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Earth's Field NMR in Antarctica: A Pulsed Gradient Spin Echo NMR Study of Restricted Diffusion in Sea Ice

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We report on the use in Antarctica of a nuclear magnetic resonance spectrometer which utilizes the terrestrial magnetic field. Free induction decay data are used to obtain estimates of brine content, in samples of sea ice extracted from the annual ice of McMurdo Sound, in the vicinity of Cape Evans, Ross Island. Pulsed gradient spin echo experiments were performed on these samples in which the orientation of the gradient with respect to the ice growth axis was varied and the separation time between the gradient pulses was varied. Anisotropic restricted diffusion effects are apparent and we use these to tentatively model the brine pocket morphology.

INTRODUCTION

The sea ice which surrounds the Antarctic continent is a significant determinant of the global energy balance. Any effective modeling of global temperature variation depends upon an understanding of sea ice optical properties, of thermal transport properties, and of the mechanical properties which determine the process of sea ice dispersal. To understand such properties requires a detailed knowledge of this complex mixed phase material consisting of an array of platelets of pure ice, separated by rows of brine-filled pockets (*1, 2*). The salts separate in a concentrated brine, some of which drains out through vertical channels as the sea ice grows in thickness, but much of which remains entrapped between ice crystals in a porous medium. The structure of these microscopic brine pores is important in determining sea-ice complex permittivity, thermal conductivity, strength, rheology, and resistance to fracture and breakup. By its selective sensitivity to nuclear spins whose host molecules reside in the liquid state, nuclear magnetic resonance (NMR) can discriminate the protons of the ice from those which reside in the liquid water phase and hence can quantify sea ice brine content (*3*).

Because ice structure is crucially dependent on the growth history, any study of Antarctic sea ice would need to be carried out *in situ* in order to be useful. The extreme conditions of the Antarctic environment preclude the use of conventional laboratory NMR equipment, a fact we have circumvented by making use of the terrestrial magnetic field. In this paper, we report on the use of pulsed gradient spin echo (PGSE) NMR in order to investigate the structure of sea ice via the unfrozen brine. The purpose of this paper is to demonstrate that it is possible to perform NMR in this extreme environment and, in particular, that the PGSE NMR method conducted in the Earth's magnetic field is capable of providing information about brine pocket structure. A detailed examination of sea ice morphology is beyond the scope of this article and will be dealt with in another publication.

THE EARTH'S FIELD NMR METHOD

In 1902 the Australian Louis Bernacchi, a member of the *Discovery* expedition of Robert Falcon Scott, made the first measurements of terrestrial magnetism in the vicinity of McMurdo Sound. That magnetic field, approximately 65 μT in magnitude and vertical in orientation, enables us to implement the magnetic resonance measurement. A number of authors have reported on applications of Earth's field NMR (*4–6*) (in temperate climates) but, to our knowledge, there is no report of NMR experiments having been conducted in Arctic or Antarctic regions, nor of standard PGSE NMR measurements in the Earth's magnetic field.

The basic principle underlying most Earth field NMR schemes is that the poor sensitivity arising from the very low Larmor frequency can be largely offset because of two factors. The homogeneity of the field permits the use of large samples and the initial magnetization can be enhanced by means of a polarizing field pulse applied prior to the free precession. The technical requirements for a polarizing coil are much less stringent than those for a coil suitable to produce the homogeneous field needed for the evolution and detection phases of NMR experiments. In consequence, the polarizer can be somewhat rudimentary. Generally, this polarizing coil is wound coaxial with the receiver/transmitter coil and will therefore be orthogonal to the Earth's field. This means that a nonadiabatic removal of the polarizing field will leave the magnetization transverse to the Earth's field and available for direct free

