

***Interactive comment on “Impacts of ikaite export from sea ice to the underlying seawater in a sea ice-seawater mesocosm” by N.-X. Geilfus et al.***

**Anonymous Referee #1**

Received and published: 25 March 2016

**I. General comments**

The objective of the paper is to assess the impact of ikaite export from sea ice to the seawater, as clearly indicated by the title. Given that several studies propose that the inorganic carbonate chemistry in sea ice is of major influence for the polar air-sea CO<sub>2</sub> exchange, quantifying the fate of ikaite in sea ice during sea ice growth and melt is of great interest.

To address their objective, the authors analyze temperature, salinity, total alkalinity (TA) and dissolved inorganic carbon (TCO<sub>2</sub>) in both the sea ice and the seawater in an artificial sea-ice pond located at the University of Manitoba, Canada. The method applied to analyze TA and TCO<sub>2</sub> in the sea-ice is thought to measure dissolved TA and TCO<sub>2</sub> only, specifically excluding TA and TCO<sub>2</sub> found in ikaite crystals (1 mol of ikaite contains 2 mol of TA and 1 mol of TCO<sub>2</sub>). Ikaite concentrations in bulk sea ice and/or its export to the seawater was then derived by computing half of the difference between the theoretical TA concentrations in bulk sea ice if TA were to be conserved with salinity (this assumes no ikaite formation in sea ice) and the observed bulk sea-ice TA (without the ikaite-bond TA concentrations). Similar in seawater, ikaite concentrations are half the difference between the observed TA (which potentially would include imported and dissolved ikaite-bond TA) and the theoretical TA concentrations if TA were conservative with salinity.

Throughout large parts of the manuscript the authors claim that their methods would show ikaite concentrations in sea-ice, which, however is not entirely true since it could also be that ikaite was already exported from sea ice at the time when the observations were taken. In order to quantify the ikaite concentration in sea ice, the authors should have measured bulk sea ice TA concentrations of samples in which ikaite crystals were fully dissolved, and subsequently subtract from these 'new' measurements the already performed measurements of bulk sea-ice TA concentrations without dissolving ikaite. I am not sure to what extent the authors could perform additional measurements to account for this lack in observations.

**In the section 5.2 (Estimation of the precipitation-dissolution of ikaite) we clarify our**

methods used, based on TA, to estimate the precipitation-dissolution of ikaite within sea ice and seawater. We also add more precision in the section 5.2.1 where we compare our estimation with previous estimation from Rysgaard et al (2014). Then finally, when we try to estimate how much ikaite remain in the ice cover compared to the amount exported to the underlying seawater, we used our estimation and then used estimation from Rysgaard et al (2014), as suggested.

Another way to approximate the exported amount of ikaite from the storage of ikaite in sea ice might be realized by subtracting the concentrations given in Rysgaard et al. 2014 for the same experiment from the observations presented in this study.

We have implemented this suggestion in the manuscript. Thanks.

Despite of not being able to show ikaite concentrations in sea ice, the data presented on ikaite dissolution within seawater clearly supports the conclusion that ikaite is exported from the sea ice to the water column at various rates throughout the course of the experiment. However, the specific conclusion that up to 43 % of ikaite remain in sea ice while the rest is exported to the underlying water column is not supported by the presented data, and might be recomputed e.g. by using the ikaite content as given in Rysgaard et al. 2014.

We have revised our discussion of ikaite export to the underlying seawater in this light. You'll see that this revision is explained in detail in the specific comments.

Furthermore, the results showing that  $p\text{CO}_2$  below sea-ice remains undersaturated, which the authors relate to ikaite dissolution in sea-ice, is certainly a new results and important for assessing the influence of the inorganic chemistry in sea ice on air-sea ice-sea  $\text{CO}_2$  exchange processes.

Thank you.

Beyond of analyzing the fate of ikaite in sea ice and seawater, the authors further consideration the influence of ikaite export to seawater on winter ocean aragonite saturation state. This approach is new, however, needs further clarification to understand the applicability of the experimental results on the influence of the process within the present-day and future Arctic Ocean, with the specific comments given in the corresponding section.

We have substantially revised section 5.5 on the impact of sea ice growth on the Aragonite saturation state in Arctic waters. We have addressed specific comments below in this regard.

The overall structure and presentation of the paper is clear, and the language fluent. However, specific parts of the manuscript need some revisions concerning the clarity of the specific statements and the manuscripts needs a thorough read through concerning spelling and grammar mistakes.

We took a better look at the manuscript and hopefully correct the spelling and grammar

mistakes. Thanks for pointing out most of them in your review.

Finally, the sectioning and structure of the manuscript is not following the guidelines for The Cryosphere, and thus needs some more attention.

We have endeavored to correct this in the revised version. Thanks.

After addressing the suggested revisions (see following comments) I think the paper is ready for publication.

We'd like to thank the reviewer for their insightful and constructive comments, which we believe, have improved the manuscript.

## II. Specific comments

### 1. Abstract

The Abstract provides a concise and brief summary. Specific questions, which have arisen in the results sections, potentially need to be re-considered in the Abstract.

L19: How do you derive the uncertainty range of  $\pm 3$   $\mu\text{mol/kg}$ ? No details about the uncertainty range are given in section 5.2.1.

