Review on Geilfus et al. (2016)

Geilfus et al. (2016) discuss data from a most interesting sea ice formation (and a bit of melting) experiment performed at the Sea-ice Environmental Research Facility (SERF) site from 13 to 30 January 2013 at the University of Manitoba, Winnipeg, Canada. Several articles have been published already using data from this experiment (Hare et al., 2013; Rysgaard et al., 2014, Else et al., 2015). Geilfus and colleagues use measurements of total alkalinity (TA), dissolved inorganic carbon (TCO$_2$ total CO$_2$), salinity, temperature, and a few other measurements to estimate the carbon budgets in sea ice and the underlying (artificial) sea water, especially the precipitation, transfer, and dissolution of ikaite. The conservative components of the marine carbonate system, namely TA and TCO$_2$, vary due to three processes: (1) Change in salinity due to formation and melting of sea ice, (2) precipitation or dissolution of calcium carbonate, here in the form of ikaite, and (3) gas-exchange. The size of the processes can be estimated in the following sequence: (1) can be quantified by scaling TA and TCO$_2$ using salinity (Eqs. 6 & 7). (2) can be estimated from changes of TA whereby the amount of calcium carbonate precipitation (and associated TCO$_2$ decrease) is equal to half of the TA reduction; the dissolution of calcium carbonate precipitation has the opposite effect. (3) The residual TCO$_2$ variation should be due to gas-exchange, which might be, however, difficult to estimate because of uncertainties when calculating small differences.

The data (TA, TCO$_2$, T, S) seem to be of high quality, however, a detailed discussion of the time evolution of measured and derived quantities is largely missing; often only wide ranges (’0.47 to 26.71 mol’) are given. A proper analysis of the data, estimates of uncertainties, identification of surprising or contradicting findings and a proper overall budget (How to close the TA budget?) for the whole pool is largely missing. Thus I cannot recommend publication.

General comments & suggestions:

Units: the partial pressure of CO$_2$, pCO$_2$, should be given in μatm (and not ppm; ppm refers to the mixing ratio of CO$_2$, xCO$_2$).

We have replaced “ppm” with “μatm” in each instance where the pCO$_2$ is discussed in the manuscript. Thanks.

Which program/package do you apply for carbonate system calculations? Which equilibrium values do you use? For a recent discussion compare Orr, Epitalon & Gattuso (2015).

We made our carbonate system calculations using the CO2sys_v2.1.xls spreadsheet [Pierrot et al., 2006] with the dissociation constants from Goyet and Dickson (1989) and others constants advocated by DOE (1994). We refer the reviewer to line 434 of the original manuscript. This information is still present in the revised version of the manuscript (L 502).

Specific comments & suggestions:

1. L 30: CO$_2$ emissions & oceanic uptake: Sabine et al., 2004 is an excellent paper, however, I suggest to cite more recent estimates (for example, IPCC 2013, or Global
Thanks for the suggestion. In the IPCC 2013 report, the introduction for Ocean biogeochemical changes, including Anthropogenic Ocean Acidification (Chap. 3, Observation Oceans, pages 291) read: “The oceans can store large amounts of CO₂. The reservoir of inorganic carbon in the ocean is roughly 50 times that of the atmosphere (Sabine et al., 2004)”. So we feel that the Sabine citation is original work and therefore the most relevant one to use in this instance.

2. L 31: 5-14% of the global ocean CO₂ uptake: based on which values? We’ve added the actual Tg C yr⁻¹ values to the text. The manuscript now reads: “The Arctic Ocean plays a key role in these processes, taking up from -66 to -199 Tg C year⁻¹, contributing 5-14% to the global ocean CO₂ uptake (Bates and Mathis, 2009), primarily through primary production and surface cooling (MacGilchrist et al., 2014).”

