Review of tc-2014-88

This is a review of the manuscript Impact of snow cover on CO_2 dynamics in Antarctic pack ice by N.X.G. Geilfus et al. It relates to the Cryosphere Discussions manuscript Number tc-2014-88. Below I cite from the manuscript in italic font.

General comments - summary

The paper presents an analysis of carbon chemistry in sea ice from the Bellingshausen Sea, Antarctica. It focuses in particular on the temporal evolution of pCO_2 in bulk ice and brine over the coarse of one month, comparing the pCO_2 evolution for two sites with different snow conditions, for a succession of warming and cooling events. Main findings proposed are (i) the CO_2 system was primarily controlled by physical and thermodynamic processes, with total alkalinity (TA), total dissolved inorganic carbon (TCO_2) and CO_2 partial pressure (pCO_2) of bulk ice and brine salinity all increasing/decreasing with cooling/warming of the ice; (ii) the ice was undersaturated in CO_2 with respect to the atmosphere, and thus acted as a sink for atmospheric CO_2; (iii) the temperature fluctuations were reduced for the site with thicker snow cover, with the associated CO_2 system parameter response, as well as the CO_2 ice-atmosphere fluxes showing the same behaviour.

The paper addresses, with the evolution of the CO_2 system, an important aspect of sea ice biogeochemistry in general, as well relevant questions concerning ocean-ice-atmosphere exchange of CO_2. The paper is well structured and most paragraphs are easy to read and understand. Observations are presented properly (in figures and text). Although the findings/conclusions are not very strong (the effect of a snow cover on sea ice temperature is well known from both model and observational work, and the present study thus only confirms basic knowledge), I would rate them worth-publishing, in particular due to the vertical profiles in pCO_2 observations presented. However, in my opinion does the interpretation of the results (in the discussion and conclusion sections) lack important aspects of sea ice physics and carbonate chemistry, while it is sometimes too speculative. In particular the validity of the methods used needs to be discussed in more detail. I summarize the deficits in the following key points:

→*Thanks for these overarching comments. We'll endeavour to address these issues below, as the reviewer has made specific comments which bring together all the ideas mentioned above in their synopsis.*

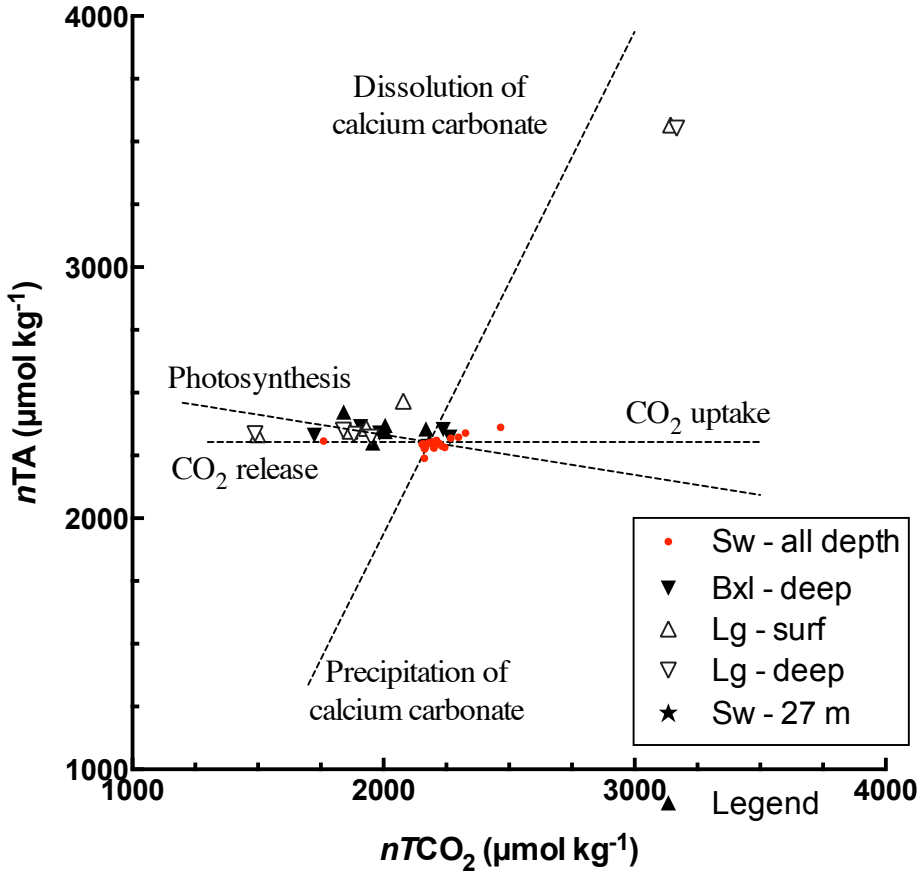
I. Dilution and concentration of brines by internal freezing/melting appears to be the process that regulates carbon parameters, yet this is not well communicated. Rather the authors often mention the (indirect) role of temperature and porosity, while in the presentation data plots of brine salinity versus carbon parameters are lacking. Also the role of other factors (CO_2 solubility, precipitation/dissolution of Calcium Carbonate and/or Ikaite crystals) is mentioned in the introduction yet lacking in the discussion.

→*To this end, we have changed the structure of the text, with one chapter of the discussion specifically dedicated to the role of the dilution-concentration effect on brine and therefore on inorganic carbon dynamics, spelling out how temperature changes result in physical changes in the brine volume of the ice cover affecting the pCO_2. CO_2 solubility is addressed in the discussion in connection with brine salinity, which of course is controlled by the sea ice temperature as we have mentioned. Regarding the lack of plot of pCO_2 versus salinity, we*

explain our choice at your comment about the Figure 10.

We chose not to mention calcium carbonate precipitation because we did not observe any calcium carbonate precipitate during our survey, so thoughts on the subject would be entirely speculative.