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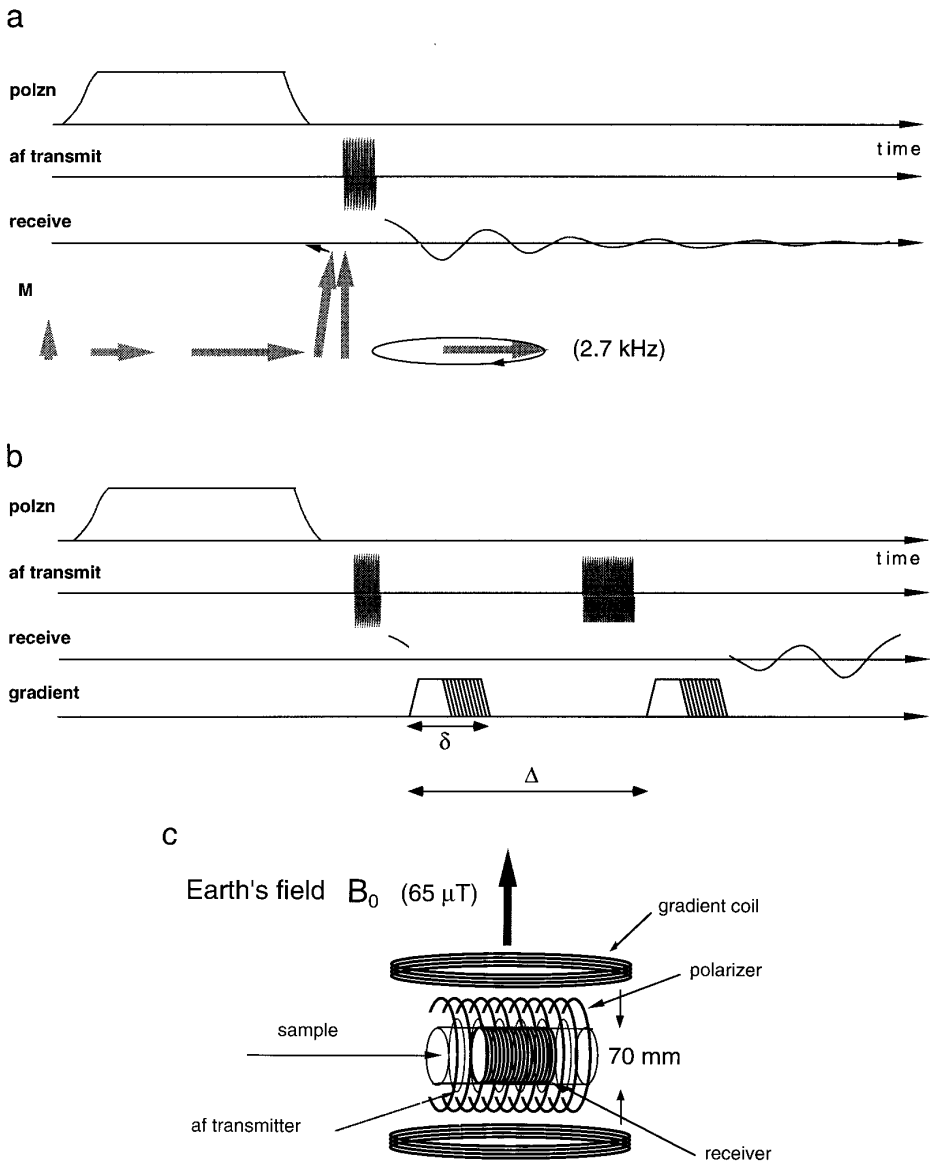


FIG. 1. (a) Schematic representation of the method used to obtain NMR signals using the Earth's magnetic field. (b) Pulse sequence used for PGSE NMR experiments. (c) Schematic diagram of probehead showing arrangement of coils and sample space. Full details are given in Ref. (*7*).

precession detection. In fact, such nonadiabatic removal is seldom perfect and any discrepancy results in an inevitable loss of available signal amplitude. We prefer to remove the field adiabatically, allowing the magnetization to return without loss to the terrestrial field direction.

