**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "**Introducing the bromide/alkalinity ratio for a follow-up discussion on "Precipitation of salts in freezing seawater and ozone depletion events: a status report", by Morin et al., published in Atmos. Chem. Phys., 8, 7317–7324, 2008"** *by* R. Sander and S. Morin

S. Morin

morin.samuel@gmail.com

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We thank Eric Wolff for his invigorating comments and apologize for the time it has taken to address them.

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1 Answer to the points raised by Eric Wolff

Both the approach of Sander et al. (2006) and Morin et al. (2008) rely on a similar kind of scenario for bromine explosion, which is quickly summarized here. At temperature below 0°C, the chemical composition of seawater brine is governed by thermodynamic equilibrium, which fixes the concentration of bromide, carbonates and other chemical species. For "highly soluble" species (i.e., not participating in precipitation processes), this results in cryoconcentration due to the removal of solid ice (as measured e.g. by Richardson (1976)). For precipitating species such as carbonates, the concentration pathway depends on temperature and at present its best estimate is what was given in Morin et al. (2008) based on the FREZCHEM model. At a given temperature, the chemical composition of the brine predicted by thermodynamics corresponds to the starting chemical composition of the medium from which bromine explosion may occur.

We agree with Eric Wolff that, within a given parcel parcel which contains brine (or brine-derived media such as aerosol or salty snow) and gaseous species, what matters first is the comparison between the initial total alkalinity and the initial total acidity in the parcel. If the total initial acidity overcomes the total initial alkalinity, bromine explosion occurs. In the opposite case, bromine explosion cannot occur. A reasonable assumption is that the initial total alkalinity in the parcel resides in the brine. The total initial alkalinity is thus imposed by the temperature (see paragraph above) and the amount of brine in the parcel. Whether bromine explosion is likely to occur or not is thus only driven by initial atmospheric acidity, the amount of brine and its temperature of formation. So, we agree here with Eric Wolff that the initial bromide/A_T ratio alone is not telling us whether bromine explosion is going to occur.

Further action: The manuscript will thus be substantially modified to clarify this point, prior to the submission of any revised manuscript.

2 Clarification of the discrepancy between the convention of Sander et al. (2006) and Morin et al. (2008)

At 273 K and with a salinity of 35.0 permil, the A_T of seawater is on the order of 2 mmol kg^{-1}. Morin et al. calculated that at 255 K, the A_T in the brine is on the order of 3 mmol kg^{-1}. In contrast, in their calculations carried out at 240 K, Sander et al. (2006) used A_T concentration in the aerosol on the order of 20 mmol kg^{-1} for the no-precip case, and 14 mmol kg^{-1} for the case with 30% carbonate precipitation. Indeed, in their calculations, carbonate precipitation is superimposed on A_T cryoconcentration leading to a 10-fold increase in A_T (like other dissolved species such as Cl$^-$ and Br$^-$ as indicated in Table 1 of Sander et al.) without carbonate precipitation. A 30% depletion of A_T due to carbonate precipitation thus actually results in a 7-fold increase of A_T in terms of the comparison with the molality at 0°C. Morin et al. (2008) always compare the A_T values in terms of molality at a given temperature and at 0°C, which explains why they never observe any A_T depletion.

The first implication of this clarification is that, if one assumes that the concentration in the brine represents the concentration in the medium from which bromine explosion may occur, the results of Morin et al. (2008) do actually not contradict the results of Sander et al. (2006). Indeed, Morin et al. (2008) predict essentially the same bromide molality in the brine as Sander et al. (2006) for a given temperature, and predicted A_T molality values are about 4-5 times lower than the low A_T case (referred to as "30% precipitation" in Sander et al., 2006) that quickly leads to bromine explosion according to Sander et al. (2006). It is thus obvious that carrying out model runs using the predictions of Morin et al. (2008) for the chemical composition of the brine would also predict significant and quick bromine explosion and ozone depletion.

Further action: the revised manuscript will contain the exact conditions for the Sander et al. (2006) model runs, and how do they compare to Morin et al. (2008) predictions using the same conventions.

