

## ***Interactive comment on “Temperature dependent halogen activation by N<sub>2</sub>O<sub>5</sub> reactions on halide-doped ice surfaces” by F. D. Lopez-Hilfiker et al.***

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Authors Response to Referee 1

This is a very nice study of reactive uptake of N<sub>2</sub>O<sub>5</sub> by halide-doped ice. It nicely indicates that the exposed (as far as heterogeneous reaction is concerned) surface of such ices consists of a region which behaves as though it was a liquid brine - as predicted by thermochemical models. Furthermore, the differential reactivity of bromide and chloride observed in liquid systems is maintained at the frozen surface, which has interesting implications given the different eutectic temperatures of NaBr and NaCl. I have only a couple of minor comments concerning the manuscript.

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\*\*\*We thank the reviewer for his/her careful reading and comments. Our responses are given below, denoted by the \*\*\*.

1. On page 6089, it may be good to give the other (non-NaX) components in the artificial seawater; in particular, are carbonates expected to be important? What is the pH of the pre-freezing solutions?

\*\*\*A table of the components in the artificial seawater is now provided from the manufacturer. Carbonates are certainly present at their typical molar ratio. No additional buffer (nor acids or bases) is added to the seawater. Thus the pH becomes < 8.2 with prolonged exposure to ambient air, and when exposed to the N<sub>2</sub>O<sub>5</sub> (with trace HNO<sub>3</sub> present) the pH likely falls further. The effect of additional acidity would be interesting to study.\*\*\*

2. Page 6093: Is the result shown in Fig 2 (at 242 K) representative of the other temperatures as well?

\*\*\*Figure 2 is representative of what is observed when exposing N<sub>2</sub>O<sub>5</sub> to a frozen seawater solution (Cl:Br 650:1) at 242 K. It isn't very representative of colder temperatures (potentially higher Br<sub>2</sub>) but is similar to what we observe at higher temperatures (a few percent yield of Br<sub>2</sub>) when using frozen seawater.\*\*\*

3. Page 6094: Please expand/explain the "expected" diffusion-limited loss rate calculation. Also, please state whether the total ionic strength is constant for each type of experiment reported.

\*\*\*We have added text to explain further the expected diffusion limited loss rate calculation. The important assumption in those estimates is the value of the reactive uptake coefficient ( $\gamma$ ) on a halide-doped ice. For a  $\gamma$  above  $1e-4$ , the geometry, pressure, and flow velocity of our reactor are such that the loss of N<sub>2</sub>O<sub>5</sub> is limited by its diffusion to the wall. This conclusion is based on using a standard approach to estimate the diffusion time scale in a laminar flow tube for transit from the flow center

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line to the wall (approximately  $r^2/D$ , where  $r$  is the tube radius) and comparing this diffusion timescale to the N<sub>2</sub>O<sub>5</sub> lifetime measured in the reactor – they were the same to within experimental error implying that the N<sub>2</sub>O<sub>5</sub> gamma at the wall is  $> 1e-4$ . The gamma measured for N<sub>2</sub>O<sub>5</sub> on pure water-ice is 0.03 (see Hanson and Ravishankara reference), consistent with our lower-limit estimate for halide-doped ice.

We have also added a note that clarifies changes to the total ionic strength of the solutions that were frozen. All solutions were made with artificial seawater. The total ionic strength was constant for solutions having the same Cl:Br ratio except when we performed experiments as a function of dilution where we intentionally decreased the total ionic strength by diluting seawater with pure water before freezing (Figure 4). When we adjusted the Cl:Br ratio to be different from seawater, we ADDED NaBr to the seawater solution. The largest adjustment was to bring Cl:Br from 650:1 to 30:1. The ionic strength thus changed by a few percent.\*\*\*

4. Figs 3-6: What (if anything) is the difference between "normalized yield" and "yield"? I assume the yield is per N<sub>2</sub>O<sub>5</sub> reacted; is that not the normalization?

\*\*\*We have added a clarification to explain "normalized yield" in the text and figure caption. Figure 4 is essentially one determination of the effect of dilution, with replicate determinations of the yield at each dilution factor, but not replicate determinations of dilution from a given starting solution. We therefore normalized the yields (e.g., ClNO<sub>2</sub> per N<sub>2</sub>O<sub>5</sub> reacted) determined at each dilution factor to the average total halogen yield obtained from many determinations (such as those shown in Figure 5) on pure frozen seawater. Thus, any variability in the measured yield (for example, due to calibration drifts on that particular day) were normalized away so the effective change due to dilution was better isolated. The normalization was small – a 25% correction.\*\*\*

5. Page 6097: At 230K, will not the bromide have precipitated, as I believe its eutectic is 245K?

\*\*\*The Cl:Br ratio in sea-ice brines at 230 K that we report was taken from the  
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FREZCHEM model predictions, see Morin et al ACP 7317-24, 2008 (their Figure 6, which compares well with the work of Koop). We have tried to more clearly note that the estimate is not our own. Significant precipitation of bromide is expected to occur near the eutectic (237K), but, importantly, not necessarily complete precipitation occurs. The Cl:Br ratio remaining in the brine (or QLL) is also more an indication of the relative precipitation of chloride salts compared to those containing bromide, and not the total fraction of bromide precipitated. We did not probe the temperature dependence of the halogen yield much below 240K, except in one experiment with frozen seawater – the Br<sub>2</sub> yield was at its lowest, the cause and robustness of that particular result remain to be determined.\*\*\*

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6085, 2012.