A Nuclear Magnetic Resonance Investigation of Brine Inclusions in Antarctic and Artificial Sea Ice

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Acknowledgments

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Contents

Abstract

The aim of this thesis is to use Nuclear Magnetic Resonance (NMR) techniques to examine the brine pockets in sea ice. Both the movement of the brine pockets within the ice, and the movement of the brine within the brine pockets is examined. The experiments are carried out using Earth's field NMR on sea ice in situ in Antarctica, and high field NMR equipment on artificially grown sea ice in New Zealand. The field work involved probe design, construction, and use. Investigations were carried out on brine content, and brine diffusion rates. The laboratory work involved growing realistic artificial sea ice, designing and constructing a temperature control system for the high field NMR machine, and carrying out experiments on the artificial sea ice samples. The brine pockets' morphology and distribution was examined. The brine and brine pocket movements over time, with a controlled temperature gradient, were also investigated. The results from the field work clearly showed multiple diffusion rates in sea ice, both faster and slower than that of water. The lab work showed that realistic sea ice had been grown, and that there was a migration of brine pockets in the direction of the temperature gradient.

Preface

This thesis investigates the properties of brine inclusions in sea ice. It is comprised of two parts, one part involved field work using Earth's field Nuclear Magnetic Resonance (NMR), on in situ sea ice in Antarctica. The other part was laboratory work carried out on artificial sea ice with a high field NMR machine in New Zealand.

Previous work done in 1995 and 1997 indicated that there was a brine diffusion rate in the sea ice faster than that of free water, however, the ice sampled was significantly disturbed in the course of the experiment. The probe that was used in 1997 was placed over, and sampled, an ice core that was connected at the base to the ice sheet. However, a large amount of ice around the ice core had to be removed to allow for the probe's gradient coils to be placed over it. The field work component of this thesis involved improving the probe used in 1997 to incorporate the gradient coils into the probe head. This alleviated the need to remove extra ice from around the core being sampled, and therefore caused less sample disturbance and allowed more cores to be examined due to the reduction in time required to set up the equipment. In order to incorporate the gradient coils, the field profiles of the gradient coil and the sensitivity profile of the transmit/receive coil had to be determined. This enabled us to choose the best gradient coil, configuration, position, and number of turns, taking into account the physical constraints imposed by the pre-existing probe head and drilling equipment. Software had to be developed to compensate for the gradient field inhomogeneities caused by the proximity of the coils to the sample. Another probe was also constructed to further reduce the disturbance to the ice sampled. This probe sampled the undisturbed region outside the probe. In order to do this however, the signal from the ice had to be received from outside the coils, causing a reduction in signal strength.

The lab work was designed to complement and extend the field work. Much larger signals were obtainable with the high field NMR system, enabling precise imaging and diffusion measurements to be made. The lab work undertaken involved growing

realistic artificial sea ice, designing and constructing a temperature and temperature gradient control system for both the growing of the ice, and the NMR machine, and completing imaging and diffusion experiments. Three-dimensional images were taken of the entire sample to ensure that the artificial sea ice sample created was a realistic and accurate representation of naturally formed sea ice. A series of two-dimensional images were also taken over a period of time, to track the migration of the brine pockets. Diffusion weighted images were taken to enable the diffusion rates to be accurately correlated with brine pocket morphology and migration. Sea ice has a local co-ordinate system, caused by the individual ice crystal orientation within the ice sheet. The orientation of the NMR machine axes is not necessarily aligned with the local axes, and therefore software had to be written to enable the difference in axes' orientation to be detected, and compensated for, to examine the diffusion rates in the local co-ordinate system.

Chapter 1

SEA ICE

1.1 Antarctic sea ice

The annual sea ice of the southern ocean, and its associated snow cover, play a number of important roles in the ocean atmosphere climate system, in ocean circulation and in structuring the marine ecosystem. Sea ice, which is between 1 and 2 meters thick and covers an area of approximately 20 million square kilometers in winter, greatly reduces the exchange of heat, gas, and momentum between the ocean and the atmosphere [1].

