

Photochemical production of molecular bromine in Arctic surface snowpacks

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Following the springtime polar sunrise, ozone concentrations in the lower troposphere episodically decline to near-zero levels¹. These ozone depletion events are initiated by an increase in reactive bromine levels in the atmosphere^{2–5}. Under these conditions, the oxidative capacity of the Arctic troposphere is altered, leading to the removal of numerous transported trace gas pollutants, including mercury⁶. However, the sources and mechanisms leading to increased atmospheric reactive bromine levels have remained uncertain, limiting simulations of Arctic atmospheric chemistry with the rapidly transforming sea-ice landscape^{7,8}. Here, we examine the potential for molecular bromine production in various samples of saline snow and sea ice, in the presence and absence of sunlight and ozone, in an outdoor snow chamber in Alaska. Molecular bromine was detected only on exposure of surface snow (collected above tundra and first-year sea ice) to sunlight. This suggests that the oxidation of bromide is facilitated by a photochemical mechanism, which was most efficient for more acidic samples characterized by enhanced bromide to chloride ratios. Molecular bromine concentrations increased significantly when the snow was exposed to ozone, consistent with an interstitial air amplification mechanism. Aircraft-based observations confirm that bromine oxide levels were enhanced near the snow surface. We suggest that the photochemical production of molecular bromine in surface snow serves as a major source of reactive bromine, which leads to the episodic depletion of tropospheric ozone in the Arctic springtime.

Proposed substrates for Arctic halogen activation include open water, frost flowers, sea ice, surface snow, blowing snow and aerosols⁷. To test the effectiveness of various snow and ice surfaces for bromine activation, ten outdoor snow chamber experiments were conducted during the March–April 2012 Bromine, Ozone and Mercury Experiment (BROMEX) in Barrow, Alaska. As listed in Table 1, locally obtained samples included first-year sea ice, brine icicles that drained through the base of uplifted sea-ice blocks, several different layers of snow located on first-year sea ice, and surface snow on the tundra. Real-time chemical ionization mass spectrometry was used to monitor Br₂ production⁹ from the snow/ice samples in a perfluoroalkoxy-coated chamber, through which clean air, with and without ozone, was allowed to flow. Br₂ was observed only when snow samples were

exposed to ambient sunlight, as shown in Fig. 1 and in the Supplementary Information. This indicates active snowpack photochemistry. On O₃ addition, chamber Br₂ concentrations increased, consistent with the autocatalytic bromine explosion mechanism, described below.

Photochemical production of the hydroxyl radical (OH) in the snowpack condensed phase and the subsequent oxidation of bromide explains the initially observed Br₂ production. Photoactivated release of Br₂ into the atmosphere was previously proposed to explain boundary-layer ozone destruction beginning at polar sunrise². In our experiments, ~3 ppt of Br₂ was produced from naturally sunlit tundra surface snow with O₃-free air flow (Fig. 1b and Supplementary Fig. S9). This is consistent with laboratory-based observations of Br₂ production from condensed-phase OH formation and subsequent reaction with bromide within the surface liquid layer of frozen solutions of chloride, bromide, iodide and nitrate¹⁰. Condensed-phase photolysis of H₂O₂ and nitrite (NO₂⁻) has been shown to produce ~96% of the OH in the Barrow snowpack, with nitrate (NO₃⁻) suggested to be an important precursor elsewhere¹¹. Although H₂O₂ photolysis produces OH leading to Br₂ formation, H₂O₂ also reacts with Br₂ and can inhibit Br₂ release¹². For our chamber experiments, the suggested initialization mechanism of Br₂ release to the interstitial snowpack air is shown in Fig. 2, wherein nitrite and H₂O₂ photolysis lead to condensed-phase OH production and reaction with bromide under acidic conditions within the quasi-brine layer that forms at the snow grain surface^{10,13}.

The most efficient Br₂ production was observed for tundra snow and the top 1 cm of surface snow above first-year sea ice. These samples were characterized by lower salinity, lower pH (4.6–6.3) and higher Br⁻/Cl⁻ molar ratios (1/148–1/38) compared with the snow and ice samples (sea ice, brine icicles and basal snow directly above sea ice) that did not exhibit Br₂ production (bromide/chloride ratios of 1/526–1/230, pH 7.3–9.5; Table 1). The basal snow, collected from the sea-ice surface to 8 cm directly above first-year sea ice, was impacted by the upward migration of brine¹⁴. In contrast, the top layer of surface snow above the first-year sea ice was impacted by atmospheric aerosol and trace gas deposition, which led to the observed higher Br⁻/Cl⁻ ratios¹⁴ and lower pH. The

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Table 1 | Snow and ice compositions corresponding to the ten chamber experiments.

