

**Halogen activation
via interactions with
environmental ice
and snow**

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**Halogen activation via interactions with
environmental ice and snow**

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Received: 15 March 2012 – Accepted: 19 March 2012 – Published: 5 April 2012

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

The role of ice in the formation of chemically active halogens in the environment requires a full understanding because of its role in atmospheric chemistry, including controlling the oxidizing capacity of the atmosphere. In particular, ice and snow are important for facilitating multiphase oxidative chemistry and as media upon which marine algae live. This paper reviews the nature of environmental ice substrates that participate in halogen chemistry, describes the multiphase reactions that occur on such substrates, presents the field evidence for ice-mediated halogen activation, summarizes our best understanding of ice-halogen activation mechanisms, and describes the current state of modeling these processes at different scales. Given the rapid pace of developments in the field, this paper largely addresses advances made in the past five years, with emphasis given to the polar boundary layer. The integrative nature of this field is highlighted in the presentation of work from the molecular to the regional scale, with a focus on understanding fundamental processes. This is essential for developing realistic parameterizations and descriptions of these processes for inclusion in larger scale models that are used to determine their regional and global impacts.

1 Introduction

Ice and snow substrates, while long considered to be bystanders in environmental chemistry, are now known to play important roles in a variety of atmospheric chemical phenomena ranging from the scavenging of volatile organic compounds by falling snow (Lei and Wania, 2004), to participation in photoreduction processes associated with deposited mercury (Durnford and Dastoor, 2011), and to sequestration of persistent organic pollutants (Brown and Wania, 2008). This review focuses on the role that ice and snow play in the formation of volatile halogen-containing molecules in the coldest parts of our atmosphere, for example in the boundary layer at high latitudes and the

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upper troposphere-lower stratosphere (UT-LS). It is likely that similar processes occur in all snow-covered regions of the globe.

Ice-halogen chemistry was first explored for its importance to the Antarctic ozone hole, a phenomenon in which the majority of ozone within the polar stratospheric vortex is depleted annually for months at a time (summarized in Solomon, 1999). A conceptual advance in our understanding of atmospheric chemistry arose through coupled laboratory, field and modeling studies that demonstrated that interactions with polar stratospheric clouds convert relatively long-lived halogenated species to more reactive species that ultimately lead to ozone destruction. For example, compounds such as ClONO₂, HOCl and HCl adsorb to cloud surfaces, and are converted via heterogeneous reactions to gas phase Cl₂ which is readily photolyzed:



This chemistry largely occurs on particles that are not composed of pure ice, but rather solid nitric acid hydrates or supercooled solutions of sulfuric and nitric acid. This multiphase chemistry has similarities to that which prevails in the polar boundary layer on sea ice surfaces, blowing snow and the snowpack, as well as potentially in the UT-LS on ice crystals. In particular, the chemistry in Reaction (R2) proceeds on surfaces and in the bulk, likely through ionic processes facilitated by the dissociation of HCl on the ice surface, as described below.

Research related to ice chemistry in the Arctic and Antarctic boundary layers has accelerated in recent decades, motivated by observations of ozone depletion events (ODEs) that coincide with elevated levels of atmospheric brominated compounds (Barrie et al., 1988), now known to be largely reactive species such as BrO, Br and HOBr (as summarized in Simpson et al., 2007b). Ozone loss can occur rapidly via well-known gas phase catalytic processes involving bromine radicals, such as Br and BrO. In addition, measurements of active iodine in polar regions have been made (e.g. Saiz-Lopez et al., 2007b).

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Formation of reactive halogens and subsequent destruction of ozone significantly changes the oxidizing conditions of the boundary layer. For example, mercury compounds, oxidized by halogen radicals, are deposited to the surface during ODEs (Schroeder et al., 1998; Steffen et al., 2008). Similarly, reactions with halogen radicals reduce the lifetimes of dimethyl sulphide and other organic compounds that are normally controlled by OH. In addition, due to changes in HO_x cycling, OH levels themselves may be affected.

Recently, it has been shown that a large degree of variability in ozone in the Arctic is correlated with exposure to sea ice (Gilman et al., 2010; Jacobi et al., 2010), which likely indicates catalytic loss of ozone by halogens.

Ozone levels in the UT-LS can also be affected by heterogeneous reactions such as Reactions (R1) and (R2) occurring on ice and other particle surfaces (Borrmann et al., 1996; Borrmann et al., 1997). Very low temperatures in the UT-LS promote formation of thin cirrus clouds over a large fraction of the Earth's surface area. Very short-lived substances (VSLs) containing halogens decompose to release halogen atoms in this region. However, air masses in the UT-LS are not as dynamically isolated as they are in the polar stratosphere and boundary layer in winter and spring, so attribution of ozone depletion to ice chemistry in the UT-LS is difficult.

While the gas phase reactions for destruction of boundary layer ozone by halogen radicals are analogous to those that proceed in the polar stratosphere, the sources of the halogens to the gas phase and the means by which they can be recycled and maintained in reactive forms are distinctly different. In the stratosphere, where residence times can be years and where photodissociation rates are enhanced by the energetic UV fields, the halogen sources are well known and include both chlorofluorocarbons and halons. By contrast, in the polar boundary layer where photodissociation of small brominated organics of biological origin does not proceed fast enough at low solar angles, the focus of most recent research has been on snowpack and sea ice surface chemistry occurring on saline surfaces. Reactive processes, either driven photochemically or by gas-surface chemical interactions, have been studied as a means by which

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sea salt halides are oxidized to more reactive forms. For example, one of a number of processes identified involves HOBr oxidation of bromide, which can either recycle active bromine or lead to its autocatalytic release: (Fan and Jacob, 1992; Mozurkewich, 1995; Vogt et al., 1996):



This is a multiphase process which, depending upon the substrate, may or may not proceed faster under acidic conditions.

The role of bromine in boundary layer ODEs was recognized very early on, and it motivated early research in the field. More recently, however, the complexity of the interrelationships between gas-surface chemistry, photochemistry, and biological processes has been recognized (Dominé and Shepson, 2002). For example, it is now known that nitrate in snow photodissociates into reactive nitrogen forms (Honrath et al., 2002; Beine et al., 2008), a process that generates OH radicals within the snowpack. Similarly, H₂O₂ photolysis is an important source of OH (Anastasio et al., 2007). Sunlight also leads to the release of small volatile organic compounds (VOCs), either through direct photolytic processes or indirectly via reactions with OH or halogen radicals (Grannas et al., 2007). Biological processes play an additional role through sea ice algae that convert inorganic halides into organic forms that are released to the ice environment.

Common to these processes is the presence of ice, whether in the form of cirrus clouds, fresh sea ice, multi-year sea ice, frost flowers, snowpack, or blowing snow. These materials present a range of microenvironments in which inorganic and organic halogenated species can interact, including the disordered layer of enhanced mobility water molecules that exists on the surface of a pure ice crystal, at the grain boundaries forming within polycrystalline ice, or within the highly concentrated brine that co-exists with sea ice. The chemistry occurring in these materials is complex, as described in this review. Freeze concentration effects driven by freezing of sea water greatly enhance solution ionic strengths and lead to enhanced rates of chemical reaction. Similarly, ice

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surface acidity may vary widely from nearly neutral conditions associated with sea water to highly acidic conditions produced by deposition to the snowpack of Arctic Haze aerosol, transported from pollution sources in mid-latitudes (Barrie et al., 1981). Lastly, the physical structures of the ice substrates are important. Sea ice contains brine microchannels that permit transport of reactants over large distances. By contrast, the snowpack from freshly fallen snow will be highly porous and with high surface area, where transport rates at the snow surface will be determined by wind pumping (Colbeck, 1997; Cunningham and Waddington, 1993).

The goal of this paper is to summarize the role that ice and snow substrates play in promoting the formation and transformations of reactive halogenated species in the atmosphere. It is hoped that a comprehensive review will highlight current knowledge and future needs for studies in different environments, such as snow-covered regions in the mid-latitudes. This paper complements the 2007 review of Simpson et al. (2007b) that focussed on the detailed relationship between active bromine and ozone depletion events in the polar boundary layer. This paper is distinguished from Simpson et al. (2007b) by providing a more fully developed molecular level description of the halogen interactions with ice and snow throughout the environment. In addition, issues that have arisen in the past five years are given special attention, such as biological sources of halogens in ice covered regions, photochemical and freezing-induced mechanisms for halogen release, observations and potential sources of active iodine, interpretation of satellite measurements of active bromine, and recent advances in modeling these processes.

2 Inorganic halides and ice

This section describes the physical nature and composition of different substrates upon which halogen activation may occur in the polar boundary layer; see Fig. 1.

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2.1 Sea ice

As sea water freezes, exclusion of solutes from the ice matrix results in the formation of low salinity ice and high salinity brine. Depending on growth dynamics, temperature, and initial salinity, the brine will be located within inclusions in the bulk ice or at the ice surface as a liquid or slushy layer (with salinities of 100 PSU, where PSU refers to practical salinity unit which is roughly equivalent to the salt mass fraction, expressed in parts per thousand). As temperatures decrease, pressure changes force the brine up through the ice surface via a process known as brine expulsion. As the brine cools, salts reach their solubility thresholds and precipitate, leading to chemical fractionation. For example, at 265 K, the precipitation of mirabilite ($\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) results in a relative depletion of Na^+ and SO_4^{2-} in the brine. Below 251 K, hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) precipitates, leading to bromide enrichment relative to chloride. Overall, these processes lead to enriched bromide concentrations at young sea ice surfaces. The relative affinity for polarizable ions, such as Br^- and I^- , for the water-air interface may also enhance bromide relative to chloride at the surface (Jungwirth and Tobias, 2001, 2006; Gladich et al., 2011). The age of the exposed/underlying sea ice is an important determinant for salinity; multi-year sea ice has less accessible salt because most of the brine will have drained away during the summer melt (Simpson et al., 2007a).

2.2 Frost flowers

2.2.1 Frost flower formation

Under cold and calm conditions, the formation of new sea ice may be associated with frost flower growth. Frost flower blooms are especially common in coastal regions where offshore winds create new shore leads which can freeze over (Domine et al., 2005). As temperatures drop and sea water freezes, air which is supersaturated with water vapor condenses at imperfections at the surface. The highly saline brine that forms at the ice surface is wicked up by the ice skeleton through the effects of surface

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tension and concentration gradients. Style and Worster (2009) have shown theoretically and experimentally that frost flowers can also grow when supersaturated air is produced immediately above an ice surface which is sublimating into a cold, dry atmosphere. Frost flower fields typically last for only a few days, at which point they may be buried by the snow or melted by surface flooding (Perovich and Richter-Menge, 1994). Due to the recent interest in frost flowers, field studies (Alvarez-Aviles et al., 2008; Obbard et al., 2009; Domine et al., 2005; Perovich and Richter-Menge, 1994) and laboratory studies (Style and Worster, 2009; Martin et al., 1995, 1996; Roscoe et al., 2011) have focused on gaining a better understanding of the frost flower growth process and chemical composition.

2.2.2 Halide levels in frost flowers

As a result of brine wicking, frost flowers are covered in a highly saline brine (≈ 100 PSU), which is about three times more saline than sea water (< 35 PSU) (Perovich and Richter-Menge, 1994; Roscoe et al., 2011), although the salinity is not uniformly distributed (Perovich and Richter-Menge, 1994) and is a function of frost flower age (Roscoe et al., 2011). For example (Alvarez-Aviles et al., 2008) measured frost flower salinities ranging from 16 PSU (mature frost flower tip) to 75 PSU (bulk young frost flower). The enhancement in salinity is demonstrated by Fig. 2, which shows measured frost flower, brine, sea ice and sea water salinities sampled at the Weddell Sea and Mertz Glacier (Rankin et al., 2002). Depending on location, growth time and temperature, frost flowers may become enriched in certain ions over others (Obbard et al., 2009). The precipitation of mirabilite at warm temperatures leads to the formation of frost flowers which are depleted in sulfate (Rankin et al., 2002, 2000). Since bromide does not precipitate until temperatures reach 245 K (ice/ $\text{NaBr}\cdot 5\text{H}_2\text{O}$ eutectic) (Koop et al., 2000), bromide is not expected to be fractionated in the majority of frost flowers and its enhanced concentration should be due to freeze-concentration effects alone.

If temperatures drop low enough for NaCl to precipitate, the bromide to chloride ratio may increase with temperature in the frost flowers and associated brine. For example,

at 240 K Koop et al. (2000) found that the chloride concentration had increased by a factor of 11 in brine while the bromide concentration has increased by a factor of 38. Kalnajs and Avallone (2006) measured Cl^-/Br^- ratios ranging from 269–367, much lower than the corresponding sea water ratio of 650, for frost flowers collected from the Barne Glacier, Antarctica, suggesting that a bromide-enhanced brine has wicked up.

2.2.3 Frost flowers as a direct source of halides

Rankin et al. (2002) first proposed frost flowers as a potentially important source of reactive bromine. Kaleschke et al. (2004) provide a parameterization for potential frost flower (PFF) area which is based in part on laboratory studies for frost flower growth (Martin et al., 1996) and depends on the open water fraction and the surface air temperature. This approach allows PFF to be calculated from satellite-based imaging and meteorological data. In the Kaleschke et al. (2004) study they showed that areas of high PFF were strongly correlated with enhanced column BrO and concluded that frost flowers are the source of reactive bromine in bromine explosion events. However, a trajectory study by Simpson et al. (2007a) showed that BrO levels in air masses arriving at Barrow, Alaska did not correlate with PFF contact.

Early on, frost flowers were estimated to have a specific surface area (SSA) similar to fresh snow leading Rankin et al. (2002) to estimate a total surface area (TSA) ranging from 50–1000 m^2 per m^2 of ice surface. As a result, it was believed that frost flowers would provide a large surface area for bromide activation. However, subsequent SSA measurements of field (Domine et al., 2005; Obbard et al., 2009) and laboratory frost flowers (Roscoe et al., 2011) reveal that the SSA is only slightly larger than the underlying sea ice. For example, Obbard et al. (2009) measured SSA for frost flowers collected from Hudson Bay ranging from 63 to 299 $\text{cm}^2 \text{g}^{-1}$ with a mean of 162 $\text{cm}^2 \text{g}^{-1}$. Similarly, Domine et al. (2005) measured SSA for frost flowers of 185 $\text{cm}^2 \text{g}^{-1}$ from which they calculate a TSA of 1.4 m^2 per m^2 of ice surface. Based on the small TSA, these studies conclude that the direct role of frost flowers in bromide activation may have been overstated.

