

Reply to Anonymous Referee #2

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:

“One may estimate that the total amount of bromide diffusing from the ice bulk to the surface is $0.2 - 1.6 \times 10^{10}$ 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. Due to lack of diffusion coefficients of bromide in ice, the diffusion coefficients of HNO_3 in crystalline ice at -15°C of $100 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ (Thibert and Dominé, 1998) was used as upper limit and a diffusion coefficient of HCl at -15°C of $3 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ as lower bound was used in this calculation. Further, the aqueous concentration of $6.2 \mu\text{M}$ and the specific surface area of each snow sample as derived by the microCT data (Table 1) was used.”

**Other points

Line 26: The text states “tropospheric O_3 reduction”, but this is misleading since the global tropospheric O_3 mixing ratio is increasing. Better wording would be “tropospheric O_3 sink”.

Thank you! Fixed.

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

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

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

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

I. 84. Samples were annealed at -5 C for 7 days. Why such a long annealing time? Why the focus on minimizing grain boundaries?

I. 88. This line also discusses 7 days of annealing. Is this in addition to the 7 days described on line 84, or is the same annealing description repeated twice? Or were samples were annealed in the reactor tubes for 7 days?

Thank you for pointing us to this inconsistency. The samples were stored once at -5°C . Grain boundaries have a 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."

I. 127. UV illumination of N_2/O_2 mixtures can also make NO_x in addition to O_3 . Was there any attempt to detect whether NO_x was formed? Any evidence of NO_x reactions, e.g., formation of nitrate in the O_3 -exposed snow?

We have focused on the ozone loss as observable and have not tried to detect NO_x or nitrates. We would like to note that the O_2 was illuminated at 185 hv – which photolyzes O_2 but not N_2 . Since we routinely use O_3 to titrate NO for NO_2 calibration, we note that our UV O_3 generator is NO_x 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 O_3 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 O_3 loss of undoped snow.

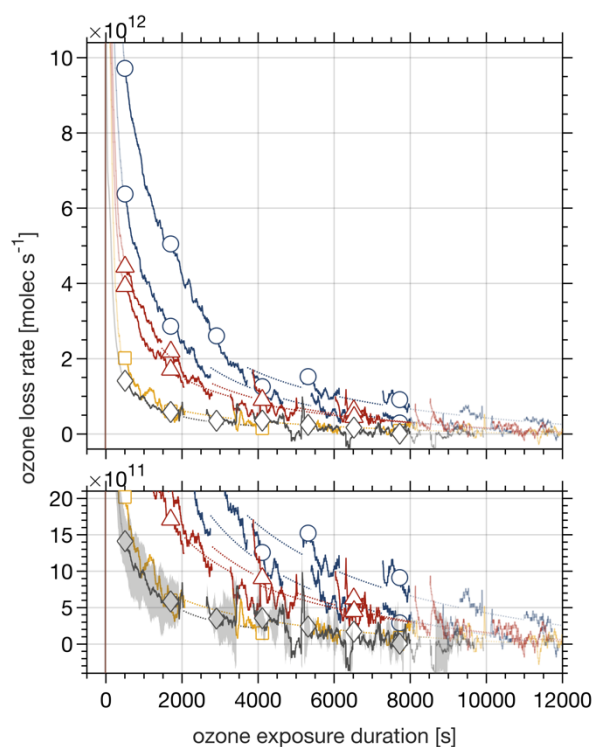


Figure 1: Ozone loss rate with duration of exposure. The snow samples with a bromide concentration of $6.2 \mu\text{M}$ experienced 0 days (blue lines, open circles) and 12 days (yellow line, open squares) of metamorphism with a temperature gradient of $31 \text{ }^\circ\text{C m}^{-1}$. The lower panel 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 $-20 \text{ }^\circ\text{C}$ (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 $4.7\text{-}6.2 \times 10^{12}$ molecules cm^{-3} for individual samples. Temperature during ozone exposure was $-15 \text{ }^\circ\text{C}$. At time 0, ozone in the carrier gas was passed over the snow samples.

