

Associate Editor Decision: Reconsider after major revisions (11 Dec 2014) by Dr Christine Klaas

Comments to the Author:

The second round of review on the new version of the manuscript has raised several new issues (see anonymous reviewer comments below) concerning presentation of results (in particular, melt pond data missing, temperature effects on carbonate system, figure formats) and analysis of data (conclusions not supported by robust quantitative analysis of the carbonate system given available information). It is my opinion that these issues need to be addressed before acceptance of the manuscript for publication.

We have made the necessary corrections to the manuscript. We agree that the caption of figure 5 was unclear so it has been improved. We think the contour plot used for figure 5 is the best way to illustrate our results. To facilitate comparison between the sea ice (figure 3), brine and melt ponds (figure 5) and the seawater results (figure 6), we now present these data in similar contour plots.

The impact of the temperature on our pCO₂ data is discussed in the manuscript. We include a section describing the temperature evolution during our survey. Care has been taken to ensure the pCO₂ data are always mentioned at the in situ temperature in the manuscript.

Concerning the dissolution of ikaite crystals, numerous studies suggested that ikaite precipitation could have a strong impact on the inorganic carbon dynamics within sea ice (Dieckmann et al 2008, 2010; Rysgaard et al 2007, 2011, 2014). Therefore, it is essential to describe what has been done on this subject during our survey. Moreover, the dissolution of ikaite crystals explained the evolution of some parameters and the relationship between TA and TCO₂ during our survey.

Reviewer's comments:

Abstract:

- L24-26: 'The percolation of this low pCO₂ melt water into the sea ice matrix dilutes the brine resulting in a strong decrease of the in situ brine pCO₂ (to 20 μatm).'

This sounds as if pCO₂ is a conserved quantity (a substance) that can be mixed. However, pCO₂ does not follow a linear mixing relationship. It is a strong function of temperature and depends on DIC and pH.

My suggestion: change wording when talking about pCO₂ and mixing.

We changed the text to read: « *The percolation of this low salinity and low pCO₂ melt water into the sea ice matrix decreased the brine salinity, TA and TCO₂ and lowered the in situ brine pCO₂ (to 20 μatm).* »

- L525-528 'Therefore, if we take into account a mean uptake CO₂ of -1 mmol m⁻² d⁻¹, over the minimum and maximum Arctic sea ice extend during spring and summer thaw (90 days), we derive an uptake from 7.2 to 16.4 Tg of C yr⁻¹.'

Where are these numbers from? This process requires a long time period (90 days) and large area (6 to 15 Million km²) and is still small compared to the current estimate of 70 to 200 Tg C yr⁻¹ uptake by the Arctic Ocean (compare, Bates and Mathis, 2009, Takahashi et al., 2009) and it is not clear how much of the uptake during the melting season might be compensated by outgassing

during ice formation.

This section was unclear so it has been reformulated beginning on line 529:

'Considering the mean F_{tot} after melt pond onset ($= -1.15 \text{ mmol m}^{-2} \text{ d}^{-1}$) over $8.4 \times 10^6 \text{ km}^2$ of sea ice (i.e. the difference between the maximum and the minimum annual Arctic sea ice extents (Dieckmann and Hellmer, 2010)) over a 90-day duration (the length of the spring and summer melt period), we derive an uptake for this annual melt period of $-10.44 \text{ Tg C yr}^{-1}$, in addition to existing annual estimates of Arctic oceanic CO_2 uptake.'

From lines 541 to 551, we compare this estimation with previous work from Rysgaard et al. (2011), Bates and Mathis, (2009) and Takahashi et al. (2009). Bates and Mathis, (2009) and Takahashi et al. (2009) only accounted for oceanic interaction with the atmosphere and considered sea ice an impermeable barrier to CO_2 fluxes. Our study suggests that sea ice acts as a sink for atmospheric CO_2 in addition to the overall uptake described by Bates and Mathis (2009) and Takahashi et al (2009).