However, looking at the ratio TCO2/TA we will be able to confirm the potential presence or not of precipitates. Indeed, if precipitation of calcium carbonate occurs in the ice it will reduce TA and TCO_2 (in a ratio 1:2). In the following figure, we plot nTCO2 versus nTA (normalized TA and TCO2 to avoid any influence of the salinity). If precipitation of calcium carbonate occurs, our samples should be located close to the theoretical trend of precipitation / dissolution of CaCO3. As you can see, this is not the case, excepted at one occasion, the first sampling date at the Liege site.



II. The large differences between bulk ice and brine pCO_2 call for a more (self-)critical discussion, including the question if the applied procedure to obtain the pCO_2 profiles of bulk ice gives useful information at all.

→*We now devote a substantial portion of the discussion section to the differences in bulk ice and brine pCO_2 results, including critical examination of the methods. More appropriately, we surmise that the differences the reviewer has brought up may actually be a result of their measurement of different parts of the sea ice system rather than them resulting in two*

different data points by measuring exactly the same thing. Please see the last paragraph of the discussion section b. Note that, as now described in the text, we believe that both methods have their specific weaknesses, and we do not see why trusting one less than the other. We are however constantly striving to improve the accuracy of the methods employed, as well as create new ways to measure important parts of the sea ice carbonate system.

III. Brine convection is mentioned several times. The relevant sea ice properties and physical conditions allowing for convection need to be clarified, and the discussion of different convection conditions should be revised here and there in the paper.

→*We changed the term of brine convection by 'overturning of brine' (as specifically mentioned in the publication of Lewis et al [2011]), or 'vertical redistribution of brine'. Although the Rayleigh numbers calculated by Brabant [2012] indicate that it was indeed convection that occurred, we are not concerned about the nomenclature, and instead simply wish to impress upon the reader that our results indicate the liquid brine within the sea ice was re distributed vertically which resulted in changes to the carbonate system. We also add more information on this subject in the manuscript, as described in our responses to your specific comments below.*

IV. The effect of snow cover on CO_2 dynamics - a central aspect according to the title, should be better outlined by giving examples of scenarios of CO_2 evolution in growing and melting sea ice.

→*Agreed. And as suggested by other reviewer, as the impact of the snow is not really the main idea of the manuscript, we changed the title as "Sea ice pCO_2 dynamics and air-ice CO_2 fluxes during the SIMBA Experiment – Bellingshausen Sea, Antarctica'.*

V. One aspect that might be important for sea ice properties, CO_2-dynamics and evaluation and validity of methods and results, is missing in the discussion: the ice at the two sites was structurally different (mainly columnar at Brussels versus mainly granular at Liege).

→*Please see our responses to specific comments below.*

In the following specific comments I outline the deficits and suggest necessary improvements.

Specific comments

P 3265, L 5-19 –>Here most (Ikaite formation is not mentioned) processes affecting the carbon system are mentioned. Later in the paper there should be made an attempt to compare them quantitatively (in terms of expected variation).

→*The precipitation/dissolution of calcium carbonate in the ice is mentioned at the P3265, L 11-12. As explained in my previous respond, and according to the figure joined, we did not observe any precipitation of calcium carbonate. Therefore we are unable to discuss the role of this precipitation in our manuscript.*

P 3266, L 2 –> could strongly impact, better just impacts

→*We changed it as suggested.*

P 3268, L 17 - P 3269, L 20 –> I am missing a note on the determination of the brine salinity. The conversion between electrolytic conductivity and practical salinity that most

conductivity instruments use is only valid to 42, while Fig. 5 contains values as large as 70.

→*To avoid this problem, we diluted the samples using ultrapure water. We included this precision in the manuscript.*

P 3269, L 21 –> subsequent analysis - how much time did it take between sampling and analysis? This might have an effect on the measurement quality.

→*The ice was sampled in Oct. 2007 and the analyses were performed during the year 2013. The ice samples were stored all time in a freezer at -30°C, impeding any exchange with the atmosphere as, at this range of temperature, the sea ice brine volume was significantly lower than the permeability threshold (5%) as described by Golden et al [2007]. Storage in the dark will cancel primary production and the effect on photosynthesis on CO_2. Bacterial activity could in principle occur, but at these low temperatures rates must be negligible. Storage temperature is below reported bacterial rates in literature. We have already tested, in a few occasions, the impact of storage on gas composition for oxygen. It was clear in these tests that no significant change occurred after 3 to 4 years of storage. If bacterial activity did happen it would result in increased CO_2 concentrations. However, pCO_2 in bulk ice was very very low indicating that this was not the case, and that CO_2 diffusing into the ice core during storage was also not taking place. Thus, we assume that the storage of the ice will not affect the quality of our measurements.*

P 3270, L 1-4 –> After 24 h, the ice sample was assumed to have returned to the brine volume and chemical conditions at the in situ temperature.... Such a return is, after expulsion of brine from the core, very unlikely. I comment more on this aspect in the methods discussion.

→*In the paper presenting the method (Geilfus et al., 2012 - Journal of Glaciology, 58(208), 287-300) tests performed on ice samples (with bulk salinities of 4-6-8-10-16-23) showed that it takes less than 4 hours to warm up the ice from -30°C to -2°C. To ensure an optimal equilibration between our sample and the standard gas, we extend the equilibrium time to 24 hours. Also, the samples are selected in the very central part of the core (between 3 and 7 centimeters from the outside surface of the core), making it unlikely that brines were expelled from that part of the core during storage. More information is provided with the detailed comments from P 3277, L 26 - P3278, L 11.*

P 3270, L 6 –> This method is only valid if the ice is permeable at the in situ conditions. This condition is probably not the only problematic issue of the method (see last note on return of ice to in situ conditions: the validity will depend on the question to what degree the in situ microstructure will be restored after cooling/storage/warming). However, as you frequently mention/assume a 5% threshold for permeability, you should then indicate in the presentation below (Fig.6) for which samples this condition may not be fulfilled.

