



Hydrohalite in cold sea ice: Laboratory observations of single crystals, surface accumulations, and migration rates under a temperature gradient, with application to “Snowball Earth”

Bonnie Light,¹ Richard E. Brandt,² and Stephen G. Warren^{2,3}

Received 26 November 2008; revised 6 March 2009; accepted 8 April 2009; published 17 July 2009.

[1] When NaCl precipitates out of a saturated solution, it forms anhydrous crystals of halite at temperatures above +0.11°C, but at temperatures below this threshold it instead precipitates as the dihydrate “hydrohalite,” NaCl · 2H₂O. When sea ice is cooled, hydrohalite begins to precipitate within brine inclusions at about −23°C. In this work, hydrohalite crystals are examined in laboratory experiments: their formation, their shape, and their response to warming and desiccation. Sublimation of a sea ice surface at low temperature leaves a lag deposit of hydrohalite, which has the character of a fine powder. The precipitation of hydrohalite in brine inclusions raises the albedo of sea ice, and the subsequent formation of a surface accumulation further raises the albedo. Although these processes have limited climatic importance on the modern Earth, they would have been important in determining the surface types present in regions of net sublimation on the tropical ocean in the cold phase of a Snowball Earth event. However, brine inclusions in sea ice migrate downward to warmer ice, so whether salt can accumulate on the surface depends on the relative rates of sublimation and migration. The migration rates are measured in a laboratory experiment at temperatures from −2°C to −32°C; the migration appears to be too slow to prevent formation of a salt crust on Snowball Earth.

Citation: Light, B., R. E. Brandt, and S. G. Warren (2009), Hydrohalite in cold sea ice: Laboratory observations of single crystals, surface accumulations, and migration rates under a temperature gradient, with application to “Snowball Earth,” *J. Geophys. Res.*, *114*, C07018, doi:10.1029/2008JC005211.

1. Introduction

[2] Sea ice has a substantial salt content, which distinguishes it from other naturally occurring ice types in Earth’s cryosphere. The salt is derived from the ocean from which the ice freezes. Numerous small inclusions of brine are trapped at the ice-ocean interface as the ice grows, with sizes from 10 μm to 10 mm. These inclusions can have average number densities as high as 20 mm^{−3} [Weeks and Ackley, 1982; Perovich and Gow, 1991, 1996; Light et al., 2003], and yield ice salinities up to 20‰ (parts per thousand) in young, thin ice. The presence of these inclusions within the ice causes the mechanical, thermal, structural, and optical properties of sea ice to be distinct from those of fresh ice. These properties often depend strongly on temperature, because of freezing-equilibrium relationships which dictate the fractional volumes of ice, gas, brine, and precipitated salt.

[3] Temperatures within sea ice exhibit a wide range of values. At the ice-ocean interface, the temperature is at the salinity-determined freezing point of the saltwater beneath. Temperatures at the upper surface of the ice, however, span the range between 0°C when the ice is melting and values commonly as low as −25°C in the winter, depending on the geographical location and the presence and thickness of an insulating snow cover. Present-day annual cycles for ice-covered seas include a cold season characterized by ice growth at the bottom (the ice-ocean interface) and snow accumulation on the top surface, and a melt season typically characterized by bottom ablation, and in the Arctic, significant upper surface ablation. In the northern hemisphere, the pervasive accumulation of liquid water in surface melt puddles on sea ice is a distinguishing feature of the summer melt season. While the overall pattern of this annual cycle is fairly well understood in our present climate, it may have been significantly different during other regimes in Earth’s climatic history. In particular, the “Snowball Earth” events of the Neoproterozoic (600–800 million years ago) [Hoffman and Schrag, 2002] may have been characterized by a frozen ocean with tropical surface temperatures below −30°C in all months [Pollard and Kasting, 2004, Figure 7; Pierrehumbert, 2005, Figure 2].

[4] Efforts to simulate the sequence of climatic states of a Snowball Earth event using a climate model can only be as reliable as the collective parameterizations of physical

¹Polar Science Center, Applied Physics Laboratory, University of Washington, Seattle, Washington, USA.

²Department of Atmospheric Sciences, University of Washington, Seattle, Washington, USA.

³Astrobiology Program, University of Washington, Seattle, Washington, USA.

processes they represent. Earth's climate is sensitive to the albedo of sea ice. On the modern Earth, sea ice is restricted to middle and high latitudes, where its exposure to sunlight is limited. On the low-latitude ocean of Snowball Earth, by contrast, ice would be exposed to large fluxes of solar energy, making the global climate much more sensitive to sea ice albedo. The albedo of sea ice depends on the thickness of the ice, its salt content, the persistence of surface melt puddles, and the vigor of summer melt processes that ablate, retexture, and desalinate the upper surfaces. A climate model that relies on an albedo parameterization devised and tuned for sea ice in Earth's present climate may be inappropriate for simulating sea ice in a fundamentally different climatic regime.

[5] In particular, the low surface temperatures of Snowball Earth would have precluded summertime surface melting and production of surface meltwater on ice-covered seas. Without a warm season sufficiently intense to produce liquid water at the surface, flushing processes that desalinate the ice [Untersteiner, 1968] would not have occurred. As a result, salt in the upper regions of the ice would not be routinely washed into the ocean. In contrast to the present-day situation, where the surface layers of multiyear ice are freshened by the flushing of liquid water and salt throughout the melt season, long periods of dry surface sublimation could have acted to concentrate salt at the ice surface.

[6] The major ions dissolved in seawater are the cations Na^+ , Mg^{2+} , Ca^{2+} , K^+ , and anions Cl^- and SO_4^{2-} , with Na^+ and Cl^- the most abundant. Within brine inclusions in first-year sea ice, these ions initially occur in approximately the same ratios as in seawater [Bennington, 1963]. While the bulk salinity of young sea ice is determined by the salinity of the ocean and the rate of ice growth, the salinity of an individual brine inclusion is determined strictly by the temperature of the ice. As the ice cools, freezing-equilibrium relationships dictate an increasing salinity of the brine (by freezing ice) and the precipitation of certain crystalline solids. Solids that are known to precipitate include ice, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ (ikaite), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (mirabilite), $\text{NaCl} \cdot 2\text{H}_2\text{O}$ (hydrohalite), KCl (sylvite), and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ [Ringer, 1906; Gitterman, 1937; Nelson and Thompson, 1954; Richardson, 1976; Dieckmann et al., 2008]. Ringer and Nelson and Thompson postulated that calcium in the seawater system precipitates as $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (antarcticite); however, more recent work by Marion et al. [1999] indicates that the bulk of the calcium more likely precipitates as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), in accord with the observations of Gitterman [1937]. A consequence of these two different pathways for the freezing of seawater is a discrepancy in the expected eutectic temperature of seawater (-53.8°C if antarcticite precipitates as compared to -36.2°C if gypsum precipitates [Marion et al., 1999]).

[7] The predominant salt in Earth's modern oceans is NaCl , and the most abundant salt to precipitate in sea ice is hydrohalite. In the seawater system, hydrohalite begins to precipitate at -22.9°C , and further cooling results in additional precipitation until the source of Na^+ is exhausted at the eutectic.

[8] General circulation models (GCMs) indicate that a weak hydrological cycle would have existed on Snowball Earth, with net precipitation at middle and high latitudes and net sublimation at low latitudes. In the model of

Pollard and Kasting [2004] the region of net sublimation spanned 30°N – 30°S ; in the model of Pierrehumbert [2005] it was narrower, approximately 10°N – 10°S . On the low-latitude ocean the ice would therefore usually not be covered by snow. Instead, the sublimation could result in a surface accumulation of salt crystals, in which case the physical and optical properties of these crystals would have strong implications for the surface energy budget of the ice cover.

[9] The salt composition of the Neoproterozoic oceans would have differed from that of present-day oceans; in particular, if the ocean was anoxic, sulfate would have been absent at the initiation of freezing [Schrage et al., 2002]. However, it seems reasonable to assume that oceanic composition during the Snowball Earth events would still have been dominated by Na^+ and Cl^- , as in the present-day ocean. This assumption leads us to hypothesize that a lag deposit of hydrohalite could have formed on frozen ocean surfaces during a Snowball Earth event, and this deposit likely would have caused the disposition of incident solar radiation to be notably different from that of modern sea ice. This possibility was mentioned by Warren et al. [2002, section 7].

[10] The aim of this paper is to assess some properties of hydrohalite and constrain some of the formation mechanisms of a hydrohalite lag deposit on cold sea ice surfaces. Considering the ubiquitous presence of NaCl and water on Earth's surface, surprisingly little is known about the properties of hydrohalite, either as single crystals or accumulated deposits. The mineral only persists at temperatures below 0.11°C , and has been documented in nature only in relatively rare circumstances: bottom sediments in Lake Bonney in Taylor Dry Valley, Antarctica and isolated Siberian saline lakes during winter [Craig et al., 1974]. To further our understanding of this mineral, we examine single hydrohalite crystals, present laboratory measurements of hydrohalite accumulations on laboratory-grown sea ice, and assess the likelihood of formation and survival of natural hydrohalite deposits on saline ice.

2. Hydrohalite in Saline Ice

[11] Empirical observations of the freezing-equilibrium relationships in seawater have been carried out to establish the sequence of salt precipitation, the chemical composition of precipitates, and the temperature-dependent mass fractions of ice, brine, and dissolved and solid salts as seawater cools below its freezing temperature of -1.8°C .

[12] Numerical thermochemical models of the freezing-equilibrium chemistry of seawater predict the temperature of initial precipitation and the temperature-dependent mass of the various precipitates in seawater. Spencer et al. [1990] and Marion and Grant [1994] have predicted these quantities in reasonable agreement with the empirical observations.

[13] These numerical simulations also predict freezing-equilibrium relationships for the simpler binary and tertiary systems, where observations and models exhibit excellent agreement. The NaCl - H_2O binary system is represented by the freezing-equilibrium diagram shown in Figure 1. Figure 1 describes freezing equilibrium for brine in equilibrium with ice (left-hand side), brine and NaCl (right hand

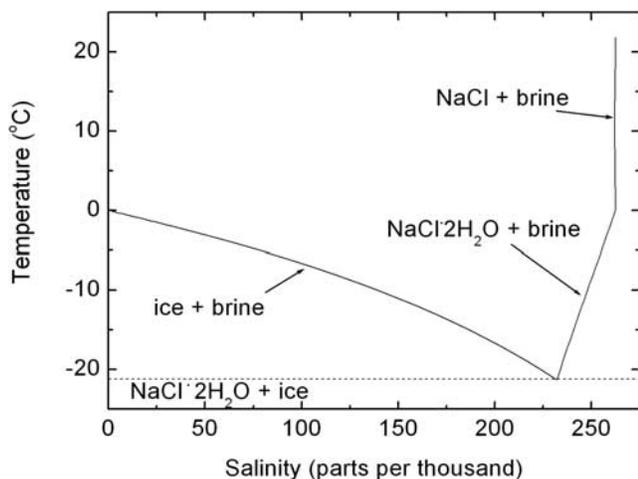


Figure 1. Freezing-equilibrium relations for the binary NaCl-H₂O system. Results from FREZCHEM [Marion and Grant, 1994].

side, temperatures greater than 0.11°C), brine and hydrohalite (right-hand side, temperatures below 0.11°C), and the ice hydrohalite eutectic (temperature -21.2°C , salinity 230‰). Hydrohalite is a stable phase in the NaCl-H₂O system below 0.11°C; above this temperature it melts incongruently to NaCl (halite) and a NaCl-saturated solution [Craig *et al.*, 1974; Marion and Grant, 1994].

[14] While the full seawater system has numerous species that precipitate, the binary NaCl-H₂O system precipitates only ice, anhydrous halite (NaCl), and hydrohalite. In the seawater system, the eutectic temperature refers to the temperature at which the entire system is solid (-36°C or -54°C , depending on which path is taken [see Marion *et al.*, 1999]). Each precipitate has a temperature of initial precipitation, and this precipitation then continues as the sample is further cooled, until one of the ions becomes depleted, limiting additional salt formation. In seawater, the major salt, hydrohalite, begins to precipitate at -22.9°C . At -30°C , 87% of the NaCl has precipitated [Richardson, 1976]. In contrast, the binary system has a simpler behavior. Above the eutectic temperature (-21.2°C), the sample is composed strictly of liquid brine and solid ice, liquid brine and solid salt, or only liquid brine, depending on the salt concentration. Below the eutectic temperature, the entire mixture is solid.