Now we can read:

"These estimations are in the same range as previous work from Rysgaard et al. [2011] who estimated an overall budget for Arctic sea ice between 14 and 31 Tg of C yr^{-1} depending on whether the precipitation of calcium carbonate took place in the ice or not. Other estimates of carbon uptake by the Arctic Ocean include Takahashi et al. [2009], who estimated oceanic uptake of 121 Tg of C yr^{-1} for an area north of 66°N while Bates and Mathis [2009] estimated an uptake between 66 and 199 Tg of C yr^{-1} for the Arctic Ocean. However, these works considered sea ice an impermeable barrier, ignoring the potential role of ice-covered seas on gas exchange between the ocean and the atmosphere. We surmise that melting sea ice may play an important role in mediating the exchange of CO_2 between the atmosphere and ocean at high latitudes and could provide an additional uptake to the previous estimation from Bates and Mathis (2009) or Takahashi et al., (2009)."

Outgassing of CO_2 during sea ice formation is still poorly estimated. Only one study has reported direct measurements of CO_2 outgassing over growing natural sea ice (Geilfus et al 2013). However, the amount of CO_2 expelled from sea ice to the underlying seawater associated with the brine rejection is also unknown and could offset the observed outgassing. This is far beyond the scope of this manuscript though it is an important consideration that merits further attention.

- L 75-77 'The discharge of melt water through the ice cover is proportional to the ice permeability and the hydraulic pressure gradient in the brine system.'

You may add '(Darcy's law)' at the end of the sentence.

Thank you. We have made the suggested addition.

- L 104 pCO_2 between 0 and 188 μatm -> pCO_2 below the detection limit (GIVE VALUES OF DETECTION LIMIT HERE) instead of "0".

The pCO_2 range reported (from 0 to 188 μatm) was measured using a calibrated Li-Cor 6262 gas analyzer and is reported as such (Geilfus et al. 2012). The detection of the Li-Cor 6262 goes from 0 to 3000 ppm.

- L 117 'measurements of TA, TCO_2 and pCO_2 on bulk sea ice' really means:

measurements of TA, TCO₂ and pCO₂ of sea ice molten in the laboratory in a closed container in order to avoid gas-exchange (right?). Please specify.

We have changed the text to read as follows:

“The evolution of the carbonate system was examined using measurements of total alkalinity (TA) and total dissolved inorganic carbon (TCO₂) on melted bulk sea ice, as well as in brine and melt ponds samples. In situ pCO₂ was measured on bulk sea ice, brine and melt ponds in association with CO₂ flux measurements over sea ice and melt ponds.”

Remark:

The (equilibrium) pCO₂ for a water sample of a certain chemical composition (TA, TCO₂, salinity) is a strong function of temperature. Thus it is important to always report pCO₂ together with temperature. This applies especially when reporting pCO₂ values of ‘bulk sea ice’.

Which temperatures (in-situ? temperature after melting the ice? lab temperature?) correspond to the reported pCO₂? Please give this information also in the figure legend.

For clarity:

- Lines 152-154: *“The pCO₂ was measured in situ (noted as pCO₂[in situ]) in brine, melt pond water and under-ice seawater using a custom-made equilibration system.”*
- 158-161: *“The in situ temperature was measured using a calibrated temperature probe (Testo 720®, ±0.1°C precision) simultaneously at the inlet and outlet of the equilibrator. Temperature correction of pCO₂ was applied assuming that the relation of Copin Montégut [1988] is valid at low temperature and high salinity.”*

In the methods section regarding the measurement of bulk ice pCO₂ (pCO₂[bulk]), on lines 193-205, the manuscript reads:

“The general principle of the method is to equilibrate the sea ice samples with a mixture of N₂ and CO₂ of known concentration (referred to as the “standard gas”, 146 µatm) at the in situ temperature and rapidly extract the gases into a Varian 3300 gas chromatograph under vacuum. The ice sample is cut to fit tightly the container (4 x 4 x 4.5 cm) to both minimize the headspace volume and keep this headspace constant. The standard gas is injected at 1013 mbar into the container. Then the container with the ice sample is placed in a thermostatic bath setup at the field in situ temperature for 24 hours. This timing is chosen to ensure that the sample is re-equilibrated to the brine volume and chemical conditions at the in situ temperature. A quick injection into the gas chromatograph then allows the reconstruction of the equilibrium brine pCO₂ at the in situ temperature.”

We have reported that the bulk ice pCO₂ data at the in situ temperature.