→*The ice structure won't affect the carbonate system of the ice samples and won't affect the method to measure the bulk ice pCO_2, as describe in the methodological paper (Geilfus et al 2012, Journal of Glaciology). The changes in the ice structure are inherent to any ice sample storage and temperature change since the initial extraction of the core to its storage for long (and even short) period of time and we can't avoid it. Only 3 point of the station on Oct. 16 had a brine volume slightly lower than 5% (4.1 - 4.4 - 4.6%). We will add a note in the figure caption of the Fig. 6 on this.*

P 3271, L 8 –> calculated brine salinity - you need to give a reference how brine salinity is computed, and you should write in the previous paragraph that calculated brine salinity is simply determined from temperature (If it is Cox and Weeks (1983), you may mention this in the beginning of the methods section).

→*We add to the methods section the following precision: "Calculated brine salinity profiles were determined from the in situ ice temperatures (after Cox and Weeks [1983])."*

P 3271, L 21 –> exhibiting an inverse relationship - Of course, this is due to calculation of brine salinity from temperature. It is not a particular result for your data (as an unexperienced reader might conclude from the text).

→*We can delete this sentence. You are right it doesn't bring new results in our dataset.*

P 3271, L 25-26 –> which is considered as the percolation threshold above which columnar sea ice is considered permeable to fluid transport - this is no result of your work and belongs to the discussion or conclusion sections.

→*Indeed, this is not part of our results. However, we moved this information in the introduction section where we first introduce the notion of sea ice permeability because it is still useful to the reader.*

P 3272, L 17 –> calculated brine salinities - sea note above P 3271, L 8

→*We deleted this sentence as suggested.*

P 3275, L 4-7 –> were nearly isothermal and likely permeable throughout, as the 5 brine volume was above 5% (Fig. 4, Golden et al., 2007). Subsequently the succession of warm and cold events with passing atmospheric fronts (Fig. 3) affected the temperature gradient within the ice cover significantly. - The note on the permeability appears a bit misplaced here, as the whole paragraph is about the thermal response.

→*Indeed, and as precision on the permeability threshold has already been given, we could delete the part: 'and likely permeable throughout, as the 5 brine volume was above 5% (Fig. 4, Golden et al., 2007).'*

P 3275, L 15-23 –> At the Brussels Site... - These considerations about convection are incomplete. First, note that you only have calculated brine salinities, yet there might not necessarily thermodynamic equilibrium when temperature changes take place on timescales of 1-3 days - the brine salinities may differ (indeed, it is what your data from brine sackholes appear to indicate). But also in case of thermodynamic equilibrium, I find it speculative to propose convection during the cooling period mentioned. First, the brine salinity gradient between 1 and 6 October is rather weak. Second, it is not only the salinity gradient that controls convective stability, yet also the permeability of the ice, that depends strongly on porosity, which in turn is lowered upon cooling. Brine channel convection that circulates large amounts of fluid within the ice is thus more likely to take place during warming, when porosity and permeability are increased. It may thus also well be that the higher porosity allowed rather for convection at the Liege site where the ice was warmer. While, on page 377, line 4, the work by Brabant (2012) is mentioned, where Rayleigh Numbers have been evaluated to discuss convection for the Liege and Brussels sites, one should note the many uncertainties in such approaches (e.g. Vancoppenolle et al.: Technical

Note: On the use of the mushy-layer Rayleigh number for the interpretation of sea-ice-core data, The Cryosphere Discuss., 7, 3209-3230). Finally, it should be avoided to base substantial parts of the discussion on a not peer-reviewed reference (Brabant, 2012).

→*In Lewis et al, [2011] 'brine convection' is not mentioned with those authors choosing to use the phrase 'overturning of brine, leading to an exchange with the underlying seawater'. Lewis et al., [2011] showed pictures of freshly extracted ice cores, thick section analyses and underwater photographs of brine drainage taken from underneath the ice. Brabant [2012] calculated the Rayleigh number and the nutrient distribution at these sites to confirm the observations of Lewis et al., [2011]. Although these data are not part of the peer-reviewed literature, neither is the technical note the reviewer has referenced and a final version of that work in The Cryosphere not foreseen, so we have to be careful with arguments for thesis data or against thoughts on a subject that remain unpublished. Calculations in a thesis are not the least bit speculative so we are more than confident of their inclusion in our work. We would be happy to include all these data in this paper were it not for a work currently in preparation containing these and other data. Finally, for this manuscript, we provide these data to help the reader to understand how the ice is affected by the variations of the air temperature.*

Now in the text, in a dedicated section entitled 'Impact of atmospheric forcing and snow thickness on the physical properties of the ice cover' we can read:

"The high brine salinities associated with the cold ice temperature at the top of the ice resulted in an unstable salinity gradient within the ice cover (Figure 4). This may have initiated overturning of brine and the mixing with underlying seawater with brine moving downward through the ice cover to be replaced by underlying seawater moving upward [Lewis et al., 2011]. To confirm this hypothesis, Lewis et al., [2011] reported presence of dissolution features observed on freshly extracted ice cores and thick sections as well as under-ice photographs clearly showing brine drainage at the ice bottom. In addition, analysis of the Rayleigh numbers (Ra) provided by Brabant [2012] suggests that brine drainage occurred at the Brussels site between 1 and 6 October (Ra >10) and between 11 and 16 October (6<Ra<7) which is also confirmed by vertical nutrient distribution in the sea ice [Brabant 2012]. At the Liège site, thicker snow muted thermal fluctuations within the sea ice reducing the magnitude of changes in brine volume and salinity. Hence, the variations in brine salinity and in the resulting density gradient were more moderate at Liège (Figure 4), resulting in a lower Ra [Brabant 2012]. It is also possible that some natural variability in the sea ice at the two sampling locations existed, though given the textural evidence of dynamic processes at Liège [Lewis et al., 2011] one might intuit that variation within salinity especially would be greater at Liège but that was not observed."

