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Interactive comment on "Snow heterogeneous reactivity of bromide with ozone lost during snow metamorphism" *by* Jacinta Edebeli et al.

Anonymous Referee #2

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The authors examine the ozone reactivity of bromide-doped laboratory "snow" and the effect of temperature-gradient metamorphism. They find that metamorphism shuts down the reactivity, apparently because it buries the bromide away from the air-ice interface. The paper is interesting because of its connection between snow physics and chemistry and implications for the reactivity of natural snow.

***Major point

Overall, the manuscript is interesting and deserves to be (eventually) published. But the writing of the manuscript is a problem: it is often difficult to follow, non-linear, and sometimes rambling. It needs significant attention from the first author but also the senior authors.

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Page 9 is one example. First, the entire page is one paragraph, as occurs on a number of pages. It would be much better to break the text into smaller paragraphs, each with a main theme. Second, the discussion circles around and around, repeating topics (e.g., the assumed diffusion coefficient) rather than linearly dealing with one topic and then moving on to the next. It makes it difficult to follow the arguments. The paper is already short, but could probably be shortened (and strengthened) by removing repetition, using a more logical flow, and removing extraneous ideas.

**Other points

Line 26: The text states “tropospheric O3 reduction”, but this is misleading since the global tropospheric O3 mixing ratio is increasing. Better wording would be “tropospheric O3 sink”.

l. 71. What is "environmental snow" and how is it different from Arctic snow?

l. 81. How were the artificial drops produced? Paint sprayer?

l. 84. Samples were annealed at -5 C for 7 days. Why such a long annealing time? Why the focus on minimizing grain boundaries?

l. 88. This line also discusses 7 days of annealing. Is this in addition to the 7 days described on line 84, or is the same annealing description repeated twice? Or were samples were annealed in the reactor tubes for 7 days?

l. 127. UV illumination of N2/O2 mixtures can also make NOx in addition to O3. Was there any attempt to detect whether NOx was formed? Any evidence of NOx reactions, e.g., formation of nitrate in the O3-exposed snow?

Figure 1. What are the solid lines that connect the symbols? Continuous ozone measurements? Are the symbols then just the continuous result at specific times or is it something else? Make it clear in the caption that "undoped" means no added bromide for the grey line. How much variability was there in O3 loss rates for the undoped samples?

l. 162. It’s not clear what is meant by “Taken the large variation in the ozone loss of samples exposed to metamorphism. . .”

l. 168. This paragraph is not easy to understand. Part of the problem is starting with the "result", i.e., comparison of O3 loss rates, before describing all of the steps that make this comparison meaningful.

l. 183. The sentence that starts “In summary, we conclude. . .” seems out of place. It is not a summary of the previous portion of the paragraph and it is a point that was made (or at least implied) in the earlier discussion of Figure 1.

l. 186. Here the authors attribute the background loss rate to “ozone self-reaction”, but is there any evidence from previous studies (e.g., in solution) that there is an appreciable O3-O3 reaction? This proposed mechanism is too specific given the lack of evidence. Also, on the next page the authors attribute the background loss to impurities, not to ozone-ozone reactions. The impurities hypothesis seems more likely.

l. 189. This is excellent agreement, but it’s not “perfect”, since current loss rate is up to 2x higher than the past rate.

l. 205. I wouldn’t expect that the snow made here is acidic. Are there pH measurements of the melted solution?

l. 220. This low coverage isn’t necessarily evidence that bromide loss limits ozone depletion, since it’s difficult to compare a bromide surface coverage with a gas-phase ozone concentration. A clearer controlling factor is instead the number of ozone molecules lost compared to the number of bromide ions initially on the ice.

l. 228. What’s the reference for this diffusion coefficient?

l. 243. Solutes have been found at grain boundaries, but the sentence indicates that this location is different from “micropockets”. My understanding of micropockets is that represent any liquid-like inclusion within the ice matrix, including at grain boundaries. If the authors want to use “micropockets” in a more specific way, they should define the

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term.

l. 250. The use of parentheses to indicate a parallel sentence meaning is confusing. Better to have two separate, clear sentences.

l. 254. It’s not clear why this possible (but hugely uncertain) number of micropockets is interesting. The number is highly sensitive to the radius, of which we only know an approximately upper bound. Furthermore, the estimate of the number of micropockets seems to have little bearing on whether micropockets can be "excluded" as a major location for bromide. The ozone data indicates that approximately 3/4 of the bromide is present internally in ice, whether in micropockets, at grain boundaries (if these are not part of micropockets) or as solid solution. How does a highly uncertain micropocket number estimate change this?

l. 257. The ozone depletion data argues strongly against all of bromide being present at the air-ice interface. So why the need for lines 257-258 to say this point again?

l. 269. What does it mean that the snow is “fully connected”? The snow that was not exposed to the temperature gradient looks as "fully connected" as the one that was exposed. Is it not?

l. 280. What does it mean that the particles “show edge structures” and why is this important? It seems that any solid-gas system will have edges.

Table 1. What is n for each of the four conditions?

l. 302. Early only one diffusion coefficient was presented, but now the issue is presented again, but with a range of values. This range should be presented in the initial discussion of diffusivities and either a best value, bounding value, or range should be presented in both locations.

l. 302. “10-12” needs to be formatted (superscripted “-12”).

l. 303. 40 - 220 nm/s is a diffusion rate or speed, not a distance.

l. 304. What is the ice-growth diffusion mechanism? It is not clear how the comparison of rates supports this (unspecified) mechanism.

If the rate of bromide diffusion is 1 - 2 orders of magnitude faster than the rate of ice growth, one would expect uniform bromide distribution throughout the growing ice, meaning also some at the interface. But the experiments suggest no Br- at the interface in the snow that experienced the temperature gradient.

One interesting link to previous work: past modeling in solution (Finlayson-Pitts and Tobias) has shown that Br- is enriched at the air-solution interface. But the results in Fig. 1 for the T-gradient snow indicate that bromide is not present at the air-ice interface.

l. 309. Aren't the micropockets (by definition) already covered with ice? If so, this discussion of ice growth on brine drops seems to miss the point.

l. 328. "Burial of acidic trace gases with atmospheric relevance has previously been discussed for these volatile species (Huthwelker et al., 2006)." Rather than give this vague statement, it would be better to make a specific statement about the past results that are relevant to the current work.

l. 331. Why use "only" to qualify the HCl uptake?

l. 346. "As a consequence. . ." This is an interesting point.

l. 369. This last sentence is no longer referring to bromide? If not, it does not fit with the rest of the paragraph.

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