Interactive comment on "Dynamic ikaite production and dissolution in sea ice – control by temperature, salinity and pCO_2 conditions" *by* S. Rysgaard et al.

Anonymous Referee #2

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General comments:

The authors studied the dynamic ikaite precipitation and dissolution in an outdoor pool experiment. They showed that the ikaite concentration decreases with sea ice depth and the relationship between ikaite concentration and temperature. The finding regarding the dynamic change in ikaite concentrations is interesting, assuming that the authors' statement about the ikaite dissolution due to snow deposition can be confirmed. Nevertheless, this study suffers from several fundamental problems that affect their results and the discussion. First, they applied an indirect method for ikaite concentration quantification, which seems rather complex and since this method is based on many assumptions and simplifications, it is difficult to assess the uncertainties of their data. Although they mentioned that 9 replicate measurements were done for one sample, no statistic analysis was given in their manuscript. So the question is why the ikaite concentration was not measured by ICP (by dissolving the ikaite in acid and then Ca concentration can be determined by ICP), which they also used for major ions measurements of ASW as mentioned in the methods.

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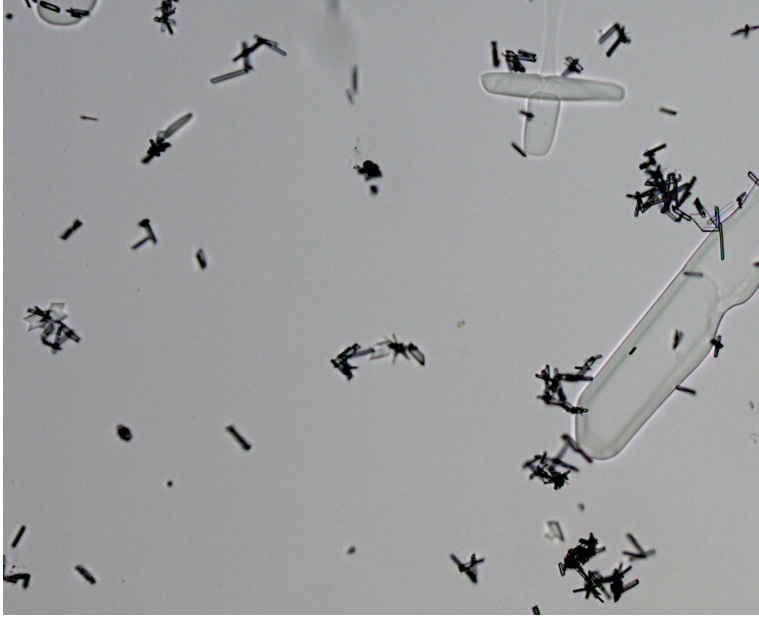
Figure 1. Image of mirabilite (large transparent crystals) and gypsum (smaller black ones due to camera contrast) from melting sea ice in ethanol at -5°C). Mirabilite dissolves when temperature increases to 0°C (it is only stable at lower temperatures).
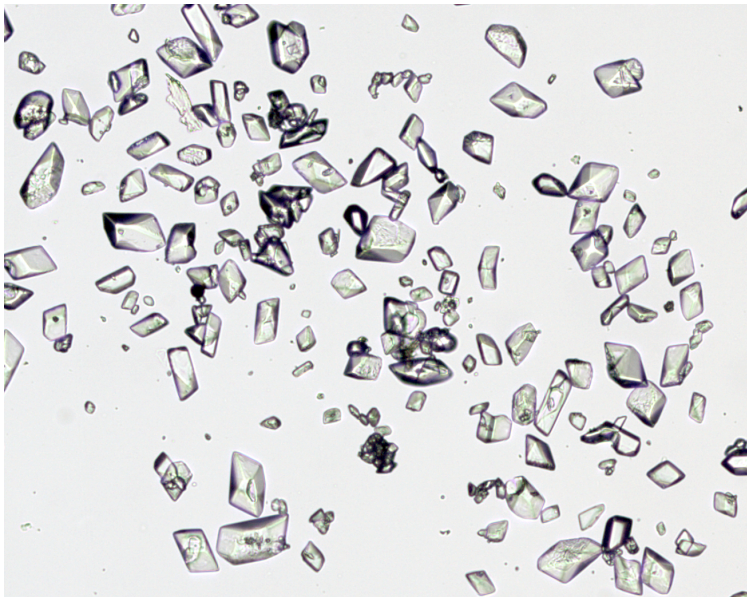