Regarding the bulk ice pCO₂ calculated from TA_{ice} and TCO_{2ice} (noted as pCO₂[bulk_calc]), the information related to the correction of the temperature was omitted in the previous version of the manuscript. We have added these details on lines 262-265:

“From TA_{ice} and TCO_{2ice}, we computed a bulk ice pCO₂ (noted as pCO₂[bulk_calc])

using the CO₂ dissociation constants of Mehrbach et al. [1973] refitted by Dickson and Millero [1987] and applying the temperature correction of pCO₂ using the relation of Copin Montégut [1988].'

All our pCO₂ data are reported at the in situ temperature.

L 119 'Percolation of melt water from ponds was tracked using the isotopic ratios δD and $\delta^{18}O$ within bulk sea ice and brine.'

A few sentences to explain the method for detection of melt water percolation with the help of isotopic compositions might be in order here. Give, for example, typical values of δD and $\delta^{18}O$ in snow, sea ice, and seawater and may be hint why they are different from each other.

We have added the following details beginning on line 207:

'Due to differences in the isotopic composition of snowmelt, seawater and sea ice (sea ice is highly depleted in ¹⁸O and D), the infiltration of meteoric water can be traced through the sea ice system based on stable isotope measurements [Eicken et al., 2002].'

- L 336-337: 'Melt pond formation and subsequent percolation of melt water into the ice cover are visible in the brine system from the isotopic ratio data (Figure 3,5).'

I understand what you want to say, however, I suggest rewriting the sentence under 'Results'.

We have made the change as suggested by the reviewer.

-> Low values of δD (down to -119.2‰) and $\delta^{18}O$ (down to -23.9‰) were observed in the upper 20 cm of the ice column. These values are much lower than typical bulk sea ice values (GIVE RANGE OF TYPICAL VALUES OF ISOTOPIC COMPOSITION HERE). They can be explained by the percolation of melt water (GIVE RANGE OF TYPICAL VALUES OF ISOTOPIC COMPOSITION HERE) from melt ponds into the underlying sea ice column.

"isotopic ratio data" is isotopic composition instead

The low δD and $\delta^{18}O$ observed in the ice are not due to the percolation of melt water from melt ponds. More specifically, lines 339-343 state:

"The percolation of snowmelt through the ice cover and its refreezing into the ice matrix formed interposed ice [Landy et al., 2014]. The formation of interposed ice as described by Freitag and Eicken [2003] and Polashenski et al. [2012] could explain the low salinity and low values of $\delta^{18}O$ (down to -23.9‰) and δD (down to -191.2‰) observed in the upper 20 cm of the ice cover."

"Within the brine system, the low isotopic composition observed in the brine at 20 cm depth on 10 June (-15.2‰ and -118.1‰, respectively, after melt pond formation) and at 20 and 40 cm depth on 17 June (-10.4‰ and -87.5‰, respectively) can be explained by the percolation of melt pond water (-10.1‰ and -93.4‰, respectively) into the underlying sea ice cover (Figure 5)."

Section 'Results':

- In my opinion the interesting results are not properly described. Let's look at

bulk sea ice temperature for example. The authors write ‘The mean ice temperature increased from -2.9oC on 4 June to -1.5oC on 12 June (Figure 3). From 10 June, the temperature of the top 20 cm of the ice was slightly negative (-0.5oC to 0oC) while the rest of the ice thickness remained around -1.5oC.’

When looking at the temperature profile I immediately recognize various other features/patterns worth mentioning as, for example, the high temperatures (above -1oC, i.e. well above the melting point of sea water with salinities > 30) at the bottom of the ice on June 12, 17, and 19, the rather unusual temperature profile with several maxima inside the ice column on 12 June, the increase in mean temperature over the observation method is not monotonic (compare data from June 8 to June 9).

“... ice was slightly negative (-0.5oC to 0oC)”

Write “... ice was between slightly negative (-0.5oC) and the melting point.” instead.

