Comments to reviewers (Vancoppenolle) – The Cryosphere

Thanks for a constructive and helpful review.

The authors claim later that TA ≈ CaCO3 in the surface layers. But careful examination of the figure indicates that this is not true (CaCO3 > TA near the top). In this context, more info on sampling and observational errors would have been useful. The surplus of CaCO3 is not enormous. Therefore, this is probably fine. But me, reader, was left with the vague impression that something was wrong there.

The analysis of TA and CaCO3 is not made on the same ice corers. This has been made clearer in our revision.

Major comments:

Describe your sampling strategy in more details. Support this with a table, with the actual numbers, for TA, TCO2, CaCO3, T and S. Also mention from which core they are from. Just to cut down any ambiguity.

We have described sampling strategy in more details. We think it is too much with a table. In stead we have provided a summary of our sampling strategy in the end of the Methods.

The thermodynamic regime of your sea ice cover seems not typical at all of Arctic sea ice, but rather looks like Antarctic sea ice, with a deep snow cover and high salinities. The ice proves to be both quite cold and saline, which arguably may favour CaCO3 formation. As your site is very peculiar, you must acknowledge this early on (in the abstract?)

The polynya site is representative of thin Arctic sea ice whereas the ICE I location is representative of fjord ice in the Arctic where there is a large source of winter precipitation (snow). It is not like Antarctic snow on ice as it is very dry and very cold (unlike Antarctic ice). There is also no surface flooding. The location is typical of sea ice in fjords or where large moisture sources are available to the Arctic winter climate system. We have added this in the description of the location in methods.

The X-ray table is abstruse. There are no titles in the columns. You nowhere explain what the numbers mean. I'm not a crystallographist at all. But the standard reader of that journal neither is. Explain more, both in the table and in the text, or remove.

We have changed the Table.

The modelling exercise has the same problem. You say, I use that model, but you don't even explain what are the basic principles, and how temperature determines your *computations. Hence, this part is at this stage unhelpful. Explain in one or two sentences: i) basic principle of the model; ii) what are your controlling factors (including T); iii) what is the ice fraction and brine salinity in your equilibrium state*

More details on the FREZECHIM model have been provided: “The production of ikaite in the sea ice cores was modeled by FREZCHEM (version 10), an equilibrium chemical thermodynamic model parameterized for concentrated solutions (up to 20 moles/kg(H_2O)) and sub-zero temperatures (done to -70 ºC) (Marion et al., 2010). The model uses the Pitzer approach to correcting for activity coefficients of solutes in concentrated solutions. Our calculation was done by following the freezing process of seawater with the same chemical composition as the local seawater under the local pCO_2 values; the thermodynamic constants used were the default values provided with the model. It should be noted that FREZCHEM modeling is based on the assumption that chemical species in the sea ice environment (ice, brine, and air) have reached thermodynamic equilibrium, and that most of the thermodynamic constants used in the model were extrapolated to low temperatures rather than being directly determined experimentally. Nevertheless, the model has shown promising applications in exploring cold geochemical processes associated with seawater freezing among many others (Marion et al., 1999; 2010).

The discussion of the physical drivers of ikaite formation is unconvincing. Extensive invokation of downwards brine expulsion is made, while this is typically a minor process (Notz and Worster 2009). In addition, more important mechanisms (e.g. full depth brine convection) are likely at work.

We have avoided the term expulsion.

Detailed comments:

page 5039

> *Abstract: I didn’like the term "bottom layer" here and throughout the paper. Be more precise. The last sentence does not help. Instead of vaguely telling what you do, you should rather explain what comes out of what you’ve done.*
>
> We have avoided the term “bottom layer”. Last sentence in Abstract has been rephrased.
>
> *line 12 surfaceice typo*
>
> Ok thanks – corrected

page 5040

** I’m more familiar with the Assur 1958 reference, but this might be the same paper.*

It is the same paper. Reference ok as presented.

page 5041line 8* *I don't understand why this sentence is here.*

To make the reader aware that CO2 can leave the sea ice with dense brine.

What is the difference between brine drainage and brine expulsion ? Base on Notz and Worster JGR 2009.