3 Br/A_T and the triggering of ODEs

Up to this point it is not relevant whether brine represents aerosol, salty snow or the brine itself possibly covered with frost flowers). In the simulations carried out by Sander et al. (2006), it was assumed that bromine explosion would occur within brine-derived aerosols. Under such an hypothesis, one has to evaluate what is the chemical composition of aerosols derived from the brine. Indeed, it is debatable whether the chemical composition of the brine will be similar (in terms of mol/kg of solution) to that of the aerosol, or if further evaporation of water in the aerosol will lead to additional evapoconcentration. This effect has to be cumulated to the effects of cryoconcentration.

In Morin et al. (2008) it was clearly mentioned that physical separation of the brine and the precipitates should occur otherwise redissolution of the precipitates upon acidification would mitigate the impact of carbonate precipitation on alkalinity. While this is perfectly conceivable that such a physical separation occurs prior to the injection of aerosols into the atmosphere from the brine, the situation inside the droplets is different. Under the assumption that the kinetics of carbonate re-dissolution in aerosols is quicker than acidification, the impact of precipitation of carbonates on A_T during evapoconcentration can be neglected. The "effective A_T" value can be calculated, for a given temperature, from the A_T value in the brine (determined by the FREZCHEM runs) and scaled with the evaporation factor:

$$A_T(\text{aerosols, effective}) = A_T(\text{brine}) \times f \tag{1}$$

If no evaporation occurs, f = 1. Evaporative processes lead to f values larger than 1. A further assumption is that f corresponds to a saturated NaCl solution (i.e., evaporation stops when the concentration of Na+ reaches its precipitation threshold). According to Richardson et al. (1976), this threshold lies between 4 and 5 mmol kg-1. Assuming that the droplets quickly evaporate to reach the state of a saturated NaCl solution, f is

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given by:

$$f = \frac{[\text{Na}^+](\text{sat.})}{[\text{Na}^+](\text{brine})} \quad (2)$$

Thus,

$$A_\text{T}(\text{aerosols, effective}) = A_\text{T}(\text{brine}) \times \frac{[\text{Na}^+](\text{sat.})}{[\text{Na}^+](\text{brine})} \quad (3)$$

Figure 1 shows the corresponding aerosol A_T values, in the two cases where $[\text{Na}^+](\text{sat.})$ = 4.0 and 5.0 mol kg^{-1}, as a function of the temperature of the brine. It is observed that below -7°C in all cases, evapoconcentration leads to A_T values below the value of 14 mmol kg^{-1} used by Sander et al. (2006). Even taking into account the evapoconcentration of alkalinity in airborne aerosols, it seems that the situation modeled by Sander et al. (2006), in terms of the alkalinity of aerosols, seems to be rather conservative (effective A_T values are rather on the order of 5 mmol kg^{-1} at temperatures on the order of -20°C, that is about one third of the initial alkalinity used by Sander et al., 2006, in their model study.)

As a by-calculation, it is worth noticing that equation (3) can be rewritten as:

$$A_\text{T}(\text{aerosols, effective}) = \frac{A_\text{T}(\text{brine})}{[\text{Br}^-](\text{brine})} \times \frac{[\text{Br}^-](\text{brine})}{[\text{Na}^+](\text{brine})} \times [\text{Na}^+](\text{sat.}) \quad (4)$$

The term first ratio is the A_T/bromide ratio in the brine, the second one is constant as long as no significant precipitation occurs for either bromide or sodium (it is equal to the sea water ratio), and the third term is also a constant that characterizes the chemical concentration of the droplets (total salinity of the droplets). This formulation indeed

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makes the A_T/bromide ratio to appear. The higher the ratio, the higher the alkalinity of the droplets, so the more difficult the acidification hence the ODEs.

In conclusion, it turns out that even if they were based on somewhat different grounds, the studies by Sander et al. (2006) and Morin et al. (2008) do not contradict each other as much as claimed in Morin et al. (2008). Indeed, as shown above, clarifications pertaining to the very definition of "alkalinity depletion" and the combination of evaporoconcentration -implicitly implemented by Sander et al. (2006)- with the calculations of Morin et al. (2008) shows that, under all the hypotheses and assumptions stated above, the conclusions of Sander et al. (2006) are physically and chemically correct. The calculations presented above indeed show that the A_T/bromide ratio is a relevant variable that describes the initial alkalinity of aerosol droplets prior to acidification, hence drives whether ODEs may occur (in conjunction with total acidity of the atmosphere and the amount of aerosols in the air).

