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Interactive comment on “Physical controls on the storage of methane in landfast sea ice” *by* J. Zhou et al.

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REVIEWER 3 (comment #1): The manuscript by Zhou et al. delivers an import contribution to our understanding of the physical controls on methane within sea ice, something which has previously been shown to be important for CO2, too. I think some parts of the article are well explained, and I agree partly with their conclusions. However, other parts are less convincing presented. Alternative explanations for the observed concentration patterns, such as biological activity, are too easily dismissed. The intuition of the authors that biological processes are minute might be correct, but I’m not convinced that their argument - based on a statistical analysis - shows it, too. This statistical analysis was done on 4 samples taken in the course of 10 days, and only on the impermeable part of the ice core. Methanogenic and/or methanotrophic

activity might have been different in the top and bottom part of the sea ice, but this is not shown. Nonetheless, as the methane standing stocks over this subset of the ice-column did not differ statistically over this small period, it was concluded that biological activity played no role. However, it might just be that those 10 days in April represented a period of low biological activity, and this does not exclude methane production and consumption processes outside of this period, such as early winter. One way to better assess this, would’ve been to take samples and incubate them to assess a potential methane production rate under controlled conditions (e.g. varying brine and temperature conditions). In fact, such measurements have been done for sea ice from the same location (Barrow, Alaska), and these were presented last year at a large meeting of the Pergamon Arctic methane group in Kiel. I’m aware of the fact that these results are not peer-reviewed yet, but they will probably show up in the literature soon. If so, this shows that biological production and consumption of methane is in fact happening in the ice. For more information, see page 15 of the abstracts of this conference: http://www.geomar.de/fileadmin/content/service/veran/wissenschaftlich/2013/All_abstracts_
symposium.pdf

AUTHORS: We acknowledge the suggestion of the reviewer about incubation, but we did not sample enough ice samples to do so, as the initial purpose was to looking at how physical processes may affect the concentrations of methane in sea ice. However, as reviewers2 and 3 were both concerned about potential significance of methane consumption and production in the ice, we modified the revised manuscript accordingly. Details are given in response to the comment #9 (see below).

REVIEWER3 (comment #2): Microbiological controls can, therefore, not be so easily dismissed. Perhaps the authors are less experienced in that field, as evidenced by the mixup of ’methanotrophic activities’ in line 16, page 123, where it should’ve read ’methanogenic activities’, which is the exact opposite. The same goes for line 25 of that page. I’m willing to forgive such a mistake, but it does lower confidence in the authors’ ability to properly exclude a microbiological explanation behind their results. Perhaps teaming up with a microbiologist who has experience with processes within the sea ice would've helped to strengthen the argument that microbiological processes are minute, and physical processes are dominant. I still think, however, that this publication adds significantly to our knowledge of the physical controls on methane fluxes in sea ice, but microbiological activity should be more seriously considered as a viable contributor, rather than dismissing this on a simple statistical test on a small subset of the data. I would therefore recommend for a major revision which addresses the remarks above, and explores alternative hypotheses behind the observed concentration patterns more thoroughly.

AUTHORS: We apologize for the major mistake about methanogenic and methanotrophic activities. Although we do not understand how this mistake was not corrected in the submitted version, we are grateful to the reviewer for noticing that mistake. We have also improved our discussion about the biological impact on the CH4 concentrations in ice. For instance, we compared the turnover time of CH4 oxidation with the lifetime of our landfast sea ice (Revised version in Word, p. 9, L17-20), and we made additional plot on the relationships between chlorophyll-a and CH4 concentrations and between phosphate and CH4 concentrations in ice (Revised version in Word, Appendix A).

REVIEWER3 (comment #3): Some other, more specific remarks, are as follows: - page 122, line 17-22: perhaps it's better to cite the latest IPCC report. The GWP of methane has been raised, as well as the contribution to radiative forcing. Also, concentrations of CO2 are more close to 400 ppm these days.

AUTHORS: The reviewer3 is completely right. The reason for the old citation is that the latest IPCC report was not published yet when we first submitted the paper. We will modify this in the revised version.

REVIEWER3 (comment #4): - page 122, line 23-25: again, the IPCC AR4 is seriously outdated. Besides, the quoted numbers are not mentioned in that IPCC chapter. I

would suggest to refer to Kirschke et al (2013), who recently presented updated numbers for both the ocean, as well as global emissions.

AUTHORS: We will modify this in the revised version. Thanks for the update.

REVIEWER3 (comment #5): - page 123, line 16 and 25: as mentioned above, this should be 'methanogenic', not 'methanotrophic'. Methanotrophy is the consumption of methane, not production.

AUTHORS: Thank you again for noticing that big mistake. We have modified this in the revised version.

