

Interactive comment on “Dynamic ikaite production and dissolution in sea ice – control by temperature, salinity and $p\text{CO}_2$ conditions” by S. Rysgaard et al.

Anonymous Referee #1

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Rysgaard et al.: Dynamic ikaite production and dissolution in sea ice – control by temperature, salinity and $p\text{CO}_2$ conditions.

General Comments Rysgaard et al. present observations of the ikaite content with depth and time in sea ice and its surface features (frost flowers and brine skim) grown and investigated at an outdoor experimental facility in the course of one month. The ikaite content is based on ‘dissolving crystal’ counts under the microscope and their conversion to ikaite molar concentration. The idea is that all ‘black spots’ on photographic sea ice slides disappearing upon warming are dissolving ikaite crystals. This tenet is carried over from their previous article on method development as an assumption (P6080 L28), which is confusing because it suggests that it is yet to be substantiated.

C3080

ated in a controlled experiment. In other words, the counts and their quantification as ikaite have a degree of uncertainty which requires rigorous evaluation if this promising method is to be used in carbon budgets in sea ice.

As outlined below, the Title of the article is misleading as the study does not provide any observational evidence for control on ikaite dynamics by $p\text{CO}_2$, while the evidence for direct and singular temperature control, although expected in terms of ikaite solubility and internal brine compositional changes with temperature, is tenuous. The salinity control in the Title is not explicitly touched upon in any section of the manuscript. Further, the thread used in the Introduction anticipates the use of the presented observations in carbon budgets in sea ice, which is not fulfilled. Consequently, the interpretation needs to be trimmed to match the potential of the offered observations and available evidence from published experimental and field studies, the latter being currently absent from the manuscript. At best, the manuscript reports the dynamic temporal distribution of ikaite in sea ice in the SERF experimental facility, which is valuable in itself, provided that the sampling assumption mentioned above is shown to be secure.

Specific comments

Methods

P6079, L7-8: This statement may be true in terms of ionic composition (SERF seawater contained all major ions present in standard seawater) but salinity-normalization to $S=35$ reveals that the concentrations of some of the pertinent ions in SERF seawater were substantially different from those in standard seawater, i.e., Ca^{2+} was 15% higher, Mg^{2+} was 50% lower, and sulphate was 27% lower than standard seawater. As a result, the ionic strength of the SERF seawater is 10% lower ($I=0.653$ at $S=35$) than standard seawater ($I=0.721$). Some amendment is needed to reflect this fact.

P6080, L28, & P6081, L6-12: The core of the dataset and narrative in this manuscript is based on this assumption. In the absence of even a brief mention in this manuscript of

C3081

confidence-building validity tests, I conclude that this assumption is previously untested for reliability. Provide assurance that this assumption is safe in the presence of substantial quantities of mirabilite predicted by the FREZCHEM model. For example, a standard seawater freezing FREZCHEM run at constant atmospheric pCO₂ predicts that the mirabilite to ikaite ratio (on a g/g basis) rises to 21 at -7°C and to 39 at -10°C. In other words, the authors need to provide evidence that the photographic technique can reliably quantify ikaite in the presence of mirabilite and, also, gas bubbles.

P6082, L16-19: I cannot see the relevance of running the FREZCHEM with the 'standard seawater' and the 'average bulk sea ice' compositions as input parameters when the exact initial composition of the SERF seawater is known. If the ionic and chemical composition of the residual seawater in the experimental basin did not change in the course of the experiment, the internal brines in the SERF sea ice should have the conservative ionic and chemical composition of SERF seawater as a function of salinity-temperature changes at thermal equilibrium plus or minus any chemical and biological reaction products. As I understand it, carbonate, sulphate, and chloride solid salt precipitation and dissolution in sea ice are solid/brine reactions not solid/bulk-sea-ice reactions. This much is stated by the authors on P6087 L5-6. The 'average bulk sea ice' composition as an input parameter is suitable for hyposaline (S < 35) starting seawater composition, such as in the Baltic. The resulting trends in Fig. 3 (standard seawater and average bulk sea ice) are therefore irrelevant and, therefore, confusing.

