

Interactive comment on “Ikaite crystals in melting sea ice – implications for $\vec{p}CO_2$ 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 CO₂ 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 (TCO₂). As a result, they calculated that mixing of melt water with this chemical composition in the surface oceanic mixed layer will depress the pCO₂ in the mixed layer, which can lead to a flux of atmospheric CO₂ into

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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 TCO₂ is less so. The authors propose a link between bulk ice TA/TCO₂ concentrations and the depression of the pCO₂ 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.

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.
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 TCO₂ than TA from sea ice (by what mechanism?) can give rise to molar TA and TCO₂ ratios of 2. Therefore, a TA:TCO₂ = 2 is not exclusively diagnostic of the presence of CaCO₃ 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 CaCO₃ minerals.
3. P1017, L12-13: CaCO₃ is also a store for TCO₂ upon dissolution.
4. P1017, L19: ‘ikaite single crystals’ should be corrected to ‘single ikaite crystals’.
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, TCO₂, and Chl were obtained from 3 ice cores, and, from P1020, L4-5, ikaite crystal microscopy and distribution with depth in the ice were

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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 -18°C and processed elsewhere. Is this what happened? This information needs to be clearly stated here.

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

7. P1021, L25-26: Which TA and TCO₂ 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.

8. P1022, L27 – P1023, L1-2: See comment 2 above. I can think of TCO₂ loss from brine by CO₂ degassing during the permeable early stages of sea ice formation and growth effectively reducing the TCO₂ without changing TA, leading to TA:TCO₂ » 1 subsequently in the brine (note, $\Delta TA:\Delta TCO_2 = 0$ in this case). 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 TCO₂ ratio (before dissolution) in the sea ice to the observed values.

9. P1025, L1: A more detailed description of the calculation of the air-sea CO₂ 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 pCO₂ depression? For this type of comparison, it would be useful to present the same calculation with a bulk sea ice TA:TCO₂ ratio of 1, i.e., the same as surface seawater.

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

11. P1025, L15-16: This is the first time that pH findings are mentioned without any

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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 TCO₂ as explained in the Methods.

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