

Interactive comment on “Photochemical chlorine and bromine activation from artificial saline snow” by S. N. Wren et al.

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This manuscript describes elegant experiments examining production of halogens from artificial snowpack and should be published in ACP. The article is well written and clearly describes the experiments, results, and atmospheric implications. The manuscript supports snowpack halogen activation via the "bromine explosion" mechanism, and also gives insight into how chlorine can be activated. The temperature and pH dependence of dihalogen production is studied and is interesting and has important atmospheric implications. I support publication of this article in ACP. Below, I have a couple of general comments and some small specific comments.

– general comments –

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On page 14172, line 16, the concept of depletion of snow bromide is mentioned. Is it possible to give some quantification to the mass balance of bromide at the surface based upon these experiments? Specifically, it seems like the calibration of the CIMS means that total liberated bromine atoms per time liberated from the snow are measured. Integration of these produced bromine atoms over time should then indicate mass loss of bromide from the snow. How does this mass loss compare to the initial mass of bromide in the snow? I would presume that the liberated bromine is much less than bromine frozen into the snow, which would then mean that some bromide is not available on the surface and/or diffusion of non-surface bromide to the surface is a limiter of bromide available for reaction. This calculation may be very crude, but it might give interesting insight into the nature of bromide on the surface and/or limitations on bringing bromide to the surface.

On page 14176, section 3.6, there is a discussion of the necessity for acid pH, and relatively low pH appears important. That is a very important result of this work with important atmospheric implications. Do the authors have an idea of the mechanistic reason for necessity of such acid pH? The pKa of HOBr is about 8.7, and that of HOCl is reported as about 7.5. Both of these pKa values would indicate that all of these acid pH values (including the value of 5.9, where dihalogen production was not observed), both hypohalous acids should be highly protonated. The trend in lower pKa for HOCl than HOBr appears to be in agreement with the observations of reduced production of chlorine at pH 4.3 while bromine is still produced. However all of the pre-freezing pH values are quite low compared to these pKa values. Can the authors speculate mechanistically about why these pH values are required?

– specific comments –

p14168, line 15. I presume that the temperatures reported later are those of the reaction chamber (5K warmer than the chiller), but please clarify this point.

p14168, line 25. What is the pressure at the region of the SF₆⁻ ion source? Does

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the electron attachment occur at near atmospheric pressure, or at close to the IMR pressure (2.5 Torr)?

p14169, line 6. A bias of -14V is mentioned here, and also another bias is mentioned earlier. What potentials are these compared to (are they compared to the chamber wall or the mass spectrometer or what)?

p14169, line 24. How was the Cl₂ final mixing ratio measured? Same question for the Br₂ mixing ratio in the standard?

p14170, line 14. I think this should say counts per second for the ion source.

p14170, line 25. I think that the resistivity of pure water is 18 M-ohm * cm. The "cm" is missing.

p14171, line 1. Please relate the impurity level in these NaCl samples to that of sea water.

p14171, line 21. I think the unit of chamber volume should be centimeters cubed (squared is listed).

p14172, line 1. Was bromide analyzed for in these samples or not? Please mention.

p14175, line 14. This wording is a little confusing. A reduction in the photolysis rate is listed as Cl₂»BrCl. That could be read that Cl₂ is much faster than BrCl or much more reduced. Please reword to be clearer.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 14163, 2013.