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

R. Sander et al.

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We thank reviewer #1 for his helpful comments and we would like to make the following replies:

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> I can see how the proposed aerosol generation mechanism
> will become fact without proof in future papers.
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We agree with the reviewer that there is always a danger of hypotheses becoming “fact” by repeated citation. However, this is certainly not our intention. Instead, we hope that our article stimulates more studies to prove (or falsify) our hypothesis. Especially laboratory studies investigating the exact degree of carbonate precipitation in cold, highly concentrated brine are urgently needed. This point is emphasized in the conclusion

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section of our manuscript.

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> I feel the authors vastly overstate their case, starting
> with the title. The CaCO3 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.
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Overstatement is a matter of degree. We have shown that all previous studies have not addressed the triggering of the bromine release. This is a key step which is not yet explained. We have provided a very plausible explanation of the trigger for the bromine explosion. However, to address the reviewer's concern, we have now added the word "potential" to the title. We do not think that a question mark would be appropriate because it would look like we'd argue against the importance of carbonate precipitation instead of proposing it.

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> 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.
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Here, we do not agree with the reviewer. Many reactions have been listed in the literature that produce the first Br atom which starts the autocatalytic cycle:

- Br^- + O_3 (Oum et al. (1998), Rudich et al. (1998), Anastasio and Mozurkewich (2002), Hirokawa et al. (1998))
- Br^- + OH (Mamou et al. (1977))
- Br^- + NO_3 (Sander and Crutzen (1996), Rudich et al. (1998))

- Br^- + N_2O_5 (Behnke et al. (1994), Finlayson-Pitts et al. (1990))
- Br^- + HSO_5^- (Mozurkewich (1995))
- photolysis of organic bromine species (Moortgat et al. (1993))
- photolysis of organic iodine species and subsequent interaction with the bromine chemistry (Vogt et al. (1999))

We do not think that lack of initiation is a limiting factor for bromine explosions.

> 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.

In our view we need to distinguish two separate issues. There are no serious objections to the discovery of the fact that regions experiencing potential frost flower conditions are the source regions of BrO clouds. This was clearly shown by Kaleschke et al. (2004). However, we do agree that there are several hypotheses trying to explain the mechanistic reason for this correlation. This is why we use the term “potential frost flower conditions” instead of “frost flowers”. Our carbonate precipitation mechanism does not depend on the actual availability of frost flowers. It will also work if aerosols form from brine-covered snow or directly from the brine, as illustrated in Fig. 1c.

> 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 exists a large body of information on this topic

> in the cryosphere physics literature.

Hitherto, it was thought that the sole source of sea salt aerosol is bubble bursting from open water. The more recent interpretation is that the sea ice surface is a significant source of sea salt to Antarctica. This change of paradigm took place only in the last few years (Wagenbach et al. 1998; Rankin et al. 2002; Kaleschke et al. 2004; Wolff et al. 2006). To the authors best knowledge there exists no significant work about sea salt aerosol from a sea ice surface before 1998 in the literature.

> Similarly the issue of CO2 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 CO2, see e.g. Semiletov et al. 2004,
> GRL, 31, L05121, doi:10.1029/2003GL017996.).

The referee is sure that there is a lot to find in the oceanography record. This is true for temperatures above -1.9 °C and typical salinities of sea water. However, for lower temperatures and brine salinities the information is sparse. A comprehensive review about the properties of sea ice was given by Weeks and Ackley (1986). They state that “all experimental work to date has ignored the carbonate content of the brine, although $\mathrm{CaCO_3 \cdot 6H_2O}$ would appear to be the first solid salt to form during the formation of sea ice”. More recently, Marion (2001) remarked the lack of equilibria data at subzero temperatures.

The referee mentioned the work of Semiletov et al. (2004). The question of $\mathrm{CO_2}$ exchange over sea ice is an important one. Semiletov et al. report interesting data about $\mathrm{CO_2}$ fluxes over melt ponds and fast ice. Such measurements over new leads and frost flowers at cold temperatures would be very desirable. However, this aspect exceeds the scope of our paper.

> I am wondering whether the question about acidity of

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> 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.

Yes, we do think that understanding the acidity is very important! Initially, when the Arctic ozone depletion events (ODEs) were discovered, it was implicitly assumed that there is always enough anthropogenic acidity to allow acid-catalyzed chemistry to occur. Later, ODEs were also discovered in the much cleaner Antarctic but the question of acidity was not raised anymore. We consider it very important to find out whether ODEs are anthropogenic or natural. And also, if they are natural, how are they affected by anthropogenic acidity? We need to understand these issues in order to explain ODEs.

> 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.

We agree that refering to Antarctic measurements is confusing in the section about the Arctic conditions and have removed the citation.

> A better reference about Arctic snow would probably be the
> work of Beine et al [...] 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).

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Thanks for pointing out these references. Acidic snow is consistent with our mechanism because it is likely that the falling snow flakes have scavenged old (i.e. processed), acidic aerosol particles. Thus (in contrast to the brine) we expect them to be acidic. Regarding the measurements of Beine et al., they suggest that sea-salt deposition turned the snow alkaline. This is consistent with our understanding if the sea-salt that turned their samples alkaline originated directly from the open water, and not from regions experiencing potential frost flower conditions.

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> 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.
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We have added this information to Table 1 in the revised manuscript.

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> 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.
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Yes, this is a good point. We have now added a few lines about ODEs to the introduction.

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> The paper is thankfully short, but at the expense of solid
> testing which could (and probably should) have been done.
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This is a somewhat imprecise criticism. Testing has indeed been done already but we decided to focus on the main results instead of diluting them with the presentation of too many additional sensitivity studies. For example, we briefly mention in the manuscript our sensitivity studies varying the aerosol lifetime and the degree of carbonate precipitation.

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