

## Exclusion of Sodium Chloride From Ice During Freezing

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### ABSTRACT

An apparatus was designed and built to freeze aqueous solutions directionally at a constant rate with a planar interface. Solutions of 1.65% NaCl (28.2 mM) were then frozen with stirring (to prevent brine concentration at the ice/water boundary) at 2.5 mm/hr, a rate appropriate with that found in natural water systems. Samples were taken along the growth (time) axis and chemically analyzed to determine ion distribution coefficients, a measure of the efficiency of salt exclusion. Distribution coefficients were found to vary with salt concentration and ice crystallography.

Key words: Distribution coefficient, Exclusion, Freezing, Ice, Sodium chloride

### INTRODUCTION

It is well known that solutes are rejected from ice when saline solutions freeze. The extent of this rejection depends significantly upon the freezing rate, as well as other factors such as the degree of solution agitation, convection and even imposed electrical potentials (Jost 1960). Most past work has concentrated upon total bulk solute without attention to individual ionic species. Ammonium salts have been extensively studied because the ammonium ion fits well substitutionally into the ice lattice (Brill 1957, Gross et al. 1975); fluoride has typically been the preferred anion because of its size (it is the smallest anion in the periodic table). In addition to  $\text{NH}_4\text{F}$ , its hydrogen analog,  $\text{HF}$ , has also been used for comparative purposes for ice physics studies. However, neither is of widespread interest because neither is very common in the environment (precipitation, fresh or ocean water). The major ions of interest to environmental researchers are  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{H}^+$  while those of interest to Arctic marine scientists are  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The long-term objective of this work is to determine the efficiency of freeze-exclusion of the three predominant anions,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ , in aqueous geochemical systems. The efficiency of ion exclusion during freezing is given by the effective dis-

tribution coefficient,

$$K = C_i / C_1$$

where  $C_i$  is the ion concentration in the ice and  $C_1$  is the concentration in solution (Pfann 1966). Since ice excludes impurities when it forms, distribution coefficients for aqueous salt solutions are generally much less than unity. Freezing is thus an efficient, although energetically costly, method of purifying saline water for industrial and consumer use. Initial results from this work, the determination of  $\text{Cl}^-$  in ice frozen from brackish NaCl water, are reported here.

### EXPERIMENTAL

Since the rate of freezing has such a strong influence upon the amount of impurities incorporated into ice, salt solutions were frozen at a constant rate,  $\pm 1\%$ . Several freezing techniques, such as zone refining and the use of glycol-chilled cold plates, were investigated and modified but none succeeded in freezing ice 1) unidirectionally, 2) at a constant formation rate, and 3) with a planar interface. (A planar interface is required for sampling to insure that each sample represents ice frozen from a uniform time interval.) A listing of freezing techniques tried and results obtained is given in Table 1.

Table 1. Techniques investigated to freeze solutions.

<i>Freezing method</i>	<i>Comments</i>
Bulk	Cannot control rate or direction or achieve planar interface
Chilled plate	Can freeze unidirectionally and obtain planar interface but difficult to control rate
Heating unit in cold room (modified zone refiner)	Can control rate and direction but impossible to get planar interface
Freezer in warm room	Meets all three requirements: unidirectional freezing at a constant rate with a planar ice/water interface. Freezing rate: 2.56 mm/hr

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Figure 1. Schematic of apparatus used to freeze salt solutions unidirectionally at a constant rate ( $\pm 1\%$ ) with a planar ice/water interface. Unit consisted of a  $-38^{\circ}\text{C}$  freezer in a  $+2^{\circ}\text{C}$  coldroom. During a typical "freezing run" a polyethylene bag containing the sample solution is slowly ( $2.56\text{ mm/hr}$ ) lowered into the freezer. To maintain thermal and chemical homogeneity in the residual solution, it was stirred mechanically for two minutes every fifteen minutes.

Using a  $-38^{\circ}\text{C}$  freezer in a  $+2^{\circ}\text{C}$  room (Fig. 1) a modified version of Gross' (1975) technique was devised and an apparatus developed that met the three above requirements. The room temperature was set at  $2^{\circ}\text{C}$  to reduce convective heat losses to the surrounding air. The annular heater in the freezer lid produces a sharp temperature gradient at the ice/water interface and meets the above requirements. Using this technique, I froze solutions of single salts slowly ( $2.56 \pm 0.02\text{ mm/hr}$ —an environmentally typical rate) with stirring to prevent brine concentration at the ice/water interface.