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2.2.4 Frost flowers as an indirect source of halides

It has also been suggested that frost flowers may be indirectly responsible for halogen activation by acting as a source of sea-salt aerosol (Rankin et al., 2000). The main evidence for this is the observation that both frost flowers and fractionated sea-salt aerosol are sulfate-depleted with respect to sea water (Rankin et al., 2000, 2002; Wagenbach et al., 1998). For example, frost flowers collected from the Weddell Sea and near the Mertz Glacier were found to have a sulfate/sodium weight ratio of 0.05–0.10, much lower than the standard seawater ratio of 0.25 but similar to that observed for wintertime aerosol at Halley base of 0.107 (Rankin et al., 2002). Beaudon and Moore (2009) were the first to observe a frost flower chemical signature in Arctic snow. Snow samples collected from the winter snowpack at the western edge of the Vestfonna ice cap were fractionated in sodium and sulfate with a $\text{SO}_4^{2-}/\text{Na}^+$ ratio of 0.092 which is lower than that of sea water but similar to that measured for Antarctic frost flowers and aerosol.

Although it has been proposed that frost flowers are a source of sea-salt aerosol, the mechanism of aerosol production from frost flowers is not known. Frost flowers are mechanically rigid and difficult to fracture (Alvarez-Aviles et al., 2008; Obbard et al., 2009; Domine et al., 2005) and frost flower breakage has yet to be directly observed in the field. Obbard et al. (2009) were the first to observe pieces of broken frost flowers but these pieces were too large to have been lofted. In addition, aerosol formation during the growth of laboratory frost flowers was not observed under various wind conditions (Roscoe et al., 2011). However, wind scouring of the highly saline frost flower surface may be important and it has also been suggested that frost flowers may indirectly affect halogen chemistry by contaminating adjacent snow (Obbard et al., 2009; Morin et al., 2008). Also, blowing snow may cover frost flowers thus facilitating a bromine explosion within the snowpack (Morin et al., 2008).

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2.2.5 Salty snow

It has been proposed that blowing saline snow on sea ice could be a source of reactive bromine (Yang et al., 2008; Jones et al., 2009; Yang et al., 2010); this mechanism is discussed in more detail in Sects. 5 and 6. It has also been proposed that a bromine explosion could also occur in the interstitial air within a salty snowpack (Morin et al., 2008). Several processes lead to enriched snow salinity. The upward migration of sea-salt enriched brine from the sea ice to the snowpack by capillary forces can affect snow salinity. Flooding, the infiltration of seawater through cracks or brine-drainage channels that connect the ocean to the sea-ice surface, also introduces brine to the basal snow layer. Enriched salinities (>2 PSU) have been observed to a height of 0.1–0.2 m (Massom et al., 2001; Domine et al., 2004; Toyota et al., 2011b) although most of the enrichment is expected within the basal snow layer (Massom et al., 2001; Toyota et al., 2011b), where salinities have been observed to range from 0.43–36.9 PSU (Toyota et al., 2011b). The salinity at the top of the snowpack is primarily affected by (a) the deposition of sea-salt aerosol generated by sea spray from the open ocean or nearby leads and polynyas and (b) precipitation dilution. Snow at the top of the snowpack is generally associated with lower salinities. For example, Massom et al. (2001) measured salinities ranging from 0.1–2.0 PSU in blowing snow collected just above the surface. Although the salinity above a height of 0.2 m is fairly low, wind scouring can re-expose salty snow surfaces (Simpson et al., 2007a). Snow blowing across bare sea ice may also acquire additional salt which may be deposited to the snowpack. Domine et al. (2004) observed large amounts of Cl^- and Br^- to be deposited to snow by wind, rapidly increasing ionic concentration. Jones et al. (2009) also measured high salt concentrations in surface snow and snow pits.

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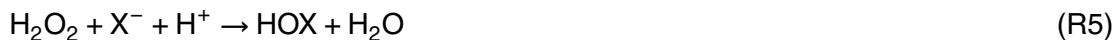
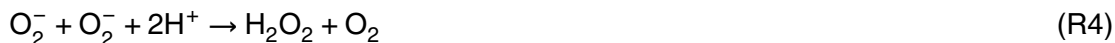


3 Organohalogenes and ice

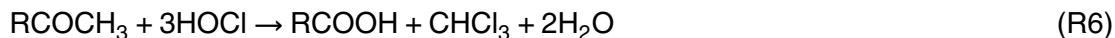
Sea ice is a habitat for organisms, such as microalgae, that are capable of enduring extreme environments. Recent studies have revealed that such sea ice microalgae are a source of organohalogenes. Naturally produced halocarbons are a group of compounds consisting of one to three carbon atoms with one to three halogen atoms. Some are short-lived in the troposphere, with atmospheric lifetimes shorter than 6 months. The compounds listed in Table 1 are all naturally produced, however, some have additional anthropogenic sources (CHBrCl₂, CHBr₂Cl and CHBr₃).

3.1 Production mechanisms

Investigations of halocarbon release have mostly focused on micro- and macro-algae from subtropical and tropical regions (Laternus, 1996; Laternus et al., 1996; Goodwin and North, 1992; Collén et al., 1994; Tokarczyk and Moore, 1994). The suggested mechanism is through the scavenging of superoxide radicals formed during photosynthesis. This involves several enzymatic processes from the conversion of O₂⁻ to H₂O₂ (Reaction R4) through the enzyme superoxide dismutase (SOD), to the reduction of H₂O₂ to water through haloperoxidases (Reaction R5) (Moore et al., 1996; Theiler et al., 1978).



where X = Cl, Br, I. During the reduction of H₂O₂, it is most likely that HOCl is formed, which will rapidly react with bromide, and if present iodide, forming HOBr and/or HOI (as described in Sect. 4). Halocarbons can then be formed through the reaction of HOCl, HOBr and HOI with the dissolved organic matter through the haloform Reaction (R6, written for X = Cl), or less likely, through addition Reaction (R7).



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The haloform reaction is known to produce all of the above mentioned halocarbons except iodomethane. All the brominated compounds correlate with CHBr_3 , which is the main contributor of organo-bromine (Abrahamsson et al., 2004; Granfors et al., 2011). For the iodinated cases, CH_2I_2 contributes the most to organo-iodine, however, it is seldom at concentrations above detection limits in open oceans (Carpenter et al., 2007).

The formation of halocarbons is, thus, dependent on both photosynthesis (Cota and Sturges, 1997; Abrahamsson et al., 2004) and respiration, since all respiring cells produce H_2O_2 . Evidence that respiration is important is that production of halocarbons has been observed during dark conditions (Collén et al., 1994; Cota and Sturges, 1997), and in sea ice brine where the pigment echinenone was present, which indicates the presence of bacteria (Theorin et al., 2012).

In polar areas only a few attempts have assessed the rate of production by sea ice algae. For cultures of organisms living on ice, production rates for bromoform have been determined to vary between $0.1\text{--}48 \text{ pmol } \mu\text{g chl a}^{-1} \text{ h}^{-1}$ (Cota and Sturges, 1997; Sturges et al., 1993). Another approach was presented by Theorin et al. (2012), who incubated sea ice brine and found comparable production rates, $3\text{--}33 \text{ pmol } \mu\text{g chl a}^{-1} \text{ h}^{-1}$. From these data, using the values given for primary productivity in the Arctic and the Antarctic (Horner et al., 1992; Gosselin et al., 1997), the total annual production of bromoform has been estimated to be in the range of $1\text{--}100 \text{ Gg}$. Measurements of organo-halogens in polar waters and atmosphere are summarized in Table 2.

3.2 Fluxes from seawater in polar areas

Reviewing halocarbon fluxes from seawater in polar areas is difficult since measurements in these areas are scarce and the few measurements are dependent on time and location of sampling. Carpenter et al. (2007) performed measurements within 40 km

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from the Antarctic sea ice in the spring/summer and found positive saturation anomalies for CHBr_3 and CH_2I_2 . The mean bromoform sea-air flux of $32 \text{ nmol m}^{-2} \text{ day}^{-1}$ and the mean saturation anomalies of 780 % were similar in magnitude to global shelf values, and the surface maxima in halocarbon concentrations were associated with melt-water from nearby sea ice. Hughes et al. (2009) estimated the air-sea flux of CHBr_3 and CH_2Br_2 from water measurements on the west side of the Antarctic Peninsula. The mean value of $84 \text{ CHBr}_3 \text{ nmol m}^{-2} \text{ day}^{-1}$ and $21 \text{ nmol CH}_2\text{Br}_2 \text{ m}^{-2} \text{ day}^{-1}$ during ice-free periods could be important if representative of the large areas of ice edge blooms in the Southern Ocean. Flux measurements at off-shore sites related to the summer ice edge were $8.3\text{--}19 \text{ nmol m}^{-2} \text{ day}^{-1}$ for CHBr_3 and $1.9\text{--}3.6 \text{ nmol m}^{-2} \text{ day}^{-1}$ for CH_2Br_2 (Abrahamsson et al., 2004). Hughes et al. (2012) measured CH_2Br_2 and CHBr_3 in coastal waters of the western Antarctic Peninsula, and found large interannual variations for CHBr_3 but not for CH_2Br_2 . They derived mean CHBr_3 emission rates of 117 and $29 \text{ nmol m}^{-2} \text{ day}^{-1}$ for diatom bloom and non-bloom waters, respectively, and suggest that CHBr_3 can be an important bromine source for the boundary layer under non-bromine explosion conditions.

A different view is given by Mattsson et al. (2012) who measured CHBr_3 and CH_2ClI in sea water and air in Antarctic waters. CHBr_3 was clearly undersaturated in a majority of the sampling sites while CH_2ClI had a saturation anomaly varying between -90% and 310% . Chuck et al. (2005) measured halocarbons in sea water and air at 60°S in February-March and found CHBr_3 , CHBrCl_2 , CHBr_2Cl to be under-saturated in sea water and CH_3I to be close to equilibrium with air.

3.3 Fluxes from sea ice

Sea ice may be a barrier to the transport of gases from seawater to the atmosphere. However, in ice-covered oceans, sea ice can also act as a source of halocarbons when they are produced within sea ice brine (Theorin et al., 2012). Halocarbon concentrations in sea ice brine are often higher than those measured in sea water (Granfors

et al., 2011; Theorin et al., 2012) and during periods of biological production and melting, sea ice will contribute halocarbons to the atmosphere. One uncertainty is the rate of transport for biogenic halocarbons through sea ice, which has not yet been determined in the field. However, diffusion coefficients for gases such as oxygen and SF₆ have been experimentally derived by Loose et al. (2011) giving diffusion coefficients (*D*) on the order of 10⁻⁵ to 10⁻⁴ cm² s⁻¹. Estimation of *D*-values for CHBr₃, CH₂ClI and CH₂Brl in sea ice during freezing by Granfors et al. (2011) resulted in a *D* on the order of 10⁻⁴ cm² s⁻¹. This would mean that *D* is approximately 100 times larger for CHBr₃ and CH₂ClI and a 1000 times larger for CH₂Brl than the diffusion coefficients in water that can be derived for halocarbons using constants given by Wilke and Chang (1955). The faster diffusion is possibly due to gas phase transport of the volatile halocarbons in gas bubbles formed in the ice during freezing, either trapped in the ice during the freezing process or formed due to supersaturation caused by the formation of gases through respiration or photosynthesis (Mock et al., 2002).

Recent laboratory studies in a cold room have shown that iodinated halocarbons diffuse very slowly through consolidated ice, suggesting that movement from under the ice through to the brine on its surface may be slower than release from neighbouring open leads (Shaw et al., 2011). The slow diffusion times through the brine channels opens up the possibility for chemical change to occur to the halocarbons while in the sea ice substrate.

3.4 Frost flowers

In addition to inorganic halides, it has also been shown that frost flowers are a source of organo-Br and organo-I to the atmosphere. The concentrations found in the frost flowers reflected the concentrations found in brine, organo-Br 140–360 pmol l⁻¹ and organo-I 1.2–5.1 pmol l⁻¹. As mentioned in Sect. 2, the lifetime of frost flowers is relatively short and, during these events, an additional source of organo-Br and organo-I might be present (Granfors et al., 2011).

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3.5 Snowpack

Alkyl halides are present in snowpack interstitial air, sometimes at mixing ratios higher than the surrounding atmosphere, suggestive of a photochemical source (Swanson et al., 2007). Measurements were conducted at both mid-latitude and polar sites, and a wide range of organohalogen species were observed. It is hypothesized that the molecules are formed within the quasi-liquid layer of the ice crystals by nucleophilic attack of a halide ion to an alcohol. However, a biological source cannot be ruled out. Described in the Supplement are calculations of the photochemical lifetimes of such species when in the interstitial air of a variety of snowpacks, from melting snow to a coastal snowpack to cold polar snow. As shown in Fig. 3, it is noteworthy that the lifetimes of the organoiodides within the snowpacks are sufficiently short that considerable photochemistry may be occurring within this environment.

4 Molecular level understanding of multiphase oxidation chemistry

The above sections have mostly addressed the bulk availability of halogenated species, and this section addresses their multiphase chemistry at a molecular level. In particular, while ice chemistry is distinct from bulk-phase aqueous chemistry, it nevertheless has strong connections to this long-standing field. Through this work it was recognized that a variety of atmospheric oxidants are active in the aqueous phase. Also, the speed of oxidation reactions generally increases with increasing atomic number, e.g. the ratios of the rate constants for reactions with dissolved O_3 are $1/10^5/10^{12}$ for $Cl^-/Br^-/I^-$ (Buxton et al., 1988; Liu et al., 2001). Finally, aqueous reactions are frequently accelerated by acidic conditions (Eigen and Kustin, 1962; Liu et al., 2001).

The first evidence that analogous chemistry may occur on ice and ice-like substrates came from ozone hole studies. Although we know now that stratospheric halogen activation occurs largely via aerosol and clouds that are composed of ice under only the coldest conditions (Solomon, 1999), many of the earliest lab studies were conducted

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on ice surfaces at temperatures below 190 K. It was shown that reactions involving adsorbed forms of HCl and HBr proceed rapidly with other halogenated molecules. In general, surface phase ionization and solvation processes are crucial for such chemistry to occur. The details of this chemistry have been reviewed previously (Abbatt, 2003; Huthwelker et al., 2006).