Experiment date	Sample type	pH	Br ⁻ (μM)	Br ⁻ /Cl ⁻	Br ₂ observed?
14 March 2012	Sea ice	7.3	161 (13)	1/526 (1/158)	No
13 March 2012	Brine icicles	9.5	677 (48)	1/230 (1/18)	No
16 March 2012	Basal snow (0–8 cm) above sea ice	7.5	61 (6)	1/434 (1/49)	No
21 March 2012	Sintered snow (8–18 cm) above sea ice	5.3	2.19 (0.09)	1/468 (1/177)	*
26 March 2012	Surface snow (top 1 cm) above sea ice	5.6	11.4 (0.6)	1/99 (1/22)	Yes
8 March 2012	Tundra surface snow	4.8	0.16 (0.02)	1/148 (1/24)	Yes
19 March 2012	Tundra surface snow	6.3	0.40 (0.03)	1/38 (1/5)	Yes
27 March 2012	Tundra surface snow	4.9	0.082 (0.009)	1/120 (1/36)	Yes
8 April 2012	Tundra surface snow	4.6	0.24 (0.02)	1/128 (1/14)	Yes
9 April 2012	Tundra surface snow	5.0	0.27 (0.03)	1/60 (1/8)	Yes

Average pH, bromide (Br⁻) concentration and bromide/chloride (Br⁻/Cl⁻) molar ratio are shown for each melted sample with an indication of whether Br₂ was detected for that sample experiment. Standard deviations of multiple analyses are shown in parentheses. Chloride, nitrate, nitrite and sulphate concentrations are shown in Supplementary Table S1. As discussed in the Supplementary Information, the measured snow chemistry is similar to previous observations made across the Arctic region. * indicates that Br₂ was observed only for added [O₃] > 100 ppb.