[15] Despite detailed information about the sequence of precipitation, there are few observations of the characteristics of individual crystals or of accumulations of the various precipitated salts in the seawater system. Nelson and Thompson [1954] used a 100 L container to concentrate seawater by freezing. They created a mixture of ice, brine, and precipitated salt whose solid fraction and salinity varied with temperature. They reported observing monoclinic crystals of hydrohalite that formed initially as white “spherulites” on the bottom and lower walls of the vessel. As the temperature was decreased, the spherulites increased in size and number. In addition, they began to form on the undersurface of the ice and eventually grew together into large masses of crystals in the bottom portion of the container. Spherulites also began to form throughout the

ice, suggesting that ice and hydrohalite exhibit close association. Nelson and Thompson observed that most of the ice eventually had a bright white color because of the ubiquitous presence of hydrohalite crystals.

[16] Little has been published about the physical properties of individual hydrohalite crystals since the 1800s, so we briefly review those papers here. The early workers used optical crystallography, measuring angles of numerous crystal faces, to infer the angles and axis ratios of the unit cell. All those studies were done prior to the invention of X-ray crystallography. Mitscherlich [1829] established the stoichiometry, by drying the crystals, determining that there are two waters of hydration. He also showed that the hydrates of NaCl, NaBr, and NaI are isomorphous. Frankenheim [1836] established that NaCl · 2H₂O is monoclinic. Hankel [1841] determined the axis ratios as a:b:c = 0.6044:1.0:0.8854 and the monoclinic angle as $81^{\circ}42'$, but noted that his interfacial angles did not agree with those measured by Frankenheim. Groth [1906] reviewed these papers and also quoted a personal communication from Gossner. According to Groth, Gossner reworked Hankel’s observations and determined axis ratios a:b:c = 0.6824: 1.0: 0.6367 and the monoclinic angle $109^{\circ}43'$ (corrected by Porter and Spiller [1956] to $107^{\circ}43'$). Gossner also grew his own crystals and determined unit cell dimensions that disagreed with Hankel’s: a:b:c = 1.1108: 1.0: 1.2357; $\beta = 114^{\circ}56'$. The conclusion of Groth was that either there are two different hydrates, or else the single compound NaCl · 2H₂O may exhibit polymorphism. Gossner apparently did not determine the number of waters of hydration, but he did report a measured density of 1.48 g cm^{-3} . The information from Groth was summarized by Porter and Spiller [1956]. Alternatively, Adams and Gibson [1930] carried out measurements that they used to calculate a density of 1.63 g cm^{-3} . The higher value appears to be more commonly accepted [Kaufmann, 1960].

[17] Light [1995] estimated the optical refractive index for hydrohalite using Lorentz-Lorenz theory [after Davidson *et al.*, 1986] along with knowledge of the molar refractivities of NaCl and H₂O, and Gossner’s crystal density. The resulting estimate for the refractive index was 1.43 ± 0.02 . A revised estimate using the density measured by Adams and Gibson [1930] predicts a refractive index of 1.49 ± 0.02 .

[18] Hydrohalite crystals have been identified in saline lakes of the Antarctic dry valleys by Craig *et al.* [1975]. They pointed out that hydrohalite is readily distinguished from halite by its noncubic morphology. They reported the crystals to be clear and colorless, birefringent, and exhibiting the monoclinic prism form.

[19] Perovich and Grenfell [1981] and Light *et al.* [2004] observed that the optical properties of sea ice show dramatically enhanced scattering when cooled below the eutectic temperature, and they attributed this scattering to the presence of hydrohalite crystals. Light *et al.* [2004] used an equivalent sphere formulation [Grenfell and Warren, 1999] to estimate an effective radius of $1.7\text{ }\mu\text{m}$ for the hydrohalite crystals present in their samples. Those observations considered only the bulk properties of sea ice with hydrohalite crystals suspended in brine inclusions. Little information exists about the ability and tendency of hydrohalite to

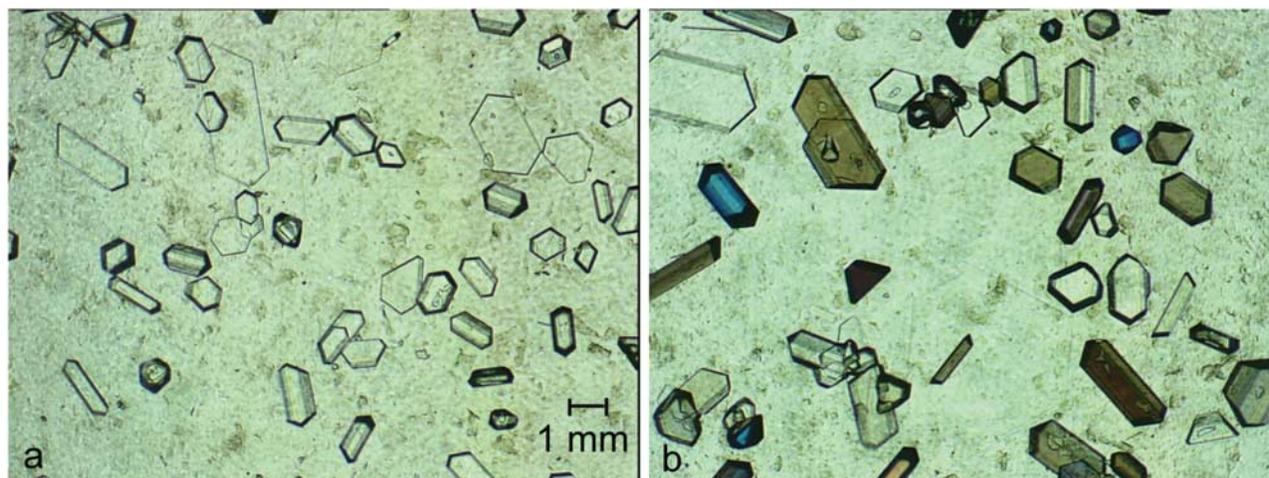


Figure 2. Images of individual hydrohalite crystals suspended in brine at -15°C , photographed in (a) transmitted light and (b) transmitted light with slightly crossed polarizers. Note that crystals appear colorless in Figure 2a but demonstrate birefringence in Figure 2b. The scale in the lower right corner is 1 mm.

nucleate, the size distributions of typical collections of crystals, or the appearance or likelihood of formation of a hydrohalite lag deposit on sublimating sea ice.

3. Experimental Approach

[20] While instances of naturally occurring hydrohalite are presently rare on Earth, samples of natural sea ice do precipitate hydrohalite when transported to the laboratory and cooled below -22.9°C [Light *et al.*, 2003]. These chilled samples are observed to take on a patchy, bright white appearance. Likewise, the precipitation of hydrohalite is evident in cold, laboratory-grown sea ice [Perovich and Grenfell, 1981]. The bright patches are caused by enhanced backscattering from hydrohalite concentrated within brine inclusions. Hydrohalite within brine inclusions has been imaged [Light *et al.*, 2003], but successful extraction of individual hydrohalite crystals has not been documented and is complicated by its close association with ice.

[21] For the purpose of isolating single crystals of hydrohalite suitable for observation, we used the binary NaCl- H_2O system to avoid the complexities of working with the full seawater system. To grow hydrohalite crystals, we used a method described by Kaufmann [1960], where solutions are formed on the branch of the freezing-equilibrium relation that maintains hydrohalite in equilibrium with saturated brine, with no ice present (right-hand branch in Figure 1). Mixtures along this branch contain loose, single crystals of hydrohalite, and these crystals were easily removed from the solution for observation. Surface accumulations of hydrohalite were also examined in the laboratory. To form a surface accumulation of salt, samples of ice were grown in a cold room laboratory from NaCl solution with salinity similar to that of seawater, in buckets that were insulated on the sides and base. The ice grew by conduction of heat vertically upward, resulting in “congelation ice”; i.e., ice formed by freezing of water to the bottom of an existing ice layer. Congelation ice is contrasted to frazil ice, in which ice crystals form in the water column and subsequently aggregate to form a cohesive layer. In frazil ice the

crystal axes are randomly oriented; in congelation ice they tend to be aligned. Both structures occur in natural sea ice floes [e.g., Weeks and Ackley, 1982].

[22] Once the ice stopped growing, it was cooled to a temperature below the eutectic temperature of the binary system. The buckets of cold ice were then kept in a subsaturated environment, encouraging sublimation. The sublimation resulted in an accumulation of salt at the ice surface. This “model” of cold sea ice was useful for studying the properties of surface deposits. The salts accumulated because the ice sublimated and because the buckets were kept isothermal, preventing the saline inclusions from migrating away from the surface. In nature, however, the formation of a deposit would only occur where the rate of sublimation exceeds the rate at which brine inclusions migrate along a temperature gradient from cold to warm. To investigate this process, experiments were also carried out to estimate rates of migration for brine inclusions under a temperature gradient.

[23] All three studies (single crystals, surface accumulations, and migration rates) were conducted in a freezer laboratory at the University of Washington; they are discussed in the following sections.

4. Single-Crystal Observations

[24] NaCl was dissolved in water at room temperature to make a saturated solution. The solution was cooled to -3°C and then filtered to remove NaCl crystals that may have formed at temperatures $>0.11^{\circ}\text{C}$. The clear filtrate was then further cooled to -15°C , following the right-hand branch of the freezing-equilibrium relations shown in Figure 1. As the solution cooled, crystals of hydrohalite precipitated, but no ice formed. At -15°C a significant mass of precipitated hydrohalite had nucleated, but some loose crystals were present at all temperatures between the melting temperature (0.11°C) and the eutectic temperature (-21.2°C). By growing hydrohalite crystals without growing ice, single crystals were easily removed from the solution for direct observation.

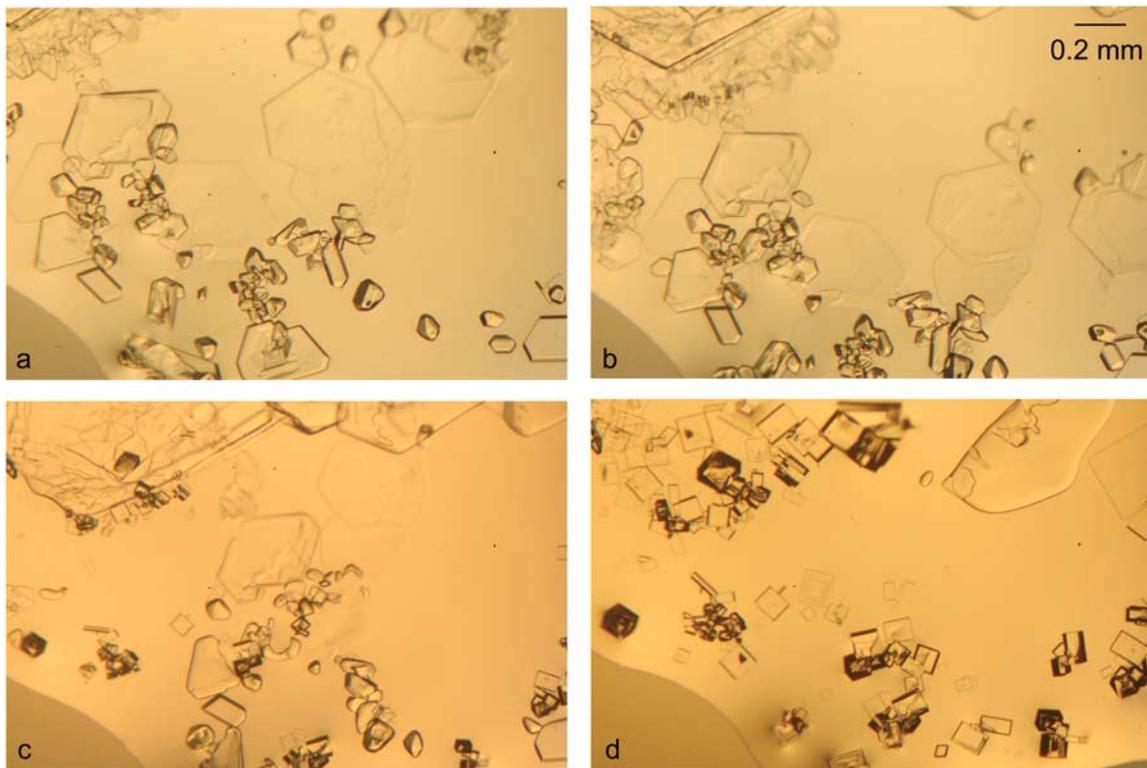


Figure 3. Image sequence showing individual hydrohalite crystals melting into halite crystals. The initial temperature was -2.1°C . The puddle that formed upon melting was saturated, so the hydrohalite crystals did not all dissolve as the temperature warmed above 0.1°C . Images were taken at (a) 0, (b) 29, (c) 42, and (d) 67 min as the room warmed.