As Sect. 2 has illustrated, the structure of boundary layer snow and ice will promote a mix of both aqueous and solid phase processes. In pristine environments, falling snow and a fresh snow pack will promote surface chemistry at the atmosphere-ice boundary. Alternatively, sea ice and frost flowers consist of both ice and concentrated brines, so that bulk aqueous phase processes will occur in these saline environments. We start with a molecular-level description of relevant surfaces, and then describe multiphase oxidative processes.

4.1 Microscopic view of the substrate

4.1.1 Brines and quasi-liquid layers

At the interface between the gas phase and solid ice phase, there exists a disordered region referred to as the quasi-liquid layer (QLL) (Döppenschmidt and Butt, 2000; Wei et al., 2002; Rosenberg, 2005; Li and Somorjai, 2007; Kahan and Donaldson, 2007). Water molecules adopt a more random orientation than in the crystalline form, giving rise to an environment different from both bulk ice and the liquid water surface. The thickness of the QLL increases with increasing temperature (Döppenschmidt and Butt, 2000) and in the presence of impurities (Döppenschmidt and Butt, 2000; McNeill et al., 2006). There is evidence to suggest that reactivity in/on the QLL may also be unique and thus care should be taken in modeling the QLL using known liquid-phase kinetics (Kahan and Donaldson, 2007; Kahan et al., 2010a,b; Kuo et al., 2011). When high ionic strengths are involved (e.g. sea ice), the concept of a pure QLL will not be applicable (Kuo et al., 2011). Instead, separation of liquid brine from solid ice is thermodynamically predicted.

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4.1.2 Halide distribution

Koop et al. (2000) suggested that both sea-salt aerosols and seawater on the ice pack will be partially liquid at temperatures as low as 230 K with increasing bromide and chloride concentrations as well as with decreasing temperature. Recent work suggests that enriched surface concentrations of halides can be adequately predicted using a thermodynamic analysis. Cho et al. (2002) presented a formulation derived from ideal solution thermodynamics for predicting both the volume fraction of the unfrozen phase as well as the concentration of excluded solutes. The authors studied dilute solutions of NaCl using NMR spectroscopy to probe brine pockets within the ice matrix and found measured concentrations and liquid fractions to be in good agreement with their predictions.

More recently, Křepelová et al. (2010) studied the surface of frozen NaCl solutions using x-ray photoelectron spectroscopy and found the composition of the unfrozen phase at the surface to be well predicted by the NaCl-H₂O phase diagram. Wren et al. (2010) studied the kinetics of the heterogeneous ozonation of bromide at the surface of frozen NaBr solutions and found the kinetics to be consistent with formation of a brine at the surface whose composition reflects the expected bulk composition. Molecular dynamics simulations by Carignano et al. (2007) and Bauerecker et al. (2008) also showed that Na⁺ and Cl⁻ ions are excluded from the ice matrix during freezing into QLLs located at the interfaces. However, recent work by Wren and Donaldson (2011) has shown that surface enrichment due to freezing is not always well predicted by thermodynamics.

4.1.3 Surface affinity of halides

There now exists extensive theoretical (e.g. Jungwirth and Tobias, 2001; Jungwirth et al., 2006; Jungwirth and Tobias, 2006; Gladich et al., 2011) and experimental (Petersen et al., 2004; Ghosal et al., 2005; Clifford and Donaldson, 2007) evidence to suggest that the heavy halide ions are surface active. The affinity of these ions for the

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air-aqueous interface may have important implications for halide activation chemistry occurring at the surface of a liquid brine layer. In particular, the strong surface affinity of iodide may compensate for its naturally low sea water concentration. However, the degree of surface enhancement is complicated because there are cross ion effects, and surface enhancement may not be the same depending on the mix of ions (Wingen et al., 2008; Gladich et al., 2011; Richards et al., 2011).

4.1.4 Acidity of sea ice surfaces and aerosol

Attention has been paid to the acidity of sea ice and brine substrates, given that pH may play a role in halogen activation (see below). In particular, Kalnajs and Avallone (2006) measured the pH of melted frost flowers, sea ice and non-frost flower snow. The pH of the frost flower samples is similar to sea water, suggesting that acidification by trace atmospheric gases did not occur. In comparison, the pH of Arctic snow has been found to range from 4.6–6.13 (de Caritat et al., 2005). However, bulk (i.e. melted sample) pHs do not necessarily reflect the effective surface pH.

Sander et al. (2006) were the first to propose that the precipitation of calcium carbonate during freezing could sufficiently reduce the buffering capacity of sea-salt aerosol, compared to that before freezing. In particular, they modeled that initially alkaline aerosol reached pH 3 when 30 % of the carbonate precipitated, with the acidification being due to oxidation of atmospheric SO₂ and NO₂. They suggest that the decrease in pH triggers bromine explosion chemistry. Morin et al. (2008) used improved thermodynamic data and found that the identity of the precipitating calcium carbonate polymorph determines potential changes in alkalinity. When calcite precipitates at 271 K, the alkalinity of the brine is reduced to a third of that of sea water. However, when ikaite (CaCO₃·6H₂O) precipitates at 268 K, the alkalinity of the brine never drops below its initial value. This concept is illustrated in Fig. 4, taken from Sander and Morin (2010), when carbonate precipitation is “turned off” the total alkalinity increases with decreasing temperature due to freeze-concentration of the brine. When calcite precipitates the alkalinity is removed from the brine and so alkalinity drops below the seawater value.

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However, precipitation of ikaite cannot fully compensate for the freeze-concentration effect and so alkalinity never drops below the seawater value. The discovery of ikaite in sea ice (Dieckmann et al., 2008, 2010) suggests that of the two polymorphs, ikaite is more likely to precipitate.

5 4.1.5 Non-reactive interactions of halogenated gases with Ice

Laboratory exposure of halogenated gases to snow and ice surfaces leads to substantial uptake for hydrogen halides such as HCl, HBr and HI (Abbatt, 2003; Huthwelker et al., 2006). Because of its high abundance in the stratosphere, HCl has also received considerable interest from theoreticians (Girardet and Toubin, 2001; Toubin et al., 2003; Bianco and Hynes, 2006). The question of whether HCl adsorbs molecularly or readily dissociates at the ice surface is clearly of importance for halogen activation (Bianco and Hynes, 2006; Horn et al., 1992). In particular, recent modeling results show that at submonolayer coverage and very low temperatures (tens of degrees Kelvin), molecular HCl can co-exist on ice with ionized HCl (Buch et al., 2002) and that some calculations predict that the dissociation mechanism is not thermally activated (Gertner et al., 1998; Svanberg et al., 2000). In these models, the ionization is driven by the number of dangling hydrogen bonds, with favorable sites offering 3 dangling H-bonds on the ice surface. Instead, other models predict efficient solvation of Cl^- when it is incorporated in the first ice layer (Gertner and Hynes, 1996; Gertner et al., 1998), as shown in Fig. 5. Those processes are favored by the higher water activities present at higher temperatures, providing a plausible mechanism for the increasing degree of HCl ionization with increasing temperature seen in experiments.

For other species, molecular dynamics (MD) simulations have been recently performed on liquid water, as a model for the aqueous surface that might arise on ice surfaces. For example, MD simulations have been carried out for the uptake of the ClO radical at the surface of liquid water (Du et al., 2009). Simulation results show that the ClO radical has a higher propensity to be adsorbed on the air-water interface than to be dissolved in the bulk, thus opening up the possibility for interfacial chemistry.

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4.2 Heterogeneous processes

In this section we address what is known about heterogeneous oxidation chemistry involving reaction of halide ions with a number of oxidants. We note that many of the studies below follow-on from earlier work on halogen activation conducted to understand polar stratospheric ozone. From this work, it was learned that ionic mechanisms dominate in many systems, such as Reactions (R1) and (R2) which are driven in large part by the dissociation of HCl on the surface (Sodeau et al., 1995; Banham et al., 1996; Horn et al., 1998). We discuss this chemistry in the following sub-sections by oxidant.

4.2.1 HOBr, HOCl

The heterogeneous reactions of HOBr play a central role in boundary layer ozone depletion and potential UT-LS chemistry on cirrus clouds. This arises because HOBr represents a significant fraction of the total active bromine budget, whereas HBr plays a minor role. A major advance arose from the recognition that heterogeneous bromine activation may proceed autocatalytically if gas phase HOBr oxidizes condensed phase bromide leading to the ultimate production of more than one HOBr gas phase molecule (Fan and Jacob, 1992; Mozurkewich, 1995; Vogt et al., 1996). This has led to the term “bromine explosion” to refer to the rapid rise of active bromine that can ensue.

Initial laboratory studies, many motivated by stratospheric issues, demonstrated that a general class of reactions proceed on ice surfaces involving the hypohalous acids, HOCl and HOBr (Hanson and Ravishankara, 1992b; Abbatt and Molina, 1992; Abbatt, 1994):



where X, Y = Cl, Br.

As described in this section, HCl and HBr adsorb strongly to ice, likely existing in a dissociated form; the hydrated halides may be similar in chemical nature to those

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in concentrated brines. In particular, under the partial pressures of HBr used in the laboratory, the ice surface is likely to melt to form a thermodynamically stable solution in which the strong acids are fully dissociated (Hanson and Ravishankara, 1992a), as occurs with HCl at somewhat higher partial pressures. HOCl and HOBr are considerably weaker acids than the hydrogen halides, and so they adsorb to ice surfaces to a lesser extent (Hanson and Ravishankara, 1992b; Abbatt and Molina, 1992). Under the low temperatures used for these studies, these reactions proceed rapidly with close-to-unity HOX uptake coefficients for surfaces exposed to HY. These studies build upon aqueous chemistry work. For example, the rate constants for the analogous aqueous reactions are extremely rapid, with the rates highest for the larger, more polarizable halides (Eigen and Kustin, 1962; Beckwith et al., 1996). Unless the acidity is very high, Reaction (R8) proceeds via a mechanism whereby the proton reacts with an HOX·Y⁻ intermediate.

Laboratory experiments have confirmed that the central reaction of the bromine explosion, Reaction (R3), will readily occur. In particular, the mass accommodation coefficient of HOBr to deliquesced salt particles and ice is large (Abbatt, 1994; Abbatt and Waschewsky, 1998). Also, Br₂ is formed when frozen NaCl/NaBr solutions are exposed to HOBr (Kirchner et al., 1997; Adams et al., 2002; Huff and Abbatt, 2002), as shown in Fig. 6. Most importantly, Adams et al. (2002) illustrated that HOBr reacts with frozen NaCl/NaBr solutions forming Br₂ initially, and then BrCl when the surface becomes depleted of bromide. In the environment, if an ice surface has been processed by reaction with HOBr or other oxidants, then BrCl may be observed as a product in place of Br₂. These reactions occur over a wide range of solution acidities, with little impact on yields or kinetics. Studies at polar boundary layer temperatures have confirmed that analogous chemistry is driven by the uptake of HOCl and HOI to frozen salt solutions (Huff and Abbatt, 2000; Holmes et al., 2001). In particular, with HOI, the product of the reaction with frozen NaCl/NaBr solutions is IBr until all the bromide is depleted, at which point ICl starts to form.

In summary, laboratory studies provide convincing evidence that HOBr heterogeneous chemistry central to the Arctic boundary layer bromine explosion proceeds rapidly, forming gas phase Br₂, so long as sufficient surface bromide is available. Surface acidity appears to not play a significant role in the chemistry, in contrast to studies conducted with aqueous salt solutions, for which acidity was required for bromine release to occur (Fickert et al., 1999). The chemistry proceeds sufficiently rapidly that mass transfer from the atmosphere to a snowpack/ice surface is very likely rate limiting, as described by Huff and Abbatt (2000). HOCl and HOI also react rapidly, in an analogous manner to HOBr.

4.2.2 Ozone

The first evidence that ozone can oxidize halides in an ice substrate demonstrated that frozen seawater liberates gas phase Br₂ when exposed to O₃ (Oum et al., 1998). These experiments were conducted just below freezing, and Br₂ concentrations were observed to rise in sync with increasing exposure to ozone. This bromine activation process is important given that it can occur in the dark, prior to polar sunrise, and it may provide the seed bromine that becomes amplified through the HOBr-driven bromine explosion reactions described above. For this reason its mechanism has been the focus of much research.

Early work implied that an interfacial reaction plays an important role. Reaction between gas phase ozone and aqueous bromide particles proceeds faster than predicted by bulk phase kinetics (Anastasio and Mozurkewich, 2002; Hunt et al., 2004). Also, changes in the spectral properties of the near-surface region of aqueous solutions indicate an interfacial reaction (Clifford and Donaldson, 2007). The detailed mechanism of this interfacial process is not well known, but likely goes through a Langmuir-Hinshelwood-like process (Oldridge and Abbatt, 2011), as observed for a large number of ozone heterogeneous reactions. Spectroscopic observation of frozen sodium bromide solutions and iodide solutions indicates that similar chemistry occurs below freezing as for aqueous substrates (Oldridge and Abbatt, 2011; Wren et al., 2010).

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A question that arises is whether the same reaction mechanism proceeds faster interfacially or predominantly in the bulk brine phase. This has direct relevance to environmental modeling because a highly reactive interfacial layer may be readily depleted of bromide by ozone, thus leading to reduced halogen supply to the atmosphere. Or, does replenishment of bromide from within the bulk occur rapidly? Quantitative separation of the bulk and surface phase kinetics in one study indicates that the surface layer reaction dominates, for 253 K frozen solutions of NaCl/NaBr with compositions close to those of seawater (Oldridge and Abbatt, 2011). Under conditions of higher ozone concentrations than are atmospherically relevant, the bulk reaction dominates the kinetics but in the atmospheric regime the kinetics are better described by a surface reaction with Langmuir-Hinshelwood-like kinetics. The same study showed that surfaces formed by freezing solutions that are both acidic and neutral promote fast kinetics (Oldridge and Abbatt, 2011), consistent with the rate determining step of the reaction mechanism not involving a proton. The lab studies do not report rapid diminution of halogen production rates with time, as might occur if bromide is being depleted at the surface. This indicates that there is rapid replenishment of bromide from the bulk brine to the surface.

In summary, we are confident that ozone readily oxidizes iodide and bromide when present in frozen solutions such as sea ice or when marine aerosol is deposited to the snowpack. There is no evidence that chloride is oxidized if the other halides are present. Under atmospheric conditions, the reaction occurs most rapidly at the interface, via a process that is not accurately modeled using bulk-phase parameters.

