APPLICATION OF THE DIELECTRIC PROFILING
TECHNIQUE TO ICE CORE STUDIES

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Abstract: The dielectric profiling (DEP) technique is described and some of
the differences between it and standard electrical tools used in ice core analysis are
discussed. The results of DEP analysis on two cores from different regions of
Antarctica, Dolleman Island and Mizuho Station are described. DEP measure-
ments on the Dolleman core are related to the chemical composition of the core,
showing that DEP can provide a high accuracy measure of total ionic content of the
ice. The measurements on the Mizuho core are compared with earlier dielectric
measurements on the same core which show dramatic changes over the 15 year
period between the measurements. A mechanism which can explain the changes
and other effects noted from d.c. conductivity (ECM) experiments, is suggested.
The mechanism is based on the theory of d.c. conduction via liquid acid veins at
triple junctions in the ice.

1. Introduction

Reynolds (1985) showed that there were great differences in the dielectric be-
(haviour between ice recovered from warm coastal areas of polar regions and that
recovered from the cold interiors. Furthermore, the discovery, whilst sounding ice
sheets by radar, of internal reflections deep within the ice (Robin et al., 1969) is evidence
of natural dielectric variability (Paren and Robin, 1975; Millar, 1981). A chemical
explanation of these variations is possible, since trace levels of impurity have been
shown to affect the dielectric behaviour of ice grown from dilute solutions in the
laboratory (Camplin et al., 1978; Gross et al., 1978; Takei and Maeno, 1987). Prior
to the development of the dielectric profiling (DEP) technique (Moore and Paren,
1987), there existed no similar evidence for natural ice. The standard electrical tech-
nique used to characterize changes in the chemical content of ice cores is the ECM
method developed by Hammer (1980). The ECM technique has identified the deposi-
tion of acidic precipitation following volcanic events, and also annual cycles in Green-
land precipitation (Hammer, 1980). A freshly cut surface is required, along which
two electrodes (1.5 mm²), 1 cm apart are drawn, with a high (typically 1000 V) voltage
applied to the electrodes. The current flowing between the electrodes is related to the
acid content and thermal history of the ice, but is independent of the salt concentra-
tion (Hammer, 1980; MacCagnan et al., 1981).

The dielectric profiling (DEP) technique has practical advantages over ECM

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profiling. The method does not require a direct contact between ice and electrodes, maintaining the ice in pristine condition. The method is totally non-destructive and gives repeatable measurements with an applied voltage of only 1 V. The system is based on a Wayne Kerr 6425 multi bridge and HP 85 microcomputer (Fig. 1). A 1 m length of core can be studied at 5 cm intervals at 42 frequencies between 20 Hz and...
300 kHz in 20 minutes. Accuracy in capacitance and conductance is around 0.5% over most of the measurement range. The electrode assembly (Fig. 2) contains 20 ‘LO’ electrodes each consisting of curved segments 5 cm in width. Together they span a 1 m length of core. Guard electrodes at each end of the 1 m section and along the sides of the electrodes serve to keep the electrical field within the area occupied by the ice core. All the curved sections have the same radius of curvature as the ice core. Usually two adjacent electrodes are connected to the bridge and the remaining electrodes earthed. The sequence of measurements is controlled by the microcomputer. The complete set of capacitance and conductance measurements for each electrode combination along a core is stored by the HP85 on magnetic tape.

This paper describes DEP measurements on two Antarctic ice cores. The two cores are very different in several important respects: the type of source area and therefore probable chemical composition, their ages since drilling, and even the drilling technique used to recover the cores. One core was recently recovered from Domegman Island, a coastal region of the Antarctic Peninsula; the other is a much older core from Mizuho Station in an elevated, inland region of East Antarctica.

2. Curved Electrode Geometry

Previous dielectric measurements on ice have employed parallel plate capacitor geometry. The theoretical behaviour of this geometry is somewhat simpler than that of the curved electrodes used in DEP. Therefore, it is useful to present a simple analytical treatment of the expected geometric capacitance that such electrodes will exhibit.

