1   **Snow heterogeneous reactivity of bromide with ozone lost during snow metamorphism.**

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10   **Abstract.** Earth's snow cover is very dynamic on diurnal time scales. The changes to the snow structure during this
11   metamorphism have wide ranging impacts such as on avalanche formation and on the capacity of surface snow to exchange
12   trace gases with the atmosphere. Here, we investigate the influence of dry metamorphism, which involves fluxes of water
13   vapor, on the chemical reactivity of bromide in the snow. For this, the heterogeneous reactive loss of ozone ~~in the dark~~ at a
14   concentration of 5-6 × 10^{12} ~~molecules~~molecule cm^{-3} is investigated in artificial, shock-frozen snow samples doped with 6.2
15   μM sodium bromide and with varying metamorphism history. The oxidation of bromide in snow is one reaction initiating polar
16   bromine releases and ozone depletions. We find that the heterogeneous reactivity of bromide is completely absent from the
17   air-ice interface in snow after 12 days of temperature gradient metamorphism and suggest that burial of non-volatile bromide
18   salts occurs when the snow matrix is restructuring during metamorphism. Impacts on polar atmospheric chemistry are
19   discussed.

20   **1 Introduction**

21   Snow on Earth hosts chemical reactions that impact the composition of the atmosphere (Dominé and Shepson, 2002; Grannas
22   et al., 2013). One example is the oxidation of bromide and the subsequent release of bromine from arctic snow (Abbatt et al.,
23   2010; Saiz-Lopez and von Glasow, 2012). This reactive halogen species participates in ozone destroying chemical cycles in
24   the gas phase. Ozone is one of the main oxidants in the lower atmosphere with impact on atmospheric composition, health,
25   and climate (Simpson et al., 2007). Recent improvement in global atmospheric chemistry models indicate that halogen
26   chemistry ~~is responsible~~accounts for about 14% of the global tropospheric ~~O_3 reduction~~ozone sinks (Schmidt et al., 2016). In
27   addition, the reactive halogen species are potent oxidants for organics and, of particular interest, gas phase mercury (Simpson
28   et al., 2007; Simpson et al., 2015). Oxidized mercury partitions readily into condensed phases from where it may enter the
29   ocean and the food-web upon seasonal snow melt (Steffen et al., 2008).

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Dominé et al. (2008) argued that the efficient chemical reactivity in snow is linked to its physical properties. Snow is a porous matrix that is dense enough to provide a large surface area for heterogeneous reactions, but not too dense to limit transport and light penetration as seen in soil, for example. The heterogeneous oxidation of bromide by ozone, a potential pathway for bromine release both in the dark and in sunlight (Abbatt et al., 2010), has been shown to be very efficient on ice and brine surfaces (Wren et al., 2010; Oldridge and Abbatt, 2011; Edebeli et al., 2019). The high rates on aqueous solutions have been linked to an ozonide intermediate and its stabilisation at the surface (Artiglia et al., 2017). ~~Consequently~~Taken that the bromide needs to be accessible to gas-phase ozone for an efficient heterogenous oxidation, the location of these chemical ~~reactants~~ ~~their~~reactant - its distribution between the air-ice interface and other reservoirs in the interior of the snow - is a key determinant for their chemical reactivity (Bartels-Rausch et al., 2014; Hullar and Anastasio, 2016; McFall et al., 2018). Field studies have revealed a high heterogeneity in bromine release and bromide concentration in snow and have attributed this heterogeneity to the initial source of bromide and to post-depositional changes of the location (Jacobi et al., 2012; Pratt et al., 2013).

One prominent post-depositional mechanism is dry metamorphism shaping the structure and physical properties of snow with impact on heat transfer, albedo, and avalanche formation (Blackford, 2007; Dominé et al., 2008; Schweizer, 2014). Snow at Earth's surface that is exposed to varying temperature gradients with time undergoes continued sublimation and deposition during metamorphism with complete re-building of the entire snow matrix every few days (Pinzer et al., 2012). Earth's snow cover can be exposed to temperature gradients between 10 ~~K~~°C m^{-1} to 100 ~~K~~°C m^{-1} (Birkeland et al., 1998). Dominé et al. (2015) showed that such temperature gradient conditions can prevail on a seasonal scale: in low-arctic tundra, snow is exposed to a temperature gradient mostly above 20 ~~K~~°C m^{-1} between mid-November and early February. The consequences are changes in the isotopic composition of the snow with implications for ice core dating (Steen-Larsen et al., 2013; Steen-Larsen et al., 2014; Ebner et al., 2017). Further, Hagenmuller et al. (2019) observed dust particles being incorporated into the ice matrix of snow driven by the intensive water vapor fluxes during dry, temperature gradient metamorphism.

With the turnover of snow grains and the movement of water vapor, contaminants may be redistributed between the surface and bulk of the snow grains: Studies investigating the adsorption and uptake of trace gases such as nitric acid and hydrochloric acid with growing ice have observed higher uptake than in ice at equilibrium (Kärcher and Basko, 2004; Ullerstam and Abbatt, 2005; Kippenberger et al., 2019). Kippenberger et al. (2019) has shown that the burial of volatile acids is a strong function of acidity, growth rate, and temperature. At equilibrium, adsorption of acidic trace gases leads to the acids or their anions entering the ice phase at considerable concentration only within the interfacial region of a few nm depth, as recently observed for hydrochloric acid and volatile organic acids (Krepelova et al., 2013; Bartels-Rausch et al., 2017; Kong et al., 2017; Waldner et al., 2018).

Therefore, recrystallization in snow might have a significant impact on the fraction of contaminants or reactants located at the air-ice interface of snow and thus on the heterogeneous chemistry of ions in snow. Laboratory studies investigating temperature

65 gradient metamorphism effects in natural and artificial snow have observed a strong influence of metamorphism on the elution

66 behaviour of ions such as ammonium, fluoride, chloride, calcium and sulphate. Whereas calcium and sulphate were found to

67 be enriched at the air-ice or ice-ice interface during snow metamorphism, ammonium, fluoride, and chloride were buried in

68 the bulk of the snow (Hewitt et al., 1989, 1991; Cragin et al., 1996; Trachsel et al., 2019).

69

70 Here, we study the effect of sublimation and growth of ice during snow metamorphism on bromide reactivity in well controlled

71 laboratory experiments. The sodium bromide used in this study is non-volatile and field studies have related its mobility in the

72 snowpack to its vivid photochemical transformation into volatile bromine. Bromine is released to the air and may re-deposit

73 on the snow surface after formation of stickier ~~species, such as HOBr~~bromine compounds (Toom-Sauntry and Barrie, 2002).

74 The objective of this study is to investigate the heterogeneous reactivity of bromide oxidation by gas-phase ozone in the dark.

75 To assess the surface concentration of bromide and its change during temperature gradient metamorphism~~.~~ the gas-phase ozone

76 loss is monitored in this study. Bromide concentration in the doped snow samples (6.2 µM) is ~~on the lower end of observations~~

77 ~~in environmental~~typical for snow ~~, but slightly higher than that observed in snow in the~~ on Arctic sea ice (Pratt et al., 2013).

Experimental

79 Snow samples were prepared by shock-freezing aqueous solutions (Bartels-Rausch et al., 2004; Trachsel et al., 2019) and

80 stored in a metamorphism box with a well-defined temperature gradient at the WSL Institute for Snow and Avalanche Research

81 SLF in Davos (Trachsel et al., 2019). After the exposure to the temperature gradient, the structurally intact individual samples

82 were exposed to ozone in a packed-bed flow tube set-up to derive the impact on the reactivity with gas-phase ozone (Bartels-

83 Rausch et al., 2004). The structure of snow samples before and after metamorphism was imaged by X-ray microtomography

84 (Trachsel et al., 2019).

Sample preparation

86 Artificial snow was produced by spraying and shock freezing droplets of a sample solution in liquid nitrogen using a homebuilt

87 sprayer (Bartels-Rausch et al., 2004; Trachsel et al., 2019)~~. The sample solution was either ultrapure water (18 MΩ quality,~~

88 ~~arium pro, Sartorius, Göttingen, Germany) (undoped snow) or 640 ppb sodium bromide (NaBr, Sigma Aldrich, >99.0%) in~~

89 ~~ultrapure water (doped snow).~~. The samples were left overnight at –45°C and then, stored isothermally at –5 °C for 7 days to

90 anneal and to minimize internal grain-boundaries (Blackford, 2007; Riche et al., 2012)~~.~~. The samples were returned to ~~–~~- 45 °C

91 after this isothermal treatment to slow down further changes with time and stored up to 54 days at - 45 °C prior to the

92 metamorphism experiments to reach a quasi-steady-state. The snow was sieved using pre-cleaned stainless-steel sieves

93 (Retsch, Germany) in a –20°C cold laboratory at the WSL Swiss Snow and Avalanche research Institute (SLF, Davos,

94 Switzerland). Snow grains in the size range 300 – 600 µm were packed into the 12.0 ± 0.1 cm long glass reactor tubes with 2.4

95 ± 0.1 cm internal diameter. ~~All samples were stored isothermally at -5 °C for 7 days to minimize grain boundaries and up to~~

96 ~~54 days at - 45 °C prior to the metamorphism experiments for logistic reasons (see Results and Discussion).~~

97

98 The sample solution was either ultrapure water (18 MΩ quality, arium pro, Sartorius, Göttingen, Germany) (undoped snow)

99 or an aqueous sodium bromide (NaBr, Sigma Aldrich, >99.0%) solution in ultrapure water (doped snow). The bromide

00 concentration in the sieved snow crystals was 6.2±0.18 μM (498 ± 14 ppbw) (in the doped snow) and <0.12 μM ((<10 ppb) in

01 the undoped snow) as determined by ion chromatography (Metrohm (Herisau, Switzerland) 850 Professional IC, 872 Extension

02 Module, 858 Professional Sample Processor autosampler). A Metrosep A Supp 10 column (Metrohm) was used and the eluents

03 were a 1.5 mM Na_2CO_3 and 0.3 mM $NaHCO_3$ in a 1:1 mixture followed by 8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ in a 1:1

04 mixture with a flow rate of 0.9 ~~ml~~cm^3 min^{-1}. Possible instrumental drifts were monitored by measuring a standard after every

05 20th sample.

Metamorphism

07 For the temperature gradient metamorphism experiments, samples were exposed to a gradient of 31 ~~K~~°C m^{-1} for 12 days in a

08 snow metamorphism box mounted in a cold room at –8 °C (at SLF, Davos, Switzerland). The metamorphism box was a heavily

09 insulated box with a heating plate set to –4 °C at the bottom. Over this plate, there was a ~ 2-3 cm thick layer of ice from

10 ultrapure water. The sample holders were mounted on a disk with a 0.5 cm layer of ice made with ultrapure water in contact

11 with the snow grains to increase thermal contact (Pinzer and Schneebeli, 2009). The spaces between the sample tubes were

12 filled by sieving in snow. The box was then covered with a thin plastic film in contact with the filled-in snow and caps of the

13 samples to avoid losses due to sublimation. This set-up resulted in an effective temperature at the bottom and at the top of the

14 snow samples of -4.4 ± 0.1 °C and -8.1 ± 0.1 °C~~.~~, respectively.

15

16 After the temperature gradient metamorphism treatment, the samples were stored at –45°C. For comparison, additional samples

17 were stored isothermally at -20 °C at SLF, Davos, Switzerland for 12 days. In total, 12 samples were prepared from the

18 homogenized snow batches: 2 undoped and 2 doped samples that experienced 12-days temperature gradient metamorphism, 2

19 undoped and 2 doped samples without temperature gradient metamorphism, 2 undoped and 2 doped samples that experienced

20 iso-thermal metamorphism. ~~The~~Two replica samples – those of the doped snow that was exposed to temperature

21 metamorphism for 12 days and the replica of the undoped snow that was not exposed to temperature gradient metamorphism

22 - could not be analysed due to technical failures during the experiments.