Since estimation of ikaite precipitation-dissolution is based on TA, we used the uncertainty of the TA measurement,  $\pm 3$   $\mu\text{mol/kg}$ . However, as the precision our TA measurement is clearly mentioned in the “site description, sampling and analysis” section, we have removed this information from the abstract.

L19: The specific percentage of the fraction of ikaite should be derived as detailed in the comments to section 5.3.

We deleted this part as this estimation was wrong. See comments in the section 5.3 further in the review.

We also modified the abstract and conclusion to fit better with our discussion.

### 2. Introduction

The introduction gives a solid general background on the processes related to the inorganic carbonate chemistry in sea ice and its influence on the air-sea  $\text{CO}_2$  exchange. Nevertheless, the authors need to state more detailed why it is important to understand and quantify the fate of ikaite in the sea ice, specifically in the second last paragraph (L81-88).

We modify the structure of the introduction to highlight the link between precipitation of ikaite within sea ice and the potential sea ice pump for atmospheric  $\text{CO}_2$  associated with it, depending on the fate of the crystals within sea ice.

L40-46: “Release of  $\text{CO}_2$  (from sea ice to the atmosphere)... from open water.” → Please be precise whether you mean air-sea-ice fluxes or air-sea fluxes.

We have amended this text for clarity. It now reads:

“Release of CO<sub>2</sub> from sea ice to the atmosphere has been reported during sea ice formation from open water (Geilfus et al., 2013a) and in winter (Miller et al., 2011; Fransson et al., 2013) while uptake of CO<sub>2</sub> by sea ice from the atmosphere has been reported after sea ice melt onset (e.g. Semiletov et al., 2004; Nomura et al., 2010; Geilfus et al., 2012; Nomura et al., 2013; Fransson et al., 2013; Geilfus et al., 2014; 2015).”

L68: “...in the Arctic...”: this should be also true for the Antarctic.

We deleted “in the Arctic” to make it a more general statement.

L79: “...will increase TA...”: high TA in meltwater will certainly not increase the seawater TA, since the release of TA upon sea-ice melt dilutes surface ocean TA concentration since bulk sea ice TA concentrations (brine + ikaite) are always lower than TA concentrations of seawater, which is also supported by your data.

We changed the manuscript as followed: “Melting sea ice stratifies surface seawater leading to decreased TA, TCO<sub>2</sub> and pCO<sub>2</sub>, in the sea surface, enhancing air-sea CO<sub>2</sub> fluxes (Rysgaard et al., 2007; 2009).”

L87: “However, the...”: This sentence would make more sense in the last paragraph, possibly after the second sentence.

We would like to keep it that way. In the last paragraph we are mentioning: “We gain the ability to carefully track carbonate parameters in the ice, in the atmosphere, and in the underlying seawater, while growing sea ice in a large volume of seawater, so that conditions closely mimic the natural system.” Which is our solution to the difficulties to detect the signal of carbon component release in a water column of several hundred meters (lines 87-88).

L95-97: This is not a full summary of the paper, since you also look into  $\Omega_{\text{aragonite}}$ .

We added few the following: “We also discuss that dissolution of ikaite crystals exported from sea ice in the underlying seawater can potentially hamper the effect of oceanic acidification on  $\Omega_{\text{aragonite}}$ .”

### 3. Site description, sampling and analysis

L151-153: They way you write this sounds like you do the same as Rysgaard et al. 2014. However, you derive the ‘ikaite’ concentrations by the difference between (TA<sub>ice</sub>\*-TA<sub>ice</sub>)/2, and only compare it to the concentrations estimated from microscope inspection as given in Rysgaard et al. 2014.

We deleted the section “The abundance and concentration of ikaite crystals precipitated within sea ice has been estimated by inspection under microscope as the samples melted.” So that it does not seem like we have replicated the method and analysis provided by Rysgaard et al., (2014).

#### 4.1. Sea ice and seawater physical conditions

L187: It seems strange that there is only a salinity stratification, however, in the temperature field the pool seems well mixed. How do you explain this?

Maybe the stratification related to the temperature is too small to be observed. The y-axis ranged in only 1.5°C.

## 4.2 Carbonate system

It is not really introduced why you look at  $nTA$  and  $nTCO_2$ . To facilitate reading and understanding you should explain this a little more detailed.

The reason to normalize TA and  $TCO_2$  is to remove the potential impact of salinity changes on both parameters and to estimate the role of other processes such as precipitation/dissolution of calcium carbonate and/or gas exchanges. We are not sure how to more clearly impress the dependence of TA and  $TCO_2$  on salinity with more clarity.

L191-192: values given for seawater concentrations of TA and  $TCO_2$  at  $t=0$  are different from the values given in Table 1.

The seawater TA and  $TCO_2$  ( $TA_{sw}$  and  $TCO_{2sw}$ ) are the concentrations reported during sea ice growth. These values are different from the values reported at  $t=0$  on 11 January (see Table 1,  $TA = 2453$  and  $TCO_2=2341$ ) because the sea ice started to grow on 13 January. The differences between 11 Jan ( $t=0$ ) and 13 Jan (when ice growth commenced) may be due cooling of the seawater, gas exchanges...

We decided not to include these values in the plot because only the plots related to TA and  $TCO_2$  in seawater will start on 11 January while all the others plots will start on 13 January when data collection commenced.

L200: Additionally provide concentrations of  $nTA$  and  $nTCO_2$  at  $t=0$ .