[25] Collections of individual hydrohalite crystals were imaged through a microscope using unpolarized transmitted light (Figure 2a) or transmitted light through partly crossed polarizers (Figure 2b). The unpolarized image indicates colorless crystals with sharp edges and lengths $0.5\text{--}4\text{ mm}$. Since these crystals were grown in a container much larger than the size of a typical brine inclusion in sea ice, the observed crystal size is much larger than the sizes expected for crystals precipitating in sea ice. The colors in the polarized image indicate birefringence. Monoclinic crystals typically exhibit birefringence; cubic crystals such as halite do not. Under quiescent conditions, our observations suggest that large volumes of cold NaCl solution may become supersaturated, as we found that the solutions would occasionally need to be gently stirred to induce hydrohalite crystals to nucleate. When crystals were permitted to grow slowly in a jar, it was not uncommon to observe edge lengths of 10 mm .

[26] This method of producing hydrohalite crystals is distinct from that used by *Craig et al.* [1975], where crystals were synthesized by evaporation of a saturated NaCl solution at temperatures below 0°C . The crystals grown by evaporation, like those grown by precipitation, tended to be large, with typical edge lengths of 5 mm reported. That technique of growing crystals by evaporation also uses the right-hand side of the freezing-equilibrium curve, as no ice is formed. If, however, hydrohalite crystals are grown in the presence of ice (left-hand branch of the freezing-equilibrium curve) and temperatures are reduced below -21.2°C , the

solution forms a eutectic solid, and the hydrohalite crystals that form tend to be extremely fine grained [*Craig et al.*, 1975].

[27] An experiment was conducted to observe the melting of hydrohalite crystals into cubic NaCl crystals. Figure 3 shows a time series of four panels. In Figure 3a, a collection of hydrohalite crystals is shown assembled on a microscope slide. The crystals were extracted from bulk solution, and were placed in a droplet of saturated brine. Subsequent images show crystals being slowly warmed to their melting temperature, 0.11°C . As warming progressed, some crystals partially or completely dissolved in the brine, such that the brine maintained its temperature-determined salinity. At temperatures above 0.11°C (Figure 3d), all the hydrohalite crystals had melted to form cubic NaCl. These observations occurred within 1 elapsed hour.

[28] Experiments were also carried out to observe the stability of hydrohalite crystals. Crystals that were retained in saturated brine remained stable indefinitely, as long as the temperature remained below 0.11°C . Individual crystals removed from a saturated solution and left in the open air remained stable only so long as the air was kept saturated. The photograph in Figure 4a shows two assemblages of hydrohalite crystals after removal from the brine in which they were both grown, at -15°C . Figure 4b shows the same two assemblages after storage for 3 days at -15°C . The collection on the left of the photograph was stored in an enclosure with saturated air; the collection on the right was kept in a subsaturated environment. The saturated environ-

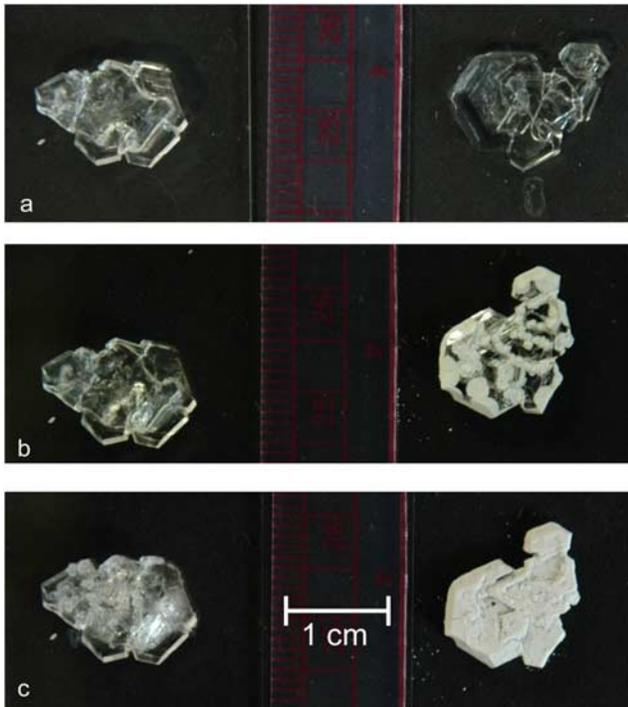


Figure 4. Images of hydrohalite crystals. (a) Two piles of crystals recently extracted from a saturated solution at -15°C . (b) The same crystals after 3 days (right) in saturated air and (left) in subsaturated air, still at -15°C . (c) The same crystals after another day in the same enclosures at -8°C . Smallest increments on scale denote 1 mm.

ment was created by placing ice along with the crystal sample in a plastic enclosure. The dry environment was created by placing the sample on a glass microscope slide in a small plastic enclosure containing desiccant. Within this time, the crystals in the saturated environment retained their translucent appearance, whereas those in the desiccated environment began to acquire an opaque white coating. Figure 4c shows the two assemblages after 1 additional day of storage at -8°C . The sample stored in the dry environment became completely coated with the white surface. A sample of the coating was scraped off the crystals and viewed under a microscope. The material appeared fractured and disorganized; no cubic NaCl crystals were identified. We speculate that this white coating results from the loss of hydration waters from the exposed surfaces of the hydrohalite crystals. These experiments suggest that the surface of hydrohalite can readily lose water if exposed to subsaturated air. This appears to happen only at the crystal surface. Even after 2 weeks in subsaturated air, the crystals retained their overall monoclinic form and appeared to have translucent interiors when broken open. The appearance of hydrohalite crystals under these various environmental conditions has implications for the albedo of cold saline ice in nature.

5. Hydrohalite Surface Accumulations

[29] Nowhere on modern Earth is sea ice known to produce significant surface accumulations of precipitated

salt. In our current climate, temperatures within the sea ice cover drop low enough for hydrohalite precipitation only during intervals in the winter and spring and only where the surface is largely free of snow. During the Arctic summer, salt near the ice surface is typically flushed into the ocean by draining surface meltwater. As a result, the uppermost regions of multiyear ice are typically almost devoid of salt. In the Antarctic, the prevalence of snow covered seasonal ice typically precludes the presence of a cold, sublimating ice surface. Where Antarctic sea ice is blown free of snow, environmental conditions sufficiently cold and dry may persist only a few days or weeks, which may not be long enough to permit the formation of a salt crust. However, under the cold, dry conditions that would have been present at low latitudes on a “hard snowball” ocean, where annual sublimation could exceed precipitation, conditions may have been favorable for the accumulation of salts at the ice surface.

[30] To observe the properties of a surface accumulation of hydrohalite crystals, we prepared samples of laboratory-grown congelation ice in the freezer laboratory. A 25‰ solution of NaCl dissolved in water was placed in round buckets (volume 11.8 L, diameter 0.276 m). The binary NaCl-H₂O system was used as a proxy for the seawater system in the laboratory-grown sea ice. The solution concentration was intentionally chosen to be smaller than the 30–34‰ generally found in the Arctic Ocean [Steele *et al.*, 2001], so as to prevent excessive concentration of salt in the bottom of the bucket as the ice grew and rejected salt into the water below. The predominant ions in the seawater system are Na⁺ and Cl⁻ (together, 86% by mass), so the binary system was expected to be a good proxy for seawater. To encourage the growth of congelation ice, the buckets were insulated on their bases and sides, causing ice growth to be predominantly at the bottom of the existing ice rather than in the water column or on the sides of the bucket. The ice cover was grown in the laboratory at -8°C . Once the ice stopped growing, the air temperature was reduced to -30°C . The lower temperature initially caused some additional ice growth into the high-salinity brine beneath the ice before the temperature of the remaining liquid cooled to the eutectic temperature. The high-salinity unfrozen liquid at the base of the ice, as well as the brine inclusions distributed throughout the ice, became eutectic mixtures of ice and hydrohalite. After storage at -30°C for a few days, the entire sample was presumed solid, although the base of the ice was never examined. It was assumed that the inclusions at least in the uppermost half of the sample had number densities and size distributions within the range expected for natural sea ice.

[31] While it was only possible to view the samples from the top surface, it was apparent that the samples took on an optically thick, bright white appearance. Previous studies have noted this appearance to be indicative of the presence of hydrohalite crystals within brine inclusions [Nelson and Thompson, 1954; Perovich and Grenfell, 1981]. The bucket samples were then stored in a frostless chest freezer. As the ice surface sublimated, the precipitated crystals of hydrohalite were left behind. As the ice continued to sublimate, the accumulation of crystals thickened.

[32] Figure 5 shows a sequence of photographs of a sample of laboratory-grown ice in various stages of salt

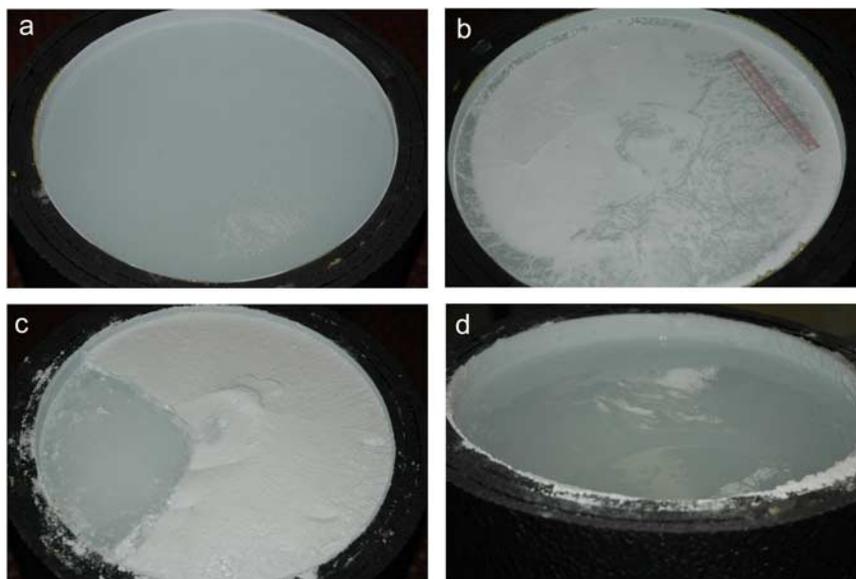


Figure 5. Bucket photos at (a) -8°C (no hydrohalite crystals), (b) -30°C (no surface accumulation but hydrohalite crystals within brine inclusions), (c) -24°C (hydrohalite surface accumulation after 6 months of sublimation in a chest freezer; partially scraped), and (d) melting surface at -20.4°C .

accumulation. Figure 5a shows a freshly grown sample at -8°C . At this temperature, no hydrohalite had precipitated within the ice. Figure 5b shows the bucket after it was cooled to -30°C for 1 day. There was no accumulation at the surface, but the ice appeared much brighter, as a result of the formation of hydrohalite within brine inclusions. Figure 5c shows a hydrohalite crust that accumulated after 6 months storage in the chest freezer. To show the contrast in appearances between the bare ice and the ice with a salt crust, a wedge of the crust was cut away. The accumulation was close to 10 mm thick in places. The bright appearance of the salt crust results from the considerable light scattering caused by the accumulation of small crystals.

[33] The texture of the salt accumulation was soft and powdery. Crystals were easily lofted from the surface by gently blown air, in contrast to the cohesive, abrasive deposits of halite on dry lakes in deserts. The powdery texture and easy dislodgement are suggestive of small crystals, consistent with the observation of *Craig et al.* [1975], where fine crystals had formed as a result of hydrohalite precipitation in the presence of ice, as would be expected to occur within individual brine inclusions. Such a fine powder could be subject to drifting by winds on Snowball Earth.