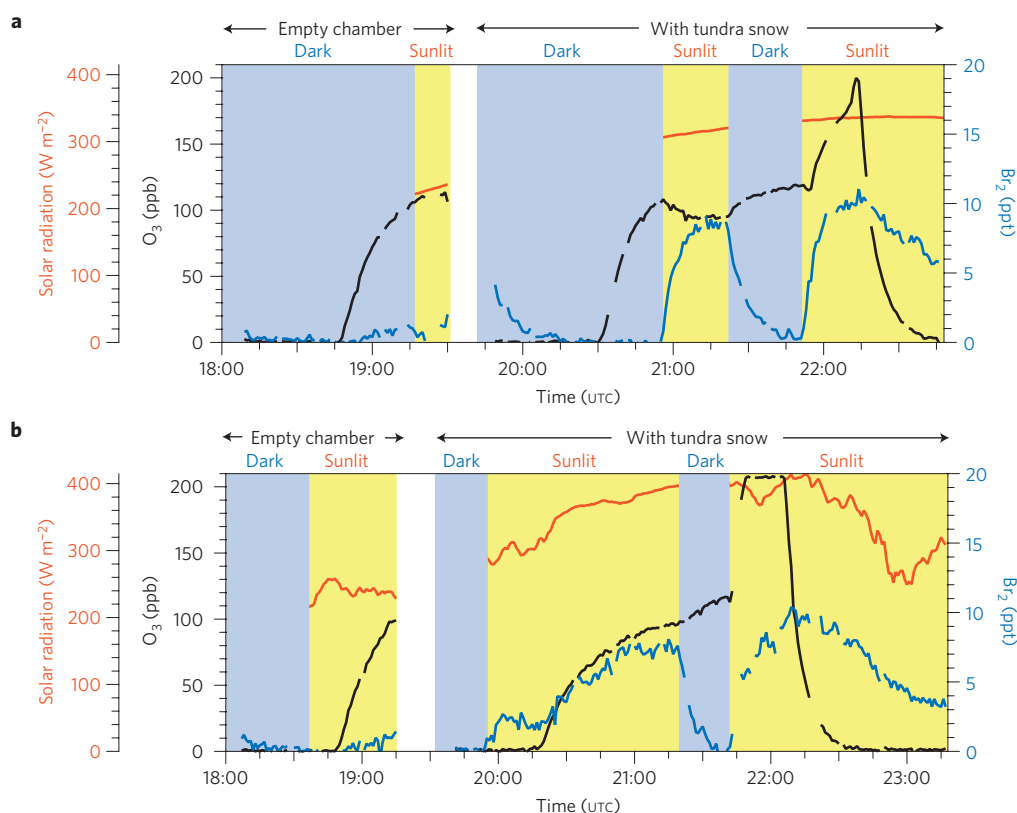


Figure 1 | Br₂ production during snow chamber experiments. **a, b**, Two example tundra surface snow chamber experiments: 27 March 2012 (**a**) and 9 April 2012 (**b**). See Supplementary Information for the other eight experiments with various snow or ice samples. For each experiment, a background test was first conducted using the empty chamber, followed by addition of a snow or ice sample. Br₂ and O₃ concentrations (blue and black lines, respectively) were monitored both in the dark and exposed to solar radiation (orange line), as shown by the light blue and yellow shaded portions of the plots. The Br₂ concentration uncertainty was estimated as 16% + 1 ppt.

sintered snow (8–18 cm above sea ice) collected between these two samples, characterized by a lower pH (5.3) and higher Br⁻/Cl⁻ ratio (1/468), showed Br₂ production only at high O₃ concentrations (>100 ppb) in the sunlight. These trends suggest that frost flowers and brine on the new sea-ice surface, characterized by high pH and low Br⁻/Cl⁻ ratio¹⁵, are not a direct halogen activation source.

Consistent with the snow chamber observations, laboratory studies have shown increased Br₂ production for frozen acidic

salt solutions^{10,16,17}. This acidity dependence is reflected in the proposed mechanism of initial Br₂ formation, wherein HO·Br⁻ reacts with H⁺ to form Br⁻ within the quasi-brine layer of the snow grains (Fig. 2)^{12,17}. A previous study¹⁶ reported higher gaseous HOBr uptake coefficients and reaction probabilities for acidified NaBr/NaCl ice films; however, in similar experiments¹⁸ a pH dependence of Br₂ production from frozen salt surfaces was not observed. Laboratory studies have also shown increased Br₂ production for increasing bromide/chloride ratios of salt