Figure 2. Ikaite crystals immediately after melting a sea ice sample from upper part (close to 0°C). We do not need to melt sea ice in ethanol to see ikaite crystals as they are still visible after sea ice melt. However, ikaite also dissolves completely, but it takes longer (minutes to hours depending on the size of the crystal)
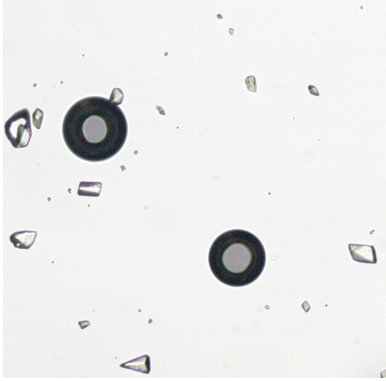
Figure 3. Two bubbles appear as circular black circles with a darker color inside. They are surrounded by ikaite crystals. Bubbles are seldom present in the microscopic image, but when they are they can be neglected by either neglecting the image or only use part of the area in the calculation.

In addition we will include more details on the method an estimate of the uncertainties – see below.

Second, the authors applied results from FREZCHEM model in comparison with their findings, however, as mentioned in the specific comments, the reason that they chose "two compositions" to bracket the expected ikaite concentration range does not make sense. Therefore, the further discussion based on these results should be reconsidered. In the end, No CO_2 measurements are presented in this study even though it is considered (even in the title) as one of the parameters investigated. Assuming only one pCO_2 for the complete investigation is not reasonable. Taking into account the temperature changes and thus the permeability will change dramatically which will not allow every part of sea ice to be in equilibrium with the atmospheric pCO_2 at all times. Therefore I do not see it appropriate to compare their findings with the results from the FREZCHEM model.

RESPONSE: We have revised Figure 3. As shown below, we have removed both the S=10 and S=35 curves, and replaced with the range of SERF seawater with different pCO_2 values. Thinking it over this makes more sense and will address another point raised by this reviewer below. We had S=35 seawater before because of the field data from natural seawater which have now been removed.

Specific comments:

Title

The title is misleading. Throughout the manuscript, there is little discussion on the effect of salinity and pCO_2 conditions on ikaite production and dissolution. For example, Salinity effect on ikaite precipitation and dissolution should refer to its thermodynamic and kinetic effects. However, it seems that the authors simply took it as a change in calcium and DIC concentrations.

RESPONSE: We will change the title to: Temporal dynamics of ikaite in

experimental sea ice.

Abstract

P 6077, L 1-3: The statement on ikaite stability is not correct. Ikaite can be even more stable than calcite and aragonite at room temperature under high pressure (Van Valkenburg et al. 1971).

RESPONSE: We have removed the sentence.

L 6: "little is known" is not true. There are already several papers published on this topic, including the papers from authors in this manuscript.

RESPONSE: Certainly little is known of the spatial and temporal dynamics of ikaite in sea ice. If we count the amount of sea ice cores investigated globally they are perhaps 50 (that is less than a square meter of sea ice). We will like to keep the sentence.

L 14: the statement is very confusing. It is understandable that ikaite will be dissolved at warm conditions. However, from which evidence, the authors concluded that it is "under acidic conditions"? My understanding towards the pH change is that the pH during this warming process should increase rather than decrease. Since the brine salinity is decreasing and the dilution will greatly enhance the brine pH. Besides, by stating "acidic conditions", it might mislead to pH lower than 7, and this should not be the case for brine pH.

RESPONSE: Snow has a pH of 5 to 6. In addition, it will isolate the sea ice from a cold atmosphere thereby increase brine volume in sea ice and the contact with low pH of snow also. For more information on this see Hare et al. 2013 Marine Chemistry 154, 46-64. In order not to confuse the reader we just remove acidic here. Realize it comes suddenly here without further explanation.

Methods

P 6079, L 7-8: The statement on their artificial seawater is not precise, as pointed out below for Table 1.

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 Mg^{2+} 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.

P 6080, L 1-3: why the ionic strength is not derived from FREMCHEM? Especially the chemical compositions in their artificial seawater were not proportional to those in the standard seawater.

