

## ***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 CO<sub>2</sub> fluxes between the atmosphere and sea ice/melt ponds in the Resolute Passage, Nunavut (74.726°N, 95.576°W,) in June 2012.

P.7493, L.1 “ To discard concentration – dilution effect, we normalized TA<sub>ice</sub> and TCO<sub>2ice</sub> 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 follow-

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ing NT<sub>Aice</sub> and NT<sub>CO<sub>2ice</sub></sub> values (capital ‘N’ for  $S = 33.2$  normalization; all values in  $\mu\text{mol kg}^{-1}$ ): upper 20 cm:  $S = 33.2$   $S = 5$  NT<sub>Aice,June4</sub> = 3107 (nT<sub>Aice,June4</sub> = 468) NT<sub>CO<sub>2ice,June4</sub></sub> = 2291 (nT<sub>CO<sub>2ice,June4</sub></sub> = 345) NT<sub>Aice,June17</sub> = 11700 (nT<sub>Aice,June4</sub> = 1762) NT<sub>CO<sub>2ice,June17</sub></sub> = 6912 (nT<sub>CO<sub>2ice,June4</sub></sub> = 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 TCO<sub>2</sub> values (p.7498) is not adequate. How to explain the high TA and TCO<sub>2</sub> values in melt ponds?

P.7499 “nT<sub>Abr</sub> and nT<sub>CO<sub>2br</sub></sub> remained relatively constant, until at least a period of melt water percolation, which corresponded to a significant rise in both nT<sub>Abr</sub> and nT<sub>CO<sub>2br</sub></sub>. This increase suggests that despite the low salinity promoting the low TA and TCO<sub>2</sub>, melt ponds and surface brine absorb CO<sub>2</sub> from the atmosphere.”

COMMENT/QUESTION: Uptake of CO<sub>2</sub> from the atmosphere by melt ponds leads to an increase of TCO<sub>2</sub> (however: is this a quantitative explanation?), however, it has no impact on TA! Remark: The authors know that pCO<sub>2</sub> uptake has no impact on TA (“An exchange of CO<sub>2</sub>(gas) will affect TCO<sub>2</sub> while TA will remain constant.” P.7501, L.16)

P.7499 “From 4 to 10 June, the decrease of the in situ brine pCO<sub>2</sub> 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<sub>2</sub> is not supported by measurements (ikaite has not been quantified).

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<sub>2</sub>? How does this compare with recent observations of ikaite

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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<sub>2</sub> according to Reaction (R1)." (P.7498) How much ikaite dissolution is necessary to explain observed changes in pCO<sub>2</sub>? How does this amount of ikaite compare to the quantities of ikaite found so far?

Specific comments:

- I suggest dropping 'in situ' in front of pCO<sub>2</sub>

- Abstract: "The low in situ pCO<sub>2</sub> observed in brine and melt ponds results in CO<sub>2</sub> fluxes of -0.04 to -5.4 mmol m<sup>-2</sup> d<sup>-1</sup>." -> "The low in situ pCO<sub>2</sub> observed in brine and melt ponds results in air-ice CO<sub>2</sub> fluxes of -0.04 to -5.4 mmol m<sup>-2</sup> d<sup>-1</sup> (negative sign for fluxes out of the atmosphere)."

- 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 pCO<sub>2</sub> still remains low, promoting a continuous but moderate uptake of CO<sub>2</sub> (-1 mmol m<sup>-2</sup> d<sup>-1</sup>)."

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.

- Abstract: "The potential uptake of atmospheric CO<sub>2</sub> 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 CO<sub>2</sub> associated to Arctic sea ice needs to be further explored and considered in the estimation of the Arctic Ocean's overall CO<sub>2</sub> budget."

COMMENT/QUESTION: What is meant by 'potential uptake'? Who estimated the

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range of 7 to 16 Tg of C (I guess per year)? How to relate the local fluxes in units of mmol m<sup>-2</sup> d<sup>-1</sup> to the regional (Arctic) fluxes in units of Tg C yr<sup>-1</sup>?