3. L 47-48: 'During the earliest stages of sea ice formation a small fraction of CO₂-supersaturated brine is expelled upward onto the ice surface promoting a release of CO₂ to the atmosphere (Geilfus et al., 2013a).’ It might be interesting to elaborate a bit more on 'expelling brine': When does it occur? How much brine can be expelled? Level of CO₂-supersaturation? Salinity of the expelled brine? Not much is known about upward brine expulsion. During sea ice formation, salty brine is expelled upward to the ice surface, but mainly downward into the ocean below. Often the formation of a brine skim is associated with the formation of frost flowers. A complete description of frost flowers formation during the same experiment as this study could be found in Galley et al (2015), Micrometeorological and thermal control of frost flower growth and decay on young sea ice, Arctic, vol 68, n°1, pp79-92. In Galley et al., (2015), salinity of the brine skim is up to 85. However higher salinity (100<) are reported in Geilfus et al (2013) or Barber et al (2014), doi:10.1002//2014JD021736. If we know about the salinity of the brine skim, we don’t know how much brine is expelled upward compared to what is expelled downward. However, the millimetric layer of brine skim reported at the surface of the ice and its ephemeral nature during the very onset of ice growth suggests that brine is mainly exported downward.

4. L 50: 'physical concentration’??? I suggest dropping 'physical’ We followed the suggestion, thanks.

5. L 60: Eq. (3) is an approximation to the TA definition given by Dickson (1981). In your experiment you use a special form of artificial seawater (ASW). It would be interesting how much total borate is in the ASW and how this is taken into account in the calculation of pCO₂ from TA and TCO₂. We have modified equation 3 to fix a mistake in the original version. As mentioned in the original manuscript (line 105), the composition of the ASW can be found in Rysgaard et al., (2014). The borate concentration in the ASW was not measured, and therefore we can’t discuss its influence on TA and TCO₂. Since 96.5% of the carbonate in seawater is accounted for by carbonate and bicarbonate (eq 3), while the rest is comprised of protons, hydroxides as well as borate, silicate and phosphate, we are confident in the assessment of TA presented here.
6. L 78-80 ’The mixing of meltwater, that is low in TCO$_2$, pCO$_2$, and high in TA due to brine dilution and ikaite dissolution, with seawater will increase TA and decrease the pCO$_2$ of the underlying seawater, enhancing the air-sea CO$_2$ fluxes (Rysgaard et al., 2007; 2009).’ pCO$_2$ of seawater is not a ‘substance’ that can be ‘mixed’: it is the equilibrium partial pressure of seawater and does not follow a linear mixing relationship. TCO$_2$ in meltwater is low compared to (artificial) seawater. Meltwater pCO$_2$ is low compared to atmospheric CO$_2$ because of low TCO$_2$ and not enough time for gas-exchange and equilibration with the atmosphere. I don’t know why meltwater TA should be higher than in ASW, because the ikaite was precipitated from ASW and then dissolves again.

When sea ice melts, it does not return it its original seawater composition. Melt water is different from seawater in many ways, including its TA. It is also substantially less saline, for example.

We changed the text in the manuscript as followed: “Melting sea ice stratifies surface seawater leading to decreased TA, TCO$_2$ and pCO$_2$, in the sea surface, enhancing air-sea CO$_2$ fluxes (Rysgaard et al., 2007; 2009).”

7. L 92-95 ‘We gain the ability to carefully track carbon parameters in the ice, in the atmosphere, and in the underlying seawater, while growing sea ice in a large enough volume of seawater, so that conditions closely mimic the natural system.’

However, there are various differences to the natural system; to name only a few: no leads for heat & gas-exchange, no horizontal ice movement impacting mixing of the underlying water, no ‘biology’ (which here simplifies the analysis of the carbonate system), the pressure build-up during the first part of the experiment. These differences should be mentioned and possible consequences for data interpretation should be discussed, especially with respect to comparison with the real world.

It is true that the SERF mesocosm does not exactly mimic the natural environment. The main goal of the SERF, and of this experiment is to have a simplified or constrained version of an ice-covered ocean. We aim in this way to gain an improved understanding of inorganic carbon dynamics from the initial sea ice growth to its melt. Once the physical-chemical processes are completely understood given the constrained SERF system, we will endeavour to add complexity to the SERF system in future experiments.

