

Response to the corrections of the research paper:

**Quantification of ikaite in Antarctic sea ice
To be considered for publication in The Cryosphere.**

We are grateful to the Editor in Chief and the two reviewers for considering this paper. We have taken into account all the comments and suggestions, and there is no doubt that the reviewers comments have enabled us to improve the manuscript a great deal. Below we have paraphrased comments from all reviewers (in italics & blue font) and made clear where and how we have altered the MS. Since we have modified the manuscript, the line numbers have been changed due to addition/deletion of text. In order to show where suggested changes were made we have added new line numbers in parenthesis for each comment.

Thank you.

Yours truly,

Michael Fischer
Department of Polar Biological Oceanography
Alfred Wegener Institute for Polar and Marine Research
Bremerhaven
Germany
Tel: +49 (0) 471 4831 1842
email: Michael.fischer@awi.de

Reviewers' comments:

Reviewer #1: Review of Fischer et al., "Quantification of ikaite in Antarctic sea ice" submitted to The Cryosphere Discussions.

However, there are missing several important supportive data in the manuscript to follow the data analysis and the discussions. As 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.

We agree that some data are missing. We have provided this data in the manuscript where the data were available and structured the paper in a way that it is easier to follow.

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 lose the crystals. Did you lose any brine in the sampling of cores?

Authors agree that the data originally provided were insufficient. Data of the exact date and time of sampling, air, and surface temperatures have been added to table 1. Brine temperature, brine salinity, and time of sampling were added to table 2. Unfortunately we cannot provide vertical temperature and bulk salinity values for table 2 since these data are from brines, which were collected in sackholes of 30 cm depth. Instead we provided such profiles from ice cores we collected separately in two new figures (Fig. 8 and Fig. 9) including the time of collection. We also calculated the brine volume and demonstrated with a dashed red line whether sea ice was permeable or not. We specifically took great care not to lose brines during coring.

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 kilometres away from each other at different times. I'm 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.

We agree that a temporal study should be conducted at the same location. And this is what we did. In Line 14-20 there is no statement, that we compared the ice cores from the SIPEX and the DDU campaign with the aim of doing a temporal study between these sites. On page 509 line 3 it is pointed out, that we did the temporal study only off Terre Adelie by collecting ice and brine from sackholes. However, we agree that it is easier for the reader to have the samplings dates. We added the dates of samplings to both table 1 and table 2. We also

rephrased and restructured the paragraph p513 line 19 as: It is not possible to determine the temporal development of CaCO_3 in the sea ice investigated during the DDU campaign. This is due to the extreme variability in CaCO_3 concentrations even on small scales. The reason for this heterogeneity might be due to the inherent variability in many sea ice properties ranging from temperature, salinity, texture, chemistry and lastly biological activity. The spatial and temporal heterogeneity are already apparent on small scales as shown by the studies during the DDU campaign. Thus, it is difficult to draw conclusions on the temporal evolution of the precipitation of ikaite. (Line 184 in the attached manuscript)

Page 509, line3-5 I do not follow how sackholes could minimize bias from spatial heterogeneity. Please clarify.

We clarified this by restructuring as: At the main sampling site, sackholes (D-SH1 to D-SH7) of 30 cm were cored every two or three days for a temporal analysis of brine and ice. All samples were collected within an area of 10 m x 10 m to minimize bias due to spatial heterogeneity.
(Line 75 – 76)

Page 509, line16 20 All sea ice samples were melted under climate controlled room conditions where temperature did not exceed 4°C. Recent knowledge (Rysgaard et al., submitted to the Cryosphere Discuss.) shows that ikaite crystals disposed in a droplet of water and raised above 4°C will dissolve in a few hours. However, if the ikaite crystal is covered by oil it will stay stable over days, even though temperature goes up to 21°C. This suggests that other things than temperature alone will dissolve the crystal. This is a kindly suggestion, but I think the ikaite crystal's reaction with the atmospheric CO_2 may cause ikaite to dissolve as their action with CO_2 in the atmosphere changes the pH of the ikaite crystal's surroundings. Thus, when exposing your ikaite crystals to atmospheric CO_2 during your melting procedure (swirling) you may start losing the crystals and thus under estimate 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".

