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 TCO₂ and salinity-normalized TA and TCO₂ during a 17 dayperiod. Measured air-ice CO2 exchange during the study is also presented. The investigation of sea ice processes and underlying water in a confined setup in an outside environment processes of salinity changes, with mainly the ikaite precipitation/dissolution and CO₂ 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.

We stopped the experiment when sea ice was still present in the tank, which explain why the initial seawater conditions are not met at the end of the experiment. We have endeavored to make this clear in the revised version of the manuscript.

Important discussion and uncertainty investigations are missing regarding the contradictions of the results.

There are no contradictions of the results presented here as far as we can tell.

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.

We have made every attempt to clarify these and other points in the specific comments below.

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.

Essential data are not missing from the work, and we see no specific comments to that effect. Revision of the section regarding in the seawater TA in light of the comments of the other two reviewers should clarify this for the reviewer.

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.

Rysgaard et al., (2014) simulated the precipitation of ikaite using SERF seawater and the FREZChem model (Marion 2001) and show that ikaite will start precipitate at -4°C. This suggests that the temperature of the water column, during the whole experiment, is warm enough to dissolve ikaite crystals.

Regarding our methods to estimate the ikaite precipitation within sea ice, we used the same technique as presented by Dieckmann et al., (2008) who is the first to report ikaite within sea ice. We recognize that melting sea ice at +4°C over night is probably not the best method, but it is widely used in different studies (e.g. Dieckmann et al 2008, 2010, Geilfus et al 2013 and Nomura et al 2013). We can't affirm that no ikaite dissolution take place during the melt of the ice samples. This is also discussed in the section "estimation of the precipitation-dissolution of ikaite" as a possible bias of the method. However, the melt of the ice samples is fast (happen over night) compared to the duration of 17 days for the whole experiment where the ikaite have more time to dissolved.

The water column temperatures were between -3°C and -7°C during the study and about -1°C at the end of the study.

The water column temperature can't be ranging from -3 to -7°C, that's sea ice (see figure 2).

There is lack of information on temperature, salinity, TA and TCO₂ 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.

We stopped the experiment when sea ice was still present in the tank which explain why we are not going back to the initial salinity in the pool and why we can' close the TA budget. In the first submitted manuscript, we did not attempt to do a TA budget. We did try to close a TCO₂ budget, including the ikaite precipitation-dissolution, airice gas exchanges and ice-seawater TCO₂ exchange. Unfortunately, as stated in the manuscript we could not close the budget and uncertainty in the methods were too big. This conclusion will be the same in an attempt to do a TA budget.

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.

We did some estimation and the lost of water due to the sea ice/seawater sampling is negligible (see further comments).

To estimate how much water is removed from the pool due to sea ice sampling, we consider that we collected 5 ice cores during each sampling day. Therefore, we will remove 103 L of seawater out of the pool. According to the dimension of the pool (line 100, L= 18.3 m, l=9.1 m and depth= 2.6m) 103 L corresponds to 0.023% of the total volume of the pool. The impact on the salinity and TA will be negligible.

What about TA and TCO₂ in the snow, brine and brine-skim, where these analyzed?

These factors could be discussed if they impact the results and maybe also used correcting the calculations.

We did not measure TA and TCO₂ in the snow or in the brine, and data on TA and TCO₂ on brine skim and frost flowers were too scarce to conclude anything and were therefore not presented in this study.

In parts of the result, the air-sea CO₂ flux is not considered and left out in the statement of processes when calculating the changes in TCO₂, which is an important process driving the changes in TCO₂ (except for biological production) although with relatively small effect. However, this is later discussed in the manuscript.

We disagree with the reviewer about the location of the air-sea flux discussion, leaving it where we feel it's most applicable and pertinent in the discussion about the CO_2 fluxes and how they affect the TCO_2 exchanges we make the TCO_2 budget.

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).

The wind data presented in more than one other paper to which we refer in the work and are not presented here because we used the chamber technique to measure the CO₂ flux at the sea ice surface. The reviewer will understand of course that the chamber technique, prevents the impact of wind on the flux measurement. See a more complete response in the specific comments section.

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.

Thanks for the references; we made sure to cite these works properly in the manuscript.

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

We've endeavored to improve the written English in the work.

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".

We changed it into "estimates".

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".

The first sentence now reads:" The precipitation and fate of these ikaite crystals within sea ice is still poorly understood."

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.

We have made the proposed revision.

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.

See previous comments.