[34] Figure 6 shows a series of images documenting the appearance and texture of a laboratory-grown surface salt accumulation. Figure 6a shows a close-up view of a cutaway edge of the accumulation. At this location, the accumulation was approximately 8 mm thick. The uppermost surface of the accumulation (less than 1 mm thick) was somewhat cohesive; the lower portions were much less dense and appeared loose and flaky. Figure 6b shows a close-up view of the same crust with a knife blade inserted into the crust. It is apparent that the crust is optically thick, as it is difficult to see the blade through the approximately 1 mm thick slice of material. This image also shows how fragile the crust is, showing the bowed surface and crum-

bling material around the location where the blade was inserted. Figure 6c shows an image of loose material extracted from the accumulation. Even when disaggregated, the material appears opaque white, indicating that individual crystals are small and highly scattering. Figure 6d shows a photomicrograph of the detailed structure of a sample of this material, in unpolarized transmitted light. Spike-shaped fingers emanate from clusters of individual crystals. The smallest discernable unit appears to be pebble-shaped features with diameters of order $10\ \mu\text{m}$. The crystals shown in the crust sample are distinct in shape and morphology from the single crystals extracted from solution shown earlier in Figures 2 and 4.

[35] A sample of the loose material was taken from the surface and was placed in a beaker in the freezer laboratory. A portion of it was used as a control sample, kept at the same temperature as the bucket sample. Another portion was reserved for estimating its density and observing its properties upon rapid warming. This part of the sample was weighed immediately. A mass-volume analysis was used to estimate a bulk density for the accumulation of $0.18\ \text{g cm}^{-3}$, which, on the basis of the estimated crystal density of $1.63\ \text{g cm}^{-3}$ [Adams and Gibson, 1930], would indicate a porosity of 89%. The material was then removed from the freezer laboratory and placed at room temperature, where the low-density, flaky structure quickly transformed to a wet, saturated slurry of cubic NaCl and water. The slurry was permitted to dry overnight, and again weighed. It was found that 62.3% of the material (by mass) remained after desiccation. This is approximately the mass fraction of NaCl expected (61.9%) for a pure hydrohalite sample, indicating that the crust was composed of essentially pure hydrohalite, and did not contain significant quantities of ice.

[36] The bucket sample and the control sample were then observed as the temperature in the freezer laboratory was gradually increased. After each 1 K rise in temperature, the crust thickness was measured and photographed, and the

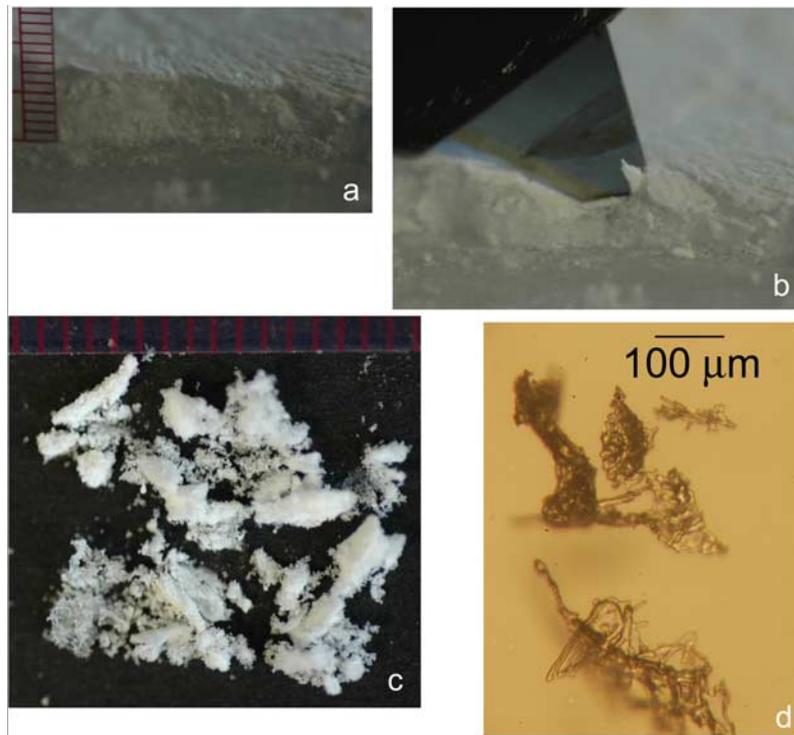


Figure 6. Photos of cutaway in crust. (a) Brackets are drawn to show the uppermost surface and the looser, more flaky part of the accumulation. The smallest interval on the scale is 1 mm. (b) The same surface as in Figure 6a, with a knife blade inserted into the crust. (c) Macro photograph of loose hydrohalite crystals. (d) Microphotograph of loose hydrohalite crystals.

crust-ice interface temperature was recorded. As the temperature rose above -21.2°C , the accumulation began to erode. Figure 5d shows the crust at -20.4°C . At the time of this photograph, the temperature of the crust had been above -21.2°C for 3 days. The crust was wet, its thickness was significantly reduced, and a surface melt puddle had begun to form on the low-lying portions of the ice.

6. Temperature-Gradient Migration Experiments

[37] The objective of the experiments in the previous section was to trace the formation and demise of a surface accumulation of hydrohalite. Of course, prerequisite to the formation of a salt crust on the ice surface is the availability of salt in the upper portions of the ice cover. Brine inclusions form at the base of the ice, at the ice-water interface, and become trapped in the ice as further growth accretes additional ice. But these inclusions are not static in the ice, as they will migrate from cold to warm areas within the ice. In the case of a cold upper surface and a warm ice-ocean interface, net downward motion of salt in the ice cover is expected, as explained below. Brine migration is slow enough that its cumulative effects may take years to show significant brine redistribution. In present-day sea ice, the events of a summer melt cycle have considerably larger effect on the distribution of salt within the ice than the relatively slow temperature-gradient migration of individual inclusions [Kingery and Goodnow, 1963]. However, on the “hard snowball” ocean, where no surface melt processes could operate, the temperature-gradient migration of brine

within sea ice may have been a significant factor for determining whatever redistribution of salts occurred within the ice. If salt inclusions migrate faster than the surface ablates, salt will not accumulate at the surface. We therefore designed experiments to measure the migration of saline inclusions within sea ice.

[38] While sea ice is growing, there exists a vertical temperature gradient within the ice. The ice-ocean interface will be at the freezing point of seawater (-1.8°C for salinity of 32‰), but the ice-air interface will be colder. Temperature gradients can be very large in rapidly growing, thin ice, but generally decrease as the ice grows thicker. During the winter, temperature gradients of 20 K m^{-1} are common in meter thick ice.

[39] Under a temperature gradient, embedded inclusions of brine will migrate from the cold end to the warm end of the ice, regardless of the direction of the gravitational field [Whitman, 1926; Hoekstra et al., 1965; Jones, 1973]. This results from the diffusion of solute along a concentration gradient within individual inclusions. A brine inclusion under a temperature gradient has solute with lower concentration at the warm end of the inclusion than at the cold end. The resulting diffusion of solute from high concentration (low temperature) to low concentration (high temperature) requires melting at the warm end and freezing at the cold end to maintain freezing equilibrium. Such melting and freezing drives the net motion of inclusions toward the warmer region of the ice. This process has been called brine pocket diffusion, or, in the metallurgical literature, temperature-gradient zone melting.

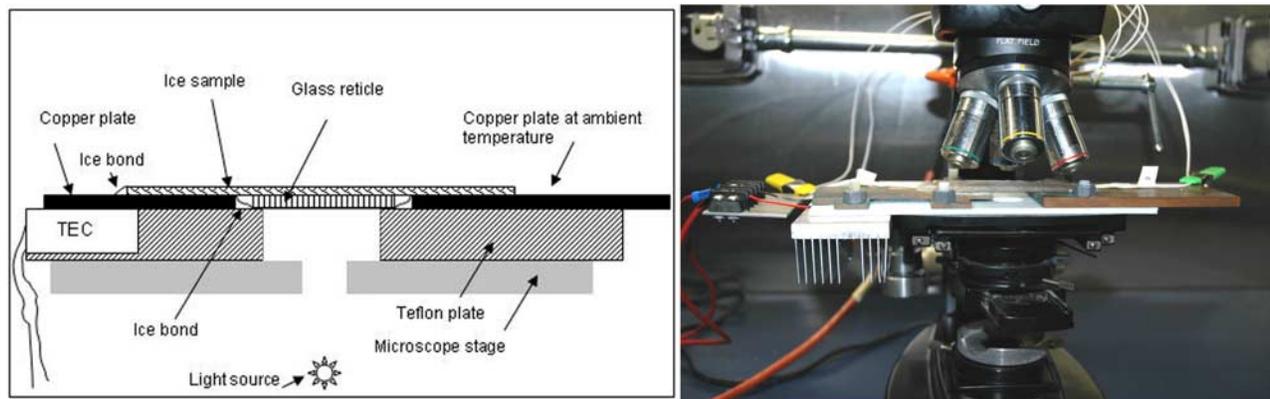


Figure 7. Schematic and photograph of temperature-gradient stage on microscope. The equipment and experimental method are described in Appendix A.

[40] Migration of salt does not require liquid inclusions. Even in subeutectic ice, salt crystals migrate under a temperature gradient. This occurs because of a layer of mobile water molecules surrounding the crystals at the ice-salt interface that is thicker at the warmer end [Wettlaufer, 1998], resulting in upward flow around the salt crystal, pushing the crystal down [Shreve, 1967]. As the temperature decreases, this layer of mobile water molecules becomes thinner, slowing the migration rate.

[41] Hoekstra *et al.* [1965] (hereinafter referred to as HOW) investigated brine pocket diffusion, in part to determine whether it could be responsible for the low salinity typically found at the surface of multiyear ice. Their laboratory observations focused on inclusions of NaCl brine and KCl brine implanted into single crystals of glacier ice. Migration of liquid inclusions, as well as subeutectic solid KCl inclusions, was documented. Their measurements were carried out between -17°C and -7°C for temperature gradients of $1-3\text{ K cm}^{-1}$. They did not study the migration of inclusions in natural sea ice, nor did they consider the

migration of inclusions containing precipitated hydrohalite, as their observations were limited to the two binary systems at temperatures above -17°C .

6.1. Experiment

[42] We have extended the experiments of HOW to lower temperatures, and in ice more representative of natural sea ice. We carried out migration experiments on individual samples of both natural sea ice and laboratory-grown NaCl ice. The apparatus is shown in Figure 7; the experimental details are given in Appendix A. An example of one migration experiment is shown in Figure 8, which is also discussed in Appendix A.

[43] Figure 9 shows the migration rates we measured, along with those that HOW reported for pure NaCl ice. Most of our data are for natural sea ice. All data have been normalized to the magnitude of the temperature gradient. Only brine inclusions whose shape remained approximately constant were included in these data, and displacements were monitored by tracking the leading edges of individual

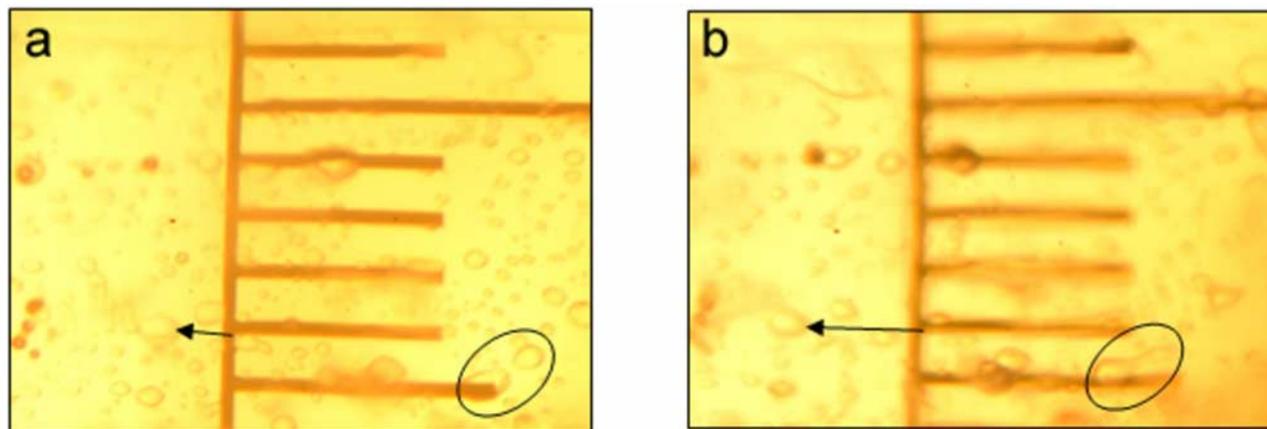


Figure 8. Migrating brine inclusions in natural sea ice. Temperature at the location of the migrating inclusions was -7.8°C ; the temperature gradient was 0.55 K cm^{-1} (high temperature on the left, low temperature on the right). Tick marks on the reticle are $100\ \mu\text{m}$ apart. (a) Before temperature gradient applied. (b) After application of a temperature gradient for 5.5 h. The arrow in Figure 8a points to the cold end of one inclusion; the arrow in Figure 8b points to the cold end of the same inclusion after it has migrated. An additional set of migrating inclusions is circled.