We have conducted this experiment in a way to purposefully exclude biology from the system to focus on the physical and chemical controls of the carbonate system. In particular, we aimed to i) determine what the main processes responsible for the changes in the inorganic carbon system during a event of sea ice growth and melt and ii) determine the exchanges between the ice, the underlying seawater and the atmosphere. We were mainly focused on the precipitation of ikaite within sea ice and its fate in the system in order to follow on and augment the results of previous and concurrent SERF experiments (e.g. Rysgaard et al., 2014). In this regard, SERF is a made useful by the “constraints” it imposes, for example its volume is fixed. This allows us to look at the potential exchange between the ice cover and the underlying seawater, which so far has proved too complicated to do in the natural environment.

8. L 104 ‘(ASW) formulated by dissolving large quantities’: formulated ⇒ generated, fabricated
We changed “formulated” to “made”.

9. L189-191 ‘TA and TCO$_2$ in seawater, noted as TA$_{sw}$ and TCO$_2$$_{sw}$, were sampled at the sea ice-seawater interface, 1.25 and 2.5 m depth. However, as the variations of TA and TCO$_2$ over the 3 depths are quite small (SD = 8.75 and 4.5 μmol kg$^{-1}$, respectively), we consider the average concentration.’ Do you really mean ‘variations’ of TA (with a standard deviation of 8.75 μmol kg$^{-1}$) or differences of TA between the 3 levels. If the latter: give mean difference ± SD.

The text now reads: “An ANOVA test over the 3 depths revealed that the means are not statistically different (p<0.01) so we consider the average concentration of the three depths in the following analysis.”

10. L 204-205’ The pCO$_2$$_{sw}$ then oscillated from 360 to 365 ppm during sea ice growth.’

⇒ ‘The pCO$_2$$_{sw}$ then varies from 360 to 365 μatm during sea ice growth.’

Thanks we have made the suggested change.

11. L 219 ‘minimums’ ⇒ minima

Thanks we have made the suggested change.

12. L224-228: Air-ice CO$_2$ fluxes: Although it’s good to know the ranges of CO$_2$-fluxes, in the current context it would be even more interesting the fluxes integrated over time.

We can’t integrate the fluxes over time as if more fluxes were measured, we will have more CO$_2$ released to the atmosphere, which doesn’t make sense. In the section 5.4, we averaged the fluxes over the whole experiment to estimate how much CO$_2$ is exchange between the ice and the atmosphere and in the table 2, the number of mole of CO$_2$ exchanges are indicated day by day.

13. L 238-240 ‘For this 2013 experiment, Rysgaard et al. (2014) discussed the precipitation of ikaite within the ice cover in detail, reporting high concentrations of ikaite (> 2000 μmol kg$^{-1}$) at the surface of the ice and ikaite precipitation up to 350 μmol kg$^{-1}$ in bulk sea ice.’ The concentrations, especially at the surface, are impressive. In the current context (TA and TCO$_2$ budgets for the whole pool) it would be good to obtain integrated values, at least rough estimates.

Ikaite precipitation concentrations have been integrated through the entire ice thickness and are provided in the original manuscript at the figure 7, as explained in the manuscript and in the figure caption. They are also reported in Rysgaard et al (2014).

14. L 244 please drop ‘Therefore’

Thanks we have made the suggested change

15. L 255 please drop ‘However,’

Thanks we have made the suggested change

16. L 256-257 Try to avoid repetition (‘2:1 ratio’): ‘As illustrated in Figure 6, an exchange of CO$_2$ does not affect TA while the precipitation- dissolution of ikaite affect TA and CO$_2$ in a ratio 2:1.’