4.2.3 Hydroxyl radical

OH is an efficient oxidant of aqueous halides via an acid-assisted mechanism (Finlayson-Pitts et al., 2003). Two studies have examined whether gas phase OH radicals heterogeneously oxidize aqueous halides. Notably, gas phase OH was generated photochemically from the photodissociation of O₃ in the presence of water vapor and deliquesced NaCl particles (Oum et al., 1998). Cl₂ was observed to form at rates

considerably faster than can be accounted for by bulk phase chemistry, leading to the suggestion that facile surface chemistry takes place, perhaps involving two OH·Cl⁻ complexes:



5 The net reaction is the same as if Cl⁻ oxidation were proceeding in the bulk phase but, instead, the chemistry is thought to be driven by high concentrations of surface complexes that form from elevated surface concentration of halides. Also, a proton is not included in the rate-determining step, so that the predicted rate of the chemistry is pH independent, unlike the more traditional bulk-phase pathway.

10 Exposure of high gas phase OH concentrations to aqueous and desiccated solutions of both pure NaBr and mixed NaCl/NaBr yielded Br₂ (Frinak and Abbatt, 2006; Sjostedt and Abbatt, 2008). Only considerable OH exposure, presumably to the point that Br⁻ is consumed, leads to the observation of Cl₂ as a gas phase product in the aqueous case. The oxidation is efficient, with the measured yield of Br₂ consistent with nearly every OH radical being involved in oxidation of Br⁻.

15 The only study of halogen release from frozen solutions via OH oxidation has observed similar results (Sjostedt and Abbatt, 2008). Again, preferential oxidation of the large halides was observed, with the primary product being Br₂, but significant levels of IBr and BrCl being observed as well. The observation of oxidized iodine, in the form of IBr, is interesting because iodide was present in the frozen solutions at extremely low levels (≈10⁻⁵ M). This is consistent with iodide being preferentially oxidized over the smaller halides. Cl₂ was never observed as a product. Indeed the Br₂ product signal showed no indication of depletion with time, indication that there is a mechanism for replenishment of bromide to the substrate surface, presumably by diffusion through a brine.

20 To conclude, these studies indicate that halides within ice films are readily oxidized by gas phase OH radicals. It is apparent that iodide and bromide oxidation will proceed before chloride oxidation, but chloride oxidation may occur if the larger halides are

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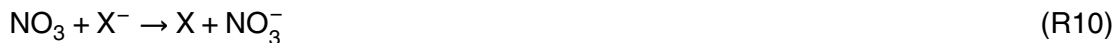
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absent. As with HOBr and O₃ chemistry, these processes proceed rapidly on pH neutral substrates but with somewhat higher efficiency at low pH.

4.2.4 N₂O₅/NO₃

For many years it has been recognized that reactive nitrogen oxides are able to oxidize condensed phase halides (Finlayson-Pitts et al., 2003). These studies were largely conducted on desiccated salts and involved a range of oxidants, including NO₂ and N₂O₅. This early work set the stage for subsequent investigations on the oxidation of aqueous solutions by both NO₃ and N₂O₅ which have illustrated that oxidation also occurs with bulk phase solutions. In the case of NO₃, halides are oxidized readily (Finlayson-Pitts et al., 2003):



Once the halogen atom is formed, it will readily yield dihalogens as described above. No studies with NO₃ have been conducted on frozen salt solutions but it is likely that the same chemistry will prevail.

For N₂O₅, most attention has been given to the ClNO₂ product that arises when chloride concentrations are sufficiently high in solution that the hydrated NO₂⁺ intermediate reacts with Cl⁻ rather than with H₂O (Behnke et al., 1997). N₂O₅ also reacts with dissolved bromide to form BrNO₂ (Schweitzer et al., 1998). Similar chemistry occurs when halides are present within an ice substrate. Early reports of this chemistry were motivated by understanding polar stratospheric processes, and experiments were conducted with low temperatures (<200 K) and HCl delivered from the gas phase (Leu, 1988; Tolbert et al., 1988). The findings were that N₂O₅ is lost only slightly faster on an ice surface to which HCl has been exposed than to a bare ice surface, but the products change, likely due to ClNO₂ formation. Analogous studies have since been performed with HBr, yielding BrNO₂ as the product (Seisel et al., 1998). The only N₂O₅ study conducted with frozen NaCl/KBr solutions reports that the ratio of ClNO₂ to Br₂ products is controlled by the ratio of the Cl⁻ to Br⁻ ratio in the brine, which in turn

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was demonstrated to vary as expected with temperature (Lopez-Hilfiker et al., 2012). In particular, Br₂ was produced ~30× more efficiently than ClNO₂, so correspondingly lower concentrations of Br⁻ in the brine can lead to equivalent yields of Br₂ and ClNO₂.

4.3 Photochemical processes

A detailed analysis of the photochemical complexities associated with many species relevant to polar atmospheric chemistry has been given in a recent review (Anastasio et al., 2012). By focusing primarily on halogens, the material discussed below complements both that work and Grannas et al. (2007). In addition, we provide an estimate of photochemical lifetimes of a wide variety of species in different modeled snowpack environments in the Supplement (see Fig. 3).

Several snowpack inorganic compounds undergo direct photochemistry to generate important atmospheric oxidants that can drive halogen chemistry, most notably nitrate ions, nitrite species (NO₂⁻ along with nitrous acid or the nitroacidium ion, H₂ONO⁺), and hydrogen peroxide. All absorb sunlight reaching the troposphere and range from very weakly absorbing H₂O₂, which has a molar absorptivity at 300 nm of approximately 1 M⁻¹ cm⁻¹ to HONO with a peak molar absorptivity of 57 M⁻¹ cm⁻¹ at 370 nm. The rate of photolysis also depends on upon the quantum yield, concentration of absorbing species, and intensity of photolyzing radiation. Therefore, although H₂O₂ is relatively weakly absorbing, the H₂O₂ concentration and quantum yield in the snowpack are large enough to make its photolysis significant (Anastasio and Chu, 2009; Chu and Anastasio, 2005; King et al., 2005; Chu and Anastasio, 2007; France et al., 2011, 2012). Understanding the photochemistry of HO_x, NO_x and NO_y species on ice is therefore particularly important because of the impacts of their products on the release of active halogens. For conditions in Halley Bay, Antarctica, the rate of OH formation in snow grains from H₂O₂ photolysis is 70 nmol l⁻¹ h⁻¹, which is an order of magnitude higher than the sum of the rates of OH or NO_x formation from photolysis of NO₃⁻ and NO₂⁻ (Anastasio et al., 2012). For Arctic Springtime coastal snowpacks in Barrow, Alaska the relative contribution of hydroxyl radical production by H₂O₂, NO₃⁻ and, NO₂⁻ photolysis

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were reported as 60 %, 4 % and 16 % respectively (France et al., 2012). This means that nitrate and nitrite ions are less important sources of OH in snow grains compared to H₂O₂ photolysis (Anastasio and Robles, 2007; Chu and Anastasio, 2005; Yang et al., 2002; France et al., 2012) and the generation rate of OH in snow grains is greater (by as much as a factor of about 10) than the production rate of NO_x. The optical properties of the snowpack are critical in calculating the production rate of hydroxyl radicals in the snowpack and sea-ice: France et al. (2007) and France et al. (2010) illustrate how the snowpack morphology, solar zenith angle, snowpack depth and overhead ozone column can all effect the production rate of hydroxyl radicals in the snowpack.

Such a rapid production of OH implies rapid oxidation of snow-grain organics, which probably leads to the observed release of volatile organics (Anastasio and Robles, 2007; Sumner et al., 2002). Just as organics can be oxidized, so too can photochemically produced OH oxidize dissolved halides. A recent report has shown that gas phase halogens, such as Br₂ and IBr, can be released when OH radicals are generated by photolysis of frozen halide-nitrate ion solutions (Abbatt et al., 2010), as shown in Fig. 7. Nitrogen dioxide and HONO were also formed in the chemistry where the nitrate ions were the source of the hydroxyl radicals, which subsequently oxidised the halide ions present. Yields of halogens were higher in acidic solutions, supporting higher rates of OH generation. While this chemistry is likely occurring in a brine solution, there is also the potential for interfacial chemistry given the experiments described earlier, where exposure to gas phase OH was shown to lead to the halogen release from a variety of frozen sodium halide substrates.

Although many natural and anthropogenic organic compounds are present in high latitude/altitude and related ice, their photochemistry has been thought to have little direct effect on halogen activation, aside from photochemical decomposition of some short lived organohalides in the snowpack (see Sect. 3 and Supplement) and by organics acting as an OH sink. However, it is of note that simulations of the photochemical behaviours of persistent organic pollutants, such as polychlorinated biphenyls (PCBs), in artificial snow recently enabled simultaneous monitoring of their photochemical

changes and volatilization fluxes from the solid matrix. The PCBs studied underwent reductive dehalogenation reactions upon irradiation at $\lambda > 290$ nm which competed with a desorption process responsible for the pollutant loss from snow (Matykiewiczová et al., 2007).

In addition, the influence of chromophoric dissolved organic matter (CDOM) which is available in polar sea ice may have an important but indirect effect on the photochemical processes discussed above. Specifically, these materials may absorb light at wavelengths similar to those absorbed by nitrate ions and hydrogen peroxide. In this context it has been shown that photo-bleaching of CDOM in sea-ice brine occurs with differential efficiencies at different Antarctic sites. The implication is that at the locations where the photobleaching is efficient, increased UV penetration would result and more effective photolysis of the species which produce the halide oxidants would follow (Ortega-Retuerta et al., 2010). Very recent work demonstrates that the UV penetration depth is not only affected by the concentration of CDOM in snowpack but also the concentrations of humic and black carbon within the snowpack (France et al., 2012). It is interesting that snow impacted by sea spray, and thus containing high halide concentrations, has a reduced light penetration depth and a reduced hydroxyl radical production rate relative to similar snowpacks unaffected by sea spray (France et al., 2011).

The direct influence of photoactive species on halogen activation may also be important. For example, recent spectroscopic studies performed on air-salt water interfaces suggest that the photooxidation of halides by chlorophyll leads to the formation of halogen atoms and other halogenated species (Reeser et al., 2009). It is possible that such photoactive organic species may similarly mediate halogen activation on frozen media.

At the theoretical level, halogen-ice photochemistry has received recent interest. Woittequand et al. (2009), computed the absorption spectra for HF and HCl at the ice surface considering a physisorbed state. Ončák et al. (2008) then modeled the absorption spectra using on the fly quantum dynamics HF, HCl and HBr on $(\text{H}_2\text{O})_N$ clusters for $N = 0-5$. Three structures were considered clusters with intact HX, contact ion structures and solvent separated ion pairs. Upon either partial or full acidic dissociation of

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HX (see Sect. 4.1) a charge transfer-to-solvent band emerges. This CTTS band shifts the onset of the absorption spectrum by 40–60 nm to larger wavelengths for both HCl and HBr, making the molecule more susceptible to photodissociation.

4.3.1 Freeze-induced processes

5 Slow freezing of seawater leads to salt exclusion into salty brines, as described in Sects. 2 and 4.1, opening up the potential for subsequent “freeze-induced” processing to take place (Pruppacher and Klett, 1997; Kurková et al., 2011). The resultant multi-component systems are only completely solid below the eutectic point, and even then supercooling can result. Between their freezing and eutectic points both liquid and
10 solid co-exist in equilibrium and under such a condition, liquid can reside in the QLL or in small structural holes between the grains of solid ice variously known as “micropockets”, “microveins” or “triple junctions” (Pincock and Kiovsky, 1966; Betterton and Anderson, 2001). These locations have been observed in both laboratory and field ice samples using techniques such as NMR spectroscopy (Cho et al., 2002). They can also
15 act as sites for “freeze concentration” and acidity changes, which can lead to unusual chemical pathways (Takenaka et al., 1996).

Inorganic ions are not necessarily incorporated into ice with the proportions originally present in their parent aqueous solutions. Substantial electrical potential differences between the solid ice and unfrozen liquid can be generated. For example, for the cases
20 of sodium chloride and sodium hydroxide, the chloride ions are incorporated more into the ice lattice as HCl, whereas Na^+ and OH^- remain in the liquid phase (Workman and Reynolds, 1950). Behaviour of this type leads to measurable pH differences at surfaces and can be important in exerting control on the chemistry (Cheng et al., 2010; Robinson et al., 2006; Anastasio et al., 2012). Reactions may take place subsequently during the
25 freezing process and the differential incorporation of ions into the ices, which generate transiently charged interfaces, can provide interesting kinetic effects. However, it has been shown that the concentration of the rejected solutes remaining in the liquid phase during freezing is the prime factor accounting for faster kinetics in most cases. The

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impact of “freeze-concentration” on polar chemistry has not been evaluated. A key study has outlined a modified acceleration model for reactions in ice especially relevant to higher order processes (Takenaka and Bandow, 2007).

The effect of freezing on a variety of acidified and neutral, nitrite ion and halide-containing mixtures has been investigated (O’Driscoll et al., 2006, 2008). Several trihalide ions were formed, including I_2Cl^- , I_2Br^- , ICl_2^- , and IBr_2^- , in mechanisms suggested by spectroscopic data to involve INO (iodine nitrogen oxide) and the nitroacidium ion, $[H_2ONO]^+$. Hence the freeze-concentration effect was utilized to operate in liquid “micropockets” containing various halides within water-ice structures. The nitroacidium ion acted as an efficient proton transfer chaperone to the chloride- and bromide-containing interhalide ions to eventually give $[Br-I-Br]^-$ and $[Cl-I-Cl]^-$ ion precursors to the interhalogens, IBr and ICl.

This chemistry was subsequently modified to mimic naturally occurring conditions more closely and also to incorporate the use of hydrogen peroxide as an oxidant. In contrast to the earlier work, the freeze-induced production of IBr_2^- was thereby observed to occur up to $pH < 5.1$, i.e. comparable to the polar snowpack (O’Sullivan and Sodeau, 2010; O’Sullivan, 2011). Other products monitored, namely nitric oxide and molecular iodine, play significant roles in atmospheric compositional change (O’Driscoll et al., 2008). The various types of bromine release mechanisms discussed above have recently been invoked in a cloud seeding study in coastal Antarctica with reference to the bromine and nitrate ion variabilities found there (Antony et al., 2010).

5 Field evidence for halogen activation in the polar boundary layer

Halogen activation from ice surfaces has been the focus of many field studies and this section focuses on the latest developments in the measurements of such species in polar latitudes.

