

Interactive comment on “Inorganic carbon dynamics of melt pond-covered first year sea ice in the Canadian Arctic” by N.-X. Geilfus et al.

Anonymous Referee #1

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General comments:

The author investigated the carbonate system in sea ice in first year landfast sea ice and CO₂ fluxes between the atmosphere and sea ice/melt ponds in the Resolute Passage, Nunavut (74.726°N, 95.576°W,) in June 2012.

- P.7494, L.1 “ To discard concentration – dilution effect, we normalized TA_{ice} and TCO_{2ice} to a salinity of 5 »

COMMENT/QUESTION: Normalization is useful, however, I’m not convinced that a salinity of 5 is the most appropriate choice. I suggest using a value close to seawater salinity to facilitate comparison with under ice conditions. If taking the seawater salinity value $S = 33.2$ (P.7496, L.6) for normalization one obtains the following NTA_{ice} and NTCO_{2ice} values (capital ‘N’ for $S = 33.2$ normalization; all values in $\mu\text{mol kg}^{-1}$): upper 20 cm: $S = 33.2$ $S = 5$ NTA_{ice}, June4 = 3107 (nTA_{ice}, June4 = 468) NTCO_{2ice}, June4 = 2291 (nTCO_{2ice}, June4 = 345) NTA_{ice}, June17 = 11700 (nTA_{ice}, June4 = 1762) NTCO_{2ice}, June17 = 6912 (nTCO_{2ice}, June4 = 1041). The resulting values are higher (4 June) or much higher (17 June) than typical seawater values and thus need explanation. Which processes can explain these large changes over a time span of about two weeks? The discussion about the normalized values of TA and TCO₂ values (p.7498) is not adequate. How to explain the high TA and TCO₂ values in melt ponds?

→ *We decided to choose the normalization to a salinity of 5 because 5 is the mean salinity of sea ice. Our samples salinity ranged from almost 0 (melt ponds samples) to 50 (brine samples). The problem of normalized samples within the salinity range 0 – 1 to a seawater salinity ($S=32$) is that we will end up with really high TA and TCO₂ samples (e.g. if $S=0.7$, TA= 246, TCO₂ = 138 on June 17, nTA at a salinity of 5 = 1757, nTCO₂ at a salinity of 5 = 985 while nTA at a salinity of 32 = 11245 and TCO₂ at a salinity of 32 = 6308). These values are extremely high. Moreover, it doesn’t really matter at which salinity the data are normalized. The ratio will also be the same. So if sea ice had a higher nTA and nTCO₂ than seawater, it will always be higher, no matter if the normalization is at 5 or 32. In addition, having these values normalized at a salinity of 5 allows easier comparison with previous study of Geilfus et al (2012) who used also the normalization at a salinity of 5. The explanations for the high TA and TCO₂ values in melt ponds are found in the next comment.*

- P.7499 “nTA_{br} and nTCO_{2br} remained relatively constant, until at least a period of melt water percolation, which corresponded to a significant rise in both nTA_{br} and nTCO_{2br}. This increase suggests that despite the low salinity promoting the low TA and TCO₂, melt ponds and surface brine absorb CO₂ from the atmosphere.”

COMMENT/QUESTION: Uptake of CO_2 from the atmosphere by melt ponds leads to an increase of TCO_2 (however: is this a quantitative explanation?). However, it has no impact on TA! Remark: The authors know that pCO_2 uptake has no impact on TA (“An exchange of $\text{CO}_{2(\text{gas})}$ will affect TCO_2 while TA will remain constant.” P.7501, L.16).

→ Indeed, we did not explain these observations properly. Looking at figure 9, the melt ponds and brine data are located between the theoretical trend of calcium carbonate dissolution and the CO_2 uptake. The dissolution of calcium carbonate will promote the increase of TA and TCO_2 (in a ratio of 2:1) while the uptake of CO_2 will promote the only increase of TCO_2 . The uptake of CO_2 has been measured and reported in the manuscript (P7496 L21-26). The presence of calcium carbonate, as ikaite, and its dissolution, has been discussed P7494 L15-20 and P7498 L3-15. Both processes explain the increase of TA and TCO_2 observed in the upper layer of the brine and in the melt ponds.

To make the text clear, we deleted the sentence “This increase suggests that despite the low salinity promoting the low TA and TCO_2 , melt ponds and surface brine absorb CO_2 from the atmosphere” P7499 L6-8.

However, more information is given later associated with the discussion of Figure 9 where we now state: “The dissolution of the ikaite crystals will increase $n\text{TA}$ and $n\text{TCO}_2$ (in a ratio 2:1) in the upper brine layer and melt pond while the uptake of CO_2 will only increase $n\text{TCO}_2$. This explains the high $n\text{TA}$ and $n\text{TCO}_2$ reported in the Figure 5.’