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

We agree and have removed this statement.

I. 168. This paragraph is not easy to understand. Part of the problem is starting with the "result", i.e., comparison of O_3 loss rates, before describing all of the steps that make this comparison meaningful.

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

"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). Oldridge and Abbatt (2011) described coated wall flow tube studies on frozen sodium bromide/sodium chloride/water mixtures at -15°C and Wren et al. (2010) reported on a laser-induced fluorescence study with sodium bromide/water mixtures at

- 20°C. The studies by Wren et al. (2010) and by Oldridge and Abbatt (2011) were done with an initial sodium bromide concentration of 10 mM and a gas-phase ozone concentration of 1×10^{14} molecule cm^{-3} and 80×10^{14} molecule cm^{-3} , respectively. Oldridge and Abbatt (2011) have argued that this multiphase reaction proceeds in the liquid fraction of sample containing bromide-brine that is in equilibrium with ice between 0 °C and the eutectic temperature where the salt precipitates. The eutectic temperature of sodium bromide is at or below -28 °C (Stephen and Stephen, 1963). ... Despite the differences in the concentration of bromide in the solutions used to freeze the films, the similar concentration of bromide in the brine during ozone exposure makes a comparison of the experimental results feasible. For the comparison, the reported uptake coefficients of 1.5×10^{-8} and $4-2 \times 10^{-8}$, respectively (Wren et al., 2010; Oldridge and Abbatt, 2011), were transferred...»

I. 183. The sentence that starts “In summary, we conclude. . .” seems out of place. It is not a summary of the previous portion of the paragraph and it is a point that was made (or at least implied) in the earlier discussion of Figure 1.

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

I. 186. Here the authors attribute the background loss rate to “ozone self-reaction”, but is there any evidence from previous studies (e.g., in solution) that there is an appreciable O₃-O₃ reaction? This proposed mechanism is too specific given the lack of evidence. Also, on the next page the authors attribute the background loss to impurities, not to ozone-ozone reactions. The impurities hypothesis seems more likely.

I. 189. This is excellent agreement, but it’s not “perfect”, since current loss rate is up to 2x higher than the past rate.

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 $1.1-1.9 \times 10^{12}$ 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 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.»

I. 205. I wouldn't expect that the snow made here is acidic. Are there pH measurements 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.

I. 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.

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

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

I. 243. Solutes have been found at grain boundaries, but the sentence indicates that this location is different from "micropockets". My understanding of micropockets is that represent any liquid-like inclusion within the ice matrix, including at grain boundaries. If the authors want to use "micropockets" in a more specific way, they should define the term.

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

"Chemical species, besides water, and ions can 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).»

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

"We propose that the brine forms liquid patches on the surface and filaments along the grain boundaries at the interface as observed for higher concentrated frozen salt solutions (Blackford et al., 2007). A homogenous film covering the total snow surface is unlikely: A back-of-the-envelope calculation with the total amount of 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 for the specific surface area of the doped snow samples. This is unfeasible, because the thickness of an ice monolayer is roughly 0.3 nm. Whether the unreactive fraction of the bromide is located in a solid solution or in micropockets within the ice matrix is beyond the scope of this work, both compartments explain its non-reactivity."

I. 250. The use of parentheses to indicate a parallel sentence meaning is confusing. Better to have two separate, clear sentences.

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

"One may estimate that the total amount of bromide diffusing from the ice bulk to the surface is $0.2 - 1.6 \times 10^{10}$ molecules per 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. Due to lack of diffusion rates of bromide in ice, the diffusion rates of HNO_3 in crystalline ice at -15 °C of $100 \text{ e}^{-12} \text{ cm}^2 \text{ s}^{-1}$ (Thibert and Dominé, 1998) was used as upper limit and a diffusion rate of HCl at -15 °C of $3 \text{ e}^{-12} \text{ cm}^2 \text{ s}^{-1}$ 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.”