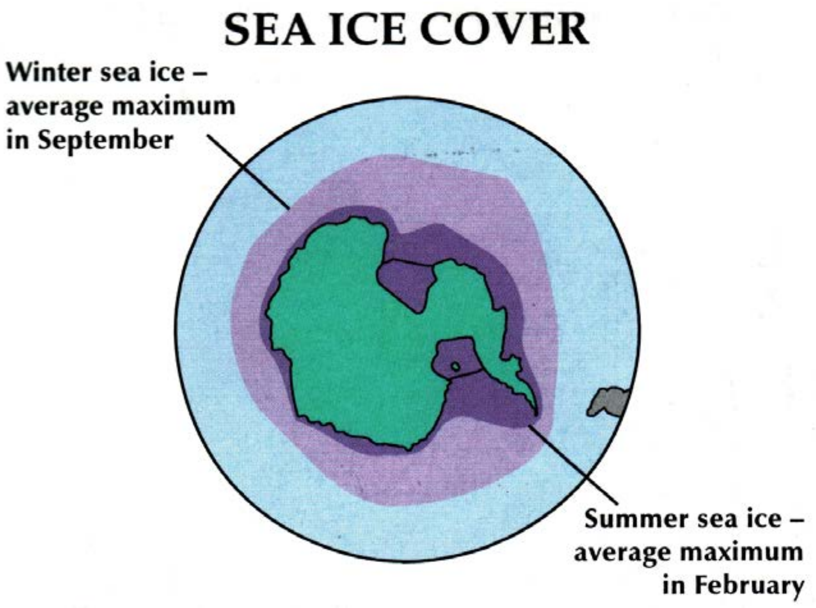

Figure 1 Antarctica, and it's seasonal ice cover.

Compared to open water, which reflects only 5% of sunlight, snow-covered ice reflects over 90% of short-wave radiation, and significantly reduces both the absorption of solar radiation at the surface, and the amount of light available for photosynthesis under the ice. The sea ice is a very effective insulator, greatly restricting the loss of heat from the relatively warm ocean (-1.9^{O}C) to the much colder polar atmosphere (which can be colder than -40^{O}C). During winter, the turbulent heat loss from leads (cracks in the sea ice that can be many kilometers long) can be two orders of magnitude greater than that from ice covered ocean [1]. In the carbon dioxide cycle, seasonal ice cover limits carbon dioxide exchange while subduction of surface water acts as a carbon dioxide sink [2]. The ice influences ocean structure and circulation, since during ice formation and growth the ice releases salt into the underlying ocean, increasing density and inducing the formation of dense, cold, and saline Antarctic Bottom Water. This is transported northwards, setting up deep convection currents that contribute to the upwelling of nutrients and to the overall thermohaline circulation (water movement driven by salinity and temperature differences) of the global ocean. The movement of ice northwards during the summer further influences the meridional heat and freshwater transport. Melting of the sea ice releases freshwater and algae spores to the ocean, increasing stability and stimulating phytoplancton growth [2].

1.2 Sea ice crystal formation

The crystal structure of sea ice is controlled by many natural causes. For one-year-old ice, the most important of these are the conditions of ice formation, i.e. the temperature, salinity, and wind-induced mixing of water during the formation and growth of the ice.

The crystals formed by the freezing of sea water are in general more or less uniform platelets of pure ice. This is due to the water molecules forming layers of hexagonal rings upon freezing. The most important characteristic of the lattice is that there is only one principal hexagonal axis of symmetry (c-axis), which is the optic axis of the ice crystal [3]. The optic axis is perpendicular to the plane of hexagonal rings, which is called the basal plane, (see figure 2). A ray of light incident on the crystal parallel to the c-axis passes through it in the usual way, with oblique incidence birefringence taking place, which is an important factor in determining the optical and reflective properties of ice.