Introduction

Lines 35-36. The references mentioned, do they report on sequestration of atmospheric CO₂ below the mixed layer or only into the surface mixed layer? Do they have evidence that the ice-brine pump actually exports atmospheric CO₂ below the mixed layer (i.e. sequestration for longer periods)? There are other studies (not so recent) of CO₂ sequestering which are more relevant, e.g. CO₂ 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".

Thanks for the reference of Brown et al (2016), I did not see the final version of the publication yet as it is just accepted for publication (end of March 2016). We changed our sentence as suggested.

Line 39. I suggest removing "CO₂", and start the sentence with "The carbonate chemistry...". What do you mean with "heterogeneous"? Do you mean that the distribution or concentrations are heterogeneous?

We followed the suggestion and change the sentence by: "The carbonate chemistry in sea ice and brine is spatially and temporally variable, which leads to complex CO_2 dynamics with the potential to affect the air-sea CO_2 flux (Parmentier et al., 2013)."

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.

Reference added

Line 46. What is the sea ice pump, please explain why and how pCO₂ is controlled? We changed the structure of the text to make sure the sea ice pump is clearly explained: "The specific conditions leading to ikaite precipitation as well as the fate of these precipitates in sea ice are still not fully understood. Ikaite crystals may remain within the ice structure while the CO₂ formed during their precipitation is likely rejected with dense brine to the underlying seawater and sequestered below the mixed layer. During sea ice melt, the dissolution of these crystals triggered by increased ice temperatures and decreased bulk ice salinity will consume CO₂ and drive a CO₂

uptake from the atmosphere to the ice. Such mechanism could be an effective sea ice pump of atmospheric CO₂ (Delille et al., 2014). In addition, ikaite stored in the ice matrix could become a source of TA to the near-surface ocean upon its subsequent dissolution during sea ice melt (Rysgaard et al., 2007; 2009)."

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.

Reference added.

Lines 54-55. Please add the reference Fransson et al. (2013). Reference added.

Lines 56-60, Equations. The definitions of some parameters are missing, please add. Yes, thanks we now define all parts of the equations that are mentioned in the text.

Lines 67-69. Please add the reference Fransson et al. (2013) for mentioning the study of brine rejection (with CO₂ and TCO₂) 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.

Reference added.

Line 75. Change (Eq. 3) to (Eq 1).

Thanks for the correction.

Line 82. What do you mean with "carbon-bearing materials". Please explain.

Now the sentence reads: "One of the major unknowns is the fate of ikaite, TCO_2 and CO_2 released from sea ice during winter."

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.

Thanks for the reference. The work of Fransson et al (2013) show how difficult it is to detect the signal of carbon components release into the water column, as stated in our manuscript. Especially as they only found evidences on 4 stations compared to the 18 stations sampled in their studies (Chap. 50, p20 on the Fransson et al (2013) publication).

Line 93. Change "carbon" parameter to "carbonate" parameters. Thanks for the correction.

Line 94. What is "large enough volume"?

We deleted the word "enough". Now the sentence reads: "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."

Line 95. Change "a 3 weeks experiment" to "17-days experiment".

We changed it into "During this experiment'.

Lines 96-97. After "main processes..." please add "...assuming no biological processes". Thanks, we have made the recommended addition.

Lines 99-109. Tank and experiment descriptions: I suggest adding a table with salinity, temperature, TA, TCO₂ 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.

We did not measure any nutrients in the artificial seawater. Since they were not measure during this experiment, it's difficult make any meaningful comments on the subject and so we refrain from doing so.

Table 1 shows the seawater conditions at 3 stages of the experiment: 1) the initial seawater conditions prior to sea ice formation 2) at the end of sea ice growth prior to melt and 3) the last measurements made in the pool, once the ice was melting.

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)?

We did not track the changes of volume in the pool during the experiment. However, considering that we collected 5 ice cores during each sampling day, we will remove 103 L of seawater out of the pool. According to the dimension of the pool (line 100, L= 18.3 m, l=9.1 m and depth= 2.6m) 103 L corresponds to 0.023% of the total volume of the pool.

We did have artificial mixing in the tank. This detail was added to the manuscript in the "Site description" section: "Four 375 W pumps were installed on the bottom of the pool at each of the corners to induce a consistent current. The pumps were configured to draw water from their base and then propel it outward parallel to the bottom of the pool. The pumps were oriented successively at right angles to one another, which created a counterclockwise circulation of 2-3 cm s⁻¹ (Else et al., 2015)."

The pool was well mixed as suggested by the T and S profile observed during the experiment (as explained line 184-187) so the distribution of TA and ikaite should be homogeneous.