I. 254. It’s not clear why this possible (but hugely uncertain) number of micropockets is interesting. The number is highly sensitive to the radius, of which we only know an approximately upper bound. Furthermore, the estimate of the number of micropockets seems to have little bearing on whether micropockets can be "excluded" as a major location for bromide. The ozone data indicates that approximately 3/4 of the bromide is present internally in ice, whether in micropockets, at grain boundaries (if these are not part of micropockets) or as solid solution. How does a highly uncertain micropocket number estimate change this?

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

I. 257. The ozone depletion data argues strongly against all of bromide being present at the air-ice interface. So why the need for lines 257-258 to say this point again?

With all respect, we think that the question whether or not impurities form a homogeneous film on snow or ice is still raising intensive discussions and is worth mentioning. (F. Dominé et al., J. Phys. Chem. A, **117**, 4733-4749 (2013).) We have shortened the manuscript elsewhere and hope that this supporting argument now won’t disturb the reading.

I. 269. What does it mean that the snow is “fully connected”? The snow that was not exposed to the temperature gradient looks as "fully connected" as the one that was exposed. Is it not?

Prior to temperature gradient the individual spheres that have been originally frozen still dominate the picture. The referee is right, that there are connections between the individual particles from the start due to fast sintering. But these bonds are weak and limited to a few points of contact. Fully connected referred to the individual spheres no longer being visible in the snow structure. We have reworded the section to make it clearer:

“In the microCT image of the snow sample prior to metamorphism individual spheres with 300 – 600 μm diameter are visible (Fig. 2, upper image). With developing snow metamorphism, the spheres get increasingly bonded and a new porous snow structure forms, while the recognition of the individual snow particles is lost (Fig. 2, lower image).”

I. 280. What does it mean that the particles “show edge structures” and why is this important? It seems that any solid-gas system will have edges.

We thank the referee for this comment. The appearance of edged structures is typical for temperature gradient metamorphism and we thought that it has occurred to some extent during isothermal storage or transport of the sample.

After reconsideration and comment of one of our co-authors, we agree with the referee. The angular structures may also have formed during isothermal storage. The minimal energy surface represents a polyhedron with rounded corners. (Löwe, H., Spiegel, J., & Schneebeli, M. (2011). Interfacial and structural relaxations of snow under isothermal conditions. Journal of Glaciology, 57(203), 499-510. doi:10.3189/002214311796905569). Thus, the faceted structures visible in Fig. 2a) are indeed formed during isothermal metamorphism.

We have deleted the particular section in the manuscript.

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

Table 1 now lists all individual experiments and we hope it is clearer that n is 1 for all but the 5 experiments without added bromide that were averaged in Figure 1.

I. 302. Early only one diffusion coefficient was presented, but now the issue is presented again, but with a range of values. This range should be presented in the initial discussion of diffusivities and either a best value, bounding value, or range should be presented in both locations.

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

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

Thank you, all points fixed.

I. 304. What is the ice-growth diffusion mechanism? It is not clear how the comparison of rates supports this (unspecified) mechanism.

If the rate of bromide diffusion is 1 - 2 orders of magnitude faster than the rate of ice growth, one would expect uniform bromide distribution throughout the growing ice, meaning also some at the interface. But the experiments suggest no Br⁻ at the interface in the snow that experienced the temperature gradient.

One interesting link to previous work: past modeling in solution (Finlayson-Pitts and Tobias) has shown that Br⁻ is enriched at the air-solution interface. But the results in Fig. 1 for the T-gradient snow indicate that bromide is not present at the air-ice interface.

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.jpcllett.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.jpccb.7b06981, 2018.)

I. 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.»

I. 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).»

I. 331. Why use “only” to qualify the HCl uptake?

Thank you, fixed.

I. 346. “As a consequence. . .” This is an interesting point.

Thank you for this judgement.

I. 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)."