23

24 Structural changes in the samples were assessed using an X-ray computer micro-tomography scanner (Scanco micro-CT 40)

25 with a resolution of 10 μm. This microCT was operated at –20°C. Details of operations of the microCT scans have been

26 described by Pinzer and Schneebeli (2009). The reconstructed microCT images were filtered with a Gaussian filter (support 2

27 voxels, standard deviation 1 voxel) and the threshold for segmentation was applied according to Hagenmuller et al. (2014).

28 Structural parameters of the segmented ice structure were extracted with the software tools of the microCT device (Image

29 Processing Language, Scanco Medical) to calculate the porosity and specific surface area.

Packed bed flow tube experiments

31 Samples were exposed to ozone at –15°C. Before exposure, about 2 cm of the samples were scraped off from the top and

32 bottom of the samples to avoid potential contamination from contact with the ice layer on the disk in the metamorphism box

33 or the caps for the sample holder/reactor tubes. An exception to this is one of the 0-day doped samples where 3 cm were shaved

34 off. Afterwards, the mass of each snow sample during the ozone exposure was determined based on the weight of the filled

35 and empty sample tube. The sample tubes were placed in the reactor cell, an insulated cooling jacket, at –15°C. The sample

36 was allowed to temperature equilibrate for an hour before exposure to gases. Humidified airflow of ~200 ~~ml~~cm^3 min^{-1} O_2 and

37 ~200 ~~ml~~cm^3 min^{-1} N_2 was delivered through the sample for 30 minutes to condition the sample. The total flow rate through the

38 sample was set between 339 ~~ml~~cm^3 min^{-1} to 352 ~~ml~~cm^3 min^{-1} at norm temperature and pressure of 273.15 K and 1013.25 bar.

39 This airflow was humidified to a water vapor pressure of ice at –15.0 ± 0.3 °C.

41 Ozone was generated by passing the N_2/O_2 airflow through a pen ray Hg UV lamp. The ozone flow was also humidified before

42 delivery to the sample. The ozone flow was alternated between a bypass and the sample to control for drifts in ozone

43 concentration. Ozone concentration was monitored using a commercial analyser (Teledyne, model 400E). The average ozone

44 concentration for each experiment was slightly different due to the day to day variability in the efficiency of the ozone

45 generator. For all experiments, ozone concentrations varied from 163 to 212 ppb (4.7-6.2 × 10^{12} ~~molecules~~molecule cm^{-3}). The

46 maximum variability during any one experiment was less than 5 ppb after attaining initial stability at the start of the experiment.

47 This drift was accounted for during analysis using fitting routines.

49 To confirm perfect flow conditions in the packed bed flow tubes, the chromatographic retention of acetone was determined

50 for some samples at -30°C. Once the ozone experiment was finished, the samples were exposed to a flow of acetone in

51 humidified N_2 (Bartels-Rausch et al., 2004). The observed retention time of acetone at -30°C matched calculations based on

52 the air-ice partitioning coefficient (Dominé and Rey-Hanot, 2002; Winkler et al., 2002; Peybernes et al., 2004; Bartels-Rausch

53 et al., 2005; Crowley et al., 2010) and the specific surface area of the snow sample as derived by microCT measurements for

54 the undoped and doped samples after temperature gradient metamorphism.
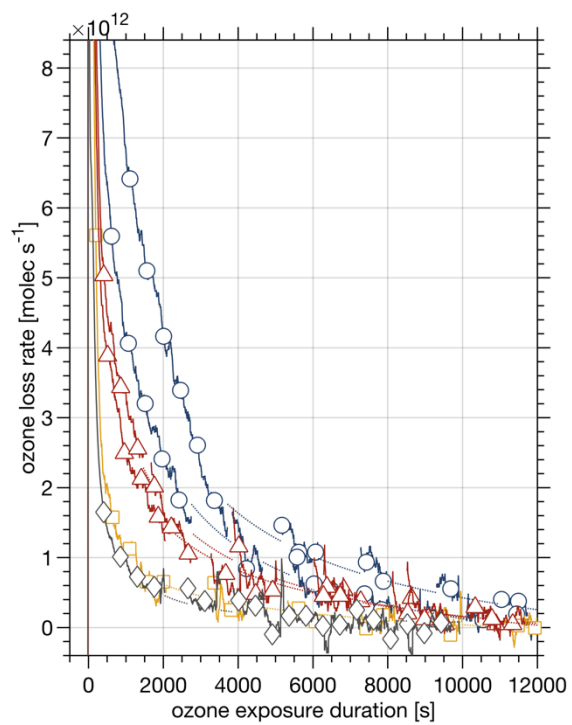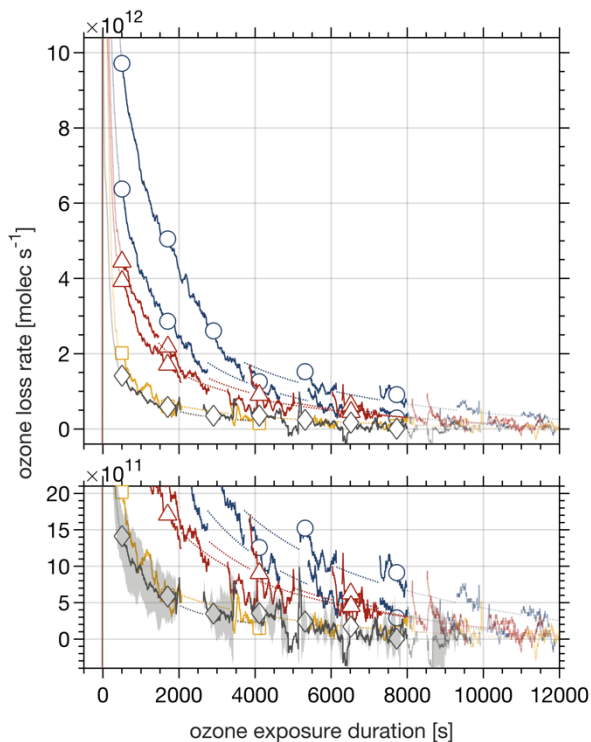
Figure 1**: Ozone loss rate with duration of exposure.** The snow samples with a bromide concentration of 6.2 μM experienced 0 days (blue lines, open circles) and 12 days (yellow line, open squares) of ~~temperature gradient~~ metamorphism with a temperature gradient of 31 ~~K~~°C m^{-1}. The lower panel is a zoom to the data. Ozone data were recorded continuously (lines), the markers are guides. The dotted lines are guide to the eyes, for periods where ozone loss data are not available (see text for details). Also shown are the ozone loss rates of snow samples after 12 days of isothermal metamorphism at -20 °C (red lines, open triangles). The grey line (open diamonds) denotes the average ozone loss rates of 5 ~~undoped~~ samples with no bromide added and with ~~and~~ without exposure to temperature gradient metamorphism. The shaded area in the lower panel shows the standard deviation. The gas phase mixing ratio of ozone varied between 4.7-6.2 × 10^{12} ~~molecules~~molecule cm^{-3} for individual samples. Temperature during ozone exposure was -15 °C. At time 0, ozone in the carrier gas was passed over the snow samples.

Figure 1 shows ozone loss rates for snow samples prior to and after exposure to ~~temperature gradient~~dry metamorphism. The ozone loss rate was derived based on observed changes in gas-phase ozone concentration downstream of the flow tube packed with the snow sample. The ozone loss curves can be classified into three regions:

1. All samples show a high (> 9×10^{12} molecule s^{-1}) loss rate during the initial period of ozone exposure up to 500 s. This observed loss is attributed to the reaction of ozone with traces of impurities, to a delay by switching the gas flows, and to the residence time of the ozone gas in the porous snow and is not further analysed.
~~1.~~2. In the intermediate time regime from about 500 s to 8000 s, the ozone loss rate is largest for the two samples doped with 6.2 μM bromide prior to ageing under laboratory-controlled ~~dry metamorphism with a constant~~ temperature

7

gradient ~~of 31 K m^{-1}~~ metamorphism with 4×10^{12} ~~molecules~~ molecule s^{-1} and 7×10^{12} ~~molecules~~ molecule s^{-1} at 1000 s duration of ozone exposure (Fig. 1, blue lines, open circles). ~~The differences in ozone loss rate of these two samples can be assigned to variations in sample mass and in the amount of bromide at the air-ice interface (see below).~~ The loss rate was reduced by a factor of about 4 ~~-~~ - 7 in the snow sample that experienced temperature gradient metamorphism with 1×10^{12} ~~molecules~~ molecule s^{-1} at 1000 s duration of ozone exposure (Fig 1, yellow line, open square). This loss rate is indistinguishable from that in the samples without added bromide with a mean of 1×10^{12} ~~molecules~~ molecule s^{-1} at 1000 s for 5 samples ~~and with a standard deviation of 0.4×10^{12} molecules~~ molecule ~~s^{-1}~~ ~~at~~ ~~1000 s~~ (Fig. 1, grey line, open diamonds).

~~This observed loss is attributed to the reaction of ozone with traces of impurities. Furthermore, the residence time of the ozone gas in the porous snow structure contributes to the apparent loss rate at the start of the experiments.~~ Also shown is the loss rate from 2 samples that experienced isothermal metamorphism for 12 days at -20 °C (Fig. 1, red lines, open triangles). The loss rate is only slightly reduced compared to the samples before exposure to metamorphism. ~~Taken~~ strongly supporting the ~~large variation in~~ driving role of the ~~ozone loss of samples that were not exposed to metamorphism, we refrain from discussing this difference further. Despite the uncertainty caused by the variation in observed ozone loss, the ozone loss in samples without exposure to~~ temperature gradient ~~metamorphism (Fig. 1, blue and red lines) are significantly higher than the loss rate after temperature gradient metamorphism. Before we elaborate on the mechanism of this loss, we start by discussing details of the apparent loss rates.~~.

3. After about 8000 s ozone exposure, the ozone loss rates of all experiments approach zero loss of ozone. The raw data curves levelled off approaching a steady loss rate of 1.1-1.9$\times 10^{12}$ molecule s^{-1}. This background loss rate may be attributed to the reactive uptake of ozone to ice driven by a self-reaction on the ice surface (Langenberg and Schurath, 1999), which is the main phase in the frozen solution samples investigated here. Langenberg and Schurath (1999) described a reactive ozone uptake coefficient on ice of 7.7-8.6$\times 10^{-9}$ at -15 °C and at ozone gas-phase concentrations similar to our work. The uptake coefficient normalizes the loss rate to the collision rate of ozone with the ice (or snow) surface. A loss rate of 0.86-0.90$\times 10^{12}$ ~~molecules~~ molecule s^{-1} can be derived based on the reported uptake coefficient for the experimental conditions of our doped samples prior to ~~temperature gradient~~ metamorphism, in good agreement with our observations. Because this loss rate is not related to the bromide in the samples, it has been subtracted from the data discussed and shown in Fig. 1.

Ozone loss compared to previous work

The reaction of gas-phase ozone with frozen solutions containing bromide has been studied in great detail previously (Wren et al., 2010; Oldridge and Abbatt, 2011; Abbatt et al., 2012; Wren et al., 2013) ~~(4-7×10^{12} molecules s^{-1}) agrees well with loss~~

10 ~~rates of 2-6 × 10^12 molecules s^-1 as derived based on earlier experimental work.~~ Oldridge and Abbatt (2011) ~~reported an uptake~~

11 ~~coefficient of 1.5 × 10^-8 in~~described coated wall flow tube studies on frozen sodium bromide/sodium chloride/water mixtures

12 at -15°C and Wren et al. (2010) reported ~~4 ± 2 × 10^-8 in a laser-induced fluorescence study with sodium bromide/water~~

13 ~~mixtures at - 20°C. The uptake coefficient normalizes the loss rate to the collision rate of ozone with the surfaces. In this work,~~

14 ~~we refrain to report the results as uptake coefficient, as only the surface area of the snow is known, but not the surface area~~

15 ~~covered with reactive sodium bromide (see below). To compare to our work, the reported uptake coefficients were transferred~~

16 ~~into loss rates based on the specific surface area of the snow sample used in this work and an ozone concentration of 4.7-~~

17 ~~6.2 × 10^12 molecules cm^-3.~~on a laser-induced fluorescence study with sodium bromide/water mixtures at - 20°C. The studies

18 by Wren et al. (2010) and by Oldridge and Abbatt (2011) were done with an initial sodium bromide concentration of 10 mM

19 and a gas-phase ozone concentration of ~~1 × 10^14 molecules~~1×10^{14} molecule cm^-3 and

20 ~~80 × 10^14 molecules~~80×10^{14} molecule cm^-3, respectively. Oldridge and Abbatt (2011) have argued that this multiphase

21 reaction proceeds in the liquid fraction of sample containing bromide-brine that is in equilibrium with ice between 0 °C and

22 the eutectic temperature where the salt precipitates. The eutectic temperature of sodium bromide is at or below -28 °C (Stephen

23 and Stephen, 1963).