RESPONSE: This sentence should not have been there; it's removed.

P6080, L 6-8: the samples were stored in -20oC before analysis. How this change in temperature from in situ affects the results? Please clarify.

RESPONSE: FF and BS samples were transported to the cold lab (-20C) until analyses (microscopic examination and x-ray diffraction) that was performed within 1-2 hour. This relative short time did not effect ikaite concentrations. However, when cores are stored at -20C for 48 h we observe an increase in the ikaite concentration. In addition, bulk pH concentrations increases with longer storage time indicating that the carbonate system is changing if cores are stored. In the revision, we will make it clear that samples were processed within 1-2 h after coring.

P 6080, L15-17: Only 20-150mg of sea ice was used for measurement. Is this amount of samples representive? How large is the uncertainty? As far as I know, the brine in sea ice is highly heterogeneous, so the ikaite distribution in sea ice should not be homogenous. Thus, the results based on such small amount of samples must have very high uncertainties.

RESPONSE: The standard error of the mean (SE) varies across the different dates and ice sections. Across all dates and sea ice sections the average standard error of the mean was 0.35 (range of variability; 0.07-0.6) x mean value. Example: Mean and SE of sea ice ikaite concentrations in central part of sea ice 23 January is 200 ± 70 μmol/kg sea ice. We have added more on this in the revised manuscript.

P6080, L 29: How was the sea ice sample area determined? Since only very little amount

of sea ice was melt for measurement. The melt sea ice should be more or less hemispheric, with different height.

RESPONSE: The microscope slides contained counting cells. The amount of crystals was documented within 1-3 counting cells and then multiplied with the number of cells that was covered by melt water after sea ice had melted. More details will be provided in our revision.

P 6081, L 4-5: The authors declared 9 replicate images were taken, however, the uncertainties resulting from this method were never mentioned.

RESPONSE: See comment previous response.

P 6082, L20-21: Assuming the system is always open to a constant pCO2 is not reasonable. Taking into account the temperature changes and thus the permeability will change dramatically which will not allow every part of sea ice to be in equilibrium with the atmospheric pCO2 at all times.

RESPONSE: See comments above. We will revise Figure 3 to include a range of pCO2.
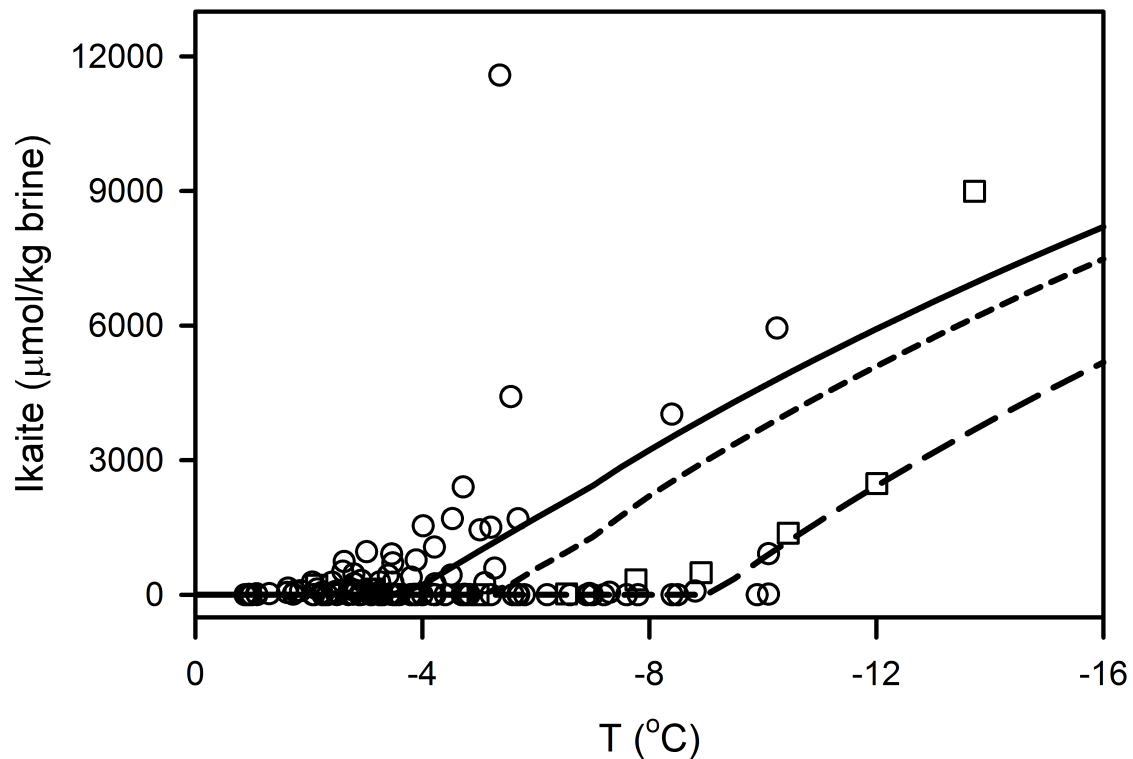
New Figure 3. Production of ikaite in sea ice, expressed as brine concentration, as a function of temperature. Symbols are observed ikaite concentrations at SERF from this work (circles: measurement within 30 min of sample collection; squares: samples taken on Jan. 24 after the snow clearance). The lines show equilibrium ikaite concentrations modeled by

