Review of the manuscript by Geilfus et al. Impact of ikaite export from sea ice to underlying seawater in a sea ice-seawater mesocosm

The manuscript describes a mesocosm experiment with artificial sea ice and seawater and the precipitation of ikaite and the impact of the exported ikaite on the underlying water using the SERF artificial outside seawater tank, the University of Manitoba in Winnipeg, Canada. The authors show data and results mainly as the changes and evolution in measured seawater TA and TCO_2 and salinity-normalized TA and TCO_2 during a 17 day-period. Measured air-ice CO_2 exchange during the study is also presented. The investigation of sea ice processes and underlying water in a confined setup in an outside environment with mainly the processes of salinity changes, ikaite precipitation/dissolution and CO_2 gas exchange affecting the carbonate chemistry (assuming insignificant effect of biological processes) is new and interesting. However, the idea of solid ikaite export to the water column and the effect of ikaite on the underlying water such as aragonite saturation state has been presented and discussed in a few publications, which should be referred to. These publications also describe sea ice processes and evolution of the sea ice and underlying water in natural sea ice. However, the estimates of the amount of ikaite exported out from the sea ice to the water beneath compared to the ikaite precipitation in sea ice are new and valuable. I think it is an interesting approach and important study in a controlled environment but it needs improvements. There are too many unclear calculations, figures, statements and missing uncertainty discussions. Hence, the manuscript requires substantial revision and cannot be published in its present form. However, I encourage publication after major revision.

General comments:

Parts of the results are not convincing with measured TA in the seawater being higher at the end of the experiment (melt) than at the start of the experiment. Important discussion and uncertainty investigations are missing regarding the contradictions of the results. Some figures are unclear, and calculations are not well described and are sometimes difficult to follow and reconstruct, such as the mole calculations of ikaite as well as the result of 57% of ikaite exported from the ice. Essential data are missing and a description of the evolution of the TA in the underlying water is missing. The uncertainty discussion on ikaite dissolution during analysis and not in the water column is missing and not mentioned in the method section. There are also unclear explanations of some of the contradicting results.

I also have concerns about the statement and conclusion about ikaite dissolution in seawater as ikaite probably does not dissolve at temperatures <0°C, such as the temperature in the underlying water. The seawater samples were stored at +4°C so the ikaite was probably dissolved or near dissolution before or at analysis, and not in the water column. The water column temperatures were between -3°C and -7°C during the study and about -1°C at the end of the study. There is lack of information on temperature, salinity, TA and TCO_2 at the end of the experiment when the ice was melted. This should be mentioned in the method and discussion sections, to be able to close the TA seawater budget from start to end, which seems to be a problem. The seawater salinity and TA could change during the study since freshwater in the form of sea ice is removed every time an ice core is collected, and same for seawater. What about TA and TCO_2 in the snow, brine and brine-skim, where these analysed? These factors could be discussed if they impact the results and maybe also used correcting the calculations.

In parts of the result, the air-sea CO_2 flux is not considered and left out in the statement of processes when calculating the changes in TCO_2, which is an important process driving the changes in TCO_2 (except for biological production) although with relatively small effect. However, this is later discussed in the manuscript. The information on wind speed is missing, it is essential for gas exchange to occur between ice and air. Metrological data could perhaps be presented in a table and moved to site description/method since this is not a result of this paper and already presented by Rysgaard et al. (2014).

Important and highly relevant references are missing in the introduction and discussion sections, such as Fransson et al. (2013) and Chierici el al. (2011), which performed the first studies of the carbonate chemistry and aragonite saturation (ocean acidification) in natural sea ice and underlying water during a full ice season in the Arctic. I suggest that these references are cited and mentioned in the discussion section. There are other relevant references that I suggest to be included, see Specific comments.

The manuscript would benefit from language correction by English native person.

Specific comments

Line 1. The title may not inform the reader what this manuscript is about. I suggest changing “Impacts” (on what?) to “Estimates” or “indications”.

Abstract

Line 12. This sentence suits better in introduction, it is not the result of the manuscript. I suggest removing the sentence and start the next sentence with “The fate ….”.

Line 14 and throughout the manuscript. As far as I can see, the experiment was performed during 17 days, not month-long experiment or three weeks, as is also written at various places in the manuscript. Please change to “17 days long” or just mentioned the dates.

