

Referee #1

Rysgaard et al.: Dynamic ikaite production and dissolution in sea ice – control by temperature, salinity and pCO₂ conditions.

General Comments Rysgaard et al. present observations of the ikaite content with depth and time in sea ice and its surface features (frost flowers and brine skim) grown and investigated at an outdoor experimental facility in the course of one month. The ikaite content is based on ‘dissolving crystal’ counts under the microscope and their conversion to ikaite molar concentration. The idea is that all ‘black spots’ on photographic sea ice slides disappearing upon warming are dissolving ikaite crystals. This tenet is carried over from their previous article on method development as an assumption (P6080 L28), which is confusing because it suggests that it is yet to be substantiated in a controlled experiment. In other words, the counts and their quantification as ikaite have a degree of uncertainty which requires rigorous evaluation if this promising method is to be used in carbon budgets in sea ice.

As outlined below, the Title of the article is misleading as the study does not provide any observational evidence for control on ikaite dynamics by pCO₂, while the evidence for direct and singular temperature control, although expected in terms of ikaite solubility and internal brine compositional changes with temperature, is tenuous. The salinity control in the Title is not explicitly touched upon in any section of the manuscript. Further, the thread used in the Introduction anticipates the use of the presented observations in carbon budgets in sea ice, which is not fulfilled. Consequently, the interpretation needs to be trimmed to match the potential of the offered observations and available evidence from published experimental and field studies, the latter being currently absent from the manuscript. At best, the manuscript reports the dynamic temporal distribution of ikaite in sea ice in the SERF experimental facility, which is valuable in itself, provided that the sampling assumption mentioned above is shown to be secure.

RESPONSE: We will change the title to: Temporal dynamics of ikaite in experimental sea ice.

Specific comments

Methods

P6079, L7-8: This statement may be true in terms of ionic composition (SERF sea- water contained all major ions present in standard seawater) but salinity-normalization to S=35 reveals that the concentrations of some of the pertinent ions in SERF seawater were substantially different from those in standard seawater, i.e., Ca²⁺ was 15% higher, Mg²⁺ was 50% lower, and sulphate was 27% lower than standard seawater. As a result, the ionic strength of the SERF seawater is 10% lower (I=0.653 at S=35) than standard seawater (I=0.721). Some amendment is needed to reflect this fact.

RESPONSE: The seawater was formulated to mimic a S=32.9 seawater instead of

S=35, which was not made clear in the original text. We will add the following in the text: “The artificial seawater was formulated by dissolving large quantities of various rock salts into local groundwater to mimic the major ion composition of natural seawater (S=32.9). Most ions were within 15% deviation from the natural composition, with the exception that the concentrations of Mg²⁺ and sulfate were 49.1% and 26.5% lower, respectively (Table 1)”.

We will also revise Table 1 as follows.

Table 1. Seawater composition used at SERF and in the FREZCHEM modeling.

Composition	SERF seawater (Ex 2.2)	Natural seawater (S=32.9) ^a	Difference (%)
Na ⁺ (mol kg ⁻¹)	0.4719	0.4569	3.3
K ⁺ (mol kg ⁻¹)	0.009796	0.009945	-1.5
Ca ²⁺ (mol kg ⁻¹)	0.011478	0.010020	14.5
Mg ²⁺ (mol kg ⁻¹)	0.026167	0.051456	-49.1
Cl ⁻ (mol kg ⁻¹)	0.5134	0.5318	-3.5
Br ⁻ (mol kg ⁻¹)	0.00092	0.00082	12.9
SO ₄ ²⁻ (mol kg ⁻¹)	0.02021	0.02750	-26.5
pH	8.2		
TA (umol kg ⁻¹)	2380		
S	32.9	32.9	

^a Extrapolated from the S=35 standard seawater (Millero, 2006) to S=32.9.

