

Interactive comment on “Quantification of ikaite in Antarctic sea ice” by M. Fischer et al.

Anonymous Referee #1

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Review of Fisher et al., “Quantification of ikaite in Antarctic sea ice” submitted to The Cryosphere Discussions.

This study is based on the collection of sea ice cores during two expeditions to Antarctica during the spring-summer transition of 2007; one of them to an offshore region, another to a coastal site. Sea ice cores were collected and melted for the quantification of CaCO₃ and the determination of its crystal form. Ikaite crystals are observed throughout the entire sea ice column, even in snow, with the highest concentrations in surface layers. A spatial study of the distribution is included and the difference in time for collection of cores is used to speculate on the temporal distribution patterns. Finally, a global potential estimate is made of the importance of ikaite dissolution on the CO₂ uptake in ice-covered seas. Few studies are reported on ikaite in sea ice and as such, this work deserves publication. However, there are missing several important supportive data in the manuscript to follow the data analysis and the discussions. As

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I read the manuscript, these data are available and I would strongly suggest these to be included, so the reader will have a chance to follow what is going on. In addition to lack many important details, the manuscript is several places so unclearly written that it is not easy to follow. I recommend publication after major revisions.

Specific comments:

Page 508, line 10-11 Even though a general description of the ice conditions during the expedition can be found in Worby et al (2011), these data are so important to interpret your data that they should be included in the present paper. Especially data of the exact date and time for sampling and analysis should be included in Table 1 as well as air and surface temperatures. Furthermore, vertical temperature and bulk salinity measurements should be provided for sea ice (in Table 2). These are basic data. In addition, brine volumes should be calculated and whether the sea ice is permeable or not (>5%, <5%) should be included as well. We are approaching summer and melting of the sea ice will dissolve the ikaite and you will loose the crystals. Did you loose any brine in the sampling of cores?

Page 508, line 14-20 In order to make a temporal study that is not affected to heterogeneity one would think that the way to do this was to visit the same location twice. Not to compare data hundreds of kilometers away from each other at different times. Im not very impressed by this part of the study. As the manuscript is written, the reader has absolutely no chance to follow this discussion as no time for collections are given. I suggest, these are provided in Table 1.

Page 509, line 3-5 I do not follow how sack holes could minimize bias from spatial heterogeneity. Please clarify.

Page 509, line 16-20 All sea ice samples were melted under climate controlled room conditions where temperature did not exceed 4C. Recent knowledge (Rysgaard et al., submitted to the Cryosphere Discuss.) shows that ikaite crystals disposed in a droplet of water and raised above 4C will dissolve in a few hours. However, if the ikaite crystal

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is covered by oil it will stay stable over days, even though temperature goes up to 21C. This suggests that other things that temperature alone will dissolve the crystal. This is a kindly suggestion, but I think the ikaite crystal's reaction with the atmospheric CO₂ may cause ikaite to dissolve as the reaction with CO₂ in the atmosphere changes the pH of the ikaite crystal's surroundings. Thus, when exposing your ikaite crystals to atmospheric CO₂ during your melting procedure (swirling) you may start losing the crystals and thus underestimate their presence. This is especially important in the present study as it is stated in your abstract that "this is the first quantitatively study of hydrous calcium carbonates".

Page 510, Line 1-5 Quantification of ikaite. It is not clear to me from the description how this is done. First you filter your samples containing the ikaite crystals. Then you store them in 75% ethanol at -18C. How much ethanol per crystal? Do you rinse the crystals before they were added to the storage vial? Seawater contains around 400 mg Ca²⁺ per liter. Then you evaporate the ethanol in your samples and dry them at 60C. Then they are treated with HNO₃ and then you calculate the amount of ikaite based in the measurement of calcium. What was assumed? Add a few more details here.

Page 510, line 13-25 Sack holes. It is difficult to judge this section without temperature and salinity measurements included – see above comments. There are several problems with sack holes that need to be tested and clearly shown not to be a problem. (1) If sea ice is cold, permeability is low and brine rises very slowly in the sack hole. Water can be sampled for nutrients etc, but gasses may exchange with the atmosphere. This seems not to be the case in the present study although no data are provided to test this – they should be. (2) If sea ice is permeable, you will risk to contaminant brine with seawater as the increasing pressure gradient will push water from the surface water into your sack hole. One way to test this is to compare your measured brine salinity from the sack hole with the calculated one based on bult salinity, temperature and brine volume calculations. Did you do that, and if so how did they compare? How fast did the brine rise in your sack holes?

