

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

Anonymous Referee #1

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Review of “Carbonate precipitation in brine - the trigger for tropospheric ozone depletion events”, by Sander et al.

Consensus exists that lower tropospheric ozone depletion events (ODEs) in polar regions during the spring are due largely to catalytic destruction of ozone by Br atoms. The Br atoms are believed to originate from the activation of sea salt Br⁻ ions in the so-called bromine explosion mechanism. In this paper the authors address the question how the bromine explosion can take off since particles derived from sea water might be expected to be alkaline while the bromine explosion is acid-catalyzed. They argue that at the low temperatures prevailing during the time that ODEs are observed, calcium carbonate (CaCO₃) will precipitate, thereby reducing the buffering capacity of the sea water and facilitating its acidification. This is an interesting hypothesis, and by

performing a few scenario calculations with a box model the authors find that in fact it is not inconsistent with, and may help explain both Arctic and Antarctic ODEs.

However, there is a problem with the style of this paper. First, I feel the authors vastly overstate their case, starting with the title. The CaCO_3 precipitation might well occur, but running a few scenario calculations is hardly proof, so a question mark at the end of the title seems in order. And in any case, while it would trigger the bromine explosion (reactions R1-R3), I would argue that the first Br atom (or hypobromous acid (HOBr) molecule) is more justifiably the ODE trigger - and that is more than simply an academic question. Another case where a hypothesis becomes fact is on page 7078 where it is stated that region experiencing potential frost flower conditions are the sources of BrO clouds. Not true, this is a hypothesis (albeit an attractive one) without proof. Such practices should be avoided (I can see how the proposed aerosol generation mechanism will become fact without proof in future papers). These two examples are indicative of the tone of the paper in general.

The paper appears rather poorly vetted. I find it for instance worrying that the section about the aerosol generation mechanism is only supported by references to chemical literature. I would be very surprised if there did not exist a large body of information on this topic in the cryosphere physics literature. Similarly the issue of CO_2 dissolution at low temperatures. I am sure there is a lot to find in the oceanography literature on this topic (after all, there is for instance the question of whether the Arctic Ocean is a source or sink for CO_2 , see e.g. Semiletov et al. 2004, GRL, 31, L05121, doi:10.1029/2003GL017996.).

I am wondering whether the question about acidity of aerosols and snow in the Arctic really is all that problematic anyway. The aerosols are probably acidic almost from the start due to anthropogenic pollution especially sulphate. It is a little deceiving to claim that they are initially alkaline and argue that this is consistent with the observations from Kalnajs and Avallone since those data pertain to Antarctic frost flowers. A better reference about Arctic snow would probably be the work of Beine et al (<http://www.atmos->

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chem-phys.net/3/335/2003/acp-3-335-2003.pdf) who report that fresh snow at Ny Alesund was reported to be alkaline. Note that fresh snow at Alert appeared to be mostly acidic, at least in spring when ODEs occur (Toom-Sauntry and Barrie, AE, 36, 2683, 2002). While on this topic, I feel the actual aerosol composition that was used for the box model calculations should be given in the current paper.

So in conclusion, an interesting hypothesis, but at a minimum the paper should be rewritten to make it clear that that is all it is. While on this point I also recommend to include in the introduction a reference to ODEs and indicate that the topic relates to those; as written now, this follows from the abstract but that is not the same. The paper is thankfully short, but at the expense of solid testing which could (and probably should) have been done.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7075, 2006.

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