We have added the values in the table 1. Thanks.

### 5.1. Key processes affecting the carbonate system

L240: “up to 350  $\mu\text{mol/kg}$ ”, however, in Fig. 7c only up to to 100  $\mu\text{mol/kg}$  for the same dataset.

In line 240 of the original manuscript, 350  $\mu\text{mol kg}^{-1}$  is a maximum reported by Rysgaard et al (2014) using their method of microscopically observing crystals. We mean to state their results here so that our data showing average ikaite concentrations in the ice cover ranged from 0 to 100  $\mu\text{mol kg}^{-1}$  reported in figure 7 is put in some context. To clarify, we have revised this text to read:

“We compared the direct microscopy observations by averaging the amount of ikaite precipitated throughout the ice thickness for each sampling day from Rysgaard et al., (2014) (Fig. 7c, white dots) with our estimation of the amount of ikaite based on the difference between  $TA_{(ice)}^*$  and  $TA_{(ice)}$  (Fig. 7c, black dots).”

We have also revised the figure caption of the Figure 7 for the sake of clarity: “Evolution of (a)  $TA_{(ice)}$  averaged throughout the ice thickness at each sampling day (black dots) and  $TA_{(ice)}^*$  (dashed red line) ( $\mu\text{mol kg}^{-1}$ ) and (b)  $TCO_{2(ice)}$  averaged throughout the ice thickness at each sampling day (black dots) and  $TCO_{2(ice)}^*$  (dashed red line) ( $\mu\text{mol kg}^{-1}$ ), (c) Estimation of the ikaite precipitation/dissolution from half of the difference between  $TA_{(ice)}^*$  and  $TA_{(ice)}$  ( $\mu\text{mol kg}^{-1}$ ) (black dots) compared to the average amount of ikaite precipitated throughout the ice thickness for each sampling day from Rysgaard et al., (2014) (white dots). The vertical black dotted line on 26 January mark when the heat was turned back on.”

## 5.2. Estimation of the precipitation-dissolution of ikaite

L260:  $\text{TCO}_2$  is not conservative with salinity due to potential gas phase of  $\text{CO}_2^*$  (Eq. 2)

We revised the text to read:

“Assuming no biological effect, ikaite precipitation/dissolution and gas exchange, TA and  $\text{TCO}_2$  are considered conservative with salinity.”

L271: Here the explanation of positive and negative signs is wrong: When the difference  $(\text{TA}_{\text{ice}}^* - \text{TA}_{\text{ice}})/2$  is positive, then the observed TA concentration is lower than what would be expected from the theoretical conservation with S. Hence, TA is either in the form of ikaite crystals somewhere in the ice matrix or being exported potentially in ikaite form from the ice matrix to the seawater. In contrast, when the difference is negative, then it implies that more TA is observed in the brine than would be expected from the theoretical conservation with S, indicating dissolution of ikaite in brine. In contrast, in seawater, when the difference  $(\text{TA}_{\text{sw}}^* - \text{TA}_{\text{sw}})/2$  is positive then ikaite is imported and dissolved in seawater releasing ikaite-bond TA, and if negative then TA is exported from seawater to somewhere else.

We agree that this section was unclear. We changed the text as: “We assume that the difference between  $\text{TA}_{(\text{sample})}^*$  and the observed TA is only due to the precipitation or dissolution of ikaite crystals. In case of ikaite precipitation (*i.e.*  $\text{TA}_{(\text{sample})}^* > \text{TA}_{(\text{sample})}$ ), half of this positive difference corresponds to the amount of ikaite precipitated within the ice. This ikaite may either remain or may be exported out of the ice. A negative difference (*i.e.*  $\text{TA}_{(\text{sample})}^* < \text{TA}_{(\text{sample})}$ ), indicates ikaite dissolution.”

L272: “...implies a lack...” this is wrong, it implies that more TA is observed in sea ice. Please rewrite this sentence according to the changes above.

See previous comment for Line 271 above. Thanks.

### 5.2.1 Sea ice

L279: “...is a result of ikaite precipitation...”: it might also be the export of ikaite to the sea-water, see comments to L271 section 5.2, and L292, L302.

See previous comment. For Line 271 above. Thanks.

L296: “...found good agreement with small differences...” This statement is too positive for the time until the 17th of January 2013. As you state in L302 “ikaite crystals could have been formed and then exported into the underlying seawater...” In other words, for this period the comparison between the ikaite concentrations observed in Rysgaard et al. 2014 and your data suggests that your data shows concentration of  $\text{TA}^*$  being exported to the seawater rather than the ikaite concentration stored in the sea ice matrix.