Figure 3 shows a cross section view of the electrodes. For a parallel plate capacitor, $
\frac{C}{t} = \frac{\varepsilon_0 A}{t}$

where $C$ is the capacitance, $\varepsilon_0$ is the permittivity of free space (8.854 pF m$^{-1}$), $A$ is the electrode area and $t$ is the separation of the electrodes. In a curved electrode $t$ is not constant, but an average value of $1/t$ can be found. The separation of the plates, $t$, at any point is $2y = 2r \cos \theta$, then

$$
\frac{1}{t} = \frac{1}{t} \frac{1}{t} \frac{d\theta}{d\theta} = \frac{1}{4r \phi} \int_{\phi}^{\phi} \frac{d\theta}{\cos \theta}
$$

![Fig. 3. Diagram to show the calculation of the geometric capacitance of curved electrodes.](image)
\[
A = 2r/\phi, \text{ where } l \text{ is the length of the electrode, therefore}
\]
\[
C = \varepsilon_0 l \left[ \ln \tan \left( \frac{\pi}{4} + \frac{\phi}{2} \right) \right]
\]

(1)

It can be seen from eq. (1) that the capacitance of the electrodes is independent of \( r \), the radius of curvature, and depends only on the length of the electrode and the angle of arc \( 2\phi \) of the electrodes. Equation (1) is only an approximation to the true geometric capacitance since no account has been taken of the curvature of the field between the electrodes due to the field making contact with the electrodes at right angles. This effect implies that \( l \) is underestimated and the true geometric capacitance is therefore lower than that given in eq. (1). The values of air capacitance found experimentally using four sets of electrodes were in satisfactory agreement with the values predicted from eq. (1). Typical values of air capacitance for the electrode geometry of Fig. 2 with a length of 10 cm was about 1 pF, with variations between electrodes at different frequencies of 5%.

Changing one electrode from a curved section to a flat section positioned at half the core diameter does not change the geometry of the electric field, but simply halves the average value of \( 1/l \). This implies that DEP profiling of half cores will be directly comparable to measurements on whole cores after correcting for the difference in air capacitance. Such a simple comparison is not possible if cutting the core results in other than a half core being measured. The electric field will then be distorted from that expected in the complete core.

In order to separate the true air capacitance from any stray capacitance contribution which should be dependent on frequency and vary from electrode pair to electrode pair, an average air capacitance for an electrode pair was found. This average was found from measurements in the most accurate frequency range of the bridge (100–50000 Hz) for each electrode pair. Stray capacitances were then found as the differences between this average and the measured capacitance. Any measured conductance was considered a stray term since dry air should be a good insulator. All ice core data could then be corrected and converted to permittivity and conductivity values.

3. Dielectric Analysis

The ice core within its protective polythene sleeve, sandwiched between the electrodes of the DEP system, is equivalent to an ice sample in series with two blocking electrodes. Gross et al. (1980) state that two conditions are necessary for easy analysis of the bulk ice properties of the blocking system: (1) the blocking layers should be perfect insulators and chemically inert, and (2) the blocking layers should be sufficiently thick (compared to other sample dimensions) that the space charge polarizations are independent of applied voltage. Sixou et al. (1967) found that the condition of linearity is met if \( Q \), the ratio of ice sample thickness to the total blocking layer thickness, is less than 100. In the ice cores studied with DEP, the value of \( Q \) based on the thickness of the polythene alone is around 300; however, there is an additional blocking layer of air due to the irregular surface of the cores and the small differences
in diameter between the cores and the electrodes. In practice typical values of $Q$ were around 20 to 50. Under these conditions the ice-blocking electrode configuration is represented as a small number of overlapping simple Debye dispersions with relaxation times $\tau_i$ and dispersion strengths $\Delta \varepsilon_i$. The complex permittivity $\varepsilon^*$ of the system is then

$$\varepsilon^* = \varepsilon_{\infty} + \sum_{i=1}^{m} \frac{\Delta \varepsilon_i}{1 + j\omega \tau_i}$$