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5.1 In-situ measurements of bromine and chlorine

The idea that halogens are activated on the sea ice, perhaps with involvement from frost flowers or other highly saline surfaces, gained traction from a number of observations including Foster et al. (2001), Tackett et al. (2007), and other observations summarized in Simpson et al. (2007b). However, recent measurements and satellite observations by Jones et al. (2009), and modeling studies (Yang et al., 2008), have raised the possibility that halogen activation can also be initiated following blowing snow events, and subsequent aerosol chemistry. In particular, Jones et al. (2009) conducted measurements at Halley Bay on the Weddell Sea in Antarctica, showed a satellite-observation of a BrO “cloud”, along with a surface-based ODE, which followed a blowing snow event at that site. Surface snow and snow pit analyses showed that bromide was significantly enriched at the surface after the wind event, and that bromide at the surface decayed significantly after the event, implying that it was then oxidized.

In a follow-up study, Jones et al. (2010) used 1987 Halley ozonesonde data to show that ozone loss between 1 and 3 km altitude was always associated with significant atmospheric depressions, windy conditions, and lofted or blowing snow. Published ozonesonde data from other Antarctic stations, some of which were accompanied by ground-based or satellite BrO observations, further supported a link between blowing snow, halogen activation and ozone loss. Begoin et al. (2010) linked satellite observations of column BrO with a cyclonic weather system to infer that Arctic BrO events can indeed be triggered by blowing snow events. During the OASIS2009 campaign at Barrow, AK, Frieß et al. (2011) conducted simultaneous measurements of BrO and aerosol extinction vertical profiles. These measurements showed that elevated BrO often coincided with enhanced aerosol optical depth, and that there were sometimes enhanced layers of BrO and aerosol extinction. However, enhanced BrO and aerosol extinction were also sometimes close to the surface. Two example days are shown in Fig. 8, which shows AOD and BrO vertical profile data retrieved from the MAXDOAS, for 11 and 14 April 2009 at Barrow. Those observations imply that indeed activation

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of bromine on aerosol surfaces can be an important mechanism, e.g. as shown for 14 April. However, even for 11 April 2009, when the enhanced BrO is surface-based, that enhanced BrO was well-correlated with AOD. These observations point out the need for 1-D profiles of the halogen atom precursors (Br_2 , BrCl , and Cl_2) along with aerosol size, number and composition data. The relationships between blowing snow and halogen activation have not been directly observed, during or after blowing snow events. In the future, the autonomous “O-Buoys” (Knepp et al., 2010; Bauguitte et al., 2011) will provide useful data to confirm if these events occur.

During the OASIS2009 campaign, Liao et al. (2011b) conducted measurements of bromine species, including Br_2 , HOBr, and BrO, via chemical ionization mass spectrometry (CIMS). The HOBr and Br_2 data are consistent with the Fan and Jacob (1992) mechanism, in that HOBr was observed with a diurnal profile consistent with daytime photochemical production, and night-time uptake on surfaces with simultaneous production of Br_2 . Buys et al. (2012) report high resolution observations of Br_2 , BrCl and BrO made in coastal Antarctica using CIMS during Austral spring in 2007. Focusing on night-time data only (which, for Br_2 and BrCl , are free from potential the HOBr interference as shown by Neuman et al., 2010), the authors report mixing ratios of Br_2 , BrCl and BrO up to to 45 pptv, 6 pptv, and 13 pptv, respectively.

It has also become important to understand the impact of temperature on halogen activation and chemistry, given that the Arctic climate is rapidly changing, and this is having a large impact on the extent and nature of sea ice (Serreze and Barry, 2011). Recently, Pöhler et al. (2010) conducted measurements of BrO from the Amundsen Gulf in the eastern Beaufort Sea. They found that maximum BrO concentrations increased linearly as the temperature decreased from 258 K, perhaps due to precipitation of $\text{NaCl}\cdot 2\text{H}_2\text{O}$ and concurrent concentration of Br^- in the quasi brine layer, as described earlier. Pöhler et al. (2010) interpret the greater flux of active bromine at low temperature to a greater temperature gradient in the near-surface layer. This observation is consistent with the Arctic observations of Tarasick and Bottenheim (2002), that severe ODEs only occur with surface temperatures below 253 K. However, care should

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be exercised in interpreting such observations for ozone itself, since the temperature observed during ODEs may not correspond to the temperature that applied during the chemical depletion, which may occur upwind (Tarasick and Bottenheim, 2002; Avallone et al., 2003).

Progress on Arctic chlorine chemistry has been slower than for bromine. Jobson et al. (1994) first showed that chlorine atom chemistry was important, as supported by observations of other species (Muthuramu et al., 1994). Read et al. (2007) recently observed evidence for chlorine atom chemistry at Halley Bay, with calculated Cl atom concentrations during ODEs as large as 3×10^4 molecules cm^{-3} , and thus not significantly different from those calculated during ODEs in the Arctic. However, as discussed by Keil and Shepson (2006), the previous observations of Br/Cl indicate that there must be a source of chlorine atoms other than BrCl.

Chlorine chemistry and bromine chemistry in the gas phase are intimately linked, as Reaction (R11) is important to bromine recycling. In addition, the reaction of chlorine atoms with VOCs is an important source of HO_2 , which participates in bromine recycling via Reactions (R12) and (R3).



The importance of chlorine chemistry was demonstrated by Pöhler et al. (2010), who observed OClO in the early morning hours at concentrations as high as 25 pptv in the Amundsen Gulf.

5.2 Interpretations of BrO satellite measurements

Since the work of Wagner and Platt (1998), Richter et al. (1998), and Chance (1998), ground based-DOAS has been significantly extended with the series of satellite-borne UV-Vis nadir instruments (GOME/ERS-2 (Richter et al., 1998), SCIAMACHY/ENVISAT (Bovensmann et al., 1999), GOME-2/MetOp-A (Munro et al., 2006), and OMI/Aura

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(Levelt et al., 2006)) from which the now familiar global maps of the BrO vertical column density (BrO^{VCD}) are derived. A particular characteristic of the BrO maps in polar regions are the BrO “hotspots”: vast areas over the sea ice zone with enhanced BrO^{VCD} which are evident during the spring months. The frequently observed BrO hotspots have recently been defined as regions where BrO^{VCD} is elevated by at least $2 \times 10^{13} \text{ molec cm}^{-2}$ relative to the zonal mean (Salawitch et al., 2010). From the earliest observations they have been assumed to be associated with boundary layer bromine release.

While satellite observations provide unsurpassed information on BrO spatial distribution, the derived vertical column measurement of BrO cannot in itself verify assumptions about bromine sources because of the lack of vertical profile information; indeed, there has been much uncertainty about the extent to which elevated column BrO may have contributions from the boundary layer, free troposphere, or stratosphere, perhaps related to low tropopause heights. The satellite data can, however, be used to derive a tropospheric VCD by subtracting a stratospheric component from the total VCD as discussed below.

Early approaches were based on the assumption that there was little longitudinal variability in stratospheric BrO (Richter et al., 1998; Wagner and Platt, 1998; Wagner et al., 2001). This key assumption, that all variability in the BrO^{VCD} would arise in the troposphere, was recognized at the time as being a potential source of error to the analysis (Richter et al., 1998). Recent approaches have used numerical models to derive stratospheric BrO^{VCD} (e.g. Theys et al., 2009; Salawitch et al., 2010; Theys et al., 2011). Theys et al. (2009) used the BASCOE 3-D chemistry transport model to derive stratospheric profiles of total inorganic bromine (Br_y). They argued that the key steps for deriving the BrO profile involved proxies for both stratospheric dynamics and photochemistry. For example, given the equivalent lifetimes of Br_y and stratospheric ozone, they used the correlation between Br_y and O_3^{VCD} to parameterize stratospheric dynamical processes in the stratosphere. Modelled BrO profiles were successfully validated

by comparison with ground-based, balloon-borne and satellite limb observations of stratospheric BrO.

In Salawitch et al. (2010) stratospheric Br_y was derived from assimilated CFC-12 profiles (Wamsley et al., 1998). Stratospheric BrO was then obtained from the BrO/Br_y ratio output from the Whole Atmosphere Community Climate Model. The authors used aircraft profiles of BrO measured during the ARCTAS (Jacob et al., 2010) and ARC-PAC (Brock et al., 2011) campaigns to derive the tropospheric BrO^{VCD}, and using this suite of data, explored observed BrO “hotspots”. In contrast to the traditional view described above, Salawitch et al. (2010) showed that, on occasion, the spatial pattern of hotspots mirrored that of stratospheric markers: tropopause height, satellite-measured O₃^{VCD}, and modeled stratospheric BrO^{VCD}. On other occasions, enhancements of BrO in the troposphere, often above the convective boundary layer, were large enough to affect the BrO^{VCD}. It thus appeared that BrO hotspots observed in the satellite-derived BrO^{VCD} could arise from enhancements in either the troposphere or stratosphere.

Theys et al. (2011) analyzed GOME-2 data to arrive at results that generally supported Salawitch et al. (2010). For the strong polar BrO hotspots, the authors found that the hotspots could not be explained by stratospheric influence alone. Supported by simulations with the p-TOMCAT model Yang et al. (2010) and Theys et al. (2011) further concluded that these hotspots were consistent with the release of bromine from sea salt aerosol generated during blowing snow events, which themselves are linked to low pressure systems and hence a lower tropopause height; see Fig. 9. This conclusion is consistent with the studies of Jones et al. (2009, 2010) and Begoin et al. (2010). Further support for the rapid evolution of some BrO from blowing snow was provided by Choi et al. (2012) using aircraft observations coupled with satellite data.

5.3 IO measurements in polar regions

The detection of reactive iodine species in the polar regions has only been made during the last decade. In the Antarctic, iodine monoxide (IO) has been detected using

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ground-based techniques such as zenith sky spectroscopy (Frieß et al., 2001), active long-path DOAS (Saiz-Lopez et al., 2007b) and multi-axis DOAS (Frieß et al., 2010), and from space (Saiz-Lopez et al., 2007a; Schönhardt et al., 2008). Surprisingly, IO mixing ratios up to 20 pptv have been observed in the coastal Antarctic boundary layer during springtime (Saiz-Lopez et al., 2007b). The IO seasonal cycle is remarkably similar to that of bromine oxide (BrO) showing a distinct maximum in spring and a secondary peak during autumn. The satellite measurements of IO have been a major development in polar halogen research, providing confirmation of active iodine chemistry over coastal and continental Antarctic. These high levels of iodine may have widespread impact on catalytic ozone destruction in the Antarctic lower troposphere, yet the sources of such a large iodine burden remain an open question (Saiz-Lopez and Boxe, 2008; Frieß et al., 2010; Saiz-Lopez et al., 2011). In particular, it has been suggested that large mixing ratios of IO up to 50 ppbv can be confined within the snow-pack and would then interact with the overlying atmosphere (Frieß et al., 2010). Alternatively, recent observations (H. Roscoe, personal communication, 2012) of I₂ around the Weddell Sea suggest that molecular iodine is an important precursor, as suggested in Saiz-Lopez and Boxe (2008).

It has been suspected for some time that iodine chemistry must be occurring in the Arctic springtime, as witnessed from the excess iodide observed in the fine aerosol at Alert (Barrie et al., 1994). However, in the Arctic regions, IO has only been measured at very localized scales at much lower levels than in the Antarctic, in contrast to BrO. For example, Hönninger (2002) observed one instance of IO using MAXDOAS at Alert, Nunavut. However, in the Amundsen Gulf, Pöhler et al. (2010) observed no IO above their detection limit of 0.3 pptv. In contrast, at Hudson Bay in the Canadian sub-Arctic, IO mixing ratios up to 3.4 pptv have been recently observed using long-path DOAS (Mahajan et al., 2010). This level of IO is enough to significantly enhance the rate of ozone depletion by bromine radicals through coupling between IO and BrO. However, the presence of detectable IO was sporadic and seemingly coinciding with iodocarbon emissions from open water polyynyas that form in the sea. It is clear that

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methods affording lower limits of detection for IO are needed, and that more routine measurements in the Arctic are needed to understand the apparent differences in iodine chemistry between the north and south polar regions.

6 Model predictions and implications for the polar boundary layer

In this section we discuss halogen activation studies over environmental ices using 0-D, 1-D, and 3-D models in both the ozone depleting (ODE) and non-ozone depleting regimes. Given the complicated nature of the multiphase activation of halogens from environmental ices, it is essential to develop models that describe in sufficient detail the nature of this chemical system and its coupling to atmospheric transport processes. In remote regions, bromine activation has been the major focus of recent work. The non-linear nature of the chemistry makes modeling an essential tool to gain insight into processes occurring. The complicated meteorological situation, including rapidly changing boundary layer heights, must be modeled to correctly describe measurements.

6.1 Models used to understand bromine measurements and ozone over environmental ices

The dominant source of reactive bromine over environmental ices has been treated as frozen seawater. Bromide in seawater is much less abundant than chloride but, as described above in Sect. 4, is more easily oxidized. In addition, bromide is in contact with the atmosphere in many forms, as described in Sect. 2 (see Fig. 1). Recent model studies have focused on process level understanding and devising scenarios to explain bromine activation and ozone loss under different conditions. Mechanisms that have been included in models include:

1. A mechanism that relates gaseous bromine to frost flowers (e.g. Rankin et al., 2002; Kaleschke et al., 2004). For example, sea-salt aerosol particles produced from frost flower fields (Piot and von Glasow, 2008).

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2. Release of gas phase bromine from sea-ice or from snow-covered sea-ice via a combination of multiphase reactions (Simpson et al., 2007a; Toyota et al., 2011a).
3. Bromine release from blowing snow, e.g. via uplifting of salt-containing snow to the atmosphere, followed by sublimation to form aerosol (Yang et al., 2008), or via reactions occurring on saline blowing snow (Jones et al., 2009)
4. Reactions in/on the snow pack (e.g. Thomas et al., 2011).

While it is not clear which mechanisms cause ODEs, most predict increased bromine release with increased wind speed, which increases surface-air exchange. Some also predict higher concentrations of halogens with increased boundary layer stability. The difficulty with all modeling associated with halogen release from environmental ices is the complexity of the chemical and physical processes involved. Sections 2 and 4 have illustrated that physical properties such as liquid layer thickness, surface acidity, and surface concentrations still have large uncertainties. Difficulties also include a lack of knowledge as to where trace species exist in environmental ices, as knowledge of their location is lost upon melting the sample to measure the concentration. Therefore, even initial concentrations of reactants can be difficult to define, as discussed in Thomas et al. (2011). The chemical complexity illustrated by lab studies also makes the results difficult to include in models. Ultimately, parameterizations and simplified chemistry is needed, with sufficient detail to both explain observations and capture the important physical chemistry.