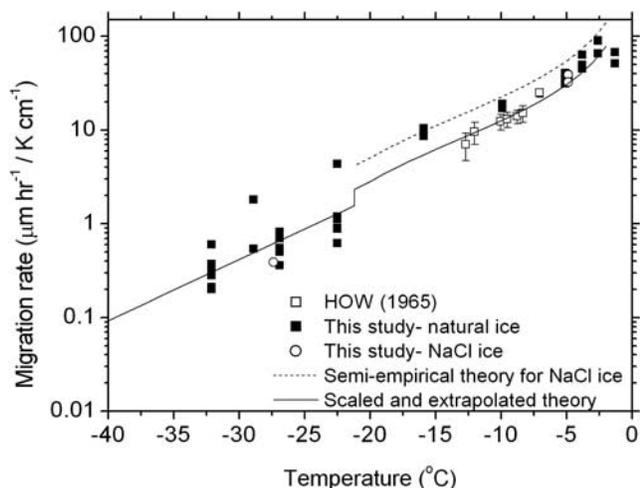


Figure 9. Observed and predicted migration rates for brine inclusions and salt crystals under an imposed temperature gradient. The semiempirical theory is a theoretical result of *Seidensticker* [1966], adjusted downward to match observations of *Hoekstra et al.* [1965] (see text).

inclusions. For each temperature studied, the progress of 1–10 inclusions was followed. These inclusions were always in the same sample (which remained mounted on the microscope stage once the experiment started), but were typically in different fields of view. As a result, the individual inclusions measured at a particular temperature were originally at roughly the same depth in the ice core, separated by no more than 10 mm horizontally.

[44] We also made some migration measurements using NaCl ice instead of natural sea ice, at -5°C and -27°C (circles in Figure 9). The data at -5°C served as a comparison between inclusions containing only the pure binary and inclusions containing the full complement of salts. Data collected on the binary system at -27°C were intended to serve as a proxy for very cold inclusions in the natural system. Inclusions near the ice surface on Snowball

Earth would often be composed entirely of ice and precipitated salt, with no liquid present. We did not have the capability to attain such low temperatures in our facility, so we simulated them with subeutectic NaCl ice.

[45] Figure 10 shows the migration of an inclusion containing only solid hydrohalite. The inclusion appears opaque, indicative of the presence of small crystals. The images were captured before and after application of a temperature gradient for 33 days, showing that the crystal moved toward the warm end of the sample (left hand side). The grid was applied to the imagery to illustrate the relative displacement. The reticle used for calculating the actual displacement is not shown on these images. In contrast to the natural ice samples, whose inclusions should contain both liquid brine and solid salt at the lowest laboratory temperatures, the NaCl ice sample in Figure 10 should have contained only solid hydrohalite and ice. However, it does appear that some of the inclusions surrounding this crystal inclusion, in the same field of view, are liquid and therefore likely supersaturated solutions that had not yet precipitated hydrohalite (arrows in Figure 10).

6.2. Comparison With Theory

[46] It would be valuable to have a theory to explain the measurements, and to use for extrapolating our results to temperatures lower than those measured. We use the theory of *Seidensticker* [1966], who attempted to explain the HOW measurements. This method requires knowledge of the diffusivity of NaCl. As there are no direct measurements in the necessary temperature and concentration ranges, *Seidensticker* determined diffusivity following the method of *Robinson and Stokes* [1959], which requires both the activity coefficient of a NaCl solution, and the limiting electrical conductivity at infinite dilution of the Na^+ and Cl^- ions. We used the temperature dependence of the concentration of a freezing NaCl solution reported by *Hall et al.* [1988] to determine the activity coefficient by applying the parameterization of *Archer* [1992]. The temperature dependence of the viscosity of pure water [*Cho et al.*, 1999] was needed along with concentration to determine limiting

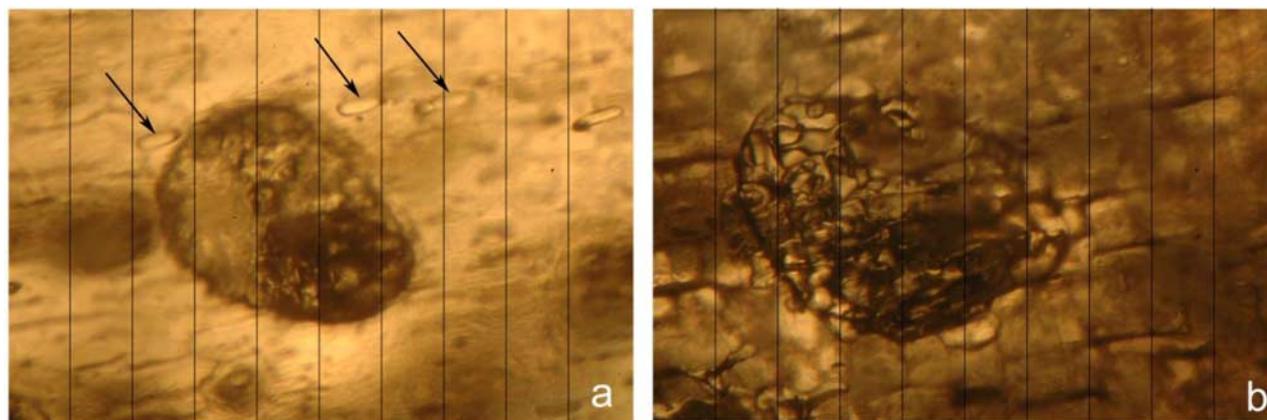


Figure 10. Migrating feature in the binary NaCl-H₂O system at -27.4°C . The large oval inclusion is a mass of solid hydrohalite crystals. The temperature gradient is from right (cold) to left (warm). (a) Before temperature gradient applied. The small inclusions indicated by the arrows appear to be liquid. (b) After application of temperature gradient for 33 days. The arbitrary grid was placed on the image to illustrate net displacement of the migrating feature since the reticle was not imaged in these two photographs.

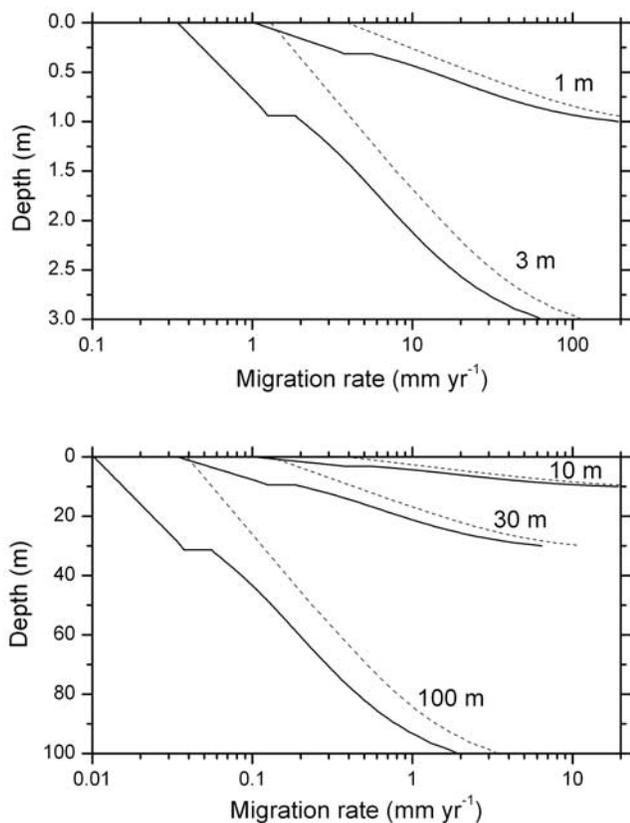


Figure 11. Computed migration rate of brine inclusions as a function of depth, in ice of various thicknesses, with temperature increasing linearly from the top surface at $T_s = -30^\circ\text{C}$ to the bottom surface at $T_f = -2^\circ\text{C}$. Solid line is computed using the solid line in Figure 9. Dashed line is computed using the dashed line in Figure 9, extrapolated through the highest data points at -22° and -28°C , to provide an upper limit to migration rates.

electrical conductivity using the parameterization of *Anderko and Lencka* [1997].

[47] *Seidensticker's* [1966] results paralleled the measurements of HOW for both KCl and NaCl, but were too high. The experimental results for NaCl could be matched by scaling the theoretical result by the factor 0.56. *Seidensticker* thought this mismatch might be caused by inadequate knowledge of the ionic diffusivity and its dependence on temperature and concentration. Our results using *Seidensticker's* method, but with the updated data indicated in the previous paragraph, gave results very similar to those of *Seidensticker* (dashed curve in Figure 9). We scaled the dashed line down by the factor 0.56 to obtain the solid curve passing through the HOW results.

[48] *Seidensticker's* [1966] theory is applicable only for liquid inclusions. However, for KCl, the same trend of migration rate on temperature appears to continue below the KCl eutectic (-11°C) in the HOW data. There is a discontinuity at the eutectic temperature, accurately measured in the KCl data of HOW, such that the migration rate of a solid KCl crystal is smaller than that of a liquid KCl inclusion, by the factor 0.65. We assume this same fractional discontinuity for NaCl, and then extrapolate below the eutectic temperature in Figure 9 with a straight line

whose slope is obtained by fitting a line to the scaled theory between -6°C and -21°C .

[49] Because of the unexplained adjustments and the extrapolations by analogy that were required to develop the semiempirical theory, we offer it just as a guide for what we might expect the behavior to be for NaCl ice, and of course natural sea ice could behave differently. This extrapolation was done before we began the experiments, when we had only the HOW data, and Figure 9 shows that extrapolation of the adjusted semiempirical theory does fall within the experimental results we now obtain.

6.3. Discussion of Migration Rates

[50] The migration of liquid brine and precipitated salt inclusions in ice was measured for temperatures between -3°C and -34°C (Figure 9). The migration rates range from 0.2 to $100 \mu\text{m h}^{-1}(\text{K cm}^{-1})^{-1}$, faster at high temperature. In a natural ice cover, the actual migration would be expected to occur at almost all of the observed rates at some location in the ice, at some time. Inclusions near the relatively warm ice-ocean interface would always migrate fastest; inclusions near the top ice surface would migrate much more slowly during the cold season. The observed rates appear to be small relative to plausible sublimation rates. The fastest migration rates would occur near the ice surface in warm, thin ice. Figure 11 shows migration rates computed as a function of depth in ice of thickness 1–100 m, using a surface temperature of -30°C , which is considered typical for the equatorial ocean during the cold phase of a Snowball Earth event [*Pollard and Kasting, 2004; Pierrehumbert, 2005*]. The solid line in Figure 11 was computed using the solid line in Figure 9. We also compute an upper limit to the migration rates, by using the dashed line in Figure 9 and extrapolating it through the highest data points at -22 and -28°C . We can then compare these rates to expected sublimation rates. On the “hard snowball” ocean, the net sublimation at the equator might be $\sim 3 \text{ mm a}^{-1}$ [*Pollard and Kasting, 2004, Figure 9*]. When the ice thickness reaches 10 m, which should occur within a few years, the “upper limit” migration rate is $< 1 \text{ mm a}^{-1}$ in the top 2 m of the ice; i.e., smaller than the sublimation rate. With sustained low surface temperatures, the ice would thicken, the migration would become much slower, and the propensity to accumulate salts greater. It therefore seems unlikely that brine migration could outrun the advancing sublimation front on a sea ice surface at low latitude on Snowball Earth.