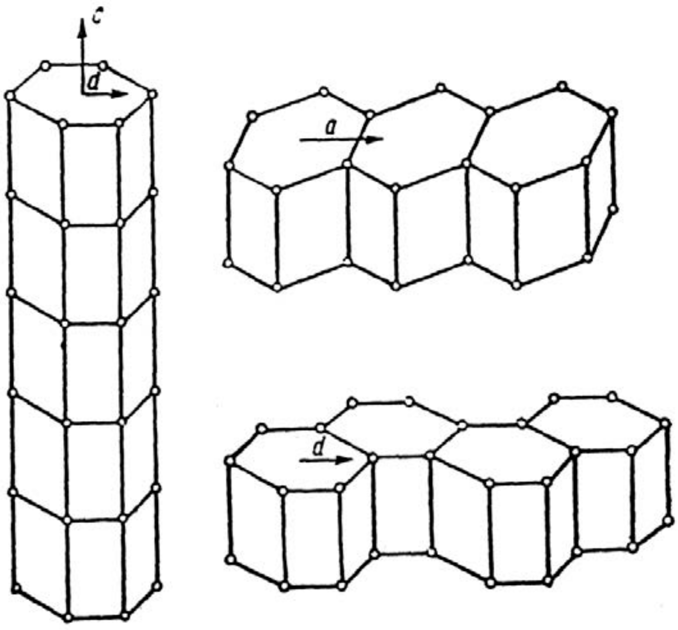

Figure 2 Formation of ice needles and plates with growth of ice crystals along different axes [3].

In the plane it is possible to distinguish two directions: the a-axis passing through the middle of one side of the hexagon and the direction inclined by 30^{O} to the a-axis, called the d-axis. The difference between the properties of ice along these two directions is small, so in the basal plane the ice is nearly isotropic. The growth of ice crystals follows the direction of these axes, if the crystal grows in the direction of the c-axis, needles are formed, if it grows in the a- or d-axis thin layers are formed. With simultaneous growth in the direction of the c- and a-axes, ice plates are formed [3]. The principal direction of growth of crystals is determined by the anisotropy of the surface energy of different faces of the ice crystal. The surface energy of the lateral faces (growth along the a- and d-axes) is substantially less than the surface energy of the tight packed plane (growth in the direction of the c-axis). Therefore the growth of the ice crystal mainly follows directions parallel to the basal plane. Crystals growing at the lower surface of the ice are deprived of one degree of freedom of growth (lateral) and further increases in size are determined by the law of geometrical selections. With vertical growth therefore, there will be a majority of crystals whose basal planes are oriented vertically and optic axis horizontally. Crystals with a disadvantageously oriented optic axis will be rapidly absorbed by their growing neighbours and cut off from the water, this is called individual suppression of cells.

In the case of lateral growth, a crystal with its basal plane disposed horizontally will prevail [4].

The chief characteristic of the crystal structure of sea ice, as compared to fresh-water ice, is the small size of the crystals. This is explained by the fact that the ions of all the salts in sea water reduce the range of action of the crystallisation nuclei so that the nuclei concentration is higher [3]. The presence of liquid and solid layers between the grains hinders and retards the growth of crystals once formed, which also leads to a decrease in size. The micro-crystalline structure of sea ice substantially influences the deformation and strength of the ice cover.

Sea ice cover consists of individual grains that are formed from more-or-less uniformly orientated plates of pure ice (elemental plates) with an average thickness of 0.5-0.6 mm, separated from each other by layers containing cells with brine. The distance between neighbouring rows of cells in the crystal, measured in the c-axis direction, is called the cell spacing [3]. The macroscopic crystals of ice therefore possess a "platy" substructure which substantially influences their physio-chemical properties. Foreign inclusions and brine are mainly displaced to the inter granular boundary. However, a considerable part of the brine remains in cells between the plates but within the grains [1]. These cells have an average diameter of 0.05 mm and their lengths vary widely.

1.3 Sea ice structure

The initial freezing occurs near the surface of the seawater to produce a soup of frazil crystals [5] which freeze together to produce flat sheet nilas, or in the presence of waves, solid ice pancakes, (see figure 3). These pancakes may consolidate to produce a continuous ice sheet [6].

Figure 3 Pancake ice at the edge of the ice sheet in November 1999.

This frazil ice is formed from grains that have randomly orientated optical axes due to the turbulent mixing during formation. Once the initial layer of ice prevents the turbulent mixing of the water due to wind and waves, the overwhelming majority of crystals will have nearly horizontal optical axes (c-axis) [7]. In this case, below the transition layer the ice becomes columnar (filamentary) in structure and the crystals are considerably elongated in the direction of the heat flux. The mean grain diameter ‘d’ increases in proportion to the increase in distance ‘z’ from the top of the ice (figure 4).