Lines 16, 20, 25 and throughout the manuscript: “dissolution of ikaite” has to be explained or used properly. Ikaite will probably not dissolve in the cold water (<0°C), so please add information to explain what you mean with “dissolved ikaite”. You may write “presence of ikaite dissolved during analysis”. Perhaps you have proofs on the dissolved ikaite in the underlying water (before storage or analysis), then please add that information.

Introduction

Lines 35-36. The references mentioned, do they report on sequestration of atmospheric CO_2 below the mixed layer or only into the surface mixed layer? Do they have evidence that the ice-brine pump actually exports atmospheric CO_2 below the mixed layer (i.e. sequestration for longer periods)? There are other studies (not so recent) of CO_2 sequestering which are more relevant, e.g. CO_2 uptake in the Arctic Ocean due to brine rejection (e.g. Anderson et al., 2004) from brine rejection, and (and very recent) Brown et al. (2016) that may also be referenced? There may also be modeling results. Maybe use other reference or change to "sequestration into the mixed layer below the ice".

Line 39. I suggest removing "CO_2", and start the sentence with "The carbonate chemistry…". What do you mean with "heterogeneous"? Do you mean that the distribution or concentrations are heterogeneous?

Lines 41-45. I suggest to add the reference of Fransson et al. (2013) for both CO_2 release in winter and CO_2 uptake during ice melt.
Line 46. What is the sea ice pump, please explain why and how pCO_2 is controlled?
Line 53. Please add the reference Nomura et al. (2013) (after Dieckmann et al., 2008), they also found ikaite crystals in natural Arctic sea ice.
Lines 54-55. Please add the reference Fransson et al. (2013).
Lines 56-60, Equations. The definitions of some parameters are missing, please add.

Lines 67-69. Please add the reference Fransson et al. (2013) for mentioning the study of brine rejection (with CO_2 and TCO_2) and effect on the carbonate chemistry in under-ice water (upper 10 m) after the studies by Semiletov et al., (2004); Rysgaard et al., (2007; 2009). Fransson et al. (2013) performed a seasonal study of natural sea ice and under-ice water covering a period from ice formation to ice melt in the Canadian Arctic. I suggest that this reference has to be cited and later discussed.

Line 75. Change (Eq. 3) to (Eq 1).
Line 82. What do you mean with "carbon-bearing materials". Please explain.

Lines 86-88. The carbonate chemistry was examined by Fransson et al. (2013) in the under-ice water where the signal of brine rejection and ikaite was observed at 2 m beneath the sea ice, so please add this information and reference. However, deeper down in the water column, this signal was gone.

Line 93. Change "carbon" parameter to "carbonate" parameters.
Line 94. What is "large enough volume"?
Line 95. Change "a 3 weeks experiment" to "17-days experiment".
Lines 96-97. after "main processes…" please add "…assuming no biological processes" .

Lines 99-109. Tank and experiment descriptions: I suggest adding a table with salinity, temperature, TA, TCO_2 of the artificial seawater. Are there any nutrients in the artificial seawater? What has been debated is that ikaite has shown a relationship to nutrient

concentrations (phosphate, nitrate?). I suggest mentioning this in the description of the site and in the discussion, and I suggest adding the reference Hu et al. (2014) for the discussion, where they found that phosphate is perhaps not essential for ikaite precipitation, that was previously thought.
What was the volume of the water in pool at the start (open water) and end (melt) dates? Did you track the changes in volume of the water during ice formation and ice growth, and when removing the seawater samples?
Did you have artificial mixing in the tank? Was the tank water well mixed so that all solid ikaite (and TA) was well distributed in the water column? Did you check if there was solid ikaite at the bottom of the tank or are you sure that all ikaite was well mixed and distributed over the entire water column, and was later dissolved (in the sample)?
How much of the pool ice cover was used for the experiment, sampling all over the ice cover?

Lines 110-114. How was salinity in the seawater sample and melted sea ice measured?

Lines 115-119. Do you have data on wind speed? That is important for the discussion of ice-air CO_2 fluxes.