The experimental scheme is illustrated in Fig. 1a. Following an initial polarization pulse of 30 mT lasting on the order of 6 s (a few T_1 relaxation times), the nuclear magnetization is restored adiabatically to the vertical orientation. Free induction decays and spin echoes are then generated using appropriate resonant audiofrequency (AF) pulses in a manner exactly akin to conventional NMR, the difference being the length of these pulses at around 10 ms. Furthermore, our apparatus has several novel features including automated and flexible process control, direct digital detection of the 2.72-kHz Larmor precession, and the incorporation of magnetic field gradient coils which permit pulsed gradient spin echo diffusion measurement. The use of a common clock for pulse sequence and AF synthesis results in phase stability sufficient for accurate signal averaging. A serendipitous outcome of our operation under Antarctic field conditions was that the signal-to-noise ratio improved by over an order of magnitude relative to measurements conducted in New Zealand, because of the absence of audiofrequency electromagnetic interference. In addition, because of the long T_2 values and the homogeneous Zeeman field, the acquired FID data had an exponential envelope with a time constant on the order of 1 s, giving a spectral linewidth of less than 1 Hz following Fourier transformation. The use of the area

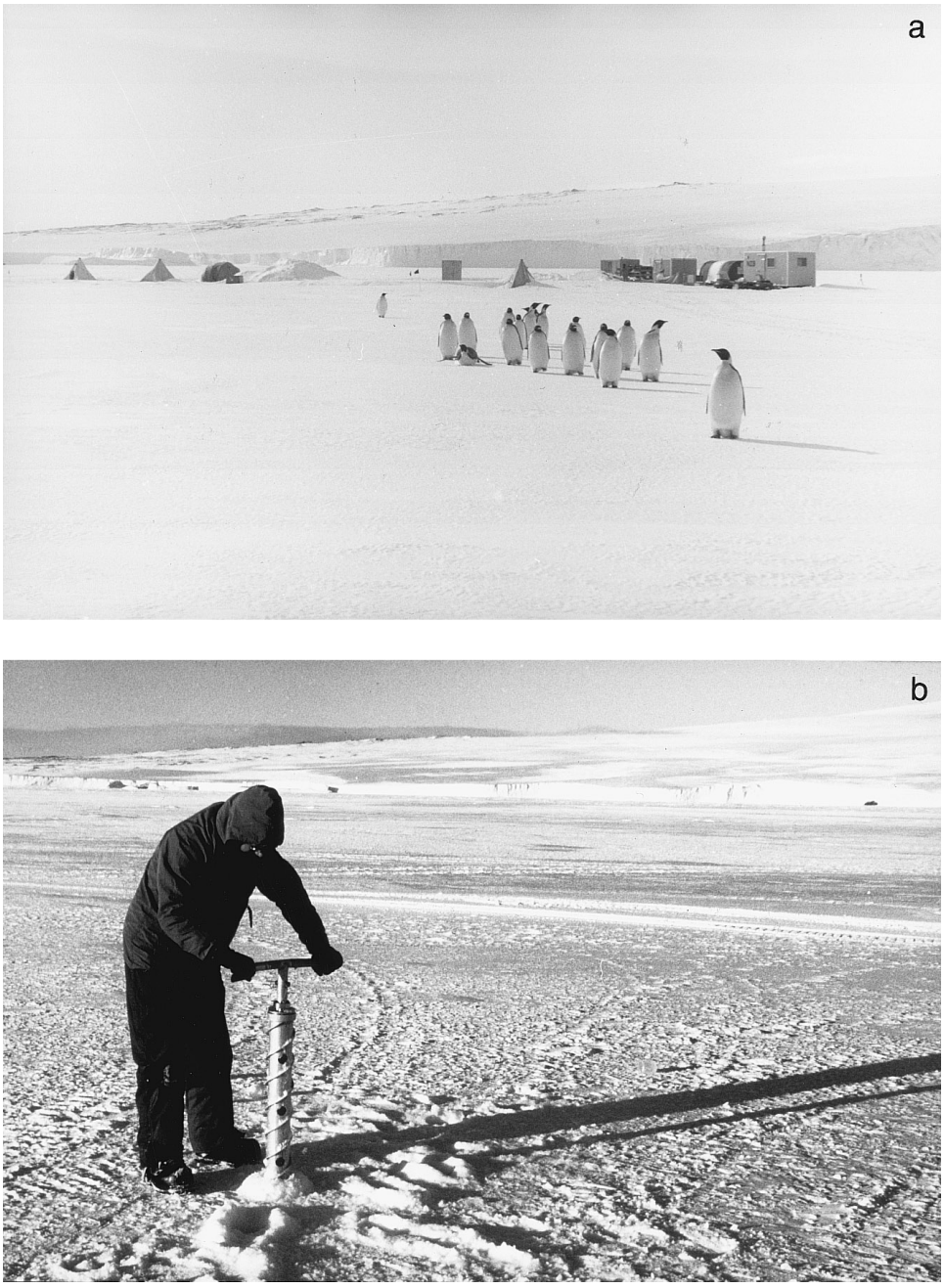
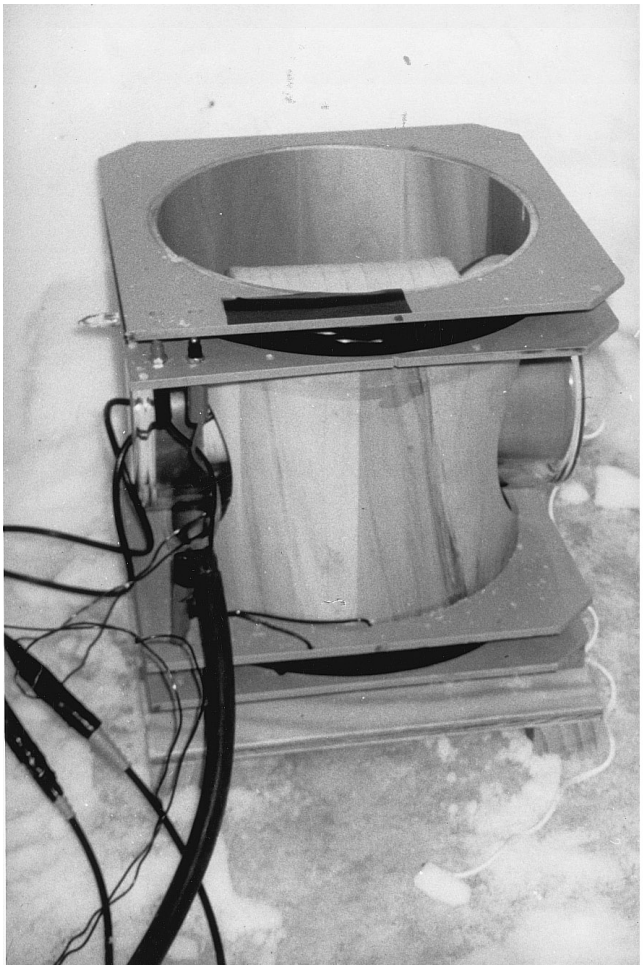