The high temperature (from -0.5°C to 0°C are mentioned in the results section and discussed in the Discussion section. The temperature and salinity profiles are quite standard for melting sea ice (see for example Eicken et al 2002, Eicken 2003). The high temperatures (>-1°C) observed at the bottom of the ice are not unusual as the ice cover is melting. The unusual temperatures observed in the figure 3 mentioned by the reviewer are maxima in the mid section of the core on June 12. These anomalous high values are probably due to warming of the ice during the temperature measurement in the field as a result of positive air temperatures at the time of measurement so they do not merit description in the text. We have included this caveat in the Results section (line 230)

- The description of salinity profiles is incomplete as: ‘Bulk ice salinity ranged from 7.5 to 0 (Figure 3). The top 20 cm of the ice had salinities around 0 while the bulk salinity of the central part of the ice decreased from 7.5 to 4 during the survey.’

Salinities in the upper 15 cm are indeed quite low (below 1) on June 9 and 12, however, not ‘around 0’ for the other samples, and actually comparable to values in the central part of the ice column on June 4. The salinities near the bottom of the sea ice are worth mentioning: high values on June 4 and 9 in contrast to relative low values on and after June 17.

We have changed the text to read as follows:

‘Bulk ice salinity ranged from 7.5 to 0 (Figure 3). The bulk ice salinity of the upper 15 cm decreased from 5.2 on 4 June to 0.1 on 9 June, then increased to 2.7 on 21 June. The central section of the ice cover (0.2 to 1m depth) decreased from 7.5 to 4 during the survey. The bulk ice salinity at the sea ice interface with the water column decreased from 7.4 on 4 June to 2.7 on 21 June.’

- L 288 to 299: For the melt ponds only ranges of observed data are given The values of nTA and nTCO2 are plausible, however, cannot be calculated from the ranges given in this section. The authors should present the whole data set for the melt ponds. The maximum values for nTA and nTCO2 for the melts ponds are smaller than the maximum values for nTA and nTCO2 in the upper 20 cm of sea ice. How are the observations of melt ponds and sea ice related in time and space?

We have presented the whole melt pond data set in Figure 5. The main features are described and discussed in the manuscript. We have changed the figure caption of figure 5 for clarity as follows:

'Temporal evolution of brine (0.2, 0.4, 0.75 and 1m depth) and melt ponds (0m) $p\text{CO}_2$ [in situ](μatm), salinity, isotopic composition of $\delta^{18}\text{O}$ and $\delta\text{D}(\text{‰})$, TA and nTA ($\mu\text{mol kg}^{-1}$), TCO_2 and $n\text{TCO}_2$ ($\mu\text{mol kg}^{-1}$).'

We have also added references to Figure 5 in the Results section related to melt ponds.

- Fig. 5: The profiles of measurements in brines (Fig. 5) should be shown in the same form as in Fig. 3 to allow for comparison.

We believe that figure 5, as presented in our manuscript is the most efficient way to show our result. It provides the most useful illustration of the evolution of our parameters during the experiment and the color code allows for quick, accurate reference to temporal changes. To facilitate comparison between sea ice, brine/melt ponds and seawater data we changed the brine/melt pond and seawater figures to the same contour format as figure 5.

- More detailed descriptions of the data are required also for the other quantities. These detailed description are necessary as foundation for the discussion that should relate the observations in a meaningful way.

A detailed description of the whole data set is in the manuscript. We changed the figure 3, 5 and 6 to contour colours plot to facilitate comparison between the datasets.

5. Discussion

The discussion is largely qualitative although many quantitative data are available. One could, for example, estimate how much low-salinity water from melt ponds is necessary to explain the large changes of S, δD , and $\delta^{18}\text{O}$ in the upper 20 cm of sea ice. Further: what are the consequences for other quantities (TA, nTA, ...)?

We have determined the impact of sea ice melt on the exchange of CO_2 with the atmosphere and how sea ice melt will affect the oceanic uptake of CO_2 in this manuscript.

Quantifying how much low-salinity melt water is necessary to explain or observations an interesting thought, but unfortunately we don't have the ^{18}O data on fresh snow to try to make a budget of the dilution processes because we arrived to find coarse wet snow at the site (line 128), indicating melt began before we arrived. Therefore, any attempt to make a budget, as suggested by the reviewer, would be conjecture.

L 328-329: 'Over the course of our study period, the vertical temperature gradient within sea ice decreases, leading to nearly isothermal ice cover.' This would belong under 'Results', however, I don't see that this statement is supported by the data.