Lines 127-130. Method of samples: the procedure of the TA analyses after removing ikaite shpuld be mentioned in this section and later discussed. Did ikaite dissolve during strorage and analysis of the seawater sample or in the water column? Please define when dissolution took place. This is valid throughout the manuscript.
Did you analysed TA in snow and brine? What about frost flowers? I assume that at the high TA occasions at the ice surface on the 16-17 January and 22-23 January, there were probably brine skim on top of the ice, including TA and maybe ikaite, which may be lost when you remove the snow and/or the ice core. Did you sample the bottom of the tank? Could there have been solid ikaite?
Could solid ikaite have escaped from the sea ice to the underlying water during the collection of sea ice? This was discussed in Fransson et al. (2013) as a possible factor of the high TA values found at 5-15 m under the sea ice, apart from the natural ikaite export from the ice.

Lines 130 and 144. How much $HgCl_2$ did you add to the samples and what was the volume of the sample?

Lines 141-142 and throughout the manuscript. You mentioned that the seawater and melted sea ice samples were stored in +4°C to avoid the dissolution of ikaite. How do you explain why the ikaite was dissolved in the water column under the sea ice?

Lines 153-155. I suggest a figure or table with brine volume for each day during the study. That is needed to understand why and when the ikaite can escape from the sea ice. This specific data should be mentioned in the discussion section as well. Have you checked brine-volume corrected TA?

Results

Lines 166-171. The metrological and salinity data is not part of the results, is already presented by Rysgaard et al. (2014) and could be moved to the site description and methods as background data.

Line 191. SD = 8.75 should have only one decimal (due to the accuracy and precision of the measurements), please change to SD=8.8. Do you mean SD="standard deviation"? "variations of …. are quite small", do you mean that "they are almost within the uncertainty of the analytical methods"?

Lines 191-195. I suggest to also write the TA and TCO_2 differences from start to end. That helps to understand the figures.
Line 208. Same as earlier, is this melted sea ice with or without ikaite? If this is in melted sea ice including ikaite crystals, you need to clarify the bulk sea ice as "melted (including ikaite)". Please explain and add to method.

Line 208-223. I would like you to present the averaged salinity used for sea ice.

Lines 225-226. Did you measure CO_2 ice-air exchange on top of the snow or did you remove the snow? This will give different flux results. Please explain.
Line 227. Add "from source" to get "switched from source to sink for…."

Line 225-228. It seems that from the measured CO_2-flux measurements, the sea ice acts as a net CO_2 source, and not a net CO_2 sink for atmospheric CO_2. This is contradictory to what is discussed about sea ice as a CO_2 sink. Please explain in discussion section.

Lines 229-230. The references mentioned confirm that the measured CO_2 fluxes are in the same order of magnitude. Please add numbers and direction of the CO_2 flux in their studies and perhaps discuss more in the discussion section.

Discussion
Line 237. What do you mean with "very low"?
Lines 236-238. The biological processes are assumed to have insignificant effect on the carbonate system. Did you check the bacterial activity in bulk sea ice both the start and the end of the experiment? I suggest that this is mentioned in the method description. It would be valuable to relate the estimated microbial activity ($gCL^{-1}h^{-1}$) and algal Chl a ($\mu g\ L^{-1}$) to the changes you measure in TCO_2 (in $\mu mol\ kg^{-1}$) to obtain a better idea of the biological impact of TCO_2.
What is the biological activity and effect of TCO_2 in the underlying water, particularly the microbial activity could be significant? Did you measure microbial activity in the seawater before and after the experiment?

Line 252. Same as earlier about "dissolution of ikaite in water column and sea ice".

Lines 260-261. This statement is not valid as is. Please change to: “Assuming no biological effect, ikaite precipitation/dissolution and gas exchange (TCO_2), TA and TCO_2 are considered conservative with salinity. Thus we can calculate…”

Line 257. Repetition: a ratio 2:1.
Line 269. Add “assumed to be only due to…” after “…this experiment are..”.

Lines 271-274. Please explain better what you mean with “lack of TA”. What do you mean with either dissolved or exported out of the sample? What means “exported out of the seawater sample”?

Lines 277-278. “ikaite is precipitated and CO_2 released from the ice to the atmosphere ; both processes reduce $TA_{(ice)}$ and $TCO_{2(ice)}$.” This statement should be changed since $TA_{(ice)}$ is not reduced by CO_2 exchange.

