

## ATMOSPHERIC CHEMISTRY

# Arctic snowpack bromine release

Snow and ice influence the climate and chemistry of the polar atmosphere. Field experiments in Alaska point to the significance of surface snow for polar ozone depletion events.

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Sea ice and snow help to shape climate at the poles. These surfaces reflect incoming solar radiation, diminishing its ability to warm the planet. Icy surfaces also mediate chemical reactions that affect the composition of the atmosphere<sup>1,2</sup>. The formation and proliferation of gaseous halogens in polar, snowy environments in spring is one example of such ice-mediated interactions, whereby chemical reactions in the ice facilitate the conversion of halogen-containing compounds to more volatile, reactive species<sup>2,3</sup>. These halogens — particularly bromine — chew up pollutants such as ozone and mercury, leading to the rapid depletion of tropospheric ozone during polar spring, and the deposition of biologically sensitive mercury to the surface. However, the exact source of these chemically reactive halogens has remained uncertain. Writing in *Nature Geoscience*, Pratt and colleagues<sup>4</sup> show that surface snow can serve as a source of bromine to the Arctic atmosphere.

The connection between ozone depletion and bromine activation was discovered roughly 25 years ago. It was found that ozone levels close to the surface could rapidly drop to near-zero levels in spring, coincident with an increase in the concentration of chemically reactive bromine-containing compounds<sup>5</sup>. A large fraction of this reactive bromine was found to consist of the free radical bromine monoxide, the gas-phase species that ultimately leads to ozone loss. When reactive bromine species such as bromine monoxide encounter halide-containing surfaces, such as sea ice, a sequence of reactions is initiated that accelerates bromine release<sup>6</sup>. This sequence of events is referred to as a 'bromine explosion'.

It has been challenging to quantitatively connect atmospheric bromine observations to studies of the relevant chemistry conducted in the laboratory, and to model simulations that attempt to couple the chemistry and the meteorology. As a result, the original source of reactive bromine has remained uncertain. Different candidates have had their time in the



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**Figure 1** | Surface snow and sea ice near Barrow, Alaska. Near-surface ozone concentrations fall to near-zero levels during polar spring, coincident with a rise in atmospheric bromine concentrations. Icy surfaces are thought to supply this bromine, but the exact source has remained uncertain. In a series of outdoor chamber experiments, Pratt and colleagues<sup>4</sup> show that surface snow serves as a source of chemically reactive bromine to the Arctic atmosphere in spring.

spotlight, including bromine-containing organic compounds released from marine environments — since shown to be unimportant. Today, bromide ions — a natural component of the sea salt found on icy surfaces affected by marine inputs — are thought to serve as an important source of bromine<sup>2,3</sup>. However, realistic representations of real-world icy substrates are hard to generate in laboratory experiments and computer models, making it difficult to quantify their contribution to the atmospheric bromine pool.

To address this uncertainty, Pratt *et al.*<sup>4</sup> assessed the potential for bromine production in various snow and ice substrates in a series of outdoor chamber experiments near Barrow, Alaska. They used real-time chemical ionization mass spectrometry to monitor bromine emissions from the icy substrates. Surface snow that

accumulated on tundra and first-year sea ice was the most efficient bromine source; sea ice, frozen brines and basal snow showed no evidence of bromine production. Importantly, light was required for the liberation of gas-phase bromine from surface snow, implying some form of photochemical activation, as postulated previously<sup>7</sup>. And the presence of ozone accelerated bromine release, indicative of ozone-induced bromine proliferation.

Pratt *et al.* propose a chemical mechanism to explain their observations. They suggest that light triggers the formation of hydroxyl radicals in the snowpack through well-known chemistry. These radicals then react with bromine-containing salts in the briny layers of salty snow, or at the surface of an ice crystal, in line with laboratory findings<sup>8</sup>. They suggest that the reactions that comprise the

bromine explosion lead to an accelerated rise in bromine concentrations within the interstitial air in the snowpack. Finally, when the snowpack is ventilated by wind, the bromine is released to the atmosphere, where it can participate in the chemical reactions that affect atmospheric ozone and mercury.

Pratt *et al.* show that the more saline surfaces — such as frozen brines and first-year sea ice — are less important when it comes to bromine chemistry than surfaces that have been exposed to the atmosphere, such as the upper level of the snowpack. This points to the potential importance of acidic conditions, shown in laboratory studies to play a role in the generation of reactive bromine. Specifically, it is possible that ice samples derived from ocean water are buffered by the marine carbonate–bicarbonate system, and so are less acidic than snow samples exposed to atmospheric gases such as nitric and sulfuric acid. If so, this points to a potential anthropogenic influence on polar bromine chemistry,

given that human activities generate atmospheric acids.

The study by Pratt *et al.* illustrates one way in which bromine can be released into the Arctic atmosphere. There is observational evidence that other pathways are also likely to be important, including the recycling of reactive bromine by snow and salty particulates generated during storms<sup>9,10</sup>. The extent to which meteorological conditions govern the relative importance of these processes is unclear, but wind is required in both cases. Equally uncertain is the chemistry involved in bromine generation, in particular the significance of spatial and temporal variations in surface acidity, salinity and morphology.

Pratt and colleagues<sup>4</sup> report significant bromine release from real-world snow. The findings lend much more confidence to the suggestion that halogens released from icy surfaces help to explain polar ozone depletion events. Summer-time and multi-year sea ice are at record low levels in the Arctic, being replaced by additional open

ocean and first-year sea ice, both of which are often covered with salty snow. Whether the rising fraction of young sea ice will enhance snowpack bromine production and release, and concomitant changes in atmospheric chemistry, remains to be seen. □

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