FIG. 2. (a) Field camp near Mt. Erebus used in our 1995 visit to McMurdo Sound. The Barne Glacier is visible in the background. (b) Process of ice core removal using auger. (c) Probehead tent with Mt. Erebus in background. (d) The probehead assembly with sea ice core sample inside. The gradient coils are visible at the top and bottom of the probe.

under this peak to determine the signal amplitude provided a high degree of bandpass filtering which helped to optimize the available signal-to-noise ratio. The entire system is controlled, and data acquired, using a Tecmag NMR system interfaced to a Macintosh IIci computer. Technical details of the equipment have been published elsewhere (*7*) and in the present paper we shall be concerned principally with the Antarctic application.

The NMR system has been used in Antarctica during the spring season (October/November) in both 1994 and 1995, on each occasion at locations near Cape Evans, Ross Island, the site of Robert Falcon Scott's winter quarters during the ill-fated Terra Nova expedition of 1910–1912. Figure 2 shows photographs of the camp site, the process of core removal, and the probehead. A photograph of the complete apparatus is given in Ref. (*7*). The probehead was located in a standard polar tent while the NMR electronics were in a second tent some 10



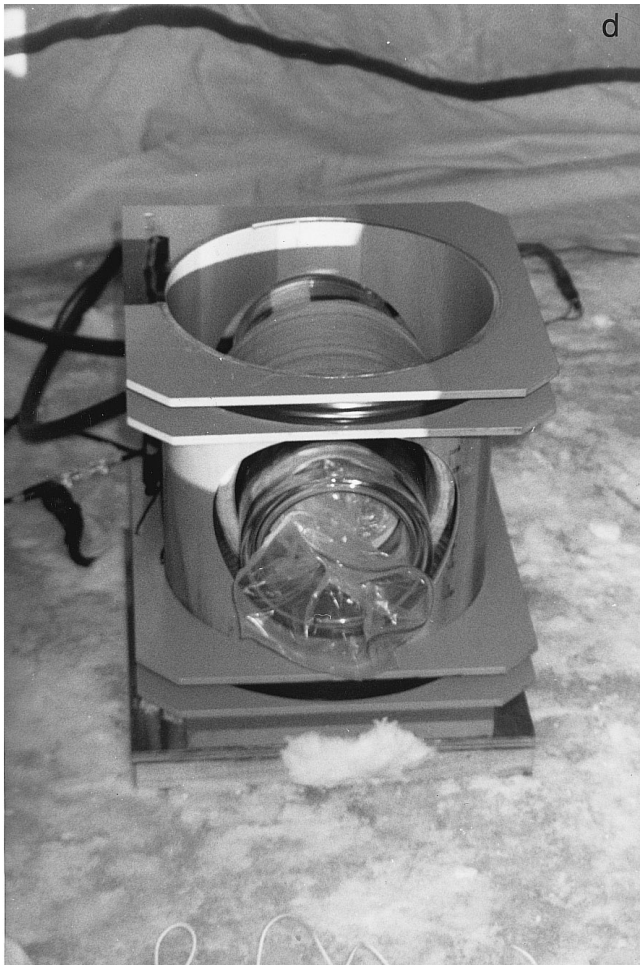


FIG. 2—*Continued*

meters distant and were powered by a 20-kW diesel generator located a further 50 m away. By means of a specially constructed auger (*8*), core samples of 65-mm diameter were removed from the sea ice at intervals of 200 mm from the surface to the ice–water interface at 2200 mm depth. Following extraction from the requisite depth, each ice core was cut to a length of 120 mm and the temperature measured at each end. It was then inserted in the NMR probehead and following completion of the NMR experiment the temperature was measured again. Although the probehead contained a dewar which provided thermal isolation for the samples from the NMR coils, typical temperature changes over the course of the experiment were on the order of or less than 2°C.

During the 1995 season, 45 core samples were examined. The free induction decay data, used to obtain brine content, was acquired in around 5 min, whereas the spin echo measurements, used to obtain relaxation time and diffusion information, required another 15 min. Subsequently, core samples were weighed and then melted in order to measure salinity. The salinity and temperature data can be used to calculate a brine fraction using the sea water phase diagram (*9*) and the correlation between the calculated brine content and that measured directly by NMR is demonstrated in Fig. 3. The agreement is good, allowing for the uncertainty in the calculated values due to their sensitivity to small errors in the temperature measurement.

PGSE NMR MEASUREMENTS ON SEA ICE

By means of spin echo measurements we determined the brine proton T_2 values to be in the range 500–1000 ms depending on the depth of the sample below the sea ice surface. These values were sufficiently long to permit PGSE NMR diffusion measurements to be undertaken. The pulse sequence used is shown in Fig. 1b; Fig. 4 gives a schematic illustration of the way in which ice core samples could be loaded into the apparatus with different orientations with respect to the magnetic field gradient. The sequence repetition time was 3 s and 24 acquisitions were used to provide the required signal averaging.

In pulsed gradient spin echo NMR the spin echo amplitude associated with molecules in unrestricted Brownian motion with diffusion coefficient D decays exponentially as (*10*)

$$E = \exp[-\gamma^2 g^2 \delta^2 D(\Delta - \delta/3)].$$

We worked with constant amplitude gradient pulses of 0.0045 T m^{-1} generated by a Maxwell pair coil set using 2.2 A current pulse from a Kepco ATE 25-10 power supply. The area under the gradient pulses was typically stepped over 12 values in a two-dimensional experiment by varying the pulse duration, δ, from 20 to 80 ms. Because of the large inductance of the gradient coils these pulses had rise and fall times on the order of 10 ms.