24

25 The concentration of sodium bromide in the reactive solutions in equilibrium with ice is a sole function of temperature, and

26 thus ~~identical~~with a concentration of 3.4 M during the ozone exposure at -15° similar even for our samples that were frozen

27 from aqueous solutions with 6.2 µM bromide. For this calculation, the freezing point depression data by Stephen and Stephen

28 (1963); Rumble (2019) was used.

29

30 Despite the differences in the concentration of bromide in the solutions used to freeze the films, the similar concentration of

31 bromide in the brine during ozone exposure makes a comparison of the experimental results feasible. For the comparison, the

32 reported uptake coefficients of 1.5×10^{-8} and $4\text{-}2 \times 10^{-8}$, respectively (Wren et al., 2010; Oldridge and Abbatt, 2011), were

33 transferred into loss rates based on the specific surface area of the snow sample used in this work and an ozone concentration

34 of $4.7\text{-}6.2 \times 10^{12}$ molecule cm^-3. The loss rate prior to temperature gradient metamorphism found in the work presented here

35 agrees with loss rates of $2\text{-}6 \times 10^{12}$ molecule s^-1 as derived based on these earlier experimental works. Uncertainty in this

36 comparison comes from the very low ozone concentration of ~~5 × 10^12 molecules~~5×10^{12} molecule cm^-3 used in ~~this~~the study

37 presented here. Based on the results by Oldridge and Abbatt (2011), one would expect increasing ~~uptake coefficients with~~

38 ~~lower ozone concentrations that can be assigned to a surface reaction. In summary, we conclude that the oxidation of bromide~~

39 ~~by ozone leads to the loss of ozone in the initial period of the experiments. Figure 1 further shows how the ozone loss rates~~

40 ~~strongly decrease with the duration of ozone exposure. After about 8000 s ozone exposure, the raw data curves levelled off~~

41 ~~approaching a loss rate of 1.1-1.9 × 10^12 molecules s^-1. Please note, that this loss rate has been subtracted from the data~~

42 ~~discussed and shown in Fig. 1. This background loss rate is attributed to the ozone self reaction on the ice surface. Support~~

comes from earlier work by~~surface reaction rates with lower ozone concentrations. Further, the surface coverage and the volume of the reactive sodium bromide brine at the interface might vary significantly due to the differences in sample geometries and in sample preparation. Please note that in this work, we refrain from discussing the results as uptake coefficient, as generally only the specific surface area of the snow is known, but not that of the reactive brine~~ ~~Langenberg and Schurath (1999) describing a reactive ozone uptake coefficient on ice of 7.7-8.6 × 10⁻⁹ at -15 °C and at ozone gas-phase concentrations similar to our work. A loss rate of 0.86-0.90 × 10¹² molecules s⁻¹ can be derived based on the reported uptake coefficient for the experimental conditions of our doped samples prior to metamorphism, in perfect agreement with our observations stated above~~.

Location of impurities

The striking loss of heterogeneous reactivity during temperature gradient metamorphism raises the question of the location of the reactive bromide in the shock-frozen, artificial snow samples before metamorphism. Snow can host impurities in several compartments (Bartels-Rausch et al., 2014): Chemical species, besides water, and ions can be molecularly embedded within the ice matrix (solid-solution), molecularly adsorbed at the air-ice interface, in liquid or solid patches at the air-ice interface, in micropockets within the ice matrix including the ice-ice interface (at grain boundaries). Clearly, only bromide in direct contact with the gas phase, that is located at the air-ice interface or within the bulk at a distance that allows sufficient diffusion to the interface, is accessible to gas-phase ozone and thus reactive. In the following, we elaborate on the feasibility of bromide being hosted in these distinct departments in the samples used here.

Shock freezing aqueous solutions may preserve the homogeneous distribution of solutes also in the ice matrix from where the bromide might diffuse to the air-ice interface and heterogeneously react with the ozone. In the following, this reacto-diffusive loss is estimated. Due to lack of knowledge of the diffusion coefficient of bromide in ice, the diffusion coefficient of HNO_3 in crystalline ice at -15 °C of 100×10^{-12} cm^2 s^{-1} (Thibert and Dominé, 1998) was used as upper limit and a diffusion coefficient of HCl at -15 °C of 3×10^{-12} cm^2 s^{-1} as lower bound was used in this calculation. Further, the aqueous concentration of 6.2 µM and the specific surface area of each snow sample as derived by the microCT data (Table 1) was used. Based on these assumptions, one may estimate that the total amount of bromide diffusing from the ice bulk to the surface is 0.2 - 1.6×10^{10} ~~molecules~~molecule each second. This is much less than the ozone loss observed in our experiments, clearly showing that the bromide is not present homogeneously in the ice matrix of the snow samples after shock freezing.

Exclusion of bromide to the ice-air interface during freezing has been observed by others at higher concentration (Wren et al., 2010). We find exclusion of bromide from the rapidly growing ice during shock-freezing even though the aqueous concentration is significantly lower than the typical solubility limits for ions in ice (details below), which might also be related to kinetic effects during fast ice growth. Thibert and Dominé (1997, 1998) derived solubilities of up to 0.1 mM to 1 mM for HCl and up to 0.06 mM to 0.6 mM for HNO_3 in ice at -8 °C to -35 °C, respectively. These data describe the equilibrium

76 between gas-phase acid and solid solution and may serve as estimate for the solubility limit of sodium bromide in ice. Even

77 though it is thus very likely that the ice might hold 6.2 µM of bromide as solid solution (total amount of bromide divided by

78 the total ice volume), the measured ozone loss rates indicate that sufficient amounts of bromide to form brine are excluded to
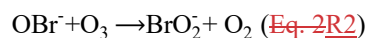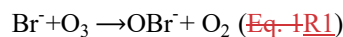
79 the ice-air interface after shock freezing.

80

81 We propose that the brine forms liquid patches on the surface and filaments along the grain boundaries at the interface as

82 observed for higher concentrated frozen salt solutions (Blackford et al., 2007)
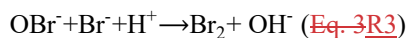
83 ~~The cumulative loss of ozone is 0.9-1.7 × 10^{16} molecules for snow doped with 6.2 µM bromide without exposure to~~

84 ~~metamorphism and 6.3 × 10^{14} molecules for the doped sample after exposure to 12 days temperature gradient metamorphism.~~.

85 A homogenous film covering the total snow surface is unlikely: A back-of-the-envelope calculation with the total amount of

86 bromide doped to the samples and with a concentration of 3.4 M gives a brine layer with a thickness of only ~0.1 nm at -15°C

87 for the specific surface area of the doped snow samples. This is unfeasible, because the thickness of an ice monolayer is roughly

88 0.3 nm. Whether the unreactive fraction of the bromide is located in a solid solution or in micropockets within the ice matrix

89 is beyond the scope of this work, both compartments explain its non-reactivity.

90 **Quantifying the bromide loss**

91 ~~The cumulative loss was derived by integrating the area below the loss rate curves in Fig. 1 between 500 and 8000 s and~~

92 ~~subtracting the cumulative loss of the undoped sample to account for the presence of impurities also in the samples doped with~~

93 ~~bromide. For this analysis, the missing data in periods where the carrier gas was bypassing the snow to monitor the ozone~~

94 ~~concentration delivered to the flow tube were estimated using a power fit to the data (Figure 1).~~ Now that we have established

95 the ozone loss rate and the number of ozone molecules lost in total, we address the amount of bromide that is oxidised by the

96 ~~ozone.~~ Generally, the products and reaction mechanism of the bromide oxidation by ozone in the aqueous phase strongly

97 depend on reaction time, reactant concentration and pH (Haag and Hoigne, 1983; Heeb et al., 2014). For non-acidified

98 conditions, as in our study, hypobromous acid (HOBr/OBr$^-$) is the main product (~~Eq. 1~~R1) that may react further with ozone

99 (~~Eq. 2~~R2) to form bromite (BrO$_2^-$), disproportionate to bromide (Br$^-$) and bromate (BrO$_3^-$), or self-react to dibromine monoxide

00 (Br$_2$O) (Heeb et al., 2014). Despite uncertainties in the precise product distribution in this study, ozone is lost in our study in

01 the initial reaction with bromide and to some extent in the subsequent oxidation of hypobromous acid to bromite resulting in

02 1-2 ozone molecules lost per bromide ~~molecule~~ion. In particular at acidic conditions as relevant for atmospheric waters and

03 ices (Abbatt et al., 2012; Bartels-Rausch et al., 2014)~~,~~; bromine is formed and released to the atmosphere in a sequence of

04 reaction steps (~~Eqs. 1~~R1 and ~~2) that consume 0.5 ozone molecules per bromine molecule . The release of bromine has also~~

05 ~~been observed in experiments with frozen sea-salt mixtures that contain bromide .~~ R3).

06

07 Br$^-$+O$_3$ →OBr$^-$+ O$_2$ (~~Eq. 1~~R1)

08 OBr$^-$+O$_3$ →BrO$_2^-$+ O$_2$ (~~Eq. 2~~R2)

09    $OBr^- + Br^- + H^+ \rightarrow Br_2 + OH^-$ (~~Eq. 3~~R3)

10

11   Thus, assuming a net loss of 1 ozone molecule per bromide molecule, one might estimate about 0.9 ~~and 1.~~7 ~~× 10^{16}~~7×10^{16}

12   molecules of bromide are available for the multiphase reaction with ozone in the two porous snow ~~prior to metamorphism. To~~

13   ~~put this number into perspective, this amount of bromide corresponds to a formal surface concentration of 4-5 × 10^{12} molecules~~

14   ~~cm^{-2} assuming, for comparison reason, that the bromide is located at the surface. Taken that the adsorption of most trace gases~~

15   ~~can be described by a Langmuir isotherm saturating at around 3 × 10^{14} molecules cm^{-2}, the formal Langmuir surface coverage~~

16   ~~would be approximately 1 %. This low coverage supports the argument that the decreasing trend of the ozone loss rates with~~

17   ~~duration of ozone exposure observed for the doped~~ samples prior to metamorphism ~~is caused by depletion of the~~. Assuming

18   a net loss of 2 ozone molecules, 1.8 and 3.3×10^{16} ~~molecules~~molecule of available bromide can be estimated for the two

19   samples. The cumulative loss was derived by integrating the area below the loss rate curves in Fig. 1 between 500 and 8000 s

20   and subtracting the cumulative loss of the undoped sample to account for the presence of impurities also in the samples doped

21   with bromide. For this analysis, the missing data in periods where the carrier gas was bypassing the snow to monitor the ozone

22   concentration delivered to the flow tube were estimated using a power fit to the data (Figure 1). ~~through the oxidation by~~

23   ~~ozone.~~The cumulated amount of reacted bromide can ~~further~~ be compared to the total amount of bromide of 4 ~~6 × 10^{16}~~ and

24   6×10^{16} molecules initially added to the snow sample. Apparently, 22 % - 26 % and 44 % to 52 % in maximum of the bromide

25   was accessible to gas-phase ozone~~, the majority of bromide was not available for reaction~~ prior to metamorphism.