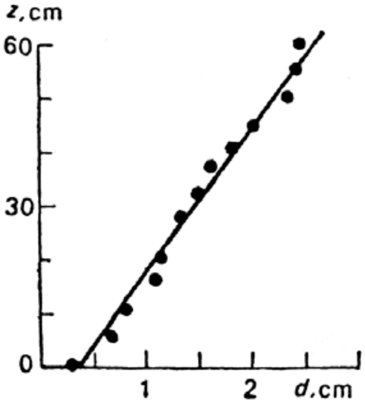

Figure 4 Mean grain size d vs distance z to upper surface of ice [3].

With the growth of the ice, the heat insulation of the zone of crystallization, i.e. the underneath of the ice, increases. The temperature gradient in that zone is therefore reduced, and so the growth of crystals is retarded but individual crystals are larger.

The cell spacing (distance between pure ice plates within the crystal) increases when the growth rate declines. Therefore, in general, the distance between the layers of cells with brine increases in proportion to any increase in the thickness of ice. The crystal structure of the ice under conditions of permanent low temperatures is very stable. The original dimensions, form and orientation of the crystals are preserved for a very long time, metamorphosis of the ice being slight. Transformations take place along the inter-crystalline surfaces and are mainly associated with the migration of brine [1].

1.4 Migration of brine

The amount of brine in sea ice depends not only on the salinity and temperature, but also on migration. Ice crystals contain very little salt, most salts are found in the space between ice crystals either in the solid or liquid state, the proportion determined by the temperature. The brine is contained in the inter crystalline layers, in capillaries and in the form of closed cells of varying form. The migration of brine takes place under the influence of a number of factors. The major factors are believed to be: the temperature gradient in the ice, affecting the concentration of brine in the cell along the direction of this gradient; the effect of gravity, facilitating the downward drainage of brine; the effect of hydrostatic pressure, squeezing out the brine from the cells; and surface tension on the brine inclusions [3].

Much of the brine that initially leaves the sea ice upon ice formation in autumn, migrates through brine channels or capillaries [8]. These can extend for many cm through the ice sheet and cause extended filamentary structures beneath the ice sheet, see figure 5. These filamentary channels are due to the brine, which has been cooled by the atmosphere, freezing the seawater around it.

