

***Interactive comment on “Ikaite crystals in melting sea ice – implications for pCO<sub>2</sub> and pH levels in Arctic surface waters” by S. Rysgaard et al.***

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General comments

This article presents biogeochemical data from a single ice floe in decay, drifting in the Arctic Ocean in the summer, with a view to estimating the impact of its decay (melting) on the air-sea CO<sub>2</sub> exchange potential. This is an actively investigated field of research at present, relevant to sea ice scientists, cold region biogeochemists, and modellers.

The authors found that the concentration of total alkalinity (TA) of the bulk ice was twice that of total dissolved inorganic carbon (TCO<sub>2</sub>). As a result, they calculated that mixing of melt water with this chemical composition in the surface oceanic mixed layer will depress the pCO<sub>2</sub> in the mixed layer, which can lead to a flux of atmospheric CO<sub>2</sub> into the surface ocean an order of magnitude higher than the primary production rate in the same ice floe. This is a convincing argument, but the analysis of the bulk ice TA and TCO<sub>2</sub> is less so. The authors propose a link between bulk ice TA/TCO<sub>2</sub> concentrations and the depression of the pCO<sub>2</sub> in the mixed layer during melting via the presence and cycling of ikaite in sea ice, which they extracted, photographed, identified, and experimented on. This is quite possible, but their analysis needs refinement for clarity; some number-crunching will also help check its plausibility (see, comments 2, 3, 7, 8, 9, and 11). Below, I give some detailed points that may be of help.

**We acknowledge the positive and constructive comments by this reviewer and answer them in details below.**

Specific comments

1. P1016, L17-18: The work of Geilfus et al. (2012) (J Geophys Res, 117, C00G10, doi: 10.1029/2011JC007118) and Loose and Schlosser (2011) (J. Geophys. Res., 116, C11019, doi: 10.1029/2010JC006509), is relevant and worth mentioning here.

**We have added these recent references as suggested.**

2. P1017, L1-4: This statement is confusing. It is not the concentrations but the concentration changes relative to a reference concentration, such as the concentration in surface seawater, which can bear the stoichiometric fingerprint of a particular geochemical process. As the authors state in the preceding statement, more efficient loss of TCO<sub>2</sub> than TA from sea ice (by what mechanism?) can give rise to molar TA and TCO<sub>2</sub> ratios of 2. Therefore, a TA:TCO<sub>2</sub> = 2 is not exclusively diagnostic of the presence of CaCO<sub>3</sub> minerals in the sea ice. On the other hand, if the ratio of the concentration changes of these parameters in sea ice relative to surface seawater were 2, i.e., if  $\Delta TA:\Delta TCO_2 = 2$ , that would be a more definitive diagnostic of the presence of CaCO<sub>3</sub> minerals. 3. P1017, L12-13: CaCO<sub>3</sub> is also a store for TCO<sub>2</sub> upon dissolution.

**Indeed we do argue on the basis of a  $\Delta TA:\Delta TCO_2 = 2$ ; Assuming that the sea-ice is formed from normal sea-water in equilibrium and exhibiting a  $TA:TCO_2 = 1$  (An assumption that seem perfectly fair to most). Our point is that when  $TA:TCO_2 = 2$  in sea ice it is highly unlikely a signal from the water column. Also not from primary productivity, which is low – see later parts of manuscript. Most likely explanation is  $CaCO_3$  produced in sea ice. We have never observed  $TA:TCO_2 = 2$  conditions in the water column – only slightly above 1. The above sentence refers the ratio being relative to the water column. Thus, we would like to keep things as written.**

4. P1017, L19: ‘ikaite single crystals’ should be corrected to ‘single ikaite crystals’.

**Suggestion followed.**

5. P1018, Methods: How many ice cores were processed for what parameters? I understand from Fig. 2 that bulk sea ice temperature, salinity, and brine volume were derived from 10 ice cores, TA, TCO<sub>2</sub>, and Chl were obtained from 3 ice cores, and, from P1020, L4-5, ikaite crystal microscopy and distribution with depth in the ice were conducted on 1 core on 29/6. Mineral phase identification by X-ray diffraction was performed on material extracted from the reserved core stored at -18C and processed elsewhere. Is this what happened? This information needs to be clearly stated here.

**Yes, this is what we did. We have added more details to this section.**

6. P1019, L25: Artificial seawater? Wa must be the weight of deionized water.

**Thanks. Correction made.**

7. P1021, L25-26: Which TA and TCO<sub>2</sub> concentrations are averaged here for the detection of a temporal trend? For example, averaging the depth profile of each parameter in each of the 3 ice cores (i.e., as understood from Fig. 2) would justify the statement of a lack of temporal trend.

**TA and TCO<sub>2</sub> conditions in individual cores were compared and showed to temporal trend. Average condition of each date is shown in Table 2. That’s why we have calculated the mean profiles and the standard deviation as shown in Fig. 2. We have made a reference to Table 2.**

8. P1022, L27 – P1023, L1-2: See comment 2 above. I can think of TCO<sub>2</sub> loss from brine by CO<sub>2</sub> degassing during the permeable early stages of sea ice formation and growth effectively reducing the TCO<sub>2</sub> without changing TA, leading to  $TA:TCO_2 \gg 1$  subsequently in the brine (note,  $\Delta TA:\Delta TCO_2 = 0$  in this case).