We have revised the text to read:

“We compared the direct microscopy observations by averaging the amount of ikaite precipitated throughout the ice thickness for each sampling day from Rysgaard et al., (2014) (Fig. 7c, white dots) with our estimation of the amount of ikaite based on the difference between  $\text{TA}_{(\text{ice})}^*$  and  $\text{TA}_{(\text{ice})}$  (Fig. 7c, black dots). Both ikaite measurements are of the same order of magnitude however the average ( $22 \mu\text{mol kg}^{-1}$ ) and maximum ( $100 \mu\text{mol kg}^{-1}$ ) of direct observations presented by Rysgaard et al. (2014) were lower than our estimated average ( $40 \mu\text{mol kg}^{-1}$ ) and maximum of up to  $167 \mu\text{mol kg}^{-1}$  over

this whole experiment. Deviations are likely due to methodological differences. Here, sea ice samples were melted to subsample for TA and  $TCO_2$ , Ikaite crystals may have dissolved during melting, leading to an underestimation of the total amount of ikaite precipitated in the ice. However, the difference between  $TA_{(ice)}^*$  and  $TA_{(ice)}$  provides an estimation of how much ikaite is precipitated in the ice cover, including those crystals potentially already exported to the underlying seawater. The method used by Rysgaard et al., (2014) avoid the bias of ikaite dissolution during sea ice melt with the caveat that crystals need to be large enough to be optically detected. If no crystals were observed, Rysgaard et al., (2014) assumed that no crystals were precipitated in the ice, though ikaite crystals could have been formed and then exported into the underlying seawater prior to microscopic observation of the sample, which may explain the difference observed between both methods during initial sea ice formation (15-18 January) when the ice was still very thin. In addition, the succession of upward percolation events could have facilitated the ikaite export from the ice cover to the underlying seawater. Estimations from both methods show similar concentrations when the ice (i) warmed due to snowfall (18-23 January) and (ii) cooled once the snow was removed (on 23 January). Once the ice started to melt (26 January), Rysgaard et al., (2014) reported a decrease in the ikaite precipitation while in this study we reported a negative difference between  $TA_{(ice)}^*$  and  $TA_{(ice)}$ , possibly indicating that ikaite dissolved in the ice.”

L309: “...negative difference ... indicating that ikaite dissolved in the ice or were exported to the water column.”: A negative difference between  $TA_{ice}^*$  and  $TA_{ice}$  does not necessarily mean that ikaite is exported, but it definitively implies that it is dissolved in brine. See comment to L271.

We have revised the text to read:

“Once the ice started to melt (26 January), Rysgaard et al., (2014) reported a decrease in the ikaite precipitation while in this study we reported a negative difference between  $TA_{(ice)}^*$  and  $TA_{(ice)}$ , possibly indicating that ikaite dissolved in the ice.”

## 5.2.2. Water column

L324: Are the values of  $TCO_{2sw} - TCO_{2sw}^*$  here similar to  $nTCO_2$  such as for TA?

I don't understand the question.

L326-328: Please also explain the effects for the sea-ice covered period.

We've added: “During sea ice melt, increased vertical permeability resulting in increased liquid communication through the sea ice volume from below likely in part dissolved ikaite crystals still residing in the ice at that time, and also will have created a downward crystal export mechanism. As the ice melt advanced, patches of open water occurred at the surface of the pool. Therefore, uptake of atmospheric  $CO_2$  by the undersaturated seawater likely occurred, increasing the  $TCO_{2(sw)}$ .”

L329-351: Given that the dissolution of ikaite is a fast process in the order of seconds to minutes, a time delay in  $pCO_2$  rise of 1 day would suggest that during this day ikaite release to the seawater must have been continuously large. Please discuss this more precisely.

We are not so sure that the dissolution of ikaite crystals occurs that quickly. At  $-1^\circ C$  (average temperature of the water column) the dissolution of ikaite will be a slow



process. In Dieckmann et al (2008), the first publication reporting ikaite within sea ice, they melted bulk sea ice over night at +4°C. This method was used by Dieckmann et al (2008, 2010), Geilfus et al (2013), Nomura et al (2013) and this study. This strongly suggests that ikaite dissolution is not a fast process, especially not in a matter of seconds.

We agree that ikaite release from the ice to the water column must have been quite large and happening continuously during the melt. We added this idea in the manuscript in the section 5.3 ‘Ikaite export from the ice cover to the water column’

### 5.3. Ikaite export from the ice cover to the water column

L360: “...of ikaite precipitated and remained within the ice cover...” See comment to L271, it could also be the amount of ikaite being exported.

We changed the text accordingly.

L366-367: Since  $(TA_{ice}^* - TA_{ice})/2$  could be ikaite crystals in sea ice and/or exported ikaite crystals from sea ice it is not straight forward to derive the percentage of ikaite being exported or remained in the sea ice using this dataset. To derive ikaite concentrations in sea ice, you should measure sea ice concentrations with dissolved ikaite and subtract your observations from these new measurements. If this is unfeasible, you might instead consider to use the ikaite concentrations as given in Rysgaard et al. 2014 to compute an estimate of the fraction of ikaite remaining in sea ice.

We did this exercise and change the whole section. It now reads:

“The difference between  $TA_{ice}^*$  and  $TA_{ice}$  provides an estimation of ikaite precipitated within the ice, including potential ikaite export to the underlying seawater, so it cannot be used to determine how much ikaite remained in the ice versus how much dissolved in the water column. However, Rysgaard et al., (2014) indicate ikaite precipitated within the ice based on direct observations. Using the ikaite concentration reported in Rysgaard et al (2014) (and shown in Fig. 7c), the sea ice volume (in  $m^3$ ) and density, we calculate that 0 to 3.05 mol of ikaite precipitated within the ice cover during sea ice growth (Fig. 8b and Table 2). This amount decreased to 0.46 and 0.55 mol during the sea ice melt (28 and 29 January, respectively). Increased ikaite dissolution in the water column when the ice began to melt (from 11.5 to 20.9 mol) indicates that 9.4 mol of ikaite were stored in the ice and rejected upon the sea ice melt. This amount is about three times the amount of ikaite precipitated in the ice estimated by Rysgaard et al., (2014) at the end of the growth phase (3.05 mol, Table 2), suggesting more work is needed best estimate ikaite precipitation within sea ice.”

