

## ***Interactive comment on “Halogen activation via interactions with environmental ice and snow” by J. P. D. Abbatt et al.***

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The review article represents a significant contribution to the synthesis of current halogen chemistry and its relationship to snow and ice. The manuscript is well written and extensively referenced. It achieves a good balance of recent findings and is generally well structured, although I have comments on a few areas that might be improved below. I support publication of the work in ACP.

Specific comments:

p8679, I2: I found the first two sentences of this paragraph to be a bit long and complex for the first introduction. I would suggest starting with the third sentence and reworking the first two sentences into the first paragraphs. Specifically, the first sentence seems to

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imply that ice controls the oxidation capacity of the atmosphere in general as opposed to in certain regions at certain times.

p8681: In this introductory section, some references could be added to key papers to support things discussed. Clearly some parts of the introduction are made to lead into later discussion, which is often stated explicitly. However, some past work that is not really discussed in this review should have key references to past work to be stated in the introduction. For example, it would be useful to reference a paper or two on the reactions of halogens with DMS and hydrocarbons. References to the prevalence of UTLS cirrus clouds and dynamic coupling of that region would be good.

p6882, I7: The topic of multiphase chemistry and acidity is referenced in discussions below, so that could be mentioned or a key reference or two could be added here.

p8684, I8: This section seems to say all brine is expelled upward. I'm not sure if the balance between upward and downward brine motion is known, but a lot, probably the majority, of brine is expelled downwards.

p6884, I9: It should be stated that below thermodynamic thresholds precipitates may form. The manuscript later discusses calcite / ikaite precipitation, and if only thermodynamics controlled that situation, calcite would precipitate upon cooling before ikaite would be formed. Additionally, the process of the precipitation can enrich brine in a species, which may affect overlying atmospheric chemistry, but to observe net enrichment in aerosol, ice, or snow samples after melting, physical separation of the brine from the precipitate is needed. Thus precipitation could affect gas-surface reaction without being observed in bulk sample (melted) analysis.

p8684, I12 and region: This section should clearly say where brine is being discussed. It is said that the precipitation of hydrohalite leads "...to enrichment of bromide compared to chloride." That is true in the residual brine, but the opposite is true in the precipitate.

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p8685, I12: This section could be reworded for better clarity of the composition of the coating brine. Specifically, if the bulk salinity of melted frost flowers is ~100PSU, then the coating brine must be more concentrated than that bulk composition. Otherwise, there would be no ice left to form the supporting ice skeleton. If thermodynamics controls the system, then the brine that coats (or is possibly included within) has a composition controlled by the ambient temperature and the phase diagram. Generally salinities in this section are bulk melted salinity and should be clearly stated as such.

p8685, I25: It is said that bromide is not expected to be fractionated. What is really meant is that bromide is not expected to precipitate. Bromide is fractionated with respect to chloride in the brine (the chloride precipitated). Also note the discussion above about the necessity for physical separation of brine from precipitate to observe the fractionation in bulk melted samples (e.g. frost flowers or snow).

p8686, I1: I believe that the numbers quoted from Koop et al.'s paper is from a calculation. The wording seems to imply that the concentrations were an experimental finding of that paper. Maybe reword to "Koop et al, (2000) calculated...". It should also be noted that Arctic FF seldom get terribly cold due to the proximity of the underlying sea water and thin ice. After frost flowers mature or if they produce atmospheric particles, they are often colder.

p8687, I6: Although it is true that frost flowers are depleted in sulfate with respect to sodium and that snow is often depleted in the same way, it is not a clear inference that frost flowers' fragments contaminated the snow. Other brines that separate from precipitated mirabilite crystals would also show sulfate depletion with respect to sodium. For example, brine that wicked up snow that had experienced <-8C would show sulfate depletion without involvement of frost flowers. Thus, the presence of depleted brine is more a signature of processing of the brine than necessarily of frost flowers.