REVIEWER3 (comment #6): - page 123, line 27: why such old references on this issue? Much has been written since about the likelihood of methane release from clathrates (which decreased). A good review on the matter is O'Connor et al. (2010), for example.

AUTHORS: We have modified this in the revised version. Thanks for the update.

REVIEWER3 (comment #7): - page 125, line 18: I see that the N2 came from a Belgian supplier. Can I therefore assume that the analysis was done in Belgium, too? What kind of influence would this have had on your analysis? Were the samples transported at -30 degrees from Alaska to Belgium, or not?r

AUTHORS: Reviewer2 was also concerned by the transport and the storage of the ice samples, and whether the cooling chain has been interrupted. Below is the comment we have provided: The ice cores were collected in Alaska and stored in the laboratory in Barrow (BASC) at -35 °C. Then they were transported by plane from Barrow to Anchorage, then shipped from Anchorage to Antwerpen (Belgium) in a reefer (-30°C), then trucked to the cold storage facilities of Nobert Dentressange, and then to the laboratory of glaciology (Brussels, Belgium). Multiple temperature sensors were transported with the ice cores, and according to the records of these temperature sensors, the cooling chain was interrupted for 4 hours during the transport from BASC to Anchorage but the temperature remained below -20 °C all the time. Then in our laboratory of glaciology (Brussels, Belgium), the ice cores were stored between -30°C and -35 °C. We would like to highlight that the transport and storage of the ice cores followed the same procedures as for the continental ice cores. Furthermore, that transportation at low temperature is required as we also expected to measure other biogenic gas as O2, CO2 on the ice cores. So it is important to limit biological activities. Because of the low temperature of the ice, humidity of the air may induce slight freezing at the surface of the cores, but we systematically removed the outer parts of the ice samples before each analysis, to avoid contamination of our CH4 concentrations in sea ice by the CH4 of the surrounding atmosphere.

We believe that we have put considerable effort and money to ensure the quality of our data, but we are open to any additional suggestions that the reviewer may have on good practices for the future transport and storage of our sea ice samples.

REVIEWER3 (comment #8): - page 126, line 14: are you sure there's no methane left behind in the pure ice matrix? What if you would take the pure ice separate, melt it, and repeat the procedure, would there be absolutely no methane released?

AUTHORS: According to Week (2010), the crystallographic structure of sea ice, hence the arrangement of the water molecules in space does not allow the incorporation of impurities in general. Sometimes, we may find defects in the ice structure, but only a few number of foreign atoms and molecules (HF, F-, Cl-, NH4+ and NH4F), which have the appropriate charge and size, may be incorporated in the pure ice structure (i.e., pure ice matrix). Separating pure ice crystal from brine and bubbles is not a trivial operation, but we can assume that there is no CH4 in the pure ice matrix as outline below. First, CH4 incorporation in ice matrix is possible in clathrates, but requires high pressure, and we thus do not expect to find this in sea ice. Second, our CH4 concentrations in brine (that are deduced using CH4 concentrations in ice and brine volume fractions) were similar to the observed CH4 concentrations in seawater; this would not be observed if there CH4 in the ice matrix. Therefore, it is very likely that

there is no CH4 in the pure ice matrix.

REVIEWER3 (comment #9): - page 132, line 25 to page 133, line 2: These processes all probably contribute quite a lot to the observed profile. But the consumption and production of methane by microorganisms has to be considered as well.

AUTHORS: (1) We suggest that methane oxidation should be minor in sea ice, because methane turnover time is much longer than the lifetime of landfast sea ice, following the recommendation of reviewer1. (2) methane production is oxic conditions may be minor as well, as we could not find any relationship between chlorophyll-a and methane, and between phosphate and methane, while Damm et al., 2008 and 2010 found good relationship between these variables where they suggest methane production in oxic seawater. In addition, we have tried to contact Niko Finke for details about their isotopic measurements made on ice samples that were also collected in Barrow, but we have not received any answers yet. The methane oxidation rate they mentioned in their abstract were huge in comparison to the concentrations of methane we have measured in sea ice, but as the numbers were only mentioned in abstract and not in a peer-reviewed paper, and we do not have any details about the methodology, we feel uncomfortable to include the numbers in our manuscript.

REVIEWER3 (comment #10): - page 133, line 3: The use of the word 'believe' is a bit colloquial here. Better would be to hypothesise it or, better still, to show it.

AUTHORS: We changed the word "believe" into "assume".

REVIEWER3: (comment #10) - page 133, line 15: 'The presence of bubbles is suggested', but at line 20 you say they were observed. So are you certain they are there or not? Are there pictures? Perhaps show some more from your 2013 paper which is referenced in line 21.

