Response to Anonymous Referee #2

We would like to thank Anonymous Referee #2 for his/her careful reading of this manuscript and constructive suggestions. We have addressed all of his/her comments in the revised manuscript, and describe in detail changes made below in the order in which they were raised by the reviewer. All page numbers and line numbers are in reference to those in the revised version of the manuscript, except where indicated otherwise. For clarity, the text of the reviewer's comments are in **black**, while the authors' responses are in blue.

This study reports experiments related to the photochemical halogen release from frozen sea water mimics. The results provide novel information on the halogen oxidation processes and important basis for the interpretation of field data. It becomes apparent that the most important parameters controlling halogen release are the relative proportions of chloride, bromide and iodide, pH and the structure of the frozen system, in terms of the way in which the combination of crystalline ice and brine are exposed to the gas phase. Since there is also a significant debate in the community on especially the latter two, these aspects could also be illuminated a bit better as detailed below. Overall, the experiments have been carefully designed and analysed, and the analysis of the results is associated with a proper discussion of uncertainties and related caveats (e.g., related to molecular chlorine detection in presence of ozone). The careful discussion of the halogen cycling reactions and their kinetics is appreciated. I therefore recommend this study for publication with only a few minor suggestions.

Comments:

1) Since the study also tries to differentiate the relative roles of photochemically produced radicals and ozone for halogen release, I wonder why no experiments have been done with ozone only for reference. While such experiments have been done in the past, indeed, exactly because of the complexity of the system in terms of microstructure, the corresponding 'ozone induced baseline dark halogen release' could have been assessed for comparison.

Our experiments were inspired by the field work of Pratt et al. (2013) and Raso et al. (2017) that suggested evidence of photochemically-initiated halogen production, the testing of which was the primary focus of this paper. We appreciate the author's comment and acknowledge that such dark experiments with ozone only would have allowed for a more direct comparison of our results with previous laboratory experiments, such as Oum et al. (1998) and Oldridge and Abbatt (2011), discussed in our paper on lines 102-106. However, since Pratt et al. (2013) demonstrated that $O_3 + Br^-$ was relatively unimportant as a Br_2 source under normal atmospheric O_3 conditions without radiation, we focused on the role of OH as an initiator.

2) The authors several times discuss potential surface reactions occurring on liquid brines, I caution that diffusive exchange even over micrometer ranges is very fast, so that all halide ions present in liquid brine are available for reaction. The kinetics may indeed be limited by a surface process, but this is maybe not the important question, because as observed by the authors, it seems rather that the exchange between

compartments may be limiting. If brine in a grain boundary is connected to the surface, diffusion is long enough to allow reaction and release within the experimental time scales. Therefore, the question remains where the less available halide ions are, if brine pockets are probably not buried below ice in such thin films. The way the films were frozen, the ice likely started to grow from the Pyrex glass walls.

We thank the Referee for this comment. The recent work from Malley et al. (2018), cited line 388) discusses the brine distribution in frozen surfaces in much more depth, and we look forward to experiments inspired by this work that will provide further clarity on this issue. But, we expect that the less-available ions are locked in the bulk ice, as discussed in lines 386-407 of the revision.

3) Could the authors please mention more precisely the irradiation conditions and how they were assessed? Has some actinometry been performed?

We have reproduced the solar irradiance spectrum of the solar simulator bulbs in Figure S1. No actinometry was performed, but we do not attempt in this paper to simulate the actual ambient radiant fluxes, but rather discuss the relative rates of production, and the roles of pH, and OH and O_3 in the gas phase on those rates.

4) pH: As the authors mention in the experimental part, this is a challenging aspect. I think a short discussion is adequate there and in the discussion section to emphasize the buffer concentrations used in relation to the halide ions, and in what way this may have affected both the physical properties and the halogen / radical chemistry.

The hydroxyl radical can react with acetic acid, as well as with bisulfate to form sulfate radical:

$\cdot OH + HSO_4^- \rightarrow H_2O + SO_4\cdot^-$ $\quad$ $k = 4.7 \times 10^5\ M^{-1}\ sec^{-1}$

$CH_3CO_2H + \cdot OH \rightarrow H_2O + \cdot CH_2CO_2H$ $\quad$ $k = 9.2 \times 10^6\ M^{-1}\ sec^{-1}$

However, the OH reactions rates with the halides are considerably faster ($k_{Cl^-} = 3 \times 10^9\ M^{-1}\ sec^{-1}$, $k_{Br^-} = k_{I^-} = 1.1 \times 10^{10}\ M^{-1}\ sec^{-1}$). We calculate that the sulfate radical would contribute less than 0.1% to halide oxidation, compared that from OH-halide oxidation. Because this is only believed to influence the results to a minor degree, we have included the desired discussion in the Supplemental Information, Lines 3-28.