We only had access to the bottom of the pool in the spring once the pool was drained, having no mechanism to look for ikaite crystals while the pool was full of water.

How much of the pool ice cover was used for the experiment, sampling all over the ice cover?

We add the precision in the manuscript and a reference to Else et al (2015) who presented a schematic view of SERF. The manuscript now reads: "Sea ice and seawater samples were obtained from a confined area on the North side of the pool to

minimize effects on other experiments (e.g. Else et al., 2015)."

Lines 110-114. How was salinity in the seawater sample and melted sea ice measured? The manuscript, lines 184 reads: "Bulk ice and seawater samples salinity was measured on bulk ice and seawater samples using a Thermo Orion 3-star with an Orion 013610MD conductivity cell and values were converted to bulk salinity (Grasshoff et al., 1983)."

Lines 115-119. Do you have data on wind speed? That is important for the discussion of ice- air CO₂ fluxes.

The wind could be an important component in the amplitude of the air-ice CO_2 fluxes measured by eddy covariance. However, in this study air-ice CO_2 fluxes were measured using the chamber technique in the purposeful absence of wind. Therefore we can't link the magnitude of the air-ice CO_2 fluxes to any wind speed.

Lines 127-130. Method of samples: the procedure of the TA analyses after removing ikaite should be mentioned in this section and later discussed. Did ikaite dissolve during storage and analysis of the seawater sample or in the water column? Please define when dissolution took place. This is valid throughout the manuscript.

The lines 127-130 states on how we took seawater samples with a peristaltic pump through an ice core hole. We did not remove any ikaite crystals from our seawater samples and never mentioned anything like that in the manuscript.

It may be possible that ikaite was present as crystals in the seawater samples and dissolved therein during storage. Since both TA and TCO_2 were measured adding acid in the samples, in all likelihood any ikaite "present" in the sample will have been dissolved.

Did you analysed TA in snow and brine?

We did not measure TA in snow or 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.

We did some measurements of TA and TCO_2 in the frost flowers. But we don't have enough data to support anything, which is why this is not presented in the manuscript. Yes the high TA and TCO_2 reported on 16-17-22-23 January are due to the presence of brine skim. Which is why, in the manuscript we are linking these high concentration to the high salinity at the surface of the ice.

Did you sample the bottom of the tank? Could there have been solid ikaite?

At the end of the experiment we did not look for ikaite or any other precipitates at the bottom of the pool. In addition, the heating coil sitting at the bottom of the pool will make the dissolution of ikaite very likely. The pool was ice-free for a few days after the end of our measurement period before another experiment took place at SERF. We only had access to the bottom of the pool in the spring once the pool was drained.

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.

The section from Fransson et al (2013) discussing the possible lost of ikaite during the ice core collection read: "However, if we assume that bacterial respiration occurred in the entire ice core during the study period, this would result in more negative CO₂-gas flux (C_T loss) or less positive flux. In addition, the effect of solid CaCO₃ may be underestimated due to the loss of CaCO₃, A_T and brine at ice-core extraction."

I believe the authors are referring to the possibility of lost of brine, and by extension ikaite, due to core extraction from the ice cover. This is of course a possibility, as you are pulling an ice core out of the ice cover, you may lose brine, gases and ikaite crystals. This is not a new problem in sea ice research and we, like many others, have not developed a coring method that overcomes this problem.

According to Rysgaard et al., (2012) brine loss during the core extraction could be approximately 10 percent (±5 %) based on unpublished data collected during the IPY-CFL project in 2008.

Lines 130 and 144. How much HgCl₂ did you add to the samples and what was the volume of the sample?

We now include the requested information as follows:

"Samples were stored in 12 ml gas-tight vials (Exetainer, Labco High Wycombe, UK) and poisoned with 12 μ l of saturated HgCl₂ solution and stored in the dark at 4°C until analysed."

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?

No, the lines 141-142 reads: "The bagged sea ice samples were then melted in the dark at 4°C to **minimize** the dissolution of calcium carbonate precipitates (meltwater temperature never rose significantly above 0°C)." We can't affirm that no ikaite dissolution take place during the melt of the ice samples. This is also discussed in the section "estimation of the precipitation-dissolution of ikaite" as a possible bias of the method.

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?

We added a figure panel on the figure 2 showing the brine volume concentration in the ice cover during the whole experiment. We add some text in the section "sea ice and seawater physical conditions".

I'm not sure to understand what is the 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.