We want to keep this precision to make sure that any reader (even those not familiar with this concept) will understand how and why we can estimate the precipitation-dissolution of ikaite through the changes in TA observed during this experiment.
17. A negative difference (i.e. $TA_{\text{sample}}^* < TA_{\text{sample}}$), implies that a lack of $TA$ is observed in the sample compared to what is expected based on the observed salinity changes (Fig. 2). This suggests that ikaite crystals were either dissolved or exported out of the sample (sea ice or seawater). A negative difference $= TA_{\text{sample}}^* - TA_{\text{sample}}$. I don’t understand the sentence: ‘negative difference’ means $TA_{\text{sample}}^* > TA_{\text{sample}}^*$, i.e. there is more TA in the sample than expected from salinity scaling; dissolution of ikaite (that was imported from somewhere else) would indeed increase TA; export of ikaite (that has been precipitated in the sample) would imply a decrease of sample TA.

This section was unclear. If $TA_{\text{sample}}^*$ is higher than $TA_{\text{sample}}$ (positive difference), it implies that a process is responsible for decreasing the $TA_{\text{sample}}$. In this case study, ikaite precipitation will decrease $TA_{\text{sample}}$. If the difference between $TA_{\text{sample}}^*$ and $TA_{\text{sample}}^*$ is negative, this suggests a process is responsible for increased $TA_{\text{sample}}$, in our case that will be the dissolution of ikaite crystals.

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

18. Both processes reduce and $TCO_2_{\text{ice}}^*$: outgassing of CO$_2$ (one of the two processes) does not change $TA_{\text{ice}}$, please rewrite sentence accordingly.

We changed the text as followed: “Greater $TA_{\text{ice}}^*$ and $TCO_2_{\text{ice}}^*$ compared to the averaged observed $TA_{\text{ice}}$ and $TCO_2_{\text{ice}}$ (Fig. 7a, b) are expected as ikaite is precipitated and CO$_2$ released from the ice to the atmosphere (Fig. 5, 6). Half the difference between $TA_{\text{ice}}^*$ and $TA_{\text{ice}}$ is a result of ikaite precipitation (Fig. 7c, black dots).”

19. Figure 7: (1) $TA_{\text{ice}}^*$ looks like you have continuous (or at least many) measurements. Please give some info.

As explained in the manuscript, $TA_{\text{ice}}^*$ is calculated based on the actual measurements. We changed the representation to make it easier to understand for each reader.

(2) I’m wondering how much of the difference between $TCO_2^*_{\text{ice}} - TCO_2^*_{\text{ice}}$ can be explained by ikaite precipitation alone and suggest to show this in another panel added to the Fig. 7.

We have a full discussion regarding the exchanges of $TCO_2$ between the ice cover, the underlying seawater and the atmosphere (Section 5.4). In this section we discuss how much CO$_2$ is released to the atmosphere and how much is exchanged with the underlying seawater when ikaite precipitation is subtracted from that calculation in the budget. We therefore refrain from adding additional panels to Figure 7.

20. Table 1: to display 4 values only, a table is not required, however, it would be good to extend the table and give values of $TA_{\text{sw}}^*$, $TCO_2^*_{\text{sw}}$, $TA_{\text{ice}}$, $TCO_2^*_{\text{ice}}$, $S_{\text{sw}}$, $T_{\text{sw}}$, $S_{\text{ice}}$, $T_{\text{ice}}$ for the time points at which you took $TA_{\text{ice}}$ samples.

The goal of the table 1, as explained in the original manuscript on line 247 and in the table caption is to show the initial seawater conditions at the beginning of the
The table now shows the pool conditions at t=0, (11 January), on 25 January (prior to the beginning of sea ice melt) and on 29 January (at the end of the experiment), as asked by reviewer 1. We refrain from extending the table as requested by this reviewer as that would be duplication of the data already found in the figures provided.

21. L 286-288 'The upward percolation of seawater observed from 15 to 18 January might complicate the picture of the effect of sea ice temperature on ikaite formation.' I bit more detailed description what happened here would be useful (or can it be found somewhere else, reference?).