We begin with a discussion of recent box modeling work on halogen release during bromine explosion events, followed by recent one-dimensional models. Finally we present results from three-dimensional chemical transport models in the context of both ground based and satellite measurements.

6.2 Box models

Studies using box models proved instrumental in deciphering the “bromine explosion” mechanism in the 1990s (e.g. Fan and Jacob, 1992; McConnell et al., 1992; Vogt et al., 1996) and have been used since to investigate details of the halogen release and recycling mechanisms (Sander et al., 1997; Michalowski et al., 2000; Evans et al., 2003).

Recent box model studies have focused on the initiation step for the bromine explosion, with one issue being the pH of the bromide-containing substrates. In particular, seawater is strongly buffered, however if the bromine explosion proceeds via aqueous (as opposed to frozen) surfaces, then an acidified solution is required (Fickert et al., 1999). As described in Sect. 4, the alkalinity of aqueous brines is affected by the form of calcium carbonate that precipitates (Sander et al., 2006; Morin et al., 2008). Sander and Morin (2010) have introduced the bromide/alkalinity ratio, which is a more relevant metric to study the preconditions of bromine explosions than simply alkalinity. Due to changes in the amount of available water through cryo- and evapoconcentration the bromide molality increases strongly during cooling of a salt solution, and therefore the precipitation of ikaite together with the concentration effects can facilitate the occurrence of a bromine explosion. A physical separation of the precipitated material and the solution is required for this mechanism to work as otherwise the precipitate would get dissolved upon acidification of the solution.

On the other hand, as pointed out in Sect. 4, there is experimental evidence from ice and frozen solution experiments that the variation of pH is less important than for bromide activation from aqueous solutions. For example, Adams et al. (2002) showed that the pH of NaCl/NaBr solutions before freezing did not have a significant influence on halogen release arising from HOBr uptake.

Box models are also often used to understand measurements of OH, NO_x, and/or halogens made over snow and ice (e.g. Sjostedt et al., 2007; Chen et al., 2007; Bloss et al., 2010; Liao et al., 2011a). These types of 0-D models do not directly include

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the influence of environmental ices, but instead constrain many species to measured values in order to determine the influence of chemistry occurring over snow/ice on the oxidation capacity of the boundary layer (e.g. the ratio OH/HO_x). While these studies have their drawbacks, they are useful for determining if the observed halogens have an influence on oxidation, for example if the measured ratio of OH/HO_x is affected. Given they are constrained by measurements of longer-lived species, they may not determine, for example, the influence of halogens on ozone.

Recently Bloss et al. (2010) looked at the interaction between NO_x and halogen chemistry using parameterized halogen and NO_x sources in a 0-D model to understand chemistry in the Antarctic boundary layer. Their model showed that conversion of NO to NO_2 was dominated by reaction with halogen oxides, highlighting the need to further study halogen- NO_x interactions over environmental ices.

Recent box modeling also investigated the sensitivity of ODE development to other reactants, as well as the implications for the oxidation capacity of the atmosphere (Piot and von Glasow, 2009). This study found that elevated mixing ratios of HCHO , H_2O_2 , DMS , Cl_2 , and HONO reduced Br and BrO levels but increased HOBr and HBr , while additional volatile organics had the opposite effect. Increased HOBr and HBr concentrations speed up the release of bromine from aerosol, but also increased the deposition of bromine. Elevated levels of NO_y led to increased bromine deposition and less ozone depletion.

Connected to bromine explosions and ODEs are concurrent atmospheric mercury depletion events (AMDEs), in which gaseous elementary mercury (GEM) is transformed into reactive gaseous mercury (RGM) and particulate mercury (Schroeder et al., 1998). The recent review on AMDEs by Steffen et al. (2008) highlighted the difficulties in modeling the interaction between halogens and mercury as many reaction pathways and rates are still uncertain. Xie et al. (2008) used a multiphase box model to conclude that Br atoms were the most important Hg oxidants, using known chemistry. Using a different box model, Hedgecock et al. (2008) also included a simple parameterization of re-emission of reduced mercury from the snow. They concluded that the

net deposition of mercury was irrelevant, however a limitation is that their model did not include advection.

6.3 One-dimensional models

An attempt to reproduce a bromine explosion event using a 1-D model from first principles using salt aerosol from frost flowers was presented by Piot and von Glasow (2008). Even though this mechanism now appears not to be the most likely (see Sect. 2), this study demonstrated the role of bromide containing aerosol in bromine activation. It also showed without recycling of deposited bromine compounds on snow an ODE does not occur and O_3 loss is limited. These results might also help in investigating the role of blowing snow for bromine release. Earlier work using 1-D models was key in showing that sea-salt aerosol alone cannot produce the levels of reactive bromine present during ozone depletion events (Lehrer et al., 2004) and suggested that halogen release from the sea-ice surface may be a significant source of halogens.

Thomas et al. (2011) were the first to develop a chemically sophisticated coupled 1-D snow-atmosphere model (MISTRA-SNOW), which they applied to conditions of the Greenland plateau during a three-day period during summer 2008. This study focused on the remote Arctic, far away from oceanic bromine sources and ODEs. This study treated the surface of snow grains as a reactive, initially acidic aqueous layer that contained bromide, chloride, and nitrate. By modeling multiphase chemistry in all model levels, they could explicitly simulate activation of bromine and NO_x in interstitial air and subsequent transport to the atmosphere. They showed that halogen activation could be occurring even in pristine environments with relatively low bromide impurities in the surface snow. Modeled interstitial air transport processes included both wind pumping and molecular diffusion. High wind speeds increase snow pack ventilation and are important for reproducing the observed atmospheric bromine mixing ratios. They reproduced observed diurnal cycles and mixing ratios of BrO and NO, which had a minimum at mid-day due to variation of the boundary layer height, while the interstitial air BrO mixing ratio peaks at mid-day (Fig. 10). They also discussed connections

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between bromine and nitrate chemistry over snow-covered regions, which occur both in the condensed and gas phases, and pointed out the importance of recycling of bromine on aerosol. The results showed a model can describe the chemistry and physics of a coupled snow-atmosphere system.

5 An emerging topic in this field is the mechanism for iodine activation. A 1-D chemical transport model was developed to explain measurements of very high IO and BrO at Halley, Antarctica (Saiz-Lopez et al., 2008). This model suggested that rapid cycling of higher iodine oxides might be responsible for this long apparent lifetime of IO. Iodine chemistry increased O₃ depletion by about 3 times compared to bromine chemistry alone. It was found that the addition of iodine chemistry significantly enhances the shifts in the OH/HO₂ and NO/NO₂ ratios caused by halogen chemistry. Very large iodine precursor fluxes were required to reproduce measured IO levels.

6.4 Three-dimensional models

15 The ultimate goal is to connect 0-D and 1-D process studies to 3-D chemical transport models operating that are used to understand processes at wider spatial and temporal scales. In recent years, scenarios that may explain bromine liberation have been included in 3-D models. In these studies the bromine source is parameterized using likely sources, which has resulted in simulation of polar spring bromine explosions and ODEs. In an earlier 3-D model, boundary layer BrO mixing ratios were estimated based on prescribed satellite-derived BrO columns (Zeng et al., 2003), however our understanding of satellite derived tropospheric BrO columns is still developing (see Sect. 5.2). More recent studies have included bromine release from sea-salt aerosols produced from abraded frost flowers (Zhao et al., 2008), deposited ozone on ice/snow as a trigger for bromine oxidation followed by recycling due to HOBr, BrONO₂, and HBr deposition (Toyota et al., 2011a), and bromine release from sea-salt aerosols produced during blowing snow events (Yang et al., 2008, 2010). Although there are significant differences in the details of the bromine release included, all of these models employ parameterizations linking the bromine release with environmental conditions, such as

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wind speed, temperature, humidity, and boundary layer height. Connecting bromine release to these factors results in better agreement with measurements, strongly indicating that enhanced bromine concentrations in the atmosphere that cause ODEs are closely connected to the meteorological conditions. For example, increased snow-atmosphere chemical exchange is associated with high wind speeds. More chemically sophisticated treatments of halogen activation in 3-D modeling are needed in order to validate current mechanisms and to capture the details of the release processes in 3-D models.

One issue under consideration is that blowing snow events are frequently observed in both the Arctic and Antarctic. The extreme meteorological conditions during blizzards include high surface wind speeds that can lift a number of snow particles (that contain impurities of bromide and chloride) into the air. In particular, when wind speeds reach a threshold speed of $\sim 8 \text{ m s}^{-1}$, snow particles can be dislodged from the snowpack. Above $\sim 12 \text{ m s}^{-1}$ these particles can be lofted into the atmosphere (Jones et al., 2009) where their large surface area is available for multiphase chemistry. Yang et al. (2008) linked a sublimation process of uplifted snow grains to formation of aerosol with sea-salt components. Using their model they obtain an absolute sea-salt production rate which is 35 times greater than the ocean source under typical Antarctic conditions (Yang et al., 2008). The produced sea-salt aerosols may release gas phase bromine after acidification. With implementation of this bromine source in a 3-D CTM, the major features of the satellite observed tropospheric column BrO are captured by the model as shown in Fig. 9 (Yang et al., 2010; Theys et al., 2011), although many uncertainties are clearly inherent in such modeling.

Toyota et al. (2011a) used the 3-D model GEM-AQ to reproduce tropospheric column BrO in April 2001 using a simple scheme of air-snowpack interactions. They modeled bromine release by connecting Br₂ activation to ozone deposition to snow-covered sea-ice (assuming an infinite source of bromide in the snow-pack), and included recycling mechanisms involving HOBr, BrONO₂, and HBr. The major features of satellite derived

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tropospheric BrO were reproduced using this mechanism for halogen release in the Arctic.

There are other ways that winds may impact snow chemistry. For example, based on observations of enhanced BrO over the Weddell Sea which were correlated with conditions under which there were high wind speeds and saline blowing snow, Jones et al. (2009) showed that maximum contact between gas and uplifted snow grains occurs under high wind conditions and attributed ODE events to saline blowing snow. This explanation for halogen activation may be more likely in storms with high humidity, where the extent to which snow particles can sublime to form aerosols is limited. However this mechanism of halogen release has yet to be included in a 3-D CTM. In addition, high winds increase the rate at which the overlying atmospheric air exchanges with that in the snow-pack and would also increase the importance of halogen liberation via surface processes on snow/ice (McConnell et al., 1992; Tang and McConnell, 1996; Michalowski et al., 2000; Lehrer et al., 2004; Thomas et al., 2011; Toyota et al., 2011a).

7 Halogen activation in the upper troposphere – lower stratosphere

Although this review has focussed primarily on the boundary layer, it is important to emphasize that halogen activation on other ice and snow surface will undoubtedly occur elsewhere, although at levels that are hard to evaluate. For example, in the upper troposphere/lower stratosphere (UT-LS), the combination of high water vapor concentrations and low temperatures promotes formation of cirrus clouds, which cover about one-third of the globe (Wang et al., 1996). Ice crystals are of variable size, on the order of a few to tens of microns, and are consistently being formed and precipitating. Unlike clouds at lower altitudes, cirrus can be very thin with low total water contents, and surface area densities that are not significantly larger than those in background aerosols.

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Halides are present on surfaces of cirrus crystals through gas-particle interactions. Especially important is the uptake of acidic gases, such as HCl and HBr (see Sect. 4), which occurs readily despite the surfaces having less surface disorder than is prevalent at higher temperatures. The mixing ratio of inorganic chlorine and inorganic bromine in the UT-LS are 100 and 5 pptv, respectively. Chlorine is mainly in the form of HCl (Marcy et al., 2007), and is the result of photolysis and oxidation of organic source gases such as methyl chloride, chloroform, and methyl chloroform (Law and Sturges, 2007). To some extent inorganic chlorine and bromine can be transported directly to the UT-LS, but such sources likely represent the minor fraction of total halogens in this region (Law and Sturges, 2007). Given the low mixing ratios of inorganic chlorine, the HCl surface coverage on the surface of cirrus cloud particles is expected to be low.

The importance of heterogeneous reactions that can activate chlorine in the UT-LS is reasonably well understood, in part by analogy to that occurring at higher altitudes in the chemically perturbed polar vortices (Solomon et al., 1997; Hofmann and Solomon, 1989; Borrmann et al., 1996). Detailed three-dimensional modeling (Solomon et al., 1997) showed that chlorine activation on cirrus several km above the tropopause might explain observations of enhanced ClO first observed outside the polar vortex at high latitudes (Toohey et al., 1991), and later at mid-latitudes (Avallone et al., 1993). Such enhancements, if widespread, were able explain up to half of the ozone losses at mid-latitudes. Observations at high latitudes in winter and spring (Thornton et al., 2003, 2005) support the general view that oxidation of HCl by ClONO₂ and, possibly, HOCl drives chlorine activation by forming Cl₂, i.e. via Reactions (R1) and (R2). The relative roles of water ice and background aerosols in chlorine activation in the UT-LS, however, remain poorly understood. In particular, the regions where ice chemistry would stand out most are the mid-latitude and tropical tropopause, where it is both wet and cold. In these regions, the abundance of inorganic chlorine is very small – of order tens of pptv and detection of the active halogen chlorine species (primarily ClO) is challenging. Additionally, sulfate aerosol surface area densities are relatively high, so that there is

some chlorine heterogeneous activation already, and additional surface area provided by ice does not have as dramatic effect as higher up in the ozone hole.

There are rare, but important exceptions where chemistry on ice may dominate over aerosol, such as in regions of deep convection where water vapor (and potentially, chlorine source gases) is injected into the lowermost stratosphere at low latitudes and in regions that are relatively particle-free. However, these conditions tend to be short-lived, making it difficult to coordinate observations of halogen species to test hypotheses. In two recent studies, anomalously high abundances of ClO were observed at the tropopause under conditions where abundances of background aerosols were very low (Thornton et al., 2007; von Hobe et al., 2011). In one case (Thornton et al., 2007), water vapor was subsaturated relative to ice at the time of the observations; there was a very strong correlation between active chlorine abundances and aerosol surface area densities, suggesting that even under such conditions, the presence of ice is not required for chlorine activation. Under these conditions, which were relatively warm (208–215 K), the reaction of HCl and ClONO₂ appears to be fast enough so that virtually all of the HCl is converted into active chlorine in a few hours. A key to such rapid conversion appeared to be high water content of the aerosols, such that the heterogeneous reaction coefficient was larger than would otherwise have been the case at low relative humidities.