The reference below is to a recent paper that shows evidence for depleted (and some enhanced) sulfate in snow in the Arctic:

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Krnavek, L., Simpson, W.R., Carlson, D., Dominé, F., Douglas, T.A., Sturm, M., 2012. The chemical composition of surface snow in the Arctic : examining marine, terrestrial, and atmospheric influence. *Atmospheric Environment*, 50 : 349-359. DOI: 10.1016/j.atmosenv.2011.11.033.

p8689, I25: It is not totally clear how this reaction leads to products other than the listed product (CHX3). I guess it can stop at intermediate numbers of X's added. Maybe a part of a sentence or a new sentence would make clear how this reaction leads to "all the above mentioned halocarbons".

p8691, about I22: I think it would be valuable here or in other places where halocarbons are discussed to talk about the seasonal timing of halocarbon fluxes compared to the timing of ODEs. Alternatively, the month of these halocarbon flux observations could be put into the context of the typical months of ODEs. It seems like the halocarbon fluxes, being biological, would be later than most of ODEs, but maybe the references address the timing issue. Similarly, the return of the hard UV required to photolyse these compounds would happen later in the ODE season.

p8692, I24: Liquid-phase concentrations of organo-Br and organo-I compounds in frost flowers and brine are discussed. Is it possible to relate these to an emission flux? If not, could further work be suggested to improve understanding?

p8696, I3: There is a discussion of iodide having a high surface propensity but low sea water concentration, which can compensate. That is true, but one should also note that if there is little iodide in solution, it can be depleted in concentration by gas-surface activation reactions. Thus, even if it were there at the start, the activation reaction will be limited by the low concentration of iodide in the sea water.

p8696, I22: Around here, please discuss that nucleation difficulties can allow calcite to not precipitate before ikaite despite the order of their listed precipitation temperatures.

p8705, I9: The word "effect" should be "affect", the verb form.

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p8707 and 8708, section 4.3.1: This section "Freeze-induced processes" is somewhat repetitive to other sections and also doesn't seem to belong as a sub-section of 4.3 (Photochemical processes). I would suggest shifting this material to other sections and eliminating this section number. I would move the first paragraph to section 4.1.1 (brines and QBL) and then eliminate repetition. I would then move the other sections to 4.1.2 (Halide distribution). Some of the later reaction discussion could be moved into parts of 4.2.

p8708, I19-21: I don't understand what this sentence means. Can it be clarified?

p8710, I16: It is discussed that nighttime only data are shown. Do they mean that BrO was 13pptv at night? Typically BrO goes to zero at night. Please clarify.

p8711, I18: These reactions seemed a bit out of place. The first reaction (R11) does couple Br and Cl cycles, as the text discusses. How chlorine produces HO<sub>2</sub> is discussed in the text, but then the reaction is not really shown. I might suggest having a section of 4.2 that would discuss reactions coupling halogens (e.g. Cl and Br) and also the role of HO<sub>2</sub>, and thus HO<sub>x</sub> production mechanisms in the production of halogen events.

p8715, I18: It should be mentioned that in addition to the easier oxidation of Br than Cl, Cl has increased reactive losses (e.g. Cl + CH<sub>4</sub>), leading to shorter catalytic chain lengths. Thus, Cl remains active shorter than Br.

p8726, I6: The sources of halocarbons are discussed here. I think a discussion of timing of biological versus inorganic sources would be valuable.

p8726, I10: I think the example shown here should be discussed in the main text, and this section should be about things concluded and open issues.

p8728, I1: The halogen activation chemistry is so nonlinear that it is not clear that moderate changes in actinic fluxes (e.g. due to blowing snow) would have drastic effects and "require more than one release scenario.". I would instead indicate that

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some ODEs are seen at high wind speed, some at low wind speed, which is maybe stronger evidence for multiple release mechanisms.

p8729, I3: It should be noted that winter ice loss in the central Arctic is not predicted in the near term by many sea ice models. Thus, a likely ice scenario is first more first year ice in winter time (due to increased ice loss in summer) followed by ice losses in all seasons.

p8758, table 1: These lifetimes seem short for Arctic springtime conditions (high overhead ozone columns and low sun angles lead to very low photolysis rates). Please clarify in the text how they were calculated (e.g. for what conditions), and how the conditions may differ in the Arctic spring.

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 8677, 2012.

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