26

27   ~~This result raises the question of the initial location and phase of the sodium bromide in the shock frozen, artificial snow~~

28   ~~samples. Shock freezing aqueous solutions may preserve the homogeneous distribution of solutes also in the grains. With the~~

29   ~~low aqueous concentration of 6.2 μM and a diffusivity of solutes in ice of 100 × 10^{-12} cm^2 s^{-1}, one may estimate that the total~~

30   ~~amount of bromide diffusing from the ice to the surface where it reacts with ozone is 1.6 × 10^{10} molecules each second. This~~

31   ~~is much less than the ozone loss observed in our experiments clearly showing that the bromide is not present in the snow~~

32   ~~samples as homogeneous solid solution. Due to lack of diffusion rates of bromide in ice, the diffusion rates of HNO_3 in~~

33   ~~crystalline ice at -15 °C of 100 × 10^{-12} cm^2 s^{-1} (Thibert and Dominé, 1998) was used as upper limit in this calculation.~~

34   ~~Interestingly, the data by Dominé and co-workers also allow to estimate solubility of sodium bromide in ice as solid solution,~~

35   ~~that is in thermodynamic equilibrium. In their well controlled experiments, derived solubilities of up to 0.1 mM to 1 mM for~~

36   ~~HCl at 265 K to 238 K and up to 0.06 mM to 0.6 mM for HNO_3 in ice. These data describe the equilibrium between gas phase~~

37   ~~acid and solid solution and may serve as estimate for the solubility limit of sodium bromide in ice. Clearly, the apparent~~

38   ~~concentrations of 6.2 μM used in the experiments described here is lower than the estimated solubilities in ice. That we find a~~

39   ~~significant fraction of bromide at the air-ice interface confirms that freezing seldomly results in thermodynamic equilibria. The~~

40   ~~initial distribution of impurities in frozen ice is rather a function of the rate at which the freezing front proceeds . Exclusions~~

41   ~~of bromide to the interface of ice during freezing has been observed by others at higher concentration . Another reservoir,~~

besides the air-ice interface, to which solutes in shock-frozen salt solutions are expelled are micropockets. Micropockets have been observed in natural ice cores, interestingly in the interior of the ice matrix rather than at the ice-ice grain boundaries . Detection in shock-frozen solutions in the laboratory is hampered by the sensitivity limit to detect these features with a diameter of ~2 μm or less in laboratory ice . and have concluded that in shock-frozen caesium chloride (sodium nitrate) solution with a concentration of 1mM (50 μM), the brine might accumulate to some extent in micropockets, based on indirect evidence. Similarly, have shown, that the brine of a 100 mM magnesium nitrate solution is not completely expelled to the air-ice interface and suggest that micropockets are present as well. Thermodynamics dictate that the sodium bromide in the heterogeneous, multi-phase mixtures forms liquid brine with a concentration of 3.4 M (1.6 M) during the ozone exposure at -15°C (metamorphism with a mean temperature of -6°C). For this calculation, the freezing point depression data by was used. The eutectic temperature of sodium bromide is at or below -28 °C (Stephen and Stephen, 1963). With a total amount of 4-6 × 10^{16} bromide molecules in the samples, 2-3 × 10^{-8} l (4-7 × 10^{-8} l) solution are formed at -15 °C (-6°C). Interestingly, this total amount of brine would fit into 500 (230) micropockets 1 μm in diameter at -6 °C (-15 °C). Based on this estimate, we cannot exclude the presence of micropockets during metamorphism and during the ozone exposure in flow tubes in the interior of the ice or at the surface of the ice where they are often called patches. On the contrary, a homogenous film covering the total snow surface is rather unlikely. Such a brine layer would have a thickness of only 0.2 nm at -6°C (0.1 nm at -15°C) with a concentration of 3.4 M.

59
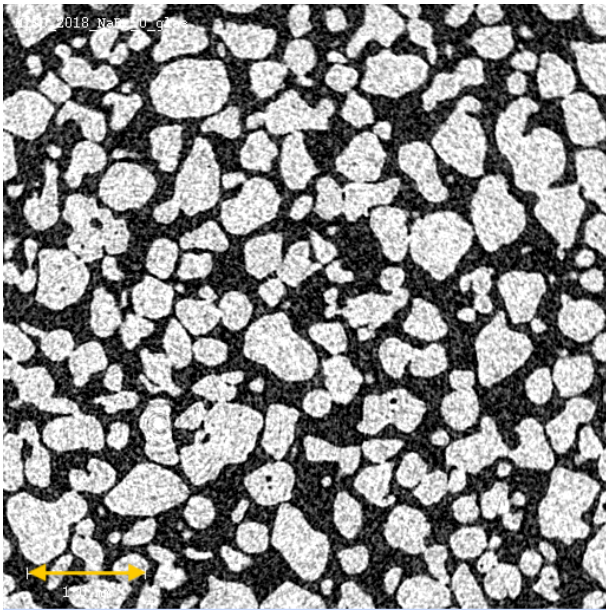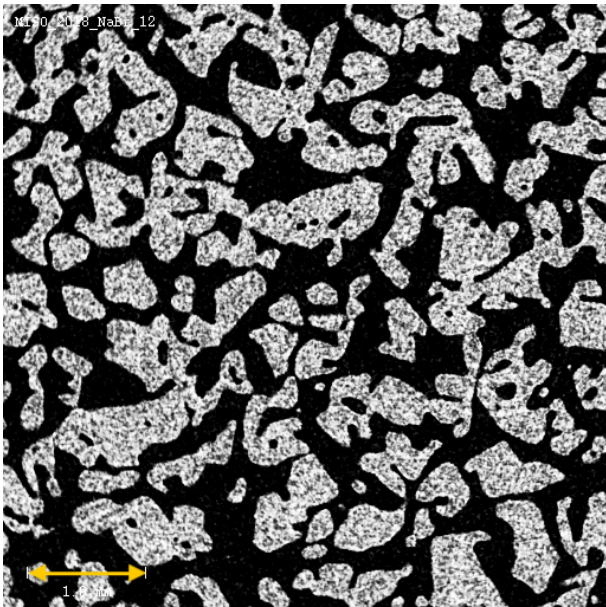
60 **Figure 2: MicroCT images showing cross-sections of the doped snow samples after 0 days (upper) and 12 days (lower)**
61 **exposure to temperature gradient metamorphism.** White areas show the ice phase, black represents interstitial air. The
62 scale bar (yellow arrow) denotes 1 mm.

Structural Changes to the snow.

Table 1 lists the physical properties of the snow samples. The specific surface area (SSA) and the porosity are within the range observed for hard wind-packed snow and depth hoar in the field (Legagneux et al., 2002; Zermatten et al., 2011; Calonne et al., 2012).

Despite the uncertainty in the precise initial location of bromide, this study clearly shows that temperature gradient metamorphism leads to a loss of heterogeneous reactivity with time. We interpret the entire loss of bromide that was initially available for heterogeneous chemistry to bromide burial driven by the locally growing ice during temperature gradient metamorphism. The structural changes to the snow during the 12 days temperature gradient metamorphism are visualised by X-ray microtomography (microCT) images in Fig. 2. During In the microCT image of the snow sample prior to metamorphism a coarseindividual spheres with 300 – 600 µm diameter are visible (Fig. 2, upper image). With developing snow metamorphism, the spheres get increasingly bonded and fully connecteda new porous snow structure grows outforms, while the recognition of the individual snow particles. is lost (Fig. 2, lower image). This reconstruction is a direct consequence of the temperature gradient in snow resulting in water vapour pressure gradients which induce fluxes of water vapour from warmer to colder regions. This gas phase movement of water is limited to short distances. In the experiments described here, the locally and continuously sublimating and growing snow, with an ice growth rate of 2 nm s^{-1} (Trachsel et al., 2019), leads to about 5 complete renewal cycles of the snow structure during the 12-days temperature gradient metamorphism (Pinzer et al., 2012). Despite the large local water turnover rate, Table 1 shows that the specific surface area (SSA) did not significantly change during the temperature gradient metamorphism. A convenient side effect of these little changes is that the kinetic experiments (Figure 1) were done with samples of similar specific surface area. That changes in SSA do not necessarily reflect water turn-over rates during metamorphism has been discussed before (Pinzer et al., 2012). The SSA andThe samples that porosity are within the range observed for hard wind-packed snow and depth hoar in the field (Legagneux et al., 2002; Zermatten et al., 2011; Calonne et al., 2012). In the microCT image of the snow sample prior to metamorphism individual spheres with 300 – 600 µm diameter are visible. The particles show edged structures even in absence of temperature gradient metamorphism (Fig. 2 upper graph). Samples were stored isothermally at -5 °C for 7 days and up to 54 days at - 45 °C prior to the metamorphism experiments (Fig. 2 upper image), show also facets, as is typical for isothermal snow (Kämpfer et al., 2005; Löwe et al., 2011). The tendency to eliminate differences in surface energy is the driving force in isothermal metamorphism ; this leads to much smaller fluxes of water vapour and consequently significantly slower re-structuring compared to temperature gradient metamorphism . Consequently, we would not have expected edge growing in the structure. We attribute this structural change to small but unintended gradients during isothermal storage of the sample. The intention of the isothermal storage at -5 °C was to allow time to eliminate internal grain boundaries . In line with the lower water vapour fluxes in isothermal metamorphism, Figure 1 clearly shows that the ozone loss rate is significantly higher in isothermally stored, doped sampled than that of the undoped samples after 12 days of isothermal metamorphism at -20 °C. Due to the fluctuation in the ozone loss rate observed in the samples prior to temperature gradient exposure, we refrain from discussing whether the

99

00

Table 1: ~~Morphology of~~Settings for the snow samples; ~~temperature gradient metamorphism age is~~The number of days ~~in~~gives the ~~metamorphism box.~~duration of metamorphism. Br denotes the concentration of bromide as derived by ion chromatography; SSA is the specific surface area ~~(± 6%~~as derived from the microCT scans with an typical error of ± 6% (Kerbrat et al., 2008). ~~ε is porosity~~The density was derived based on the weight of the snow sample and the volume of the sample holder. The mass denotes the amount of snow during the ozone exposure experiments and the surface area denotes the total surface area of the snow during the ozone exposure experiments. Each experiment with added bromide and an average of the 5 experiments with no added bromide is shown in Figure 1 and discussed in this work.

	Br [μM]	SSA [cm g^{-1}]	density of snow [g cm^{-3}]	mass [g]	Surface area [cm^2]
0 days	6.2	183	0.33	17	3118
0 days	6.2	183	0.32	11	2018
12 days, 31 °C cm^{-1} gradient	6.2	162	0.41	14	2268
12 days, isothermal	6.2	143	0.45	16	2281
12 days, isothermal	6.2	143	0.35	14	1996
0 days	<0.12	195	0.35	13	2540
0 days	<0.12	195	0.3	10	1953
0 days	<0.12	176	0.3	12	2113
12 days, 31 °C cm^{-1} gradient	<0.12	167	0.371	14	2336
12 days, 31 °C cm^{-1} gradient	<0.12	167	0.390	17	2836

08

09

10 The observed burial of bromide during the temperature gradient metamorphism may be attributed to a combination of growing

11 ice, covering the bromide present at the air-ice interface with neat ice, and diffusion of the bromide into the growing ice as

12 described in our previous work (Trachsel et al., 2019). ~~Diffusion rates of bromide in crystalline ice are not known. Diffusion~~

13 ~~rates of HCl, HNO₃, and formaldehyde in crystalline ice at -6 °C range from 7-240 × 10-12 cm²·s⁻¹, which allows us to~~

14 ~~calculate a mean diffusive distance of 40 – 220 nm s⁻¹. This diffusive distance is thus larger than the ice growth rate of 2 nm s⁻~~

15 ¹ supporting the ice-growth diffusion mechanism. Whether the bromide remains agglomerated forming micropockets under

16 the growing ice, or forms a solid-solution in the growing ice remains somehow speculative. A recent study by Wu et al. (2017)

17 showed that bromide is likely to be incorporated in the ice with recrystallization especially at low concentration. Molecular

18 dynamics simulations by Wu et al. (2017) showed that the charge density around a bromide ion does not result in very large

19 disruptions of the local ice structure as observed for other ions such as fluoride.. Therefore, they concluded that incorporating

20 bromide into the ice structure may be energetically feasible. Revisiting the micropockets and patches addressed above, one

21 could propose that these micropockets could Patches at the interface may also be covered by the growing ice in line with

22 Nagashima et al. (2018), who observed preferential growth of ice onto of brine droplets compared to the neat ice surface.