P6080, L28, & P6081, L6-12: The core of the dataset and narrative in this manuscript is based on this assumption. In the absence of even a brief mention in this manuscript of confidence-building validity tests, I conclude that this assumption is previously untested for reliability. Provide assurance that this assumption is safe in the presence of substantial quantities of mirabilite predicted by the FREZCHEM model. For example, a standard seawater freezing FREZCHEM run at constant atmospheric pCO₂ predicts that the mirabilite to ikaite ratio (on a g/g basis) rises to 21 at -7°C and to 39 at -10°C. In other words, the authors need to provide evidence that the photographic technique can reliably quantify ikaite in the presence of mirabilite and, also, gas bubbles.

RESPONSE: We added a brief description of the method, and why it works. We aim to make a methods paper on this matter. It is correct that mirabilites are present in sea ice, but not at temperatures around 0°C. It has dissolved! And mirabilite (see Figure 1 below) crystals look different from gypsum (Figure 1) and ikaite (Figure 2). Bubbles are easily distinguished (Figure 3) as they appear as large circles – and we avoid including this area on the calculation. All crystals forms have been identified by x-ray techniques. We also did an ICP-MS analysis of the ikaite crystals, which confirmed the presence of high levels of calcium. We did not report this in the manuscript as it was done qualitatively. Isolating ikaite crystals from sea

ice for subsequent chemical analysis is not straightforward as they dissolve rather rapidly.

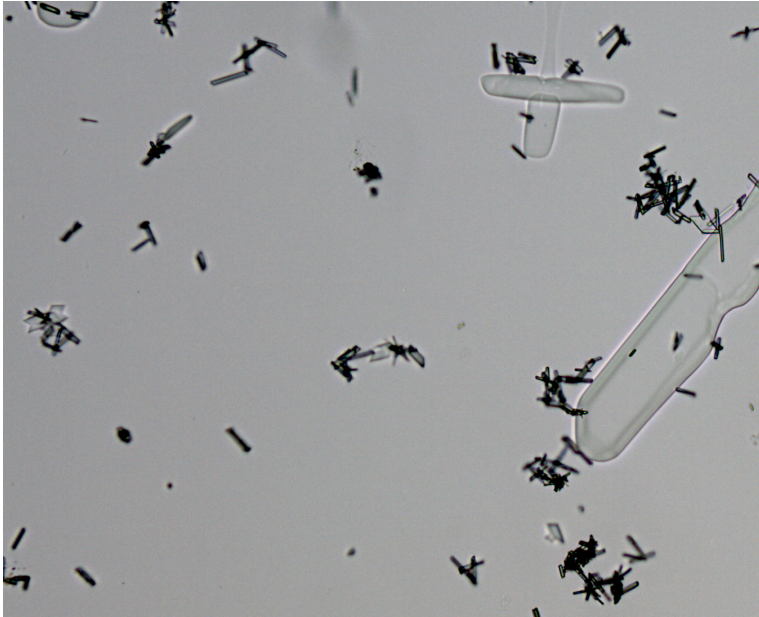


Figure 1. Image of mirabilite (large transparent crystals) and gypsum (smaller black ones due to camera contrast) from melting sea ice in ethanol at -5°C). Mirabilite dissolves when temperature increases to 0°C (it is only stable at lower temperatures).