We agree that ikaite crystals will start to dissolve above 4°C, this is why we took special care about the temperature. However, as we clarified on page 509 lines 16 to 28, we did not swirl every sample. Those samples, which were swirled, were checked under the microscope for signs of dissolution, which were never observed. Therefore we are convinced, that even if a reaction of ikaite with the atmospheric CO_2 would start to occur, this is negligible, since the samples did not experience any mechanical stress that would have accelerated equilibrium reactions.

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 -18°C. How much ethanol per crystal? Do you rinse the crystals before they were added to the storage vial? Seawater contains around 400mg Ca^{2+} per liter. Then you evaporate the ethanol in your samples and dry them at 60°C. Then they are treated with HNO_3 and then you calculate the amount of ikaite based in the measurement of calcium. What was assumed? Add a few more details here.

Unfortunately we don't understand the question "How much ethanol per crystal?" This question can't be answered, since the volume of ethanol (ca. 2ml) in the vial never changed and therefore the amount of ethanol per crystal varies with the number of crystals present in

the samples. We always put the filters in a 2ml Safe-Lock Tube (Eppendorf Germany), which we then filled with ca. 2ml 75% v/v ethanol. However, for a better understanding we rephrased the part as: The filters with crystals were then placed in a plastic vial (Safe-Lock Tubes 2ml, Eppendorf, Germany) and subsequently filled with 75% v/v ethanol and frozen at –18°C for later mineralogical phase identification and quantitative measurements. Line 92 in the attached manuscript

We didn't rinse the crystals since we used a vacuum pump for filtration so that the melt water was completely pumped through the filter, leaving a dry sample. Therefore we are convinced that no additional calcium was left on the crystals. For a better understanding we changed the sentence in Line 20 on page 509 as: The melt water was filtered through 0.2 µm polycarbonate filters using a vacuum pump and the volume determined. (Line 91)

Page 510, line 13 -25 Sackholes. It is difficult to judge this section without temperature and salinity measurements included – see above comments. There are several problems with sackholes 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 sackhole. 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 contaminate brine with sea water as the increasing pressure gradient will push water from the surface water into your sackhole. One way to test this is to compare your measured brine salinity from the sackhole with the calculated one based on bulk salinity, temperature and brine volumetric calculations. Did you do that, and if so how did they compare? How fast did the brine rise in your sackholes?

Temperature and salinity data are now provided in table 2 (see above). We tested the measured brine salinities versus the calculated ones based on the equation of Petrich & Eicken 2010. The measured brine salinities were slightly higher or equal to the calculated values, therefore we can conclude that brine was not contaminated by seawater. We provided S and T for brine in table 2 so that the reader is able to follow. We added a sentence as: Comparison of theoretical values of brine salinity (calculated according Petrich and Eicken (2010)) versus measured values (table 2) showed that brine was not influenced by seawater (Fig. 8 and Fig 9.) (Line 163 – 164)

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 of temporal differences? See previous comment.

We clarified this. The temporal study was only conducted during the DDU campaign. See above.

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.

We agree and now provide the data in the tables. See above

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?

We agree. The data is now provided, see above. For an easier understanding we rephrased the sentences as: When brine is normalized to a salinity of 35, (see Papadimitriou et al. (2007)) dissolved organic nitrogen (DON₃₅) and dissolved organic carbon (DOC₃₅) concentrations increase non-linearly over a period of time. In our study, phosphate (normalized to S=35) shows the same trend as DON₃₅ and DOC₃₅ at the beginning, it did not increase over time and remained low.
(Line 155 – 158)

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 some thing completely else? Biology is abroad term.

We can't answer this question, since we have not measured primary productivity or bacterial activity and therefore cannot relate the NO₃ values to any specific biological activity.

Page 512, line 8-10 How can TA decrease 400 uM 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 5mg 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.

Not finding any correlation between TA and ikaite precipitation is not unexpected with averaging out of properties in bulk samples. We normalized TA and nutrient data since they are conservative (Papadimitriou 2007, Zeebe and Wolf-Gladrow 2001). Ikaite in sea ice is present in a solid phase and does not change directly with altering salinity. As a result these parameters cannot be normalized in a simple manner and are presented and discussed as measured. On page 512 Line 22 we explained it in more detail: "However, it is still not clear at what point in time ikaite precipitation occurs, and our interpretation is confounded because the various biogeochemical parameters measured during sample collection do not reflect conditions at the time of precipitation." However, we provided the bulk concentrations as described above. We added some more details and changed the paragraph in the discussion section (Page 512, line 25 in the discussion paper) as: For example the question arises why a TA decrease by 400 μmol did not result in a correlation with the precipitation of calcium carbonate. As discussed above, the measurements reflect only a small time frame in the seasonal carbon cycle within sea ice and not necessarily the conditions at time of precipitation. Observations of higher values of hydrous calcium carbonate precipitation in older land fast ice (Fig. 6) also raise the question if precipitation also takes place during subsequent sea ice growth or if ikaite, after it has formed in young sea ice, remains stable under various conditions until the sea ice melts and therefore do not alter TA or the carbonate system itself.
(Line 174 in the attached manuscript)