We remove expulsion from the sentence. Main thing here is that CO2 can escape the sea ice with the brine.

If you to use brine motion to elaborate on how your reaction works in the sea ice environment, you must be more precise. I would tend to describe this reaction as being driven by brine concentrations. But in this context, the reasoning could be the opposite: in brines, concentrations of all salts are much higher than in seawater, but the stocks are very low. Besides, if brine concentrations are the relevant values, speaking of brine motion could be meaningless. Desalination has no impact at all on brine values. Desalination changes brine volume and bulk salinity, but not brine salinity, which solely depends on temperature, if one assumes equilibrium.

We avoid going into that discussion. We just mention brine drainage as stated above. Main thing is that ikaite crystals grow to a size that they become trapped in sea ice. On the other hand CO2 can escape the sea ice.

line 9 "within sea ice interstices". If you mean that they lose contact with brine then use "between pure ice crystals with no contact with brine?". What do you mean by "pushed to the right" ? Do you mean that there is a CaCO3 deficit in the brine solution ?

We recognize that this sentence may be confusing. We have reformulated it to:

Brine drainage from sea ice is expected to result in a removal of dissolved CO2 along with salts. If precipitated ikaite crystals become trapped between pure ice crystals (narrow sites), then CO2 can be lost from the ice while bulk alkalinity is preserved.

Methods

** The ice conditions seem very peculiar. You must say slightly more. Did you choose that site on purpose? Given the very deep snow, it is very likely that negative freeboard was widespread. Did you measure freeboard ? Or, do you have indirect indications of negative freeboard, e.g., did you see slush on the base of the snow layer? A quick computation suggests that you could easily have highly negative freeboard if the snow was dense enough. Then, the question is, was the snow old (high density) or fresh (low density)?*

The sites were chosen by purpose as they represent a fast ice and polynya site. This year a lot of snow was present – this was not planned. However, lots of snow is regularly observed along and off East Greenland. More details on freeboard have been given in our revision.

Was there ice algae on the site? Was the site chosen to avoid ice algae? Ice algae would reduce nutrients and nitrates could affect TA. I understand that the authors don't want to elaborate on biological aspects, but this information could be useful for future use of your study.

There was very little light. And very little ice algae. Idea was to show that chemical processes still occur in sea ice in the wintertime, even though no ice algae are present. This was part of the logic of the site selection.

You must be more precise in acknowledging the potential sources of errors. The key issue is the temperature cycle you impose to your samples before observation. Add a paragraph to describe the different source of errors. Keeping your ice cores at -20°C may produce $CaCO_3$. If the time they are kept at this temperature is very short, that should be fine. But what if the (unknown) ikaite production rate is very high?

We have added a paragraph of the issue to keep ice corers at -20C: Samples for S, TA, TCO_2 were processed immediately in the field laboratory. Samples for S were melted at 20C and analyzed on site. Sea ice samples for TA and TCO_2 were melted at 0C in gas tight bags and preserved with HgCl in gas tight vials until analysis. Crystals for ikaite determination were immediately processed in the field laboratory. Crystals for ikaite determination on x-ray were kept frozen (-20C) until analysis a month later. Photo documentation showed that crystal morphology did not change due to storage. And since x-ray analysis only were used to identify crystals as being ikaite the prolonged freezing period prior analysis should not affect the results obtained. However, it is important that preservation of TA, TCO_2 and quantification of ikaite is done in the field. These samples should not be stored at low temperatures before analysis as $CaCO_3$ could be produced during the storage.

You must precisely say whether you measured S, TA, $CaCO_3$ from the same ice core or not.

Samples are from separate cores – this has been clearly stated in the revision.

page 5042

** Period missing line 29*

That's strange – it is not missing in our original submission. Something must have gone wrong in the translation.

** Line 29. Why 1.07mm2 ? This numbers falls from outer space at present.*

That’s due to the optics of the microscope and the setting applied. No need to explain further.

page 5043

** "The area of the melt sea ice sample was determined..." how can one measure the area of a liquid?*

Many ways, but the easiest is to count the cells on the glass plate covered by melt water.