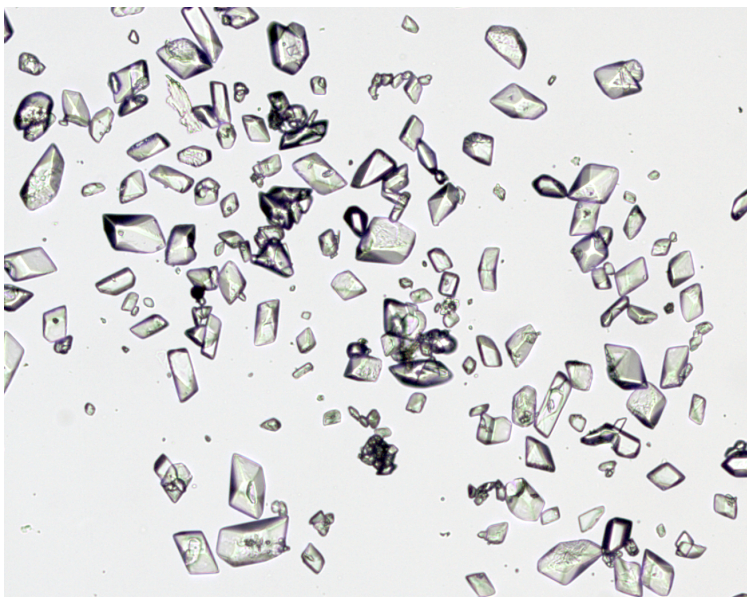


Figure 2. Ikaite crystals immediately after melting a sea ice sample from upper part

(close to 0°C). We do not need to melt sea ice in ethanol to see ikaite crystals as they are still visible after sea ice melt. However, ikaite also dissolves completely, but it takes longer (minutes to hours depending on the size of the crystal)

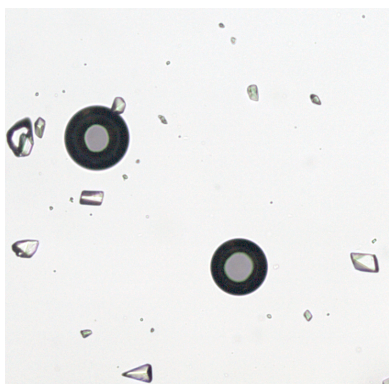


Figure 3. Two bubbles appear as circular black circles with a darker color inside. They are surrounded by ikaite crystals. Bubbles are seldom present in the microscopic image, but when they are they can be neglected by either ignoring the image or only use part of the area in the calculation.

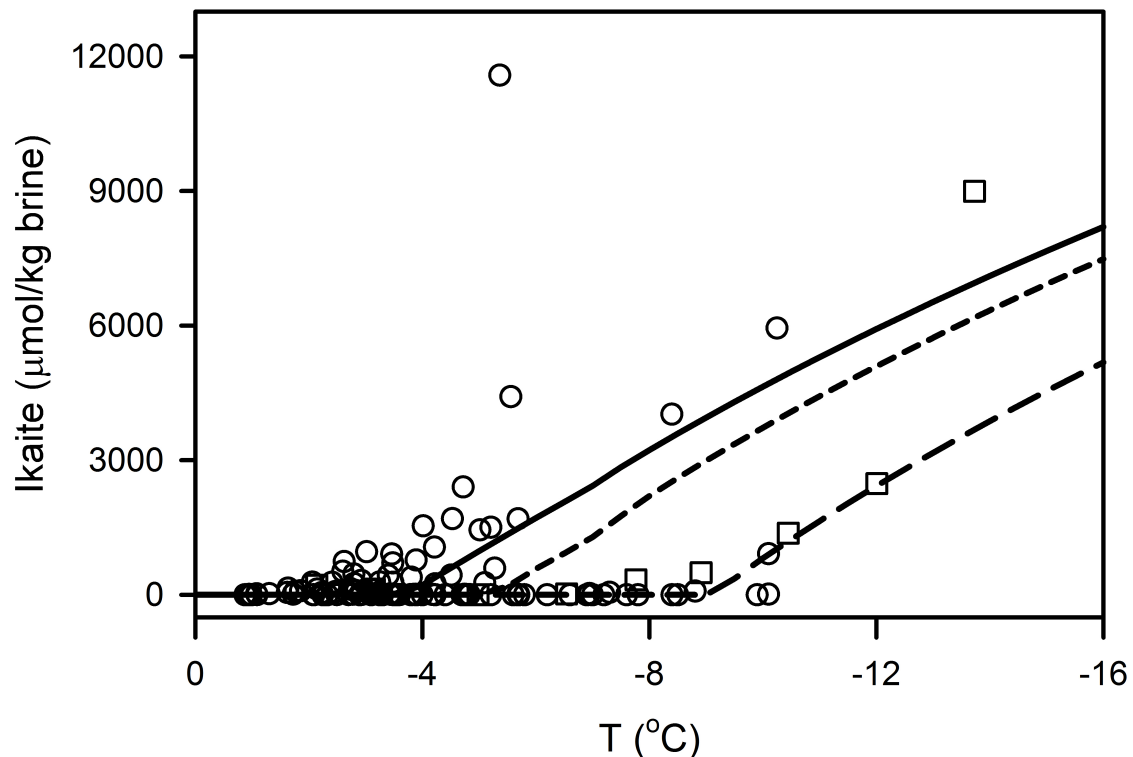
P6082, L16-19: I cannot see the relevance of running the FREZCHEM with the ‘standard seawater’ and the ‘average bulk sea ice’ compositions as input parameters when the exact initial composition of the SERF seawater is known. If the ionic and chemical composition of the residual seawater in the experimental basin did not change in the course of the experiment, the internal brines in the SERF sea ice should have the conservative ionic and chemical composition of SERF seawater as a function of salinity-temperature changes at thermal equilibrium plus or minus any chemical and biological reaction products. As I understand it, carbonate, sulphate, and chloride solid salt precipitation and dissolution in sea ice are solid/brine reactions not solid/bulk-sea-ice reactions. This much is stated by the authors on P6087 L5-6. The ‘average bulk sea ice’ composition as an input parameter is suitable for hyposaline ($S \ll 35$) starting seawater composition, such as in the Baltic. The resulting trends in Fig. 3 (standard seawater and average bulk sea ice) are therefore irrelevant and, therefore, confusing.