[51] The migration rates reported here show substantial variability for inclusions measured at the same temperature, and are somewhat higher than the earlier measurements of HOW in the overlapping temperature range. The variability among measured migration rates for different inclusions at a single temperature was, in some cases, nearly a factor of 10 (e.g., see the data for -22.5°C , where values extend from 0.6 to $4.3 \mu\text{m h}^{-1}(\text{K cm}^{-1})^{-1}$). The observed variability in the present study may be attributed to uncertainties in experimental methods, including the accuracy and repeatability of measuring small displacements, the effects of fluctuations in temperature, and differences in composition of inclusions. It may be that at $T < -23^\circ\text{C}$ the faster migration rates result from supercooled brine which has not yet nucleated hydrohalite crystals.

[52] With regard to variation in the composition of individual inclusions, *Harrison* [1965] pointed out that dissolved gases may play a role in the migration of brine inclusions, which would not necessarily be expected to be uniform across inclusions, even within a single sample. While some brine inclusions clearly nucleate an enclosed gas bubble, others appear not to. The effect of included gas bubbles on brine migration has not been studied. This is a separate issue from the migration of gas bubbles directly in ice, as would be observed in glacial ice [e.g., *Stehle*, 1967]. Other variations in the composition are related to the salt content of individual inclusions. Inclusions in natural sea ice have more complex chemistry than the pure NaCl-H₂O inclusions studied by HOW.

[53] In natural sea ice, brine embedded within the ice would be expected to have uniform ionic composition, such that the abundance of individual ions is exclusively a function of temperature. Variations in the ion content of individual brine inclusions at the same temperature could occur where the fraction of precipitated solid deviates from that predicted by freezing equilibrium. Since the onset of both ikaite and mirabilite precipitations occur above -8.2°C [*Marion and Grant*, 1994; *Richardson*, 1976; *Marion et al.*, 2009], some quantity of precipitated salt would be expected to exist at all lower temperatures. If any of the salt fails to nucleate and the brine becomes supersaturated, this would lead to variations in the ionic content of the brine. The delayed precipitation of hydrohalite within cooling brine inclusions has been described previously [*Light et al.*, 2003] and could cause variations in the salt content of the brine. Furthermore, the size or number of any precipitated crystals could vary significantly between brine inclusions, as these properties could be closely associated with brine inclusion size. Observations by HOW and *Harrison* [1965] discerned no dependence of migration rate on inclusion size. This was true even for cases where the diameter of adjacent inclusions differed by a factor of 3. But those studies were carried out in the pure binary system at temperatures above the onset of hydrohalite precipitation.

[54] Inclusion size could, however, be important beyond the dynamics of the melting and freezing processes involved in brine pocket migration. Large inclusions that extend into the colder portion of the sample could have different chemical equilibrium than neighboring inclusions that do not extend so far. Efforts were made to sample migrations at temperatures other than the onset temperatures of mirabilite and hydrohalite precipitation. The effect of these factors on the migration of brine inclusions has not been studied. However, HOW showed that for KCl, once the binary cools to the eutectic temperature, the migration rate of the solid inclusion is considerably slower than the liquid inclusion. This result suggests that the presence of precipitates could significantly slow the migration speed of brine inclusions.

[55] The migration experiments carried out by HOW considered only NaCl and KCl brines artificially introduced into single crystals of glacial ice. The advantage of their approach is that it examined the question of temperature-gradient migration in the context of simplified chemistries within a simplified ice structure. Their results showed that KCl brine migrated faster than NaCl brine, so we expect that the migration of seawater brine with the full complement of salts would not be identical to either binary system.

[56] For most of our work we used natural ice samples cut from thick, first-year congelation ice, rather than samples cut from laboratory-grown NaCl ice, for two reasons: they contain the full complement of salts found in natural seawater, and they tend to have more uniform, vertically oriented structural properties than samples grown in the laboratory. However, we did carry out some experiments with laboratory-grown NaCl ice, for comparison with the earlier results of HOW. Observations taken on natural ice indicate higher migration rates than those made on NaCl brine by HOW for the temperature range where they overlapped, -7 to -13°C (Figure 9). This was not surprising, since HOW had found KCl inclusions to migrate faster than NaCl inclusions, by a factor of ~ 2.4 . Surprisingly, our migration measurements of the pure NaCl system were found to have rates identical to our measurements of the full seawater system at -5°C .

[57] Samples of laboratory-grown NaCl ice were also used to study the migration of inclusions known to be composed exclusively of a eutectic salt-ice mixture with no liquid present. This experiment would have been difficult to do with natural ice in the laboratory, because natural sea ice inclusions do not become completely solid until cooled to -36°C or below, and our laboratory could not be maintained so cold. Solid, subeutectic NaCl inclusions were thus used as a proxy for solid, subeutectic seawater inclusions.

[58] For binary solutions, a sharp reduction in migration rate is expected once liquid inclusions become solid. HOW observed this transition for the KCl-H₂O system. In the natural seawater system, there should always be some solid precipitate in each brine inclusion at temperatures below the initial precipitation of mirabilite. It is not clear to what extent the migration of standard seawater brines, which are dominated by NaCl, are affected by the presence of other ions, but we do expect differences in the migration rates of inclusions that contain liquid brine and those with only solid salt.

[59] However, the result shown in Figure 9 indicates that the migration rate for the solid NaCl-2H₂O inclusion (open circle at -27.4°C) is comparable to results at approximately the same temperature for inclusions in natural ice, which presumably contained liquid brine. One possible explanation for this result is that the natural ice inclusions had largely precipitated and the small amount of liquid brine left had little effect on the migration of the inclusions. There is a range of migration rates for the natural samples at each temperature measured. This range may result from varying degrees of precipitation. It is also possible that the natural samples contain impurities in the brine which are capable of altering the migration rate.

6.4. Off-Axis Migration

[60] There may also be structural reasons for the range of observed migration rates and the distinction between migration rates in natural sea ice and migration rates in the samples studied by HOW. While HOW found migration rates to be independent of crystal orientation, their inclusions were artificially introduced into pure ice samples, and single inclusions were not arranged in linear strings with preceding and trailing neighbor inclusions. *Harrison* [1965] observed migration rates to be independent of the angle

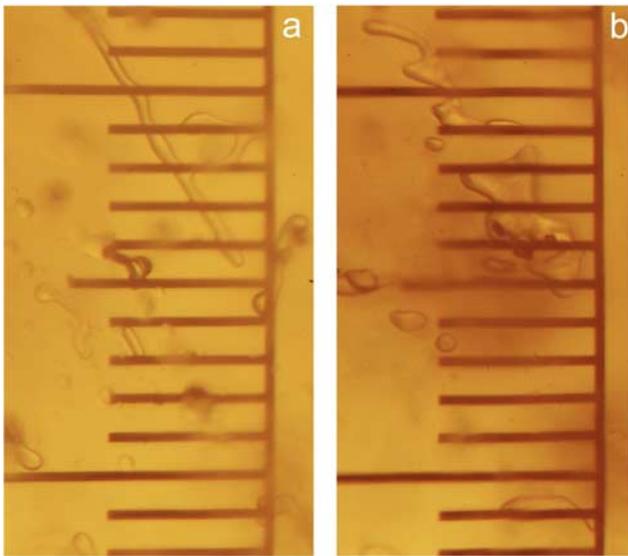


Figure 12. Migrating brine inclusion in “off-axis” ice. The temperature gradient is from right (cold) to left (warm). (a) Before temperature gradient applied. (b) After application of temperature gradient for 75 h. Tick marks on the reticle are 100 μm apart.

between the temperature gradient and the *c* axis of the host crystal for inclusions of NaCl or KF. In our studies, natural ice samples were desired so that the temperature gradient could be applied in the same direction as the ice growth. This meant that the *c* axes were aligned perpendicular to the temperature gradient, and ice crystal platelets (containing the *a* axis) aligned parallel to the temperature gradient. Strings of brine inclusions developed parallel to the temperature gradient, and the long axis of each inclusion was typically parallel to the temperature gradient. We decided to investigate whether there is a tendency for inclusions to migrate more rapidly when the temperature gradient is aligned with platelet boundaries that separate strings of brine inclusions. Although the mechanism would be different, an analogy could be made to the deformation of glacier ice preferentially by shearing on basal planes.

[61] We therefore observed the migration of brine inclusions in a sample where the *c* axis was intentionally misaligned. *Harrison* [1965] found brine inclusions occasionally to migrate along a direction other than the direction of the temperature gradient. In those instances (about 5% of the total), the inclusion migrated preferentially along the *c* axis.

[62] In our experiment, a sample was mounted with *c* axis $\sim 40^\circ$ from the direction of the temperature gradient (by contrast, all samples shown in Figure 9 were mounted at approximately 90°). When a temperature gradient was applied to this sample, the inclusions began migrating along the temperature gradient, across the platelet boundary (Figure 12). In the process, the inclusions formed instabilities and divided into smaller inclusions. The observed migration rates for these “off axis” inclusions were approximately an order of magnitude smaller than the rates for samples with *c* axis perpendicular to the temperature gradient at comparable temperature. This experiment did not demonstrate migration along a direction other than that of

the temperature gradient (in contrast to *Harrison*’s), but does suggest that migration is slowed considerably when not along the platelet boundary. Furthermore, this was the only instance where we observed inclusions to break apart when a temperature gradient was applied. HOW often observed breakup of the artificial inclusions of brine that they created in fresh ice, but their inclusions were initially much larger than those found in natural sea ice.

7. Further Discussion of Migration Rates and Surface Crusts

[63] Our migration rate observations suggest that migration in cold ice is sufficiently slow that accumulation of salt at the ice surface can be expected on the low-latitude ocean during the early stages of a Snowball Earth event. This accumulation would alter the optical properties of the ice cover, enhancing the surface albedo. In the laboratory, the accumulation of fine-grained salt crystals at the ice surface caused increased backscattering. The details of this increased backscatter depend on inherent optical properties of the crystals, crystal grain sizes, crystal shape, and the density of the accumulation. Reflectance measurements have begun; they will be reported elsewhere.

[64] The photographs of the sublimation lag deposit in Figure 6 indicate characteristic crystal sizes 5–100 μm in diameter. These crystals are considerably smaller than the crystals shown in Figures 2 and 3, which had been grown from bulk solution. Crystals grown in bulk solution precipitate at temperatures above the eutectic as the solution saturates, without simultaneous formation of ice. By contrast, crystals forming a surface accumulation nucleated in small brine inclusions as the ice temperature dropped below the eutectic temperature, so their size was limited by the salt content of the inclusion. They also appear to be less regular in shape (Figure 6d).

[65] In the sublimation experiments reported here, a loosely arranged structure of hydrohalite crystals was left to accumulate as the ice surface sublimated. The bulk density of the accumulation probably depends on the bulk salinity of the ice. High-salinity ice would have more and/or larger hydrohalite crystals, possibly resulting in a higher-density crust. When exposed to the atmosphere, other processes such as wind drifting would affect the density. In the laboratory, crystals in the accumulation were easily lofted.

[66] Analysis of the crust material from NaCl ice indicates that it was composed largely of hydrohalite. Relative to the mass of the freshly sampled crust, the dried portion of the crust was found to be slightly heavier than expected for pure hydrohalite. This suggests that there may have been some impurities in the crust material, or that perhaps the very uppermost surface layer may have lost some of its water of hydration prior to sampling.

[67] The crust was stable at temperatures below the binary eutectic, -21.2°C . Once the temperature increased above this point, hydrohalite in contact with the ice forced some ice melt and then dissolved in the liquid. This liquid (with salinity 230‰) then appeared to drain into the ice, creating numerous small channels. Once the crust was largely dissolved, the surface appeared pitted and mushy.

[68] In our laboratory studies, highly saline liquid melt puddles periodically formed on the ice surface as it was warmed above -21.2°C . When the ice became permeable the puddles drained through the ice. When the ice became impermeable, meltwater ponded at the surface.

[69] Use of the binary system ensured that at temperatures below -21.2°C , no liquid existed within the laboratory-grown ice or in its crust. In the natural seawater system, however, a small amount of liquid would still exist even after the hydrohalite had largely precipitated. The role of this liquid in the formation of a salt crust has not been specifically examined. For natural sea ice containing the full complement of salts, it may be that the presence of liquid would prevent a salt crust from forming until the temperature was considerably lower than -22.9°C . The exact temperature would depend on the exact ionic composition of the ocean.