Figure 5 compares the echo attenuation obtained from a representative core sample (temperature −6°C, salinity 5.9 ppt, and taken at a depth of 1400 mm) with that found using a pure water reference. For the core sample experiment the gradient was applied in a direction transverse ($g_\perp$) to the vertical axis of the core samples. The results shown in Fig. 5 are remarkable in two respects. First we note the steepness of the initial decay in the sea ice sample at −6°C, indicating, paradoxically, a faster apparent diffusion than that of pure water at 7°C. This result suggests that the brine in the ice sample is not in thermodynamic equilibrium. Second, we note the strong biexponentiality of the echo attenuation. Ironically, the enhanced diffusion which dominates the initial decay has conferred the advantage of revealing a baseline of inhibited diffusion which would have otherwise been inaccessible given the strength of the available magnetic field gradient. This residual signal due to inhibited diffusion is more than 10 times the intrinsic noise level and represents in excess of 20% of the brine.

The data shown in Fig. 6 are also for core samples at −6°C of salinity 5.9 ppt and taken at a depth of 1400 mm. However, in these sets the gradient pulse spacing, Δ, was varied from 108 to 245 ms, thus providing a means of investigating the existence of any restrictions to molecular diffusion. Figures 6a and 6b show spin echo attenuations as a function of evolution time for orientations in which the magnetic field gradient is applied respectively transverse ($g_\perp$) and parallel ($g_\parallel$) to the vertical axis. In both cases we have schematically represented the data by using simple biexponential decays to guide the eye.

In the case of the Antarctic ice data shown in Fig. 6a, we note that the echo attenuation curve is independent of effective diffusion time, $(\Delta - \delta/3)$, as can be seen from the similarity of the data obtained with different values of Δ. We interpret these data as being consistent with a brine pocket model in which a large fraction of these pockets have dimensions, measured along the gradient direction, which are sufficient for rapid and unrestricted motion. Furthermore, the independence of the echo amplitudes in Fig. 6a over a factor of 2 in evolution time tells us that this rapidly diffusing water remains completely unrestricted over these times.

The results for the parallel orientation of gradient are very different. Here the rapidly diffusing water becomes more restricted once the evolution time reaches 200 ms. Clearly the brine with enhanced diffusion occupies pores which are highly anisotropic, an anisotropy which is consistent with light scattering studies (*11*). Given the relationship $\langle z^2 \rangle = 2D\Delta$, we are led to the conclusion that the dimension at which longitudinal restriction becomes apparent is on the order of 40 μm while the transverse dimension of the large pores is larger than 40 μm.

An interesting aspect of the data shown in Fig. 6a is the fact that both the slowly and rapidly decaying components appear to be associated with diffusion coefficients which are independent of the observation time, $(\Delta - \delta/3)$. In particular we are led to conclude that the slowly decaying fraction does not correspond to water which is completely confined (in which case it

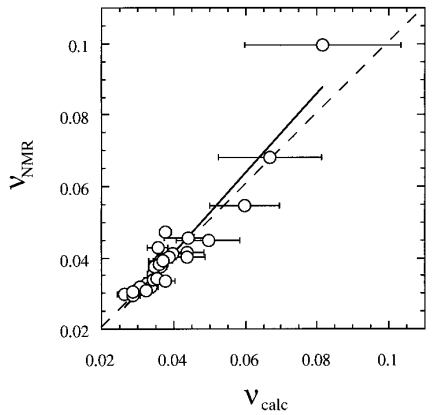


FIG. 3. Correlation of NMR measured brine volume fraction, ν_{NMR} ($m^3_{brine}/m^3_{sea\ ice}$), in Antarctic sea ice from McMurdo Sound to calculated value based on measured sea ice temperature and salinity. Linear regression of the data (—) yields $\nu_{NMR} = -0.0035 + 1.12\ \nu_{calc}$, with correlation coefficient 0.952. The dashed line of slope 1 is shown for reference.

would exhibit $D_{eff} \sim (\Delta - \delta/3)^{-1}$, but instead corresponds to a component with an asymptotic diffusion coefficient of greatly reduced value. This strongly suggests that the water is moving tortuously between connected pores with narrow throats.