- P.7489, L.3 "... pCO<sub>2</sub> between 0 to 188 μatm ...". COMMENT/QUESTION: What is the detection limit of pCO<sub>2</sub>?

- 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.

- P.7491, L.19 "were bring back" -> were brought back - P.7491, L.1 "TCO<sub>2</sub> was determined by CO<sub>2</sub> equilibration chamber coupled to an infrared CO<sub>2</sub> analyzer with a precision of ±2 μmol kg<sup>-1</sup>."

COMMENT/QUESTION: Please explain. I guess: infrared analyzer -> mixing ratio of CO<sub>2</sub> -> pCO<sub>2</sub> -> [CO<sub>2</sub>] & finally calculate TCO<sub>2</sub> from [CO<sub>2</sub>] and alkalinity (?). Does the precision of ±2 μmol kg<sup>-1</sup> refer to TCO<sub>2</sub> or [CO<sub>2</sub>]?

- 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'.

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

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

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

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- P.7495, L.13 "with concentrations ranging from 20  $\mu\text{atm}$  to . . ." -> "with values ranging from 20  $\mu\text{atm}$  to . . ."

- P.7496, L.18 "The in situ  $\text{pCO}_2$  at the seawater surface . . ."

COMMENT/QUESTION: I'm not sure what the authors mean by 'in situ  $\text{pCO}_2$ ': I guess they mean the surface seawater equilibrium partial pressure (often denoted by  $\text{PCO}_2$ , i.e. using capital P).

- P.7496, L.19 "(negative flux denoting uptake of  $\text{CO}_2$ )" -> "(negative values denoting flux of  $\text{CO}_2$  out of the atmosphere)"

- P.7500 "On 19 and 21 June, the bulk ice  $\text{pCO}_2$  in situ slightly increased while the in situ melt ponds  $\text{pCO}_2$  slightly decreased to reach the same range of concentration."

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

- P.7500, L.26 "To test the sackhole technique's ability to sample uncontaminated brine, we compared  $\text{TABr}$  and  $\text{TCO}_2\text{br}$  with a  $\text{TA}$  and  $\text{TCO}_2$  estimated from the calculated brine volume (Cox and Weeks, 1983; Leppäranta and Manninen, 1988) and  $\text{TAice}$  and  $\text{TCO}_2\text{ice}$  (Fig. 8). Both methods yield similar  $\text{TA}$  and  $\text{TCO}_2$  concentrations (from 102 to 4425  $\mu\text{mol kg}^{-1}$ ), with a similar relationship between  $\text{TA}$  and  $\text{TCO}_2$  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)  $\text{TABr}$  and  $\text{TCO}_2\text{br}$  with a  $\text{TA}$  and  $\text{TCO}_2$  estimated from  $\text{TAice}$  and  $\text{TCO}_2\text{ice}$  and the calculated brine volume (Cox and Weeks, 1983; Leppäranta and Manninen, 1988).

- COMMENT/QUESTION: From Fig.8 one cannot see how good  $\text{TCO}_2\text{br}$  and  $\text{TCO}_2$  estimated from  $\text{TAice}$  and brine volume fit to each other: Which data correspond to each other?. I suggest splitting Fig. 8 into 2 panels: one for  $\text{TCO}_2$  over  $\text{TCO}_2$ , the

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other for  $\text{TA}$  over  $\text{TA}$ .

- 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  $\text{TASw}$  and  $\text{TCO}_2\text{sw}$  was associated with the low isotopic ratio of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  occurring over a very short period (Fig. 6)."

COMMENT/QUESTION: The decrease of  $\text{TASw}$  and  $\text{TCO}_2\text{sw}$  is probably related to the decrease of salinity (mentioned earlier, right?). I'm missing information about sea ice thickness and its development over time.

- 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:  $\text{TCO}_2$ ,  $\text{TA}$ ,  $\text{T}$ ,  $\text{S}$ . Let me suggest again to scale (normalize) all  $\text{TCO}_2$  &  $\text{TA}$  values to seawater salinity (S50 m).