- P.7499 “From 4 to 10 June, the decrease of the in situ brine pCO_2 is mainly due to the drop in brine salinity associated with rising temperature and the dissolution of ikaite.”

COMMENT/QUESTION: The contribution of dissolution of ikaite to decrease in pCO_2 is not supported by measurements (ikaite has not been quantified).

→ Indeed, but we observed ikaite crystals and only few crystals. Moreover, the precipitation of calcium carbonate is strongly suggested by the Figure 9 and the ration between $n\text{TCO}_2$ and $n\text{TA}$. This suggests that ikaite crystals were present in the ice and were dissolved due to the high temperature reported in the ice. Therefore, we could not make an exact estimation of how much ikaite crystals were present in the ice.

COMMENT/QUESTION: The manuscript contains interesting new measurements. It is, however, mainly descriptive. I’m missing a detailed analysis of the data. The results shown in Fig. 9 are most interesting, however, the discussion remains on the qualitative level. How much ikaite precipitation/dissolution is required to explain the observed changes in TA and TCO_2 ? How does this compare with recent observations of ikaite in sea ice? Another example: one could ask whether the large change of salinity (from 33.2 to 31.4) in the water layer directly underneath sea ice can be explained by local melting or if advection of a different water mass is required. Another example is the dissolution of ikaite: “As previously suggested, the dissolution of ikaite crystals during sea ice melt likely contributed to a lowering of in situ brine pCO_2 according to Reaction (R1).” (P.7498) How much ikaite dissolution is necessary to explain observed changes in pCO_2 ? How does this amount of ikaite compare to the quantities of ikaite found so far?

→ According to the definition of TA and TCO_2 (c.f. Zeebe et Wolf-Gladrow 2001, CO_2 in

seawater) the precipitation of 1 mole of calcium carbonate will reduce TCO_2 by 1 and TA by 2 moles (these information as also found in the manuscript, P7501 L16-17). During this study, the average concentration of TA and TCO_2 decrease in bulk sea ice from 403 to 283 and from 325 to 225 $\mu\text{mol kg}^{-1}$, respectively. Therefore, this range of variation corresponds to a precipitation of up to 60 μmol of ikaite. This amount is extremely low compared to the amount of ikaite precipitation reported by Rysgaard et al (2014) or Barber et al (2014) who reported precipitation of ikaite crystals up to 2000 and 3000 μmol , respectively. Unfortunately, as explained in the manuscript, we were unable to quantify the precipitation of ikaite. However, our observations and figure 9 indicate precipitation of calcium carbonate within the ice. The evolution of the brine $p\text{CO}_2$ is not only due to the dissolution of ikaite crystals, but also due to the brine dilution by melting sea ice. Assuming an average brine sample with a $p\text{CO}_2$ of 400 μatm , a salinity of 22 and TA of 1439 $\mu\text{mol kg}^{-1}$ and TCO_2 of 1340 $\mu\text{mol kg}^{-1}$ at -0.8°C (the mean brine characteristics during our survey). The $p\text{CO}_2$, according to CO2sys, will be 146 μatm and the concentration of $[\text{CO}_2]$ will be 10.2 $\mu\text{mol kg}^{-1}$. Therefore, decreasing the $p\text{CO}_2$ of this brine sample to 0 will only ask the dissolution of 146 μmol of ikaite. This amount is, again, in the lower end of the amount of ikaite precipitated found in the literature.

Specific comments:

- I suggest dropping 'in situ' in front of $p\text{CO}_2$

→ We considered your suggestion and have decided to define the three $p\text{CO}_2$ sources as follows:

- in situ bulk ice $p\text{CO}_2$ will be noted $p\text{CO}_2[\text{bulk}]$,
- bulk ice $p\text{CO}_2$ computed from TA_{ice} and $\text{TCO}_{2\text{ice}}$ will be noted $p\text{CO}_2[\text{bulk_calc}]$,
- in situ brine/melt ponds/seawater $p\text{CO}_2$ will be noted brine/melt ponds/seawater $p\text{CO}_2[\text{in situ}]$.

In the manuscript, as we discuss all of these different measurements, it seems appropriate to make the distinction between the 3 kinds of data.

- Abstract: "The low in situ $p\text{CO}_2$ observed in brine and melt ponds results in CO_2 fluxes of -0.04 to $-5.4 \text{ mmol m}^{-2} \text{ d}^{-1}$." → "The low in situ $p\text{CO}_2$ observed in brine and melt ponds results in air-ice CO_2 fluxes of -0.04 to $-5.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ (negative sign for fluxes out of the atmosphere)."