FREZCHEM, as 1 kg of SERF seawater (S = 32.9, TA = 2380 µmol/kg) freezes from 0 to -16 °C under different pCO2 values: 390 µatm (solid line), 1000 µatm (short dashed line), and 5000 µatm (long dashed line).

Results

P6083, L 9-17: Ikaite concentration was converted from the counting area, however, no statistic analysis was ever presented. Especially, the result from Fig. 1d, there is only one crystal. How could this one crystal be representive?

RESPONSE: The difference in the amount of crystals from upper to lower layers is shown here. The one crystal in the bottom layer is because the concentration here is low. We could also have shown an image with no crystals – which would have been confusing. We do not say the one crystal is representative. Some of the 9 images do not contain crystals for this layer, others do. According to the statistics above 1 ikaite crystal would have a SE of ± 0.35 (range 0.07 to 0.6).

P6083, L 27: How was the "less than 7%" derived?

RESPONSE: A unit cell (a, b, c, alpha, beta, gamma) that is 8.816 8.317 11.042 90 110.612 90 has a volume of 757.8 cubic angstroms. A rectangular prism with relative dimensions of 1 x 1.06 x 1.32 is rectangular box of 8.816 8.317 11.042 90 90 90, which has a volume of 809.6 cubic angstroms. So our approximate rectangular box could be argued to over-estimate the volume by about 7%. These details will be provided in a revised manuscript.

P 6085, L 9-12: It stated that after warming up the sea ice, "ikaite crystals in the sea ice to dissolve completely". However, warm sea ice has high permeability, ikaite might be released to underlying seawater instead of dissolved in sea ice. Please clarify.

RESPONSE: In principle they could. However, we did not capture any ikaite crystals in our sediment traps deployed just beneath the sea ice (Parallel study). So, most likely they dissolved. However, we rephrase the sentence to; "ikaite crystals in the sea ice to dissolve"

Discussion

P 6086, L 3-4: the statement is not correct. Here, the authors conflate different processes that are relevant. First, the precipitation of ikaite will dramatically decrease the brine pH and enhance the solution pCO2. Due to the increasing high pCO2, CO2 is released. Nevertheless, the solution should still be less alkaline instead of high alkaline. The high surface pH found in the study of Hare et al. (2013) is bulk pH not brine pH, which is more likely due to the dilution processes (the decrease in salinity resulting in the increase of pH).

RESPONSE: We are talking bulk sea ice conditions. Will be included in a revision. Hare et al. did measure brine directly, which showed a pH range of 8-8.5.

P6087, L 5-6: Not clear what is the Causality here.

RESPONSE: Fig. 3 has changed and the text here will change as well in the revision.

P 6087, L 15-19: Here, the authors explained the reason why two compositions (standard seawater (S=35) and seawater resembling bulk sea ice (S=10)) were chosen for their discussion, "because the current version of FREZCHEM (13.3) treats the aqueous and solid phases as a closed system and cannot account for loss of salts to the underlying water during ice formation." However, this statement suffers fundamental problem. It does not matter if the model accounts the brine solution (salt) loss or not, since "ikaite concentrations are reported as per mass of brine". If the brine (salt) is expelled to the underlying water during ice formation, the remaining brine in the sea ice is also becoming smaller. Nevertheless, the concentration of chemicals in sea ice will not be influenced by the loss of salt. Therefore, I don't see the necessity to run the model at S=35 and S=10, since these two model results are not relevant to their experimental conditions at all.