P6082: Provide evidence that the assumption of constant brine pCO₂ at atmospheric equilibrium is justified. Field and experimental data indicate a large range of pCO₂ conditions in sea ice, to name but a few: Geilfus et al. (2012, *J. Glaciol.* 58, 287-300), Miller et al. (2011, *J. Geophys. Res.* 116, C00G04, doi: 10.1029/2011JC007143), Miller et al. (2011, *J. Geophys. Res.* 116, C02028, doi: 10.1029/2009JC006058), and Delille et al. (2007, *Limnol. Oceanogr.* 52, 1367-1379.).

Discussion P6086, L21-24: The statement about the hypothetical contribution of the ikaite content in FF and BS to the total ikaite content is redundant in view of the next

C3082

statement on L24-25, which is based on the actual observations.

P6087, L1: Clarify what the observed relationship was between sea ice temperature and ikaite concentration.

P6087, L9: In order for the FREZCHEM to solve the CO₂ system in the brine, it requires 2 parameters when one is stated here (TA). Clarify the second parameter used here.

P6087, L20: By the authors' statement here, the observations of the ikaite content in the SERF sea ice do not follow the curved increase with decreasing temperature past the temperature threshold predicted by FREZCHEM at atmospheric pCO₂. Provide context (also in the Introduction) why temperature is considered here the primary independent variable in the precipitation of ikaite in sea ice. Clarify what 'general' means in the statement on L25-27.

P6088, L2: Explain 'sufficiently', which implies a threshold in the concentration increase for precipitation to begin.

P6088, L4: The temperature threshold of ikaite precipitation is very specific to the input parameters in the FREZCHEM model. Clarify why the range of threshold temperatures here.

P6088, L5-6: The thermodynamic solubility product of ikaite is $K_{sp} = a_{Ca} a_{CO_3} a_{H_2O}^6$ (Bischoff et al., 1993, *J. Geol.* 101, 21-33). Clarify how the IAP reported here is related to the K_{sp} , and the precipitation and dissolution of ikaite.

P6088, L16-24: In L16-18, the authors suggest slower ikaite precipitation rate than seawater-ice-air heat exchange following snow clearance to explain why the observed ikaite concentration was lower than that predicted from the FREZCHEM model. In other words, although the brine-ice-air system thermally re-equilibrated rapidly, the ikaite-brine system did not. Further on (L20-22), it is stated that the delayed 'response' of ikaite is due to slow latent heat change in sea ice. These two statements are contradictory. Furthermore, as the authors state on P6087, L20, the ikaite data do not fit the

C3083

'direct temperature control' model of the FREZCHEM predictions. Additionally, 'direct control' of a parameter on another would imply a positive correlation between temperature and ikaite concentration as seen in the FREZCHEM trend at constant pCO₂. Such a correlation is not provided here, and it is not visually obvious. Hence, the statement about 'direct temperature control' is uncorroborated. In short, it is unclear how the authors deduce 'direct control' of temperature on ikaite concentration.

P6089, 5-6: The term 'inhibition' of precipitation implies kinetic effects under supersaturation ($IAP > K_{sp}$) conditions in the presence of the 'inhibitor' ions. The authors use this term to explain the lower ikaite concentrations they determined in the lower middle part of the sea ice viewed from the perspective of bulk sea ice chemical composition. This shift in perspective is confusing because ikaite precipitation and dissolution is a brine/solid reaction. Provide information on the saturation state of the brine with respect to ikaite, which is a more appropriate term and concept to use, to explore this pattern in the ikaite distribution in sea ice.

P6089, L9-12: Downward transport implies ice permeability conducive to such transport. Provide permeability information from observations to support this statement.

P6090, L3-27: It is unclear on what evidence the pCO₂ enters the proceedings this late in the Discussion and, crucially, the Title of this manuscript. The authors do not present pCO₂ data either from the SERF system or from field and experimental studies available in the literature to support this latter part of the Discussion or, indeed, the Title. Provide published evidence that whether ikaite precipitates or dissolves in sea ice is a function of the brine pCO₂. Speculation is healthy provided that it is firmly rooted in published evidence in the absence of commensurate data in the study. In the same vein, the Title is misleading for the same reason and should be changed. Finally, it will be useful to provide some analysis of the current dataset along the lines of inorganic carbon mass balance in sea ice. Field studies have documented from geochemical analyses of brines the fractional contribution of CaCO₃ precipitation to the inorganic carbon mass balance in sea ice and can be used for meaningful comparisons.

C3084

Interactive comment on The Cryosphere Discuss., 7, 6075, 2013.

C3085