Agreed. However, we present these data in a section called "sea ice and seawater

physical conditions". This section is needed to make sure the reader knows how the physical conditions of both the ice cover and the underlying seawater are evolving during the experiment. This section leads directly on from the methods section at the very beginning of the results.

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"?

We changed that part and made an ANOVA test to confirm the TA and TCO₂ means of the 3 depths are not statistically different. The manuscript now reads: "We performed an ANOVA test over the 3 depths and the means are not statistically different (p<0.01). Therefore we will consider the average concentration."

Lines 191-195. I suggest to also write the TA and TCO₂ differences from start to end. That helps to understand the figures.

Both values of TA and TCO₂ at the beginning and at the end of the experiment are already given in the text (L 191-195 of the original manuscript) and in the table 1.

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.

In the methods section, we state that we are melting bulk sea ice samples (ikaite still included within the ice samples), we do not know of a method to remove the ikaite from the samples without melting them.

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

In this section we refrain from mentioning the averaged bulk ice salinity. Here we present TA and TCO₂ in bulk sea ice and the normalized TA and TCO₂ in sea ice (noted as nTA and nTCO₂), so mention of average bulk salinity would likely muddy the water for the reader. The only time we mention average sea ice salinity is when we introduce the calculation of the expected TA and TCO₂ based on sea ice salinity. The manuscript specifies that TA, TCO₂ and S are averaged throughout the ice cover where that information is pertinent.

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.

We did not remove the snow cover from the ice to measure the air-ice CO_2 fluxes. The snow removal just at the location of the chamber will not make our estimation of the air-ice CO_2 fluxes representative for the whole ice covered pool. In addition, removing the snow will allow the ice to cool down quite rapidly (as illustrated in the figure 2, when we removed the snow on 23 January), promoting a release of CO_2 from the ice to the atmosphere. The exact role of the snow cover in term of air-ice CO_2 fluxes is not well known and is worth dedicated studies, but that is beyond the scope of this work.

We changes the manuscript as followed (to include the notion of snow over sea ice): "The CO₂ fluxes measured at the variably snow-covered sea ice surface (see Figure 2b), ranged from 0.29 to 4.43 mmol m⁻² d⁻¹ show that growing sea ice released CO₂ to the atmosphere (Fig. 5)."

Line 227. Add "from source" to get "switched from source to sink for...."

Thanks for the correction.

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.

In these lines we mean to indicate that we found that sea ice was a source of CO_2 to the atmosphere during growth and a sink for atmospheric CO_2 during melt. In the discussion, we attempted to do a TCO_2 budget. We mention the ice cover is, on average over the duration of the experiment, releasing 0.08 mol of CO_2 to the atmosphere. This is consistent with the reported measure of air-ice CO_2 fluxes from the lines 225-228.

The ability for the ice to act as a sink or source for atmospheric CO_2 is not only linked to the air-ice exchange of CO_2 , but also to where this CO_2 is going. In this manuscript we also calculate how much TCO_2 is exported from the ice to the underlying seawater and we confirmed that sea ice primarily export TCO_2 to the water column.

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.

We have added the necessary amendments to the new text, which now reads: "These ranges of air-ice CO₂ exchanges are of the same order of magnitude as fluxes reported on natural sea ice using the same chamber technique in the Arctic during the initial sea ice growth (from 4.2 to 9.9 mmol m⁻² d⁻¹ in Geilfus et al., 2013) and during the spring-summer transition (from -1.4 to -5.4 mmol m⁻² d⁻¹ in Geilfus et al., 2015). In Antarctica air-ice CO₂ fluxes were reported during the spring-summer transition from 1.9 to -5.2 mmol m⁻² d⁻¹ by Delille et al (2014), from 0.3 to -2.9 mmol m⁻² d⁻¹ (Geilfus et al., 2014) and from 0.5 to -4 mmol m⁻² d⁻¹ (Nomura et al., 2013)."

Discussion

Line 237. What do you mean with "very low"?

Very low was poor word choice, so we have revised the text to read: "During this experiment, neither organic matter nor biota were purposely introduced into the pool; the observed range of bulk ice microbial activity (5.7 x 10⁻⁹ on 14 January to 7.5 x 10⁻⁷ g C L⁻¹ h⁻¹ on 21 January) and algal Chl *a* (0.008 on 14 January to 0.002 µg L⁻¹ on 21 January) were too low to support any biological activity (Rysgaard et al., 2014). Therefore biological activity is unlikely to have played a role."