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.

We assumed equal growth conditions for the young and older fast ice, which we investigated. We agree that from the data alone we cannot draw this conclusion. We therefore rephrased this sentence and moved it into the paragraph above. See above. (Line 177 – 181 in the new manuscript.)

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.

Analyses of the ice structure (see Meiners et al. 2011) provide the necessary evidence. We added the citation as: Higher values of calcium carbonate in some middle layers of sea ice were attributable to rafting of floes subsequent to sea ice formation (see Meiners et al. (2011)).
(Line 196 – 197)

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

We clarified this, See above revisions.

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 snap shot 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 meltwater 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.

The authors agree that such estimation is on “thin ice”. Following the review, we therefore deleted this part from the manuscript. As you noted, we do not exactly know if CaCO₃ precipitation occurs in a dynamic cycle or if it just forms in young sea ice and stays there (see your comment above). We assumed a precipitation once and have taken the lowest and the highest values, which resulted in the huge range of our estimation. We deleted the part and restructured the paragraph as: Previous studies have pointed out the importance of sea ice for the carbon uptake in polar oceans due to i.e. CaCO₃ precipitation (Rysgaard et al., 2009, 2011; Delille, 2006; Tison et al., 2002; Nedashkovsky et al., 2009). An estimation of the contribution of calcium carbonate precipitation to the polar carbon cycle would be useful. However, the large heterogeneity observed in the distribution of ikaite will make such an estimate highly uncertain. In addition also the large amount of ikaite in the snow has to be

taken into account. Considering the vast areal extent of sea ice in the polar regions the high concentrations of ikaite found in sea ice and in the snow would be a significant addition to the polar carbon flux. (Line 232 - 239)

The abstract was edited according to this.

The conclusion was also rephrased as: We showed the heterogeneous occurrence of CaCO_3 in sea ice. Large scale quantification of CaCO_3 precipitation in different types of sea ice and during the entire season in both the Arctic and Antarctic is necessary to validate these findings and to provide a quality data set to estimate its contribution to the polar carbon cycle. (255 - 258)

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.

The authors don't agree. We consider it as justified speculation since we discuss the occurrence of the mineral in the top layer and its implications for the carbon cycle.

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.

Will be corrected by copernicus

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

We added the information. See above.

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

We added the salinity, temperature, and sampling date of the brine. Bulk values of sea ice are provided in Fig. 8 and 9. The numbers refer to brine, which was collected in sackholes. The ikaite values are from the ice cores adjacent to the sackholes (SIPEX cruise) or from ice cores obtained during drilling of the sackhole (DDU campaign). To clarify this we added a sentence in the caption as: Ikaite values are from ice cores. All other values are sampled directly from brine obtained from sackholes.

Ikaite in sea ice is present in a solid phase and does not change directly with altering salinity. As a result these parameters cannot be normalized in a simple manner and are presented and discussed as measured. See comments above.

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

For the conventional geostatistical spatial interpolation using the simple kriging method, we applied a regular grid. Using this regular grid instead of random sampling points allows an

evaluation of the 2-dimensional distribution. A Morans I value would not provide any additional information. We edited the figure by adding white lines, indicating sampling points. We edited the caption as: ... on a 20 m x 20 m grid with sample points every 5 m by 5 m (shown by intersections of the white lines and at the edges).

Reviewer #2:

The authors present the first quantitative study of calcium carbonate as ikaite within sea ice. This study is based on 2 field trips to Antarctica (on pack ice and landfast sea ice). Sea ice cores and snow were sampled and melted to determine and quantify the precipitation of CaCO_3 as ikaite. Ikaite was observed in all samples throughout the entire sea ice column with a maximum of concentration at the top layer of the ice. The authors examined its horizontal spatial distribution and speculated on the temporal evolution of the precipitation of ikaite. Finally, they discussed its importance to the carbon cycle in polar oceans.

