

Interactive comment on “Carbonate precipitation in brine – the trigger for tropospheric ozone depletion events” by R. Sander et al.

Anonymous Referee #2

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The authors present an intriguing hypothesis: calcium carbonate precipitation from freezing sea water greatly reduces the buffering capacity of the resulting brine and subsequently produced sea-salt particles. This allows the “bromine explosion” to occur much more quickly than if all of the seawater carbonate needed to be neutralized by acids. The hypothesis is explored and supported using a few model runs of heterogeneous chemistry under both Arctic and Antarctic conditions.

This paper should itself be a trigger for further laboratory, field, and modeling studies of the importance of carbonate precipitation in bromide oxidation in polar regions. While I have a few questions and suggestions below, I recommend publication after these issues are addressed.

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1. Sea-salt particles I. It is not clear from the manuscript how the particles are treated. Are they considered to be well-mixed, liquid particles with a composition based on sea salt (minus the corresponding amount of CaCO_3) in equilibrium with the ambient relative humidity? Or are the particles frozen and only a portion of the halides are available for reaction? What are the concentrations of major sea-salt components (e.g., Na^+ , Cl^- , Br^-) in the particles?

2. Sea-salt particles II. The LWC values used in the model (on the order of $1\text{E}-10 \text{ m}^3 \text{ m}^{-3}$) seem very high. For example, work by Staebler et al. (JGR, 99, D12, 25429-25437, 1994) during PSE92 at Alert found particle volumes ($D_p = 0.2 - 12$ microns) on the order of $1\text{E}-12 \text{ m}^3 \text{ m}^{-3}$, with most of the volume in the submicron, presumably sulfate, particles. Are there other measurements that justify using the model LWC values for sea-salt particles?

3. Sea-salt particles III. Mechanical generation of sea-salt aerosol from frost flowers, brine, or deposited snow should produce very large particles (with a median diameter significantly larger than the 2 micron particles in the model), which will have lifetimes shorter than the assumed 3 days in the model. Using the same LWC as assumed in the model, would larger particles affect the model chemistry (e.g., because of faster removal of acidity from the boundary layer or slower liquid phase diffusion in the particles)?

4. Other sea-salt pools. Are the frost flower and brine pools included in the model chemistry? If not, how might their inclusion affect bromine activation in the model? What fractions of condensed phase bromide are in these pools and in the airborne particles in typical polar conditions?

5. Calcium carbonate precipitation. Since the extent of carbonate precipitation is the key component in the chemistry examined, it would be useful to see the set of equations, calculations, equilibrium constants, and assumptions that were used to determine Figure 2. This would be a very useful appendix for curious readers (such as this

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reviewer).

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