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Atmospheric Chemistry and Physics Discussions

Precipitation of salts in freezing seawater and ozone depletion events: a status report

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Abstract

In springtime, the polar marine boundary layer exhibits drastic ozone depletion events (ODEs), associated with elevated bromine oxide (BrO) mixing ratios. The current interpretation of this peculiar chemistry requires the existence of acid and bromide-enriched surfaces to heterogeneously promote and sustain ODEs. In a recent study, Sander et al. (2006) have proposed that calcium carbonate ($CaCO_3$) precipitation in any seawater-derived medium could potentially decrease its alkalinity, making it easier for atmospheric acids such as HNO_3 and H_2SO_4 to acidify it. We performed simulations using the state-of-the-art FREZCHEM model, capable of handling concentrated electrolyte solutions, to check the preliminary results of Sander et al. (2006). We show that the alkalinity of brine is indeed reduced to about half and a third of the initial alkalinity of seawater, at 263 K and 253 K, respectively. Such levels of alkalinity depletion have been shown to speed-up the onset of ODEs (Sander et al., 2006; Piot and von Glasow, 2008a), suggesting that carbonate precipitation could well be a key phenomenon linked with ODEs, in polar regions but also in other cold areas, such as altitude salt lakes. In addition, the evolution of the Cl/Br ratio in the brine during freezing was computed using FREZCHEM, taking into account Br substitutions in Cl–containing salts.

1 Introduction

Boundary layer ozone depletion events (ODEs) in early springtime are a widespread and recurring phenomenon in the polar marine boundary layer, both in the Arctic and Antarctic (e.g. Simpson et al., 2007, and references therein). Ozone (O_3) is known to be destroyed through an autocatalytical mechanism involving halogen radicals and oxides, in particular bromine and bromine oxide (Br/BrO). While the understanding of the gas-phase mechanism accounting for the destruction of ozone under these conditions seems to be fairly complete (Bottenheim et al., 2002), the exact nature of the medium on which Br is activated (from sea-salt brom*ide* into atmospheric brom*ine*) is

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still unresolved. Br radicals rapidly react with O_3 to form BrO. Under ODE conditions, BrO mainly self-reacts (yielding the photolabile compound Br_2) or reacts with HO_2 to produce HOBr. HOBr is water-soluble and thus is taken up into aqueous media to react with available bromide in the presence of acidity (Fan and Jacob, 1992; Fickert et al., 1999):

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \quad \text{(R1)}$$

Br_2 is highly insoluble and therefore is released into the atmosphere, where its photolysis yields two Br radicals, both of which can in turn react with ozone. By exponentially increasing the amount of atmospheric reactive bromine, this mechanism is the backbone of the so-called *bromine explosion* (Platt and Janssen, 1995) and the associated quantitative ozone destruction. The medium where reaction (R1) occurs must fulfill the three following conditions:

1. Be at the interface between the gas phase and a phase containing available bromide,
2. Have a sufficiently large surface area (accessible to gases),
3. Feature a pH low enough for reaction (R1) to significantly occur.

Simpson et al. (2007) recently thoroughly discussed the nature of media fulfilling the above-mentioned conditions. Marine aerosols, frost-flowers (or frost-flower derived aerosols) and sea-salt enriched snowpack have in common a chemical composition close to that of seawater in terms of the proportions between species. Seawater is alkaline (Zeebe and Wolf-Gladrow, 2001), and its pH is generally buffered by the carbonate system (i.e. thermodynamic equilibria between atmospheric CO_2 and dissolved CO_2, HCO_3^- and CO_3^{2-}), within 0.1−−0.2 pH-unit around an average value of 8.2 at the surface. Because of the high amount of salts dissolved in it (35 $g\,kg^{-1}$ on average), seawater does not entirely freeze solid when exposed to subzero temperature. The

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formation of ice is accompanied with a "salting-out" of ions into an increasingly concentrated brine, as temperature decreases. For example, at –10°C, the salinity of brine is 144 g kg^{-1}, which represents a four-fold increase in salinity (Richardson, 1976). Along this gradual concentration process, some salts reach their solubility threshold and start precipitating.

In a recent modeling study, Sander et al. (2006) have proposed that calcium carbonate ($CaCO_3$) precipitation in the brine at subzero temperatures could efficiently remove most of the seawater alkalinity, hence annihilating its buffering capacity. As a consequence, small amounts of strong acids present in the atmosphere (such as NO_2, SO_2 and the associated nitric and sulfuric acids) could easily lower the pH enough for reaction (R1) to proceed. Piot and von Glasow (2008a) have included this process in their modeling study on the conditions necessary to trigger and sustain ozone depletion, and have found that the alkalinity depletion rate was critical for the onset and the sustainment of ODEs. However, Sander et al. (2006) calculated the fraction of remaining alkalinity in brine as a function of temperature using the data of Richardson (1976) for major ions concentrations and computing variables relevant to the carbonate system using thermodynamic constants only valid above 0°C and for a salinity of 35 g kg^{-1}. The validity of their results might therefore be questioned, in a context of strongly non-ideal solutions where elevated activity corrections must be considered to correctly account for chemical equilibria.