Up to now, few studies are published on ikaite precipitation within sea ice, and this work presents the first estimation of this precipitation. However, the main purpose of this manuscript “quantification of ikaite” is really poorly explained, making it impossible for the reader to understand. The second purpose of this manuscript, as indicated by the authors, is to investigate the relationship between calcium carbonate and alkalinity, phosphate, and dissolved organic matter. However, the authors fail to provide any further information/discussion with this second objective. These data are partially available in the manuscript (page 512, lines 1-10 and in table 2), however, the authors must provide more detail on these relationships in the manuscript rather than simply refer the reader to the publication of Papadimitriou et al., 2009. This discussion is important and necessary as the conditions of surrounding the precipitation of calcium carbonate are not yet understood; relevant points could include the relationship between the ratio TA:DIC and the possible precipitation of CaCO_3 , the phosphate concentration impeding the precipitation of calcite and supporting the precipitation of ikaite (Bischoff et al, 1993), and so on.

We agree that some details were missing in the method part. We added this information as described above for review #1. We provided a discussion on the relationship of CaCO_3 and all the data we could provide. DIC cannot be provided as discussed in the following comments. Thus we can not provide any TA:DIC ratios and therefore we can not discuss it. The work of Papadimitriou provides information of normalization of brine constituents and does not provide any further data from our study area.

Page 506, lines 1-16: Defines $p\text{CO}_2$ -DON-DOC and then used only the abbreviation further in the text.

$p\text{CO}_2$ is defined as: They ascribe the high $p\text{CO}_2$ (partial pressure of CO_2) (Line 27), DON, DOC, and TA are defined as : Brine was allowed to accumulate in the sackholes and sampled with a vacuum pump and transferred into different vials for total alkalinity (TA), dissolved

organic carbon (DOC), dissolved organic nitrogen (DON), and phosphate analyses (Line 76). The abbreviations are then used throughout.

Page 508, line 2: When this field trip occurred? I guess it start in September but when did it end? What were the dates of the field work?

We added the information as: During the first campaign (Sea Ice Physics and Ecosystem eXperiment (SIPEX) onboard RSV Aurora Australis from September to October 2007)... (Line 48 – 50). The dates of sampling are provided in table 1 and 2.

Page 508, lines 8-11: Although this information is already available in another publication, it would be easier for the reader if there were a short summary in this manuscript. The reader should not have to refer to four different papers to understand and interpret the data presented here. I'm thinking about salinity and temperature profiles, the brine volume, and the ice texture.

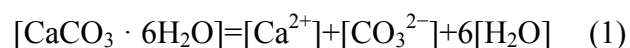
We provided the bulk salinity, ice temperature, and brine volume in two new figures (8 and 9). We reduced citations and rephrased the sentence as: Further details on ice types, bulk salinity, ice temperature, and brine volume, see table 1, Meiners et al. (2011), figure 8, and figure 9. (Line 54 - 55)

Page 508, lines 26: "These cores were cut into 2 cm section" Which cores? The text is unclear between the line 20 and 27. Please clarify the text.

We rephrased it as: Ice core D10 was taken from sea ice which had formed in autumn and had remained intact since its formation, in contrast to cores D1-D9 which were from younger sea ice. Ice cores D7 to D10 were cut into 2 cm sections. (Line 68 - 70)

Page 510, lines 6-12: The method used to quantify the amount of ikaite is not clear to me. Which is too bad as it is one of the main goals of this manuscript (title of the manuscript). More detail with respect to the method of ikaite quantification is necessary.

We rephrased the paragraph and added some more details as: To quantify the amount of ikaite within the sample, the quantity of calcium ions were determined using Inductively-Coupled Plasma Optical Emission Spectrometry (ICP OES). The Safe-Lock tubes containing the filters were rinsed with concentrated ethanol and the content was transferred to larger vials. The transferred samples were dried at 60°C until all the ethanol had evaporated, leaving only the calcium carbonate crystals. Five ml concentrated HNO₃ was added to dissociate all molecules according to equation 1 before the samples were analysed in the ICP OES. The amount of ikaite was calculated using a molar calcium/ikaite ratio of 1.



