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$_2$)
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).
Specific comments & suggestions:

1. L 30: CO₂ 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 Carbon Project)

2. L 31: 5-14% of the global ocean CO₂ uptake: based on which values?

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?

4. L 50: ‘physical concentration’??? I suggest dropping ‘physical’

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.

6. L 78-80 ‘The mixing of meltwater, that is low in TCO₂, pCO₂, and high in TA due to brine dilution and ikaite dissolution, with seawater will increase TA and decrease the pCO₂ of the underlying seawater, enhancing the air-sea CO₂ fluxes (Rysgaard et al., 2007; 2009).’ pCO₂ 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. TCO₂ in meltwater is low compared to (artificial) seawater. Meltwater pCO₂ is low compared to atmospheric CO₂ because of low TCO₂ 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.

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.

8. L 104 ‘(ASW) formulated by dissolving large quantities’: formulated ⇒ generated, fabricated

9. L 189-191 ‘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.

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.’

11. L 219 ‘minimums’ ⇒ minima

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.

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 TCO₂ budgets for the whole pool) it would be good to obtain integrated values, at least rough estimates.

14. L 244 please drop 'Therefore'
15. L 255 please drop 'However,'
16. L 256-257 Try to avoid repetition ('2:1 ratio'): 'As illustrated in Figure 6, an exchange of CO₂ does not affect TA while the precipitation-dissolution of ikaite affect TA and CO₂ in a ratio 2:1.'
17. L 271-274 'A negative difference (i.e. TA(sample)* < TA(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).'

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\text{difference} = \text{TA(sample)*} - \text{TA(sample)}
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I don’t understand the sentence: ‘negative difference’ means TA(sample) > TA(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.

18. L 278 ‘... both processes reduce and TCO₂(ice)’; outgassing of CO₂ (one of the two processes) does not change TA(ice), please rewrite sentence accordingly.
19. Figure 7:
   (1) TA*(ice) looks like you have continuous (or at least many) measurements. Please give some info.
   (2) I’m wondering how much of the difference between TCO₂*(ice) - TCO₂(ice) can be explained by ikaite precipitation alone and suggest to show this in another panel added to the Fig. 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(sw), TCO₂(sw), TA(ice), TCO₂(ice), S(sw), T(sw), S(ice), T(ice) for the time points at which you took TA(ice) samples.
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?). 15 to 18 January is the period with large differences $TA_{(ice)}^{*} - TA_{(ice)}$, $TCO_{2(ice)}^{*} - TCO_{2(ice)}$, and large discrepancy between estimates of ikaite precipitation by Rysgaard et al. (2014) and the current investigation (Fig. 7).

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 $TA_{(ice)}^{*}$ and $TA_{(ice)}$ (Fig. 7c, black dots) and found good agreement, with some small differences likely due to methodological differences.’
please give a correlation coefficient.

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?

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

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.

26. According to Fig. 8B much more ikaite has been dissolved in seawater than precipitated in sea ice: What’s your explanation?
27. L 338-340 ‘Using the equation from Copin-Montegut (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!).

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

29. L 375-377 ‘To estimate the amount of TCO$_2$ exchanged during this experiment, we convert our units to moles, using the sea ice (and seawater) thickness (in meter) and density (in kg/m$^3$) and the pool dimension (in meter).’

This is not just a conversion of units! Instead of concentrations you consider reservoir contents!

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 TCO$_2$, 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.

References