P 3276, L 2-8 –> The flooding...period. - The more likely cause for increase in TA and pCO_2 (brine salinity increase) should be mentioned first. The expression main control on the brine carbonate system sounds more complex than what most likely happens during warming: Brine is diluted by internal melting of ice, and this leads to lower concentrations of all chemical species that where not dissolved in the ice, and so also of CO_2.

→*Now the text reads:*

"At the Liège site, the pCO_2 variations were limited by small variations in ice temperature

under the thicker snow cover (Figure 4). Surface flooding on 18 and 23 October, might have hydrostatically forced high pCO_2 seawater laterally or upward through the ice matrix. An increase of the in situ brine pCO_2 and TA was observed on 18 October but these parameters decreased on 23 October (Figure 5-6). Therefore, the TA and pCO_2 fluctuations observed between the 18 and 23 October could also be solely explained by the changes in the thermal regime (cooling and then warming)."

P 3276, L 8-13 –> In addition...assumption. - How large variation in equilibrium constants would you expect, based on other systems? Would you really be able to resolve these, taking the errors, noise, and unaccounted physics into account? If not, then it is this what you should mention here, and not use the term validate.

→*We do not have concrete evidence that the equilibrium constants for the carbonate system in cold conditions are valid. However, this is the best we can do until these constants are somehow validated for sub zero temperatures. We now cite work suggesting that using these constants should be fine. We have added these references in the manuscript (i.e. Marion [2001]; Delille et al., [2007]).*

P 3276, L 23-27 –> However, convection...on 6 October... The assumption of convection is proposed due to similar brine carbonate properties sampled from sackholes on 6 October.

→*Our response to your comment for the P 3275, L 15-23 should also respond to this comment. The text as been reorganized:*

"However, it is surmised that vertical redistribution of brine between 1 and 6 October homogenized brine salinity, TA, pH_T, TCO_2 and pCO_2 between the two-sackhole depths sampled on 6 October. Sea ice temperature decreased between 11 and 16 October increasing the upper brine salinity and TA (Figure 5) while the brine volume shrank below the 5% level (Figure 4), which in theory should indicate impermeability of the sea ice [Golden et al., 2007] at that thickness, isolating the upper brine layer from those below. Therefore, large differences were observed in salinity, TA, TCO_2 and pH_T between the upper layer and lower brine samples."

A look at Fig. 5 shows that also the brine salinity of the deep and surface sackhole samples was very similar, while the temperatures and calculated brine salinities were not (the deepest sackhole brine on 6 October has a brine salinity of about 70, compared to a calculated value of 40 at 40 cm depth, Fig. 4). Hence, if the convection hypothesis is true, then the authors have sampled brine in a (convecting) non-equilibrium stage on 6 October. Such a convection event would be expected to lead to lower upper salinities, and one finds indeed some indications in Fig. 4. However, the upper salinities at the Brussels Site appear to fluctuate quite strongly, and they increase again after 6 October by a similar amount (Fig. 4). Such a behavior may better be explained by natural variability of ice properties (between the cores). This does not mean that convection is not active in this ice - it however cannot be confirmed for the proposed dates (see note above on P 3275, L 15-23). Another aspect to be mentioned here (discussed by the authors below) is that the sackhole technique may create an artificial convection pattern such that the brine sampled does not derive from the sackhole depth. The difference in brine properties between two sackhole depths may then derive from different inflow pattern into the sackholes. While these could indeed reflect the permeability of the ice, it makes a quantitative interpretation difficult, and even qualitative conclusions on convection in situ may be wrong. The discussion should

include these uncertainties and possibilities.

→*The now-named 'vertical redistribution of brine event', renamed in light of this reviewers comments, has been elucidated by Lewis et al [2011] and Brabant [2012] through salinity measurement, Rayleigh number calculation and nutrient concentrations measured in the ice, all of which is provided in the present manuscript. Our work also contains the well-known caveats regarding the sampling or brine from sackholes. We have added the following to the discussion in order to speak to the reviewer's point about inter-core variability at the sites "It is also possible that some natural intra-site variability within the sea ice existed at the two sampling locations. Given the textural evidence of dynamic processes at Liège [Lewis et al., 2011] one might intuit that variation within salinity especially would be greater at that location but it was not observed."*

P 3276, L 28 –> less permeable - Earlier you noted 5% as a threshold - why then you term it only less permeable and not impermeable?

→*We changed the text as follows:*

"Sea ice temperature decreased between 11 and 16 October increasing the upper brine salinity and TA (Figure 5) while the brine volume shrank below the 5% level (Figure 4), which in theory should indicate impermeability of the sea ice [Golden et al., 2007] at that thickness, isolating the upper brine layer from those below."

P 3276, L 27 - P 3277, L 1 –> On 16 October...lower brine samples. - The larger differences in brine salinity and carbon parameters on 16 October are expected as a consequence of larger temperature difference, - they do not need to be related to a permeability threshold. Note also that the brine from the surface sackhole had a salinity slightly above 60, which is much less than the calculated brine salinity in Fig. 4, where I estimate roughly 90 as an average for the upper 15 cm. Again, this indicates the difficulty to interpret the sackhole observations quantitatively.

→*By providing this information, we want to highlight the fact that the low brine volume content in the upper part of the ice could isolate the brine from the rest of the ice column. The temperature is low, so the brine volume is low. We modified the text to include this notion. Now we can read:*

"Therefore, large differences were observed in salinity, TA, TCO_2 and pH_T between the upper layer and lower brine samples. At Liège, thermal fluctuations in the ice cover were limited by thicker snow cover, resulting in small differences in salinity, TA, pH_T, TCO_2 and in situ pCO_2 between the upper and lower brine sample depths (Figure 5)."

P 3277, L 7-14 –> Brine...snow. Again, it appears that also pCO_2 is controlled by dilution and concentration of brine during internal melting and freezing - this can be said more clearly than in these sentences.