We have moved this sentence to the results section as suggested. Figure 3 indicates that the ice temperature increased during our survey and became almost isothermal. On 21 June the vertical temperature range is less than 1°C . Therefore we think is pretty fair to said that our ice cover become 'nearly isothermal'.

- L 337-339 'The 20 cm depth on 9 and 10 June ... had the same isotopic ratios as the melt ponds.'

No! First: the isotopic compositions cover large ranges in the melt ponds as well as in the upper 20 cm of the ice. Second: the ranges are not identical with more negative values in ice.

We have rewritten these lines as follows:

“Within the brine system, the low isotopic composition observed in the brine at 20 cm depth on 10 June (-15.2‰ and -118.1‰, respectively) and at 20 and 40 cm depth on 17 June (-10.4‰ and -87.5‰, respectively) can be explained by the percolation of melt pond water (-10.1‰ and -93.4‰, respectively) into the underlying sea ice cover (Figure 5). The combination of low isotopic composition with low salinities and warm ice temperatures (~ 0°C) collectively suggest that meltwater percolated into the ice cover, at least to a depth of 40 cm.”

- L 339-341 ‘The increase of the $\delta^{18}\text{O}$ and δD ratios in the melt ponds observed on 19 and 21 June suggests that the contribution of sea ice melt to the melt ponds had increased.’ Please show all melt pond data.

We have shown all our melt pond data.

- L 347-364 The discussion on ikaite dissolution is purely qualitative and leads to nowhere.

Precipitation of ikaite crystals has been suggested to play a significant role in the inorganic carbon chemistry within sea ice (Dieckmann et al 2008, 2010; Rysgaard et al 2007, 2010, 2011, 2013, 2014; Geilfus et al 2012, 2013; Nomura et al 2010...). Therefore it seems interesting to mention if ikaite crystals were present during our survey. We were able to observe crystals in melted bulk ice samples. Ikaite crystal dissolution decreases the $p\text{CO}_2$ and increases TA, which is observed in our survey so with thought I pertinent to discuss this. In addition, the relationship between TA and TCO_2 (Figure 9) suggests ikaite crystal dissolution occurred, and so we discuss this topic and its effects in the discussion section (lines 478 – 495) which will lead to further exploration of this specific by ourselves amongst others in further work.

- L 388 ‘... and the dissolution of ikaite.’ This statement is not supported by the data.

Please see previous response.

- Fig.9 Although some of the sea ice $n\text{TA}-n\text{TCO}_2$ data lie close to a $\Delta n\text{TA}:\Delta n\text{TCO}_2=2:1$ line through the sea water value, this does not necessarily speak for CaCO_3 dissolution as indicated in the graph. The very high $n\text{TA}-n\text{TCO}_2$ values occur in the upper 20 cm of the ice core (Fig. 3) where salinity values decrease to values well below 1. This decrease of S below 1 requires input of large amounts of freshwater (dilution of salinity from 5 to 1 requires addition of 4 kg of freshwater per kg of ice!). The low-salinity water observed in melt-ponds by the authors cannot do the job because its salinity was larger than 1. A possible explanation could be melt ponds with lower salinity (at an earlier state of development and/or with larger water input from snow). Such waters might show a TA:TCO₂ ratio much different from sea water.

Figure 9 shows the normalized TA and TCO_2 to a salinity of 5 (as mentioned in the figure caption), which removes the effect of dilution by the salinity from the plot.

Thus melt pond data located between the CaCO_3 dissolution and the CO_2 uptake relationships indicate that both calcium carbonate dissolution and CO_2 uptake may be occurring at the same time.

The decrease of salinity to value below 1 is due to fresh snow melt, melt pond water percolation into the ice matrix and internal sea ice melting.

Minor points: → *We corrected the text as suggested. Thanks for the input.*

- L 16: CO_2 flux -> CO_2 fluxes
- L 20: increase of the ice temperature -> increase in ice temperature
- L21 decrease of bulk ice salinity -> decrease in bulk ice salinity
- L 28 fluxes out of the atmosphere -> fluxes from the atmosphere
- L 34 please drop 'still'
- L 102 sea ice
- L 213: replace 'ø' by 'δ'
- L 213: drop gap between number and per-mille sign; also L 306-307 (the same convention applies for percent)