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**Follow-up discussion
on Morin et al.**

R. Sander and S. Morin

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

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Abstract

Sander et al. (2006) proposed that CaCO_3 precipitation can be an important factor in triggering tropospheric ozone depletion events. Recently, Morin et al. (2008b) presented calculations with the FREZCHEM model and concluded that their results and interpretation cast doubt on the validity of this hypothesis. In this joint publication, we have re-analyzed the implications of the FREZCHEM results and show how they can be reconciled with the proposal of Sander et al. (2006). The chemical predictions of both approaches are consistent. Although an interpretation solely based on the alkalinity change in the brine does not support the conclusion of Sander et al. (2006), we show that the bromide/alkalinity ratio (which increases during the cooling of the brine) can be used as an indicator of the potential for triggering bromine explosions.

1 Introduction

Sander et al. (2006) proposed that carbonate precipitation in brine could be a trigger for tropospheric ozone depletion events in polar regions via the following sequence:

1. Cooling of the brine increases its salinity (cryoconcentration).
2. CaCO_3 becomes supersaturated and precipitates.
3. The loss of dissolved carbonate (the major contributor to the alkalinity A_T) reduces the buffering capacity of brine on sea ice.
4. Aerosols resulting from the brine can be acidified more easily.
5. The acid-catalyzed “bromine explosion” produces reactive halogen species (e.g. BrO) in the gas phase.
6. Halogen chemistry leads to tropospheric ozone depletion events.

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This mechanism is specific to cold regions (marine boundary layer temperatures sustained below the freezing point of water), therefore deemed potentially powerful to explain the occurrence of tropospheric ozone depletion events in polar regions. The mechanism does not necessarily have to involve aerosols (as suggested in point 4 above). Indeed, any mechanism inducing physical separation of the precipitate and the brine prior to acidification would suffice (see Fig. 1 in Morin et al. 2008b). Sander et al. (2006) supported their proposal with preliminary calculations. However, due to lack of temperature-dependent data, thermodynamic constants at 273 K had to be used. In addition, activity coefficients were not taken into account. In a recent publication, Morin et al. (2008b) presented improved calculations of CaCO_3 precipitation to test this hypothesis. The FREZCHEM model was used which is able to extrapolate thermodynamic constants into the subzero ($T < 273 \text{ K}$) temperature range, and explicitly calculates activity coefficients in concentrated solutions (Marion, 2001). After the public discussion of the ACPD paper (Morin et al., 2008a), new information became available showing that out of the polymorphs of CaCO_3 , ikaite is more likely to precipitate than calcite (Dieckmann et al., 2008). Implementation of ikaite into FREZCHEM led to less carbonate precipitation. Morin et al. (2008b) now concluded that their result “strongly contradicts the predictions of Sander et al. (2006) and casts doubts on the validity of the hypothesis originally described by these authors”. In this paper we will re-analyze the implications of the FREZCHEM results and show that they can be reconciled with the proposal of Sander et al. (2006).

2 Discussion

2.1 The effect of cooling on the alkalinity of brine

For a better comparison of the two studies, plots were created that include both the results of Sander et al. (2006) and Morin et al. (2008b). Figure 1 shows the precipitation of calcium carbonate during the freezing of sea water. The black line is the

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same as that in Fig. 2 of Sander et al. (2006). In this plot, the percentage of calcium carbonate precipitation corresponds to the ratio of the alkalinity in the brine at a given temperature to its hypothetical value if no carbonate mineral was allowed to precipitate along freezing, taken at the same temperature. The red and the orange lines show the FREZCHEM results for calcite and ikaite precipitation, respectively. It can be seen that the results by Sander et al. (2006) are very similar to the FREZCHEM results for calcite precipitation. However, when ikaite is considered, the precipitation of carbonate is lower.

The alkalinity A_T of the brine as a function of temperature is shown in Fig. 2. This plot is similar to Fig. 5 of Morin et al. (2008b) but contains two additional lines: The blue line shows A_T when carbonate precipitation is artificially switched off in FREZCHEM, and the grey line shows the alkalinity of sea water at $T=273$ K. This figure requires careful interpretation. It shows that for ikaite precipitation, A_T is always above the value at 273 K. This results from two opposing effects: 1) the alkalinity increases because the brine becomes more concentrated at lower temperatures, and 2) it decreases due to carbonate precipitation. When ikaite is formed, the precipitation does not completely compensate for the cryoconcentration effect. Although ikaite precipitation still removes a substantial fraction of the alkalinity of the brine, atmospheric particles produced from brine at subzero temperature will still have an alkalinity higher than if they were produced at 273 K. This led Morin et al. (2008b) to the conclusion that ikaite precipitation in the brine prior to aerosol generation does not deplete the alkalinity of airborne particles (with respect to particles produced from unfractionated seawater above freezing), thereby challenging the conclusions of Sander et al. (2006). Indeed, interpreted this way it is difficult to see how the mechanism presented in the introduction can trigger bromine explosions at subzero temperatures.