On lines 166-171 (of the original manuscript) please note that we discuss this in greater detail:

“The air temperature at the beginning of the experiment ranged from -2°C to -26°C, which initiated rapid sea ice growth to 15 cm until 18 January (Fig. 2). During this initial sea ice growth, the sea ice was attached to the side of the pool resulting in the development of a hydrostatic pressure head that caused percolation of seawater at the freezing point upwards through the sea ice volume as the sea ice grew downwards. This resulted in repeated events of increased sea ice temperature from the bottom to the surface observed between 15 and 18 January (Fig. 2).”

15 to 18 January is the period with large differences $TA^*_\text{(ice)} - TA_{\text{(ice)}}$, $TCO_2^*_{\text{(ice)}} - TCO_2\text{(ice)}$, and large discrepancy between estimates of ikaite precipitation by Rysgaard et al. (2014) and the current investigation (Fig. 7). We discuss the differences between our methods and estimation by Rysgaard et al. (2014) in the original manuscript, from line 293 to line 305, with a specific focus on the beginning of the sea ice growth (15-18 January). Please also see the next comment for further precision.

22. L 293-297 'So, we compared the direct microscopy observations by averaging the amount of ikaite precipitated throughout the ice thickness for each sampling day from Rysgaard et al., (2014) (Fig. 7c, white dots) with our estimation of the amount of ikaite based on the difference between $TA^*_\text{(ice)}$ and $TA_{\text{(ice)}}$ (Fig. 7c, black dots) and found good agreement, with some small differences likely due to methodological differences.' Please give a correlation coefficient.

We have amended the text as follows to clarify what was initially meant by good agreement:

“We compared the direct microscopy observations by averaging the amount of ikaite precipitated throughout the ice thickness for each sampling day from Rysgaard et al., (2014) (Fig. 7c, white dots) with our estimation of the amount of ikaite based on the difference between $TA^*_\text{(ice)}$ and $TA_{\text{(ice)}}$ (Fig. 7c, black dots). 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 $TCO_2$, Ikaite crystals may have dissolved during melting, leading to an
underestimation of the total amount of ikaite precipitated in the ice. However, the difference between $TA_{(ice)}^{*}$ and $TA_{(ice)}$ provides an estimation of how much ikaite is precipitated in the ice cover, including those crystals potentially already exported to the underlying seawater. The method used by Rysgaard et al., (2014) avoid the bias of ikaite dissolution during sea ice melt with the caveat that crystals need to be large enough to be optically detected. If no crystals were observed, Rysgaard et al., (2014) assumed that no crystals were precipitated in the ice, though ikaite crystals could have been formed and then exported into the underlying seawater prior to microscopic observation of the sample, which may explain the difference observed between both methods during initial sea ice formation (15-18 January) when the ice was still very thin. In addition, the succession of upward percolation events could have facilitated the ikaite export from the ice cover to the underlying seawater. Estimations from both methods show similar concentrations when the ice (i) warmed due to snowfall (18-23 January) and (ii) cooled once the snow was removed (on 23 January). Once the ice started to melt (26 January), Rysgaard et al., (2014) reported a decrease in the ikaite precipitation while in this study we reported a negative difference between $TA_{(ice)}^{*}$ and $TA_{(ice)}$, possibly indicating that ikaite dissolved in the ice.”

23. L 298-301 'During melting of the sea ice samples, ikaite crystals may have dissolved, leading to an underestimation of the total amount of ikaite precipitate [precipitation] in the ice. This bias is avoided during direct microscopic observation of the crystals (Rysgaard et al., 2014) if crystals are large enough to allow optical detection.' Do you see a significant difference in the mean values of ikaite precipitation estimated by the two methods? See previous comment.

24. L 315-317 'According to equations 1 to 3, lower $TA_{(sw)}^{*}$ and $TCO_{2}^{*}_{(sw)}$ compared to $TA_{(sw)}$ and $TCO_{2}^{*}_{(sw)}$ (Fig. 3b, c) confirm the dissolution of ikaite in the underlying seawater.’ Eqs. (1)–(3) do not contain the quantities $TA_{(sw)}$ and $TCO_{2}^{*}_{(sw)}$. Please rewrite accordingly.