Particularly noteworthy were the observations in the tropics (von Hobe et al., 2011), when concurrent measurements clearly demonstrated the presence of large ice particles at very low temperatures. It was concluded that activation was primarily due to Reaction (R1); however, even under these conditions of high ice surface areas, temperatures below 200 K, and high solar illumination, it was not possible to distinguish between chemistry that may have occurred on ice surfaces versus that which could have occurred in background aerosol alone.

Several additional studies are worth noting. Motivated by inference of anomalously high abundances of OCIO in twilight in the Arctic lower polar stratosphere (Pierson et al., 1999), a laboratory study found generation of OCIO following uptake of ClO onto

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ice (McKeachie et al., 2004). Although such a process mainly affects partitioning within the ClO_x family, the inferred role of a $\text{ClO}-\text{H}_2\text{O}$ complex may play a role in chlorine-cirrus chemistry at mid- and lower latitudes that has yet to be explored. In addition, heterogeneous halogen activation involving bromine species in aircraft contrails and aircraft-influenced cirrus (Meilinger et al., 2005) may shift the partitioning of the radicals that influence ozone from a condition of ozone production to one of destruction (Toohey et al., 2010). Unfortunately, there are no direct observations of the important halogen species within aircraft-influenced regions.

8 Conclusions and open issues

8.1 Substrates for halogen activation

First-year sea ice is a potentially important source of reactive halogens due to its highly saline surface. The role of frost flowers may be less significant than initially expected but may indirectly influence halide activation chemistry by contributing salinity to adjacent snow. Salty snow which is lofted into the atmosphere is now being considered as an additional source of reactive bromine, although we stress that activation will probably also occur in the interstitial air within snow. The relative importance of these sources of reactive bromine may vary on regional and temporal scales. In particular, it is interesting to consider differences between the hemispheres, such as there being more acidity arising from pollution sources in the North. Differences in precipitation and temperature regimes are also important to consider, with wet, warm conditions leading to enhanced precipitation rates that will dilute snow salinity.

Finally, our detailed understanding of the molecular-level nature of sea ice and snow surface is still evolving. Without an accurate knowledge of the effective surface halide concentrations and surface pHs, the role of co-existing species such as organics, and the size of brine layers as a function of temperature, our understanding of halide

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activation will remain limited. Laboratory studies should study increasingly complex environmentally-relevant ices.

8.2 Active halogen sources

While the polar boundary layer has largely focused on the inorganic sources of active halogens, this review highlights that a number of halocarbons are associated with ice covered regions. While some of the species formed are sufficiently long-lived that they may not contribute to these active halogen loadings, the organo-iodine species and some of the organo-bromides may be important. Determining the balance between biotic and abiotic production of iodine in snow-covered regions is clearly a priority. To illustrate open issues, Saiz-Lopez and Boxe (2008) have proposed a mechanism for iodine release from sea-ice surfaces in a multiphase chemical model. This study suggested that biological production of inorganic iodine from marine algae contained within and underneath sea-ice, and subsequent diffusion through sea-ice brine channels leads to accumulation in the brine layer on the surface of sea-ice. The levels of inorganic iodine released through this mechanism could account for the observed IO concentrations in the Antarctic springtime environment, albeit large uncertainties are inherent including the possibility that HOI will react with organics present and the rates of diffusion through the ice.

On the abiotic side, during the long polar night, O_3 is the most likely candidate for initiating bromine activation. The kinetics involve a complicated surficial process only now being quantitatively understood (see Sect. 4.2). Use of bulk-phase chemistry within an assumed aqueous brine volume will likely lead to inaccurate predictions. The uptake coefficients of other species, notably OH and HOBr, are better defined, being close to unity. And so, the rates at which such species may activate halides will likely be strongly mass transfer limited, unless generated in situ within the snowpack. Of these two, HOBr will be the more important once reasonable levels of bromine activation have occurred, given the low abundance of OH. However, for the initial activation of

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bromine, OH chemistry is potentially important. The importance of N_2O_5 as a halide oxidant should not be discounted.

A major challenge in connecting laboratory results to atmospheric models is the need to know surface halide composition. It has been clearly demonstrated (for example, with HOBr; see Sect. 4.2) that the products of these heterogeneous reactions are very much dependent on the surface halide composition, which will change during the course of prolonged exposure to atmospheric oxidants. Of particular interest also is the pH of sea ice, brine and snow surfaces. While there is a strong dependence of activation on pH for aqueous substrates (Fickert et al., 1999), this dependence largely disappears on ices formed by freezing salt solutions (Adams et al., 2002). Reactions with ozone and photochemical activation can also occur via neutral substrates (Oum et al., 1998; Oldridge and Abbatt, 2011; Wren et al., 2010; Sjostedt and Abbatt, 2008). In light of these results, low surface pH can accelerate but may not be a necessary criterion for halide activation.

8.3 Role of meteorology in boundary layer ozone loss

Although it is commonly thought that a stable boundary layer is a necessary prerequisite for a bromine explosion event, vigorous meteorological conditions that give rise, for example, to blowing snow may prompt ODEs as well. Do the two different meteorological regimes correspond to different bromine sources? It is possible that air masses containing active bromine could have experienced a storm and lost their wind speed before arriving at the measurement site (Yang et al., 2010). If so, local snowpack photochemistry will be less important and might not be necessary to support a bromine explosion. On the other hand, the snowpack chemistry could be enhanced by the wind pumping process due to perturbations of winds and/or pressure. Under strong wind speeds, there could be more radical bromine-precursors being pumped into the interstitial region to accelerate bromine liberation (Toyota et al., 2011a). It is hard to judge whether pumping air into the snowpacks is more efficient than lifting particles into the air in terms of bromine activation efficiency. The actinic fluxes and

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hence photochemistry will be reduced in blowing snow likely requiring more than one release scenario. The question then arises whether the processes that control bromine explosions are driven more by dynamics or chemistry, or whether both are important. Future studies are needed using 1-D models to investigate situations with different wind speeds, varying snowpack ventilation, boundary layer height, and the resulting impact on predicted chemistry because surface concentrations are strongly modulated by boundary layer height (as shown in Thomas et al., 2011). Both 1-D and 3-D model studies should address how stability influences halogen chemistry and the extent of ozone loss due to the non-linear nature of this chemistry, which is further complicated by the complex boundary layer dynamics in the polar regions (as discussed in Anderson and Neff, 2008). Further measurement of the sea salt aerosol produced and the chemical composition of the lifted particles during blowing snow events may help us to answer this question. The chemical complexity within 3-D models must increase, to tease out the dynamical-chemical relationships.

8.4 Effects of climate change

In the Arctic, the aerial extent of perennial sea-ice has been rapidly declining (Comiso, 2002), accompanied by an increase in younger, thinner sea ice (Maslanik et al., 2007). As described above, younger sea ice has a higher bulk salinity and is more likely to be covered in a highly saline brine. Furthermore, snow layer thickness is also a function of sea ice age with thicker snowpacks on multi-year ice often accompanied by a lower salinity. Polynyas and leads, which are important for frost flower formation, are particularly prone to change in a warming climate, being areas of thinner ice and reduced ice cover (Morales Maqueda et al., 2004).

The importance of environmental ice-atmosphere chemical interactions in a changing climate was highlighted by Voulgarakis et al. (2009). Assuming complete loss of Arctic sea-ice during summer, the composition of the Arctic troposphere was simulated with and without bromine release from sea-ice. The loss of sea-ice resulted in a large ozone increase, especially during spring, attributed mainly to bromine chemistry. While

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the connections between the presence of sea-ice and halogen chemistry are not yet fully understood, this study shows that a decrease in ice and snow may significantly alter atmospheric composition. Any increase or decrease in halogen chemistry due to changes in sea ice cover will have resulting impacts on atmospheric oxidation and may impact the lifetime of pollution transported to the polar regions. Additional measurements (Jacobi et al., 2010) indicate that low ozone levels are the normal state of the Arctic spring, suggesting large-scale removal of O₃ by halogens. This points out the need to establish connections between tropospheric ozone and halogen chemistry due to the role of tropospheric O₃ in the warming of the Arctic (Quinn et al., 2008) and global climate (IPCC, 2007).

Supplementary material related to this article is available online at:
<http://www.atmos-chem-phys-discuss.net/12/8677/2012/acpd-12-8677-2012-supplement.pdf>.

Acknowledgements. This paper was prepared as a follow-up to an IGAC-sponsored workshop on Air-Ice Chemical Interactions (AICI) held at Columbia University, 2011. The authors thank IGAC for its support and the workshop co-organizers, Thorsten Bartels-Rausch and Faye McNeill. JLT would like acknowledge the support of the OPALE project funded by the ANR (Agence National de Recherche) contract ANR-616 09-BLAN-0226.

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Table 1. Naturally produced short-lived halocarbons and their estimated atmospheric lifetime (Law and Sturges, 2007).

Compound	Atmospheric lifetime (days)
CHBr ₃	26
CH ₂ Br ₂	120
CHBrCl ₂	68
CHBr ₂ Cl	79
CH ₂ BrCl	150
CH ₃ I	7
CH ₃ CH ₂ I	4
1-iodopropane	0.5
2-iodopropane	1.2
CH ₂ ClI	0.1
CH ₂ BrI	0.04
CH ₂ I ₂	0.003

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Table 2. Mixing ratios and surface water concentrations of organo-Br and organo-I. Data taken from: Carpenter et al. (2007), Yokouchi et al. (1996), Butler et al. (2007), Penkett et al. (1985), Reifenhäuser and Heumann (1992a), Reifenhäuser and Heumann (1992b), Yokouchi et al. (1994), Bottenheim et al. (1990), Yokouchi et al. (2008), Yokouchi et al. (2001), Rasmussen et al. (1982), Hughes et al. (2009), Krysell (1991), Fogelqvist (1985), Fogelqvist and Tanhua (1995), Moore and Tokarczyk (1993), Moore et al. (1993), Sturges et al. (1997), Schall and Heumann (1993), Schall et al. (1997), Abrahamsson et al. (2004), Chuck et al. (2005).

	Arctic atmosphere >60° N, pptv	Arctic water, pmol l ⁻¹	Antarctic atmosphere >60° S, pptv	Antarctic water, pmol l ⁻¹
Br	2.9–27	24–110	8.1–30	3–230
I	2.9–4.0	0.1–2.2	0.11–2.4	3–19

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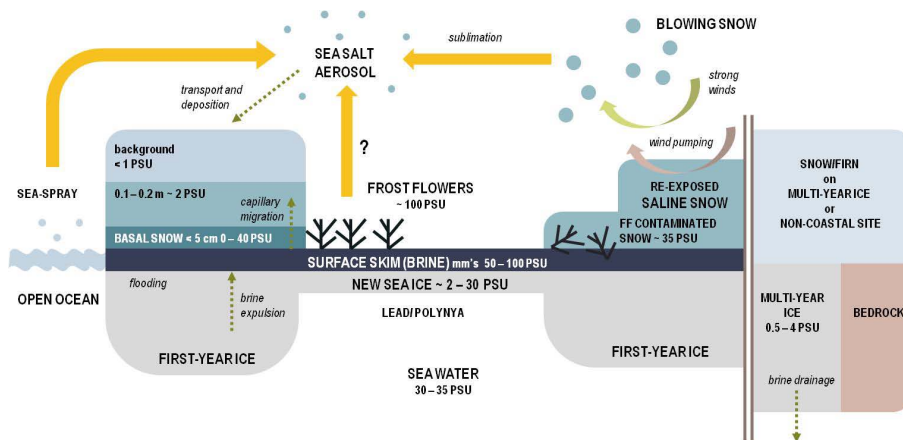


Fig. 1. Sources of halides in the polar boundary layer. A range of salinity values is indicated: frost flowers (Rankin et al., 2002), brine, new ice (Ehn et al., 2007), multi-year ice (Timco and Weeks, 2010), basal snow (Toyota et al., 2011b), snow < 0.2 m (Toyota et al., 2011b), background snow (Massom et al., 2001), frost flower (FF) contaminated snow (Obbard et al., 2009).

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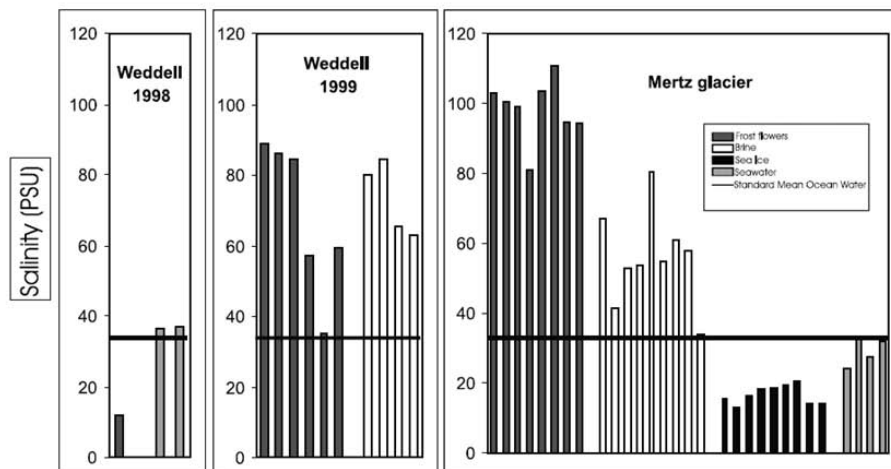


Fig. 2. Salinities of frost flowers (darker grey), slush (white), ice (black) and seawater (lighter grey). Taken from Rankin et al. (2002) with permission of the American Geophysical Union.