In polar regions, chemical fractionation associated with the precipitation of salts primarily of marine origin significantly affects the chemical composition of aerosols. For instance, mirabilite ($Na_2SO_4{\cdot}10H_2O$) precipitation below –8°C was experimentally observed by Richardson (1976). Wagenbach et al. (1998a) found depletion of sulfate in atmospheric particles in coastal Antarctica ("negative non-sea-salt sulfate") indicating that mirabilite precipitation occurs in nature as well. Jourdain et al. (2008) made similar observation in central Antarctica. Since calcium carbonate and mirabilite are likely to precipitate under almost similar conditions, it is expected that carbonate precipitation would have a major impact on atmospheric processes likewise. Calcite precipitation

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below –2°C has been described by Richardson (1976) from seawater freezing experiments under neutral atmosphere conditions (i.e. the air surrounding the freezing seawater sample was replaced by pure N_2, hence suppressing any carbonate equilibration process with atmospheric CO_2). Except the pioneering study of Gitterman (1937) and indirect evidence presented by Papadimitriou et al. (2003), no direct measurement of the level of precipitation as a function of temperature is available in the literature for conditions relevant to sea-ice formation, in part due to the difficulty of accurately measuring carbonate concentrations in seawater by conventional techniques, especially at subzero temperatures. The effects of mirabilite precipitation on the composition of aerosols are relatively easy to measure (Wagenbach et al., 1998b). In contrast, the effect of calcite precipitation is not easily detectable in the chemical composition of aerosols. The carbonate ion cannot be easily measured in this medium and the large difference between calcium and total carbonate concentrations in seawater prevents a direct observation of this effect by looking at the concentration of calcium in aerosols, using techniques which are accurate to within a few % only.

An additional potentially important effect relevant to atmospheric chemistry, associated with precipitation of ions in seawater during freezing, is the differential behavior of halogen anions. Indeed, chloride and bromide are not expected to precipitate at the same temperatures. Assuming that bromide was never precipitating during freezing, while chloride precipitates as $NaCl{\cdot}2H_2O$ below –22°C, Koop et al. (2000) speculated that this could cause a net enrichment of bromide over chloride in the brine, thus providing better conditions for the bromine activation mechanism (Vogt et al., 1996).

In the present study, we investigate the thermodynamics of seawater brine at subzero temperatures, with a focus on the behavior of the carbonate system and on the chloride/bromide ratio. Our approach relies on the use of the molal-based thermodynamic model FREZCHEM, specifically designed to handle non-ideal solutions using the Pitzer formalism and using state-of-the-art equilibrium constants (see Marion, 2001, and references therein). This allows to predict with a much greater confidence the fate of alkalinity in brine, as a function of temperature, during seawater freezing. Taking into

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account the specific chemistry of bromide, we give more accurate estimates of the Cl/Br ratio in bulk brine, as a function of temperature.

2 Methods

2.1 The FREZCHEM model

To evaluate equilibrium chemistry for seawater freezing, we used the FREZCHEM model (Marion et al., 1999; Marion, 2001; Marion and Kargel, 2008). FREZCHEM is an equilibrium chemical thermodynamic model parameterized for concentrated electrolyte solutions using the Pitzer equations (Pitzer, 1991, 1995) for the temperature range from <−70 to 25°C and the pressure range from 1 to 1000 bars. The model is currently parameterized for the Na–K–Mg–Ca–Fe(II)–Fe(III)–H–Cl–Br–SO_4–NO_3–OH–CO_3–CO_2–O_2–CH_4–H_2O system. It includes 81 solid phases including ice, 14 chloride minerals, 30 sulfate minerals, 15 carbonate minerals, five solid-phase acids, three nitrate minerals, six acid-salts, five iron oxides, and two gas hydrates.

2.2 The carbonate system in seawater and its thermodynamic properties

The intricate chemical equilibrium between carbonate species in seawater and atmospheric CO_2 is governed by the following three equations:

$$CO_{2gas} \leftrightarrow CO_{2aq} \quad \text{(R2)}$$

$$CO_{2aq} + H_2O_{liq} \leftrightarrow HCO_3^- + H^+ \quad \text{(R3)}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \quad \text{(R4)}$$

These thermodynamic equilibria can be described by a Henry's law coefficient (K_{CO_2}, for reaction (R2)) and two dissociation constants (Ka_1 and Ka_2 for reactions (R3) and (R4), respectively):

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$$K_{CO_2} = \frac{a(CO_2)_{aq}}{f(CO_2)} \quad (1)$$

$$Ka_1 = \frac{a(HCO_3^-)\cdot a(H^+)}{a(CO_{2aq})\cdot a(H_2O_{liq})} \quad (2)$$

$$Ka_2 = \frac{a(CO_3^{2-})\cdot a(H^+)}{a(HCO_3^-)} \quad (3)$$

where a(X), referring to the chemical activity of the species X, is here taken equal to $\gamma_X \cdot m(X)$. γ_X is the activity coefficient of the species X and m(X) represents its molality (in mol kg^{-1}_{water}). $f(CO_2)$ is the fugacity of CO_2, equal to $\gamma_{CO_2} \cdot p(CO_2)$, $p(CO_2)$ being the partial pressure of CO_2.