→ Thanks, we have changed the text accordingly.

- Abstract: "As melt ponds reach equilibrium with the atmosphere, the uptake becomes less significant. However, since melt ponds are continuously supplied by melt water their in situ $p\text{CO}_2$ still remains low, promoting a continuous but moderate uptake of CO_2 ($-1 \text{ mmol m}^{-2} \text{ d}^{-1}$)."

COMMENT/QUESTION: I found this a bit confusing. From the first sentence I got the impression that equilibrium is reached, whereas this is actually not the case according to second sentence (compare Fig.4). Please rewrite.

→ Indeed, we change the text as follows: This initial low in situ $p\text{CO}_2$ observed in brine and melt ponds results in air-ice CO_2 fluxes of -0.04 to $-5.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ (negative sign for fluxes

out of the atmosphere into the ocean). As melt ponds strive to reach equilibrium with the atmosphere, their in situ pCO₂ increases (up to 380 μatm) with time and the percolation of this relatively high concentration pCO₂ melt water increases the in situ brine pCO₂ within the sea ice matrix as the melt season progresses.'

- Abstract: "The potential uptake of atmospheric CO₂ by melting sea ice during the Arctic summer has been estimated from 7 to 16 Tg of C ignoring the role of melt ponds. This additional uptake of CO₂ associated to Arctic sea ice needs to be further explored and considered in the estimation of the Arctic Ocean's overall CO₂ budget."

COMMENT/QUESTION: What is meant by 'potential uptake'? Who estimated the range of 7 to 16 Tg of C (I guess per year)? How to relate the local fluxes in units of mmol m⁻² d⁻¹ to the regional (Arctic) fluxes in units of Tg C yr⁻¹?

→*Now we can read in the abstract: 'Considering the minimum and maximum Arctic sea ice extents during the melt period (90 days), we estimate an uptake of atmospheric CO₂ ranging from 7.3 to 16.4 Tg of C yr⁻¹ due to the sea ice melt pond dynamics.'*

All the details of the calculation can be found in the discussion section: 'Therefore, if we take into account a mean uptake of CO₂ of -1 mmol m⁻² d⁻¹, over the minimum and maximal Arctic sea ice extension during spring and summer thaw (90 days), we derive an uptake from 7.3 to 16.4 Tg of C yr⁻¹.'

- P.7489, L.3 "...pCO₂ between 0 to and 188 μatm..."

COMMENT/QUESTION: What is the detection limit of pCO₂?

→*The range of measurement of the Li-820 is from 0 to 20000 ppm (http://www.licor.com/env/products/gas_analysis/LI-820/).*

- P. 7489, L.25 "During our survey, the air temperature increased from 0.6 to 3.2°C, with a maximum temperature of 4.3°C observed on 19 June (Fig. 2)."

COMMENT/QUESTION: Maximum (4.3°C) is larger than the range (0.6 to 3.2°C). Please rewrite.

→*We changed the text as follows: 'During our survey, the air temperature increased from 0.6 to 4.3°C'.*

- P.7491, L.19 "were bring back" -> were brought back

→*Thanks for the correction.*

- P.7491, L.1 "TCO₂ was determined by CO₂ equilibration chamber coupled to an infrared CO₂ analyzer with a precision of ±2 μmol kg⁻¹."

COMMENT/QUESTION: Please explain. I guess: infrared analyzer -> mixing ratio of CO₂ -> pCO₂ -> [CO₂] & finally calculate TCO₂ from [CO₂] and alkalinity (?). Does the precision of ±2 μmol kg⁻¹ refer to TCO₂ or [CO₂]?

→*Indeed, this part seems to be unclear. TCO₂ has been measured, not calculated from TA and pCO₂. We add more precision in the text, as follows: 'TCO₂ was determined on a TCO₂ auto-*

analyzer (AS-C3, Apollo SciTech) via sample acidification (H_3PO_4) followed by non-dispersive infrared CO_2 detection (LI-7000) with a precision of $\pm 2 \mu mol kg^{-1}$. Both TA and TCO_2 were calibrated with certified references material from Dr. A. G. Dickson at the Scripps Institution of Oceanography.'

- P. 7494, L.9 "We assumed a conservative behaviour of dissociation constants for the range of temperature and salinity encountered in the ice cover."

COMMENT/QUESTION: It is not clear to me what you exactly mean by 'conservative behaviour of dissociation constants'.

→ The CO_2 dissociation constants are not determined for the range of salinity and temperature found within sea ice. Therefore, when we use them, we assume they are conservative for the conditions measured within sea ice. However, according to Marion (2001), the constants should be fine for the range of temperature and salinity encounter in our study. Therefore we will remove this sentence.