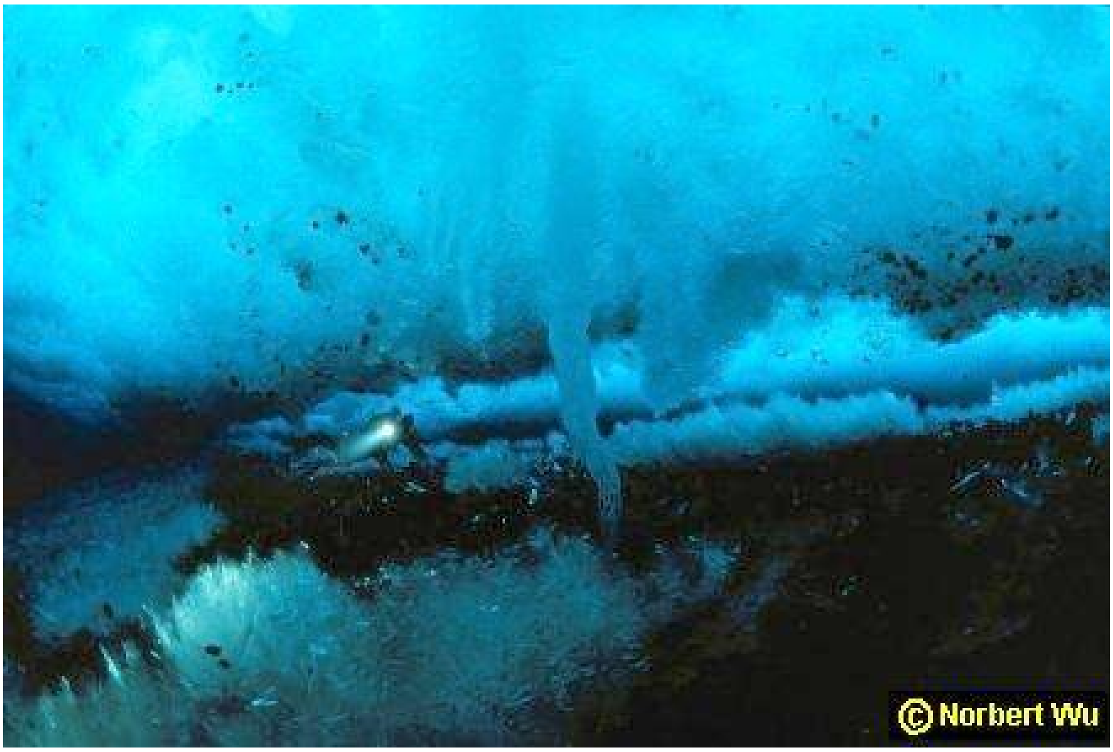

Figure 5 Brine channels extending out through the base of the ice sheet [9].

In the cold part of the year, as a result of the freezing of brine, most of the capillaries are transformed into closed cells, separated by necks of ice. Under the action of the temperature gradient these cells are displaced toward the higher temperature, in this case the ocean underneath. Since the brine in the cells is in thermodynamic equilibrium, in the zone of higher temperature (the bottom of the cell) the brine concentration is weaker than in the zone of lower temperature, (the top of the cell). As the more highly concentrated brine at the top of the cell is denser and therefore heavier, it sinks to the bottom of the cell causing the diffusion of salts within the cell [10]. This process is called Raleigh convection, (see figure 6).

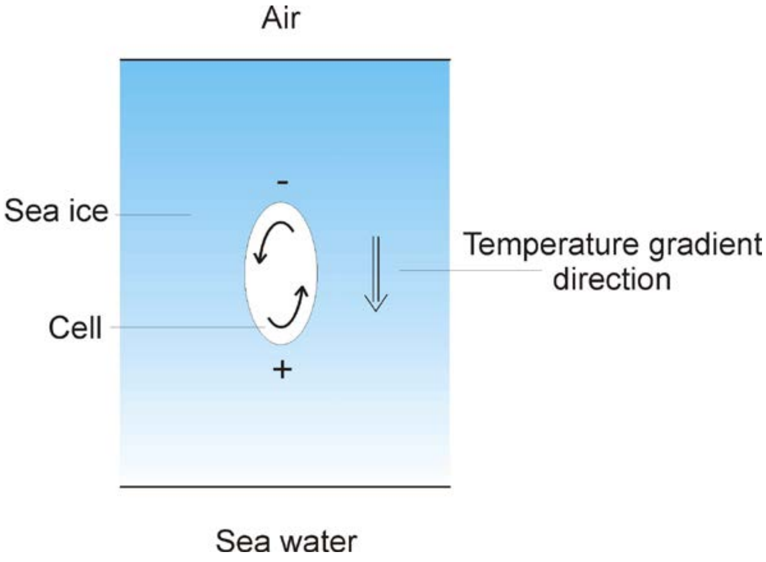

Figure 6 Raleigh convection caused by temperature gradients and gravity.

During Raleigh convection equalisation of brine concentration takes place and the temperature concentration equilibrium is disturbed. Restoration of this equilibrium requires melting of ice and dilution of brine in the part of the cell where the temperature is higher and freezing out of brine with the formation of pure ice in the zone of lower temperature. The melting of ice in the warmer part of the cell and freezing in the colder part gradually displaces the brine from the cold layers into the warmer ones until it is discharged into the water (see figure 5). The migration of the cell depends not only on the value of the temperature gradient but also on the intensity of the diffusion of salts, forces of surface tension caused by phase transitions, gravity and a number of other factors [11]. When the cells are smaller than a critical size of

40μm the surface tension is great enough to prevent Raleigh convection [12], but the diffusion of the salts will still cause migration, albeit at a reduced rate. Coalescence of individual inclusions and absorption of small inclusions by large ones also take place [13]. These transformations occur in such a way that the total surface area of the inclusions, and consequently the surface energy decreases.

For a given salinity, the amount of brine in the ice at any one time depends on the temperature. The experimental data below (figure 7) shows the decrease in brine with lowering temperature. This data is valid only when there is no migration of brine.