2.2 Introducing the $[\text{Br}^-]/A_T$ ratio

One way to overcome the discrepancy between the two interpretations is to consider $[\text{Br}^-]/A_T$, i.e. the molar ratio of bromide to alkalinity. Since bromide and acidity are both

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needed for bromine explosions, the ratio $[\text{Br}^-]/A_T$ determines how much bromine can be liberated from the solution once a certain amount of alkalinity has been neutralized. It can be considered representative of the potential for triggering bromine explosions. While cryoconcentration of the alkalinity is reduced due to carbonate precipitation, the molality of highly soluble Br^- increases considerably during freezing (Morin et al., 2008b). Figure 3 shows how $[\text{Br}^-]/A_T$ increases with decreasing temperature for both, calcite and ikaite precipitation. In the case where ikaite is set to precipitate in the FREZCHEM run, this increase is lower than for calcite, and also starts to increase at lower temperatures. Thus the temperature at which the brine is separated from the precipitate is critical. Nevertheless, the strong temperature dependence of this ratio makes this a possible explanation of the fact that ozone depletion events are mainly found in cold regions. This approach reconciles the results of Sander et al. (2006) and Morin et al. (2008b). It should be noted though, that all results and discussions presented here assume thermodynamic equilibrium. For future studies, the kinetics of precipitation and dissolution should also be taken into account, a topic which is mentioned in the current discussion of Marion et al. (2009).

3 Conclusions

A re-analysis of the FREZCHEM calculations by Morin et al. (2008b) has shown that, although ikaite precipitation is less efficiently removing carbonate than calcite precipitation, these results do not contradict the proposal of Sander et al. (2006), as long as the interpretation of the results is based on the $[\text{Br}^-]/A_T$ ratio and not just on the alkalinity of the medium where bromine activation occurs.

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References

- Dieckmann, G. S., Nehrke, G., Papadimitriou, S., Göttlicher, J., Steininger, R., Kennedy, H., Wolf-Gladrow, D., and Thomas, D. N.: Calcium carbonate as ikaite crystals in Antarctic sea ice, *Geophys. Res. Lett.*, 35, L08501, doi:10.1029/2008GL033540, 2008. 20767
- 5 Marion, G. M.: Carbonate mineral solubility at low temperatures in the Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system, *Geochim. Cosmochim. Acta*, 65, 1883–1896, 2001. 20767
- Marion, G. M., Millero, F. J., and Feistel, R.: Precipitation of solid phase calcium carbonates and their effect on application of seawater S_A-T-P models, *Ocean Sci.*, 5, 285–291, 2009, <http://www.ocean-sci.net/5/285/2009/>. 20769
- 10 Morin, S., Marion, G. M., von Glasow, R., Voisin, D., Bouchez, J., and Savarino, J.: Precipitation of salts in freezing seawater and ozone depletion events: a status report, *Atmos. Chem. Phys. Discuss.*, 8, 9035–9060, 2008a, <http://www.atmos-chem-phys-discuss.net/8/9035/2008/>. 20767
- 15 Morin, S., Marion, G. M., von Glasow, R., Voisin, D., Bouchez, J., and Savarino, J.: Precipitation of salts in freezing seawater and ozone depletion events: a status report, *Atmos. Chem. Phys.*, 8, 7317–7324, 2008b, <http://www.atmos-chem-phys.net/8/7317/2008/>. 20766, 20767, 20768, 20769
- 20 Sander, R., Burrows, J., and Kaleschke, L.: Carbonate precipitation in brine – a potential trigger for tropospheric ozone depletion events, *Atmos. Chem. Phys.*, 6, 4653–4658, 2006, <http://www.atmos-chem-phys.net/6/4653/2006/>. 20766, 20767, 20768, 20769