→*Now we can read:*

"Brine pCO_2 and, to a lesser extent, bulk ice pCO_2 both seem to follow the observed cyclical variations in the ice temperatures (Figure 6) indicating the dilution – concentration effect in large part controls the pCO_2."

P 3277, L 14-16 –> In addition, the greater changes in porosity throughout the ice column at

the Brussels site (Fig. 4) led to more variability in brine pCO_2 than in the bulk ice (Fig. 6). Please explain, why you now mention porosity as an additional factor. Do you actually mean brine dilution/concentration? The porosity is a structural that is computed from bulk ice properties (temperature and bulk salinity) - why should this then have a larger effect on brine pCO_2 than on bulk ice pCO_2? One would expect the opposite, and this casts (see also in other comments) doubt on the bulk ice pCO_2 measurements.

→*We have changed the term porosity for brine volume to address this comment and clarify the intent of this sentence. If the changes of brine volume are more important at the Brussels site, it means that changes in temperature and salinity play an increased role on the pCO_2 signature of the brines that collect in the sackhole! Our opinion is that while bulk ice pCO_2 probably most of the time does not include a brine channel, it mainly reflects changes in the secondary porosity (brine pockets, intra-crystalline brine lamellae…). On the contrary, brines in the sackholes primarily collect and overemphasize the signature of brine tubes and brine channels at all levels above the bottom of the hole. These more easily convey larger pCO_2 changes from brine volume changes in the upper layers and eventually sea water intrusions from flooding when present. . Now we can read:*

"In addition, the greater changes in brine volume content throughout the ice column at the Brussels site (Figure 4) led to more variability in brine pCO_2 than in the bulk ice due to the effects of brine dilution – concentration (Figure 6)."

P 3277, L 17-19 –> However, the flooding observed.... If this indeed was the case, and flooding had a major impact on pCO_2, one would expect larger values in the brine close to the ice-seawater interface. In Fig. 6 this does neither seem clearly evident on 18 or 23 October. The described increase in brine pCO_2 may thus again simply relate to brine concentration during cooling/internal freezing.

→*We changed the text as follows:*

"Surface flooding on 18 and 23 October, might have hydrostatically forced high pCO_2 seawater laterally or upward through the ice matrix. An increase of the in situ brine pCO_2 and TA was observed on 18 October but these parameters decreased on 23 October (Figure 5-6). Therefore, the TA and pCO_2 fluctuations observed between the 18 and 23 October could also be solely explained by the changes in the thermal regime (cooling and then warming)."

P 3277, L 20-26 –> From...measurements. - As noted above, it would be helpful to mention the discussion of the sackhole technique already in the discussion of convection, and point out the danger that the results reflect sackhole-induced convection - and not an intrinsic process in the ice. It would also be useful to present at least a rough estimate of how much CO_2 the sackhole brine might absorb from the atmosphere, either based on controlled experiments or theoretical considerations.

→*We already discussed about the 'convection' problem earlier in our response. In this part we are exactly discussing about the difference between the bulk ice pCO_2 and the in situ brine pCO_2 using the sackholes technique.*

We used the sackholes method as it was previously used by Gleitz et al. [1995] and recommended by Papadimitriou et al. [2004] as the best current method to sample brines for chemical studies (especially compared to centrifugation). Anyway, "best" does not mean

"accurate". Hence, we assessed the error due to gas exchange during filling of the sackholes. We assumed that the sackhole was half filled within 15 minutes and that brine volume increased linearly. We used in our calculation the worst scenario, meaning the larger air-brine gas gradients we observed during the experiment. We carried out a incremental computation at each minute, taking into account the increase of the brine volume, change of the concentration of the brine due to air-brine gas transfer assuming that the stopper was not air-tight (maintaining the pCO_2 gradient between brine and atmosphere) and computed the air-brine gas transfer at each minute. Air-brine gas transfer was computed using the gas transfer velocity k600 proposed by Crusius and Wanninkhof [2003] for gas exchange over a lake at low wind speed (conventional gas transfer velocity formulations lead to a transfer equal to zero with a wind speed of zero as it is the case in the sackhole), Schmidt number (Sc) were taken from Wanninkhof [1992] CO_2 and we assumed a -2/3 power dependence of Sc as is recommended at low wind speed.

	Temp. (°C)	Salinity	Concentration	Sc	k	flux	Error	Relative error
CO2	-1.1	27.76	25 ppm	2217.0	0.4184	0.50 µmol	0.08 ppm	0.34 %

Table 1 Error due to gas exchange between brine and the atmosphere during filling of the sackhole

Air-brine gases transfers and related biases on measurements are reported on the Table 1. The error on pCO_2 measurement is well below the precision, not significant and do not affect the conclusions of the manuscript.

P 3277, L 26 - P3278, L 11 –> In comparison...window. Here bulk ice pCO_2 and brine pCO_2 measurements are discussed. First I cannot understand, why small isolated brine pockets are included in the bulk ice measurement (that due to the methods section is only valid for permeable ice samples).

→*The bulk ice pCO_2 takes into account the CO_2 dissolved within the brines and into its gaseous form as gas bubbles trapped within the ice structure. The brine pCO_2 is a direct measurement of the CO_2 concentration dissolved within the brine. Therefore, if a small brine pocket is totally isolated (meaning not connected to the brine channel network) within the ice structure, it may not be possible to sample it using the sackholes technique. While, measuring the bulk ice pCO_2, we will have the possibility to take this brine pocket into account during our analysis. We added these precisions in the text. This difference may explain the difference between the two different types of measurements. For more details on the analysis of the bulk ice pCO_2, please refer to the methodological paper: Geilfus, N. X., B. Delille, V. Verbeke, and J. L. Tison (2012), Towards a method for high vertical resolution measurements of the partial pressure of CO2 within bulk sea ice, Journal of Glaciology, 58(208), 287-300.*

Second, while properly determined bulk ice and brine pCO_2 data should not differ much, they show differences of up to an order of magnitude.