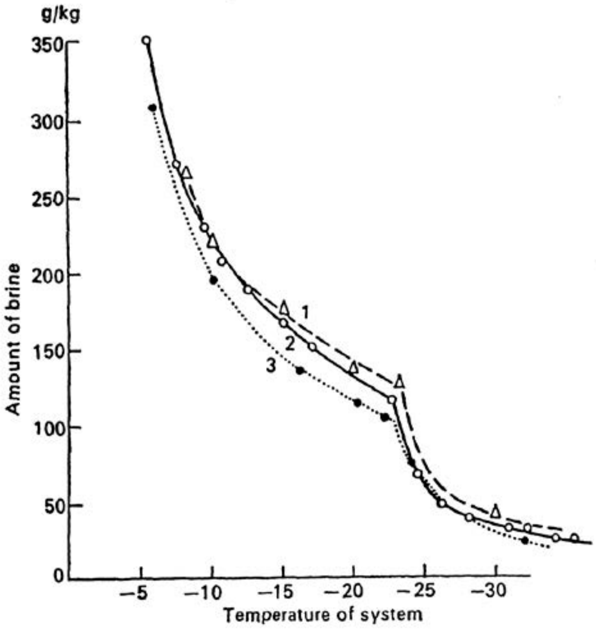

Figure 7 The mass of brine in 1kg of sea ice at different temperatures [3].

1. According to Ringer with salinity of 35.05ppt
2. According to Gitterman with salinity of 33.10ppt
3. According to Assur with salinity of 34.32ppt

The nature of the variation in the salinity of ice with time is shown in figure 8. Here both the temperature effect and the effect of drainage are represented. It can be seen that directly after the formation of ice, its salinity is reduced by almost 1/2 in two months, in winter it changes comparatively little. The transition from the winter regime of salinity to the summer regime takes place very rapidly i.e. in the course of 1-2 months.

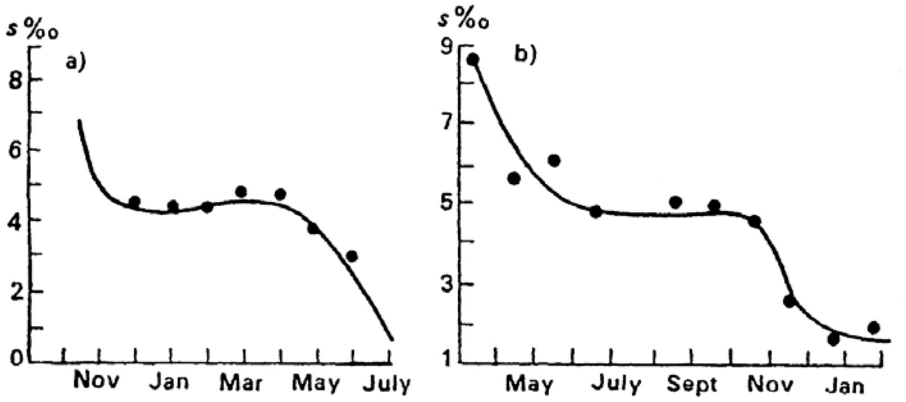

Figure 8 The change in salinity of sea ice over the winter [3].
a) In the Arctic. b) In Antarctica

After the snow cover vanishes, intense radiation melting takes place, causing pronounced structural transformations of the upper layer of the ice. Melting occurs mainly along the inter-granular layers because the brine there intensively absorbs radiant energy. When the brine freezes again a rapid growth of crystals of complex form takes place. The thickness of this intensely metamorphised layer in one-year-old ice is usually not more that 20 to 30 cm [3].

There exist a number of important differences between Antarctic and Arctic one-year-old ice. In particular, one-year-old Antarctic ice is considerably thicker at similar latitudes, than Arctic ice [14]. In the Antarctic, much of the ice consists of randomly oriented crystals characteristic of frazil ice [15, 16]. This is a result of the turbulence of the southern ocean in which pancakes are jumbled and rafted. Deep within the pack however, the open water areas become filled with ice in the Arctic manner, with ordered columnar ice forming a few centimeters below the surface [17]. It is this latter type of ice sheet which we have examined in the McMurdo Sound area. Jeffries *et al* have reported on similar structural characteristics in Arctic sea ice from the Beaufort Sea [18].