

RESPONSES TO REFEREE #1

“The author cites precipitates and temperatures of initial precipitation from McCarthy et al. (2007), yet that work deals exclusively with single-salt binary systems, not the multi-salt system of seawater. I would suggest the author confer with Marion et al. (1999) for a more appropriate description of the species and their temperatures for this system. In particular, the work of Marion et al., casts light on the lowest temperature at which liquid likely exists in sea ice (-36.2 C, not -60C as stated on page 13169, line 11) and the absence of $\text{MgSO}_4 \cdot 11 \text{H}_2\text{O}$ in the seawater system, and the much lower temperature of the initial precipitation of KCl than the -10.7 C cited (p 13169, line 15). I appreciate that the precipitation pathway presented by Marion et al. is an alternative, but that paper also presents the previously existing paradigm for the multi-salt seawater system, which also indicates no $\text{MgSO}_4 \cdot 11 \text{H}_2\text{O}$ precipitation, and the much lower temperature of KCl formation.”

Many thanks to Referee #1 for his/her comments, and especially for the very helpful suggestion of a more appropriate citation for precipitation in the seawater system. I found its discussion of the Ringer-Nelson-Thompson pathway and the alternative Gitterman pathway especially thought provoking and have change the principle citation in the paper to Marion et al. and adjusted the text accordingly...

The brine volume and chemistry of sea ice are clearly temperature-dependent, although 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 Gitterman pathway, 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 and begin to precipitate when solubility limits are reached. These include mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) which begins to precipitate by -7.3 °C, hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) which begins to precipitate at -22.9 °C, probably gypsum ($\text{Ca}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$) at -22.2 °C, and magnesium chloride at -36.2 °C (Marion et al., 1999).

“Minor points: P13169, line 5 “and the literature?””

Agreed. This has been changed to “*in the literature*”

“P 13169, line 11: “and salt saturated and when solubility limits..” should be “the brine becomes more concentrated and salts saturate when solubility limits are reached”

Agreed and changed accordingly.

“Line 18: most of the other “cations” contribute only a tiny fraction of the overall salinity...” Why “cations”? I think should be “most of the other precipitates contribute only...””

Agreed that it should not be only cations. The sentence has been changed to read,

... most of the other salts contribute only a tiny fraction of overall salinity.

“p. 13170, Line 8: who is “we”? Obbard et al., 2009? This is confusing.”

Yes, Obbard et al., 2009, or more generally anyone doing XMT of sea ice with an equivalent system. This has been clarified in these sentences as follows:

Saturated salt solutions and solid salts would have very similar X-ray attenuation coefficients, so one cannot determine analytically the phase present in brine inclusions in the reconstructed XMT images. However, an understanding of the thermodynamics of freezing seawater, allows those conducting such experiments to accurately predict what they are seeing.

RESPONSES TO REFEREE #2

Thank you for your comment on the use of XMT to investigate the phase distribution of snow samples. My apologies for misleading you with our statement 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".

My intention was not to question your results on the identification of brine – ice – solid precipitate in sea-ice. My intention was rather to underline that the quantitative assignment of brine vs. solid ice is debated. Indeed, I'll have to leave the discussion on the particular details on quantifying liquid fraction in samples with varying molarity and composition to the experts. At the end, it might be very well the performance of different instruments that make the difference, as you suggest in your comment. Therefore, I am very thankful for your comment and suggest publication as is.

Quantifying the fraction of liquid is an important point when XMT should be applied to monitor impurities in snow or lab-grown ice as concentration in the melt might be lower than that in brine of sea-ice. The key question in context of snow research is whether the phase and distribution of impurities can be investigated without the need to refer to the phase diagram. Currently, we lack experimental proof of the phase of impurities (solution vs. participate) and of their distribution within most, if not all, samples. I think we agree that XMT is a powerful method to tackle this issue, but application to snow or lab-grown ice remains a challenge. I hope that this is the message that the reader can take home from this paragraph and that this short paragraph creates interest in the use of XMT for the ice and initiate its use to observe impurities in snow samples.

I truly regret that we did not have a change to sort this out prior to publication. I would have been happy to revise the wording and to be more precise. I hope you can accept my apologies, this happened when I shortened and restructured the manuscript from its ACPD version to be published in ACP. Personally, I feel that, despite the wording being suboptimal, a correction would not help the reader more than this comment. I truly believe that the take-home message is not altered even if most readers should be misled by our statement. But I leave this to the editor.

Thank you for your review and comments. I agree with your observation that "Quantifying the fraction of liquid is an important point when XMT should be applied to monitor impurities in snow or lab-grown ice as concentration in the melt might be lower than that in brine of sea-ice. The key question in context of snow research is whether the phase and distribution of impurities can be investigated without the need to refer to the phase diagram. Currently, we lack experimental proof of the phase of impurities (solution vs. participate) and of their distribution within most, if not all, samples. I think we agree

that XMT is a powerful method to tackle this issue, but application to snow or lab-grown ice remains a challenge. I hope that this is the message that the reader can take home from this paragraph and that this short paragraph creates interest in the use of XMT for the ice and initiate its use to observe impurities in snow samples."