→*According to our previous response, the bulk ice and brine pCO_2 may differ.*

I thus feel that a more critical discussion of the bulk ice method is in order. One may imagine the following scenario of an ice sample that is cooled, stored and, prior to pCO_2 measurements, again warmed to its in situ temperature: When the bulk ice is cooled to -

23 °C, this will first result in expulsion and loss of brine, which implies a loss of CO_2. Also, during the cooling and internal freezing of the core, CO_2 concentrations are increasing above the atmospheric background, and CO_2 will be lost from the sample, as long the brine network stays interconnected. The situation becomes more complex below -23 °C, even much salt is precipitating in from of hydrohalite, and brine network connectivity will likely drop to very low values. As salt crystal formation induces density changes and brine redistribution, the microstructure after redissolution (prior to pCO_2 measurements) may finally differ from the in situ values (e.g., more salt may reside in isolated inclusions). Finally, the sample may still loose CO_2 from its outer volume (connected to its surface), even once it has become impermeable on larger spatial scales. All these factors are difficult to quantify, but upon returning to in situ temperatures, the pCO_2 will be less than in the field.

→*The reviewer is discussing about the impact of the storage (long term or not) of the ice samples for the bulk ice pCO_2 measurements, how the ice sample can go back to its in situ conditions after storage at low temperature (-30°C).*

- *We recognize that brine may have been lost upon extraction of the core from the ice (Barber and Yackel, 1999). We estimate brine loss to be approximately 5% based on unpublished data collected during the IPY-CFL project in 2008. The measurements were done by replicate samplings (core extraction) from a small area of uniform first-year sea ice (area of about 10 m^2). Salinity was measured from these cores, and the variability in the measurements was used to estimate the potential brine loss. Thus, the expectation was that the brine volumes would be approximately equal over this small area, and most of the variability would be due to variable brine drainage.*
- *The bulk ice pCO_2 were performed in the center section of the ice core to avoid any contamination during the manipulation but also because if brine were lost during the storage it will be, preferentially, from the extremities of the core, leaving the center 'undisturbed'.*
- *Also, the cores are cooled down very quickly to the storage temperature, from the outside to the inside of the core. Therefore, if CO_2 is lost it is from the outer surficial part of the core which: a) was not sampled and b) quickly formed an impermeable outer "ring" preventing loss from the inner parts*
- *The changes of the microstructure of the ice during the storage do not affect the CO_2 contents within the ice or the ability of the method to work properly. And this point has been discussed in the paper presenting the method (Geilfus et al., 2012).*
- *The precipitation of salt will not affect either the pCO_2 content in the ice because the ice is warmed up to reach its in situ temperature. Therefore any salt precipitating at low temperature will dissolve during the warming period. The main salt affecting the carbonate system will be the precipitation of ikaite. And this precipitation is strongly affected by the temperature of the ice. Indeed, ikaite will precipitate during its storage, but as the ice will warm up to its in situ temperature, these ikaite crystals will dissolve (Rysgaard et al., 2014).*
- *If all these processes where that important, they should concur to lower pCO_2s at **all** levels in **all** cores. However, 3 out of 5 bulk ice profiles are similar to the brine pCO_2 at Liège, and 2 out of 5 in Brussels…and this is coherent with our interpretation with respect to differences in thermal regime due to the insulating snow cover.*

According to the data the loss of CO_2 appears to be rather large.

→*We again do not agree, according to the Fig. 6, 6 profiles on 10 shows bulk ice pCO_2 with similar concentration than brine pCO_2. And we attempt to discuss the differences and why the surface layer of the ice is generally low.*

Moreover, the data in Fig. 6 indicate that the bulk ice pCO_2 stays at a similar level for all stations, while the sackhole brine values vary much more with temperature (as one would expect from concentration/dilution of brine). One might thus also suspect that the bulk ice method has a tendency to produce results that may rather present the cooling procedure (e.g., minimum temperature and cooling rate, sample size and open porosity fraction at its surface) than its intrinsic pCO_2.

→*The variation due to the difference in ice temperature should also be observed in the bulk ice pCO_2 just on a smaller scale. The reason why is explained in P3278 L6-11.*

If this would be the case, these data would be rather difficult to interpret. Regarding the vertical pCO_2 profiles derived, neither the absolute values nor the vertical distribution may have to do with natural conditions. The statement Therefore, the bulk ice pCO_2 values changes are less variable, reflecting mostly internal melting due to temperature and salinity changes in the ice cover needs to be tested against this hypothesis, i.e. that the bulk ice pCO_2 measurement procedure is problematic.

→ *See previous responses.*

P 3278, L 13-18 –> Dumont (2009)...pC02. I wonder if these notes deserve to be an extra paragraph. I rather suggest to include it as a note in the convection discussion. If larger variability at the Liege site may be related to higher convective activity, or to natural spatial variability between cores, or to the different structure described in Lewis et al. (2012) is a question that also arises here.

→*The lines 13-18 of the P3278 are related to Chl a concentrations in the ice. We specify that the variations of Chl a are not associated with the variations of pCO_2, excepted at one occasions, during a flooding event. Therefore why should we include this description within the convection discussion?*

P 3278, L 21 - P 3279, L 13 and Fig. 10 –> The bulk ice...Geilfus et al. (2012a). - According to this review/comments above the present data apparently require a more complete discussion, before a comparison with the Arctic should be presented. Beside the noted aspects (measurement technique, possible convection) the authors should also discuss the differences in ice type (mainly columnar at Brussels, mainly granular with strong layering at Liege), as it may well be an important aspect of permeability and potential CO_2 fluxes. This is of particular importance as Arctic sea ice is known to be primarily of columnar nature, contrasting the tendency of granular ice production in the Antarctic.

