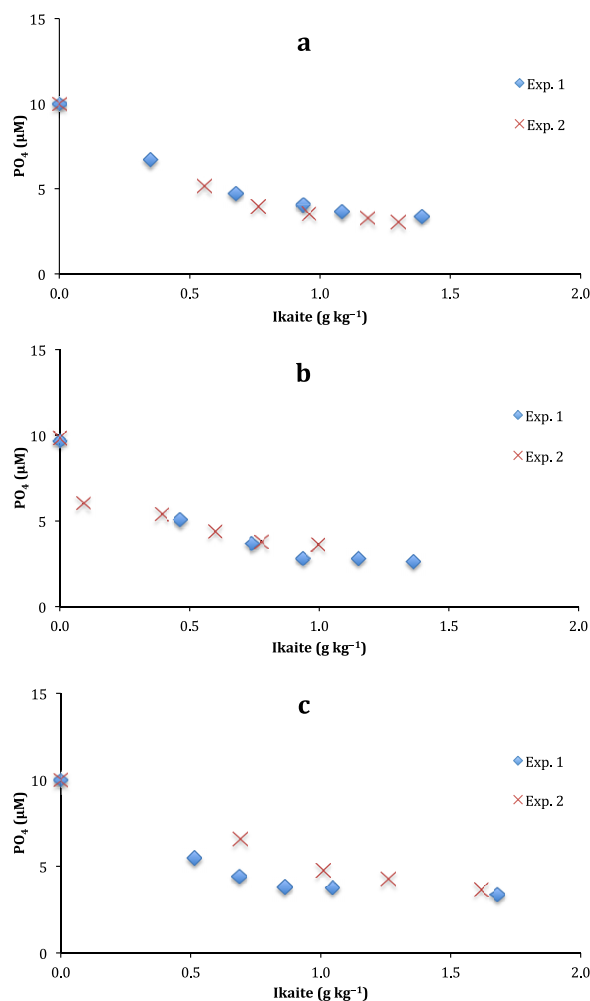


Figure 5. Coprecipitation of PO_4 with ikaite at different temperatures and an initial PO_4 concentration of $10 \mu\text{mol kg}^{-1}$, $\text{pH} = 9.0$, $S = 70$: (a) $T = -4^\circ\text{C}$, (b) $T = -2^\circ\text{C}$, and (c) $T = 0^\circ\text{C}$.

also shows that the amount of PO_4 coprecipitated with calcite is independent of temperature in the temperature range from 12°C to 32°C [Rodriguez *et al.*, 2008]. Thus, one might expect that at lower brine temperatures, the removal of 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 PO_4 Concentration on PO_4 Coprecipitation With Ikaite

Initial PO_4 concentration greatly affects the amount of PO_4 coprecipitated with ikaite (Table 1). The percentage of PO_4 removal by ikaite precipitation decreases slightly with increasing initial PO_4 concentration. This result indicates that the distribution coefficient of PO_4 in solution and PO_4 coprecipitated with ikaite ($k = C_{\text{in ikaite}}/C_{\text{in solution}}$) depends on the initial PO_4 concentration; the distribution coefficient k decreases with increasing initial PO_4 concentration. Nevertheless, the absolute amount of PO_4 removed by ikaite precipitation is still larger at higher initial PO_4 concentrations. For example, $3.6 \mu\text{mol kg}^{-1}$ PO_4 was removed at an initial PO_4 concentration of $5 \mu\text{mol kg}^{-1}$; while about $30 \mu\text{mol kg}^{-1}$ can be removed at an initial PO_4 concentration of $50 \mu\text{mol kg}^{-1}$. From this result, we can infer that if the PO_4 concentration in sea ice brine is low, the precipitation of ikaite can remove PO_4 more efficiently, while if ikaite precipitation occurs at high PO_4 concentrations, more 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 Mg^{2+} [Reddy and Wang, 1980]. As a result, although the solution Ω at the onset of ikaite precipitation is similar between $S = 0$ and $S \geq 35$ (Table 1), the difference in 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 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 PO_4 removed by ikaite precipitation since the brine salinity would not drop to zero.

4.4. Effect of Temperature on PO_4 Coprecipitation With Ikaite

The change in temperature in the studied range from -4°C to 0°C has no effect on the amount of PO_4 coprecipitated with ikaite (Table 1). The removal of 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 Ω 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°C [Feistel, 2008]. Nevertheless, a laboratory study on the coprecipitation of PO_4 with calcite