RESPONSE: We agree that the inclusion of an “average bulk sea ice (S=10) seawater” could lead to confusion. We further found an error associated with the S=10 curve in Figure 3 (the actual TA was $1200 \mu\text{mol kg}^{-1}$ instead of $800 \mu\text{mol kg}^{-1}$). We will remove it from Figure 3 and change the figure – see comments below.

P6082: Provide evidence that the assumption of constant brine pCO_2 at atmospheric equilibrium is justified. Field and experimental data indicate a large range of pCO_2 conditions in sea ice, to name but a few: Geilfus et al. (2012, J. Glaciol. 58, 287-300), Miller et al. (2011, J. Geophys. Res. 116, C00G04, doi: 10.1029/2011JC007143), Miller et al. (2011, J. Geophys. Res. 116, C02028, doi: 10.1029/2009JC006058), and Delille et al. (2007, Limnol. Oceanogr. 52, 1367-1379.).

RESPONSE: We are fully aware that brine pCO_2 is rarely at equilibrium with the

atmosphere, often much higher than the atmospheric $p\text{CO}_2$. As the current version of the FREZCHEM model cannot simulate a seawater system that is closed to the atmosphere, we used a $p\text{CO}_2 = 390 \mu\text{atm}$ in our modeling exercise as a case study. This could occur in the topmost sea ice brine (e.g., brine skim in new ice) that has degassed to reach equilibrium with the atmosphere. To encompass different $p\text{CO}_2$ values, we have revised Figure 3 (see below), which now includes modeled results of SERF seawater with $p\text{CO}_2$ ranging from 390 to 5000 μatm . Note that our main purpose of the FREZCHEM modeling was to see whether the observed levels of ikaite in sea ice are thermodynamically possible, and the answer was yes as demonstrated in Figure 3.