### 5.4. Air-seawater exchange of inorganic carbon, attempt of CO<sub>2</sub> budget

The calculation of the  $TCO_2$  export from ice to water is not clear, in particular, concerning the conversion of the air-seawater CO<sub>2</sub> flux to units of mass?

The air-ice CO<sub>2</sub> fluxes are presented in  $mmol\ m^{-2}\ d^{-1}$ . As we know the time step between each measurement, we can estimate the number of mole of CO<sub>2</sub> exchanged between the ice and the atmosphere for each day in  $mol\ m^{-2}$ . From there, using the sea ice thickness and density we can estimate how many moles are exchanged over the whole pool. We added few lines in the manuscript to clarify:



“The number of mole of  $\text{CO}_2$  exchanges between the ice and the atmosphere were calculated (noted as  $\text{CO}_{2(\text{air-ice})}$  in Table 2) using the time step between each flux measurement, the ice thickness and density. During sea ice growth 0.01 to 0.42 mol of  $\text{CO}_2$  were released from the ice-covered pool to the atmosphere. During sea ice melt uptake of atmospheric  $\text{CO}_2$  by the ice-covered pool ranged from -0.15 to -0.93 (Fig. 9, white triangles).”

Opposed to the definition of ikaite concentrations in sea ice, you here nicely explain the potential processes that cause a negative difference between  $\text{TCO}_{2(\text{ice})}^*$  and  $\text{TCO}_{2(\text{ice})}$  in lines 371-375: ...”This could be due to different processes: (i) sea ice released  $\text{CO}_2$  to the atmosphere, (ii) the precipitation of ikaite within sea ice decreased  $\text{TCO}_{2(\text{ice})}$  and (iii) sea ice exchanges  $\text{TCO}_2$  with the underlying seawater.” Unfortunately, for calculating the budget, you again assume that  $(\text{TA}_{\text{ice}}^* - \text{TA}_{\text{ice}})/2$  would be ikaite concentrations (see comment to L271, explaining that for TA both (ii) and (iii) are relevant).

Agreed, so we have revised the text to read: “Assuming we know how much ikaite is contained in the ice cover...”

L388: “up to 99 %”: please give mean range, or plot results as time series.

We have revised the text here to read: “ $\text{TCO}_2$  export from the ice to the water column ranged from 23% of the total sea ice  $\text{TCO}_2$  early in the ice growth (14 January) to 100% after the onset of melt. These estimations are comparable to the study of Sejr et al., (2011) who suggested that sea ice exports 99% of its total  $\text{TCO}_2$  to the seawater below it.”

89: “Between the beginning and the end of experiment, sea ice exported 2.8 mol.” The methodology used to derive these values is unclear, it seems as if you give the value at the end of the experiment?

Agreed. We now use the average sea ice export of  $\text{TCO}_2$  to the underlying seawater and have made this necessary correction in the text:

“On average over the whole experiment, sea ice exported 1.7 mol of  $\text{TCO}_2$  to the underlying seawater (Fig. 9), which corresponds to a  $\text{TCO}_{2(\text{sw})}$  increase of  $43.5 \mu\text{mol kg}^{-1}$  considering the average sea ice thickness and density during the experiment and the volume of the pool. However,  $\text{TCO}_{2(\text{sw})}$  increased by  $115 \mu\text{mol kg}^{-1}$  over the whole experiment (Fig. 3b), leaving an increase of  $71.5 \mu\text{mol kg}^{-1}$  in the  $\text{TCO}_{2(\text{sw})}$  that cannot be explained by the sea ice-seawater exchange of  $\text{TCO}_2$ . We postulate that as the ice melt advanced, patches of open water that opened at the surface of the pool which were undersaturated compared to the atmosphere (Fig. 3d) imported the additional  $\text{TCO}_2$  directly from the atmosphere in the form of  $\text{CO}_{2(\text{g})}$ . Considering the pool volume, the  $71.5 \mu\text{mol kg}^{-1}$  increase of  $\text{TCO}_{2(\text{sw})}$  could be explained by an air-sea water  $\text{CO}_2$  uptake of  $8.5 \text{ mmol m}^{-2} \text{ d}^{-1}$  over 3 days of sea ice melt in a 20% ice free pool. High air-sea gas exchanges rates have been observed over partially ice-covered seas (Else et al., 2011; 2013). This mechanism is also corroborated by models that account for additional sources of turbulence generated by the presence of sea ice (Loose et al., 2014).”

5.5. Impact of sea ice growth on aragonite saturation state of the Arctic Ocean in the

context of ocean acidification

The title of this chapter implies that data from the Arctic Ocean are shown, however, the discussion is solely based on the SERF 2013 data. Hence, the chapter title is misleading.

We changed the title of this section into: “Potential impact of sea ice growth and ikaite export on aragonite saturation state of the underlying seawater.

Generally the data suggests that with or without ikaite export to the seawater the seawater would be supersaturated (Fig. 10), hence, in this experiment calcifying organisms should not face any problems. You should more clearly state that you base your conclusion “potentially hamper the effect of ocean acidification in fall to winter” on the differences between  $\Omega_{\text{aragonite}}$  and  $\Omega_{\text{aragonite}}^*$ .