(Line 107 - 115)

Hopefully this provides enough information for the reader to follow the idea behind this method.

Page 510, lines 13-25: It is essential to present the brine salinity and the in-situ temperature of the brine. As I understand from the caption of table 2, this table only refers to melted ice samples. So where are the in situ brine data? Does the text here refer to the wrong samples? In table 2, where are the data from stations D1 to D10 and DSP1 to DSP25? What does the data presented in table 2 correspond to? Is it a mean of the entire ice column (for station S1-S14) or just the top 10cm? Please clarify. In addition, it is essential that you provide the sampling date if you intend on keeping the “temporal evolution” section. Is the table caption wrong, or incomplete?

We agree, it was not clear from the table caption that the data refers to brine samples. Only the ikaite values were obtained from related ice cores. Therefore this is the in situ brine data. We edited the caption as: Physico-chemical properties of brine collected from sackholes from land fast ice off Terre Adelie (DDU) in November 2007 (D-SH1 to D-SH7) and from sea ice in East Antarctic (see map) between September and October 2007 (S1 to S14). TA, DON, DOC, and nutrients are normalized to S=35. Ikaite values are from ice cores (30cm) obtained from the sackholes (D-SH1 to D-SH7, DDU campaign) and ice cores adjacent to the sackholes (S1 to S14, SIPEX cruise, sum of the first three 10 cm sections) and presented in mg l⁻¹ melted sea ice.

D1 to D10 and DSP-1 to D-SP25 are ice cores and were only analysed for ikaite. Sampling date is now provided.

Page 511, lines 20-21: Core D10 is older than the others cores and you find a higher mineral concentration. Did you see any difference in the size of the crystals? They could be less numerous but bigger as they have had more time to grow. Could you add this information? If you notice a difference, it would be really nice to show a picture/figure.

We did not observe significant differences in size range of the crystals between the samples.

Page 512, lines 1-10: Even if these data are available in the publication of Papadimitriou et al, 2009, a quick summary including salinity and temperature profiles, and temporal evolution of each variable is necessary. In addition, Rysgaard et al 2007 suggested that the precipitation of CaCO₃ could be indicated by a ratio of Ta:DIC of 2. Geilfus 2011 showed evidence of CaCO₃ precipitation but with a ratio much more lower. It will be interesting to have this information, as they should be available from your data.

The well-known work of Papadimitriou provides information of normalization of brine constituents and does not provide any further data from our study area. However, we agree that Papadimitriou 2007 would be more appropriate for citation, thus we corrected it. We agree that this information would be very interesting. Unfortunately we cannot provide the data being asked for. We performed pH measurements of brine during our study. However, we do not trust this data, since we were only able to measure pH earliest 2 hours after sampling. Even though we took care to fill the sample vials without any headspace, we cannot exclude degassing of the brine, since the vials were unfortunately not gas tight. Therefore, the pH may have changed, thus providing possible corrupt data. In addition one would need to calculate DIC out of TA and pH using dissociation constants, which are not valid for the range of salinities we observed. However, for curiosity we calculated these values using the constants of Mehrbach 1973 refitted by Dickson and Millero 2006 and

compared them. The differences of DIC were between 2 and 655 $\mu\text{mol/l}$ with an average of 186 and a standard deviation of 201 $\mu\text{mol/l}$. This already shows, that the data, which we would have obtained do not provide the necessary accuracy. We also calculated the TA:DIC ratios. Using the Mehrbach/Dickson constants we get ratios between 1.1 and 3.9 with an average of 1.9. Using the constants of Millero 2006 results in ratios between 1.1 and 2.1 with an average of 1.5. In our opinion the ratio of TA:DIC has to be used carefully when interpreting brine/bulk data of TA and DIC with respect to CaCO_3 precipitation as they are influenced by several other factors. We also think that the constants of Millero 2006 are the most appropriate ones, since their pK_1 and pK_2 values are the only constants available in the literature, which still drop with increasing salinity. All other constants increase again at the edge of their valid salinities.

With this uncertainty we don't think that the data quality is high enough to be published.