Line 285-286: What is “relatively high sea ice temperatures”? Is this temperature high enough for ikaite dissolution, “likely promote ikaite dissolution”? Please explain. I would think that it is more likely that ikaite is rejected from the sea ice to the underlying water due to increased brine volume and dissolved later (storage, analysis?). It would be good to relate this temperature increase in the sea ice to brine volume values (e.g. >5%) when the brine channels connect to each other and promote solutes and gases to escape from the ice. Presenting the evolution of the brine volume fractions in a table or figure during the study would improve some of the understanding of the results, as was suggested earlier in this review.

Line 296. What do you mean with “good agreement”? Please specify.
Lines 298-300. This sentence could perhaps be moved to the method description.

Lines 311-313. Please add “in this study” between “underlying seawater” and “is the dissolution…”. Also add “export of ikaite from the ice” before “dissolution of…” so the sentence will be: “ ….carbonate system in the underlying water in this study is the export of ikaite from the ice and dissolution of calcium carbonate”. Please change the next sentence to: “While a few studies of ikaite precipitation….”.

Lines 315-318. Please add: “according to the study by Fransson et al. (2013)” after where the crystals are dissolved”. This study needs to be mentioned since this is one of the first studies describing the carbonate chemistry (such as TA, TCO_2) evolution of the sea ice and underlying water (upper 10m) and the sea ice processes such as precipitation and dissolution of ikaite, affecting TA, TCO_2 and aragonite saturation from ice formation (in November) to ice melt (in June). They suggested that the high TA found in the upper 10 m under the sea ice was a result of solid ikaite rejected from the ice, dissolved in the water or in the sample before analysis.

Line 319. Please explain how you obtained the 66 µmol kg^{-1} maximum concentration.

Line 320. Change to “17-days long”.
Lines 336-345. I am concerned about the 1-day delay of the measured pCO_{2sw} compared to the $npCO_{2sw}$-normalized values in Figure 3d after turning on the heat. This is unclear to me since this temperature increase should be directly discerned in pCO_{2sw} and it has to be explained or discussed. Why is there a delay?
The sentence “process other than a the temperature change affected the $pCO_{2(sw)}$”. Do you have any suggestions on what other processes affected $pCO_{2(sw)}$”?

Lines 355-357. Compare with brine volume fraction.

Lines 358-367 and Figures 8a, b. The calculation procedure is difficult to follow and information on volumes of water and sea ice are missing. I am not convinced why the ikite (mole) in seawater is so large. It is mentioned in the Figure 7c caption (almost same figure as Figure 8a) that “the ikaite is estimated from half of the difference between $TA_{(ice)*}$ and $TA_{(ice)}$”, but in the figures it seem that data is not presented as “half”. Could you explain?
How was “0 to 43% of ikaite crystals remain” calculated?

Lines 376-377. Please provide numbers of your parameters such as volume, density, and pool dimensions used in the calculations.
Line 380. Was the CO_2 fluxes measured on snow and on ice from removed snow?
Line 388. Add “(up to 99% as brine)”…
Line 396-398. What was the wind speed during the study? It would be interesting to know since CO_2 fluxes are highly dependent on wind speed.

Line 430-431. This statement is not right. The effect of processes in sea ice such as ikaite precipitation and dissolution affecting the carbonate chemistry and aragonite saturation state (ocean acidification) in the under-ice water has been address in the seasonal study by Fransson et al. (2013). This study should be mentioned. However, in natural sea ice, there is also advection and other processes acting on the under-ice water, which makes the artificial mesocosm experiment a suitable environment to study effects in a more confined and controlled way.

Line 436. “sea ice decreases pH and increases $\Omega_{aragonite}$”. Could you please explain why they change in opposite directions?

Lines 438-446. There are few studies such as Chierici el al. (2011) that I suggest should be mentioned in this discussion since this is the first study of the changes of the carbonate chemistry and aragonite saturation state in the underlying water (mixed layer) during a full annual cycle in the Arctic, covering all seasons (autumn, winter, spring and summer). They found relatively low $\Omega_{aragonite}$ in winter under the ice, explained mainly by remineralisation and brine rejection. In spring, $\Omega_{aragonite}$ increased mainly as a result of primary production. Fransson et al. (2013) also studied the carbonate chemistry and $\Omega_{aragonite}$ in underlying water but focused on the upper 10m, showing more of the impacts of sea ice processes.