The solubility of calcite (Ksp) and the water autoprotolysis product (Kw) are also important for the carbonate system:

$$Ksp = a(Ca^{2+})\cdot a(CO_3^{2-}) \quad (4)$$

$$Kw = \frac{a(H^+)\cdot a(OH^-)}{a(H_2O_{liq})} \quad (5)$$

Like all thermodynamic constants, K_{CO_2}, Ka_1, Ka_2, Ksp and Kw vary as a function of the state variables temperature (T) and pressure (P) only. In the case of seawater freezing at the air/sea interface, we neglect the pressure dependency, so that all true thermodynamic constants presented here depend only on temperature.

2.3 Extrapolating to subzero temperatures

Freezing seawater simulations require parameterizations of equilibrium constants to subzero temperatures. In their seminal study, Sander et al. (2006) noticed that using



published parameterizations accounting for variations of apparent thermodynamic constants as a function of temperature of salinity out of their validity range, both in terms of temperature and salinity, lead to inconsistent results. In the current study only "true" thermodynamic constants relevant to the carbonate system are extrapolated as a function of the temperature. Figure 1 shows equilibrium constants between 273 and 298 K taken from the literature (Marion, 2001; Marion and Kargel, 2008). The values at $T < 273\,K$ are simply extrapolations of the higher temperature equations. Justification and validation of these extrapolations are discussed in Marion (2001) and Marion and Kargel (2008). The key argument was that the smoothness of the curves at $T \geq 273\,K$ should extrapolate well.

3 Results

The present study focuses on the results obtained from a model run, simulating the freezing of seawater. Table 1 summarizes the data used for seawater compositions that were inputs to the FREZCHEM model, taken from a recent reevaluation of the composition of standard seawater at S=35.00 (Millero et al., 2008).

3.1 Major ions in seawater brine during freezing

The composition of seawater during freezing to 253 K, computed using FREZCHEM, is compared to Richardson (1976) data for Na^+, Cl^-, and Ca^{2+} (Fig. 2). The Na^+ and Cl^- comparisons are excellent. The model Ca^{2+} concentration deviates slightly from the Richardson value (Fig. 2). At 253 K, the Richardson datapoint for Ca^{2+} is $0.073\,mol\,kg^{-1}_{water}$, while the FREZCHEM estimate is $0.080\,mol\,kg^{-1}_{water}$. Even if we assume that all the carbonate ions had precipitated as calcite by 253 K, the residual Ca^{2+} molality in our simulation would only be reduced to $0.079\,mol\,kg^{-1}_{water}$. A possible explanation for the discrepancy in Ca^{2+} values at 253 K could be minor differences in the initial concentrations for our ions (Table 1) and the Richardson (1976) database. But, if we

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run our simulation at the Richardson (1976) Ca^{2+} concentration (0.01055 mol kg^{-1}_{water}), that only reduces the model-calculated Ca^{2+} concentration at 253 K from 0.080 (Fig. 2) to 0.079 mol kg^{-1}_{water}. Combined uncertainties on chemical analysis of brines and in theoretical thermodynamic estimates are probably the main explanation for this slight discrepancy.

3.2 Alkalinity of brine as a function of temperature

As stated in Zeebe and Wolf-Gladrow (2001), seawater alkalinity is dominated by the carbonate system. In this work, the contribution from borate and other weak acids is neglected. Therefore, we define the total alkalinity (TA, in equivalents kg^{-1}_{water}) as:

$$TA = m(OH^-) + m(HCO_3^-) + 2m(CO_3^{2-}) - m(H^+) \quad (6)$$

Application of any chemical thermodynamic model to seawater must find a way to cope with the fact that seawater is supersaturated with respect to many carbonate minerals (e.g., dolomite, magnesite, and calcite; Morse and Mackenzie, 1990; Millero and Sohn, 1992; Marion, 2001). In what follows, we will focus our attention on calcite because this is the carbonate mineral that precipitates during seawater evaporation and freezing (Gitterman, 1937; Richardson, 1976; McCaffrey et al., 1987; Morse and Mackenzie, 1990; Millero and Sohn, 1992; Marion, 2001). One can assess the degree of supersaturation by the equation:

$$\Omega = \frac{IAP}{Ksp} \quad (7)$$

where IAP is the model-calculated ion activity product and Ksp is the mineral solubility product. With the composition in Table 1, we estimated the Ω value for calcite supersaturation using the FREZCHEM model; these Ω estimates ranged from 5.7 at 298 K to 1.1 at 253 K (Fig. 3). In what follows, we use the Ω value (Eq. 7, Fig. 3) as a K_{sp} multiplier to estimate a hypothetical solution IAP. The solutions will remain