We added this precision and changed the text as followed: “During ice growth, sea ice brine rejection appears to increase both pH (from 8.00 to 8.06) and  $\Omega_{\text{aragonite}}$  (from 1.28 to 1.65) of the underlying seawater, offsetting the effect of decreased temperature. A slight increase of  $\Omega_{\text{aragonite}}$  was predicted due to increased salinity and a proportional increase of TA and  $\text{TCO}_2$  as depicted in  $\Omega_{\text{aragonite}}^*$ . However, the effect of ikaite rejection and subsequent changes in TA strongly enhance the increase of  $\Omega_{\text{aragonite}}$ .”

- L441: Please clarify why  $\Omega_{\text{aragonite}}$  reaches its minimum during winter, since this is not supported by the data on your sea-ice growth-melt cycle. Do other observations suggest this, if yes please refer to them?

We added references in the text.

- L442: Why do you specifically only state the Arctic Ocean? In other words, do you expect different results for the Antarctic region, and if so, please explain the reasons.

We deleted “in the Arctic ocean”.

- L443-444: “...ice removal acts to impede the effect of ikaite rejection and therefore promote decreased  $\Omega_{\text{aragonite}}$ .” This calls for taking into account under-ice ikaite rejection in modeling predictions (...) in the context of sea ice rapid shrinking.”: Several modeling studies have addressed the effects of future Arctic sea-ice decay on ocean acidification and report that Arctic surface ocean acidification is related to the rate of sea-ice reduction, and also to the responses of wind mixing and stratification under reduced sea-ice conditions (e.g. Steiner et al. 2014; Yamamoto et al. 2012). Please relate the increase in  $\Omega_{\text{aragonite}}$  due to ikaite export from the ice to the surface ocean to the effects of rising atmospheric  $\text{CO}_2$  concentrations, global warming and associated Arctic sea-ice decay on  $\Omega_{\text{aragonite}}$  projected by models.

This will be a really interesting topic, but this is far beyond the scoop of this manuscript.

## 6. Conclusion

The conclusions drawn are valid and well presented except of one part: The connection between L459-462 and L462-466 is not obvious. Please be more precise here. You should state that any attempt of deriving the air-sea  $\text{CO}_2$  flux related to the carbon pump

should take into account that ikaite is exported to the underlying ocean during sea ice growth, which might reduce the efficiency of oceanic CO<sub>2</sub> uptake upon sea ice melt related to the sea ice pump.

We changed the text accordingly.

### III. Technical comments in Figures and Tables Caption

Fig. 1 Give year of experiment.

We add the information.

Fig. 2. Put panel labels in brackets.

Done.

Panel (d): y-axis units for temperature overlain on bracket.

Thanks, we fixed that.

Panel (c) and (d): units for salinity not given.

Salinity do not have units and we did not provide any units through the whole manuscript.

Panel (d): legend is missing information of what is temperature and sanity.

We fixed that.

Caption Fig. 2.

Use lower case letters for panel description.

“... snow cover”: better to use same text as in figure: ‘snow thickness’

“... black horizontal bars..”: no bars visible: maybe better use ‘black shaded areas’

Indicate colors for seawater temperature and sanity in panel (d)

Last sentence, final dot missing.

We did the changes as suggested.

Caption Fig. 3.

Use lower case letters for panel description. Indicate also that red line is calculated on the mean values of the three depth intervals. Legend in panel (a) and (b): no need for ‘Sw’ abbreviation. One space between depth value and unite.

We did the changes as suggested.

Caption Fig. 4.

Use lower case letters for panel description.

We did the changes as suggested.

Caption Fig. 6.

Use lower case letters for panel description.

We did the changes as suggested.

Caption Fig. 7.

Use lower case letters for panel description.

One space after the fist TA<sub>(ice)</sub>

We did the changes as suggested.

Fig. 8.

y-axis labels: “Ikaite” This is to imprecise, see comments to L271.

The figure caption of figure 8 now reads:

“Evolution of (a) ikaite dissolution within the water column (in  $\mu\text{mol kg}^{-1}$ ), (b) mass of ikaite dissolved in the underlying seawater (blue), mass of ikaite precipitated in sea ice (black) estimated from this study and estimated from Rysgaard et al., (2014) (white). The vertical black dotted line on 26 January mark when the heat was turned back on.”

The figure is showing the amount of ikaite within sea ice or seawater, no matter if it dissolved, precipitated or exported. Therefore, “Ikaite” as label of the y-axis should be enough.

Caption Fig. 8.

Use lower case letters for panel description.

“..amount of mol of ikaite..” mol is the unit: ‘..mass of ikaite in mol..’

We did the changes as suggested.

Fig. 9.

A flux cannot have the unit mol.

“Total  $\text{TCO}_2$  lost by the sea ice” This is the mass of  $\text{TCO}_2$  of ice cover assuming the absence of ikaite.

“Air-ice  $\text{CO}_2$  fluxes” cannot have units of mol

We changed it into: amount of  $\text{CO}_2$  exchanges between the atmosphere and the ice cover ( $\text{CO}_{2\text{air-ice}}$ , white triangle).

Caption Fig. 9.

A flux cannot have the unit mol.