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⁻¹h⁻¹) and algal Chl a (μg L⁻¹) to the changes you measure in TCO₂ (in μmol kg⁻¹) to obtain a better idea of the biological impact of TCO₂. What is the biological activity and effect of TCO₂ in the underlying water, particularly the microbial activity could be significant? Did you measure microbial activity in the seawater before and after the experiment? We added the following info into the method section:

"Bulk ice samples for biological measurements were collected between 14 and 21 January. Filtered (0.2 µm) SERF seawater (FSW) was added at a ratio of 3 parts FSW to 1 part ice and the samples were left to melt in the dark. Chlorophyll a was determined on three occasions by filtering two aliquots of the melted ice sample onto GF/F filters (Whatmann brand) and extracting pigments in 10 ml of 90% acetone for 24 h. Fluorescence was measured before and after the addition of 5% HCl (Turner Designs Fluorometer) and Chl a concentration was calculated following Parsons et al. (1984). Measurements of bacterial production were done four times during the biological sampling period by incubating 6-10 ml subsamples of the ice-FSW solution with ³H-leucine (final concentration of 10 nM) for 3h at 0°C in darkness (Kirchmann, 2001). Half of the samples were spiked with trichloroacetic acid (TCA, final concentration 5%) as controls prior to the incubation, while the remaining active subsamples were fixed with TCA (final concentration 5%) after incubation. Following the incubation, vials were placed in 80°C water for 15 minutes (Garneau et al., 2006) before filtration through 0.2 µm cellulose acetate membranes (Whatmann brand) and rinsing with 5% TCA and 95% ethanol. Filters were dried and dissolved in scintillation vials by adding 1 ml ethyl acetate, and radioactivity was measured on a liquid scintillation counter after an extraction period of 24 h. Bacterial production was calculated using the equations of Kirchman (1993) and a conversion factor of 1.5 kg C mol⁻¹ (Ducklow et al., 2003)." As shown in the previous comments, the level on bacterial production or Chl a were too low to have any impact of the TCO₂ during the experiment.

Line 252. Same as earlier about "dissolution of ikaite in water column and sea ice". See previous responses regarding your comments on L 127-141-208.

Lines 260-261. This statement is not valid as is. Please change to: "Assuming no biological effect, ikaite precipitation/dissolution and gas exchange (TCO₂), TA and TCO₂ are considered conservative with salinity. Thus we can calculate..."

Thanks for the correction.

Line 257. Repetition: a ratio 2:1.

We want to keep that repetition as it is essential that the reader understand the concept of ratio TA: TCO_2 of 2:1 to understand how we estimated the precipitation/dissolution of ikaite within sea ice and the underlying seawater.

Line 269. Add "assumed to be only due to..." after "...this experiment are..". Thanks for the correction.

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"?

We agree that this was unclear so we have revised the text to read: "The difference between $TA_{(sample)}^*$ and the observed TA is only due to the precipitation or dissolution of ikaite crystals. In case of ikaite precipitation (*i.e.* $TA_{(sample)}^* > TA_{(sample)}$), 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.* $TA_{(sample)}^* < TA_{(sample)}$), indicates ikaite dissolution."

Lines 277-278. "ikaite is precipitated and CO2 released from the ice to the atmosphere;

both processes reduce $TA_{\text{(ice)}}$ and $TCO_{2\text{(ice)}}$." This statement should be changed since $TA_{\text{(ice)}}$ is not reduced by CO_2 exchange.

This statement has been changed, now the manuscript reads: "The higher $TA_{(ice)}^*$ and $TCO_{2(ice)}^*$ compared to the averaged $TA_{(ice)}$ and $TCO_{2(ice)}$ (Fig. 7a, b) is expected as ikaite is precipitated (Rysgaard et al., 2014) and CO_2 released from the ice to the atmosphere (Fig. 5, 6); processes reducing $TA_{(ice)}$ and $TCO_{2(ice)}$."

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.

According to our method used to measure $TA_{(ice)}$ and estimate $TA_{(ice)}^*$: the difference between the $TA_{(ice)}^*$ (TA expected from the salinity changes) and the observed TA is assumed to only be due to the precipitation/dissolution of ikaite crystals. In case of ikaite precipitation (*i.e.* $TA_{(ice)}^* > TA_{(ice)}$), 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.* $TA_{(ice)}^* < TA_{(ice)}$), indicates ikaite dissolution.