New Figure 3. Production of ikaite in sea ice, expressed as brine concentration, as a function of temperature. Symbols are observed ikaite concentrations at SERF from this work (circles: measurement within 30 min of sample collection; squares: samples taken on Jan. 24 after the snow clearance). The lines show equilibrium ikaite concentrations modeled by FREZCHEM, as 1 kg of SERF seawater ($S = 32.9$, $\text{TA} = 2380 \mu\text{mol/kg}$) freezes from 0 to $-16 \text{ }^\circ\text{C}$ under different $p\text{CO}_2$ values: 390 μatm (solid line), 1000 μatm (short dashed line), and 5000 μatm (long dashed line).

Discussion P6086, L21-24: The statement about the hypothetical contribution of the ikaite content in FF and BS to the total ikaite content is redundant in view of the next statement on L24-25, which is based on the actual observations.

RESPONSE: We removed the sentence.

P6087, L1: Clarify what the observed relationship was between sea ice temperature and ikaite concentration.

RESPONSE: This has been reformulated to “we employed the FREZCHEM model to calculate theoretical equilibrium ikaite concentrations as a function of different sea ice temperatures and seawater with different pCO₂ values”

P6087, L9: In order for the FREZCHEM to solve the CO₂ system in the brine, it requires 2 parameters when one is stated here (TA). Clarify the second parameter used here.

RESPONSE: The other parameter is pCO₂. We will clarify this in the revised manuscript.

P6087, L20: By the authors' statement here, the observations of the ikaite content in the SERF sea ice do not follow the curved increase with decreasing temperature past the temperature threshold predicted by FREZCHEM at atmospheric pCO₂. Provide context (also in the Introduction) why temperature is considered here the primary independent variable in the precipitation of ikaite in sea ice. Clarify what 'general' means in the statement on L25-27.

RESPONSE: The precipitation of ikaite will only occur when the ion activity product of $a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} a_{\text{H}_2\text{O}}^6$ exceeds the solubility product of ikaite. When pCO₂, TA and total Ca²⁺ concentrations are held constant, as is the case with our modeling, temperature is the primary control of the activities of Ca²⁺ and CO₃²⁻ due to its control over brine salinity. We will clarify this in the revised manuscript.

P6088, L2: Explain 'sufficiently', which implies a threshold in the concentration increase for precipitation to begin.

RESPONSE: See our response above.

P6088, L4: The temperature threshold of ikaite precipitation is very specific to the input parameters in the FREZCHEM model. Clarify why the range of threshold temperatures here.

RESPONSE: As per our response above, the temperature threshold is dependent on the initial concentration of seawater Ca²⁺, TA and pCO₂. When Ca²⁺ and TA are held constant (as is the case shown in revised Figure 3), the threshold is dependent on pCO₂: higher pCO₂ results in a lower pH, and as a result ikaite will not precipitate until the ice is much colder. We will clarify this in the revised manuscript.

P6088, L5-6: The thermodynamic solubility product of ikaite is $K_{\text{sp}} = a_{\text{Ca}} a_{\text{CO}_3} a_{\text{H}_2\text{O}}^6$ (Bischoff et al., 1993, J. Geol. 101, 21-33). Clarify how the IAP reported here is related to the K_{sp}, and the precipitation and dissolution of ikaite.

RESPONSE: As stated in the ms, the K_{sp} used in FREZCHEM was indeed based on Bischoff et al. (1993), which was extrapolated to low temperature by Marion (2001). At each temperature, the model will calculate the IAP and compare it with the K_{sp} at that temperature. Ikaite would only be precipitated when the IAP reaches K_{sp} . For instance, with the SERF seawater at $pCO_2 = 390 \mu atm$, at $T = -3.5 \text{ }^\circ C$, the IAP is 4.55×10^{-8} which is less than the K_{sp} of 5.03×10^{-8} . Therefore, there would be no precipitation of ikaite. When the temperature is lowered to $-4 \text{ }^\circ C$, IAP exceeded the K_{sp} of 4.87×10^{-8} , and as such $214 \mu mol \text{ kg}^{-1}$ brine of ikaite needs to be formed to bring down the IAP to equal to the K_{sp} .

