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Discussions

Interactive comment on "Dynamic ikaite production and dissolution in sea ice – control by temperature, salinity and $p\text{CO}_2$ conditions" *by* S. Rysgaard et al.

Anonymous Referee #2

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

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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. 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 CO2 measurements are presented in this study even though it is considered (even in the title) as one of the parameters investigated. Assuming only one pCO2 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 pCO2 at all times. Therefore I do not see it appropriate to compare their findings with the results from the FREZCHEM model.

Specific comments:

Title

The title is misleading. Throughout the manuscript, there is little discussion on the effect of salinity and pCO2 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.

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).

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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.

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.

Methods

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

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.

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

P 6080, L15-17: Only 20-150mg of sea ice was used for measurement. Is this amount of samples representative? 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.

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.

P 6081, L 4-5: The authors declared 9 replicate images were taken, however, the

uncertainties resulting from this method were never mentioned.

P 6082, L20-21: Assuming the system is always open to a constant pCO_2 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.

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 representative?

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

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.

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 pCO_2. Due to the increasing high pCO_2, CO_2 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).

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

P 6087, L 15-19: Here, the authors explained the reason why two compositions (satandard 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 aque-

ous 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.

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-}.

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.

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.

Conclusion

P 6091, L 2: The statement made here is too vague. Since different initial conditions

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will result in different initial temperature for ikaite precipitation. The authors should indicate this finding is only valid in their study.

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.

Table 1

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).

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