Therefore, the warmer temperature observed in the ice and the negative difference between $TA^*_{(ice)}$ and $TA_{(ice)}$ indicates the ikaite dissolution. However, we are also considering the possibility for an export of ikaite from the ice to the underlying seawater to happen as the brine volume increased and the vertical permeability of the sea ice increased at that time of the experiment. This is already mentioned in the manuscript. We added the reference to the sea ice brine volume content in the ice.

Line 296. What do you mean with "good agreement"? Please specify.

This statement has been changed, now the manuscript read: "Both ikaite measurements are of the same order of magnitude however the average (22 µmol kg⁻¹) and maximum (100 µmol kg⁻¹) of direct observations presented by Rysgaard et al. (2014) were lower than our estimated average (40 µmol kg⁻¹) and maximum of up to 167 µmol kg⁻¹ over this whole experiment. Deviations are likely due to methodological differences. Here, sea ice samples were melted to subsample for TA and TCO₂, 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."

Lines 298-300. This sentence could perhaps be moved to the method description.

In the method section, we already have this sentence: "The plastic bag was sealed immediately and excess air was gently removed through the valve using a vacuum pump. The bagged sea ice samples were then melted in the dark at 4°C to minimize the dissolution of calcium carbonate precipitates (meltwater temperature never rose significantly above 0°C)." This implies what is stated on lines 298-300 of the original manuscript.

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...".

We changed the text accordingly.

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, TCO₂) evolution of the sea ice and underlying water (upper 10m) and the sea ice processes such as precipitation and dissolution of ikaite, affecting TA, TCO₂ 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.

We added the reference.

Line 319. Please explain how you obtained the 66 μmol kg⁻¹ maximum concentration.

The 66 μ mol kg⁻¹ comes, as stated in the manuscript, from half the difference between $TA_{(sw)}^*$ and $TA_{(sw)}$. It increases from 0 at the first day (as $TA_{(sw)}^* = TA_{(sw)}$) to a maximum of 66 μ mol kg⁻¹ the last day, as shown in the figure 8a and mentioned in the manuscript.

Line 320. Change to "17-days long".

We changed it into "During this experiment"

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)}"?

We changed the text as followed:

"The $pCO_{2(sw)}$ is highly correlated with the seawater temperature (Fig. 2) with a rapid decrease of $pCO_{2(sw)}$ during the first days of the experiment (13 to 15 January) and a relative constant $pCO_{2(sw)}$ until 27 January. However, on 26 January, the heat was turned back on affecting the seawater temperature on the same day (Fig. 2) while the impact of increasing temperature on the $pCO_{2(sw)}$ appeared one day later (Fig. 3d). We normalized the $pCO_{2(sw)}$ to a temperature of -1°C (after Copin-Montegut (1988), noted as $npCO_{2(sw)}$, blue line on Fig. 3d). The $npCO_{2(sw)}$, does not show major variations during sea ice growth with values around 380 μ atm. However, once the heat is turned on and the seawater temperature increased (on 26 January), $npCO_{2(sw)}$ decreased from 383 μ atm to 365 μ atm, while $pCO_{2(sw)}$ did not change in response to increased seawater temperatures until 27 January, suggesting that a process other than temperature change affected the $pCO_{2(sw)}$.

According to equation 1, the dissolution of calcium carbonate has the potential to reduce $pCO_{2(sw)}$. Therefore, during sea ice growth and the associated release of salt, TA, TCO_2 and ikaite crystals to the underlying seawater, ikaite dissolution within the seawater could be responsible for maintaining stable $pCO_{2(sw)}$ values while seawater salinity, $TA_{(sw)}$ and $TCO_{2(sw)}$ are increasing. Once the seawater temperature increased (26 January), sea ice melt likely released ikaite crystals to the underlying seawater (Fig. 2, 8a) along with brine and meltwater, a process that would continuously export ikaite from the sea ice as the volume interacting with the seawater via percolation or convection increased. The dissolution of these crystals likely contributed to keeping the $pCO_{2(sw)}$ low and counterbalancing the effect of increased temperature. We argued that once all the ikaite crystals are dissolved, the increase seawater temperature increased the $pCO_{2(sw)}$ simultaneously with the $npCO_{2(sw)}$ (27 January, Figure 3)."

Lines 355-357. Compare with brine volume fraction.

We added the figure panel of the brine volume content in the ice during the whole experiment to Figure 2. This figure is explained in the "sea ice and seawater physical conditions" conditions and show that the ice cover is mainly "permeable", according to the permeability threshold of 5% brine volume from Golden et al (2007). The only 2 occasions where the ice was "impermeable" was on 23 January, when the ice cooled down due to the snow removal from its surface and during the early sea ice growth. This suggests that brine and/or seawater could freely circulate within the ice cover, along with ikaite crystals. Therefore I don't think we need to add something in the text as we suggest 1) the ikaite rejection along with the brine and 2) the increase of the brine connectivity could facilitate the exchange sea ice-seawater.