P6088, L16-24: In L16-18, the authors suggest slower ikaite precipitation rate than seawater-ice-air heat exchange following snow clearance to explain why the observed ikaite concentration was lower than that predicted from the FREZCHEM model. In other words, although the brine-ice-air system thermally re-equilibrated rapidly, the ikaite-brine system did not. Further on (L20-22), it is stated that the delayed ‘response’ of ikaite is due to slow latent heat change in sea ice. These two statements are contradictory.

RESPONSE: We believe L16-18 is more likely, and will remove the discussion re latent heat change (L20-22). Another possibility is the difference in pCO_2 . Upon snow removal, the ice cools down rapidly and as such brine pCO_2 could be much higher than the atmospheric pCO_2 . As shown in the revised Figure 3, increasing pCO_2 will shift decrease the temperature threshold for ikaite precipitation, as well as ikaite concentration. We will include this discussion in the revised manuscript.

Furthermore, as the authors state on P6087, L20, the ikaite data do not fit the ‘direct temperature control’ model of the FREZCHEM predictions. Additionally, ‘direct control’ of a parameter on another would imply a positive correlation between temperature and ikaite concentration as seen in the FREZCHEM trend at constant pCO_2 . Such a correlation is not provided here, and it is not visually obvious. Hence, the statement about ‘direct temperature control’ is uncorroborated. In short, it is unclear how the authors deduce ‘direct control’ of temperature on ikaite concentration.

RESPONSE: As per our response above, we have revised Figure 3 that now shows the control by both temperature and pCO_2 .

P6089, 5-6: The term ‘inhibition’ of precipitation implies kinetic effects under supersaturation ($IAP > K_{sp}$) conditions in the presence of the ‘inhibitor’ ions. The authors use this term to explain the lower ikaite concentrations they determined in the lower middle part of the sea ice viewed from the perspective of bulk sea ice chemical composition. This shift in perspective is confusing because ikaite precipitation and dissolution is a brine/solid reaction. Provide information on the saturation state of the brine with respect to ikaite, which is a more appropriate term and concept to use, to explore this pattern in the ikaite distribution in sea ice.

RESPONSE: The term ‘inhibition’ has been removed and sentence reformulated. We remove Line 5 and the first half of Line 6. It’s impossible to calculate saturation state at each depth, as we would need to know precisely pCO_2 and TA at each

depth.

P6089, L9-12: Downward transport implies ice permeability conducive to such transport. Provide permeability information from observations to support this statement.

RESPONSE: The sea ice volume temperature and bulk salinity profiles (manuscript Figure 2) indicate that for a brief period between 23 and 24 Jan, the volume should have been permeable to fluid transport in light of the “rule of fives” proposed by Golden et al., 1998.

P6090, L3-27: It is unclear on what evidence the pCO₂ enters the proceedings this late in the Discussion and, crucially, the Title of this manuscript. The authors do not present pCO₂ data either from the SERF system or from field and experimental studies available in the literature to support this latter part of the Discussion or, indeed, the Title. Provide published evidence that whether ikaite precipitates or dissolves in sea ice is a function of the brine pCO₂. Speculation is healthy provided that it is firmly rooted in published evidence in the absence of commensurate data in the study. In the same vein, the Title is misleading for the same reason and should be changed. Finally, it will be useful to provide some analysis of the current dataset along the lines of inorganic carbon mass balance in sea ice. Field studies have documented from geochemical analyses of brines the fractional contribution of CaCO₃ precipitation to the inorganic carbon mass balance in sea ice and can be used for meaningful comparisons.

RESPONSE: Title has been changed. As there exist no technique for measuring reliable pCO₂ concentrations in the brine, we cannot compare with data. However, pCO₂ concentrations in the water column increase following the snow clearance experiment, indicating that pCO₂ conditions increases in the brine as well. These data will be presented elsewhere. We have reformulated this paragraph, but will like to keep the speculations.