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supersaturated (no calcite precipitation) until the aforementioned hypothetical solution IAP is exceeded by the newly calculated IAP due to either evaporation or freezing. For reasons that are still unclear, calcite does not precipitate until seawater starts to evaporate (McCaffrey et al., 1987) or freeze (Gitterman, 1937; Richardson, 1976; Marion, 2001). Shortly after seawater begins freezing at –1.9°C, our model predicts calcite precipitation associated with a rapid decline in TA.

In standard seawater and in the brine during freezing, TA is dominated by carbonate species because H^+ and OH^- do not significantly contribute to it. HCO_3^- represents about 96.5% of seawater carbonates, and this proportion remains constant during freezing, within 1%. Thus, the evolution of the molality of HCO_3^- during freezing is similar to that of TA. As a consequence of carbonate precipitation in brine, the molality of HCO_3^- is reduced during freezing. Starting with 2.11 mmol kg_{water}^{-1} at 273 K, its concentration is reduced to 1.14 mmol kg_{water}^{-1} at 263 K, and 0.71 mmol kg_{water}^{-1} at 253 K. This corresponds to a decrease of 46% and 66% of TA, respectively (Fig. 4). In other words, the alkalinity of brine is reduced to about half or a third of the alkalinity of seawater at 273 K, at 263 K and 253 K, respectively. Taking into account liquid-phase equilibria and equilibrium with atmospheric CO_2 only, the pH of the brine (calculated as $-\log_{10}(m(H^+))$) monotonously decreases from 8.20 to 7.56, when temperature decreases from 273 to 253 K.

In this study, we are representing alkalinity in terms of molality (mmol kg_{water}^{-1}). We could also represent alkalinity in terms of content (equivalents); in this case, 96% of the original alkalinity is precipitated at 253 K. This is the consequence of a combination of a reduced concentration in a reduced amount of solution. Indeed for a given amount of seawater undergoing freezing, the mass of liquid water at 263 and 253 K represents only 21%, and 12% of the total mass, respectively. However the buffering capacity in brine depends on the alkalinity in terms of concentration of carbonates in solution, not its remaining content at a given temperature.

FREZCHEM predicts a larger effect of carbonate precipitation on the alkalinity of brine than Sander et al. (2006), who predicted that even at 250 K the concentration (in

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mol L^{-1}) of HCO_3^- was reduced to only half of its value at 273 K.

3.3 Br/Cl in brine

Koop et al. (2000) were the first to consider that changes in precipitation patterns between chloride and bromide would lead to a relative enrichment in bromide during freezing. In their study, they used data from Richardson (1976) (who did not include bromide measurements) and assumed as a first guess that bromide would not precipitate during freezing. As a result, the bromide concentration is enhanced in comparison with the initial seawater composition, for temperatures lower than –22°C (Fig. 5), corresponding to the precipitation of $NaCl{\cdot}2H_2O$. Simultaneously, the molal chloride/bromide ratio decreases from its "normal" value of 650 (Table 1, Millero et al., 2008), to values as low as 250 around –30°C. This is consistent with measurements by Kalnajs and Avallone (2006), who measured Cl/Br ratios between 269 and 367 in frost-flowers grown at temperature around –35°C. However, Simpson et al. (2005) did not measure such a large change in this ratio, with Cl/Br in young (a few hours old) frost-flowers on the order of 630 (unfortunately the temperature was not given in this publication).

The inclusion of the chemistry of bromide in FREZCHEM allows for a much more accurate assessment of the chemical fractionation associated with the precipitation of brominated salts. At some point, Br^- (and all other soluble salts) must precipitate during the freezing process. During seawater evaporation, Br^- precipitates as a minor substitute for Cl^- in halite (NaCl) (McCaffrey et al., 1987). The FREZCHEM model was recently parameterized to include these Br–Cl substitution reactions at T≥273 K (Marion et al., 2007). In our current study, we assumed that we could substitute hydrohalite ($NaCl{\cdot}2H_2O$) for halite at subzero temperatures. At 253 K (Fig. 5), no chloride salts have precipitated, so, the Cl/Br ratio is still 650 (Table 1). But at 248, 243, and 238 K, our model predicts that the Cl/Br ratios have dropped to 326, 211, and 175, respectively, because Cl^- precipitates more rapidly than Br^- in hydrohalite, which leads to lower Cl/Br ratios in the solution phase. Eventually, all the Br^- will precipitate in

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the same way as Cl^- in hydrohalite, sylvite (KCl), and $MgCl_2{\cdot}12H_2O$ during seawater freezing. But most of the Br^- precipitation will occur near the eutectic as the solution phase Cl/Br ratio drops precipitously. Bromide is fractionated in these precipitation reactions with initial precipitates being lowest in Br content and final precipitates being highest in Br content.