The question remains as to the mechanism for enhanced water diffusion apparent in Fig. 5. One possibility is that by removing the core from the sea ice and placing a sectioned sample in the probe we have caused it to suffer a change in temperature sufficient to upset the delicate salinity, temperature, and gravitational gradients which were previously in balance. However, in all the samples taken, despite covering a wide range of temperatures from the surface of the ice sheet at ~ -15°C to the base at ~ -1.8°C, a similar pattern of enhancement was apparent, whatever the orientation of the sample inside the probe, and irrespective of the degree of (small) temperature change which the sample suffered during the course of the measurement. Consequently, we find it hard to accept that this behavior is an artifact associated with sample perturbation and are inclined to the view that it is intrinsic to the brine pocket structure even when in the ice sheet.

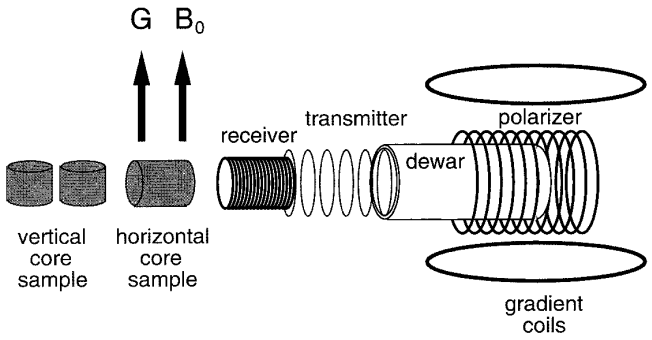


FIG. 4. Schematic showing exploded view of probe and the orientation of the sample during loading with the sea ice vertical axis direction respectively transverse (a) and parallel (b) to the gradient.

Preliminary work in the laboratory using NaCl and sea water ice samples grown under laboratory conditions and held in thermal equilibrium confirms this view.

CONCLUSION

The results presented here indicate how nuclear magnetic resonance in the terrestrial magnetic field has the potential to provide unique information about liquid phase fractions and pore (brine pocket) morphology for geophysical samples on site. In particular the PGSE NMR method has revealed some interesting anomalies indicative of anisotropic nonequilibrium brine dynamics in the brine pockets of Antarctic sea ice. Although the experiments described here are preliminary, they represent a considerable effort in apparatus development, in logistics, and in extreme measurement difficulty. Only a small fraction of the PGSE NMR and brine content data acquired in the Antarctic in 1995 have been shown here, and indeed, much further analysis is required in order to clarify the dependence of the data on the depth at which the ice core was taken from the sheet.

The work raises interesting questions about the nature of the chemical potential or buoyancy forces responsible for enhanced brine water diffusivity, and about the details of the brine pocket connectivity in sea ice. In our view such questions can best be answered in an NMR sense by extending the measurements in two directions. First, we believe that vital substantiation could be provided by NMR studies of model ice systems in the laboratory. This approach would offer the possibility of working under precise temperature control while making available a much greater range of NMR approaches,

