

Interactive comment on “pH-Dependent production of molecular chlorine, bromine, and iodine from frozen saline surfaces” by John W. Halfacre et al.

Anonymous Referee #1

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The manuscript by Halfacre et al. describes a number of laboratory experiments conducted to better elucidate the nature of halogen activation from halide-containing ices. This is an important topic in polar boundary layer chemistry, and only a couple of lab studies have been performed on this system before. So there is inherent merit to the work in that regard.

The halogen release is driven either by exposure to ozone or by illumination when an OH radical precursor, such as nitrite or hydrogen peroxide, is incorporated into the frozen solution. The experiments are performed using a flow tube that is coupled to a chemical ionization mass spectrometer operated with an iodide reagent ion. The

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solutions also contain a buffer to maintain the acidity of the solution, given that protons are required for some of these activation processes. I have a few questions concerning the experimental approach (see below) but my major comments are related to the presentation of the experimental results, although I am in general agreement with their interpretations. Some of the results themselves are new and interesting (e.g. I₂ release in the dark) but others have been showed before, albeit with different approaches (e.g. Br₂ release with light).

I'll start by saying that I found this paper very challenging to read, especially the Results and Discussion sections which were excessively wordy. The Introduction and Conclusions are fine. Given that there are only a few figures of data, I believe that the experimental results and their discussion could be much more succinctly described, perhaps cut in length by a factor of two. As opposed to describing every observation, could the major findings be emphasized? Indeed, I recommend that the authors re-write the paper so that the results and associated discussion are united, i.e. the results are discussed as they are presented. I found myself moving back and forth many times between the two sections as I was reading the paper.

The Abstract, too, could be improved. For example, the authors should explain what they mean when they state that photochemical production of Br₂ was observed (line 33). What were the conditions that led to Br₂ production? Another example is that the mechanism of the heterogeneous recycling should be mentioned (line 35). Finally, the last sentence should point out that these mechanisms, even if slow, may be important as the initiation of halogen release to the atmosphere, even if they ultimately do not constitute the major source.

Another weakness of the paper is the attempt to connect the laboratory results to those measured in the field. There are so many factors that come into play in this chemistry, I don't think we can plan to quantitatively relate the lab and the field in the manner attempted. For example, is the spatial distribution of the salts, protons, and OH precursors the same in the field snow samples as those in the lab? I believe the answer

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is no, given the totally different manner by which the ice samples are prepared. For example, how might the buffer materials (such as acetate) interact with OH in the ice? Is the surface segregation of these species the same? My advice would be to give up on the goal of making that comparison, except in the most qualitative manner. That said, I do believe that the relative rate approach for interpreting the kinetics of oxidation of different halides has merit. There could be more done interpreting these reactivity ratios in terms of the (much better) known bulk aqueous reaction rate constants.

Overall, I believe there is merit to publication of this paper after the results are presented in a more succinct manner, with caveats added for how this work is translatable to the interpretation of field measurements.

Experimental questions:

Will the acetic acid/acetate buffer be affected by volatilization of acetic acid from the ice?

I found line 128 confusing – i.e. was no iodide observed by IC? If so, what LOD was prevalent for the IC method?

For the bisulfate buffer, will OH react with bisulfate to form the sulfate radical anion, rather than react with the halide ions?

Line 150: Was it room air that went through the flow tube? If so, what contamination may result?

Line 170: What is the spectrum of the solar simulator bulbs?

Line 177: typo

Line 189: Where is the Cl₂ background coming from? Just from chloride on flow tube or plumbing surfaces?

Line 203: I am nervous of how the HOBr sensitivity is estimated, given that the CIMS instrument is not the same as used in the referenced work by Liao et al. Wouldn't it be

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wiser to just call this signal uncalibrated?

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