Cautionary notes outlined in the conclusions of Morin et al. (2008) remain valid, especially in terms of the competition between thermodynamics and kinetics. It must be pointed out too, that if bromine activation occurs somewhere else than on aerosols, the description and the calculations above would the description and the calculations above would have to be modified accordingly.

Further action: the revised manuscript will include these calculations as a justification for the relevance of the A_T/bromide ratio.

We are of course entirely open to further discussion on this topic, and look forward hearing from the reviewers soon.

Full caption of Figure 1 : A_T and Na^+ molalities in the brine (red curves, "cryoconcentrated") and in aerosols (grey and black curves, "evaporoconcentrated") as a function of temperature. Two different values of the Na^+ molality at saturation (4 and 5 mmol kg^{-1}, respectively) are considered to bracket the impact of evaporoconcentration in aerosols.

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The "evapoconcentration" curves for A_T can be directly compared to the A_T value chosen by Sander et al. (2006) to initialise their model runs in the case where carbonate precipitation is allowed, which is presented in green. Vertical dashed arrows illustrate some A_T evapoconcentration pathways for two temperatures.

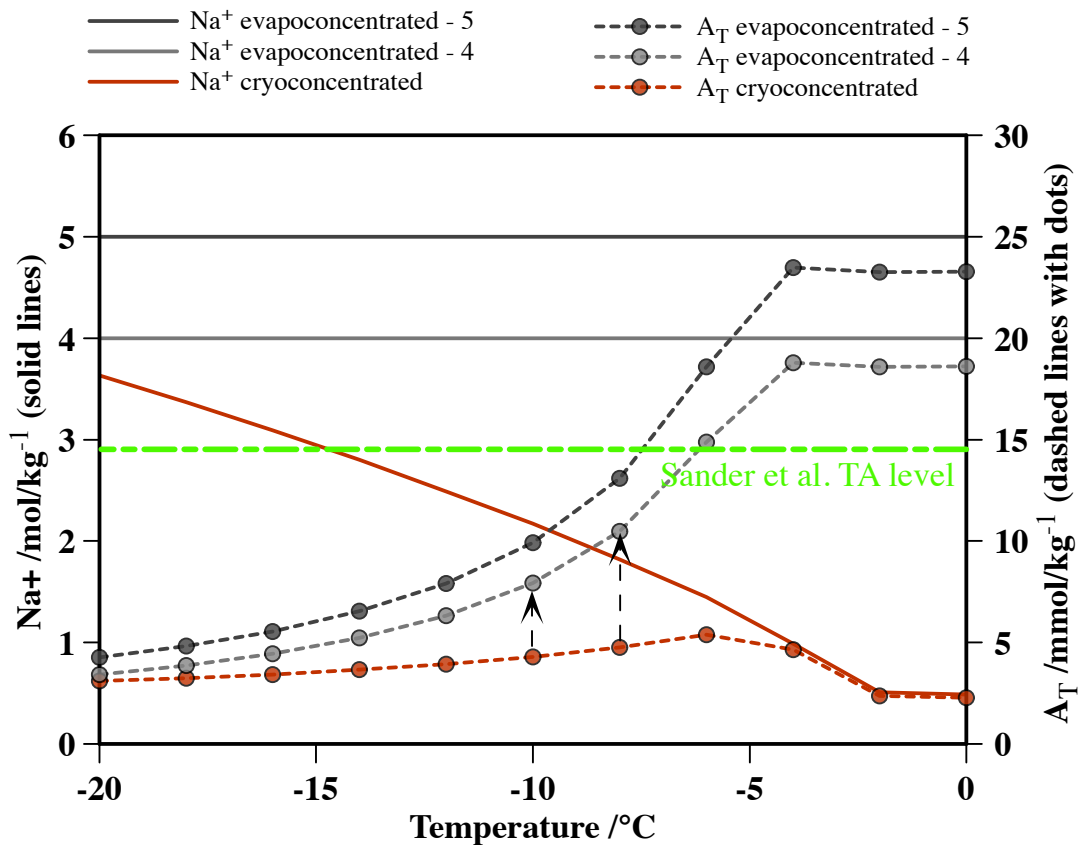Interactive comment on Atmos. Chem. Phys. Discuss., 9, 20765, 2009.

Fig. 1. A$_{\rm T}$ and Na$^+$ molalities in the brine (red curves, "cryoconcentrated") and in aerosols (grey and black curves, "evapoconcentrated") as a function of temperature.