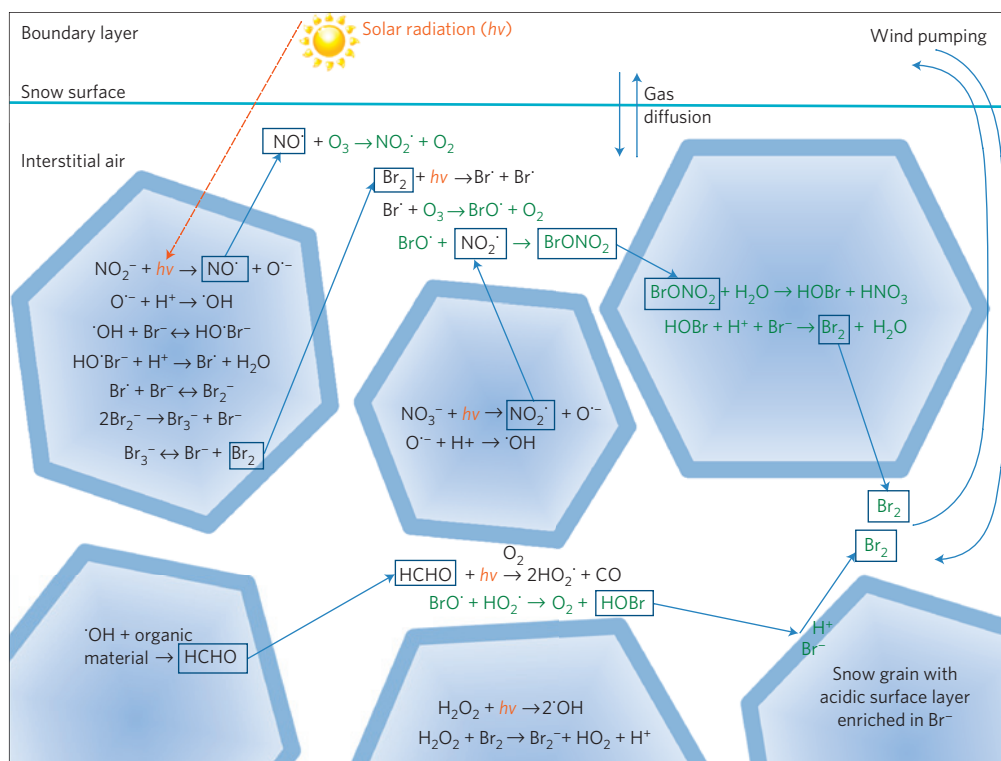


Figure 2 | Snow bromine activation and interstitial air bromine explosion. Proposed major pathways of Br_2 production^{10,12,16,17,21} initiated in sunlit, acidified snow, followed by snowpack interstitial air bromine explosion, increasing Br_2 concentrations. Although wind pumping was not active in the chamber, it is an important process for snow exposed to the atmosphere. Reaction pathways requiring O_3 are shown in green. Snow grains do not depict the actual snow morphology. The reactions drawn within the snow grains probably occur in an acidic surface quasi-brine layer^{10,13}.

solutions and ice films^{12,16,18}. Despite the faster reaction of OH with bromide, compared with chloride, the abundance of chloride at lower bromide/chloride ratios results in the dominance of the reaction of OH with chloride^{12,18}. This reduces the rate of $\text{HO}\cdot\text{Br}^-$ formation and/or increases the number of steps to Br_2 formation, reducing Br_2 production and resulting in a dependence on the bromide/chloride ratio^{12,18}. In our chamber studies, neither BrCl nor Cl_2 was measured above calculated limits of detection (5–8 ppt and 1–6 ppt, respectively, discussed in the Methods). Laboratory studies have shown preferential formation of Br_2 at higher bromide/chloride ratios¹⁸ with BrCl/Br_2 being <0.06 (ref. 17), implying BrCl levels that would not have been detectable for this study.

With Br_2 production initialized by snowpack photochemistry, the addition of increasing ozone concentrations to the chamber resulted in increasing Br_2 concentrations, consistent with the autocatalytic bromine explosion mechanism^{3,5}. On gas-phase Br_2 photolysis, reaction of bromine atoms ($\text{Br}\cdot$) with O_3 forms BrO (Fig. 2). Correspondingly, a decrease in O_3 of $\sim 10\%$ (~ 10 ppb) was observed when inlet O_3 concentrations were held constant at ~ 100 ppb and the chamber was exposed to solar radiation (Fig. 1). Subsequent reaction of BrO with gas-phase HO_2 and NO_2 radicals, produced through snowpack photochemistry¹⁹, forms HOBr and BrONO_2 , respectively (Fig. 2). The snowpack photochemical production of HO_x and NO_x is well known¹⁹, and as expected, nitrogen-containing trace gases were observed when the snow chamber contents were sunlit, as noted in the Supplementary Information. Uptake of HOBr and BrONO_2 by the acidic snow surface leads to the formation of more Br_2 , which is subsequently released to the gas phase (Fig. 2)¹⁶. Previous laboratory studies of BrONO_2 uptake on HBr -doped ice suggest hydrolysis of BrONO_2 , forming

condensed-phase HOBr , and subsequent reaction with bromide, leading to increased Br_2 release^{20,21}. Through this bromine explosion mechanism, the initial condensed-phase formation of one Br_2 molecule leads to the formation of two Br_2 molecules through heterogeneous reactions of HOBr and BrONO_2 with the available snowpack Br^- (refs 3,5).

We propose that the bromine explosion pathway occurs most rapidly in the interstitial air of the snowpack with Br_2 release to the atmosphere primarily through wind pumping⁷. As the rate of Br_2 production is dependent on the mass transfer of HOBr (ref. 22) to the snow surface, this process should be more efficient within the snowpack compared with the overlying atmosphere. Consistent with snowpack Br_2 production and interstitial O_3 destruction through the bromine explosion mechanism, Foster *et al.*²³ measured higher bromine and lower O_3 concentrations within the interstitial air of the top 6 cm of the Alert, Canada snowpack, compared with 26 cm above the snow surface. The catalytic bromine cycle also explains our chamber observation of decreased Br_2 concentrations when O_3 was no longer added because BrO , and thus HOBr and BrONO_2 , could no longer be produced. Further, when the chamber was covered to prevent photochemical reactions, the Br_2 concentrations slowly decayed, as predicted by dilution. It is important to note that Br_2 production was not observed for our snow/ice chamber samples in the dark for concentrations of added O_3 up to 140 ppb; this is in contrast to previous laboratory studies of frozen synthetic sea salt and southern California sea water, which showed Br_2 production following O_3 addition in the dark²⁴.