8. Conclusions

[70] Sea ice interacts with the climate system by raising the albedo of the ocean surface, which causes further cooling, thus favoring persistence of the ice (the “ice albedo feedback”). This positive feedback is operative at temperatures near 0°C . The observations carried out in this study indicate that precipitated hydrohalite within cold sea ice may cause an ice cover to exhibit properties distinct from the more temperate ice most common on the polar oceans at present. In particular, differences in the optical properties of the ice could change how the ice responds to shortwave forcing. Such differences have the potential to activate climatic feedback processes not only near 0°C but also near -20°C .

[71] In particular, the accumulation of salts at the ice surface has the potential to further increase the surface albedo by creating collections of small, strongly scattering crystals on the upper surface of the ice. Quantitative assessment of the albedo increase caused by such an accumulation is beyond the scope of this work, but the use of a crude experimental set up resulted in reflectance estimates greater than 0.95 at visible wavelengths (400–700 nm). This suggests an albedo comparable to that of optically thick snow with grain radii of $200\ \mu\text{m}$ [see *Wiscombe and Warren*, 1980, Figure 8]. Furthermore, the accumulation of salts at the ice surface was demonstrated to affect the melting process as well. When cold ice with a surface accumulation was warmed above its eutectic temperature ($\sim -21^{\circ}\text{C}$), highly saline melt puddles formed, dramatically darkening the ice surface. These observations of (1) increased backscatter upon cooling and (2) the revival of surface melt processes along with decreased albedo on warming, at a temperature below -20°C , reveals the possibility for an important positive “salt albedo feedback” in sea ice.

[72] The formation of a salt accumulation on the ice surface depends on whether surface sublimation can outpace the downward migration of salts through the ice. To ascertain this, observations of temperature-dependent migration rates were made in the laboratory on natural sea ice samples. Estimates from GCMs of temperatures and sublimation rates on the tropical ocean of Snowball Earth, together with the results of our migration experiments,

suggest that downward migration of salt will be too slow to prevent formation of a surface salt crust.

[73] Of the various ice types to be expected on the ocean surface of Snowball Earth [*Warren et al.*, 2002, sections 4 and 7], some now exist in Antarctica and are available for study in the field. Salt crusts have never been observed on modern sea ice. They have been observed on frozen saline lakes in the Antarctic dry valleys (P. Allen and M. Hage, personal communication, 2004), but those crusts are of mirabilite, which can form at about -8°C . Hydrohalite crusts are probably not available for study in nature, so the laboratory experiments we carried out were essential to study this particular surface type. The laboratory also allowed for precise control of environmental variables to investigate the processes of brine migration and surface accumulation.

[74] Use of the binary $\text{NaCl-H}_2\text{O}$ system as a proxy for the seawater system carried numerous advantages. It enabled isolation of a single species for study, avoided the complex chemistry and ambiguous precipitation patterns of the multisalt system, and ensured that a eutectic solid could be formed at temperatures achievable in the laboratory. The natural seawater system poses additional questions. The lower temperature for eutectic formation, the simultaneous presence of liquid brine and precipitated salts within brine inclusions, and the possibility of supersaturated brines would cause differences in how salts accumulate as the ice is sublimated and how meltwater is produced as the ice is warmed. It will therefore be important in future work to grow a salt crust by sublimation of natural sea ice rather than from NaCl ice.

[75] To further examine the role of salt crusts in climate, it will also be necessary to investigate to what extent the presence of a salt crust on the ice surface suppresses further sublimation of ice. The surface layer of salt may also alter the thermal properties of the system [*Kargel et al.*, 2007] and the growth rate of ice at the bottom. Such behavior could limit the accumulation of salts at the ice surface. Also questions about wind lofting and the redistribution of accumulated salt are ripe for study.

Appendix A: Experimental Design for Temperature-Gradient Migration

[76] A laboratory microscope was adapted to support a custom-built stage capable of being cooled as much as 10 K below ambient temperature at one end. The microscope was installed in the freezer laboratory, which maintains the room temperature anywhere between 0°C and -30°C , to within $\pm 2\ \text{K}$. The microscope stage was constructed using two copper plates; ice samples were mounted such that they bridged the gap between the two plates. The warm end of the sample was mounted on the plate extending into the ambient air of the room; the cold end was mounted on the other plate, sitting on a thermal electric cooler (TE Technology HP-127-1.0-1.3-71P). The thermal electric cooler (TEC) was equipped with a heat sink mounted below the device, under the left hand edge of the microscope. A fan was used to cool the heat sink. Figure 7 shows a schematic of the temperature-gradient stage and a photograph of the stage mounted on the microscope in the laboratory.

[77] Samples were prepared by cutting thick sections of ice on a band saw inside the cold room. Finished sample dimensions were approximately 100 mm long, 20 mm wide, and 3 mm thick. The natural ice samples were cut from a 100 mm diameter core extracted from first-year landfast sea ice off Point Barrow, Alaska. Samples of laboratory-grown ice were cut from a block of ice, 120 mm high, grown at an air temperature of -10°C . The block was grown in a rectangular Plexiglass container with insulated sides and base. All thick sections were cut with their long dimension along the direction of ice growth, so that they could be mounted on the microscope stage in the proper orientation for simulating ice with a warm lower boundary and cold upper boundary.

[78] Each thick section was prepared in the freezer laboratory at -15°C by sanding and hand polishing both faces. A warmed glass reticle was then placed on one side of the sample. Heat from the reticle melted the surface slightly, and the reticle quickly froze to the sample. The reticle served as a reference marker for measuring the displacement of individual inclusions during intervals when the temperature gradient was applied. The scale on the reticle was positioned to remain in the microscope field of view as the stage was moved forward and back. A clear glass slide was frozen to the top of the sample to help insulate the top surface from the ambient air in the cold room and to limit sublimation of the sample. The sample was mounted to the copper plates using a few drops of fresh water to form an ice bond. This ice bond ensured good thermal contact between the sample and the copper plates, and kept the ice positioned during the course of the experiment.

[79] Temperature gradients found in nature, particularly in thick ice, would be considerably smaller than the large gradients imposed in this laboratory experiment. Such large gradients were necessary to obtain measurable motion over experimentally feasible time intervals (hours to weeks). In their study, HOW addressed the scalability of temperature gradients and found that migration velocities could be normalized by the temperature gradient.

[80] To monitor the temperature of the ice, thermistors (YSI 44033) were frozen onto the copper plates at each end of the ice sample by applying a few drops of fresh water to cover the tip of the thermistor where it contacted the plate. Temperatures from the thermistors were logged using an Omnidata "Polycorder" data logger. After applying a current to the TEC, an approximately linear temperature gradient was established between the cold end of the ice sample and the point on the sample in contact with the ambient plate. The temperature at the location of the inclusions within the field of view was estimated from the temperatures logged by the two thermistors over the time between observations. The magnitude of the temperature gradient was calculated by taking the difference in average temperature from the thermistors at the warm and cold ends of the sample, and the distance between the cold end of the ice sample and the beginning of the plate in contact with the ambient air.

[81] Once mounted on the microscope, a variety of fields of view could be selected by translating the stage front to back. Typically 3–10 different fields were monitored for each thick section. To estimate the motion of individual inclusions, still photographs were taken of the ice sample in

transmitted light both before and after application of the temperature gradient.

[82] The TEC was typically supplied a current of 1.5 A and voltage 3 V. This is considerably smaller than the device rating of maximum current 3.6 A and maximum voltage 16 V. Presumably we could have achieved a stronger temperature gradient with this apparatus, but the degree to which the hot side of the TEC could be cooled was limited by space for the fan-cooled heat sink. Migration is slower at low temperature. Samples at -25°C typically required 4 weeks to measure significant displacement. The highest migration rates (for temperatures above -10°C) could be measured in less than 4 h.

[83] Since it is difficult to control relative humidity in the freezer laboratory, it was often necessary to humidify the space immediately around the sample to prevent the ice from suffering excessive loss due to sublimation. This was accomplished using a plastic bag that was fitted around the microscope stage. The bag contained an ice brick and was carefully removed each time the sample was imaged. While preventing excessive sublimation, the saturated environment around the sample also caused considerable deposition of frost on colder surfaces. This typically resulted in a thick layer of frost on the cold end of the ice, and at least some frost on the part of the ice under the microscope objective. It was difficult to image the scene through the frost, and clearing the frost proved to be difficult. To circumvent this problem, when it was necessary to image the sample, the TEC was turned off, typically 1 day in advance, and the entire sample was permitted to sit at the ambient temperature of the cold room. During this time, the frost sublimated and the optical path through the sample cleared; the sample could then be imaged clearly. It was assumed that the migration stopped when the thermistor probes indicated there was no longer a difference in temperature between the two ends of the ice, which typically occurred within a few minutes of switching off the TEC. Measures taken to control the humidity in this way were typically used only during experiments conducted in the middle of the temperature range. At high temperatures ($T > -8^{\circ}\text{C}$), the migration was fast enough that the sample did not need to be monitored for long periods. A short experiment meant minimal loss of sample through sublimation and minimal deposition of frost on the sample. At the lowest temperatures, the required time periods were long, but the entire freezer laboratory was saturated with water vapor so sublimation rates were acceptably slow.

[84] Figure 8 shows a pair of still images used to monitor the migration of a field of brine inclusions in natural first-year sea ice. The ambient temperature was -5.7°C and the cold end was held at -15.7°C . The temperature at the location of the scene in the image was estimated to be -7.8°C . The warm side is on the left, the cold side on the right. Arrows point to the position of a single inclusion both before and after the temperature gradient was applied. In Figure 8a, the arrow points from a fixed reference location on the reticle to the cold end of a brine inclusion. In Figure 8b, the arrow points from the same reference mark to the cold end of the same brine inclusion. Images were also taken several times between the times of these two images, so the progress of this particular inclusion was also monitored on shorter intervals. The change in distance from

the reference mark is taken to be the displacement of the inclusion, and the migration rate is calculated from this distance, the magnitude of the temperature gradient, and the time elapsed (5.5 h in this case). Distances were measured in the images by counting pixels using the “rectangular marquee tool” in Adobe Photoshop 7.0. A minimum displacement of 50 pixels was required for a measurement to be significant. An additional pair of migrating brine inclusions is featured within the black ovals.

[85] The sample shown in Figure 8 was unusually thin, such that the reticle and the inclusion could both be imaged without adjusting the focus of a 4× objective. In this particular sample, no inclusions obscured the view of the targeted inclusion. Typically, measurements were made in samples thicker than this one, which was selected to illustrate the technique, but not thick enough to survive the inevitable sublimation suffered during the time necessary for detectable displacement on the microscope stage. For most fields of view, it was necessary to photograph the reticle scale and then adjust the focus to image the inclusions. Because of the limited depth of field, typically two images were taken at each observation time, one with the reticle in focus and one with the inclusion in focus. In these cases, displacement of the feature was measured by assuming that the two sequential images taken at different depths could be stacked directly one on top another.

[86] Efforts were made to maintain a stable temperature gradient across the ice sample. A plastic box was placed over the microscope while the samples were not actively being imaged, and the ice sample and sample stage were typically wrapped in a plastic bag during the migration experiments. Recorded temperatures at each end of the sample show brief warmings of as much as +7.8 K at the cold end and +3.5 K at the ambient end (measured at ambient room temperature of -14°C). These warming events occurred during the laboratory defrost cycle which occurred every 12 h and lasted for 30 min. Once the defrost cycle completed, it typically took the sample about 1–2 h to be completely restored to its lower temperature. For migration measurements that exceeded 12 h, these temperature excursions were included in the calculation of the average temperature, but had little effect since their duration was relatively short.

[87] Additionally, there was a periodic temperature cycle imposed by the thermostat of the freezer laboratory. The temperature variation on the cold plate had an amplitude of 0.05 K with a period of about 3 min. The cycle was not perceptible on the warm end of the plate, as it was located well within the vapor barrier bag. As a result of this temperature cycle, some individual inclusions would have experienced cyclic growth (melting) and contraction (freezing). No effort was made to record inclusion locations at the same temperature in the thermostat cycle or the defrost cycle. In general, the gross motion of the inclusion under the temperature gradient was considerably larger than the small growth and contraction that each inclusion underwent as the sample was thermally cycled.