COMMENT/QUESTION: Fig.4: For sea ice you give 3 different pCO_2 values: (1) brine in situ pCO_2 , (2) [bulk?] sea ice pCO_2 , and (3) sea ice calculated pCO_2 . If (1) & (2) are measured quantities: what are the differences in method & meaning? Which of the pCO_2 values is 'responsible' for air-ice gas exchange?

→ In the Fig. 4, indeed, we show 3 different type of measurement of the pCO_2 .

- 1) The in situ bulk ice pCO_2 (white diamonds on Fig. 4), noted as ice pCO_2 [bulk]: these values have been measured using bulk sea ice samples. The general principle of the method is to equilibrate the sea ice samples with a mixture of N_2 and CO_2 of known concentration (referred to as the "standard gas", $146 \mu atm$) at the in situ temperature and rapidly extract the gases into a Varian 3300 gas chromatograph under vacuum (P 7492, L3-17).

This method measures all the CO_2 content in the ice samples at the in situ temperature measured during the core extraction. This method will take into account the pool of CO_2 dissolved within the brine as well as the gaseous phase, trapped within the ice as gas bubbles, under the same conditions as during the core extraction.

- 2) The bulk ice pCO_2 was also computed from the TA and TCO_2 measured on melted bulk sea ice samples within gas tight bags (P 7494, L7-10), noted as ice pCO_2 [bulk_calc].

Therefore, as the ice is melted, the carbonate system is not representative of the in situ conditions, when the ice sample was still 'ice'. The equilibrium of the carbonate system will be different, as the melting ice crystals will dilute all the CO_2 dissolved within the brine. The potential crystals of ikaite within the ice structure will be dissolved due to the increase of the temperature and decrease of salinity and this dissolution will affect the carbonate system.

- 3) Finally, we measured in situ the brine and melt ponds pCO_2 (noted as pCO_2 [in situ]) using an IRGA, Li-Cor 820 (more explanation are P 7490, L25-29; P 7491, L1-4). This method is a direct measurement of the brine pCO_2 . It doesn't take into account the CO_2 as gas bubble trapped within the ice, but only the CO_2 dissolved within the brine. The main disadvantage of this method is that brines are sampled using the sackholes technique. Therefore it is impossible to determine the exact origin of the brine (P 7501,

L2-4).

The air-ice exchanges of CO₂ are mainly due to the gradient of CO₂ between the liquid phase and the atmosphere. Therefore we have to look at the difference of CO₂ concentration between the brine/melt ponds and the atmosphere. The two methods including such information are the in situ bulk ice and brine pCO₂. A small discussion about the differences between both dataset can be found on P7500 L14-25.

In the discussion of the pCO₂ data in the figure 4, now we have revised to:

'However, the pCO₂[bulk_calc] rely on the validity of the four equilibrium constants of the aqueous carbonate system. The thermodynamic constants are assumed to be valid at subzero temperatures, but this assumption needs to be tested. Moreover, the pCO₂[bulk_calc] is not representative of the in situ concentrations because the ice sample is melted. Melt will trigger the dissolution of ikaite crystals that may have formed, strongly impacting both the TA and the TCO₂ of the resulting meltwater. On the contrary, the ice pCO₂[bulk] measured the CO₂ concentration at the in situ temperature, so it takes into account the CO₂ dissolved within the brine as well as the gaseous CO₂ (bubbles) in the ice sample.'

- P.7494, L.15 "We observed few ikaite crystals in the ice..." As we observed few crystals in the ice..."

→ *We changed the text as follows: 'We observed few minerals in the ice, which dissolved within a few minutes at room temperature.'*

- P.7494, L.25 "at the 40 cm depth" -> "at 40 cm depth"

→ *Thanks for the correction.*

- P.7495, L.13 "with concentrations ranging from 20 µatm to..." -> "with values ranging from 20 µatm to..."

→ *Thanks for the correction.*

- P.7496, L.18 "The in situ pCO₂ at the seawater surface..."

COMMENT/QUESTION: I'm not sure what the authors mean by 'in situ pCO₂': I guess they mean the surface seawater equilibrium partial pressure (often denoted by PCO₂, i.e. using capital P).