23

24 The results presented here show that after 5 complete recrystallisation cycles the bromide is absent from the air-ice interface.

25 This depletion of bromide at the air-ice interface is in excellent agreement with previous observations of other ions in snow

26 during metamorphism (Hewitt et al., 1991; Cragin et al., 1996; Trachsel et al., 2019). Elution profiles of shock-frozen snow

27 doped with a mixture of ammonium, calcium, chloride, fluoride, sodium, and sulphate revealed decreasing amounts of all ions

28 at the air-ice interface with duration of snow metamorphism up to 12 days (Trachsel et al., 2019). On longer time scales,

29 calcium and sulphate showed increasing occurrence at the air-ice interface. A further finding from Trachsel (2019) is that the

30 cation and anion tend to experience the same fate in shock-frozen snow. One might thus speculate, that the sodium in the

31 experiments presented here is likewise depleted at the air-ice interface during metamorphism. and have shown preferential

32 elution of sulfate compared to chloride and nitrate in snow samples after metamorphism. They proposed that latter ions were

33 incorporated into the ice matrix of snow during dry metamorphism, a finding that was also observed for ammonium and

34 fluoride . A more detailed and quantitative comparison A more detailed and quantitative comparison with the elution studies is

35 hampered, as the elution studies generally lack a budget of ions and give no direct link to chemical reactivity. Further,

36 meltwater or the eluent, induce changes to the snow structure (wet metamorphism) and might lead to relocation of impurities

37 (Meyer and Wania, 2008; Grannas et al., 2013).

1 Conclusion and Atmospheric Implication

39 We have presented an assessment of the effects of metamorphism on the reactivity of ozone with bromide in snow doped with

40 6.2 µM sodium bromide. loss of gas-phase ozone in bromide doped snow. Probing the presence of bromide in snow by its

41 reaction with ozone is an effective way to reveal its location that is not amenable with other methods that would offer more

42 chemical selectivity or spatial resolution but do lack sensitivity for the low impurity concentrations found in the environment.

43 Experiments were performed in the dark in snow doped with 6.2 µM sodium bromide. The artificial snow had physical

44 properties and a bromide concentration typical for natural snow, making extrapolations to the environment feasible. While

45 snow is not formed by shock freezing in the environment, riming might occur and lead to similar distribution of impurities as

46 observed in our samples. Further, we suggest that the patches of bromide at the air-ice interface represent bromide that is

deposited with sea salt aerosol on surface snow. Our observation of the ozone consumption showed that the bromide-doped snow samples lost their chemical reactivity towards gas-phase ozone during 12-days of temperature gradient metamorphism. This loss occurred without photochemistry forming volatile products. Post-depositional changes to bromide in snow have been observed in the field and have so far been explained by vivid photochemical reaction into volatile bromine. Volatile bromine might then be re-deposited on the snow surface after formation of more oxidized species, such as HOBr (Jacobi et al., 2002; Toom-Sauntry and Barrie, 2002). ~~Burial of acidic trace gases with atmospheric relevance has previously been discussed for these volatile species~~The burial of volatile trace gases into growing ice has also been discussed for acidic trace gases with atmospheric relevance (Huthwelker et al., 2006). Kippenberger et al. (2019) has studied the uptake of HCl and of oxidised organic trace gases to growing ice in Knudsen cell experiments. They observed a continuous uptake ~~only~~ of HCl that exceeded the equilibrium partitioning of HCl to ice (Zimmermann et al., 2016) scaling with ice growth rate and temperature. Growth rates were varied between 2 nm s^{-1} and 110 nm s^{-1}. ~~Post-depositional changes to bromide in snow have been observed in the field and have been explained by vivid photochemical reaction into volatile bromine. Volatile bromine might then be re-deposited on the snow surface after formation of more oxidized species, such as HOBr (Jacobi et al., 2002; Toom-Sauntry and Barrie, 2002).~~ In this study, we uniquely show that non-volatile bromide ions are effectively buried. Apparently, temperature gradient metamorphism appears to facilitate the formation of energetically most favourable impurity distributions in snow.

Our findings directly imply that for the Earth surface snow, where temperature gradients are omnipresent, burial of non-volatile solutes during metamorphism can reduce their availability for heterogeneous reactions. That only a small fraction of impurities may be chemically active in surface snow has been discussed for nitrate by Thomas et al. (2011) and Wren and Donaldson (2011). Results from this study thus emphasize that the reactivity of impurities changes dramatically with time during temperature gradient metamorphism in the field, rather than being a result of the initial deposition process.

~~Changes in chemical reactivity with gas-phase species may also hold for those species that were found accumulate at interfaces such as sulphate .~~ Clearly, the tendency to be incorporated into the ice matrix is a strong function of the chemical properties and of concentration (Bartels-Rausch et al., 2014; Trachsel et al., 2019). As a consequence, chemical species that were initially deposited together to the snow might separate to different compartments during metamorphism. The fact that bromide, for example, is driven into the ice while other potential reaction partners might leave the ice may lead to switching off other reaction pathways~~, such as~~. For instance, the oxidation by OH radicals that are produced from organics ending up outside, too far away for the OH to reach the bromide.

We argued that the driving force for the relocation are temperature inhomogeneities ~~in snow~~ and resulting water vapor fluxes~~.~~, as frequently observed in surface snow. That ice is not in thermodynamic equilibrium is moreover a ~~frequent~~common situation for atmospheric ice particles as well with common sub- and super- saturation (Gao et al., 2004). Our results therefore suggest that similar re-distribution of ions might also occur prior to snowfall.

In the case of bromide, ~~this~~the re-distribution away from the interface will suppress an initiation step in bromine explosion and ozone depletion events, both in light and in the dark, even for snow samples that ~~have an apparently~~show high ~~concentration of~~ bromide concentrations. We propose that this finding -at least partially – explains the varying reactivity of Arctic surface snow. Pratt et al. (2013) has investigated production of bromine for a range of saline snow and sea ice samples in outdoor chamber experiments and found no correlation ~~of~~with total bromide concentration in the samples and bromine release. It appeared that pristine snow, where the exchange with the atmosphere dominates its chemical composition, is more productive than snow that is in contact with sea water. Pratt et al. (2013) argued that deposition of atmospheric acids to the unbuffered surface snow drives the observed reactivity. Based on our finding, another explanation would be ~~the~~a constant flux ~~deposition~~ of bromide from the atmosphere refurbishing the ~~buried~~ bromide that is buried by temperature gradient metamorphism and thus providing reactive bromide at the air-ice interface.

This finding has significant environmental implications as it does not only stress the importance of the location of chemical species on their reactivity, but shows that this location is rapidly changing in surface snow. ~~Further,~~ One should note that incorporation of solutes into the interior of ice and snow makes them not only resistant to multiphase chemistry, but further reduces their tendency to be washed away by melt- or rain water percolating the snow. The enrichment in the snow may thus contribute to later release of toxins to the marine food web upon the complete melting of the snow (Wania et al., 1998; Eichler et al., 2001; Steffen et al., 2008; Durnford and Dastoor, 2011; Grannas et al., 2013). ~~Thus~~Further, even under current warming conditions ~~bromide~~the buried species might be ~~a~~ promising candidate for reconstructing past atmospheric composition from ice core records that have experienced melt effects (Eichler et al., 2001). ~~The enrichment in the snow may also contribute to later release of toxins to the marine food web upon the complete melting of the snow (Wania et al., 1998; Eichler et al., 2001; Steffen et al., 2008; Durnford and Dastoor, 2011; Grannas et al., 2013).~~

1 Data availability

Edebeli, Jacinta; Bartels-Rausch, Thorsten (2020). Data set on bromide oxidation by ozone in snow during metamorphism from laboratory study. EnviDat. *doi:10.16904/envidat.138*.

1 Author Contribution

TB-R, AE, MS designed the MISO project that this study was part of. JE planned and performed the flow tube experiments with help and input from MA, AE, MS, SA, TB-R. JT and JE performed, analysed, and discussed the microCT measurements with input from MS. TB-R and JE analysed the ozone uptake data and wrote the manuscript with input from MA and all other authors. All authors approved the submitted version of the manuscript. This work is part of JE doctoral thesis at ETH Zürich.

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The authors examine the ozone reactivity of bromide-doped laboratory "snow" and the effect of temperature-gradient metamorphism. They find that metamorphism shuts down the reactivity, apparently because it buries the bromide away from the air-ice interface. The paper is interesting because of its connection between snow physics and chemistry and implications for the reactivity of natural snow.

***Major point

Overall, the manuscript is interesting and deserves to be (eventually) published. But the writing of the manuscript is a problem: it is often difficult to follow, non-linear, and sometimes rambling. It needs significant attention from the first author but also the senior authors.

We thank the referee for detailed discussion of our manuscript and the generally positive feedback on the scientific quality and significance. We have significantly restructured and shortened the text removing parts that you might have felt are extraneous. We hope that you agree about the modified manuscript meeting the standards of ACP.

Page 9 is one example. First, the entire page is one paragraph, as occurs on a number of pages. It would be much better to break the text into smaller paragraphs, each with a main theme. Second, the discussion circles around and around, repeating topics (e.g., the assumed diffusion coefficient) rather than linearly dealing with one topic and then moving on to the next. It makes it difficult to follow the arguments. The paper is already short, but could probably be shortened (and strengthened) by removing repetition, using a more logical flow, and removing extraneous ideas.

Thanks for pointing to the long paragraphs. These have slipped our attention when uploading the manuscript. Shorter paragraphs and subheading have been introduced throughout the manuscript. The initial reason for discussing the diffusion at two different places of the manuscript was to clearly differentiate processes occurring during the ozone experiments and during the metamorphism as both differ in experimental settings such as temperature which impacts the diffusion. In the revised version, diffusion is no longer discussed in the context of the metamorphism and the discussion of diffusion is thus at one place:

18 "One may estimate that the total amount of bromide diffusing from the ice bulk to the surface is 0.2 - 1.6e10
19 molecules each second. This is much less than the ozone loss observed in our experiments clearly showing that
20 the bromide is not present homogeneously in the ice matrix of the snow samples. Due to lack of diffusion
21 coefficients of bromide in ice, the diffusion coefficients of HNO3 in crystalline ice at -15 °C of 100e-12 cm2 s-1
22 (Thibert and Dominé, 1998) was used as upper limit and a diffusion coefficient of HCl at -15 °C of 3e-12 cm2 s-1
23 as lower bound was used in this calculation. Further, the aqueous concentration of 6.2 µM and the specific
24 surface area of each snow sample as derived by the microCT data (Table 1) was used."

25 **Other points

26 Line 26: The text states "tropospheric O3 reduction", but this is misleading since the global tropospheric O3
27 mixing ratio is increasing. Better wording would be "tropospheric O3 sink".

28 Thank you! Fixed.

29 "Recent improvement in global atmospheric chemistry models indicate that halogen chemistry accounts for about
30 14% of the global tropospheric ozone sinks (Schmidt et al., 2016)"

31 l. 71. What is "environmental snow" and how is it different from Arctic snow? l. 81. How were the artificial
32 drops produced? Paint sprayer?

33 We agree that his statement was confusing. We focus on Arctic snow in the revised version:

34 "Bromide concentration in the doped snow samples (6.2 µM) is typical for snow on Arctic sea ice (Pratt et al.,
35 2013)."