4 Atmospheric implications

4.1 Thermodynamic predictions and their applicability to atmospheric chemistry

Based on available thermodynamic data and an up-to-date model handling chemical equilibria in seawater as a complex solution, this work demonstrates that calcite does quantitatively precipitate in brine at subzero temperatures, which is then associated with a significant depletion of its alkalinity. This process operates between 273 and 253 K, so that it could be a widespread phenomenon in brine in polar regions. Results from the FREZCHEM model suggest that half of the alkalinity is depleted between 273 K and 263 K, and that two-third of it is depleted when the temperature reaches 253 K. Based on a much more solid basis than Sander et al. (2006), who calculated chemical equilibria in seawater in a simplified manner, this result is still in qualitative agreement with their model calculations.

The pH of the brine decreases from 8.20 to 7.56, when the temperature decreases from 273 to 253 K. This increase in acidity, solely due to thermodynamic equilibria in relationship with the carbonate system, does not suffice to reach the pH threshold under which reaction (R1) occurs (Fickert et al., 1999). However this effect may combine with (and even enhance) acidification due to incorporation of atmospheric acid into brine-derived media (see below).

In terms of the Cl/Br ratio in freezing brines, the FREZCHEM results are in agreement with results linked with the hypothesis that bromine precipitation does not occur during freezing (Koop et al., 2000), because bromide is a minor substitute in chloride



salts. Although this deserves to be experimentally confirmed, this is an indication that the Cl/Br ratio is likely to decrease when the temperature drops below 253 K (–20°C), consistent with some chemical observations from polar regions (Kalnajs and Avallone, 2006).

All the results presented in this article, initiated by the Sander et al. (2006) study, rely purely on thermodynamic considerations (with the notable exception of calcite supersaturation in seawater, see Sect. 3.2). There is therefore a risk pertaining to using these results as such without taking into account kinetic effects such as metastability and in particular supersaturation. For example, seawater freezing can proceed through two pathways, widely different in terms of eutectic temperatures and behavior of key species, solely depending on the equilibration time at each temperature step during freezing (see Marion et al., 1999, for details). It is not known which pathway corresponds to sea-ice formation. Although this does not influence the chemical composition of brine between 273 and 253 K, predictions at lower temperatures are impaired by this unknown.

In order for reaction (R1) to proceed, the depletion of the alkalinity in the aqueous medium is a required but not sufficient condition: the solution also has to be acidified to pH values of below about 6.5 (Fickert et al., 1999). However if a solution that is still in contact with the precipitate is being acidified, the carbonate equilibrium will shift, leading to the release of alkalinity and therefore the precipitate still acts as buffer for the pH of the solution. If, however, the precipitate is physically separated from the solution this effect will not happen anymore. For polar regions such a separation could occur if aerosol particles are blown off from the brine solution, either in form of brine droplets or frost flower fragments. Another, possibly more likely scenario, is the covering of brine with either fresh or wind-blown snow. The brine could then be sucked up in the snow but the precipitate would remain at the bottom of the snowpack. Then photochemical reactions involving the brine in the snowpack could lead to a "bromine explosion" within the snowpack and to the release of Br_2 to the atmosphere which has been observed to occur by Foster et al. (2001) and Spicer et al. (2002).

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4.2 Bromine explosion and Ozone Depletion Events

Sander et al. (2006) and Piot and von Glasow (2008a) have studied the influence of alkalinity depletion in their modeling studies on ODEs in polar regions, with the hypothesis that under reduced alkalinity conditions, acidification by atmospheric acids, such as nitric or sulfuric acids, would be facilitated. By lowering the pH this would render reaction (R1) possible, hence favoring bromine explosion and ODEs. While Sander et al. (2006) have assumed that 30% of the alkalinity was precipitated out as carbonate, Piot and von Glasow (2008a) compared the consequence of varying the amount of precipitation from 100% (base run) to 50% and 0%. Both studies showed that alkalinity depletion is required to allow a fast acidification of brine-derived media (either brine itself, frost-flowers, sea-salt enriched snow-packs, or aerosols derived from them). Piot and von Glasow (2008a) have found that the rate of ozone destruction did not significantly vary between 50% and 100% of alkalinity suppression, which brackets our model estimate of the degree of alkalinity depletion (ca. 66% at 253 K).