→ *We noticed some mistakes in the text. Therefore we rephrased it as follows: 'The pCO₂[in situ] of the water column ranged from 259 to 469 µatm. The top 2 m of the seawater column was mainly under-saturated with respect to the atmosphere, except on June 7 where the pCO₂[in situ] was at 455 µatm. From there, the pCO₂[in situ] decreased to 269 µatm on June 23 (Figure 6).'*

- P.7496, L.19 "(negative flux denoting uptake of CO₂)" -> "(negative values denoting flux of CO₂ out of the atmosphere)"

→ *We delete this information as it is already introduced in the abstract, as asked in one of your previous comments.*

- P.7500 “On 19 and 21 June, the bulk ice $pCO_{2in situ}$ slightly increased while the in situ melt ponds pCO_2 slightly decreased to reach the same range of concentration.”

COMMENT/QUESTION: I have no idea what that means.

→ *We rephrased it as follows: ‘On 19 and 21 June, the brine $pCO_2[in situ]$ decreased to reach the same concentration as the ice $pCO_2[bulk]$.’*

- P.7500, L.26 “To test the sackhole technique’s ability to sample uncontaminated brine, we compared TA_{br} and TCO_{2br} with a TA and TCO_2 estimated from the calculated brine volume (Cox and Weeks, 1983; Leppäranta and Manninen, 1988) and TA_{ice} and TCO_{2ice} (Fig. 8). Both methods yield similar TA and TCO_2 concentrations (from 102 to 4425 $\mu mol\ kg^{-1}$), with a similar relationship between TA and TCO_2 with a R^2 of 0.96. The scatter between the two methods could be due to the impossibility of determining the exact original depth from which the brine seeped, especially if melt ponds are present at the surface of the ice cover.”

COMMENT/QUESTION: I suggest to slightly reorder the first sentence: To test the sackhole technique’s ability to sample uncontaminated brine, we compared (Fig. 8) TA_{br} and TCO_{2br} with a TA and TCO_2 estimated from TA_{ice} and TCO_{2ice} and the calculated brine volume (Cox and Weeks, 1983; Leppäranta and Manninen, 1988).

→ *We changed the text accordingly, thanks.*

COMMENT/QUESTION: From Fig.8 one cannot see how good TCO_{2br} and TCO_2 estimated from TA_{ice} and brine volume fit to each other: Which data correspond to each other? I suggest splitting Fig. 8 into 2 panels: one for TCO_2 over TCO_2 , the other for TA over TA.

→ *I agree with your suggestion, we changed the figure 8 as suggested. Therefore we had to modify the text a little. Now it reads: ‘To test the sackhole technique’s ability to sample uncontaminated brine, we compared TA_{br} and TCO_{2br} with a TA and TCO_2 estimated from TA_{ice} and TCO_{2ice} and the calculated brine volume (Figure 8) [Cox and Weeks, 1983; Leppäranta and Manninen, 1988]. Both methods yield similar TA and TCO_2 concentrations (from 274 to 3554 $\mu mol\ kg^{-1}$ and from 283 to 3189 $\mu mol\ kg^{-1}$, respectively), with a similar relationship between TA and TCO_2 with a R^2 ’s of 0.84 and 0.85, respectively. The scatter between the two methods could be due to the impossibility of determining the exact original depth from which the brine seeped, especially if melt ponds are present at the surface of the ice cover.’*

Therefore we also changed the figure caption of the figure 8. Now it reads: ‘Comparison between brine TA and TCO_2 measured on brine collected using the sackholes technique and the brine TA and TCO_2 estimated from TA_{ice} , TCO_{2ice} and the brine volume.’

- P.7501, L.9 “The only noticeable impact of sea ice melt on the underlying seawater was observed on 20 June where the decrease of TA_{sw} and TCO_{2sw} was associated with the low isotopic ratio of $\delta^{18}O$ and δD occurring over a very short period (Fig. 6).”

COMMENT/QUESTION: The decrease of TA_{sw} and TCO_{2sw} is probably related to the decrease of salinity (mentioned earlier, right?). I’m missing information about sea ice thickness and its development over time.

→Indeed, this sentence is misleading. We want to draw attention to the reader that the decrease of the surface seawater salinity observed on June 20 is probably due to the percolation of melt pond water through the ice due to the slight decrease of the isotopic ration of $\delta^{18}O$ and δD observed as the same time. Therefore we changed the sentence as follows: 'The only noticeable impact of the percolation of melt ponds water on the underlying seawater was observed on 20 June....'

The information about the sea ice thickness can be found on P7493 L5-6: 'The average ice thickness at the sampling site, as determined from cores, decreased from 130 (± 5) to 105 (± 5) cm over the sampling campaign.'

- P.7501, L.20 "To calculate these theoretical effects we assumed that seawater sampled at 50m was not influenced by the overlying melting sea ice."

COMMENT/QUESTION: Please give the seawater values at 50 m depth: TCO₂, TA, T, S. Let me suggest again to scale (normalize) all TCO₂ & TA values to seawater salinity (S50 m).