Page 512, lines 20-23; page 511 lines 9-10 It is necessary to show salinity profiles and ice texture of the ice cores. From fig 3 and 4 it is obvious that ikaite should be more likely expected at the top of the ice. The more saline layer at the top of the ice is interesting but you need to show salinity profile to argue that. In addition to the salinity distribution, the max concentration of ikaite could be also linked to the texture of the ice (i.e. frazil ice versus columnar ice). This makes sense as you sampled pack ice (station S1-14) and land fast sea ice (the others). In common sea ice, the top of the ice column is often made of frazil ice. This layer could be more saline due to a faster growth rate upon initial formation of the ice. The authors should show some salinity profiles and thin sections and discuss them in this context. In addition, did you sample the seawater underlying the ice? Do you think that ikaite crystals may be exported from the ice to the seawater suggesting that the bottom of the ice has lost some crystals? In addition, as your samples run from September to December, (end-of-winter to mid-summer), we can imagine that some brine flushing events could have occurred in the ice. That's another reason why it would be interesting to have the date of the sample (it will help to understand the figure 3 and 4) as well as the salinity-temperature profiles and to calculate the relative brine volume. Is it possible that the ice lost some crystals as the summer approached? Can you quantify that?

We deployed two sediment traps underneath the ice at Dumont Durville. We did not find any crystals in these. We do not think that ikaite is lost to the underlying sea ice, though this question still remains elusive.

In the method part we therefore added the following paragraph:

Two sediment traps MST6 (HYDRO-BIOS, 0.005 m^2 surface) and a current-meter RCM7 (ANDERRA) were deployed under the sea ice at Dumont d'Urville from 13/11/07 to 04/12/07 immediately adjacent to the temporal study site. The first sediment trap at 5 m under the ice and the second one at 25 m. Water depth at the site was 53 m. Mercuric chloride was used for fixation of the samples. Sediment trap samples were immediately analysed under the binocular microscope after the traps were retrieved. (Line 82 – 86)

In the results section as:

The sediment trap samples did not have any CaCO_3 crystals in the sample bottles.
(Line 154)

In the discussion section as:

The reasons why we did not find CaCO_3 in the sediment trap are not clear and the absence can at this stage only be attributed to several factors which cannot be verified: These include the dissolution of crystals during ice melt, which means crystals do not leave the sea ice as temperatures increase. The dissolution in the sediment trap itself before the trap was

retrieved, but this would mean that crystals, which dropped out of the ice a day before retrieval would also have dissolved.

(Line 223 - 227)

Salinity, temperature and calculated brine volume profiles are now provided in figure 8 and 9. Unfortunately we cannot provide any thin sections for the land fast ice off Terre Adelie. We don't think that structure is the key parameter for ikaite precipitation. High salinity values triggering high saturation states of ikaite in saline solutions and very low temperatures at the surface of sea ice are most likely the reason for ikaite precipitation, which, in addition, might be catalysed/influenced by other biochemical components. Salinity is driven by temperature and not by growth rate (Petrich and Eicken 2010). It is obvious that granular ice is the most likely place of precipitation since it is, as you said, common the top sea ice layers, which also contains the highest values of salinity, which are triggered by the low temperatures at the surface and not by the structure itself.

513, lines 8-11: "The occurrence of calcium carbonate in the snow.... as describes above" .I don't understand this statement, could you please clarify?

Unfortunately, it was not possible for us to understand what was meant by this question. The occurrence of ikaite in the snow is described in the results section (Fig. 7) and the thermomolecular pressure gradient is described some line above.

Page 513, lines 15-18: "concentration of CaCO₃ are on the same order of magnitude". If I go back to the page 511, lines 15-16, I read that the precipitation is on the same order of magnitude but higher. You could just say that the precipitation of CaCO₃ in land fast sea ice is more important than in pack ice and find an explanation. From the figure 3 and 4, the main difference is in the top of the ice. May be the ice texture, an indicator of genesis of the sea ice formation could be an explanation? See comment above.

We think one should be careful to say that the precipitation of calcium carbonate in land fast sea ice is more important than in pack ice. As already mentioned in review #1 this is only a snapshot in time. A possible explanation could be that CaCO₃ could precipitate during subsequent sea ice growth or that pack ice experienced different growth conditions such as higher temperatures resulting in lower salinities and thus lower values of CaCO₃. We added this part to the discussion section as: The reason why we found different values in different types of sea ice is not clear yet. One explanation could be, that CaCO₃ also precipitates during subsequent sea ice growth. Another reason could be, that sea ice is experiencing different growth conditions i.e. such as higher temperatures resulting in lower salinities and saturation states and thus lower values of ikaite.