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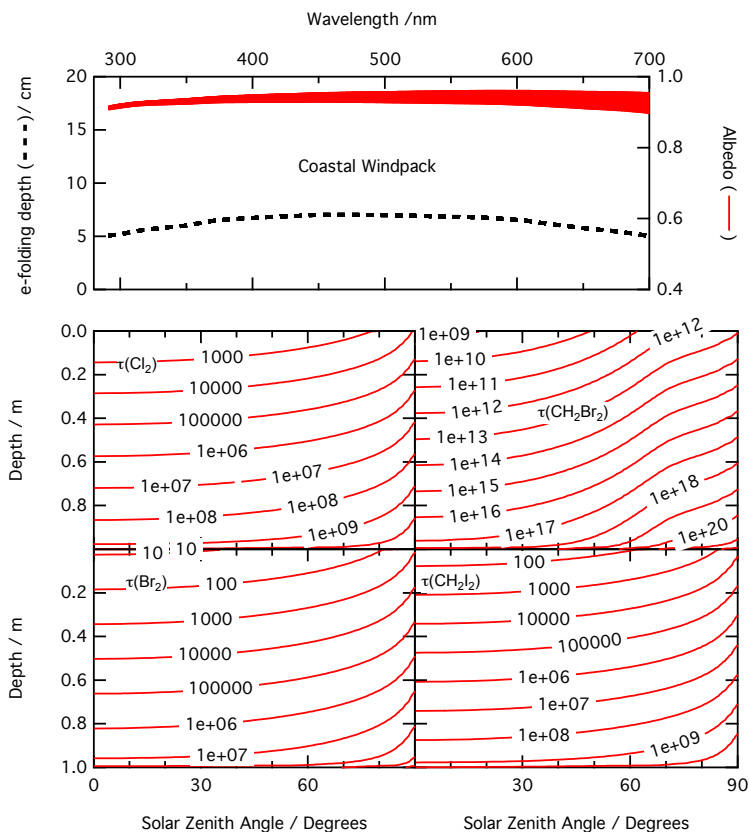


Fig. 3. Upper frame: albedo and e-folding depth for light penetration in a coastal snowpack. Lower frame: photolysis lifetime isopleths versus snowpack depth and solar zenith angle for the photolysis of select species in a coastal snowpack. See Supplement for details.

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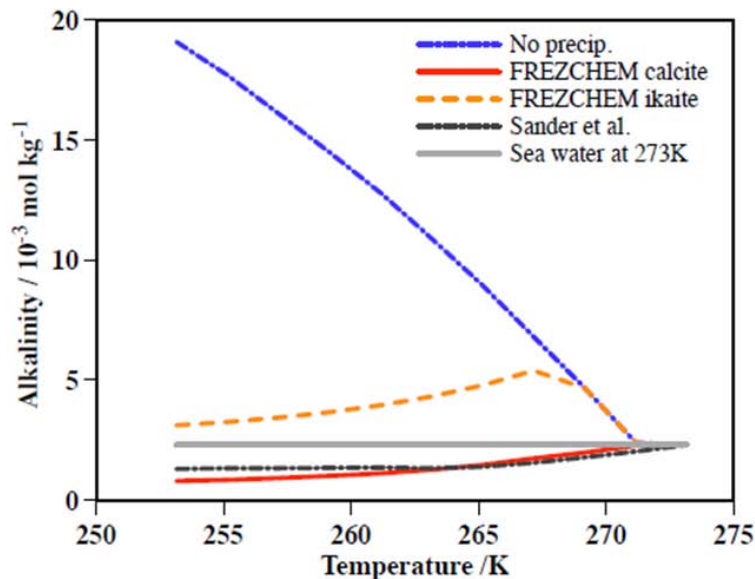


Fig. 4. Total alkalinity (AT) of the brine during the freezing of seawater as calculated by the FREZCHEM model with (a) carbonate precipitation artificially “switched off” (b) precipitation of calcite only and (c) precipitation of ikaite only. Taken from Sander and Morin (2010) with permission of the authors.

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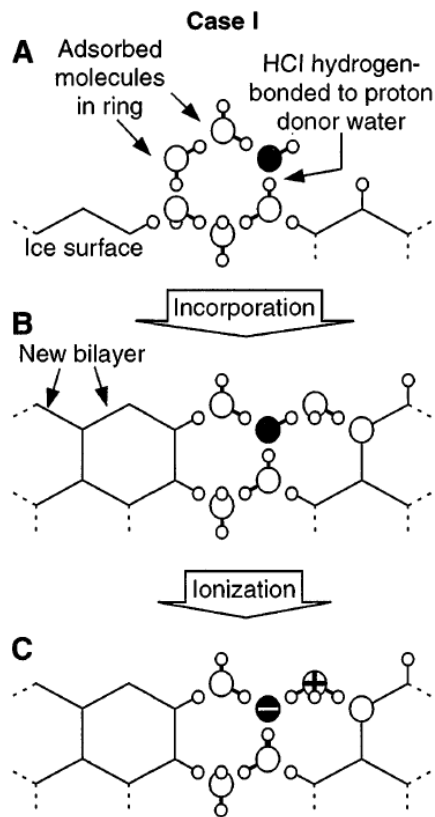


Fig. 5. Molecular dynamics model results for the adsorption of HCl molecule to an ice surface via ionization to form a chloride ion and a H_3O^+ ion, as indicated in **(C)**. Taken from Gertner, B. J. and Hynes, J. T., *Science*, 271, 1563–1566, 1996. Reprinted with permission from AAAS.

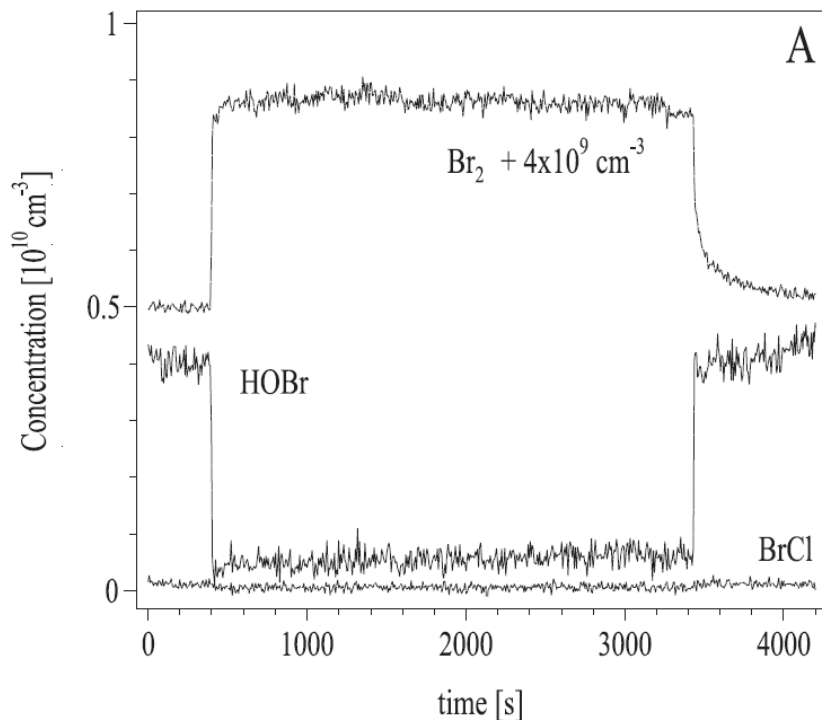


Fig. 6. Formation of Br_2 (and loss of HOBr) when gas phase HOBr is exposed to a frozen NaCl/NaBr solution at 233 K at roughly 400 s in a coated-wall flow tube. Note that no gas phase BrCl is formed. Taken from Adams et al. (2002) with permission of the authors.

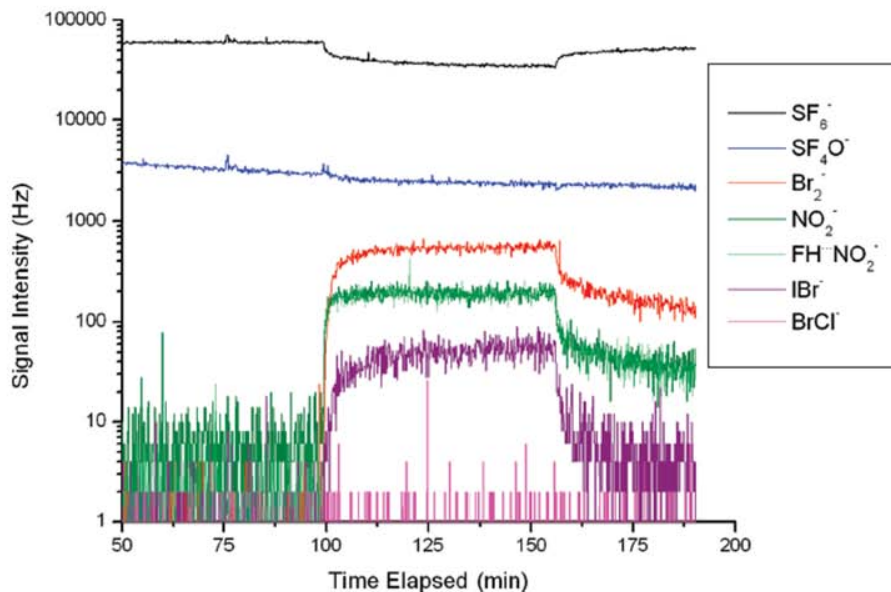


Fig. 7. Formation of gas phase halogens, primarily Br_2 (red line) upon exposure of frozen $\text{NaCl}/\text{NaBr}/\text{NaNO}_3$ mixtures to ultraviolet light at roughly 100 min. Reprinted with permission from Abbatt et al., *J. Phys. Chem. A*, 114, 6527–6533, 2010. Copyright 2010 American Chemical Society.

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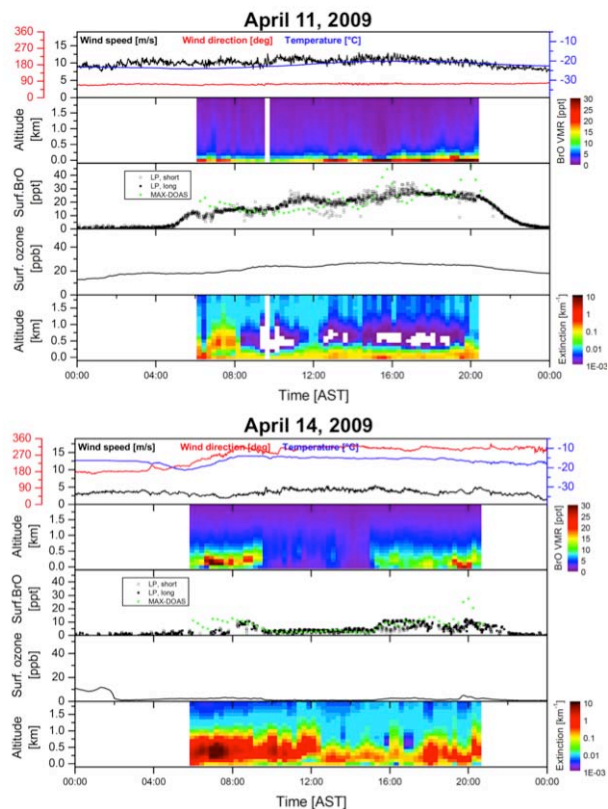


Fig. 8. Vertical profiles for BrO and aerosol optical depth (AOD) at Barrow, AK during OA-SIS2009 show that in some cases, such as for 11 April, the enhanced BrO is surface-based, while in some cases, the enhancement is aloft (14 April). However, as shown here, in both cases, BrO seems well-correlated with AOD. Figure courtesy of Udo Frieß.

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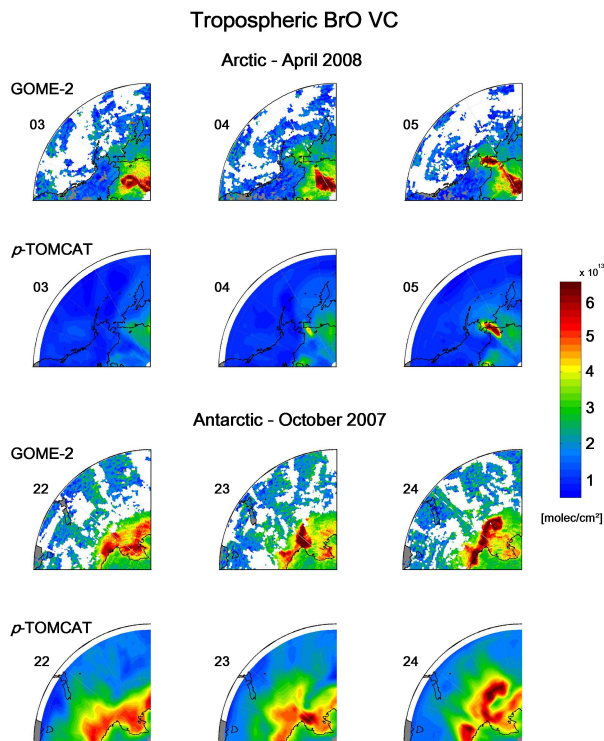


Fig. 9. Tropospheric BrO vertical columns from GOME-2 (satellite) and p-TOMCAT (model) including bromine emissions from sea salt aerosol production through blowing snow events across the Chukchi Sea region of Arctic from 3 to 5 April 2008 (upper panels) and over the Ross Sea of Antarctica from 22 to 24 October 2007 (lower panels). Taken from Theys et al. (2011) with permission of the authors.

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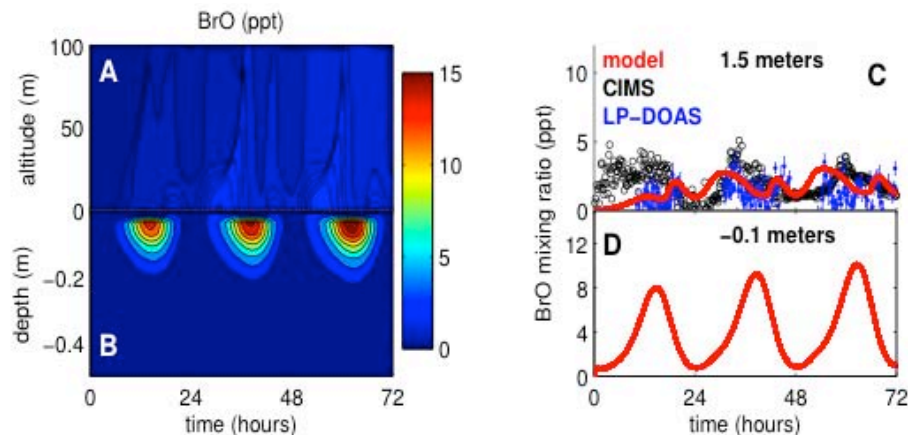


Fig. 10. Model predicted BrO using a 1-D coupled snow-atmosphere model, MISTRA-SNOW, during summer 2008 compared to measured BrO mixing ratios above the snow (C). The model predicts enhanced BrO mixing ratios in the interstitial air (B, D) due to snow chemistry. Taken from Thomas et al. (2011) with permission of the authors.

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