To date, solutions of four different chloride salts have been frozen using the technique described above. The anion concentration in each of these solu-

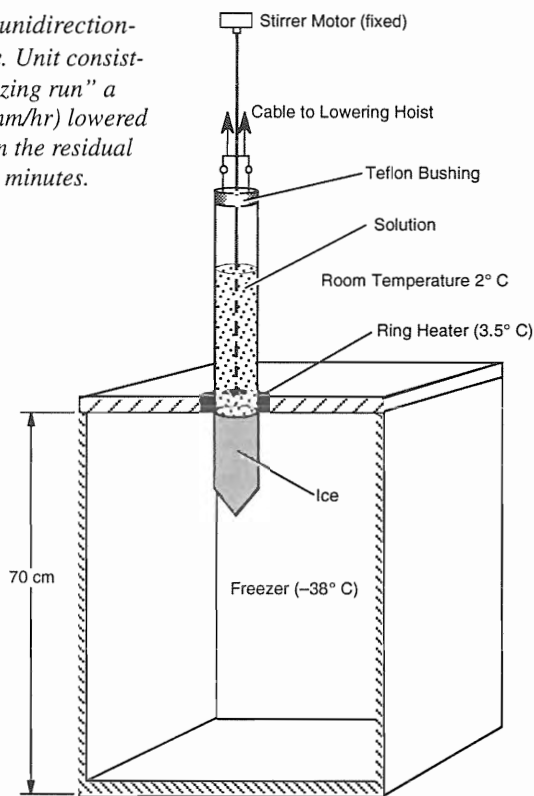


Table 2. Composition of four chloride salt solutions that were used in freezing experiments.

Salt	Salt concentration (mg/L)	Cation concentration (mg/L)
NaCl	1649	649
KCl	2103	1103
MgCl <sub>2</sub>	2863	343
NH <sub>4</sub> Cl	1509	509

In all cases the chloride concentration was  $1000\text{ mg/L}$ .

tions was the same,  $1000\text{ mg Cl}^-/\text{L}$ , while the cation concentration varied depending on its valence and the molecular composition of the salt. Table 2 shows the initial concentrations of all constituents in the four chloride solutions. Holding the chloride concentration constant permits evaluation of the effect of the counterion, in this case the cation, upon the freeze exclusion efficiency of chloride.

As of this writing, only the NaCl ice core has been analyzed. Before analysis the core was cut widthwise with a bandsaw into 10-mm-thick disks as shown in Figure 2. Each disk was then placed between crossed polars and photographs taken to determine the ice crystallography. Individual core segments were rinsed with deionized water to remove any surface contami-

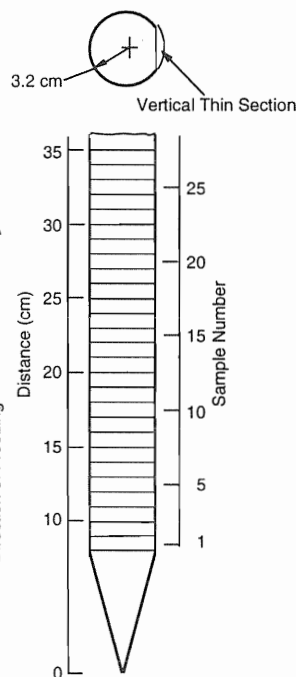
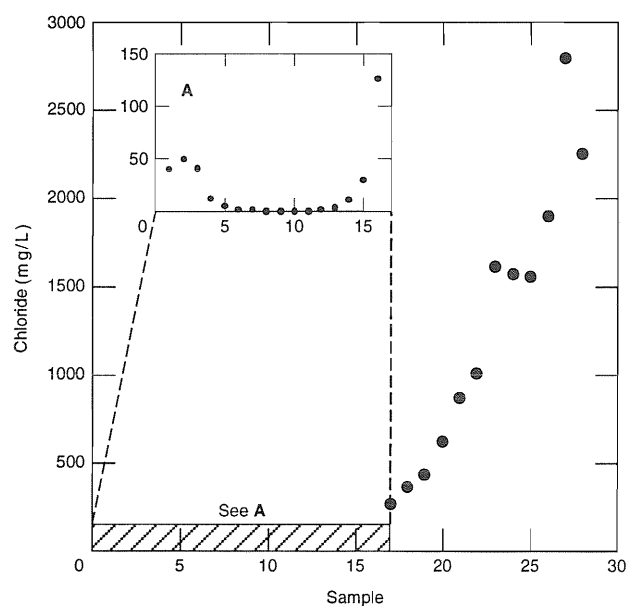


Figure 2. NaCl core sampling. Frozen salt solutions were sampled as shown above. The direction of freezing is from bottom to top. The cone-shaped segment at the bottom was designed to control the initial ice nucleation process and promote a smooth, planar, gradually advancing freezing front. Samples, 10 mm long, were cut with a bandsaw from the cylindrical section of the core, rinsed, melted and analyzed by ion chromatography.

nation and allowed to melt. Aliquots of the melted samples were taken for determination of  $\text{Cl}^-$  concentrations using a Dionex model 2010i ion chromatograph, containing an HPICE-AS3 separator column, AFS 1-2 anion fiber suppressor and 50- $\mu\text{L}$  sample loop. The eluant was 3-mM  $\text{NaHCO}_3$ /2.4-mM  $\text{Na}_2\text{CO}_3$  and the regenerant was 12.5-mM  $\text{H}_2\text{SO}_4$  both flowing at 3.0 mL/min. Analysis precision was  $\pm 5\%$ .