[88] **Acknowledgments.** This research was supported by the NASA Astrobiology Institute (NAI) and by NSF grant ANT-07-39779. We thank the principal investigator of the University of Washington’s NAI grant, Peter Ward, for encouragement. We also thank Ogden Brandt and Willy Weeks for helpful discussions on the migration of salts in ice and Donald

Archer for use of his program to calculate activity coefficients of NaCl solution.

References

- Adams, L. H., and R. E. Gibson (1930), The melting curve of sodium chloride dihydrate. An experimental study of an incongruent melting at pressures up to twelve thousand atmospheres, *J. Am. Chem. Soc.*, *52*, 4252–4264, doi:10.1021/ja01374a010.
- Anderko, A., and M. M. Lencka (1997), Computation of electrical conductivity of multicomponent aqueous systems in wide concentration and temperature ranges, *Ind. Eng. Chem. Res.*, *36*, 1932–1943, doi:10.1021/ie9605903.
- Archer, D. G. (1992), Thermodynamic properties of the NaCl + H₂O system II. Thermodynamic properties of NaCl(aq), NaCl · 2H₂O(cr), and phase equilibria, *J. Phys. Chem. Ref. Data*, *21*, 793–829.
- Bennington, K. O. (1963), Some chemical composition studies on Arctic sea ice, in *Ice and Snow: Properties, Processes, and Applications*, edited by W. D. Kingery, pp. 248–257, MIT Press, Cambridge, Mass.
- Cho, C. H., J. Urquidí, and G. W. Robinson (1999), Molecular-level description of temperature and pressure effects on the viscosity of water, *J. Chem. Phys.*, *111*, 10,171–10,176, doi:10.1063/1.480367.
- Craig, J. R., R. D. Fortner, and B. L. Weand (1974), Halite and hydrohalite from Lake Bonney, Taylor Valley, Antarctica, *Geology*, *2*, 389–390, doi:10.1130/0091-7613(1974)2<389:HAHFLB>2.0.CO;2.
- Craig, J. R., J. F. Light, B. C. Parker, and M. G. Mudrey (1975), Identification of hydrohalite, *Antarct. J. U. S.*, *10*, 178–179.
- Davidson, D. W., R. N. O’Brien, P. Saville, and S. Visaisouk (1986), Optical refraction by clathrate hydrates, *J. Opt. Soc. Am. B Opt. Phys.*, *3*, 864–866, doi:10.1364/JOSAB.3.000864.
- Dieckmann, G. S., G. Nehrke, S. Papadimitriou, J. Göttlicher, R. Steininger, H. Kennedy, D. Wolf-Gladrow, and D. N. Thomas (2008), Calcium carbonate as ikaite crystals in Antarctic sea ice, *Geophys. Res. Lett.*, *35*, L08501, doi:10.1029/2008GL033540.
- Frankenheim, M. L. (1836), Chemische und krystallonomische Beobachtungen, 2: Das Hydrat des salzsauren Natrons (Chemical and crystallographic observations, 2: The hydrate of the sodium salt of hydrochloric acid), *Ann. Phys. Chem.*, *37*, 637–642.
- Gitterman, K. E. (1937), Termicheskiy analiz morskoy vody (Temperature analysis of sea-water), *Tr. Solyanoy Lab. Vses. Inst. Galurgii Akad. Nauk SSR*, *15*, 5–23.
- Grenfell, T. C., and S. G. Warren (1999), Representation of a nonspherical ice particle by a collection of independent spheres for scattering and absorption of radiation, *J. Geophys. Res.*, *104*, 31,697–31,709, doi:10.1029/1999JD900496.
- Groth, P. (1906), *Chemische Krystallographie*, vol. 1, pp. 233–234, Wilhelm Engelmann, Leipzig.
- Hall, D. L., S. M. Sterner, and R. J. Bodnar (1988), Freezing point depression of aqueous sodium chloride solutions, *Econ. Geol.*, *83*, 197–202, doi:10.2113/gsecongeo.83.1.197.
- Hankel (1841), Ueber die Krystallform des wasserhaltigen Kochsalzes (On the crystal form of hydrated table-salt), *Ann. Phys. Chem.*, *53*, 623–624.
- Harrison, J. D. (1965), Measurement of brine droplet migration in ice, *J. Appl. Phys.*, *36*, 3811–3815, doi:10.1063/1.1713953.
- Hoekstra, P., T. E. Osterkamp, and W. F. Weeks (1965), The migration of liquid inclusions in single ice crystals, *J. Geophys. Res.*, *70*, 5035–5041, doi:10.1029/JZ070i020p05035.
- Hoffman, P. F., and D. P. Schrag (2002), The Snowball Earth hypothesis: Testing the limits of global change, *Terra Nova*, *14*, 129–155, doi:10.1046/j.1365-3121.2002.00408.x.
- Jones, D. R. H. (1973), The temperature-gradient migration of liquid droplets through ice, *J. Cryst. Growth*, *20*, 145–151, doi:10.1016/0022-0248(73)90128-0.
- Kargel, J. S., R. Furfaro, O. Prieto-Ballesteros, J. A. P. Rodriguez, D. R. Montgomery, A. R. Gillespie, G. M. Marion, and S. E. Wood (2007), Martian hydrogeology sustained by thermally insulating gas and salt hydrates, *Geology*, *35*, 975–978, doi:10.1130/G23783A.1.
- Kaufmann, D. W. (1960), Low temperature properties and uses of salt and brine, in *Sodium Chloride: The Production and Properties of Salt and Brine*, edited by D. W. Kaufmann, *ACS Monogr.*, *145*, 547–568.
- Kingery, W. D., and W. H. Goodnow (1963), Brine migration in salt ice, in *Ice and Snow: Properties, Processes, and Applications*, edited by W. D. Kingery, pp. 237–247, MIT Press, Cambridge, Mass.
- Light, B. (1995), A structural-optical model of cold sea ice, M.S. thesis, Univ. of Washington, Seattle.
- Light, B., G. A. Maykut, and T. C. Grenfell (2003), Effects of temperature on the microstructure of first-year Arctic sea ice, *J. Geophys. Res.*, *108*(C2), 3051, doi:10.1029/2001JC000887.
- Light, B., G. A. Maykut, and T. C. Grenfell (2004), A temperature-dependent, structural-optical model of first-year sea ice, *J. Geophys. Res.*, *109*, C06013, doi:10.1029/2003JC002164.

- Marion, G. M., and S. A. Grant (1994), FREZCHEM: A chemical-thermodynamic model for aqueous solutions at subzero temperatures, *CRREL Spec. Rep. 94-18*, Cold Reg. Res. and Eng. Lab., Hanover, N. H.
- Marion, G. M., R. E. Farren, and A. J. Komrowski (1999), Alternative pathways for seawater freezing, *Cold Reg. Sci. Technol.*, *29*, 259–266, doi:10.1016/S0165-232X(99)00033-6.
- Marion, G. M., F. J. Millero, and R. Feistel (2009), Salinity/temperature ranges for application of seawater S_A -T-P models, *Ocean Science. Discuss.*, *6*, 171–189.
- Mitscherlich, E. (1829), Ueber das wasserfreie und wasserhaltige Chlornatrium, Jodnatrium und Bromnatrium (On free and hydrated NaCl, NaI, and NaBr), *Ann. Phys.*, *17*, 385–388.
- Nelson, K. H., and T. G. Thompson (1954), Deposition of salts from sea water by frigid concentration, *J. Mar. Res.*, *13*, 166–182.
- Perovich, D. K., and A. J. Gow (1991), A statistical description of the microstructure of young sea ice, *J. Geophys. Res.*, *96*, 16,943–16,953, doi:10.1029/91JC01594.
- Perovich, D. K., and A. J. Gow (1996), A quantitative description of sea ice inclusions, *J. Geophys. Res.*, *101*, 18,327–18,343, doi:10.1029/96JC01688.
- Perovich, D. K., and T. C. Grenfell (1981), Laboratory studies of the optical-properties of young sea ice, *J. Glaciol.*, *27*, 331–346.
- Pierrehumbert, R. T. (2005), Climate dynamics of a hard Snowball Earth, *J. Geophys. Res.*, *110*, D011111, doi:10.1029/2004JD005162.
- Pollard, D., and J. F. Kasting (2004), Climate-ice sheet simulations of Neoproterozoic glaciation before and after collapse to Snowball Earth, in *The Extreme Proterozoic: Geology, Geochemistry, and Climate*, *Geophys. Monogr. Ser.*, vol. 146, edited by G. Jenkins et al., pp. 91–105, AGU, Washington, D. C.
- Porter, M. W., and R. C. Spiller (1956), *The Barker Index of Crystals: A Method for the Identification of Crystallizing Substances*, vol. II, W. Heffer, Cambridge, U. K.
- Richardson, C. (1976), Phase relationships in sea ice as a function of temperature, *J. Glaciol.*, *17*, 507–519.
- Ringer, W. E. (1906), Über die Veränderungen in der Zusammensetzung des Meereswassersalzes beim Ausfrieren, *Verh. RijksInst. Onderz. Zee.*, *3*, 1–55.
- Robinson, R. A., and R. H. Stokes (1959), *Electrolyte Solutions*, 2nd ed., 559 pp., Academic, San Diego, Calif.
- Schrag, D. P., R. A. Berner, P. F. Hoffman, and G. P. Halverson (2002), On the initiation of a Snowball Earth, *Geochem. Geophys. Geosyst.*, *3*(6), 1036, doi:10.1029/2001GC000219.
- Seidensticker, R. G. (1966), Comment on paper by P. Hoekstra, T. E. Osterkamp, and W. F. Weeks, 'The migration of liquid inclusions in single ice crystals', *J. Geophys. Res.*, *71*, 2180–2181.
- Shreve, R. L. (1967), Migration of air bubbles, vapor figures, and brine pockets in ice under a temperature gradient, *J. Geophys. Res.*, *72*, 4093–4100, doi:10.1029/JZ072i016p04093.
- Spencer, R. J., N. Møller, and J. H. Weare (1990), The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Mg-Cl-SO₄-H₂O system at temperatures below 25 C, *Geochim. Cosmochim. Acta*, *54*, 575–590, doi:10.1016/0016-7037(90)90354-N.
- Steele, M., R. Morley, and W. Ermold (2001), PHC: A global ocean hydrography with a high-quality Arctic Ocean, *J. Clim.*, *14*, 2079–2087, doi:10.1175/1520-0442(2001)014<2079:PAGOHW>2.0.CO;2.
- Stehle, N. S. (1967), Migration of bubbles in ice under a temperature gradient, in *Physics of Snow and Ice*, edited by H. Oura, pp. 219–232, Inst. of Low Temp. Sci., Hokkaido Univ., Sapporo, Japan.
- Untersteiner, N. (1968), Natural desalination and equilibrium salinity profile of perennial sea ice, *J. Geophys. Res.*, *73*, 1251–1257, doi:10.1029/JB073i004p01251.
- Warren, S. G., R. E. Brandt, T. C. Grenfell, and C. P. McKay (2002), Snowball Earth: Ice thickness on the tropical ocean, *J. Geophys. Res.*, *107*(C10), 3167, doi:10.1029/2001JC001123.
- Weeks, W. F., and S. F. Ackley (1982), *The Growth, Structure and Properties of Sea Ice*, *CRREL Monogr.*, vol. 82–1, Cold Reg. Res. and Eng. Lab., Hanover, N. H.
- Wettlaufer, J. S. (1998), Introduction to crystallization phenomena in natural and artificial sea ice, in *Physics of Ice-Covered Seas*, edited by M. Leppäranta, pp. 105–194, Univ. of Helsinki Press, Helsinki.
- Whitman, W. G. (1926), Elimination of salt from seawater ice, *Am. J. Sci.*, *11*, 126–132.
- Wiscombe, W. J., and S. G. Warren (1980), A model for the spectral albedo of snow. I: Pure snow, *J. Atmos. Sci.*, *37*, 2712–2733, doi:10.1175/1520-0469(1980)037<2712:AMFTSA>2.0.CO;2.

R. E. Brandt and S. G. Warren, Department of Atmospheric Sciences, University of Washington, Seattle, WA 98195-1640, USA. (brandt@atmos.washington.edu; sgw@atmos.washington.edu)

B. Light, Applied Physics Laboratory, University of Washington, Seattle, WA 98195-355640, USA. (bonnie@apl.washington.edu)