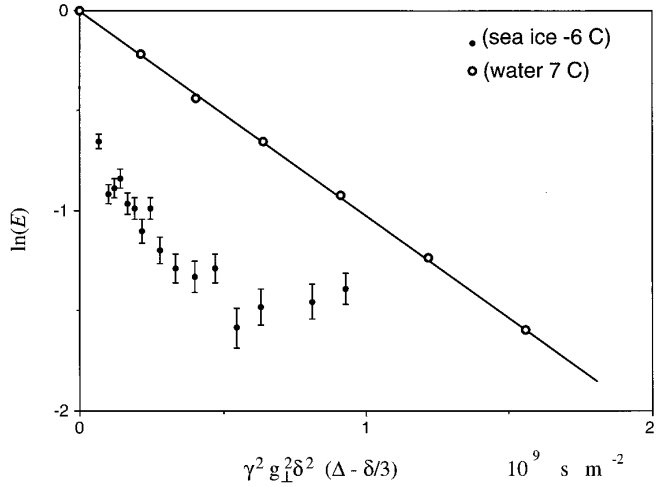


FIG. 5. Dependence of brine water spin echo attenuation on gradient pulse parameter $\gamma^2 g^2 \delta^2 (\Delta - \delta/3)$, for a sample obtained at a depth of 1400 mm (filled circles). The pulse spacing, Δ, is 108 ms. The linear data (open circles) corresponds to pure water at 7°C for which the pulse spacing, Δ, is 145 ms. For the sea ice measurement the sample is oriented as in Fig. 4a, with the gradient normal to the sea ice vertical axis. By contrast with the water sample, the brine shows evidence of fast and slow diffusion components.

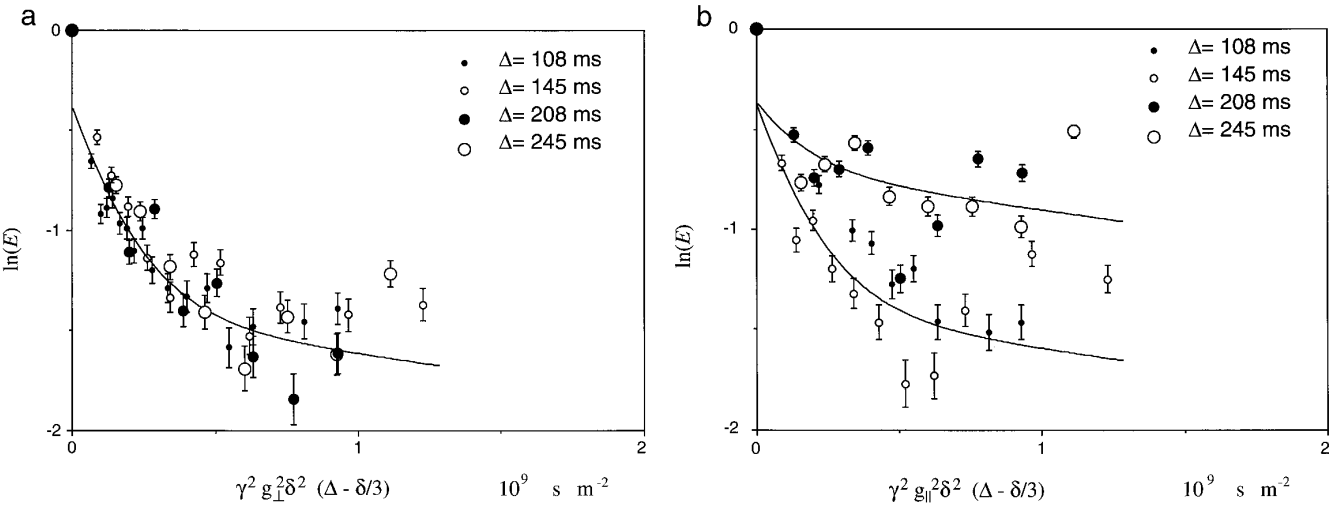


FIG. 6. Dependence of brine water spin echo attenuation on gradient pulse parameter $\gamma^2 g^2 \delta^2(\Delta - \delta/3)$, for a sample obtained at a depth of 1400 mm (filled circles) and for a range of times Δ as shown. In (a) the sample is oriented as in Fig. 4a, with the gradient normal to the sea ice vertical axis; in (b) it is oriented as in Fig. 4b, with the gradient parallel to the sea ice vertical axis. The biexponential lines are simply a guide to the eye and correspond to decay in which the fast diffusion coefficient is 2.2×10^{-9} m^2 s^{-1} (faster than that of free water) while the slow component diffusion rate is smaller by a factor of 10. In (b) the brine shows different behavior depending on the observational time scale, Δ, thus providing evidence of restricted diffusion. From the smallest to largest value of Δ used, the amplitude of the restricted component rises from 0.25 to 0.40, as indicated by the two solid lines.

including high-resolution micro imaging. Second, we see the need for a new NMR system, for use in the field, which will enable us to obtain information directly from the sea ice without the need for core removal. Both these strategies are currently under investigation at Massey University.

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