“Total  $\text{TCO}_2$  exchanges by the ice cover” This is the mass of  $\text{TCO}_2$  of ice cover assuming the absence of ikaite and  $\text{CO}_{2(\text{g})}$  in bubbles.

As mentioned in the manuscript:

The total amount of  $\text{TCO}_{2(\text{ice})}$  lost from the ice cover is estimated by the difference between  $\text{TCO}_{2(\text{ice})}^*$  and  $\text{TCO}_{2(\text{ice})}$ .

And

According to Figure 7b, the ice cover always had lower  $\text{TCO}_{2(\text{ice})}$  during the experiment ( $\text{TCO}_{2(\text{ice})}^* > \text{TCO}_{2(\text{ice})}$ ) compared to what would be expected if the  $\text{CO}_2$  simply followed brine rejection in a conservative process (i.e.  $\text{TCO}_{2(\text{ice})}^*$ ). This could be due to different processes: (i) sea ice released  $\text{CO}_2$  to the atmosphere, (ii) the precipitation of ikaite within sea ice decreased  $\text{TCO}_{2(\text{ice})}$  and (iii) sea ice exchanges  $\text{TCO}_2$  with the underlying seawater.

Therefore, the total exchanges of  $\text{TCO}_2$  from the ice take into account the precipitation of ikaite and the gas exchanges.

Fig. 3. To 5. And Fig. 7. To 9

x-axis text: use for all plots the same x-axis text, e.g. the same as used in Fig. 2.: “Day of January 2013”.

We did the change as suggested.

Table 1.

Please also give the water column conditions just before the heat was turned ON, and at the end of the experiment.

We followed the suggestion.

Table 2.

“amount”: better use ‘mass’

“ikaite”: See comment to Fig. 8. and L271.

“CO<sub>2</sub> fluxes (mol)” fluxes are defined e.g. to be changes in mass over time. How do you derive these values, please clarify this in the text, see comment to section 5.4.

The figure caption now read:

“Masses of TCO<sub>2</sub> in the water column (TCO<sub>2(sw)</sub>) and in the ice cover (TCO<sub>2(ice)</sub>), masses of ikaite within the ice cover estimated from this study and from Rysgaard et al., (2014), masses of ikaite dissolved in the water column (Ikaite<sub>(sw)</sub>) and masses of CO<sub>2</sub> exchanged between the ice and the atmosphere over the whole pool (estimation based on the air-ice CO<sub>2</sub> fluxes). All units are in mole.”

#### IV. Technical comments

L18-19: “... ikaite precipitated...”, better: ‘... ikaite concentrations of up to..’

Thanks for the correction.

L19: “... within sea ice; up to...”: wrong ‘... within sea-ice; at least...’

This sentence does not exist anymore.

L29: “Each year...”: Be more precise: e.g. ‘Currently, each year..’

Thanks for the suggestion.

L30: “... through primary production and surface cooling...”: please be slightly more precise here explaining the biological pump and the dissolution pump.

If the reader wants to know more about the biological and dissolution pump, he could use the references provided in the manuscript.

L33: Please give references, and clarify if you refer only to model and/or observational estimates.

I’m not sure what the reviewer is referring to and there are a couple of references in the sentence.

L33: “... sea ice an impermeable...” grammar mistake: ‘... sea ice as an impermeable...’

Thanks for the correction.

L47: comma missing after “formation”

Thanks for the correction.

L50: please give reference.

I’m not what the reviewer is referring to as the end of the sentence L50 has a reference.

L51: “...inorganic carbon...” → give abbreviation TCO<sub>2</sub>

No, inorganic carbon refer here to either TCO<sub>2</sub> or CO<sub>2</sub> (dissolved or as gas bubbles), which is all “inorganic carbon”.

L56: “...TA is reduced...”: Be more precise: e.g. ‘...TA in brine is reduced...’

Thanks for the correction.

L57: "...while TCO<sub>2</sub> is...": Be more precise: e.g. '...while TCO<sub>2</sub> in brine is..'

Thanks for the correction.

L59: "[CO<sub>2</sub>]": Spelling mistake: [CO<sub>2</sub>\*]: and define in text what this means

The equation as shown in the original manuscript is correct and is displayed as in Zeebe and Wolf Gladrow (2001), CO<sub>2</sub> in seawater: equilibrium, kinetics, isotopes.

L60: "[B(OH-)]": Spelling mistake: B(OH)<sub>4</sub>-]

Thanks for the correction.

L60: "[H-]": Spelling mistake: [H+]

Thanks for the correction.

L63: Also re-mention the pathway of brine to the sea-ice surface as was given in lines 47-48.

We won't repeat something wrote less than 15 lines above. In addition, the reading of the text will be less smooth.

L67: "...fluxes...": Be more precise: e.g. '...air-sea fluxes..'

Thanks for the suggestion.

L67: "...seawater and incorporated...": Grammar mistake: e.g. '...seawater and its contribution to intermediate and deep-water formation..'

Thanks for the correction.

L77: "...melting sea ice promotes...": Be more precise: e.g. '...surface warming and melting sea ice promote..'

We choose to keep "melting sea ice". Sea ice can melt from the top (surface melting) due to the increase of the radiation and from the bottom (warmer seawater, as during this experiment). Both cases lead to the melt of the ice. And the sea ice melt promotes the stratification of the underlying seawater (as during this experiment).

