Review of tc-2014-88

This is a review of the manuscript *Impact of snow cover on CO2 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 pCO2 in bulk ice and brine over the coarse of one month, comparing the pCO2 evolution for two sites with different snow conditions, for a succession of warming and cooling events. Main findings proposed are (i) the CO2 system was primarily controlled by physical and thermodynamic processes, with total alkalinity (TA), total dissolved inorganic carbon (TCO2) and CO2 partial pressure (pCO2) of bulk ice and brine salinity all increasing/decreasing with cooling/warming of the ice; (ii) the ice was undersaturated in CO2 with respect to the atmosphere, and thus acted as a sink for atmospheric CO2; (iii) the temperature fluctuations were reduced for the site with thicker snow cover, with the associated CO2 system parameter response, as well as the CO2 ice-atmosphere fluxes showing the same behaviour.

The paper adresses, with the evolution of the CO2 syste, an important aspect of sea ice biogeochemistry in general, as well relevant questions concerning ocean-ice-atmosphere exchange of CO2. The paper is well structured and most paragraphs are easy to read and understand. Observations are presented properly (in figures and text). Although the findigs/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 pCO2 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:

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 (CO2 solubility, precipitation/dissolution of Calcium Carbonate and/or Ikaite crystals), is mentioned in the introduction yet lacking in the discussion.

II. The large differences between bulk ice and brine pCO2 call for a more (self-)critical discussion, including the question if the applied procedure to obtain the pCO2 profiles of bulk ice gives useful information at all.

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.

IV. The effect of snow cover on CO2 dynamics - a central aspect according to the title, should be better outlined by gving examples of scenarios of CO2 evolution in growing and melting sea ice.

V. One aspect that might be important for sea ice properties, CO2-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).

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).

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

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.

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.

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.

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.

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).

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).

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.

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

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.

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).

P 3276, L 2-8 –> *The flooding...period.* - The more likely cause for increase in TA and pCO2 (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.

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*.

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. 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.

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

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, weher I estimate roughly 90 as an average for the upper 15 cm. Again, this indicates the difficulty to interpret the sackhole observations quantitatively.

P 3277, L 7-14 –> *Brine...snow.* Again, it appears that also pCO2 is controlled by dilution and concentration of brine during internal melting and freezing - this can be sayed more clearly than in these sentences.

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 pCO2 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 pCO2 than on bulk ice pCO2? One would expect the opposite, and this casts (see also in other comments) doubt on the bulk ice pCO2 measurements.

P 3277, L 17-19 –> *However, the flooding observed....* If this indeed was the case, and flooding had a major impact on pCO2, 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 pCO2 may thus again simply relate to brine concentration during cooling/internal freezing.

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 CO2 the sackhole brine might absorbe from the atmosphere, either based on controlled experiments or theoretical considerations.

P 3277, L 26 - P3278, L 11 –> *In comparison...window.* Here bulk ice pCO2 and brine pCO2 measurments 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). Second, while properly determined bulk ice and brine pCO2 data should not differ much, they show differences of up to an order of magnitude. 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 pCO2 measurements, again warmed to its in situ temperature: When the bulk ice is cooled to -23 ℃, this will first result in expulsion and loss of brine, which implies a loss of CO2. Also, during the cooling and internal freezing of the core, CO2 concentrations are increasing above the atmospheric background, and CO2 will be lost from the sample, as long the brine network stays interconnected. The situation becomes more complex below -23 ℃, ehen 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 pCO2 measurements) may finally differ from the in situ values (e.g., more salt may reside in isolated inclusions). Finally, the sample may still loose CO2 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 pCO2 will be less than in the field. According to the data the loss of CO2 appears to be rather large. Moreover, the data in Fig. 6 indicate that the bulk ice pCO2 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 pCO2. If this would be the case, these data would be rather difficult to interpret. Regarding the vertical pCO2 profiles derived, neither the absolute values nor the vertical distribution may have to do with natural conditions. The statement *Therefore, the bulk ice pCO2 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 pCO2 measurement procedure is problematic.

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.

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 CO2 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.

Regarding Fig. 10a, the bulk ice temperature versus bulk ice pCO2, I would rather plot pCO2 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 pCO2 apparently strongly depends. The scale should be changed, as in the present Fig. 10 only little detail can be seen.

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 ℃, compared to -30 ℃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 ℃. Salt crystal precipitation/dissolution involves large density changes, and very likely changes in the microstructure that may be fundamental for the validty of the pCO2 measurements. Please provide a comparison of all the data compared.

In Fig. 10c it appears to me that Arctic data have been obtained at lower brine porosities, with corresponding larger bulk pCO2 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 pCO2 I thus recommend that you make a statistical significance test for only the brine volume ranges for which data are available in both regions.

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, indiretly the ice temperature) that correlates with pCO2 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 CO2 transport processes), as well as structural effects that influence the validity of the method to obtain bulk ice CO2. Please distinguish this more clearly.

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 perform 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.

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.

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

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

Technical corrections

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

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

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

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.