36 l. 84. Samples were annealed at -5 C for 7 days. Why such a long annealing time? Why the focus on minimizing
37 grain boundaries?
38 l. 88. This line also discusses 7 days of annealing. Is this in addition to the 7 days described on line 84, or is the
39 same annealing description repeated twice? Or were samples were annealed in the reactor tubes for 7 days?

40 Thank you for pointing us to this inconsistency. The samples were stored once at -5°C. Grain boundaries have a
41 pronounced impact on snow physics and physical chemistry. They may host impurities, that were expelled during

freezing to the ice-ice interface and may act as shortcut for diffusion. To give the ice particles time to anneal

leading to a reduction in the grain boundaries, we stored the samples at -5°C for about a week.

"The samples were left overnight at –45°C and then, stored isothermally at –5 °C for 7 days to anneal and to minimize grain-boundaries (Blackford, 2007; Riche et al., 2012). The samples were returned to - 45 °C after this isothermal treatment to slow down further changes with time and stored up to 54 days at - 45 °C prior to the metamorphism experiments for logistic reasons."

l. 127. UV illumination of N2/O2 mixtures can also make NOx in addition to O3. Was there any attempt to detect whether NOx was formed? Any evidence of NOx reactions, e.g., formation of nitrate in the O3-exposed snow?

We have focused on the ozone loss as observable and have not tried to detect NOx or nitrates. We would like to note that the O2 was illuminated at 185 hv – which photolyzes O2 but not N2. Since we routinely use O3 to titrate NO for NO2 calibration, we note that our UV O3 generator is NOx free.

Figure 1. What are the solid lines that connect the symbols? Continuous ozone measurements? Are the symbols then just the continuous result at specific times or is it something else? Make it clear in the caption that "undoped" means no added bromide for the grey line. How much variability was there in O3 loss rates for the undoped samples?

The ozone was recorded continuously, and the symbols were only added to help differentiate the lines (in black and white prints). We have modified the figure and caption to make this clearer, also adding the standard deviation to show the variability in the O3 loss of undoped snow.

61

Figure 1: Ozone loss rate with duration of exposure. The snow samples with a bromide concentration of 6.2 µM experienced 0 days (blue lines, open circles) and 12 days (yellow line, open squares) of metamorphism with a temperature gradient of 31 °C m^{-1}. The lower panel is a zoom to the data. Ozone data were recorded continuously (lines), the markers are guides. The dotted lines are guide to the eyes, for periods where ozone loss data are not available (see text for details). Also shown are the ozone loss rates of snow samples after 12 days of isothermal metamorphism at -20 °C (red lines, open triangles). The grey line (open diamonds) denotes the average ozone loss rates of 5 samples with no bromide added and with and without exposure to temperature gradient metamorphism. The shaded area in the lower panel shows the standard deviation. The gas phase mixing ratio of ozone varied between 4.7-6.2e12 molecules cm-3 for individual samples. Temperature during ozone exposure was -15 °C. At time 0, ozone in the carrier gas was passed over the snow samples.

72

l. 162. It's not clear what is meant by "Taken the large variation in the ozone loss of samples exposed to metamorphism. . ."

27

75   We agree and have removed this statement.

76

78   We have reworded the beginning of the paragraph and hope it is easier to follow.

79   "The reaction of gas-phase ozone with frozen solutions containing bromide has been studied in great detail previously (Wren
80   et al., 2010; Oldridge and Abbatt, 2011; Abbatt et al., 2012; Wren et al., 2013). Oldridge and Abbatt (2011) described coated
81   wall flow tube studies on frozen sodium bromide/sodium chloride/water mixtures at -15°C and Wren et al. (2010) reported
82   on a laser-induced fluorescence study with sodium bromide/water mixtures at - 20°C. The studies by Wren et al. (2010) and
83   by Oldridge and Abbatt (2011) were done with an initial sodium bromide concentration of 10 mM and a gas-phase ozone
84   concentration of 1×10^{14} molecule cm^{-3} and 80×10^{14} molecule cm^{-3}, respectively. Oldridge and Abbatt (2011) have argued
85   that this multiphase reaction proceeds in the liquid fraction of sample containing bromide-brine that is in equilibrium with
86   ice between 0 °C and the eutectic temperature where the salt precipitates. The eutectic temperature of sodium bromide is at
87   or below -28 °C (Stephen and Stephen, 1963). ... Despite the differences in the concentration of bromide in the solutions
88   used to freeze the films, the similar concentration of bromide in the brine during ozone exposure makes a comparison of the
89   experimental results feasible. For the comparison, the reported uptake coefficients of 1.5×10^{-8} and $4\text{-}2 \times 10^{-8}$, respectively
90   (Wren et al., 2010; Oldridge and Abbatt, 2011), were transferred...»

91

92

95   Yes, we agree. Thank you. We have removed the sentence and restructured the paragraph.

96

We apologize for not being clear. We have rewritten this paragraph where we discuss the reactive loss of ozone on pure ice. As ice is the main surface in our samples, we conclude that this "ozone self-reaction" on ice may explain the long-lasting tail of the data. Of course, impurities might contribute, however, we think that these react away faster. We also describe the agreement as good and not perfect in the revised version.

« 3.   After about 8000 s ozone exposure, the ozone loss rates of all experiments approach zero loss of ozone. The raw data curves levelled off approaching a steady loss rate of 1.1-1.9e12 molecule s-1. This background loss rate may be attributed to the reactive uptake of ozone to ice driven by a self-reaction on the ice surface (Langenberg and Schurath, 1999), which is the main phase in the frozen solution samples investigated here. Langenberg and Schurath (1999) described a reactive ozone uptake coefficient on ice of 7.7-8.6e-9 at -15 °C and at ozone gas-phase concentrations similar to our work. The uptake coefficient normalizes the loss rate to the collision rate of ozone with the ice (or snow) surface. A loss rate of 0.86-0.90e12 molecules s-1 can be derived based on the reported uptake coefficient for the experimental conditions of our doped samples prior to metamorphism, in good agreement with our observations. Because this loss rate is not related to the bromide in the samples, it has been subtracted from the data discussed and shown in Fig. 1.»

l. 205. I wouldn't expect that the snow made here is acidic. Are there pH measure- ments of the melted solution?

We agree. We do not expect the snow to be acidic. We have not measured the pH of the molten snow as this would say little about the pH of the reactive medium.

l. 220. This low coverage isn't necessarily evidence that bromide loss limits ozone depletion, since it's difficult to compare a bromide surface coverage with a gas-phase ozone concentration. A clearer controlling factor is instead the number of ozone molecules lost compared to the number of bromide ions initially on the ice.

Thank you, we agree and have removed this section.

l. 228. What's the reference for this diffusion coefficient?

26 We always referred to Dominé's work. This section was rewritten as mentioned above.

31 We agree fully with this definition and have reworded to make this clearer.

32 "Chemical species, besides water, and ions can molecularly embedded within the ice matrix (solid-solution),

33 molecularly adsorbed at the air-ice interface, in liquid or solid patches at the air-ice interface, in micropockets

34 within the ice matrix including the ice-ice interface (at grain boundaries).»

35

36 We have also removed the detailed discussion on micropockets and now simply state:

37

38 "We propose that the brine forms liquid patches on the surface and filaments along the grain boundaries at the

39 interface as observed for higher concentrated frozen salt solutions (Blackford et al., 2007). A homogenous film

40 covering the total snow surface is unlikely: A back-of-the-envelope calculation with the total amount of bromide

41 doped to the samples and with a concentration of 3.4 M gives a brine layer with a thickness of only ~0.1 nm at -

42 15°C for the specific surface area of the doped snow samples. This is unfeasible, because the thickness of an ice

43 monolayer is roughly 0.3 nm. Whether the unreactive fraction of the bromide is located in a solid solution or in

44 micropockets within the ice matrix is beyond the scope of this work, both compartments explain its non-

45 reactivity."

46

47 l. 250. The use of parentheses to indicate a parallel sentence meaning is confusing. Better to have two separate,

48 clear sentences.

49 Thank you, we have removed the discussion of diffusion during metamorphism.

50 "One may estimate that the total amount of bromide diffusing from the ice bulk to the surface is 0.2 -

51 1.6e10 molecules per second. This is much less than the ozone loss observed in our experiments clearly showing

52 that the bromide is not present homogeneously in the ice matrix of the snow samples. Due to lack of diffusion

53 rates of bromide in ice, the diffusion rates of HNO_3 in crystalline ice at -15 °C of 100 e^{-12} cm^2 s^{-1} (Thibert and

54 Dominé, 1998) was used as upper limit and a diffusion rate of HCl at -15 °C of $3e^{12}$ cm^2 s^{-1} as lower bond was

55 used in this calculation. Further, the aqueous concentration of 6.2 µM and the specific surface area of each snow

56 sample as derived by the microCT data (Table 1) was used."

57

58 l. 254. It's not clear why this possible (but hugely uncertain) number of micropockets is interesting. The number

59 is highly sensitive to the radius, of which we only know an approximately upper bound. Furthermore, the

60 estimate of the number of micropockets seems to have little bearing on whether micropockets can be "excluded"

61 as a major location for bromide. The ozone data indicates that approximately 3/4 of the bromide is present

62 internally in ice, whether in micropockets, at grain boundaries (if these are not part of micropockets) or as solid

63 solution. How does a highly uncertain micropocket number estimate change this?

64 We have removed this section to make the manuscript more linear and clearer.

65 l. 257. The ozone depletion data argues strongly against all of bromide being present at the air-ice interface. So

66 why the need for lines 257-258 to say this point again?

67 With all respect, we think that the question whether or not impurities form a homogeneous film on snow or ice is still

68 raising intensive discussions and is worth mentioning. (F. Dominé et al., J. Phys. Chem. A, **117**, 4733-4749 (2013).) We

69 have shortened the manuscript elsewhere and hope that this supporting argument now won't disturb the reading.

70

71 l. 269. What does it mean that the snow is "fully connected"? The snow that was not exposed to the temperature

72 gradient looks as "fully connected" as the one that was exposed. Is it not?

73 Prior to temperature gradient the individual spheres that have been originally frozen still dominate the picture. The referee is

74 right, that there are connections between the individual particles from the start due to fast sintering. But these bonds are weak

75 and limited to a few points of contact. Fully connected referred to the individual spheres no longer being visible in the snow

76 structure. We have reworded the section to make it clearer:

77

78 "In the microCT image of the snow sample prior to metamorphism individual spheres with 300 – 600 μm diameter are

79 visible (Fig. 2, upper image). With developing snow metamorphism, the spheres get increasingly bonded and a new porous

80 snow structure forms, while the recognition of the individual snow particles is lost (Fig. 2, lower image)."

81 l. 280. What does it mean that the particles "show edge structures" and why is this important? It seems that any

82 solid-gas system will have edges.

83 We thank the referee for this comment. The appearance of edged structures is typical for temperature gradient

84 metamorphism and we thought that it has occurred to some extent during isothermal storage or transport of the sample.

85

86 After reconsideration and comment of one of our co-authors, we agree with the referee. The angular structures may also have

87 formed during isothermal storage. The minimal energy surface represents a polyhedron with rounded corners. (Löwe, H.,

88 Spiegel, J., & Schneebeli, M. (2011). Interfacial and structural relaxations of snow under isothermal conditions. Journal of

89 Glaciology, 57(203), 499-510. doi:10.3189/002214311796905569). Thus, the faceted structures visible in Fig. 2a) are indeed

90 formed during isothermal metamorphism.

91

92 We have deleted the particular section in the manuscript.

93 Table 1. What is n for each of the four conditions?

94 Table 1 now lists all individual experiments and we hope it is clearer that n is 1 for all but the 5 experiments

95 without added bromide that were averaged in Figure 1.

