

## ***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**

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### **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> bond in ikaite crystals (1 mol of ikaite

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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.

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.

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.

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Furthermore, the results showing that pCO<sub>2</sub> 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 CO<sub>2</sub> exchange processes.

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.

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.

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

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

## 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.

L19: The specific percentage of the fraction of ikaite should be derived as detailed in

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the comments to section 5.3.

### 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 CO<sub>2</sub> exchange. Nevertheless, the authors need to state more detailedly why it is important to understand and quantify the fate of ikaite in the sea ice, specifically in the second last paragraph (L81-88).

L40-46: "Release of CO<sub>2</sub> (from sea ice to the atmosphere) .. from open water." → Please be precise whether you mean air-sea-ice fluxes or air-sea fluxes.

L68: "...in the Arctic,": this should be also true for the Antarctic.

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.

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

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

### 3. Site description, sampling and analysis

L151-153: The 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  $(\text{TA}_{\text{ice}} - \text{TA}_{\text{ice}})/2$ , and only compare it to the concentrations estimated from microscope inspection as given in 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 tem-

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perature field the pool seems well mixed. How do you explain this?

#### 4.2 Carbonate system

It is not really introduced why you look at nTA and nTCO<sub>2</sub>. To facilitate reading and understanding you should explain this a little more detailed.

L191-192: values given for seawater concentrations of TA and TCO<sub>2</sub> at t=0 are different from the values given in Table 1.

L200: Additionally provide concentrations of nTA and nTCO<sub>2</sub> at t=0.

#### 5.1. Key processes affecting the carbonate system

L240: “up to 350 umol/kg”, however, in Fig. 7c only up to 100 umol/kg for the same dataset.

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

L260: TCO<sub>2</sub> is not conservative with salinity due to potential gas phase of CO<sub>2</sub>\* (Eq. 2)

L271: Here the explanation of positive and negative signs is wrong: When the difference  $(TA_{ice}^* - TA_{ice})/2$  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  $(TA_{sw}^* - TA_{sw})/(-2)$  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.

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.

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#### 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.

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 TA\*2 being exported to the seawater rather than the ikaite concentration stored in the sea ice matrix.

L309: “..negative difference .. indicating that ikaite dissolved in the ice or were exported to the water column.”: A negative difference between TA<sub>ice</sub>\* and TA<sub>ice</sub> does not necessarily mean that ikaite is exported, but it definitively implies that it is dissolved in brine. See comment to L271.

#### 5.2.2. Water column

L324: Are the values of TCO<sub>2sw</sub>- TCO<sub>2sw</sub>\* here similar to nTCO<sub>2</sub> such as for TA?

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

L329-351: Given that the dissolution of ikaite is a fast process in the order of seconds to minutes, a time delay in pCO<sub>2</sub> rise of 1 day would suggest that during this day ikaite release to the sea-water must have been continuously large. Please discuss this more precisely.

#### 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.

L366-367: Since  $(TA_{ice}^* - TA_{ice})/2$  could be ikaite crystals in sea ice and/or exported

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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.

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

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

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

L389: “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?

#### 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.

Generally the data suggests that with or without ikaite export to the seawater the sea-

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water 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  $\Omega_{\text{aragonite}}^*$ .

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?

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.

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 CO<sub>2</sub> concentrations, global warming and associated Arctic sea-ice decay on  $\Omega_{\text{aragonite}}$  projected by models.

#### 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 CO<sub>2</sub> 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.

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### III. Technical comments in Figures and Tables

Caption Fig. 1.

Give year of experiment.

Fig. 2.

Put panel labels in brackets.

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

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

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

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 salinity in panel (d)

Last sentence, final dot missing.

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.

Caption Fig. 4.

Use lower case letters for panel description.

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Caption Fig. 6.

Use lower case letters for panel description.

Caption Fig. 7.

Use lower case letters for panel description.

One space after the first TA(ice)

Fig. 8.

y-axis labels: "Ikaite" This is too imprecise, see comments to L271.

Caption Fig. 8.

Use lower case letters for panel description.

"..amount of mol of ikaite.." mol is the unit: '..mass of ikaite in mol..'

Fig. 9.

A flux cannot have the unit mol.

"Total TCO<sub>2</sub> lost by the sea ice" This is the mass of TCO<sub>2</sub> of ice cover assuming the absence of ikaite.

"Air-ice CO<sub>2</sub> fluxes" cannot have units of mol

Caption Fig. 9.

A flux cannot have the unit mol.

"Total TCO<sub>2</sub> exchanges by the ice cover" This is the mass of TCO<sub>2</sub> of ice cover assuming the absence of ikaite and CO<sub>2</sub>(g) in bubbles.

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

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of January 2013”.

Table 1.

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

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.

IV. Technical comments

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

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

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

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

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

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

L47: comma missing after “formation”

L50: please give reference.

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

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

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L57: “..while TCO<sub>2</sub> is..”: Be more precise: e.g. ‘..while TCO<sub>2</sub> in brine is..’

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

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

L60: “[H-]”: Spelling mistake: [H+]

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

L67: “..fluxes..”: Be more precise: e.g. ‘..air-sea fluxes..’

L67: “..seawater and incorporated..”: Grammar mistake: e.g. ‘..seawater and its contribution to intermediate and deep-water formation..’

L77: “..melting sea ice promotes..”: Be more precise: e.g. ‘..surface warming and melting sea ice promote..’

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

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

L167: “..15 cm on 18 January..”: mistake: ‘..15 cm until 18 January..’

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..’

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.

L201: “..ice started the melt..”: mistake: ‘..ice started to melt..’

L225: “..suggest..”: this is rather weak, better to write that the measurements ‘show’ this.

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

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L264-265: in the equation 'sample' means 'sw or ice'. It would facilitate reading if you would write for each component a separate equation. It is better to not put "sw" and "ice" within brackets, while the time variable should be written not in subscript and in brackets.

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

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

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

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

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

L317: "..half the difference between TA(sw)\* and TA(sw) .." mistake: '..half the difference between TAsw and TAsw\*..'

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

L322: ".. TA(sw)\* and TA(sw) ..": see comment L317

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

L346: Changes in pCO<sub>2</sub> cannot not understood from equation 3.

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

L379: Fig. 9 not 8

L379: "maximum outgassing": logical mistake: '..maximum loss of TCO<sub>2</sub>..'

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

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tion from the total..'

L392: "Fig 3c" → Fig. 3B

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

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

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

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

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

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

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

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

L457: "up to 66.." → '..up to 128..'

L462: Please give more references

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

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

#### References

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