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

S. Morin et al.

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We thank R. Sander for having read the version of our manuscript during the discussion phase. His comments are valuable as his previous work on the potential impact of carbonate precipitation in the brine (Sander et al., 2006) has sparked our interest on this issue, which ultimately yielded the present study.

Using the model FREZCHEM we checked the sensitivity of the carbonate system in the brine to the nature of the calcium carbonate that precipitates, and found that whether ikaite (Dieckmann et al., 2008) or calcite (Marion, 2001) is the calcium carbonate salt which precipitates makes a very significant difference in terms of alkalinity during freezing, at equilibrium with atmospheric CO_2. Thus the conclusion of the revised article is that the results of Sander et al. (2006) should really be viewed as preliminary and certainly not to be taken for granted in forthcoming studies dealing with halogen activation

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in polar regions.

Response to general comments

- NO_2/SO_2 : This is true that these are not strong acids, but only strong acid precursors. This has been changed in the text.
- Variations in pH during freezing : this remark was not kept in the revised version of our manuscript, given the large magnitude in the change of the alkalinity in the brine during freezing (when ikaite is set to precipitate), which is the main observation derived from the model runs.
- The separation of precipitated salts from the brine is indeed required to explain negative nss-sulfate observations, as stated in the manuscript. We have added a sketch in the paper, which summarizes potential sources of aerosol featuring a chemical composition affected by chemical fractionation in the brine prior to formation. The sentence discussed by R. Sander has been removed from the body of the manuscript.
- Equivalents : this terms has been defined in the text in terms of charges (it is useful when discussing variations of the alkalinity). Table 1 has been modified according to the suggestion of R. Sander, for clarity.
- Extrapolated values : we agree with R. Sander that extrapolated values of true thermodynamic constants could be valuable for other studies. The data used for producing Fig. 1 are attached to the revised manuscript as a supplementary file. However, given the complexity of sea-water as a chemical medium, we feel that only a thorough and accurate thermodynamic modeling such as FREZCHEM should be used with such data, when dealing with thermodynamic issues discussed here. Not only thermodynamic constants have to be extrapolated (as

shown on the Fig. 1 of the discussion paper), but also the whole thermodynamic state of the system has to take into account temperature variations (activity coefficients, density etc.). The FREZCHEM model is available upon request (a generic version is even available on the internet), and all necessary thermodynamic parameters are embedded in the model. All the necessary details are given in Marion (2001). As it is now stated in the model, it is clear that not only thermodynamics should be applied to deal with such a complex system. One way to solve the issues raised in our revised manuscript, brought about by our model runs, is to perform careful laboratory experiments, which only will be able to provide strong constraints on the chemical behavior of sea-water during freezing in polar regions, in conjunction with reactive halogen chemistry.

Technical comments

All technical comments were fixed as indicated.

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9035, 2008.

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