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Comment

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

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This paper is a well written and refreshingly concise description of a modeling study of the chemical behavior of seawater at sub-zero temperatures. This study is of value to the scientific community to help reconcile some incongruous results from modeling, satellite and in-situ measurements of atmospheric bromine, frost flowers and ozone depletion events (ODEs). It is recommended that the paper be published with minor revisions.

The authors used the FREZCHEM model to simulate carbonate and halogen salt precipitation in brine solutions at thermodynamic conditions representative of those found in polar-regions and associated with frost flower formation. The results qualitatively agree with previous modeling studies but carry greater weight due to the narrower fo-

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cus of the study and the use of thermodynamic constants that are more suitable for temperatures below 273K and salinities above 35 g/kg. The proposed temperature-alkalinity relationship could in part resolve the disagreement between observational studies suggesting a coincidence between bromine explosions/ODEs and frost flowers (eg Rankin et al. 2002), laboratory studies indicating that a lower pH is required for the release of bromine from frost flowers (Fickert et al. 1999) and in-situ bulk measurements of frost flowers and brine showing elevated pH (Kalnajs and Avallone 2006).

General Comments:

In section 4.3, the possibility of calcite re-dissolution when frost flower/ice samples are melted for analysis is discussed. There appears to be a contradiction in using this process to explain the difference between calculated pH and field observations (Gleitz et al. 1995 etc). In comparing chloride to bromide ratios between modeled brine solution and melted frost flower samples there is good agreement (9047, line 1). However, when comparing pH and alkalinity of modeled brine and measurements, there is a significant discrepancy. The authors suggest that calcite dissolution upon melting for analysis may increase the alkalinity back to sea water values (9049, line 13). It would also be expected halogen salts would similarly re-dissolve upon melting, returning frost flower samples to the sea water Cl/Br ratio of 650. It seems unlikely that dissolution on melting could affect the pH measurements and not the halogen measurements.

On page 9047 line 16 onwards, the authors discuss the implications of their findings for subsequent processes that may reduce the pH of brine derived aerosols to a low enough value to facilitate gas phase bromine release. While the process of carbonate precipitation may speed up the acidification of aerosols, it is unlikely that it is a necessary condition. The pH of sea salt aerosol inferred from measurements and modeling indicates that acidification can be a reasonably rapid process even without the removal of carbonate (albeit under warmer and possibly more polluted tropical conditions e.g. Pszenny et al. 2004 and references therein). This would suggest that carbonate pre-

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cipitation may be less important for sea salt aerosol acidification, at least in warmer areas such as the Dead Sea (as discussed in section 4.2).

On a more general level, the paper would benefit from an expanded description of the physical processes modeled and methodology used with the FREZCHEM model. For example, the authors mention the process of "salting out"; however it is not immediately clear if this is a thermodynamic or kinetic process and whether or not it is included in the model. Additional technical details as to what model runs were performed would be useful for interpreting the results. It can be inferred from figure 5 that the model was run down to temperatures of 238K, however there is no carbonate/alkalinity data is reported below 253K. Is there a limitation to the calculation of alkalinity below 253K? For comparison to observational results, particularly from the Antarctic, values below 253K would be useful.

Technical notes:

Page 9037, line 17: "0.1 – 0.2 pH-unit" should read "0.1 – 0.2 pH-units"

Page 9037, line 13: The statement: "Marine aerosols, frost-flowers (or frost-flower derived aerosols) and sea-salt enriched snowpack have in common a chemical composition close to that of seawater in terms of the proportions between species." seems to contradict the premise of the paper.

References:

Pszenny, A. A. P., J. Moldanov, W. C. Keene, R. Sander, J. R. Maben, M. Martinez, P. J. Crutzen, D. Perner, and R. G. Prinn (2004), Halogen cycling and aerosol pH in the Hawaiian marine boundary layer, *Atmos. Chem. Phys.*, 4, 147 - 168.

Rankin, A. M., Wolff, E. W., and Martin, S.: Frost flowers: Implications for tropospheric chemistry and ice core interpretation, *J. Geophys. Res.*, 107, 4683 - 4694, 2002.

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