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Atmospheric Chemistry and Physics
Discussions

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

Anonymous Referee #2

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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 re-

lated 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.

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.

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

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 emphasise 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.

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