** Lines 13-15 "Its volume". Say that you sum over all crystals.*

Suggestion followed.

** Paragraph starting line 16. Say in two words which quantity you measure with X-rays. It is not obvious at the moment.*

We have added a little more here including a revised Table.

page 5045

** line 15 less that typo*

Corrected to less than

** line 26. The ice texture interpretation is not very precise. I’m not a specialist, but please check. A quick look in the literature (eg haas et al. Jglaciol 2001) indicates that polygonal granular does not support snow ice formation, but rather superimposed ice formation.*

The shape of the crystals seen in Fig. 3a are definitely polygonal. Snow melt did not occur during our field work as temperatures remained significantly below freezing. The salinity of the ice in question was also very high thus suggesting snow ice rather than superimposed ice. Finally, polygonal ice crystals have also been observed in other types of ice than superimposed ice (e.g. in the Baltic Sea, see Granskog et al Jglaciol 2007). Please also see the reply to the other review that discusses this a bit further.

Sentence been corrected to:

The upper 35cm of sea ice at ICE I was composed of polygonal granular ice, formed through percolation and refreezing of brine and seawater into snow, i.e. snow ice

page 5046

line 10 orbicular granular ice crystals reflect frazil ice in general (see Eicken, Encyclopaedia of the Antarctic - just google it). The most likely scenario to explain an orbicular granular layer on top of the ice is just new ice formation in open water (frazil ice that consolidates). Snow ice could also form such structures. Then, why invoking brine expulsion here: it is not needed to explain textural features.

We don't believe these crystals originated as frazil ice. Their shape is still orbicular (i.e. rounded). However, compared to frazil ice, they appear to have a specific c-axis orientation (not random), they are much larger, and they have a disc like shape (flat) as noted in the text and seen in Fig. 4a. These types of granular crystals are not discussed in Encyclopedia of the Antarctic. We believe they may have formed from upward growth of ice at the sea ice surface from the freezing of a brine skim (Ehn et al. 2007). This brine is pushed to the surface by the process of brine expulsion as the new ice surface layer cools rapidly with thickness growth. The mention of brine expulsion is therefore needed to explain their presence (as well as the presence of frost flowers).

Sentence "may be related to brine expulsion to the sea ice surface" on lines 13-14 is changed to "may be related to freezing of brine expulsed to the sea ice surface"

line 19 remove "the presence of"

removed

page 5048

** The "temporal" adjective in the title section is not really supported by observations made in this paper*

Temporal has been removed.

** line 15 "dynamic conditions of" -> i would remove*

Suggestion followed

** line 16 Understanding this dynamic would be-> "Constraining the rates of ikaite formation as a function of temperature and brine chemical composition would be"*

Suggestion followed.

** from line 18 on. You must at least explain what are the basics of the model. What are the parameters you specify (in particular temperature)? It would also be nice to compare the output in terms of brine salinity and solid ice fraction of the FREZCHEM model to see whether you reach a value that is comparable to your observed-temperature-derived values. Elaborate here or in the discussion, if you can, why calculations are lower than observations.*

See our reply above. As explained in the text, the discrepancy could be due to the kinetic process and due to the extrapolated thermodynamic constants, both of which are impossible to address at this time of the model development. The important aspect from the modeling excise is that the observed distribution profile follows a similar pattern of the modeled results.

page 5049

** line 5:*

- what did you actually see moving with your microscope? solutes ? gases ? micro-organisms ?

The solutes moved. It was visible from movement of gases and particles. When increasing the temperature the movement increased. We have rephrased this sentence to appear clearer.

- "*are entrapped and transported within the brine system*" -> "*accumulate and move within brine*".

Suggestion followed.

- transport velocity -> are you sure it is a transport velocity and not diffusion ?

Yes, increasing temperature clearly show mass flow one direction.

** line 12*

- this sentence sounds as if CaCO3 crystals would freshen seawater and decrease pCO2. Be more explicit. Is the pCO2 decrease driven by the melt of TCO2-poor ice ? Would CaCO3 enhance CO2 depletion ? That question could be examined by looking at the TA-S ratio in sea ice and seawater. If the TA-S ratio is higher in sea ice than in seawater,

then the role of CaCO3 release would add a further contribution to the simple melt of the ice.