During BROMEX, aircraft-based scanner–differential optical absorption spectroscopy²⁵ (DOAS) measurements were used to examine the spatial variability of BrO , the presence of which reflects local-scale halogen chemistry owing to its short atmospheric

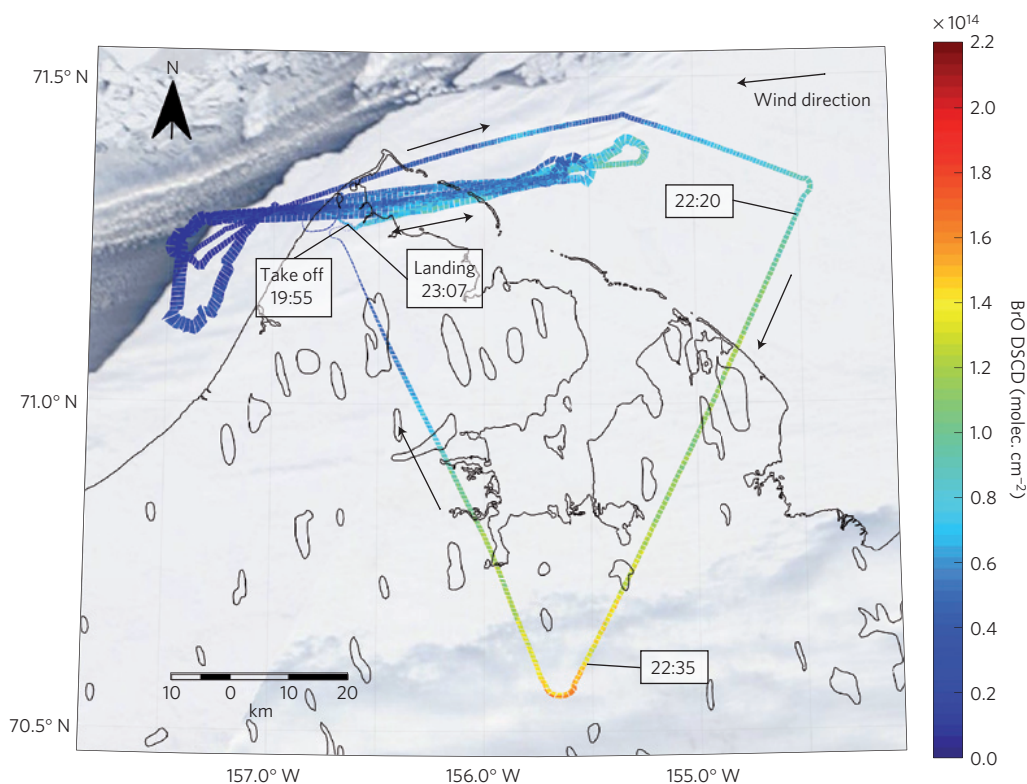


Figure 3 | Spatially resolved BrO. 24 March 2012 aircraft flight track originating from Barrow, Alaska and flying over nearby first-year sea ice, as well inland tundra to the south, at ~ 900 m above mean sea level (times in UTC). The background snow and sea-ice image is from the MODIS Terra satellite (true colour, 250 m resolution). The black traces correspond to the Alaska coastline and inland snow-covered lakes. Differential slant column densities (DSCDs) of BrO, as measured by the downward-looking scanner-DOAS system, are shown by the colourscale. The retrieved BrO DSCDs have a typical 1σ error of 1.2×10^{13} mol cm^{-2} .