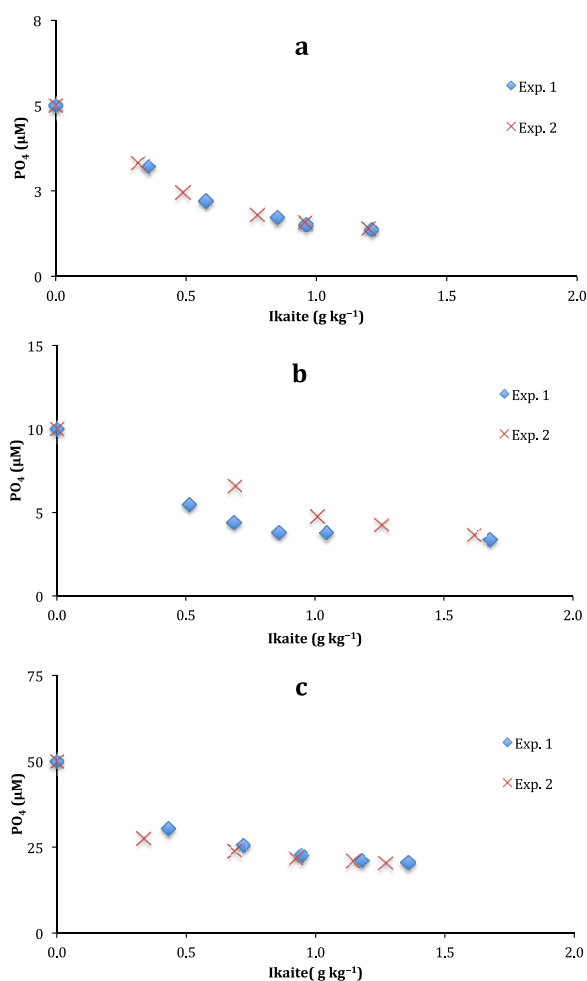


Figure 6. Coprecipitation of PO_4 with ikaite at different initial PO_4 concentrations and $\text{pH} = 9.0$, $T = 0^\circ\text{C}$, $S = 70$: (a) $[\text{PO}_4] = 5 \mu\text{mol kg}^{-1}$, (b) $[\text{PO}_4] = 10 \mu\text{mol kg}^{-1}$, and (c) $[\text{PO}_4] = 50 \mu\text{mol kg}^{-1}$.

note that with the precipitation of gypsum at lower temperatures, 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 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 PO_4 relative to nitrate is reported based on the Redfield ratio [Gleitz et al., 1995; Papadimitriou et al., 2007]. However, elevated 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 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°C and -10°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; PO_4 Equilibrium Concentrations and Percentage of PO_4 Removal by Ikaite Precipitation Under Different pH , Salinity, Temperature, and Phosphate Concentration Conditions^a

Experimental Conditions	Experimental Variations	$\log(\text{IAP})$	Ω	$[\text{PO}_4]_{\text{Eq}} (\mu\text{M})$	PO_4 Removal %
pH effect: at $S = 70$, $T = 0^\circ\text{C}$, $\text{PO}_4 = 10 \mu\text{M}$	8.5	-6.73 ± 0.025	3.02	5.8 ± 0.19	42 ± 1.9
	9.0	-6.67 ± 0.011	3.47	3.3 ± 0.04	67 ± 0.4
	9.5	-6.53 ± 0.005	4.68	0.8 ± 0.00	92 ± 0.0
	10.0	-6.48 ± 0.020	5.37	0.2 ± 0.11	97 ± 1.1
S effect: at $\text{pH} = 9.0$, $T = 0^\circ\text{C}$, $\text{PO}_4 = 10 \mu\text{M}$	0	-6.59 ± 0.021	4.17	0.3 ± 0.04	97 ± 0.4
	35	-6.68 ± 0.051	3.47	2.7 ± 0.00	73 ± 0.0
	70	-6.67 ± 0.011	3.47	3.3 ± 0.04	67 ± 0.4
	105	-6.61 ± 0.003	3.98	3.0 ± 0.05	70 ± 0.5
T effect: at $\text{pH} = 9.0$, $S = 70$, $\text{PO}_4 = 10 \mu\text{M}$	0°C	-6.67 ± 0.011	3.47	3.2 ± 0.22	68 ± 2.2
	-2°C	-6.73 ± 0.023	3.39	3.1 ± 0.73	69 ± 7.3
	-4°C	-6.74 ± 0.017	3.72	3.3 ± 0.04	67 ± 0.4
$[\text{PO}_4]$ effect: at $\text{pH} = 9.0$, $S = 70$, $T = 0^\circ\text{C}$	$5 \mu\text{M}$	-6.71 ± 0.024	3.16	1.4 ± 0.03	72 ± 0.6
	$10 \mu\text{M}$	-6.67 ± 0.011	3.47	3.3 ± 0.04	67 ± 0.4
	$50 \mu\text{M}$	-6.66 ± 0.022	3.55	20.4 ± 0.06	59 ± 0.1

^aThe standard deviation is derived from duplicate experiments.

5. Conclusions

We investigated the effect of ikaite precipitation on phosphate (PO_4) concentration under conditions representative for sea ice brine and shows that the concentration of PO_4 in solution is strongly affected by ikaite precipitation. PO_4 can be coprecipitated with ikaite. The coprecipitation of PO_4 with ikaite mainly occurs at the early stage of ikaite formation (nucleation), and 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 PO_4 removal by ikaite precipitation. The amount of PO_4 coprecipitated with ikaite increases with increasing pH and initial PO_4 concentration. Salinity ($S \geq 35$) and temperature have little effect on PO_4 coprecipitation with ikaite in ASW. The fact that 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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