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 5-6e^{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 1: 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

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 normalizes the loss rate to the collision rate of ozone with the ice (or snow) surface. A loss rate of 0.86-0.90E12 molecule 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.

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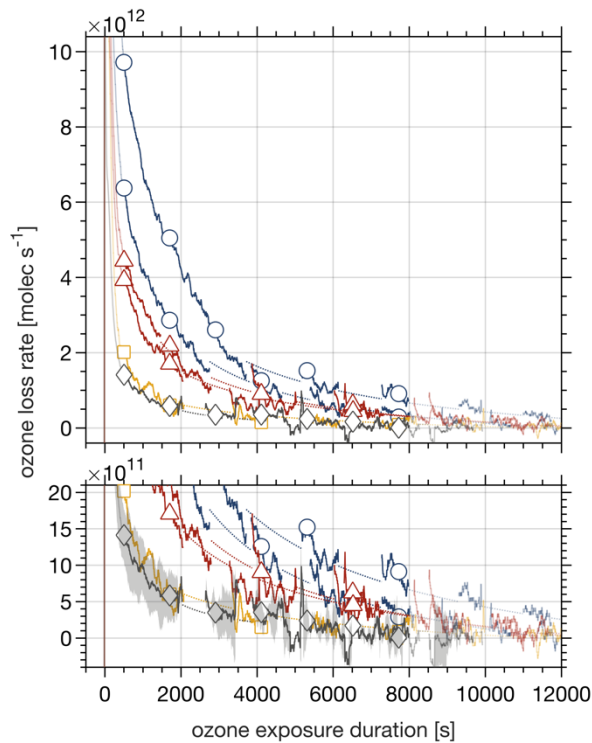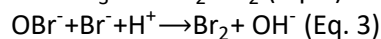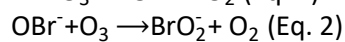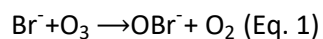

Figure 1: **Ozone loss rate with duration of exposure.** The snow samples with a bromide concentration of 6.2 µM experienced 0 days (blue lines, open circles) and 12 days (yellow line, open squares) of metamorphism with a temperature gradient of 31 °C m^{-1}. The lower panel is a zoom to the data. Ozone 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 4.7-6.2 10^{12} 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.

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

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

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

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

Thus, assuming a net loss of 1 ozone molecule per bromide molecule, one might estimate about 0.9 and 1.7 molecules of bromide are available for the multiphase reaction with ozone in the two porous snow samples prior to metamorphism. Assuming a net loss of 2 ozone molecules, 1.8 and 3.3E16 molecules of available bromide can be estimated for the two samples.»

6) The discussion of available bromide vs. observed ozone loss (page 9, lines 227 ff) states that the latter is much smaller than the former. Actually one could say that the observed ozone loss is three orders of magnitude larger than the calculated bromide flux. But what is the conclusion from this calculation?

With all respect, we tried to say exactly what you state. The larger observed ozone loss means that the smaller amount of bromide available to react is too small to explain this ozone loss. We keep the original text as follows, but hope that due to the added introduction to the location of impurities in snow, the point is clearer now:

"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 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. One may estimate that the total amount of bromide diffusing from the ice bulk to the surface is 0.2 - 1.6E10 molecule 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.»

Fixed.

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

* ozone is lost from the gas-phase in samples that have been doped with bromide prior to temperature gradient metamorphism. The loss rate agrees well with previous studies. Giving, despite the small number of experiments, confidence in the loss being driven by reaction of ozone with bromide.

* to explain the observed ozone losses, bromide needs to be present at the air-ice interface in higher amounts than predicted for a homogeneous distribution in the ice. This agrees to earlier studies. As the exclusion of impurities during freezing is certainly a question of concentration, relevance comes from the fact that this is the first chemical study with uM of bromide that is the same concentration as found in the Arctic.

* the ozone reactivity decreases after temperature gradient metamorphism. In fact, we find no bromide driven ozone loss at all in the aged snow. Main reason being that diffusion is just too slow. The life time of bromide in snow 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 the main conclusion of general relevance. Quantifying the loss further is then rather a question of how reactive the snow was prior to metamorphism which is a question on the location and thus sources of the bromide in the snow.

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

We have considerable shortened the manuscript by rearranging, removing repetitions, and removing some content. We like to point out, that discussing the phase diagram and the freezing point

depression is crucial when working with binary ice - salt mixtures and we'd argue that this discussion might indeed be longer than the presentation of the data itself. Discussing the phase diagram not carefully enough, has lead to false conclusions about the observed chemistry in the past (see Huthwelker , 2006).

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

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