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 ikaite (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 $TA_{\text{(ice)}}^*$ and $TA_{\text{(ice)}}^*$, 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?

We add the data used for the calculation. The exact values are presented earlier in the manuscript (see next comment). Data presented in the fig 8a are half the difference between $TA_{(sw)}^*$ and $TA_{(sw)}$. Regarding the estimation of ikaite remaining in the ice. We

changed the section 5.3 as followed:

"We estimated the amount of ikaite precipitated and dissolved within sea ice and seawater based on the sea ice (and seawater) volume (in m³), the sea ice and seawater density, the concentration of ikaite precipitated and dissolved within the ice cover (Fig. 7c), and the concentration of ikaite dissolved in the water column (Fig. 8a). Within the ice cover, the amount of ikaite precipitated-dissolved ranged from -0.7 to 1.97 mol (Fig 8b, Table 2), with a maximum just after the snow was cleared on 23 January. In the underlying seawater, the amount of ikaite dissolved in the pool increased from 0.47 mol on the first day of the experiment to 11.5 mol on 25 January when sea ice growth ceased. Once the ice started to melt the amount of dissolved ikaite increased up to 20.9 (28 Jan) and 26.7 mol (29 January, Table 2). The estimation of ikaite dissolution in the pool is significantly higher than the estimated amount of ikaite precipitated (and potentially exported) within the ice cover, especially during sea ice melt. Within the ice cover, the ikaite values presented here represent a snapshot of the ikaite content in the ice at the time of sampling. In the underlying seawater, ikaite dissolution increased TA_(sw) cumulatively over time.

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 m³) 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. Once the ice started to melt, the increased ikaite dissolution from 11.5 mol to 20.9 mol (28 January) and to 26.7 mol (29 January) suggests that about the same amount of ikaite is dissolved during the sea ice growth as during the first two days of the sea ice melt. The amount of ikaite dissolved in the water column after melt commenced continued to increase cumulatively, suggesting that ikaite is continuously exported to the underlying seawater as increased sea ice temperatures permit more of the volume to communicate with the underlying seawater. Therefore, we can assume than more than half of the amount of ikaite precipitated within the ice remained in the ice cover before ice melt began."

Lines 376-377. Please provide numbers of your parameters such as volume, density, and pool dimensions used in the calculations.

The size and volume of the pool is given in the section "site description", the volume of seawater-sea ice is fixed and started with a seawater depth of 2.6 m (as described in the site description section). Once the ice started to grow, the seawater depth decreases by the volume of sea ice growth. Sea ice and seawater density are calculated based on temperature and salinity using long-standing equations found in the literature.

Line 380. Was the CO₂ fluxes measured on snow and on ice from removed snow? See previous respond regarding the same question.

Line 388. Add "(up to 99% as brine)"...

We changed the text accordingly.

Line 396-398. What was the wind speed during the study? It would be interesting to know since CO₂ fluxes are highly dependent on wind speed.

See previous respond regarding the same question.

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.

The manuscript now reads: "However, any understanding of the effect of ikaite precipitation in sea ice on ocean acidification is still in its infancy (e.g. Fransson et al., 2013)."

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

We made a mistake and change the manuscript as followed: "During ice growth, sea ice brine rejection appears to increase both pH (from 8.00 to 8.06) and $\Omega_{aragonite}$ (from 1.28 to 1.65) of the underlying seawater, offsetting the effect of decreased temperature. A slight increase of $\Omega_{aragonite}$ was predicted due to increased salinity and a proportional increase of TA and TCO_2 as depicted in $\Omega_{aragonite}$." However, the effect of ikaite rejection and subsequent changes in TA strongly enhance the increase of $\Omega_{aragonite}$."

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.

We added the reference Chierici et al., (2011) and the change the text as followed: "Since the discovery of ikaite precipitation in sea ice (Dieckmann et al., 2008), research on its impact on the carbonate system of the underlying seawater has been ongoing. Depending on the timing and location of this precipitation within sea ice, the impact for the atmosphere and the water column in terms of CO_2 transport can be significantly different (Delille et al., 2014). Dissolution of ikaite within melting sea ice in the spring and export of this related high $TA:TCO_2$ ratio meltwater from the ice to the water column will decrease the pCO_2 , increase pH and $\Omega_{aragonite}$ of the surface layer

seawater. Accordingly, during sea ice melt, an increase of $\Omega_{aragonite}$ in the surface water in the Arctic was observed (Chierici et al., 2011, Fransson et al., 2013, Bates et al., 2014). However, it was difficult to ascribe this increase to the legacy of excess TA in sea ice, ikaite dissolution or primary production."