**The fact is that we observe a high  $TA:TCO_2$  ratio in the ice compared with the water. It cannot be explained by high silicate or phosphate concentrations – we checked that. The most likely explanation is that it is caused by calcium carbonates. What else could it be? Primary production is low here. We would like to keep text as it is.**

For less controversy, I suggest conversion of the bulk sea ice concentrations on a per unit brine volume or brine mass basis, salinity normalization after estimating brine salinities from ice temperature, and examination of the salinity normalized concentrations relative to surface seawater concentrations in Table 1. Alternatively, a back-of-the-envelope calculation is necessary to examine how realistic the quantity of ikaite is, which is required to dissolve, to raise the background TA to TCO<sub>2</sub> ratio (before dissolution) in the sea ice to the observed values.

**Normalizing into brine concentrations will add to the uncertainty due to the calculated brine volume and assumptions of how much of the TA and TCO<sub>2</sub> is within the brine. However, we can include a simple calculation on the quantity of ikaite, which is required to dissolve to raise the background TA to TCO<sub>2</sub> ratio. Basically, the TA:TCO<sub>2</sub> ratio in sea water do not vary much around 1. If we assume for simplicity that sea ice is formed from water with a TA:TCO<sub>2</sub> ratio of 1, the excess alkalinity caused by CaCO<sub>3</sub> is the difference between TA and TCO<sub>2</sub> in sea ice, which ranges from 162.1 to 241.5  $\mu\text{mol/kg}$  melted sea ice (See Table 1). More on this matter has been included in the revision.**

9. P1025, L1: A more detailed description of the calculation of the air-sea CO<sub>2</sub> flux from the 0.2 cm/week melting rate of sea ice would be most helpful to all readers here. Also, could it be just the freshening of the mixed layer that causes the pCO<sub>2</sub> depression? For this type of comparison, it would be useful to present the same calculation with a bulk sea ice TA:TCO<sub>2</sub> ratio of 1, i.e., the same as surface seawater.

**We have included more on this calculation as requested:**

**Assuming that all ikaite crystals dissolve in the sea ice or in the mixed layer, melting of 0.2 m sea ice with an average temperature (-1.1°C), salinity (3.9), TA (420  $\mu\text{mol kg}^{-1}$ ) and TCO<sub>2</sub> (221  $\mu\text{mol kg}^{-1}$ ) from Table 2, into a 20 m thick mixed layer with average water column characteristics of temperature (-0.2°C), salinity (32.6), TA (2203  $\mu\text{mol kg}^{-1}$ ) and TCO<sub>2</sub> (1987  $\mu\text{mol kg}^{-1}$ ) from Table 1, will result in a 3.8 ppm decrease in pCO<sub>2</sub> per week. This decrease is calculated from the resultant conditions in a 20 m mixed layer of temperature (-0.2°C), salinity (32.2), TA (2186  $\mu\text{mol kg}^{-1}$ ) and TCC2 (1970  $\mu\text{mol kg}^{-1}$ ) using the CO2SYS program – see materials and methods. Assuming no CaCO<sub>3</sub> crystals e.g. TA and TCO<sub>2</sub> concentrations are both 221  $\mu\text{mol kg}^{-1}$ , the resultant pCO<sub>2</sub> decrease will be 2.2 ppm per week. Based on average conditions during the field campaign (Table 1 & Table 2), this corresponds to an air-sea CO<sub>2</sub> uptake of 10.6 mmol m<sup>-2</sup> sea ice d<sup>-1</sup> or to 3.3 ton CO<sub>2</sub> km<sup>-2</sup> ice floe week<sup>-1</sup> (with CaCO<sub>3</sub>) and 4.9 mmol m<sup>-2</sup> sea ice d<sup>-1</sup> or 1.5 ton CO<sub>2</sub> km<sup>-2</sup> ice floe week<sup>-1</sup> (without CaCO<sub>3</sub>). It should be noted that we do not take wind mixing into account, but just consider the resultant CO<sub>2</sub> uptake of melting 0.2 m sea ice into a 20 m mixed layer after a return to initial pCO<sub>2</sub> conditions. An important finding here is that the presence of CaCO<sub>3</sub> in sea ice will double the air-sea flux as compared with melting of pure sea ice.**

10. P1025, L2-4: This is an important finding and should be stated in the Abstract.

**Thanks - we have included this in the Abstract**

11. P1025, L15-16: This is the first time that pH findings are mentioned without any prior mention in the Results and Discussion section. Some restructuring is needed here, presuming that the pH here was the pH calculated from TA and TCO<sub>2</sub> as explained in the Methods.

**We have added more on pCO<sub>2</sub> and pH in the discussion section. The background for the calculations is already provided in the Methods section.**