Carbonate precipitation could be of relevance for other regions as well. Salt lakes in cold regions including high altitude salt lakes (e.g. Salar de Uyuni in Bolivia) might provide the conditions for calcite precipitation as well, if temperatures decrease below the above mentioned threshold of about –2°C. Sedimentation could provide a physical mechanism for separation of the precipitate and the brine in salt lakes, if the lake is deep enough and vertical mixing slow, followed again by acidification either of the brine or production of aerosol particles from it. Small scale "bromine explosions" might also occur from little puddles of brine that might be present. Carbonate precipitation associated with evaporation (McCaffrey et al., 1987) could also occur in warmer areas were ODEs were reported, such as the Dead Sea (Hebestreit et al., 1999) and the Great Salt Lake (Utah, USA; Stutz et al., 2002).

Satellite images show very high BrO vertical column densities over very large regions of continental Asia in boreal spring. These extent as far South as 50° N (e.g. Wagner et al., 2001). In these regions either salty lakes (Caspian Sea) or smaller salt lakes

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would probably provide the required conditions for carbonate precipitation and therefore for facilitated bromine explosion events.

4.3 Implications for field/lab measurements

The literature on alkalinity measurements in sea-ice brine is sparse (Gleitz et al., 1995, and references therein). Gleitz et al. (1995) report field measurements of pH, temperature, salinity and total alkalinity in sea-ice cores from the Weddell Sea (Antarctica). As shown in Fig. 6, the temperature-salinity relationship in these field samples agrees well with laboratory measurements by Richardson (1976). However, Gleitz et al. (1995) did not observe a change in pH and alkalinity with temperature and salinity in these samples. It is noteworthy that, for both pH and alkalinity measurements, samples were melted to about 20°C prior to the measurements. Calcite dissolution may then have returned the alkalinity back into the solution, thus leading to non representative data. Redissolution of precipitated salts may also have affected measurements carried out on melt frost flowers (e.g. Kalnajs and Avallone, 2006, and references therein). The discovery that carbonate precipitation might strongly affect the chemical composition of most polar heterogeneous phases seems to indicate strong caveats related with how measurements should be carried out. Indeed, while filtering out crystals appears to be the best option for handling liquids (such as brine itself), it is not clear how one can in-situ filter out crystals precipitated in snow, aerosols or frost-flowers, prior to melting and undertaking chemical analyses.

As discussed before, bulk measurements of chemical parameters such as the pH of frost-flowers are likely to be hazardous to undertake. Nevertheless, what really matters is the chemical composition at the interface with the atmosphere. New insights into the pH at the surface of frozen solutions may be gained from laboratory measurements by adapting the promising interface-sensitive fluorescent probe recently developed by Clifford and Donaldson (2007). In addition, it is now established that some ions tend to segregate very close to the surface of frozen media. For instance, molecular dynamics calculations show that halides tend to be expelled from the ice matrix towards the

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ice/vapor interface (e.g. Carignano et al., 2007). Combining these approaches with the chemical composition of the brine predicted by thermodynamic considerations and governed by the precipitation of salt may shed some new light on our understanding of atmospheric chemistry in cold regions, and especially ozone depletion events.

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Table 1. Initial composition of seawater used for the simulation (S=35 00, Millero et al., 2008). The atmospheric CO_2 pressure was fixed at $0.38 \cdot 10^{-3}$ bar (380 ppmv).

	Cations Initial molality		Anions Initial molality
Na^+	0.48606	Cl^-	0.56577
Mg^{2+}	0.05474	SO_4^{2-}	0.02926
Ca^{2+}	0.01066	Br^-	0.00087
K^+	0.01058	$HCO_3^- + CO_3^{2-}$	0.00228*

* equivalents kg^{-1}_{water}, everything else are moles kg^{-1}_{water}

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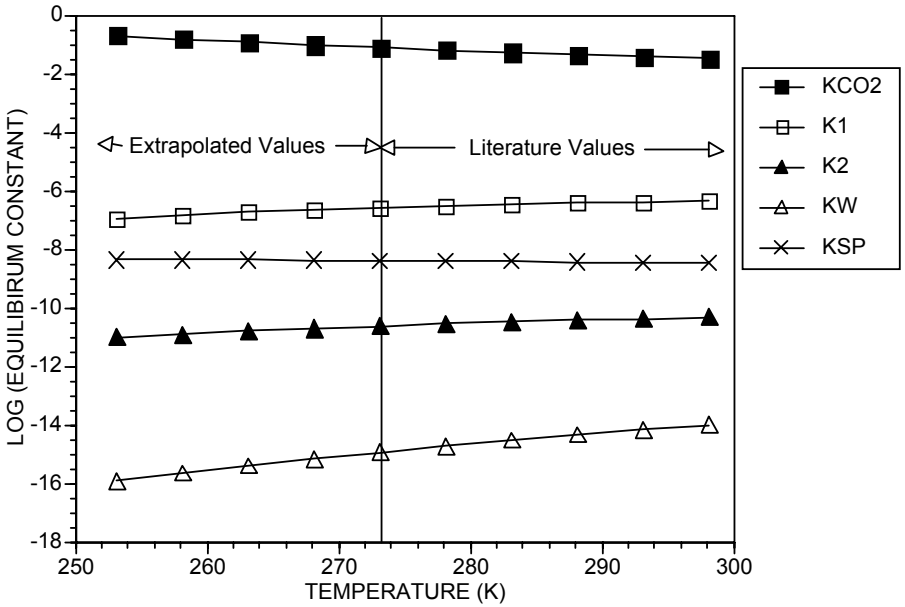