Conclusion

Line 448. "17-day".

We changed the first sentence of the conclusions. Now it reads: "We quantified the evolution of inorganic carbon dynamics from initial sea ice formation from open water to its melt in a sea ice-seawater mesocosm pool from 11 to 29 January 2013."

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

We made the requested change.

Tables

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

We added the conditions at the end of the sea ice growth and at the end of the experiment. The rest of the dataset is shown in the figures in the manuscript. We prefer these data are contained in figures because they provide more immediately meaningful information than tables can provide.

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.

We added the variables asked and changed the header.

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.

We would like to keep the figure 2 as it is even if yes a small part of the data presented in this figure were presented in the manuscript of Rysgaard et al (2014). We made some changes in the plot 2d to increase the visibility and made the plot clearer.

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.

With the changes made in the figure 2D, we can easily see the S at the beginning and the end of the experiment. We also added these data in the table 1, as asked by the reviewer 1. The salinity does not return to the start salinity, simply because we stopped the experiment while we still had ice in the pool. Therefore a significant amount of freshwater was still "unavailable" to dilute the pool back to the start salinity.

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

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.

Fig. 3 is first mentioned when we are presenting the $TA_{(sw)}$, $TCO_{2(sw)}$ and pCO_2 data in the results section. Then, in the discussion, when we are introducing $TA_{(sw)}^*$ and $TCO_{2(sw)}^*$ and discussing it, we are referring again to the figure 3 as both are shown there. It doesn't make sense to introduce $TA_{(sw)}^*$ and $TCO_{2(sw)}^*$ in the results section as the reader won't understand at that stage why we are introducing these variables. Therefore we will keep the figure 3 and the text as it is now.

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.

The black line on each panel represent the concentration measured during the experiment (TA, TCO_2 , pCO_2) and the figure caption reads: "the seawater pCO_2 (μ atm) measured in situ (black) and corrected to a constant temperature of -1°C (blue)." And "In panels (**a**) and (**b**) the black line is the average over the three depths while the dotted red line is the expected concentrations according to the variation of salinity observed and calculated from the mean values of the three depths." Therefore, the black line is defined in both the figure caption and the figure itself.

As shown here, the blue line is defined, no change needed.

 TA^* and TCO_2^* are also defined as the figure caption reads: "the dotted red line is the expected concentrations according to the variation of salinity observed and calculated from the mean values of the three depths." However, to please the reviewer, we added some information to the end of the sentence that now reads: "In panels (a) and (b) the black line is the average over the three depths while the dotted red line is the expected concentrations according to the variation of salinity observed and calculated from the mean values of the three depths $(TA_{(sw)}^*)$ and $TCO_{2(sw)}^*$, respectively)."

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?

See our responses earlier in the review on your comment on L336.

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 .

We add the text as suggested.

Figure 6. Define the green dotted line in caption.

We added the following text to the figure caption: A linear regression is shown in green for the ice samples (a) and blue for the seawater samples (b).

Figures 7. The figure 7b of changes in TCO₂ includes CO₂ flux but it does not say in the text.

The figure 7b is the evolution of $TCO_{2(ice)}$ and the expected $TCO_{2(ice)}$ according to the salinity changes. Changes of TCO_2 in sea ice are not only linked to the CO_2 (gas) exchanges, but also ikaite precipitation-dissolution and exchange of TCO_2 between sea ice and the underlying seawater.

Figure 7c does not show "half the TA" as I can see. Please explain or I missed something. We doubled check the calculation and yes, the fig 7c does show half the difference between $TA_{(ice)}^*$ and $TA_{(ice)}$.

Figure 9. What explains the large difference on the 24-25 January between ice-water exchange of CO₂ and total TCO₂ loss from sea ice?

The maximum amount of ikaite precipitated in the ice happen just after the snow clearing (after 23 January) so, the big difference on the 24-25 January are due to more TCO_2 trapped under the form on ikaite than before.

Added references:

Anderson, L.G., E. Falck., E. P. Jones., S. Jutterström and J. H. Swift. 2014 Enhanced uptake of atmospheric CO₂ 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,