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Photochemical chlorine activation from artificial saline snowpacks

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Halogen activation on snow and ice substrates has a profound influence on the oxidative capacity of the polar boundary layer. The release of reactive chlorine species is of particular interest since chlorine atoms can participate in both ozone depletion and hydrocarbon oxidation. However, the mechanisms by which halides in sea ice substrates are converted into reactive halogen species are not well understood. In this study we investigated the activation of halogens from artificial saline snow in the presence of light and ozone. Gas phase Cl2, BrCl and Br2 were detected using a chemical ionization mass spectrometer. We observe the dark release of Br2 in the presence of ozone; BrCl and Cl2 are only observed in the presence of both ozone and light. Interestingly, photo-induced release of halogens is still seen when a 320 nm or a 380 nm long-pass filter is placed in the light path. The observed halogen release is consistent with the chemistry occurring in a concentrated brine located at the surface of the snow grains. Results suggest that smaller snow grains, which present a larger total snow surface area, enhance chlorine production to a greater extent than BrCl or Br2 production. Chlorine production is shown to be strongly pH dependent, with higher chlorine yields under acidic conditions. Overall the results indicate that a mechanism involving UV-A light and ozone leads to accelerated halogen activation, which may be particularly important for releasing chlorine from bromide-depleted snow.