where $\varepsilon_{\infty}$ is the high-frequency permittivity of the system, $\omega$ is the angular frequency, and $j = \sqrt{-1}$. Notice that there is no d.c. conductivity term in eq. (2), due to the presence of the blocking layer. We are interested in the ice dielectric parameters, rather than those of the composite system. Unfortunately, for reasons that are not yet understood, the methods that are successful in the analysis of laboratory blocking systems do not give reasonable results when applied to the ice cores studied by DEP. The inversion equations used [see the appendix of Gross and Johnson (1983)] rely on an appropriate value for $Q$. This is particularly true of the equations for extracting the relaxation times of the ice and its d.c. conductivity. The extraction of the high frequency conductivity of the ice, $\sigma_m$, depends on the factor $Q/(1+Q)$ which is always close to 1 and the correction to $\sigma_m$ is very small. Additionally it has been found that the dominant relaxation frequency, $f_r$, of the main Debye dispersion of the composite is a useful indication of certain ice properties. Therefore, the difficulty of extracting true bulk ice parameters from the composite does not prevent two parameters, $\sigma_m$ and $f_r$, that are diagnostic of ice properties, from being found.

The analysis of the dielectric spectrum produced at each measurement position closely follows the techniques used by Gross et al. (1980) and earlier by D. B. Knoll described in Westphal and Iglesias (1970), and is described in detail in Moore and

![Graph showing conductivity against relative permittivity](image-url)

**Fig. 4.** A typical plot of conductivity against permittivity for a data set from the Dollemann core. The straight lines represent the dielectric dispersions that produce the fitted points. The lowest frequency dispersion is obscured by the low frequency data points.
Paren (1987) and Moore (1988b). Briefly, the analysis is based on the plots of conductivity $\sigma$ against permittivity $\varepsilon$. The $\sigma$-$\varepsilon$ diagram should show a set of straight lines representing each Debye dispersion, bent by the effects of the adjacent dispersions. The analysis program corrects each portion of the plot for the effects of its neighbours until a set of consistent relaxation parameters emerges. The program is started with a set of initial 'break points' that delimit the frequency range of each dispersion. Once a set of relaxation parameters has been calculated, the agreement between the measured dielectric data and those derived from the model. If the agreement is unsatisfactory a different set of 'break points' is generated, and this process continues until the fitting is acceptable. Figure 4 shows a typical $\sigma$-$\varepsilon$ plot for an ice core data set. The two important blocking layer composite parameters, $\sigma_0$ and $f_0$, are illustrated. Three dispersions characterize this data set which is the typical number for the Dollemann Island ice core, although occasionally two dispersions adequately describe the behaviour. This effect has also been seen from DEP measurements of other cores, and may provide an indication of certain ice properties, although the effect has not been systematically investigated.

4. Results of DEP Profiling

4.1. Dollemann island core

Dielectric measurements have been made in a cold room at $-22^\circ$C on a 133 m core from Dollemann Island, Antarctic Peninsula (70°35'S, 60°55'W, elevation 400 m, mean annual temperature $-17^\circ$C), (Moore, 1988a). The Dollemann core displays a wide range of acidities and marine salt concentrations that are typical of coastal Antarctica. A continuous 45 m section of this core has been chemically analyzed for Na$^+$, Mg$^{2+}$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$ (Mulvaney and Peel, 1988). This has produced 807 sets of dielectric and chemical data. The chemical species can be used to construct two basic chemical parameters that are representative of the neutral marine salt content, and of the acidic concentration in the core. Neutral salt is found from the total cation (excluding H$^+$) concentration of the core assuming that the non-measured cations are in sea salt ratios to Na$^+$ and Mg$^{2+}$. Salt is then given as

\[
salt = 1.05 ([Na^+] + [Mg^{2+}])
\]

if the units of concentration are $\mu$Eq $l^{-1}$. Total acid concentration is the difference in concentration between the total anions and the total cations, that is

\[
acid = [Cl^-] + [SO_4^{2-}] + [NO_3^-] - salt
\]

Again the concentrations are in $\mu$Eq $l^{-1}$, and contributions to the ionic balance of other ions such as NH$_4^+$, or terrestrial species are neglected. This assumption is supported by measurements of NH$_4^+$ and the ionic balance of the Dollemann core (Mulvaney and Peel, 1988).