Fig. 1. Temperature dependency of thermodynamic constants relevant to the carbonate system (from Marion, 2001).

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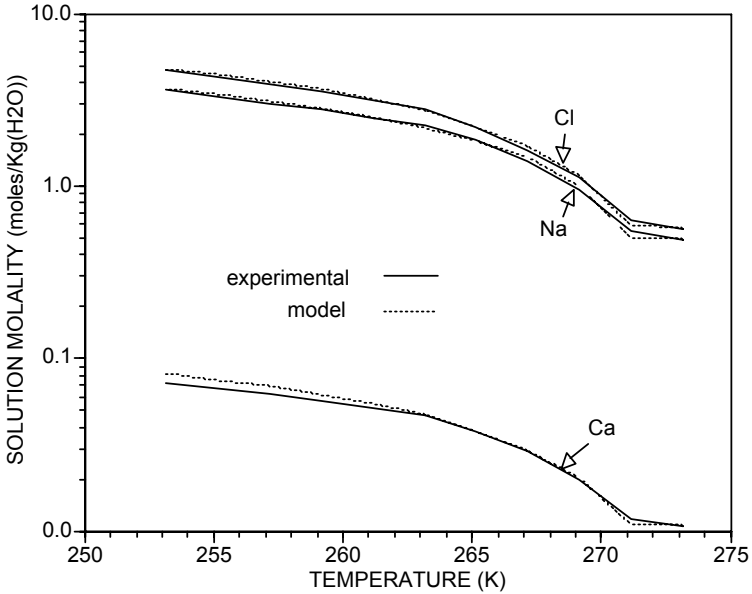

Fig. 2. Comparison of the evolution of the molality of major ions during freezing computed by FREZCHEM and measured by Richardson (1976).

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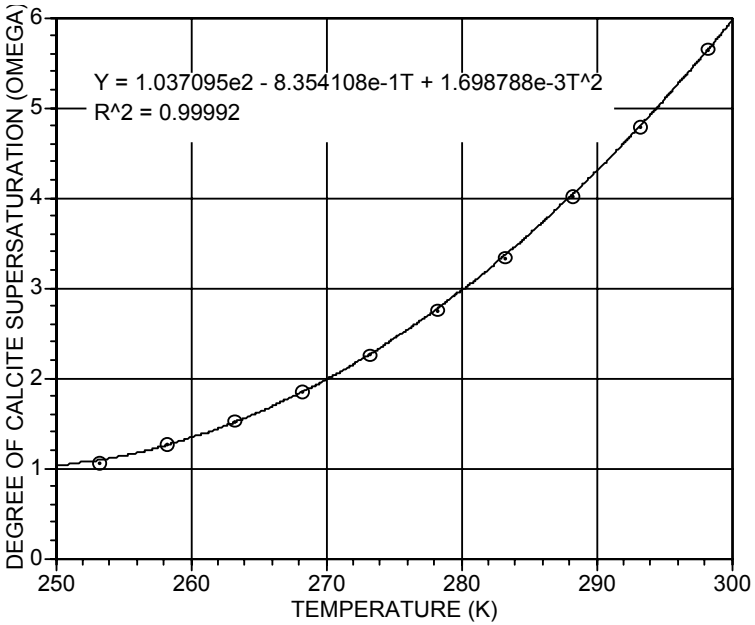

Fig. 3. Temperature dependency of the degree of supersaturation of calcite (Ω) during freezing.