→Now we have added these data to the text. It now reads: 'To calculate these theoretical effects we assumed that seawater sampled at 50 m (on average: T = -1.62°C; S = 32.43; TA = 2229 $\mu\text{mol kg}^{-1}$ and TCO₂ = 2135 $\mu\text{mol kg}^{-1}$, Figure 6) was not influenced by the overlying melting sea ice.'

- P.7501, L.26 "The concentration of algal biomass (Chl a) has been measured at the bottom of the ice and decreased from 11.1 $\mu\text{g L}^{-1}$ in 4 June to 0.05 $\mu\text{g L}^{-1}$ on 21 June (unpublished data, C. Mundy)."

COMMENT/QUESTION: What's the reason for the decrease (actually vanishing) of chlorophyll at the bottom of sea ice? Is it related to melting (compare, for example, Zeebeetal, 1996)? Zeebe, R. E., Eicken, H., Robinson, D.H., Wolf Gladrow, D., & Dieckmann, G. S. (1996). Modeling the heating and melting of sea ice through light absorption by microalgae. *Journal of Geophysical Research: Oceans* (1978–2012), 101(C1), 1163-1181.

→Several mechanisms could explain the decrease of the Chl a concentrations: 1) the warming up of the ice cover could cause brine drainage (Mundy et al., 2005), 2) additional warming of the bottom ice due to non-photochemical quenching of light absorbed by ice algae (Zeebe et al., 1996) and 3) negative physiological response of ice algae to light stress (e.g. Campbell et al., 2014).

The study of Galindo et al. (2014) (about DMS in the area, at the same period of time (June) in 2010, 2011) suggests that the vanishing of the Chl a concentration could be influenced by an enhanced ocean heat flux in addition to the increase of light transmittance. The loss of the biomass resulted from the warming and melting of the ice. We add this to the text.

- P.7502, L.29 "... pond coverage (x)..." -> "... pond coverage (fraction $0 \leq x \leq 1$)..."

→Thanks for the correction.

- P.7503, L.3 "The pond coverage (Fig. 2) was obtained six times between the date of pond onset (10 June) and the final sampling date, with a terrestrial laser scanner. In short, the scanner 5 was used to measure the surface topography of an untouched 80×160m area of sea ice and could also differentiate between ice cover and melt

ponds at the surface, thereby providing the pond fraction (Landy et al., 2014).”

COMMENT/QUESTION: This paragraph could go under ‘Methods/Results’.

→ *We would like to keep this paragraph as it is. Indeed, this kind of information could go in the methods section, but it will stand isolated as the methods are mainly referring to the carbonate system. We add this little information to make sure the reader can understand how we extrapolate our CO₂ fluxes and would therefore like to keep this as presented.*

- P.7503, L.8 “... then return to previous values ($-1 \text{ mmol m}^{-2} \text{ d}^{-1}$) when melt ponds are dominating. $p\text{CO}_2$ conditions in melt ponds are determined by a balance between equilibration with atmospheric CO_2 the continuous supply of melt water from the snow and sea ice.” -> “... then returned to previous values ($-1 \text{ mmol m}^{-2} \text{ d}^{-1}$) when melt ponds are dominating. $p\text{CO}_2$ conditions in melt ponds are determined by a balance between equilibration with atmospheric CO_2 and the continuous supply of low- $p\text{CO}_2$ melt water from snow and sea ice.”

→ *Thanks for the input.*

- P.7504, L.8 “Early in the melt period, increased ice temperatures and subsequent decreased bulk ice salinity dissolution of ikaite crystals promoted a strong decrease of TA, TCO_2 and $p\text{CO}_2$ observed in bulk sea ice and brines (Fig. 10). The decrease of $p\text{CO}_2$ causes sea ice to act as a sink for the atmospheric CO_2 ($\approx -1 \text{ mmol m}^{-2} \text{ d}^{-1}$). This sink increases (up to $-5.4 \text{ mmol m}^{-2} \text{ d}^{-1}$) during the initial formation of melt pond due to its very low $p\text{CO}_2$ levels. The percolation of melt pond water into the ice matrix will intensify the brine dilution and the decrease of the brine TA, TCO_2 and $p\text{CO}_2$ (Fig. 10).” -> “Early in the melt period, increased ice temperatures and subsequent decreased bulk ice salinity and dissolution of ikaite crystals promoted a strong decrease of TA, TCO_2 and $p\text{CO}_2$ observed in bulk sea ice and brines (Fig. 10). The decrease of $p\text{CO}_2$ causes sea ice to act as a sink for atmospheric CO_2 ($\approx -1 \text{ mmol m}^{-2} \text{ d}^{-1}$). This sink increases (up to $-5.4 \text{ mmol m}^{-2} \text{ d}^{-1}$) during the initial formation of melt ponds due to its very low $p\text{CO}_2$ levels. The percolation of melt pond water into the ice matrix will intensify the brine dilution and the decrease of the brine TA, TCO_2 and $p\text{CO}_2$ (Fig. 10).”