This is indeed a challenge. The solution may lie in the use of two complimentary techniques, XMT and another. An interesting problem for those analyzing impurities in snow.

I too am sorry that we did not have a chance to sort this out prior to publication. It is my fault for not seeing and weighing in on your paper during its interactive discussion phase. We were in the midst of a major tragedy in my family, and I didn't get back to full productivity, and see your paper, until several months later. Hopefully the availability of both of our papers will prove instructive to the reader.

LIST OF ALL RELEVANT CHANGES MADE IN THE MANUSCRIPT

P13169, line 5 - “in the literature” changed to “and the literature”?”

P 13169, line 11 - “and salt saturated and when solubility limits..” changed to “the brine becomes more concentrated and salts saturate when solubility limits are reached”

P 13169, line 18 - “most of the other cations contribute only a tiny fraction of the overall salinity...” changed to “most of the other salts contribute only a tiny fraction of overall salinity.”

P 13169, last paragraph – it originally read:

“The brine volume and chemistry of sea ice are temperature-dependent. As seawater begins to freeze, at about $-1.9\text{ }^{\circ}\text{C}$, salt ions are excluded, producing low salinity ice crystals and leaving high salinity brine in pockets and channels (Thomas and Dieckmann, 2009). As the system is cooled, the brine becomes more concentrated and salt saturated and when solubility limits are reached (between $-2\text{ }^{\circ}\text{C}$ and $-60\text{ }^{\circ}\text{C}$), salt (or hydrate) crystals begin to precipitate (Light et al., 2003). These include mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) which begins to precipitate at $-8.2\text{ }^{\circ}\text{C}$ and 4% (by weight), magnesium sulfate $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ which begins to precipitate at $-3.6\text{ }^{\circ}\text{C}$ and 17.3%, potassium chloride (KCl) which begins to precipitate at $-10.7\text{ }^{\circ}\text{C}$ and 19.7%, and hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) which begins to precipitate at $-22.9\text{ }^{\circ}\text{C}$ and 23.3% (McCarthy et al., 2007). Mirabilite and hydrohalite would comprise the majority of the precipitate, as most of the other cations contribute only a tiny fraction of overall salinity.”

This has been rewritten to incorporate the more appropriate reference suggested by Referee #1. The paragraph now reads:

“The brine volume and chemistry of sea ice are clearly temperature-dependent, although 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 Gitterman pathway, described in Marion et al., 1999. Key is that as seawater begins to freeze, at about $-1.9\text{ }^{\circ}\text{C}$, 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 and begin to precipitate when solubility limits are reached. These include mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) which begins to precipitate by $-7.3\text{ }^{\circ}\text{C}$, hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) which begins to precipitate at $-22.9\text{ }^{\circ}\text{C}$, probably gypsum ($\text{Ca}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$) at $-22.2\text{ }^{\circ}\text{C}$, and magnesium chloride at $-36.2\text{ }^{\circ}\text{C}$ (Marion et al., 1999). Mirabilite and hydrohalite would comprise the majority of the precipitate, as most of the other salts contribute only a tiny fraction of overall salinity. Each salt precipitates gradually over a range of temperatures, and at $-10\text{ }^{\circ}\text{C}$ this process would have only just begun.”

P 13170, line 8 (Conclusions): In order to clarify our use of “we”, we have changed the original text, formerly:

“Saturated salt solutions and solid salts will have very similar X-ray attenuation coefficients, so we could not determine analytically the phase present in brine inclusions in the reconstructed XMT images. However, with an understanding of the thermodynamics of freezing seawater, we can 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.”

To read:

“Saturated salt solutions and solid salts would have very similar X-ray attenuation coefficients, so one cannot determine analytically the phase present in brine inclusions in the reconstructed XMT images. However, an understanding of the thermodynamics of freezing seawater, allows those conducting such experiments to accurately predict what we are seeing.”

THE MARKED-UP MANUSCRIPT FOLLOWS

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 air-ice 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 clearly temperature-dependent, although 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 Gitterman pathway, 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 and begin to precipitate, when solubility limits are reached. These include mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) which begins to

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precipitate by -7.3 °C, hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) which begins to precipitate at -22.9 °C, probably gypsum ($\text{Ca}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$) 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 salts 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 would have very similar X-ray attenuation coefficients, so one cannot determine analytically the phase present in brine inclusions in the reconstructed XMT images. However, an understanding of the thermodynamics of freezing seawater, allows those conducting such experiments to 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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