

## ***Interactive comment on “Precipitation of salts in freezing seawater and ozone depletion events: a status report” by S. Morin et al.***

**E. Wolff (Referee)**

ewwo@bas.ac.uk

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This paper is a simple and well-written study of phase relationships expected in materials derived from freezing seawater. It is valuable, firstly as a refinement of the highly conceptual study by Sander et al that discussed how alkalinity would be lowered in the liquid phase as brine freezes. That paper highlighted the difficulty that the derived thermodynamic values could not be extrapolated to the relevant low temperatures and high salinities. This paper solves that issue by using the FREZCHEM model to do the calculations "properly". This paper adds in an interesting calculation of how Br/Cl ratios should vary in the liquid phase as temperature drops below the point at which NaCl (halite) precipitates. These two results (lowered alkalinity, and fractionation favouring bromide on surfaces) lead to two implications: firstly they clearly call urgently for real

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measurements to be made. As stated by a number of people at the recent AICI laboratory workshop on halogens and ice (Cambridge, June 2008), the measurements of pH and alkalinity in brines frozen from sea ice appear quite straightforward and really should be done. Secondly, if correct, the measurements suggest atmospheric effects relevant to ozone depletion events that should be further studied in models. I believe this paper is therefore very worthwhile, and should be published with minor changes.

The paper is in principle quite straightforward. The main technical issues concern FREZCHEM itself: I am not able to judge whether it is correct in all respects (see below) but its details have been tested in a series of papers. I do have a number of detailed comments and corrections, and I would also like to add something to the interactive comment by Kaleschke.

Kaleschke makes the point that there has recently been a paper by Dieckmann et al., apparently showing that the precipitated phase of calcium carbonate in sea ice is ikaite and not calcite. I agree that the authors need to comment on this, but it is worthwhile to look at the history of this issue. In fact, when one goes to early studies (Richardson, 1976; Weeks and Ackley, 1982), authors refer to the calcium carbonate salt they assume to be precipitated as  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  (i.e. ikaite). FREZCHEM includes 4 calcium carbonate minerals (calcite, aragonite, vaterite and ikaite); in the paper describing their incorporation (Marion, 2001), one of the authors of the present paper specifically discusses whether it is calcite or ikaite that forms when freezing seawater, and concludes that calcite is more likely. Especially in view of the Dieckmann paper, this should be discussed again here; perhaps the authors might test how it affects their predicted alkalinity (Fig. 4) if calcite precipitation is inhibited by artificially raising its  $K_{\text{sp}}$ , a manoeuvre that was proposed before (Marion, 2001).

A few detailed comments:

Page 9038, line 27: "observations"

Page 9038, line 29: As discussed above, Richardson actually discussed (by chemical

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formula) ikaite rather than calcite, although he didn't name it.

Page 9041, line 2: "or salinity"

Page 9041, line 3: "led to inconsistent" (not "lead")

Page 9042 and Fig 2: This figure is very hard to evaluate as published. I'd prefer to see it on a linear scale, or at least with the two pairs of curves on separate plots to give a vertical stretch.

Fig. 2, y-axis: "moles/kg"; not "moles/Kg";

Page 9045, line 15. Not essential, but if you just want data on the ratio of Br to sea salt in frost flowers you can also quote (Rankin et al., 2002).

Page 9046, lines 1-5. You refer here to the eutectics, and most people will know the value for NaCl, but I doubt they know the value for NaBr; it would be valuable to mention it here. Without doing a big literature survey, I found a value of 244.8 K, but there may be more "official" values out there.

Page 9047, last paragraph. The authors worry about whether the calcium salt will remain separated and unavailable. I believe it has always been assumed that the precipitated salt (whether calcite, ikaite or mirabilite) is incorporated into the growing ice structure on the sea ice surface. There are two reasons to assume this: firstly even ikaite is considerably denser than the brine, so will anchor to the underlying ice, and secondly I would have thought that any crystals in the liquid phase will act as nucleation points for ice growth that will eventually engulf them.

Page 9048, line 24: "where ODEs"

Page 9049, line 8-10. It should also be stated that the pH changes you are predicting in the temperature range of Fig. 6 is around 0.2 units (your supplementary data), which would be lost in the scatter of the measurements shown.

Marion, G. M.: Carbonate mineral solubility at low temperatures in the Na-K-Mg-Ca-

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H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system, Geochim. Cosmochim. acta, 65, 1883-1896, 2001.

Rankin, A. M., Wolff, E. W. and Martin, S.: Frost flowers - implications for tropospheric chemistry and ice core interpretation, J. Geophys. Res., 107, 4683, 2002.

Richardson, C.: Phase relationships in sea ice as a function of temperature, J. Glaciol., 17, 507-519, 1976.

Weeks, W. F. and Ackley, S. F.: The growth, structure, and properties of sea ice, CRREL Monograph 82-1, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, 1982.

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Discussion Paper

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