X-ray computed microtomography of sea ice

Comment on: A review of air-ice chemical and physical interactions (AICI): liquids, quasi-liquids, and solids in snow (Atmos. Chem. Phys., 14, 1587–1633, 2014)

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ABSTRACT

This comment addresses a statement made in "A review of air-ice chemical and physical interactions (AICI): liquids, quasi-liquids, and solids in snow" by Bartels-Rausch et al. (Atmos. Chem. Phys., 14, 1587–1633, 2014). Here we rebut the assertion that X-ray computed microtomography of sea ice fails to reveal liquid brine inclusions, by discussing the phases present at the analysis temperature.

1.0 INTRODUCTION AND DISCUSSION

Recently, Bartels-Rausch et al. (2014) published a review of the recent literature on airice interactions. In it, they state that, "using XMT is difficult when liquid is present, due to the small difference in absorption of liquid solutions and of solid ice. Hence it seems likely that the liquid features documented by Obbard et al. (2009) and Murshed et al. (2008) are to a certain degree sea salts that have precipitated at their imaging temperature of 263 K." This is misleading.

First of all, XMT is not necessarily "difficult when liquid is present." The difference in X-ray absorption between brine and solid ice is easily detectable with Oxford Instrument's SkyScan 1172 high-resolution desktop micro computed tomography system. The first scientists collecting XMT images of sea ice (Golden et al., 2007) doped laboratory saltwater solutions with CsCl in order to produce ice with enough X-ray contrast for their instrument's 8-bit camera. With the Skyscan 1172, however, the three phases - ice, brine and air - can be easily distinguished due to their inherently different X-ray attenuation characteristics and the range of intensities (4096) captured by the instrument's 12-bit camera. This is explained in our paper (Obbard et al., 2009) and is illustrated with a reconstructed grey scale image of a horizontal slice of a sample of Amundsen Sea ice showing ice (grey), brine (white) and air (black) (Obbard et al., 2009, Figure 1).

Second, at the -10 °C temperature used to obtain the results shown in our paper, the greater part of volume of the brine inclusions seen actually are liquid. This brine is so concentrated that we do not detect X-ray attenuation differences between it and the solid salts, but the fact that the largest part of the brine inclusion volume is liquid at -10 °C can be seen by reference to the phase behavior of salt solutions in the literature.

The brine volume and chemistry of sea ice are <u>clearly</u> temperature-dependent, <u>although</u> the exact freezing pathway, with respect to phases, especially precipitates, present at each temperature is still an area of controversy. In the following discussion we accept the <u>Gitterman pathway</u>, described in Marion et al., 1999. Key is that as seawater begins to freeze, at about -1.9 °C, salt ions are excluded, producing low salinity ice crystals and leaving high salinity brine in pockets and channels. As the system is cooled, the brine becomes more concentrated and salts saturate <u>and begin to precipitate</u>, when solubility limits are reached. These include mirabilite (Na₂SO₄ • 10H₂O) which begins to

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2003).

precipitate by -7.3 °C, hydrohalite (NaCl • 2H₂O) which begins to precipitate at -22.9 °C, probably gypsum (Ca₂SO₄ • 2H₂O) at -22.2 °C, and magnesium chloride at -36.2 °C (Marion et al., 1999). Mirabilite and hydrohalite would comprise the majority of the precipitate, as most of the other <u>salts</u> contribute only a tiny fraction of overall salinity. Each salt precipitates gradually over a range of temperatures, and at -10 °C this process would have only just begun.

Light et al. (2003) were interested in the effects of inclusions on the optical properties of sea ice and, in addition to conducting lab experiments, produced a model to determine temperature dependent equivalent cross-sectional area for brine pockets, tubes, gas bubbles, mirabilite crystals and hydrohalite crystals. According to their model, the equivalent cross-sectional area for all types of salt inclusions (brine pockets, brine tubes, mirabilite and hydrohalite) falls between -1.9 °C and -8.2 °C (as the brine concentration and ice crystal freezing process progresses), levels out between -8.2 °C and -21.2 °C, and then rises sharply. Also according to their model, brine inclusions (pockets and tubes) and mirabilite crystals have comparable equivalent cross sectional areas at -15 °C. At -25 °C, the hydrohalite, mirabilite, and brine tubes would have about the same equivalent cross section, about twice that of brine pockets. At -35 °C, the modeled cross sectional diameters would have dropped for brine inclusions in general (as more ice freezes out), remained about the same for mirabilite (already precipitated) but risen dramatically for hydrohalite (Light et al., 2003, Figure 16).

2.0 CONCLUSIONS

Saturated salt solutions and solid salts <u>would have very similar X-ray attenuation</u> coefficients, so <u>one cannot</u> determine analytically the phase present in brine inclusions in the reconstructed XMT images. However, an understanding of the thermodynamics of freezing seawater, <u>allows those conducting such experiments to</u> accurately predict what we are seeing. XMT is indeed an excellent method to investigate the distribution of brine in sea ice, and combined with an understanding of phase changes in sea ice can give a very good idea of liquid brine volumes and distribution. We will publish a lengthier examination of temperature dependent changes in sea ice in the near future.

3.0 ACKNOWLEDGEMENTS

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