→ *Thanks for the correction.*

COMMENT/QUESTION: (1) In Fig. 9 normalized values of TCO_2 and TA ($n\text{TCO}_2$ and $n\text{TA}$) are shown whereas you talk about TCO_2 and TA, (2) no information about $p\text{CO}_2$ is provided by Figs. 9 or 10, (3) decrease of salinity and dissolution of ikaite have opposite effects on both TCO_2 & TA (dissolution of ikaite leads to increase of both TCO_2 & TA in the molar ratio of 1:2). The sign of change (decrease or increase) of TCO_2 & TA depends on the strength of dilution versus dissolution of ikaite.

→ We kept the discussion on $n\text{TA}$ and $n\text{TCO}_2$. We add the information about the precipitation of calcium carbonate on the figure 9.

- P.7504, L.17 “As melt ponds form from melted snow and melted ice surface the in situ melt pond $p\text{CO}_2$ is low ($36 \mu\text{atm}$). The percolation of this low $p\text{CO}_2$ melt water into

the sea ice matrix dilutes the brine causing the in situ brine $p\text{CO}_2$ to decrease ($20 \mu\text{atm}$).”

COMMENT/QUESTION: In contrast to TCO_2 or TA, $p\text{CO}_2$ is not a conservative quantity and thus it does not obey a linear mixing equation. You might argue for a lowering of $p\text{CO}_2$ by considering changes in TCO_2 and TA by dilution.

→ *This is what we mean in the text. Obviously it is not clear enough, so we changed the text as follows: ‘The percolation of this low $p\text{CO}_2$, low salinity melt water into the sea ice matrix will decrease the in situ brine $p\text{CO}_2$ ($20 \mu\text{atm}$).’*

- P.7504, L.24 “in situ $p\text{CO}_2$ remains undersaturated”

COMMENT/QUESTION: In my opinion a $p\text{CO}_2$ cannot be ‘undersaturated’; a water mass can be undersaturated.

→ *Indeed, we changed the text as follows: ‘the in situ melt pond $p\text{CO}_2$ remains undersaturated’*

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Anonymous Referee #2

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This paper describes an interesting and well-conceived project of high scientific value. The study is principally well conceived and considering the locality and limitations of sea ice research has yielded interesting results. I have the following comments and suggestions:

Abstract.

The summary is concise but needs language correction there are two points, which I think are misleading. Melt ponds are a product of snow melting as well as sea ice melting. See your introduction. There should be some mention as to the role or not of the biology in the melt pond or around it. See Results and discussion.

→As mention in the introduction (P7487 L16-17), melt ponds are mainly due to the melt of snow, and, in advanced stage of melt, due to sea ice melt. In the abstract, we add this notion, as asked by the reviewer. Now we can read: ‘As sea ice melt progresses, melt ponds form, mainly from melted snow, leading to a low in situ melt pond $p\text{CO}_2$ ($36 \mu\text{atm}$). The percolation of this low $p\text{CO}_2$ melt water into the sea ice matrix dilutes the brine resulting in a strong decrease of the in situ brine $p\text{CO}_2$ (to $20 \mu\text{atm}$).’ We don’t think we should mention the role of the biology in the abstract as the role of biology, in this study, has been suggested to play a minor role in the inorganic carbon dynamic. We believe that the abstract should remain focus on the main process describe in the manuscript.

Introduction.

The introduction is fine showing a good review of the literature, and provides a solid background. However I find that the aspect that melt ponds are sometimes highly productive sites, biologically speaking is not accounted for in the introduction e.g. Phytoplankton production from melting ponds on Arctic sea ice: Lee et al. 2012.

→We don’t believe we should go for a complete review of the melt pond productivity in our introduction as the manuscript is not focused on this subject. However, the concentration reported in Lee et al 2012 ranged from 0.1 to $2.9 \text{ mg Chl a m}^{-3}$ or 0.1 to $2.9 \mu\text{g L}^{-1}$. The range of concentration we observed in this study is 1.11 to $23.15 \mu\text{g L}^{-1}$ in bulk ice and 0.08 to $0.41 \mu\text{g L}^{-1}$ in melt ponds. As the figure 9 suggests, the role of biology in our study was minor compared to other processes (dilution and dissolution of calcium carbonate). Therefore, we will keep the introduction focus on the main processes.