→*This sentence now reads:*

"Although based on limited data, Antarctic sea ice may have lower pCO2 values than Arctic sea ice at the same ice temperature (Figure 10), although differences in the sea ice texture and dynamical forcing between the two poles are important and may have substantial effects on permeability (and therefore fluxes) and should be further investigated. It is noteworthy that

the observed range of concentrations suggests that Antarctic sea ice becomes undersaturated in CO2 relative to the atmosphere early in the winter–spring transition and reaches levels not observed in Arctic sea ice until much later in the spring decay process [Geilfus et al., 2012a,b; 2014; Crabeck et al., 2014]."

We hope providing these caveats allays the reviewers concern and spurs further research into these potentially important areas.

Regarding Fig. 10a, the bulk ice temperature versus bulk ice pCO_2, I would rather plot pCO_2 versus calculated brine salinity. Due to the dependence of brine salinity on temperature such a plot will look similar, yet I rate it more useful, as it shows brine dilution/concentration, on which pCO_2 apparently strongly depends. The scale should be changed, as in the present Fig. 10 only little detail can be seen.

→*We choose to plot the bulk ice pCO_2 versus bulk ice temperature to make an easier comparison with the plot of the in situ brine pCO_2 versus brine temperature. As the reviewer notes, making the same plot using the brine salinity will result in the same plot but then the comparison with the brine will be lost. In addition, the figure 10c represents the relationship between the bulk ice pCO_2 and the brine volume fraction of the ice. We chose the brine volume fraction because it takes into account BOTH the bulk ice salinity AND the ice temperature (which is explained P3279 L9-13).*

About the scale of the figure 10: having the same scale between 10a and 10b allow the reader to realize that all data from the bulk ice (10a) are in the same range as the brine data (10b). The cloud of data is located at the same position on the X-axis. Which is a point that may be lost if the scale was different.

Next, it is important, in particular due to the uncertainty to what degree the method is valid to obtain bulk ice pCO2, to mention and discuss possible differences in the sampling, storage and measurement procedures of the different datasets. For example does the Arctic sea ice from Geilfus et al. (2014) appear to have been stored at -20 °C, compared to -30 °C in the present study. While at the lower temperature most salt will precipitate as hydrohalite, before it is redissolved prior to pCO2 measurements, this is not the case during storage at -20 °C. Salt crystal precipitation/dissolution involves large density changes, and very likely changes in the microstructure that may be fundamental for the validity of the pCO2 measurements. Please provide a comparison of all the data compared.

→ *The ice samples from Geilfus et al [2014] come from the melting period in Resolute bay. The salinity range of these samples are from -3 to 0°C. For this range of temperature, a storage at -20°C is low enough to ensure an appropriate storage impeding any gas exchange during the storage. About the precipitation of salt, yes, the storage will promote a precipitation of salt. However, as explain earlier, during the equilibrium at the in situ temperature, the salts will dissolve again. This processes is also explained in Rysgaard et al [2014]. Therefore this precipitation will not affect our measurement and we don't need to provide any comparison.*

In Fig. 10c it appears to me that Arctic data have been obtained at lower brine porosities, with corresponding larger bulk pCO_2 values. For the porosity regime where data from both regions exist, I cannot make up a large difference by eye. For the comparison of Arctic versus Antarctic bulk ice pCO_2 I thus recommend that you make a statistical significance test for only the brine volume ranges for which data are available in both regions.

→*The range of brine volumes shown in Figure 10C for the Arctic is smaller than the range of brine volumes in the Antarctic, however, these brine volume data are in no way indicative of different polar regimes and it would be ill-advised to treat them as such. Further, they are from different times in the annual cycles at both poles. The interest of this figure is to integrate the variations of T and S (in the same plot) versus the bulk ice pCO_2, as data reporting bulk ice pCO_2 are from different times of the year. Therefore, we could conclude, according to the figure 10c, that if the brine volume is low (because of low T and/or high S) the bulk ice pCO_2 is high while if the brine volume is high (because of high T and/or low S), the bulk ice pCO_2 is low.*

P 3279, L 9-10 –> The brine volume combines the effect of the high salinity and low temperature at the same time. - The brine volume is indeed the property that (in thermodynamic equilibrium) follows from bulk ice salinity and temperature, yet it does not combine these effects. Rather it is an average property of the pore space. It is the brine salinity (or, due to their relationship, indirectly the ice temperature) that correlates with pCO_2 in a clear physical manner - via brine dilution and concentration (as apparent from the in situ brine observations, Fig. 10b). The effect of brine volume or porosity is more complex, as it affects the permeability of ice in situ (and thus CO_2 transport processes), as well as structural effects that influence the validity of the method to obtain bulk ice CO2. Please distinguish this more clearly.

→ *We have deleted this sentence from the discussion.*

Due to the noted uncertainties with the procedures/methods to obtain bulk ice pCO2, I rate the sackhole brine results in Fig. 10b as physically most meaningful. As mentioned for bulk pCO2 I recommend to show in situ brine pCO2 versus brine salinity, and per- form a statistical test to determine the significance level of an eventual difference between Antarctic and Arctic brines. Also here a comparison of the sackhole sampling procedures (sampling times, depth) would be helpful to evaluate if difference in the measurement protocols might have influenced the results.

→*We are not in a position to qualitatively rate our results on a scale of "most meaningful" to "least meaningful". We have been very careful to keep any and all opinion out of our work and we would like it to remain as objective as possible. Second, any statistical testing of the difference between Antarctic and Arctic brine would be invalidated by the large differences in the ice physical properties due to the season they were sampled in amongst a myriad of other factors.*

P 3279, L 10-12 –> It should also be noted that both in the Arctic and in the Antarctic, spring sea ice can become undersaturated in CO2, while the underlying seawater is still supersaturated. - In view of the process of internal melting of sea ice during warming, implying dilution of brine, this is something one might expect. If you note this here again you should outline the mechanisms behind, eventually some possible paths of the history of pCO2 during freezing-melting, for example 1. seawater at atmospheric pCO2 freezes and pCO2 increases to values highjer than in the atmosphere, 2. sea ice looses CO2 due to this gradient as lomg the ice is permeable, 3.snow falls on the ice, which warms and, by dilution of brine, decreases pCO2, 4. Strong warming with a snow cover present dilutes the brine further, etc... Discuss, if there are differences between Antarctic and Arctic sea ice that would give rise to different scenarios.