- P.7501, L.26 "The concentration of algal biomass ( $\text{Chl a}$ ) 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, Zeebe et al., 1996)? Zeebe, R. E., Eicken, H., Robinson, D. H., WolfáÅřGladrow, 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.

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

- 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  $80 \times 160\text{m}$  area of sea ice and could also differentiate between ice cover and melt ponds

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

COMMENT/QUESTION: This paragraph could go under 'Methods/Results'. - P.7503, L.8 "... then return to previous values (-1 mmol m<sup>-2</sup> d<sup>-1</sup>) when melt ponds are dominating. pCO<sub>2</sub> conditions in melt ponds are determined by a balance between equilibration with atmospheric CO<sub>2</sub> the continuous supply of melt water from the snow and sea ice." -> "... then returned to previous values (-1 mmol m<sup>-2</sup> d<sup>-1</sup>) when melt ponds are dominating. pCO<sub>2</sub> conditions in melt ponds are determined by a balance between equilibration with atmospheric CO<sub>2</sub> and the continuous supply of low-pCO<sub>2</sub> melt water from snow and sea ice." - 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<sub>2</sub> and pCO<sub>2</sub> observed in bulk sea ice and brines (Fig. 10). The decrease of pCO<sub>2</sub> causes sea ice to act as a sink for the atmospheric CO<sub>2</sub> (≈ -1 mmol m<sup>-2</sup> d<sup>-1</sup>). This sink increases (up to -5.4 mmol m<sup>-2</sup> d<sup>-1</sup>) during the initial formation of melt pond due to its very low pCO<sub>2</sub> levels. The percolation of melt pond water into the ice matrix will intensify the brine dilution and the decrease of the brine TA, TCO<sub>2</sub> and pCO<sub>2</sub> (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<sub>2</sub> and pCO<sub>2</sub> observed in bulk sea ice and brines (Fig. 10). The decrease of pCO<sub>2</sub> causes sea ice to act as a sink for atmospheric CO<sub>2</sub> (≈ -1 mmol m<sup>-2</sup> d<sup>-1</sup>). This sink increases (up to -5.4 mmol m<sup>-2</sup> d<sup>-1</sup>) during the initial formation of melt ponds due to its very low pCO<sub>2</sub> levels. The percolation of melt pond water into the ice matrix will intensify the brine dilution and the decrease of the brine TA, TCO<sub>2</sub> and pCO<sub>2</sub> (Fig. 10). "

COMMENT/QUESTION: (1) In Fig. 9 normalized values of TCO<sub>2</sub> and TA (nTCO<sub>2</sub> and nTA) are shown whereas you talk about TCO<sub>2</sub> and TA, (2) no information about pCO<sub>2</sub> is provided by Figs. 9 or 10, (3) decrease of salinity and dissolution of ikaite have opposite effects on both TCO<sub>2</sub> & TA (dissolution of ikaite leads to increase of both TCO<sub>2</sub> & TA in the molar ratio of 1:2). The sign of change (decrease or increase) of

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TCO<sub>2</sub> & TA depends on the strength of dilution versus dissolution of ikaite.

- P.7504, L.17 "As melt ponds forms from melted snow and melted ice surface the in situ melt pond pCO<sub>2</sub> is low (36 μatm). The percolation of this low pCO<sub>2</sub> melt water into the sea ice matrix dilutes the brine causing the in situ brine pCO<sub>2</sub> to decrease (20 μatm)."

COMMENT/QUESTION: In contrast to TCO<sub>2</sub> or TA, pCO<sub>2</sub> is not a conservative quantity and thus it does not obey a linear mixing equation. You might argue for a lowering of pCO<sub>2</sub> by considering changes in TCO<sub>2</sub> and TA by dilution.

- P.7504, L.24 "in situ pCO<sub>2</sub> remains undersaturated"

COMMENT/QUESTION: In my opinion a pCO<sub>2</sub> cannot be 'undersaturated'; a water mass can be undersaturated.

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Interactive comment on Biogeosciences Discuss., 11, 7485, 2014.

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