96 l. 302. Early only one diffusion coefficient was presented, but now the issue is presented again, but with a range

97 of values. This range should be presented in the initial discussion of diffusivities and either a best value,

98 bounding value, or range should be presented in both locations.

99 l. 302. "10-12" needs to be formatted (superscripted "-12").

00 l. 303. 40 - 220 nm/s is a diffusion rate or speed, not a distance.

01 Thank you, all points fixed.

02 l. 304. What is the ice-growth diffusion mechanism? It is not clear how the comparison of rates supports this

03 (unspecified) mechanism.

04 If the rate of bromide diffusion is 1 - 2 orders of magnitude faster than the rate of ice growth, one would expect

The ice-growth diffusion mechanism has been discussed in our previous work. Basically, it addresses the

question, why the reactivity decreases while the water of the snow undergoes 5 complete recrystallisation cycles.

During one full cycle, any bromide patches initially covered by the growing ice might be exposed to the air-ice

interface again, when the water that covered them evaporates towards the end of the complete recrystallisation

cycle. The detailed mechanism is speculative, so we removed it from the discussion of this manuscript and state

the result as the apparent ability of the temperature gradient metamorphism to foster re-distribution of impurities

into the interior of the ice matrix.

When a homogeneous distribution of bromide is reached, some of it would end up at the interface and at a

distance from where it could diffuse to the interface. We discuss this aspect now early on in the manuscript where

we conclude that the amount of bromide in this region is too small to give noticeable ozone consumption:

"Shock freezing aqueous solutions may preserve the homogeneous distribution of solutes also in the ice matrix

from where the bromide might diffuse to the air-ice interface and heterogeneously react with the ozone. In the

following, this reacto-diffusive loss is estimated. Due to lack of knowledge of the diffusion coefficient of

bromide in ice, the diffusion coefficient of HNO3 in crystalline ice at -15 °C of 100e-12 cm2 s-1 (Thibert and

Dominé, 1998) was used as upper limit and a diffusion coefficient of HCl at -15 °C of 3e-12 cm2 s-1 as lower

bound was used in this calculation. Further, the aqueous concentration of 6.2 µM and the specific surface area of

each snow sample as derived by the microCT data (Table 1) was used. Based on these assumptions, one may

estimate that the total amount of bromide diffusing from the ice bulk to the surface is 0.2 - 1.6e10 molecules each

second. This is much less than the ozone loss observed in our experiments, clearly showing that the bromide is

not present homogeneously in the ice matrix of the snow samples after shock freezing"

We prefer to not discuss the surface propensity of bromide in aqueous solution, which has been revisited recently

(Gladich, I., Chen, S., Vazdar, M., Boucly, A., Yang, H., Ammann, M., and Artiglia, L.: Surface Propensity of

Aqueous Atmospheric Bromine at the Liquid–Gas Interface, The Journal of Physical Chemistry Letters, 3422-3429, 10.1021/acs.jpclett.0c00633, 2020.

Olivieri, G., Parry, K. M., D'Auria, R., Tobias, D. J., and Brown, M. A.: Specific Anion Effects on Na+ Adsorption at the Aqueous Solution–Air Interface: MD Simulations, SESSA Calculations, and Photoelectron Spectroscopy Experiments, The Journal of Physical Chemistry B, 122, 910-918, 10.1021/acs.jpcb.7b06981, 2018.)

l. 309. Aren't the micropockets (by definition) already covered with ice? If so, this discussion of ice growth on brine drops seems to miss the point.

Thank you for pointing to this inconsistency. We have reworded as follows:

"Patches at the interface may also be covered by the growing ice in line with Nagashima et al. (2018), who observed preferential growth of ice onto brine droplets compared to the neat ice surface.»

l. 328. "Burial of acidic trace gases with atmospheric relevance has previously been discussed for these volatile species (Huthwelker et al., 2006)." Rather than give this vague statement, it would be better to make a specific statement about the past results that are relevant to the current work.

Thank you. We have rewritten the section to be clearer:

«Our observation of the ozone consumption showed that the bromide-doped snow samples lost their chemical reactivity towards gas-phase ozone during 12-days of temperature gradient metamorphism. This loss occurred without photochemistry forming volatile products. Post-depositional changes to bromide in snow have been observed in the field and have been explained by vivid photochemical reaction into volatile bromine. Volatile bromine might then be re-deposited on the snow surface after formation of more oxidized species, such as HOBr (Jacobi et al., 2002; Toom-Sauntry and Barrie, 2002). The burial of volatile trace gases into growing ice has also been discussed for acidic trace gases with atmospheric relevance (Huthwelker et al., 2006).»

l. 331. Why use "only" to qualify the HCl uptake?

Thank you, fixed.

l. 346. "As a consequence. . ." This is an interesting point.

Thank you for this judgement.

l. 369. This last sentence is no longer referring to bromide? If not, it does not fit with the rest of the paragraph.

Indeed, the sentence does not refer to bromide alone:

"Based on our finding, another explanation would be a constant flux of bromide from the atmosphere
refurbishing the bromide that is buried by temperature gradient metamorphism and thus providing reactive
bromide at the air-ice interface.

This finding has significant environmental implications as it does not only stress the importance of the location of
chemical species on their reactivity but shows that this location is rapidly changing in surface snow. One should
note that incorporation of solutes into the interior of ice and snow makes them not only resistant to multiphase
chemistry, but further reduces their tendency to be washed away by melt- or rain- water percolating the snow.
The enrichment in the snow may thus contribute to later release of toxins to the marine food web upon the
complete melting of the snow (Wania et al., 1998; Eichler et al., 2001; Steffen et al., 2008; Durnford and Dastoor,
2011; Grannas et al., 2013). Further, even under current warming conditions the buried species might be
promising candidate for reconstructing past atmospheric composition from ice core records that have experienced
melt effects (Eichler et al., 2001)."

The manuscript reports on a small series of six experiments quantifying the ozone loss on bromide-doped artificial snow samples. The effect of subjecting the samples to temperature gradients for extended periods of time (days) is studied.

This is an interesting and important study possibly allowing conclusions on the avail- ability of bromide and the processes at the ice-air interface in (aged) snow. It is, there- fore, in principle relevant for understanding and modelling bromine release events ob- served in polar regions.

The manuscript contains important information relevant to the readers of ACP and should be published. However it contains a number of deficiencies and significant improvements are possible and should be made.

We thank the referee for recognizing the interesting aspects of this manuscript and for the positive judgement on the significance. We have substantially shortened and streamlined the manuscript and hope that the revised version convinces you.

1) Frequently release of volatile bromine is mentioned, however the experiments really determine loss of ozone, this fact should be stated more explicitly.

Indeed, we observe ozone loss and try to argue carefully that we assign this loss to the well-known reaction of ozone with bromide in the dark. The fact that we observe ozone loss is now mentioned prominently in the abstract, introduction, and in the conclusion again.

Abstract: "... the heterogeneous reactive loss of ozone in the dark at a concentration of $5\text{-}6e^{12}$ molecule cm^{-3} is investigated in artificial, shock-frozen snow samples doped with 6.2 μM sodium bromide …"

End of introduction: "The objective of this study is to investigate the heterogeneous reactivity of bromide oxidation by gas-phase ozone in the dark. To assess the surface concentration of bromide and its change during temperature gradient metamorphism the gas-phase ozone loss is monitored in this study. Bromide concentration in the doped snow samples (6.2 μM) is typical for snow on Arctic sea ice (Pratt et al., 2013)"

Conclusion: «We have presented an assessment of the effects of metamorphism on the loss of gas-phase ozone in bromide doped snow. Experiments were performed in the dark in snow doped with 6.2 µM sodium bromide»

2) The data given in some parts are incomplete and are given in different units, so reading the manuscript requires a pocket calculator. For instance on page 5, lines 125-131 the air flow through the samples is given in ml/minute, the ozone mixing ratio in ppb, while later (page 9) the number of ozone molecules per second is required. Although the manuscript mentions release of bromine 'in light and in the dark' one assumes that the experiments were performed in the dark, but this is not said in the manuscript. Volumes are sometimes given in ml, sometimes in cm3.

Thank you for pointing this out. We have replaced ml by cm^3 throughout the document. We still give the ozone mixing ratio (in ppb) but only in parenthesis next to the gas-phase concentration in molecule cm^{-3} for the convenience of the reader. We also mention the chemistry in the dark more explicitly. Thank you for this comment. We'd like to point out -however- that we use the well-known heterogeneous chemistry of bromide with ozone in the dark to probe the availability and reactivity of bromide at the snow-air interface. We are convinced that our results can also be directly be applied to the photochemistry of bromide with ozone.

Conclusion: "We have presented an assessment of the effects of metamorphism on the loss of gas-phase ozone in bromide doped snow. Experiments were performed in the dark in snow doped with 6.2 µM sodium bromide.»

Abstract: " For this, the heterogeneous reactive loss of ozone in the dark at a concentration of 5-6E12 molecule cm^{-3} is investigated in artificial, shock-frozen snow samples doped with 6.2 µM sodium bromide and with varying metamorphism history."

End of introduction: "The objective of this study is to investigate the heterogeneous reactivity of bromide oxidation by gas-phase ozone in the dark. To assess the surface concentration of bromide and its change during temperature gradient metamorphism the gas-phase ozone loss is monitored in this study. Bromide concentration in the doped snow samples (6.2 µM) is typical for snow on Arctic sea ice (Pratt et al., 2013)"

3) A table is missing, which summarizes the pertinent data of the experiments: Volume of the reaction chamber,
flow rate, snow density, snow surface area, number of ozone molecules lost per second, etc..

We have expanded the table. We prefer not to give give the number of ozone molecules lost per second as this
number changes with time. For more data we kindly refer to the data repository where data tables can be
downloaded.

Table 2: Settings for the snow samples; The number of days gives the duration of metamorphism. Br denotes the
concentration of bromide as derived by ion chromatography; SSA is the specific surface area as derived from the
microCT scans with an typical error of ± 6% (Kerbrat et al., 2008). The density was derived based on the weight of
the snow sample and the volume of the sample holder. The mass denotes the amount of snow during the ozone
exposure experiments and the surface area denotes the total surface area of the snow during the ozone exposure
experiments. Each experiment with added bromide and an average of the 5 experiments with no added bromide
is shown in Figure 1 and discussed in this work.

	Br [μM]	SSA [cm g^{-1}]	density of snow [g cm^{-3}]	mass [g]	Surface area [cm^2]
0 days	6.2	183	0.33	17	3118
0 days	6.2	183	0.32	11	2018
12 days, 31 °C cm^{-1} gradient	6.2	162	0.41	14	2268
12 days, isothermal	6.2	143	0.45	16	2281
12 days, isothermal	6.2	143	0.35	14	1996
0 days	<0.12	195	0.35	13	2540
0 days	<0.12	195	0.3	10	1953
0 days	<0.12	176	0.3	12	2113
12 days, 31 °C cm^{-1} gradient	<0.12	167	0.371	14	2336

12 days, 31 °C cm^{-1} gradient	<0.12	167	0.390	17	2836

39

4) Fig. 1: The figure summarizes all experimental findings of the manuscript, therefore it should be as informative and clear as possible. However, it is actually quite hard to read since most of the data are huddled in the lowest 20% or so of the plot. It would be helpful if the plot could be split in two, one ranging to 8E12 molec/s or even higher (what are actually the highest measured ozone loss rates?), one showing the data up to e.g. 3E12. Also additional lines indicating the ratio of losses at treated snow vs. losses at untreated snow could be helpful. What is the significance of the symbols (e.g. circles), do they just indicate the lines or are they measurement points?

