

Response to author comment on my review of tc-2014-88

The authors have clarified many aspects and improved the paper. However, I still find that the following points need improvements.

- The authors claim that processes related to cooling-warming of samples prior to bulk CO₂ measurements likely will not affect the results; I give some more arguments and reference from field work that indicate fundamental changes in microstructure during similar cooling-warming, and suggest possible effects on the method. These should be considered a bit more critically in the text.
- One main conclusion proposed by the authors is now: *Both techniques, measuring the pCO₂ within sea ice and brine, address different parts of the brine network.* However, in this connection the authors have corresponded with arguments (that are also mentioned in the paper) that I find confusing (e.g. that the bulk pCO₂ measurements include information from isolated brine pockets). Have I misunderstood something in the Geilfus et al. (2012) methodology paper? As I understand the latter, pCO₂ is measured from equilibration of a standard gas with the ice samples warmed to in-situ temperatures, and it is then the connected brine pore space that the gas equilibrates with, not the isolated brine pockets. If I am correct here, then this should be corrected in the paper (e.g. Line 418), and it should be noted that both the bulk pCO₂ the in situ pCO₂ methods can only measure CO₂ within interconnected brine networks.

Regarding the comparison of the methods, the conclusion that in situ brine pCO₂ and bulk ice pCO₂ relate to different fractions of the brine network (the most mobile one), is acceptable, provided the critical notes on the in situ sack-hole technique by the authors. However, a note on disadvantages of the bulk ice pCO₂ technique, especially the possible consequences of microstructure change, brine expulsion and air space (see my comments below) need to be added.

- Fig. 10 and text: A subsection 5d is termed “comparison” between Antarctic and Arctic. Based on Fig. 10 a difference between the regions is supposed, and written in the present text (L. 447...). In my opinion this should be tested statistically, even if the causes are unknown. Also, Fig. 10a would be, as noted, much more informative, if the y-scale would be changed.
- I still find some passages about brine convection speculative, mentioning too frequently the work by Brabant (2012) that is not per-reviewed. Also, if, as on Lines 331 ff., Rayleigh numbers estimated by Brabant (2012) are explicitly mentioned, then Ra should at least be defined. In my opinion, Brabant (2012) may be referenced, yet not in the detail given here.

Provided that the authors address these aspects in the specific comments, which I rate as minor improvements, I recommend the paper for publication in “The Cryosphere”.

Sönke Maus, Trondheim, 20.10.2014

Specific comments

The specific comments on the unclear topics include my original comments (including *authors text in italic*), *the authors answers in italic*, **my response in bold**.

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 CO₂. 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 CO₂ concentrations. However, pCO₂ in bulk ice was very very low indicating that this was not the case, and that CO₂ 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.*

->-> **A problem with 6 years of storage may be the possibility of crystal structure rearrangement (due to presence of liquid also at -30 °C). This may add to my arguments below, that the in situ sea ice microstructure very likely cannot be restored by cooling-warming of samples. However, my main concern, as outlined below, is the cooling process, and a relatively short time interval after it.**

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...*

->-> **Brine is not expelled *during storage* but during cooling. Also, as brine expulsion is the consequence of expansion during partial freezing of brine, and this process is expected to take place everywhere in the sample, also in the center. I comment further on this below in the note on P 3277, L 26-.**

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 pCO₂, as describe in the methodological paper (Geilfus et al 2012, Journal of Glaciology).*

—>> **According to the Geilfus et al 2012 methodological paper you mention, the method to measure bulk pCO₂ is only valid if the ice is permeable at in situ conditions. Hence, the ice structure may affect this method.**

P 3277, L 26 - P3278, L 11 —> *In comparison...window.* Here bulk ice pCO₂ and brine pCO₂ 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 pCO₂ takes into account the CO₂ dissolved within the brines and into its gaseous form as gas bubbles trapped within the ice structure. The brine pCO₂ is a direct measurement of the CO₂ 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 pCO₂, 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 pCO₂, 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*

—>> **As noted in my first review, I cannot understand, why small isolated brine pockets can be expected to be included in the bulk ice pCO₂ measurement described in the Geilfus et al. 2012 methodological paper. As I understand this method, pCO₂ is measured from equilibration of a standard gas with the ice samples. It is then the connected brine pore space that the gas equilibrates with, not the isolated brine pockets as you appear to claim here. Indeed, that Geilfus et al. 2012 mention several times that the validity of the methods requires a permeable sample, while here something different is proposed, appears confusing.**

P 3277, L 26 - P3278, L 11 —>... 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 °C, 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 °C, when 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.