RESPONSE: As per our reply above, we will remove S=10 and S=35 curves, and replace it with SERF seawater in equilibrium with various pCO2 values.

P 6088, L 5: it is rare to express the ion activity product (IAP) of calcium and carbonate in the form of {Ca2+}{HCO3-}2{H2O}5/pCO2. Since the direct reaction of ikaite precipitation is Ca2+ + CO32- +6H2O – CaCO3.6H2O, Thus, the IAP should be expressed in the term of {Ca2+}{CO32-}.

RESPONSE: One of our coauthors is an aquatic chemist who prefers to write the IAP that way. However, we are willing to change to the conventional way should the editor so desire.

P 6089, L 19-24. It is rather confusing here. As one sentence before the authors stated that they confirmed the hypothesis that CO2 is released to the atmosphere during initial ikaite precipitation, and then they said that they did not observe a high CO2 release to the air, and the explanation is "seems like most CO2 goes down with the brine". Please clarify these two conflict statements.

RESPONSE: We realize this can be confusing. Point is that although FF and BS contains many ikaite crystals per mass of ice, they contribute a minor part of the entire mass. This has been described in previous sections of the paper. We will rephrase to; First, the hypothesized release of CO2 to the atmosphere during initial precipitation of ikaite in surface layers of the sea ice can be supported by our observations of high ikaite concentration in BS and FF. One should bear in mind here, however, that although the BS and FF ikaite concentrations are high they are only an indication of a flux to the atmosphere. The size of the flux is not necessarily large. We will delete the reference to our CO2 flux measurements, as they will form the basis for more details on this matter in another manuscript.

P 6089, L 4-6: As pointed out in the comment to P 6088, L5, ikaite precipitation is

determined by the concentrations (activities) of Ca2+ and CO32- rather than HCO3-. Therefore, the authors might have problem in interpreting the role of carbonate concentrations. For example, at high pH, HCO3- concentration is low, but CO32- is high, which should favor the ikaite precipitation. And also, it is not correct to use "inhibition" here. "inhibition" should refer to kinetic effect on ikaite precipitation. However, this is obviously not the case in this statement.

RESPONSE: Again, this is due to different preferences in writing the reaction. The reaction can be written either in the form of HCO_3^- or CO_3^{2-}, and the results should be the same, as HCO_3^- and CO_3^{2-} are related. Note that under natural seawater or sea ice conditions, HCO_3^- concentration will always be higher than CO_3^{2-}, unless the pH is above pKa2 which is around 10.3. We will change the wording of "inhibition".

ConclusionP 6091, L 2: The statement made here is too vague. Since different initial conditions will result in different initial temperature for ikaite precipitation. The authors should indicate this finding is only valid in their study.

RESPONSE: We will start the sentence with, 'In our study, Ikaite precipitated in sea ice with …'

P 6091, L 14-17: Based on the same reason as to the P 6087, L15-19, the conclusion about the FREZCHEM model is not correct.

RESPONSE: In light of new Figure 3, we will revise this section. Our main points will be 1) the observed concentrations of ikaite can be reasonably described by FREZCHEM, though major limitations exist; and 2) The lower than expected ikaite in sea ice following snow removal could be due to higher pCO2 in the rapidly cooling sea ice. Now that we have removed the modeling for natural seawater, we will delete any discussions regarding the natural system.

Table 1

In the methods part, the authors stated that the SERF seawater is similar in chemical composition to natural average seawater. However, the concentration of Mg2+ in SERF seawater is largely offset from that in standard seawater. 2. If the so-called "seawater resembling bulk sea ice" is extrapolated from S = 35 standard seawater to S = 10, why the TA value is 800 μmol kg-1 (instead of 682.8)? 3. The authors should mention that the units used in this table are expressed in mol kg-1 (water) instead of mol kg-1 (soln).

RESPONSE: See comments to Table 1 above. A revised Table 1 can be found above as well.

Fig. 1 is too small, the morphology of ikaite can not be seen from these figures.

RESPONSE: We will provide a larger high-resolution figure in the revision.