lifetime (typically ~ 1 min; refs 9,26). During the example flight shown in Fig. 3, BrO was observed over the snow-covered surface of first-year sea ice and tundra. From BrO measurements using a forward-looking DOAS system, discussed in the Supplementary Information and shown in Supplementary Fig. S11, it is concluded that the observed BrO was exclusively located close to the surface. On this day, the highest BrO differential slant column densities were observed over snow-covered tundra, located ~ 75 km inland; it should be noted that other flights sometimes showed higher BrO concentrations over snow-covered first-year sea ice compared with over tundra. Bromine production and propagation through the snowpack interstitial air bromine explosion mechanism provides an explanation for these observations, which could not be explained by recycling on aerosols, as discussed in the Supplementary Information. It is also consistent with previous satellite-based observations of BrO hotspots above first-year sea ice⁷, as well as correlation of BrO concentrations with first-year sea-ice contact²⁷. This is because, on average, Arctic first-year sea ice is covered by ~ 29 cm of snow in the springtime²⁸, when sunlight can drive the photochemical reactions leading to Br₂ production. A previous study¹⁴ reported brine migration to impact snow only up to ~ 17 cm above sea ice near Alert (Canada) and Ny-Ålesund (Norway). Therefore, surface snow is most impacted by atmospheric processes, including deposition of sea salt, acidic Arctic haze aerosols, HNO₃ and HOBr (refs 14,29). In addition, the surface snow is more easily acidified than the buffered sea-ice surface³⁰, making the surface snow more conducive for halogen activation. Similar to surface snow above first-year sea ice, inland tundra snow is also impacted by atmospheric processing and can be characterized by high bromide/chloride ratios due to transport and deposition of gas-phase bromine compounds, as well as sea salt²⁹.

Snowpack photochemistry leading to interstitial air bromine explosion chemistry and Br₂ release to the atmosphere through wind pumping is an efficient and important mechanism for Arctic halogen activation, leading to ozone and mercury depletion events. The most efficient halogen activation sources were found to be acidic snow (melt water pH < 7) with bromide/chloride ratios greater than $\sim 1/200$. The identification of the prominent sources and likely mechanisms of the initiation and propagation of bromine chemistry is expected to improve our ability to simulate atmospheric composition and feedbacks within the Arctic system, particularly with the changing sea-ice landscape. The formation of Br₂ and subsequent destruction of ozone significantly changes the oxidative capacity of the Arctic troposphere, such that the lifetimes of many surface-level trace gas pollutants are significantly reduced⁷. In particular, the reaction of bromine atoms with gaseous elemental mercury, which is transported from the mid-latitudes, leads to toxic mercury deposition to Arctic ecosystems⁶. With climate change, multi-year sea ice is being replaced with first-year sea ice and expanding areas of open ocean⁸, changing the precipitation in the Arctic. An increasing fraction of first-year sea ice covered by an acidic snowpack influenced by atmospheric processing will probably lead to more prevalent Br₂ production in the Arctic. The complex interactions and climate system feedbacks between the atmosphere, ocean, sea ice and snowpack influence halogen activation, ozone depletion and mercury deposition to ecosystems in ways that we are just beginning to understand in the changing Arctic system.

Methods

The outdoor snow chamber, shown in Supplementary Fig. S1 and described in the Supplementary Information, was constructed from aluminium with

internal surfaces coated with perfluoroalkoxy to prevent surface reactions. The chamber top consisted of a 0.6-cm-thick sheet of Acrylite OP-4 (CRYO Industries), providing ~60% transmission of 280 nm radiation rising to ~92% at 395 nm; this was covered by opaque fabric for dark experiments. The main chamber (70.5 cm L × 50.0 cm W × 15.0 cm H) provided an internal volume of 53 l. Compressed air (7.4 lpm) of breathing air quality was directed through an activated charcoal hydrocarbon trap to remove volatile organic compounds, followed by a mass flow controller and an O₃ generator (model 97-0067-01, UVP). Experiments consisted of a period with no ozone added, followed by a gradual ramp of the inlet O₃ concentration to ~100 ppb, after which the inlet O₃ concentration was held constant, raised, and then lowered. After passing through the O₃ generator, air was passed through a 3.8 l polyethylene container containing ~1 l of crushed ice produced from milli-Q water to increase the air humidity. Ozone measurements were conducted using a 2B Technologies model 205 dual-beam O₃ monitor.