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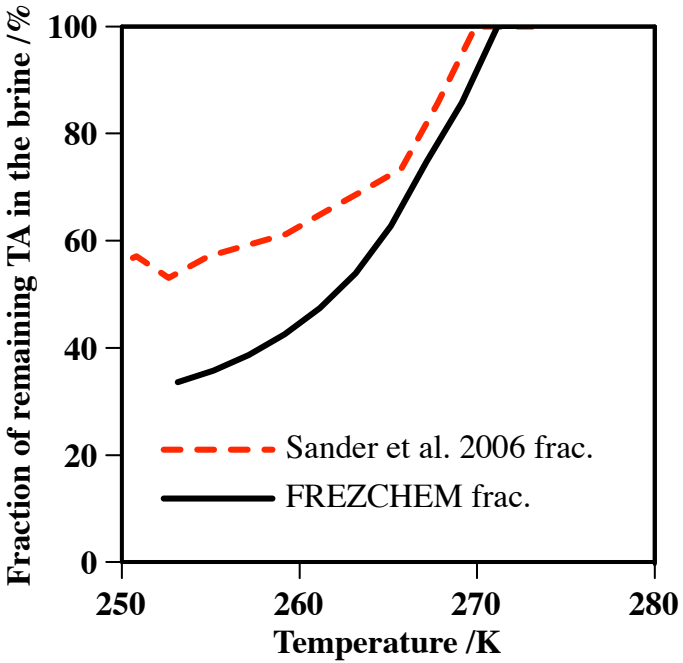

Fig. 4. Evolution of the percentage of the remaining total alkalinity (in eq kg^{-1}_{water}) of brine as a function of temperature, during freezing, calculated by Sander et al. (2006) (red dashed line) and using the FREZCHEM model (black solid line).

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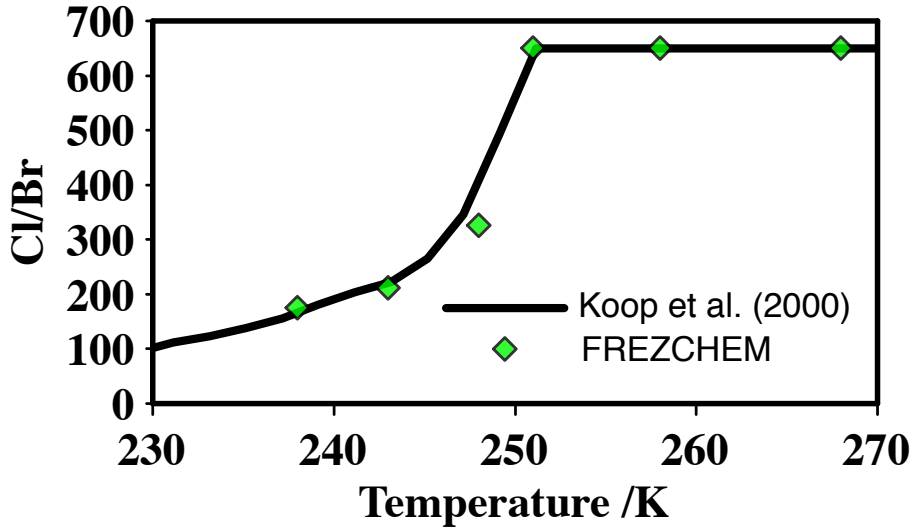

Fig. 5. Evolution of the Cl/Br ratio as a function of temperature, assuming no precipitation of bromine-containing salt (after Koop et al., 2000), and calculated with FREZCHEM.

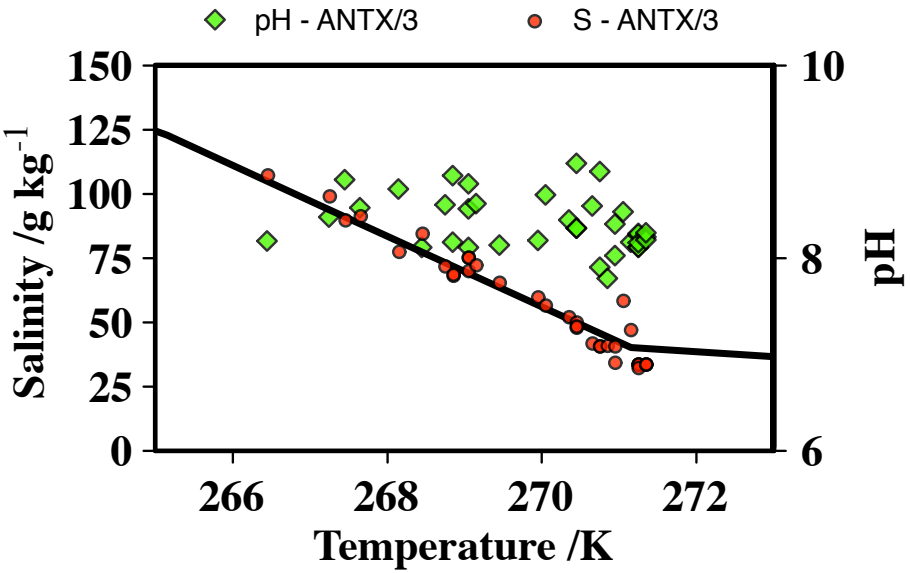

Fig. 6. Comparison of the salinity (dots) and pH (diamonds) measurements by Gleitz et al. (1995) with the laboratory determined salinity (solid line) of Richardson (1976), as a function of the temperature. Field and laboratory salinity measurements show excellent agreement. The pH does not seem to depend on the temperature (see text for details).

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