## RESULTS AND DISCUSSION

Concentrations of chloride in ice frozen from NaCl solution containing 1000 mg/L  $\text{Cl}^-$  are shown in Figure 3. Contrary to expectation the distribution coefficient did not vary linearly with the aqueous solution concentration but showed a marked dependence upon ice crystal size and number. More surprisingly, an exponential change in the distribution coefficient occurred at high solution concentrations, despite no obvious change in the ice crystallographic structure. Theoretically, one would expect concentrations in the ice to be initially low and rise as the impurities excluded from the ice accumulate at the freezing front and become entrapped as the freezing front advances. This reasoning is based on the classic theory that the exclusion efficiency or distribution coefficient is constant. The results shown in Figure 3 show that the expected form of the curve is not realized and thus other factors must be influential. While others (Gross 1968) have shown that the distribution coefficient can vary over large concentration ranges, the large multidirectional changes in ice chloride over such narrow solution concentration ranges is more complex to explain. A preliminary explanation, based on the  $\text{Cl}^-$  data



shown in Figure 3, is given below.

When impurities are incorporated into ice they can go to one of three types of locations: 1) the ice lattice, 2) the grain boundaries and triple junctions, or 3) brine pockets. The ice lattice is one of the most resistant to substitutional impurities (Glen 1974) and thus is the least favorable location and consequently can "hold" the least amount of impurities. The grain boundaries and triple junctions can incorporate much higher impurity concentrations but, because of their small size, the total amount of impurities is limited. Brine pockets, on the other hand, can incorporate not only high concentrations of impurities but large volumes as well. Brine pockets are generally formed between ice crystals and not within the crystal lattice.

The polarized-light photographs show that the first three samples of the ice core are composed of a rather large (15 or 16) number of crystals; crystal number decreases to 3 by sample 13 and finally the core becomes one single crystal. Looking at Figure 3, I believe the initial moderately high chloride concentrations are due to most of the salt being incorporated into the triple junctions and grain boundaries. As the crystal number decreases, the number of triple junctions and the grain boundary area also decreases resulting in lower chloride concentrations in the ice. Finally, when the ice core consists of a single crystal, chloride concentrations are the lowest. At this point the distribution coefficient is  $1.05 \times 10^{-3}$  ( $1.05 \text{ mg/L} \div 1000 \text{ mg/L}$ ). During the entire freezing process so far NaCl has been excluded quite efficiently, resulting in about a doubling of the solution concentration. When the solution concentration reaches approximately 2000 mg  $\text{Cl}^-/\text{L}$  or 3300 mg NaCl/L the ice lattice can no longer continue to reject the salt and brine pockets begin to form. Because the photographs were taken without magnification they do not clearly show individual brine pockets in these particular ice sections, but they do exhibit a large amount of "graininess" that could easily be caused by light scattering by brine pockets. This mechanistic change occurs very abruptly: between samples 14 and 16 the ice concentration increases by an order

Figure 3. Plot of  $\text{Cl}^-$  concentration in ice vs. sample for NaCl solution frozen directionally at a rate of  $2.56 \pm 0.02 \text{ mm/hr}$ . Samples, 10 mm long, were cut horizontally across the core in the direction of freezing so that sample 1 was the first to freeze and sample 28 was the last. All samples are from the same core; the scale changes at sample 16 to keep points on same plot. Note onset of sudden and dramatic concentration increase at samples 14–16 (10–100 mg  $\text{Cl}^-/\text{L}$ ).

of magnitude while the solution concentration increases by only about 7%. This abrupt transition is quite surprising, considering that most changes in nature occur rather gradually. At this time, the exact physiochemical process that triggers this change is not understood.

## SUMMARY AND CONCLUSIONS

The amount NaCl in ice depends not only upon the rate of freezing and degree of solution agitation but also strongly upon the mechanism of impurity incorporation into the ice. For a given freezing rate, the salt incorporation mechanism depends upon the solution concentration. At low and moderate solution concentrations (e.g.,  $\leq 3000$  mg/L) NaCl can be incorporated within the ice lattice as well as in the grain boundaries and triple junctions. At higher solution concentrations NaCl forms distinct brine pockets. Depending upon the salt incorporation mechanism, ice/solution distribution coefficients for  $\text{Cl}^-$  range from  $1.05 \times 10^{-3}$  for the ice crystal lattice to about 0.10 for ice containing brine pockets.

Future work will include the analysis of the exclusion efficiency of other salts to determine if the above effects occur at similar concentration levels for different ionic species.

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