Now the manuscript reads: “Lower $TA_{(sw)}^{*}$ and $TCO_{2}^{*}_{(sw)}$ compared to $TA_{(sw)}$ and $TCO_{2}^{*}_{(sw)}$ (Fig. 3) confirm the dissolution of ikaite in the underlying seawater as the dissolution of ikaite crystals will decrease both TA and TCO$_2$ (equations 1 to 3).”

25. Fig. 8A does not make sense to me because you compare ikaite precipitation and dissolution using concentrations in one reservoir (sea ice) which shows large relative changes in volume and in another huge reservoir (seawater). I suggest to drop Fig. 8A.

Figure 8a shows ikaite precipitated in the ice cover (black diamonds) and the dissolution of ikaite in the underlying seawater (blue triangle), both expressed in $\mu$mol kg$^{-1}$. It may not be appropriate to show both the ikaite precipitation within sea ice and the ikaite dissolution within the water column in a single plot due to the difference in reservoir. Since ikaite precipitation within sea ice is already illustrated in the figure 7, we decided to remove this information from figure 8a, but we choose to keep the figure because it is the only plot illustrating ikaite dissolution in the water column.

26. According to Fig. 8B much more ikaite has been dissolved in seawater than
precipitated in sea ice: What’s your explanation?

We add some precision about this in the manuscript in the section 5.3: “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.”

27. L 338-340 ‘Using the equation from Copin-Montégut (1988), we normalized the pCO_{2(sw)} to a temperature of -1°C (noted as npCO_{2(sw)}, blue line on Fig. 3d).’ No motivation is given for this ‘normalization’ and I don’t see why to do so. Once again: pCO_{2(sw)} is not a substance. The gas-exchange depends on the actual pCO_{2(sw)} (strongly dependent on temperature!). The lines 334-338 of the original manuscript read: “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 on the pCO_{2(sw)} only appeared one day later (Fig. 3d).” This led us to normalize the data because as you say and as it’s mentioned above, the pCO_{2} is strongly dependent on the temperature. So the question we want to answer is why, when we heated the pool, the in-situ pCO_{2} didn’t change. To answer that question, we normalized the pCO_{2} to a temperature of -1°C to remove the effect of temperature.

28. L 361 ‘Within the water column, 0.47 to 26.71 mol of ikaite dissolved.’ Please give a proper discussion of the evolution in time (Fig. 8B) and how this evolution is related to various processes. What might have caused the drop of ikaite dissolution in seawater around 20 January? How to close the TA budget? Compare also Fig. 3 We changed section 5.3 “Ikaite export from the ice cover to the water column”, to include a discussion about the evolution of the amount of ikaite dissolved in the water column and some possible conclusions. In the first submitted manuscript, we did not attempt to do a TA budget… We did try to close a TCO_{2} budget, including the ikaite precipitation-dissolution, air-ice gas exchanges and ice-seawater TCO_{2} exchange. Unfortunately, as stated in the manuscript we could not close the budget and uncertainty in the methods were too big (see your comment 30). This conclusion will be the same in an attempt to do a TA budget.

29. L 375-377 ‘To estimate the amount of TCO_{2} exchanged during this experiment, we convert mol kg^{-1} to moles, using the sea ice (and seawater) thickness (in meter) and density (in kg/m³) and the pool dimension (in meter).’ This is not just a conversion of units! Instead of concentrations you consider reservoir contents! The text now read: “To estimate the amount of TCO_{2} exchanged during this experiment, we convert our units to moles, using the sea ice (and seawater) volume (in m³) and density (in kg/m³).”

30. L 418-419 ‘Using the seawater conditions at the end of the experiment, a layer of
1cm of seawater in the pool contains 4.21 mol of TCO₂, making it difficult to close our budget. 'It’s good that you mention this uncertainty. I would like to see more uncertainty estimates in the manuscript.

Thanks

References