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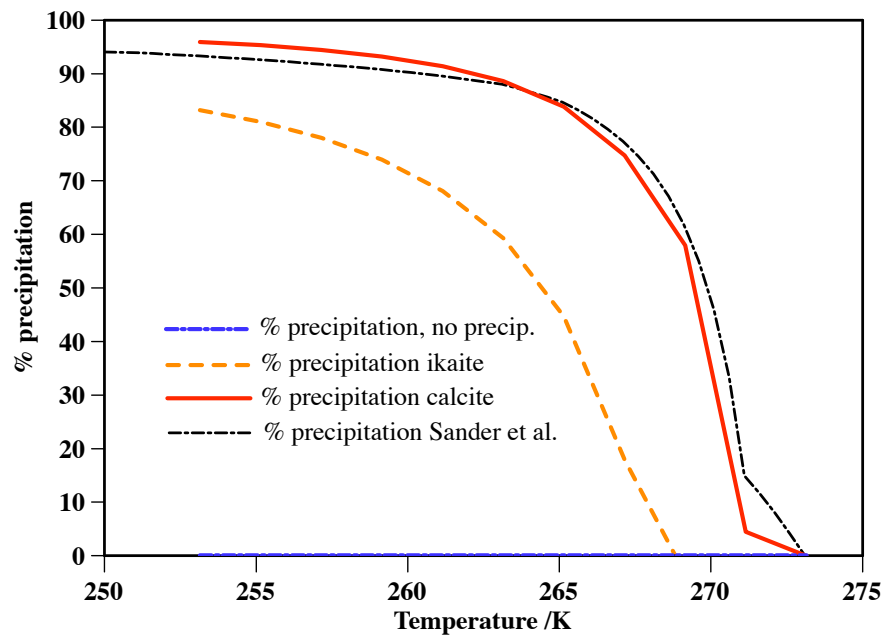
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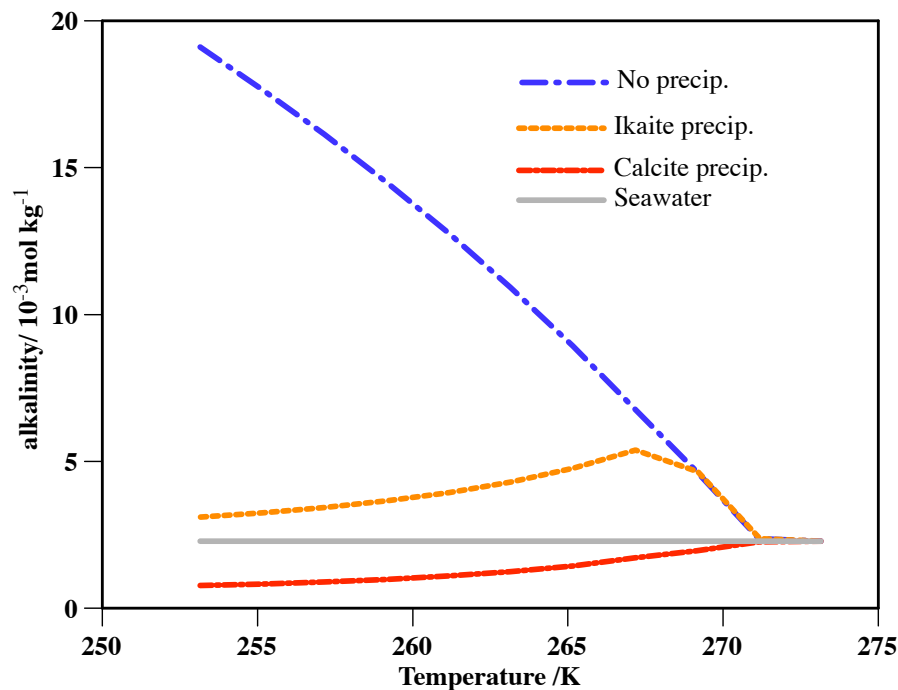
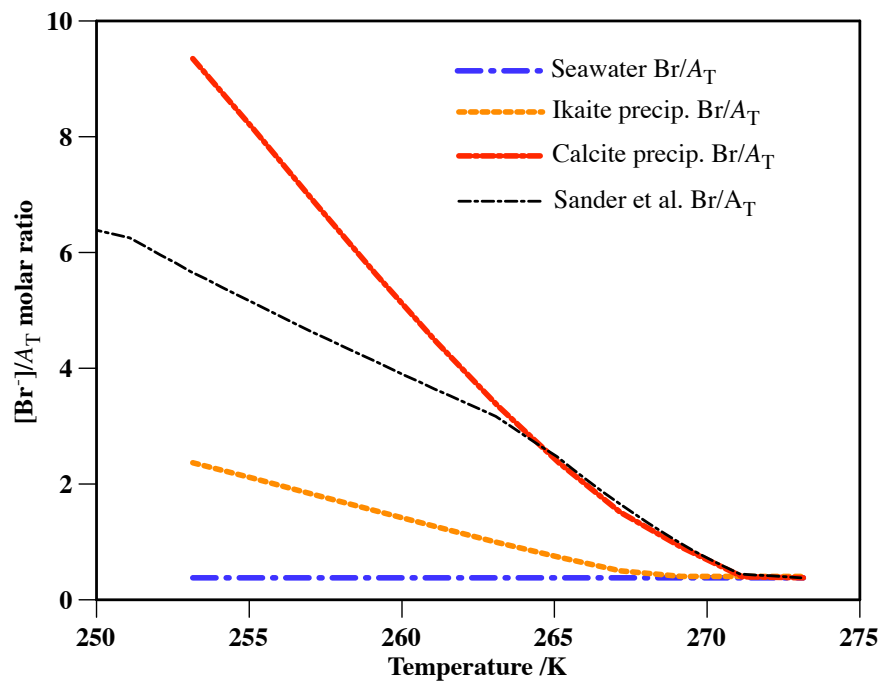


Fig. 2. Alkalinity A_T of the brine during the freezing of sea water. The definition is $A_T = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + 2[\text{CaCO}_3^0] + 2[\text{MgCO}_3^0] - [\text{H}^+]$, where CaCO_3^0 and MgCO_3^0 represent dissolved ion pairs.

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**Fig. 3.** The ratio of alkalinity to bromide during the freezing of sea water.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)