L80: "...underlying seawater...": be more precise: e.g. surface ocean → due to the enhanced summer stratification L78.

Thanks for the suggestion.

L90: "435 m<sup>3</sup>": Give dimensions rather than the volume.

The dimensions are provided few lines below, in the section "Site description, sampling and analysis".

L167: "...15 cm on 18 January...": mistake: '..15 cm until 18 January...'

If it please to the reviewer.

L170: "...This results in the increase of the sea ice temperature...": Be more precise: e.g. 'This resulted in repeated events of increased sea-ice temperatures..'

We followed the suggestion.

L197-198: it would be more intuitive to call it 'sw' and 'ice' instead of 'sample'. Delete brackets around 'sw', and 'ice', put brackets around 't' and do not write 't' in subscript.

We decided to use 'sample' in the formulas (4) and (5) to make them valid for both seawater and sea ice. In the formula description, we specifically explained that 'sample' is either sea ice or seawater. The use of the brackets around 'sw' and 'ice' is

to be consistent with the writing of  $TA_{(ice)}$  and/or  $TA_{(sw)}$  used through the whole manuscript.

L201: "...ice started the melt..": mistake: '...ice started to melt..'

Thanks for the correction.

L225: "...suggest...": this is rather weak, better to write that the measurements 'show' this.

Thanks for the suggestion.

L228: Is is not appropriate to give a range of two values.

Agreed, we have made the appropriate correction.

L264-265: in the equation 'sample' means 'sw or ice'. It would facilitate reading if you would write for each component a separate equation.

We decided to use the notation "sample" to avoid the repetition of the same equation and we will keep it that way.

It is better to not put "sw" and "ice" within brackets, while the time variable should be written not in subscript and in brackets.

We put "sw" and "ice" within bracket to be consistent with the notation of  $TA_{(ice)}$ ,  $TA_{(sw)}$ ,  $TCO_{2(ice)}$  and  $TCO_{2(sw)}$  thought the whole manuscript.

L270: "assume" this sounds like as if another value than the one-half would also make sense. You should clearly explain here were the one-half comes from: 1 mol of ikaite contains 2 mol of TA.

The text now read: "The difference between  $TA_{(sample)}^*$  and the observed TA is only due to the precipitation or dissolution of ikaite crystals."

L278: "...assume..." see comment to L270

The text now read: "Half the difference between  $TA_{(ice)}^*$  and  $TA_{(ice)}$  is a result of ikaite precipitation (Fig. 7c, black dots)."

L299: "...precipitate...": grammar mistake: '...precipitated..'

Thanks for the correction.

L304: "...differences observed": be more precise: e.g. '...differences between both methods...'

If it please to the reviewer.

L318: "...to the amount of ikaite...": be more precise: e.g. '...to the concentration of ikaite..'

If it please to the reviewer.

L317: "... half the difference between  $TA_{(sw)}^*$  and  $TA_{(sw)}$  ..." mistake: '... half the difference between  $TA_{sw}$  and  $TA_{sw}^*$ ...'

No, the text as shown in the manuscript is correct, we are always looking at the difference between  $TA_{(sw)}^*$  and  $TA_{(sw)}$ .

L319: "...amount...": imprecise formulation: '...concentration...'

Thank you.

L322: "...  $TA_{(sw)}^*$  and  $TA_{(sw)}$  ..": see comment L317



See previous comment.

L345: "...processes other than a the temperature..." → delete the 'a'

Thanks for the correction.

L346: Changes in  $p\text{CO}_2$  cannot not understood from equation 3.

Right, we changed it to equation 1.

L367: "...crystals remain contain within...": grammar mistake: '.. crystals remain within..'

Thanks for the correction.

L379: Fig. 9 not 8

Thanks for the correction.

L379: "maximum outgassing": logical mistake: '... maximum loss of  $\text{TCO}_2$ ...'

Thanks for the correction.

L386: "... substracting ... ikaite precipitation to the total": grammar mistake: '...precipitation from the total...'

Thanks for the correction.

L392: "Fig 3c" → Fig. 3B

Thanks for the correction.

L402: "...convection..." This should include all kind of transport mechanisms e.g. advection, mixing

We changed it into "mixing" which we take to include convection, diffusion, advection etc.

L400: "... measurement...": spelling mistake: '...measurements..'

Thanks for the correction.

L424: "... area ..": spelling mistake: '... areas ...'

Thanks for the correction.

L426: "... as a result of respiration.": missing process: '... as a result of respiration and dissolution..'

The undersaturation in respect with aragonite can't be enhanced by the dissolution of calcium carbonate...

L438: "...dramatically...": formulation too dramatic

We changed dramatically for strongly.

L438: "...increase the...": grammar mistake 'increase...'

Thanks for the correction.

L439: "This suggest that...": spelling mistake: 'This suggests that..'

Thanks for the correction.

L444: "... and therefore promote decreased..": grammar mistake: '... and therefore promotes a decrease of...'

Thanks for the correction.

L457: "up to 66..." → '... up to 128...'

Thanks for the correction.

L462: Please give more references

The reference provided is the original reference regarding this problematic. There is no need for additional references.

L470: "... is responsible the...": '... is responsible for the'

Thanks for the correction.

L471: "...we project that...": '... we discuss that..'

Thanks for the correction.

## References

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