This sentence has been reformulated to appear clearer. The TA:S ratio in sea ice was 84 ± 4 (ICE I) and 78 ± 0.8 (POLY I) as compared with the water column 67 ± 3 (ICE I) and 61 ± 0.2 (POLY I). Thus, the higher TA-S ratio in sea ice than in seawater show that CaCO3 release add a further contribution to the simple melt of ice.

** line 17 in the bottom layer of the sea ice -> reword, be more precise*

we have added the interval to be more precise

** lines 19 on, starting from "One explanation".*

I was not really convinced by the physical part of this argument, which relies on downward brine expulsion of CO2, which sounds quite unlikely in your situation. Clearly, you are in a system where local chemical sources and sinks must interact with physical transport by convection.

We have decided to include some of the ideas provided by the reviewer. The revision contains more details on this matter. See below and in the revised version.

These paragraphs need to be rewritten. Use the following items or reject them:

1) Brine volumes are higher than 5 everywhere (permeable ice) and the temperature gradient points downwards (unstable brine network). All these suggest that full-depth convection (see Jardon et al., JGR2013) is possible. Hence, your brine might well be convectively exchanging with seawater below. CaCO3 would extract Ca and DIC from brine and could pump them out of the liquid brine, while convection could replenish in brine the elements required to form ikaite. This all depends on the time scales associated with CaCO3 precipitation and brine convection. See Vancoppenolle et al., JGR 2010, section 6.4 where a similar argument is developed for ice algae and nutrients.

We have included a little more on this paragraph in our revision.

2) Besides, the most natural explanation is that CaCO3 stock is equal to a a temperature-dependent production rate multiplied by time. The upper layers are older and colder, hence more prone to higher ikaite stocks.

Agree – this has been highlighted further in the revision.

3) I don't know what your pH measure means, but clearly the pH of brines should be used. Full-depth convection of brine may explain an apparent downward migration of pH equivalents. Any downward transport of pH equivalents should be driven by an upward *vertical gradient of pH equivalents within brine, provided by the brine network is open.*

It is difficult to measure pH of brines. Here we report on bulk pH measurements and can only speculate on what pH is in the brine. We would like to keep the text as it is.

4) Looking at your curves, it appears that CaCO3 concentrations are higher than TA. Be more precise on the sampling and observation errors. Give TA/CaCO3 numbers in a table or put the profiles on the same plot to make this clear.

The analysis of TA and CaCO3 are not from same cores. This has been made clear.

page 5050

line 6 "Another mechanism that could affect". -> use instead something like "Physical supplies by brine convective motion that impacts the stocks of required elemets driving the ". This second paragraph could also be rewritten using the aforementionned elements.

Suggestion followed.

page 5051 *line 5 Again, brine expulsion is unlikely to be the main driver here.*

Point taken.

page 5052 *line 21 this Papakyriakou paper is not cited.*

It is now.

Figures and tables

Fig1. I don't see the dark and light stars mentionned in the caption for panel B. Besides, could you delimit sea ice and land on panel B using dark lines ?

We have changed to red and yellow stars. No.

Tab1 is not helpful. The meaning of the numbers is not detailed, no units. I would remove this table, unless it is described and explained properly.

We disagree. It is the first time that data on so many ikaite crystals and ice layers have been documented. We have improved the Table. Would like to keep it.

Fig 2. For even easier reading, you may add the name of the site for each panel and suggest what the lines mean with a legend, but this is more an advice than an order :-). If you know the location of the freeboard, add it on the plot.

Would like to keep the figure as it is.

Fig 6. You could add a line in the text to explain why the relation between crystal numbers and concentrations is not linear. Obviously, you find out smaller crystals upper in the sea ice. If you know where freeboard is, add it on the plot.

We would like to keep the legend as is. Size distributions of crystals will be a focus of an upcoming paper. No need to present this here without discussing in in details in the main text also. It is not important for the conclusions of this manuscript.