Study site, material and methods:

The study site appears to be representative of typical Arctic sea ice, as described. Methods described are fine, although I find the way the authors arrive at the average ice thickness disconcerting. To determine the ice thickness from cores does not account for the tremendous irregularity of sea ice and especially under ice topography. This is particularly crucial when the data are used to assess melting rates or growth of sea ice. The authors

should mention these constraints. A simple transect done with an auger and tape could have improved the results considerably.

→ *It is true, a simple transect will do the job more properly to estimate the ice thickness. However, a simple transect done every 3-4 days on the sampling site will ruined the all site by accelerating the melt. Off course we could do this transect at a respectable distance from the sampling site, but then someone, somehow will ask about the legitimacy at these measurements, outside of our sampling site. Moreover, during our sampling, we took ice core for: temperature – salinity – bulk ice pCO₂ – TA and TCO₂ (results described in our study) and additional core for others studies. So our estimations of the ice thickness is already done based on, at least 4 ice cores, on our sampling site.*

The fact that biological activity was not really accounted for is also disconcerting. Particularly since samples were apparently poisoned to curtail biological activity. Reference to some measurements done under the ice Page 7501 lines 26-29 is not all that convincing or adequate. See Results.

→ *Poisoned samples are standard procedure to store samples for TA, TCO₂ before analysis. And we can't really count on the possibility that we will have no biology to avoid this procedure.*

Results:

Judging by the type of fieldwork involved in this study, the authors have done a good job to compile an excellent data set.

→ *Thank you*

See my comments on the determination of ice thickness.

The authors need to reflect on the deficiencies regarding their measurements. See comments regarding the biological properties and lack of measurements

→ *Chl a has been measured during our survey and range of concentration are provided in the manuscript (same range of concentration as the Lee et al (2012) paper suggested by the reviewer). However, as suggested by the figure 5, the brine pCO₂ changed independently of the variation of Chl a and according to the figure 9, the main processes responsible for the changed in TA and TCO₂ observed in the study are the dissolution of ikaite crystals and the uptake of CO₂. Therefore this study confirms that biology has a minor role in the inorganic carbon dynamic during the melt of the ice, as already suggested by Sjøgaard et al (2013) and Glud et al (2014).*

Now we can read, in the discussion: *“The mean concentration of algal biomass (Chl a) in bulk sea ice decreased from decreased from 23.15 μg L⁻¹ in June 4 to 1.11 μg L⁻¹ on June 12 and Chl a concentration in melt ponds ranged from 0.08 to 0.41 μg L⁻¹ (unpublished data, C. Mundy and V. Galindo). The loss of the biomass could result from the warming and melting of the ice [Zeebe et al., 1996; Galindo et al., 2014]. These concentrations are in the same range as those reported by Mundy et al. [2011] and Geilfus et al. [2012b] on melting landfast sea ice in the Beaufort Sea. From the brine profiles in Figure 5 and from the trend of the sea ice samples in Figure 9, it looks like brine dilution and calcium carbonate dissolution are the main factors controlling CO₂ exchange during our observation period. It should however be underlined that most of the calcium carbonate dissolution trend holds in only 4-5 samples located in the top 20*

cm of the sea ice cover. In the lowest range of nTA and nTCO₂ (< 500 μmol kg⁻¹) which correspond to 80% of the sea ice cover (including the bottom Chl a rich 10 cm layer), the ice samples pull the trend to the left of the calcium carbonate dissolution line, suggesting an increasing influence of the algal CO₂ uptakes, strong enough to maintain the bottom ice and brines pCO₂ at low values, in the close vicinity of the nearly saturated water values at the ice-water interface. This biological effect on the TCO₂ is however probably limited to the decaying very bottom section of the sea ice cover [Søgaard et al., 2013; Glud et al., 2014].'

Discussion:

As mentioned previously I find that the omission of biological data or properties weakens the paper. Even if it were only to relate to these in the discussion and consider the significance or insignificance with potential consequences for the budgeting the authors carry out.

→ *See previous comment.*

The discussion is good but there are quite a few language errors, which I have not pointed out specifically considering that there are mother tongue authors involved in this publication.

→ *Hopefully we did the appropriate correction.*

The point that biological properties apparently only marginally affect the carbonate system, which is based on data from the literature, may in fact be so but this needs more precise discussion. The problem is that it appears that the only biological data obtained were by Mundy. What about the melt ponds?

→ *See respond above.*

I think that the discussion can be condensed somewhat by reducing the number of assumptions.

Conclusion:

Again I think that the conclusions, as the discussion would benefit from reducing the assumptions and speculation where possible.

Figures:

Figures are ok

Literature ok