AUTHORS: We meant that "the large difference between the deduced CH4 in brine . . . and the actual measurements of CH4 in brine)" suggest the presence of bubbles, and this is confirmed by the thin sections (Zhou et al., 2013).

REVIEWER3 (comment #11): - page 133, line 28-29: Could you elaborate a bit more on the physical processes behind the reduction of bubble nucleation efficiency? This is mentioned very briefly, but not really explained, which will make it harder for readers to understand why this is. Besides, this is your argument for why the concentration of methane reduces with depth. So this should be explained better, supported with references.

AUTHORS: The process is explained a few lines above. When temperature and brine salinity gradient is strong, CH4 solubility decreases, and this lead to bubble formation (lines 10-11). Therefore, in contrary, when the temperature and brine salinity gradient decrease (as the freezing front progresses), bubble nucleation from the solubility decrease is less efficient (line 28-29).

REVIEWER3 (comment #12): page 134, line 2-4: Please explain the brine volume effect better. At the moment this part is written rather confusing and more difficult to comprehend than necessary. Please rewrite in a way that it's clear how this works.

AUTHORS: we reformulate the paragraph as "We attribute this to the brine volume effect: a larger brine volume may contains a larger amount of CH4 molecules, which induces higher CH4 concentrations in bulk ice. The fact that CH4 in brine do not show the increase at the bottom of the ice supports this suggestion."

REVIEWER3 (comment #13): page 136-137, conclusion: why convince the reader that biological processes don't matter, when you admit right here that microbiological activities do affect the concentration of methane in the ice? How does this affect your results? Discussion Paper AUTHORS: We have rewritten the conclusion in the revised manuscript. It now reads as "We reported on [CH4] evolution in landfast sea ice and in under-ice water from February through June 2009 at Barrow (Alaska). Our [CH4] in sea ice and [CH4] in seawater are consistent with records from the area with CH4 release from sediment and gas hydrate destabilization (Kvenvolden et al., 1993; Lorenson and

Kvenvolden, 1995; Shakhova et al., 2010). As summarized in Fig. 4, gas exchange likely took place during initial ice growth between sea ice and the atmosphere, and the formation of cracks could lead to a decrease of CH4 at the very surface of the ice. Then when sea ice reached ca. 25 cm of ice thickness, gas bubble formation triggered by strong solubility changes could have favoured CH4 accumulation in ice. CH4 retention in the ice was twice as efficient as that of salt. However, as sea ice thickens, temperature and brine salinity gradient were no more sufficient to trigger bubble nucleation, and CH4 was then trapped in the dissolved state, as salt did. The subsequent evolution of [CH4] in sea ice layers mainly depended on physical processes, as chlorophyll-a and phosphate concentrations did not support in situ CH4 production, and as CH4 oxidation was likely insignificant. Abrupt changes in [CH4] in sea ice occurred when sea ice became permeable; these were associated with the release of gas bubbles to the atmosphere. Therefore, the main role of our landfast sea ice in the exchange of CH4 from seawater to the atmosphere was its control on the amount of CH4 that it is able to store in its impermeable layers and the duration of such storage. Although gas incorporation and sea ice permeability are two dominant factors driving CH4 concentrations in sea ice in our study site, the magnitude of these processes may be different in the other polar oceans. Indeed, the contribution of the ebullition fluxes of CH4 from sediment to the concentration of CH4 in bulk ice, the transport of CH4 through the ice, the significance of physical versus biological controls on CH4 dynamics rely on the nature of the sediment, the water depth, the physical parameters of the ice and biological activity within the ice, which may vary depending on the location. In case of a higher mix of physical and biological controls on CH4 concentrations in bulk ice, we would recommend to measure: (1) the carbon and hydrogen isotopes of CH4 in sea ice, as isotopic fractionation is highly sensitive to biological processes, and (2) the same isotopes in the sources (e.g., organic matter). Indeed, previous studies have suggested that biogenic CH4 within anoxic sediments may have carbon isotopic values as negative as -110 ‰ (Whiticar, 1999), in comparison to that formed by CH4 oxidation (-10 to -24‰ (Damm et al., 2008; Schubert et al., 2011)), but few of them have considered that the measured isotopic values in the sediment or in seawater also depend on the isotopic composition of the sources. “ REVIEWER3 (comment #14): One final remark: first time readers might be confused about the mentioning of bubbles in your paper without additional context. Sometimes it would help to say ’bubbles formed in the ice’ so readers don’t confuse this with bubbles from ebullition

AUTHORS: We checked throughout the manuscript and corrected the term where it may be confusing. Thanks for the suggestion.

Interactive comment on The Cryosphere Discuss., 8, 121, 2014.