Thank you for pointing out difficulties in reading the Figure. With all respect, we believe that the important parts of the figure are readable. Nevertheless, we have added a zoom to the figure. Thank you very much for this idea, it allowed us to also plot the standard deviation of the repeated experiments. We apologize for not being clear about the symbols. The ozone was monitored continuously, the symbols are just a help to differentiate the lines better. The figure is now introduced by:

"Figure 1 shows ozone loss rates for snow samples prior to and after exposure to dry metamorphism. The ozone loss rate was derived based on observed changes in gas-phase ozone concentration downstream of the flow tube packed with the snow sample. The ozone loss curves can be classified into three regions:

1. All samples show a high (> 9E12 molecule s^{-1}) loss rate during the initial period of ozone exposure up to 500 s. This observed loss is attributed to the reaction of ozone with traces of impurities, to a delay by switching the gas flows, and to the residence time of the ozone gas in the porous snow and is not further analysed.
2. In the intermediate time regime, the ozone loss rate is largest for the two samples doped with 6.2 µM bromide prior to ageing under laboratory-controlled temperature gradient metamorphism with 4E12 molecule s^{-1} and 7E12 molecule s^{-1} at 1000 s duration of ozone exposure (Fig. 1, blue lines, open circles). The loss rate was reduced by a factor of about 4 - 7 in the snow sample that experienced temperature gradient metamorphism with 1E12 molecule s^{-1} at 1000 s duration of ozone exposure (Fig 1, yellow line, open square).....»
3. After about 8000 s ozone exposure, the ozone loss rates of all experiments approach zero loss of ozone. The raw data curves levelled off approaching a steady loss rate of 1.1-1.9E12 molecule s^{-1}. This background loss rate may be attributed to the reactive uptake of ozone to ice driven by a self-reaction on the ice surface (Langenberg and Schurath, 1999), which is the main phase in the frozen solution samples investigated here. Langenberg and Schurath (1999) described a reactive ozone uptake coefficient on ice of 7.7-8.6E-9 at -15 °C and at ozone gas-phase concentrations similar to our work. The uptake coefficient

170   normalizes the loss rate to the collision rate of ozone with the ice (or snow) surface. A loss rate of 0.86-

171   0.90E12 molecule s^{-1} can be derived based on the reported uptake coefficient for the experimental

172   conditions of our doped samples prior to metamorphism, in good agreement with our observations.

173   Because this loss rate is not related to the bromide in the samples, it has been subtracted from the data

174   discussed and shown in Fig. 1.

175

176

177   In Figure 1, the part of the data that is not used to quantify the ozone loss is now plotted faded and the y-axis scale

178   is adopted to the fully show the range of the data used in the analysis

179

180
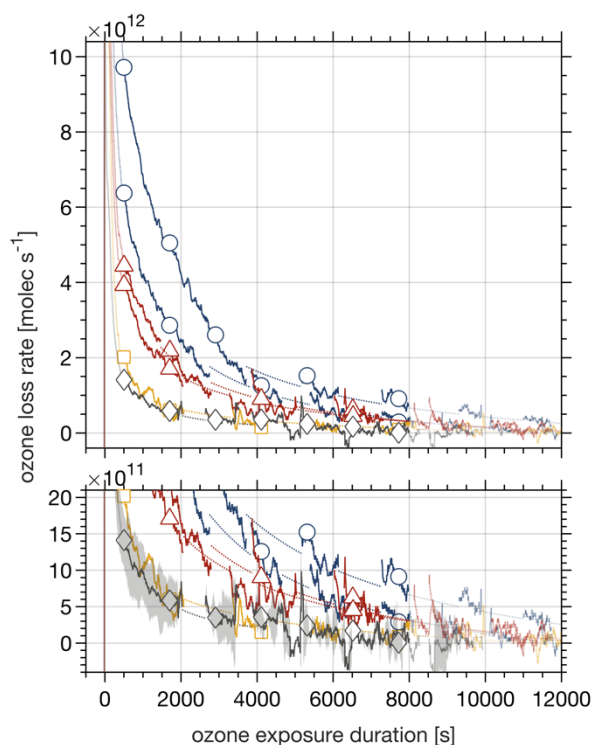
Figure 2: Ozone loss rate with duration of exposure. The snow samples with a bromide concentration of 6.2 µM

experienced 0 days (blue lines, open circles) and 12 days (yellow line, open squares) of metamorphism with a

temperature gradient of 31 °C m^{-1}. The lower panel is a zoom to the data. Ozone data were recorded continuously

(lines), the markers are guides. The dotted lines are guide to the eyes, for periods where ozone loss data are not

available (see text for details). Also shown are the ozone loss rates of snow samples after 12 days of isothermal

86 metamorphism at -20 °C (red lines, open triangles). The grey line (open diamonds) denotes the average ozone
87 loss rates of 5 samples with no bromide added and with and without exposure to temperature gradient
88 metamorphism. The shaded area in the lower panel shows the standard deviation. The gas phase mixing ratio of
89 ozone varied between 4.7-6.2 10^{12} molecule cm^{-3} for individual samples. Temperature during ozone exposure
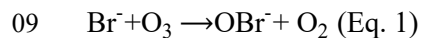90 was -15 °C. At time 0, ozone in the carrier gas was passed over the snow samples.

91

92 5) The discussion of the assumed reaction system is unclear: Why should be only 0.5 ozone molecules consumed
93 per bromine molecule (Br2)? Reaction equations 1 through 3 suggest that it is at least 2 ozone molecules. The
94 disproportionation reaction (BrO2- + BrO- ?) is missing from the scheme. What is the meaning of 'assuming a net
95 loss of 1 ozone molecule per bromide molecule'? And how is the number of 1E16 available bromide ions
96 calculated?

97 Our apologies for not being clear. We have rewritten this section:

98 «Generally, the products and reaction mechanism of the bromide oxidation by ozone in the aqueous phase strongly
99 depend on reaction time, reactant concentration and pH (Haag and Hoigne, 1983; Heeb et al., 2014). For non-
00 acidified conditions, as in our study, hypobromous acid (HOBr/OBr$^-$) is the main product (Eq. 1) that may react
01 further with ozone (Eq. 2) to form bromite (BrO$_2^-$), disproportionate to bromide (Br$^-$) and bromate (BrO$_3^-$), or self-
02 react to dibromine monoxide (Br$_2$O) (Heeb et al., 2014). Despite uncertainties in the precise product distribution in
03 this study, ozone is lost in our study in the initial reaction with bromide and to some extent in the subsequent
04 oxidation of hypobromous acid to bromite resulting in 1-2 ozone molecules lost per bromide ion. In particular, at
05 acidic conditions relevant for atmospheric waters and ices, but not applicable to our experimental settings (Abbatt
06 et al., 2012; Bartels-Rausch et al., 2014), bromine is formed and released to the atmosphere in a sequence of reaction
07 steps (Eqs. 1 and 3).

08

09 $Br^- + O_3 \longrightarrow OBr^- + O_2$ (Eq. 1)
10 $OBr^- + O_3 \longrightarrow BrO_2^- + O_2$ (Eq. 2)
11 $OBr^- + Br^- + H^+ \longrightarrow Br_2 + OH^-$ (Eq. 3)
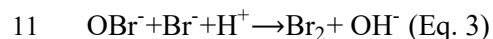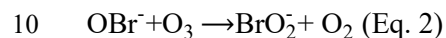
12

13 Thus, assuming a net loss of 1 ozone molecule per bromide molecule, one might estimate about 0.9 and

14 1.7 molecules of bromide are available for the multiphase reaction with ozone in the two porous snow samples

15 prior to metamorphism. Assuming a net loss of 2 ozone molecules, 1.8 and 3.3E16 molecules of available bromide

16 can be estimated for the two samples.»

17 6) The discussion of available bromide vs. observed ozone loss (page 9, lines 227 ff) states that the latter is much

18 smaller than the former. Actually one could say that the observed ozone loss is three orders of magnitude larger

19 than the calculated bromide flux. But what is the conclusion from this calculation?

20 With all respect, we tried to say exactly what you state. The larger observed ozone loss means that the smaller

21 amount of bromide available to react is too small to explain this ozone loss. We keep the original text as follows,

22 but hope that due to the added introduction to the location of impurities in snow, the point is clearer now:

23 "The striking loss of heterogeneous reactivity during temperature gradient metamorphism raises the question of the

24 location of the reactive bromide in the shock-frozen, artificial snow samples before metamorphism. Snow can host

25 impurities in several compartments (Bartels-Rausch et al., 2014): Chemical species, besides water, and ions can

26 molecularly embedded within the ice matrix (solid-solution), molecularly adsorbed at the air-ice interface, in liquid

27 or solid patches at the air-ice interface, in micropockets within the ice matrix including the ice-ice interface (at

28 grain boundaries). Clearly, only bromide in direct contact with the gas phase, that is located at the air-ice interface

29 or within the bulk at a distance that allows sufficient diffusion to the interface, is accessible to gas-phase ozone and

30 thus reactive. In the following, we elaborate on the feasibility of bromide being hosted in these distinct departments

31 in the samples used here.»

32

33 "Shock freezing aqueous solutions may preserve the homogeneous distribution of solutes also in the ice matrix

34 from where the bromide might diffuse to the air-ice interface and heterogeneously react with the ozone. One may

35 estimate that the total amount of bromide diffusing from the ice bulk to the surface is 0.2 - 1.6E10 molecule per

36 second. This is much less than the ozone loss observed in our experiments clearly showing that the bromide is not

37 present homogeneously in the ice matrix of the snow samples.»

38 7) Table 1 gives the bromide content of the samples in ppbw, while in most of the remaining manuscript bromide

39 is given in micro M. It would be helpful to include both numbers. Also, the SSA is given per gram, which is fine,

42   Fixed.

47   Here, we kindly disagree and would like to point out that we have shown:

48   * ozone is lost from the gas-phase in samples that have been doped with bromide prior to temperature gradient

49   metamorphism. The loss rate agrees well with previous studies. Giving, despite the small number of experiments,

50   confidence in the loss being driven by reaction of ozone with bromide.

51   * to explain the observed ozone losses, bromide needs to be present at the air-ice interface in higher amounts than

52   predicted for a homogeneous distribution in the ice. This agrees to earlier studies. As the exclusion of impurities

53   during freezing is certainly a question of concentration, relevance comes from the fact that this is the first chemical

54   study with uM of bromide that is the same concentration as found in the Arctic.

55   * the ozone reactivity decreases after temperature gradient metamorphism. In fact, we find no bromide driven ozone

56   loss at all in the aged snow. Main reason being that diffusion is just too slow. The life time of bromide in snow

57   assuming there is a sink at the surface, so the flux out of ice is limited by diffusion, is in the order of years. This is

58   the main conclusion of general relevance. Quantifying the loss further is then rather a question of how reactive the

59   snow was prior to metamorphism which is a question on the location and thus sources of the bromide in the snow.

65 We fully agree. This study directly links changes in chemical reactivity to snow metamorphism for the first time at
66 low concentration that are not only relevant for Earth's Arctic environment, but also low enough to potentially
67 allow the formation of a solid-solution. Certainly, investigating how many re-crystallization cycles - by varying
68 the time or the temperature gradient - are a follow up that we also highly recommend.

69 In summary, this is an interesting paper, but for the rather small amount of data it is way too long, and not many
70 conclusions can be drawn yet. The presentation could be made more clear and easier to read (see above) and in a
71 number of places the text could be considerably shortened.

72 We have considerable shortened the manuscript by rearranging, removing repetitions, and removing some content.
73 We like to point out, that discussing the phase diagram and the freezing point depression is crucial when working
74 with binary ice - salt mixtures and we'd argue that this discussion might indeed be longer than the presentation of
75 the data itself. Discussing the phase diagram not carefully enough, has lead to false conclusions about the observed
76 chemistry in the past (see Huthwelker , 2006).

77 This paper has only one conclusion: That heterogeneous reactivity is lost during snow metamorphism. We strongly
78 argue that the total loss of heterogeneous chemistry after temperature gradient metamorphism is worth publishing.
79 We think that this is one and clear conclusion from this work, not more but not less.

80 In a follow up study, we would suggest to use clean snow as for example prepared under nature identical conditions
81 in the Anastasio group and dope it with bromide – either in aerosol deposits or molecularly adsorbed. Then a study
82 with more parameter variation as you suggested and including changes to the temperature gradient should be done.

83