(Line 203 - 207)

Page 513, lines 22: "reason of this heterogeneity may be salinity, temperature, texture..." It will be nice to show these data and write a real discussion about it.

We rephrased this part slightly as: It is not possible to determine the temporal development of CaCO₃ in the sea ice investigated during the DDU campaign. This is due to the extreme variability in CaCO₃ concentration even on small spatial scales. The reason for this heterogeneity might be due to the inherent variability in many sea ice properties ranging from temperature, salinity, texture, chemistry and lastly bacterial activity. The spatial and temporal heterogeneity are already apparent on small scales as shown by the spatial and temporal

studies during the DDU campaign. Thus, it is difficult to draw conclusions on the temporal evolution of the precipitation of ikaite. (Line 208 - 214)

We only did a spatial study of ikaite and not of salinity, temperature, texture, chemistry, etc. The inherent variability in many sea ice properties is described in many publications. Thus it should be allowed to speculate.

Page 513, lines 26: The temporal evolution could be discussed only from data of station D1 to D10 as they were sampled at the same location. It makes no sense to compare data from the SIPEX cruise as they were sampled in different locations (fig1). Unfortunately, we do not have any temporal reference for stations D1 to D10. All the dates are missing. However, it will be more interesting to compare the precipitation of ikaite between the 2 different types of ice (landfast-packice) sampled in this study.

This is what we have done. We agree that it was difficult to follow. We rephrased this part, See comments for review#1. Dates for the samples are provided now. As you said the samples are from different locations and in addition they were sampled at different times. Therefore we think one cannot compare these data. This would only be possible if samples would have been obtained at the same time. It would be necessary to obtain the history of the different types of sea ice before a comparison could be done.

Page 514, lines 13-25: You should be careful of doing this estimation of the contribution of the CaCO₃ precipitation to the carbon cycle. (1) You only take into account the first 10 cm of the ice. Do you know if CaCO₃ could precipitate at the bottom of the ice, as the ice forms from the freezing seawater? Ikaite is supposed to be the first salt precipitated (Assur1958). Are you sure that you did not lose any precipitate or that ikaite could not be expelled into the underlying seawater, which could explain the low concentration of ikaite found at the bottom of the ice? In addition, as the summer draw nears, brine flushing could occur, carrying along crystals into the seawater. No quantification of either of these processes occurred in this work. (2) As you mentioned in your manuscript (page513, lines17-18), older sea ice may support continuously growing/evolving precipitation of CaCO₃. You only have a snapshot of this precipitation. What effect does ice age have on the amount ikaite precipitated? (3) As mentioned in your manuscript (page 513, lines20-22) this precipitation is very heterogenic. This leads to large but undiscussed uncertainty in your estimation. (4) The authors seem to think that as soon as this precipitation occurs, it leads to an uptake of CO₂ by the ocean. In the work of Delille (2006) and Geilfus (2011) different scenarios are explained suggesting different impacts of the CO₂ flux depending on how and where this precipitation occurs.

As written for review#1 we agree that such an estimate is uncertain. See also rephrased parts of the manuscript as described for review#1.

We don't think that ikaite precipitation occurs at the bottom of the ice, as the salinity is at seawater values. In addition this part experiences a regular turnover of the water resulting in a relatively high temperature at the freezing point of seawater. We had sediment traps underneath the ice, but we could not observe any ikaite loss to the underlying water.

We agree that we do not know the effect of sea ice age on the amount of ikaite within the ice. The large heterogeneity resulted in the huge range we have presented.

We don't think that as soon as ikaite precipitation occurs, it leads to an uptake of CO₂ by the ocean! This is why we discussed this issue in line 238 – 247 and it shows us that you support our justified speculation (Delille 2006)

Page 515, lines 19: The importance of the precipitation of CaCO₃ within sea ice has already been suggested by Rysgaard (2007), Delille (2006, 2007), Geilfus (2011).

The importance has been suggested but a full calculation and therefore an estimate of the significance of CaCO₃ precipitation i.e. for the sea ice carbon pump (Rysgaard 2007) is still missing! To our best knowledge and discussions with international colleagues, we think that the carbon pump is mainly influenced by the high pCO₂ due to the salinity effect. Thus it would be necessary to provide dissociation constants for S > 50 and subzero temperatures. However, since we have deleted the estimation, this part was deleted in the conclusion as well. See comments above.