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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

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This paper aims to discuss the effects of CaCO3 precipitation in enabling the occurrence of acid-catalysed bromine explosions and resulting tropospheric ozone depletion events. That is clearly an important topic, because it is true that the community has been living with a mainly-unspoken issue: the generally accepted mechanism requires an acidity that appears difficult to achieve. The paper takes as its starting point two recent papers, by Sander et al and Morin et al. Sander et al showed (with calculations they knew to be approximate) that calcite precipitation (from brine on frozen surfaces) would cause a big decrease in alkalinity at cold temperatures. Morin et al (with more exact calculations) actually confirmed this would be the case for calcite precipitation, but pointed out that it would not be the case for ikaite precipitation, which is believed to be the pathway that occurs. In this sense, the present paper is cast in a rather odd way: the two papers do not need reconciling (as the present paper suggests); they are already perfectly reconciled if both sets of authors accept that ikaite precipitation is what occurs, so that the calculations for calcite are irrelevant (the authors might want to clarify whether they do agree on this). The main point of the current paper though is that the alkalinity is not what is important but rather the ratio of Br- to alkalinity, which does increase with decreasing temperature even for ikaite precipitation. However, the importance of this ratio is simply stated, with no discussion of why it is important. If this paper is to go ahead, the authors need to explain why they think the ratio matters. The relevant reaction is:

$HOBr + Br^- + H^+ \rightarrow H_2O + Br_2$

It seems to me that this reaction cares about the pH, which will be determined by whether the uptake of acid from the atmosphere can overcome the alkalinity. But I can see no first order reason why it cares about the ratio of Br- to alkalinity. Atmospheric acidity has to neutralise most of 3 millimolar alkalinity (according to Figure 2) before it can even start to lower pH and be effective, irrespective of what the Br- concentration is. Once it has done this, the reaction will of course be more effective if the Br- concentration is higher, and it is true that the reaction itself consumes acidity, so that a continuing supply of acid will be required if a large proportion of the Br- in the sample is to be converted. But the fact that both Br- concentration and alkalinity are somehow involved does not justify that the ratio is important.

I'd like to think I have missed the point here, and that the authors can justify the importance of the ratio. But if so they should write down the equations that make the ratio

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relevant, and show the reader why it is. If they cannot do this, then the paper does not really warrant progress to ACP.

A minor grammatical point: page 20767, line 2 “therefore deemed potentially powerful”, replace with “and is therefore considered potentially capable of explaining the. . .”

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