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Page 511, line 15-20 The ikaite concentrations in land fast ice off Terre Adelie were generally higher (Different) than the pack ice cores. How can you then use these two locations to elaborate on temporal differences? See previous comment.

Page 511, line 25- 29 It is difficult for the reader to follow this temporal study without the sampling dates and times! They should be included.

Page 512, line 1-5 Again, provide the exact times. How can the reader judge if the normalized salts and nutrients etc. increased non-linearly with time if times are not available?

Page 512, line 5-7 Unclearly written. Does NO₃ show a trend governed by biology? What do you mean? Is that due to primary production and uptake by algae, or NO₃ production by nitrifying bacteria, or something completely else? Biology is a broad term.

Page 512, line 8-10 How can TA decrease 400 μ M and show no correlation to calcium carbonate in sea ice? As an example, Table 2 shows ikaite concentrations of around 1 mg per liter melted sea ice. How much does that correspond to in CaCO₃ normalized to a salinity of 35? A guess is 5 x bulk concentrations – again it is difficult to follow your calculations without the important data of bulk concentrations. So around 5 mg CO₃²⁻ per liter of brine. In terms of molar weight equivalents of CO₃²⁻ this should be visible. Please add some more details here or in the following Discussion.

Page 513, line 7-10 How can you conclude “it appears that hydrous calcium carbonate precipitation also takes place during subsequent sea ice growth as observed in older fast ice (Fig. 6)”? It could have been formed in young ice and just stay there.

Page 513, line 12 I would add “...middle layers of sea ice were presumably attributed...” Without the support data it is difficult to tell if floes have slid over each other. How did bulk salinities look? What about the crystal structure? They would tell.

Page 513, line 19-23 No it is not possible to determine the temporal development of

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CaCO₃ as you have not provided the dates and time for collection the cores! This makes it very difficult for the reader to follow. Furthermore, the huge distance between sites makes this an impossible task. See above comments.

Page 514, line 13-20 I would be careful to make any first estimate on the possible contribution of calcium carbonate precipitation to the carbon cycle for several reasons. Firstly, crystals may have been dissolved during the melting procedure. Secondly, because ikaite crystals may continuously form and dissolve during the season and your estimate is based on a snapshot in time. Thirdly, the large heterogeneity observed in the distribution of ikaite will make such an estimate highly uncertain. It would be nice if TA, DIC, temperature and bulk salinities were available for sea ice and the surface waters. Then you could estimate the pCO₂ in melt water and mix that into the surface water. Fill up the mixed layer with CO₂ from the atmosphere and calculate how much that would be. Do this compare with the independent ikaite crystal estimation? If these data are not available I would stay away from this.

Page 514, line 28 – Page 515, line 10 I think the paragraph with polynya and frost flowers is too long considering the short discussion. This is very speculative especially when no data are available from such areas.

References There seems to have entered some numbers behind the references that I do not think should be there. See for example Dieckmann et al (2008) on Page 517, line 7-10, where 507, 509, 510, 512 appear.

Table 1. Add the specific dates and times for each sea ice core.

Table 2 Add the temperature, bulk salinity and calculated brine volume to the table. Furthermore, it is difficult to judge what the numbers refers to. Are they mean data of the 10 cm sections of the sea ice cores? I guess they are. Then add the standard deviation of each core and the number of replicates. This will be very useful in order to follow your heterogeneity study. Why is ikaite not normalized to salinity of 35? It is difficult to compare with for example TA. Add another column where you show the

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alkalinity contribution for ikaite. Makes your discussion easier to follow.

Figure 8 I suggest you calculate the spatial autocorrelation (Moran's I, Legendre and Legendre 1998), to evaluate the 2-dimensional distributions of ikaite crystals. Data should be there.

Please also note the supplement to this comment:

<http://www.the-cryosphere-discuss.net/6/C34/2012/tcd-6-C34-2012-supplement.pdf>

Interactive comment on The Cryosphere Discuss., 6, 505, 2012.

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