—> *The reviewer is discussing about the impact of the storage (long term or not) of the ice samples for the bulk ice pCO₂ 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). 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 pCO₂ 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 CO₂ 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*

->->I expand my comments on expulsion and microstructure changes: First, as noted above, brine expulsion is a consequence of expansion during partial freezing of brine, and this density change will also affect the center of samples. In my experience samples are not sealed upon cooling, yet the necessity to expel brine (due to internal expansion) creates tiny networks through which the brine reaches the sample surface. Second, if the sample would indeed be sealed from the outside during cooling, brine expulsion being absent, I would expect that for very rapid cooling the high internal pressure leads to cracking (such cracks may be tiny, yet they could render the sample artificially permeable, influencing the

pCO₂ measurements). It is further important to note that, when the ice is warmed again, internal melting of ice leads to contraction (brine being more dense than ice), and a certain fraction of the pores will not be re-filled with brine, yet with air/gas. Note also that, when the ice is warmed again in the lab, there is no hydrostatic pressure from the underlying water, that forces the brine back into the channels. A complete restoring of in situ ice conditions during cooling-warming of samples in the lab is thus very unlikely. For the bulk ice pCO₂ measurements this may have several consequences: (i) the sample contains considerable amounts of air, influencing the methods accuracy as discussed by Geilfus et al. 2012 (e.g. the concentration of standard gas, that is reported in Geilfus et al., 2012, yet not in the present figure 10); (ii) interdispersed air and brine pockets may now fill the original channels, affecting permeability/fluxes; (iii) the permeable fraction of the pore space may have changed; (iv) as long the opposite is not proven, there may have been gas fluxes through tiny networks during cooling and storage: this may not be falsified by comparing measurements after for example 1 and 4 years, as these fluxes might take place rapidly.

- *The changes of the microstructure of the ice during the storage do not affect the CO₂ 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).
->->As noted above, microstructure during cooling-warming as well as storage changes may imply permeability changes, as well as changes in air space, and thus affect the validity of the method.*
- *The precipitation of salt will not affect either the pCO₂ 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).
->->Precipitation of salts always implies, as already noted, microstructure changes. These come in addition to the irreversible expansion and expulsion upon cooling. Please refer to D.M. Cole, The microstructure of ice and its influence on mechanical properties, Eng. Fract. Mech. 68, 1797-1822, 2001, with Fig. 8 as an example how fundamental microstructure changes after cooling below -23°C can be.*
- *If all these processes were that important, they should concur to lower pCO₂s at all levels in all cores. However, 3 out of 5 bulk ice profiles are similar to the brine pCO₂ at Liege, 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. ->->At several places in the text the authors argue that in situ brine pCO₂ and bulk ice CO₂ may relate to different fractions of the brine networks. Now it is argued with the similarity of the results for the 5 out of 10 profiles where moderate (also in these profiles values may differ more than two-*

fold) agreement is found. This is not very consequent. Also, the fact that half of the profiles do not agree, is in my opinion noteworthy when the validity of a method is concerned.

P 3278, L 21 - P 3279, L 13 and Fig. 10 → *The bulk ice...Geilfus et al. (2012a).* ...The scale should be changed, as in the present Fig. 10 only little detail can be seen. —>*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. ->->Different scales could be noted in the Figure/text. What is lost in the present scale of Fig. 10a is the possibility to distinguish the data points.*

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 process is also explained in Rysgaard et al. 2014]. Therefore this will not affect our measurement and we don't need to provide a comparison.*

->->**As mentioned above, fundamental microstructural differences between sea ice stored at temperatures below -23°C and above have been documented (noted example in Cole, 2001). Therefore the different storage conditions should be mentioned for the reader. By the way, I am not aware of a study in the literature that clearly demonstrates time scales and degree of re-dissolution of different salt precipitates in warming sea ice. There is certainly potential for precipitation-dissolution hysteresis, in particular when air and brine are interdispersed, and on timescales of hours.**

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 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.

—> *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 factors*

—>—> **A statistical test should be provided when comparing two datasets in a figure, in particular as the authors write (Line 447): “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”.**

P 3279, L 14-28 —> *During this study, ...atmosphere...* 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 CO₂ 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* —>—> **The authors do not provide the time from removing the snow to start of measurements. However, ice surface temperatures may change rather rapidly (e.g., according to $z \approx 2\sqrt{\kappa t}$ with ice thermal diffusivity κ , the upper millimeter may respond within less than half a minute). That removal of snow imposes a disequilibrium may also be critical.**