



The Importance of Calcium Carbonate (CaCO₃) Precipitation on the Bromine Explosion

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Reactive halogens play a major role in ozone depletion events (ODEs). Gas phase halogens are supplied by the so-called "bromine explosion" activating bromide (Br⁻) from aerosol or salt deposits to release Br₂ and BrCl. The bromine explosion is pH-dependent, making the problem of sea salt aerosol acidification arise. There is now growing evidence that airmasses having undergone an ODE were earlier in contact with surfaces containing brine (salty liquid layers on top of newly-formed sea ice). Recently, it has been suggested that the fractionation of brine under polar conditions (leading to bicarbonate (HCO₃⁻) precipitation), may lead to a lower buffer capacity of the brine. This would facilitate the release of bromine under clean conditions with little available gas phase acidity. We examined the influence of precipitated HCO₃⁻ as CaCO₃ out of the brine for the development of a representative ODE (major ODE after 4 days). We used the one-dimensional model MISTRA where a 2000 m thick column of air is advected over a brine-covered surface. In our model runs, deposited bromine compounds are partly re-released to the gas phase.

With complete precipitation of HCO₃⁻ relative to seawater concentration, all the bromide from sea salt aerosols is efficiently released to the gas phase via the bromine explosion process. Sea salt aerosols are rapidly acidified to a pH of about 4-4.5. Ozone decreases to less than 4 nmol/mol within 4 days. With only 50% precipitation of HCO₃⁻, emitted particles from the brine are initially buffered to a pH close to 8. The bromine explosion is delayed by about 24 hours compared to the run with complete precipitation of HCO₃⁻. After four days of simulation, ozone decreased to a minimum of 7 nmol/mol. With no CaCO₃ precipitation, the released aerosols hardly liberate bromide: ozone decreases by only 1 nmol/mol after 2 days in atmospheric layers not influenced by the re-emission from snow. Our model runs confirm that the bicarbonate precipitation is a key process accelerating the bromine explosion.