Conclusion

Line 448. “17-day”.

Line 451. Change the sentence to “….while export of ikaite from the ice and dissolution of ikaite was the main ….”

Tables

Table 1. should include more information such as all sampling occasions, not only start conditions.

Table 2. This table could perhaps also include “ikaite (mol) seawater”. In the header it should be added “sea ice” in the ikaite (mol) column.

Figures and figure captions:

Figure 2. This figure is not the result of this manuscript and has been presented in Rysgaard et al. (2014). I suggest moving it to background information for the site description. Figure 2d is very unclear and it is impossible to discern the different parameters, and should be changed. Figure 2d caption is unclear of what is what with the different colors and depths shown in the figure. I suggest separating salinity and temperature in two different figures for clarity.

It is difficult to see if the salinity is higher at the end of the experiment or not. This has to be more evident in the method and discussed, if the salinity never returns to start salinity.

Please decide if you use big (A) or small letter (a) in caption and figure, be consistent.

Figure 3. TA* and TCO_2* are defined when this figure is referred to. The parameters should be defined in the result section (when the figure is firstly mentioned) to understand the results shown in Figure 3. Figure 3d has also very unclear colors. The “blue” line should be defined in the figure caption. In addition, add and define TA* and TCO_2* in the caption (a, b) as well as add the color “black” (a,b) and “red” and “black” and “green” (c) for more consistent presentations of the data.

I am concerned about the 1-day delay of the measured pCO_{2sw} compared to the $npCO_{2sw}$-normalized values in Figure 3d after turning on the heat. This is unclear to me since this temperature increase should be directly discerned in pCO_{2sw} and it has to be explained or discussed. Why is there a delay?

Figure 5. Add “positive air-ice CO_2 flux means outgassing from the ice and negative CO_2 flux means uptake of atmospheric CO_2.

Figure 6. Define the green dotted line in caption.

Figures 7. The figure 7b of changes in TCO_2 includes CO_2 flux but it does not say in the text.

Figure 7c does not show “half the TA” as I can see. Please explain or I missed something.

Figure 9. What explains the large difference on the 24-25 January between ice-water exchange of CO_2 and total TCO_2 loss from sea ice?

Added references:

Anderson, L.G., E. Falck., E. P. Jones., S. Jutterström and J. H. Swift. 2014 Enhanced uptake of atmospheric CO_2 during freezing of seawater: A field study in Storfjorden, Svalbard. JGR Vol. 109, C06004, doi:10.1029/2003JC002120, 2004

Brown et al. (2016)

Chierici, M., Fransson, A., Lansard, B., Miller, L.A., A. Mucci., E. Shadwick., H. Thomas, J E. Tremblay., T. Papakyriakou. 2011. *The impact of biogeochemical processes and environmental factors on the calcium carbonate saturation state in the Circumpolar Flaw Lead in the Amundsen Gulf, Arctic Ocean*. JGR-Oceans. 116, C00G09, doi:10.1029/2011JC007184.

Fransson, A., Chierici, M., Miller, L.A., Carnat, G. Papakyriakou T, et al., 2013. Impact of sea-ice processes on the carbonate system and ocean acidification at the ice-water interface in the Arctic Ocean. 2013. Journal of Geophysical Research-Oceans, 118, 1–23, doi:10.1002/2013JC009164.

Hu, Y., D.A..Wolf-Gladrow, G.S. Dieckmann, C. Völker, G. Nehrke 2014. A laboratory study of ikaite (CaCO3·6H2O) precipitation as a function of pH, salinity, temperature and phosphate concentration, Marine Chemistry 162 (2014) 10–18, http://dx.doi.org/10.1016/j.marchem.2014.02.003

Nomura D, Assmy P, Nehrke G, Granskog MA, Fischer M, Dieckmann GS, Fransson A, Hu Y, Schnetger B, 2013. Characterization of ikaite (CaCO32 •6H2O) crystals in first- year Arctic sea ice north of Svalbard. Annals of Glaciology, 54(63)doi:10.3189/2013AoJ62A034