→*We decline to delve any further into listing the potential mechanisms for oversaturation of seawater beneath ice because we have not presented any data to render these mechanisms more than conjecture.*

P 3279, L 14-28 –> During this study, ...atmosphere. - The described effect of the snow cover and difference between the sites is interesting. However, I rate the following aspects as noteworthy. First, as pointed out above, the crystal structure of the ice was different at the two sites. Please discuss some more details, eventually by referring to the paper of Lewis et al. (2012).

→*We have referred to Lewis et al. [2011] repeatedly on this subject throughout our work.*

Second, removing snow lowers the surface temperature, increases the brine salinity, and thus changes the pCO2 gradient between brine and atmosphere - an important parameter that determines the surface fluxes.

→*We don't think that, within the 5 min used to do the flux measurements, the change of temperature will be so significant that the CO_2 flux will change that much. It sounds like the reviewer has access to similar measurements, so he should know that the surface temperature within the chamber does not change appreciably in 5 minutes….*

Could there be a difference between the Liege and Brussels Sites due to sampling dates?

→*Yes, there is different flux between Liege and Brussels due to different sampling dates… The ice will have different temperature, and a different pCO_2.*

With regard to the final sentence As suggested by Delille (2006), Nomura et al. (2010a, 2013), and Geilfus et al. (2012a), the magnitude of the CO2 fluxes depends on the pCO2 gradient between the ice and the overlying atmosphere, I suggest that you mention that this is a physical law that can be found in the basic literature, and discuss shortly the difficulties in predicting such fluxes, due to lack of knowledge in other parameters (surface turbulence, surface permeability, etc...).

→*You are right; this is basic physical law that we delete from the manuscript.*

P 3280, L 14-28 –> Conclusions. - Most of what should be changed here follows from the comments in the discussion. I recall the following aspects:

→*The conclusions has been changed to highlight our main observations:*

- *Spring sea ice pCO_2 swiftly responds to short term meteorological events, with redistribution processes linked to the brine network dynamics,*
- *The spring sea ice pCO_2 is undersaturated and largely controlled by the brine dilution upon warming, although a potential impact of primary production could contribute to the undersaturation,*
- *Despite episodic flooding events brining supersaturated seawater in the brine network, the spring sea ice remains undersaturated and a sink for atmospheric CO_2,*
- *Both techniques, measuring the pCO_2 within sea ice and brine, address different parts of the brine network*

L 2-7 –> That snow on sea ice modulates the heat fluxes, and thus the ice temperature, is known from many other studies. The statement that Our observations suggest that snow is

a key component in the changes occurring in the carbonate system within the sea ice, is too strong regarding the uncertainty and limited validity of the methods (sackhole brine, bulk pCO2), as well the limited flux dataset and temporal resolution of sampling. If you want to highlight the effect of snow cover on carbon chemistry, you may say that your limited observations so far support what is expected based on basic sea ice physics.

→*We delete the part making reference on the impact of the snow on the T changes in the ice cover. It is, indeed, not part of our results. We can now read:*

"The succession of warm and cold events impacted the physical properties of the sea ice and its inorganic carbon dynamics. Snow thickness modulated the heat flux to the sea ice, which impacted its salinity and therefore the sea ice carbonate system. Less snow and larger temperature variations created larger variations in brine salinity, TA, TCO_2, and brine and bulk ice pCO_2."

About the discussion on the sackholes, please see previous responses.

L 8-14 –> The conclusion on convection is speculative and I rate the data as insufficient (or insufficiently discussed) to support it clearly.

→*See previous response about the "convection". We can read in the conclusions:*

"In addition, the combination of unstable salinity gradients within the ice cover and episodic warming events initiated vertical brine redistribution at the low-snow site on two occasions homogenizing brine properties vertically. At the end of the survey, flooding occurred due to snow loading at the Liège site, bringing high pCO_2 seawater into the brine system."

L 15-19 –> In my opinion the results indicate differences in the potential and validity of the methods, not of the intrinsic in situ CO2 dynamics. Main points are (i) to what degree the sackhole brine pCO2 is reliable (how much uptake of atmospheric CO2 may take place) has not bee shown; (i) the bulk ice pCO2 measurements may reflect aspects of the sampling, storage and measurement protocol that are difficult to quantify and relate to in situ physical properties and pCO2.

→*I think we have covered all these questions in our previous comments and correction to the manuscript.*

L 20-24 –> The ice cover as a sink of atmospheric CO2 - it should be noted that the CO2 fluxes with snow on ice were only marginally different from zero. The statement that these fluxes were largely independent on the seawater conditions seems in some contradiction on what the authors mention about flooding events and convection.

→*This sentence now reads:*

"At both sampling sites, the ice cover acted as a sink for atmospheric CO_2, even despite episodic flooding by supersaturated seawater. Thus, during early spring the inorganic carbonate system in the sea ice of the Bellingshausen Sea behaved as a transition layer between the ocean and the atmosphere, reacting to atmospheric forcing and from episodic interactions with the seawater."

Any mention of convection in the work has been removed at the request of this reviewer.

Technical corrections

As I think that considerable rewriting is needed, I restrict this section to notes on the figures:

Fig. 2 –> Do you have variability in snow thickness measurements as for the ice thickness? The freeboard is difficult to see/read when printed.

→*No, unfortunately we only have the mean snow thickness, the information provided in the manuscript.*

Fig. 5 –> It would be helpful to distinguish the Liege and Brussels stations by color coding

→*Indeed, that's why, in the figure 5, Brussels stations are in black and Liege stations are in white…*

Fig. 10 –> As mentioned, a plot of pCO2 versus brine salinity (and measured and calculated) would be helpful. The y-scale in 10a should be changed.

→*We already explained our choice earlier in our response.*