Ten snow chamber experiments were performed using samples collected near Barrow, Alaska (Table 1). Five tundra snow samples, comprising blocks (~65 cm long × 45 cm wide × 13 cm high) of the top ~13 cm of surface snow, were collected from 8 March to 9 April 2012 at the measurement site ~5 km inland, southeast of the town of Barrow, and placed immediately into the chamber. Other samples were obtained from March 13 to 26, 2012 from a location ~3 km north (upwind) of Barrow on the shore-fast first-year sea ice. These samples included: a block of first-year sea ice, brine icicles collected from below first-year sea ice blocks at a pressure ridge, an 8-cm-thick block of basal snow located directly above the sea ice, a 10-cm-thick block of sintered snow above basal snow, and surface 1 cm of blown and sintered snow. Samples for ion chromatography analysis were stored in sealed polyethylene bags in a -30 °C freezer in Barrow, transported to Indiana packed in dry ice to prevent melting, and then held in a -40 °C freezer until analysis. Melted samples were analysed using a Dionex DX500 ion chromatograph with an AS11 column and suppressed conductivity detection; chloride, bromide, nitrate, nitrite and sulphate concentrations were quantified (Table 1 and Supplementary Table S1). The pH of melted, undiluted samples was measured using a calibrated Thermo Scientific Orion Star Series ISE meter.

Br₂ measurements were conducted using a chemical ionization mass spectrometer, described in ref. 9. Using hydrated I⁻ (I·(H₂O)_n⁻) as the reagent ion, Br₂ was measured at masses 287 (I⁷⁹Br⁸¹Br⁻) and 289 (I⁸¹Br⁸¹Br⁻). Background measurements were performed every ~5–15 min during chamber experiments by passing the air flow through a glass wool scrubber. Br₂ in 21 ml min⁻¹ N₂ was added to the air flow just before the start of the chamber experiment for calibration; the estimated uncertainty in the reported Br₂ concentrations was 16% + 1 ppt. For chamber periods using O₃-free air, the 3σ limit of detection for Br₂, using mass 287, was calculated to range from ~1–4 ppt (typically ~2 ppt) for a 5 s integration period (corresponding to 1 min of chemical ionization mass spectrometer measurements). Higher 3σ limits of detection (typically ~7 ppt) were calculated for high-[O₃] periods. For all experiments, limits of detection for BrCl (mass 241, I⁷⁹Br³⁵Cl⁻, assuming the same sensitivity as mass 287) and Cl₂ (mass 197, I³⁵Cl³⁵Cl⁻) typically ranged from ~5 to 8 ppt and ~1 to 6 ppt, respectively. Further details are provided in the Supplementary Information.

Airborne BrO measurements were made with a passive DOAS system²⁵ installed on the Purdue University Airborne Laboratory for Atmospheric Research, a modified Beechcraft Duchess aircraft. The Scanner-DOAS system telescope was mounted below the aircraft. The scanner system was looking downwards (nadir) and featured a whisk broom scanner that pointed the telescope from -25° to +25° (one swath) perpendicular to the flight direction. Each swath had a resolution of 128 pixels and a width about equal to the flight altitude. The telescope received sunlight that was scattered at the ground surface and thus had passed through the atmosphere below the aircraft twice. Spectra were recorded in the range from 300 to 405 nm with a resolution of 0.6 nm. The DOAS data analysis derived BrO differential slant column densities, the total columns of BrO of a light path in comparison with a reference spectrum. Further details are given in the Supplementary Information. In Fig. 3, the data are plotted on a map assigning the BrO differential slant column densities to the ground pixel according to flight position, altitude, pitch and roll.

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Author contributions

P.B.S. and K.A.P. designed the experiments, which were conducted by K.A.P. and K.D.C. K.A.P. wrote the manuscript. P.B.S., K.A.P., K.D.C. and M.C. designed the snow chamber. T.A.D. collected samples from the sea ice, provided guidance for tundra snow sampling and contributed to discussions. P.B.S., D.P., S.G. and J.Z. conducted the aircraft-based BrO measurements with aircraft assistance from B.H.S. W.R.S. and U.P. contributed to discussions and were other principal investigators of the BrO study. D.J.T. and L.G.H. provided assistance with chemical ionization mass spectrometry. All authors reviewed and commented on the paper.

Additional information

Supplementary information is available in the [online version of the paper](#). Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to K.A.P.

Competing financial interests

The authors declare no competing financial interests.