Sea salt dominates acid concentration in most of the core. The major acid, H$_2$SO$_4$, is mainly a product of the photochemical oxidation of biogenically derived sulphur. Acid shows a clear annual cycle, salt also displays an annual cycle but is much more variable (Mulvaney and Peel, 1988). Peaks in salt and acid are general-
ly out of phase since acid peaks at maximum solar flux, in mid-summer whereas salt peaks at minimum sea ice extent in autumn. By contrast central polar regions have much lower concentrations (Herron, 1982) and acid is derived from volcanic sources (Legrand and Delmas, 1987), though typical acid concentrations are more like those found in Dolleman ice. The Dolleman core is therefore a complicated core to interpret in comparison with the much simpler chemical composition of ice from the polar interiors. This complexity is compensated by the large chemical and dielectric data sets available for study from the Dolleman core.

At the high frequency end of the DEP measurements the system displays a conductivity (σm in Fig. 4), close to that of ice in the HF-VHF range which is used for radar sounding purposes. This conductivity, together with the relaxation frequency of the dominant dispersion of the composite are very sensitive to the nature of the chemical impurities in the ice. The two dielectric parameters behave in ways that are dependent on the quantity and the type of chemical impurity present (Moore et al., 1990). For example, the increase in conductivity produced by a given quantity of acidic impurity is three times that caused by the same quantity of neutral salts. Using only the two dielectric parameters it is possible to estimate the total anion ([Cl\(^-\)]+[SO\(_4^{2-}\)]+[NO\(_3^-\)]) content of the Dolleman ice to a level that explains 87% of the variance in the anions. The measured total anion concentration and that estimated from the two dielectric parameters are shown in Fig. 5.

The dependencies of conductivity and relaxation frequency on both the acid and neutral salt concentrations are linear. Moore et al. (1990) show that the coefficient relating acid to conductivity is in good agreement with that predicted from the theory of the d.c. conductivity of polar ice proposed by Wolff and Paren (1984). This model is not based on the classic Jaccard (1959) theory of ice conduction based on point defects, but instead uses the idea that veins of highly concentrated acid located at triple grain junctions are responsible for the d.c. conductivity. This theory has also

![Fig. 5. A comparison of the measured total anion concentrations (thin line) and that predicted using the DEP parameters (thick line) for the Dolleman core.](image-url)
received direct observational support from the detection of high concentrations of sulphur at triple junctions (Mulvaney et al., 1988; Wolff et al., 1988). The nature of the salt conduction mechanism is consistent with the Jaccard theory if one Bjerrum L defect were generated for each one to two salt ions present in the ice (Moore, 1988b). This indicates that a large fraction of the salt impurity is present in the ice lattice.

4.2. JARE 13 core

This core is a complete contrast to the Dollemann core. The JARE 13 core was obtained in 1972 from Mizuho Station (70°41′53″S, 44°19′54″E), 2230 m above sea level and 270 km inland (Suzuki and Takizawa, 1978). The JARE 13 core was drilled using a thermal drill, in contrast to the electromechanical drill used on Dollemann Island, however both cores are of the same diameter. The JARE 13 core has been used for many analyses since it was recovered and there is only about 25 m of the original 139 m core still available for analysis. The core was cut into halves after drilling and has been stored as 0.5 m long sections at −15°C (sometimes as warm as −5°C, Suzuki and Takizawa, 1978), for some considerable time.

DEP measurements were made on the core halves with a flat plate 'HI' electrode substituted for the curved section shown in Fig. 2. The measurements were made at −22°C so that they could easily be compared with the Dollemann data set. This temperature is also close to −24°C, one of the temperatures at which Maeno (1978) analyzed samples from the same core when it was fairly new. Maeno (1978) made measurements on flat samples cut from the core in the traditional parallel plate type of electrode assembly. At that time chemical analysis of ice cores was very difficult and reliable chemical profiles of ice cores could not be measured. Twelve spot measurements of Na⁺ and Mg²⁺ concentrations were obtained and give an average value for neutral salt concentration of 10 μEq l⁻¹ (Murozumi et al., 1978), which is only slightly less than the average value for Dollemann of 14.6 μEq l⁻¹. The very large difference in the elevations and distances from the sea between the two sites would be expected to produce much lower concentrations of salts at Mizuho than Dollemann Island (Herron, 1982). This suggests that the early chemical analyses of the JARE core were not accurate. No data are available on the acid concentration of this core; however, Fujii and Watanabe (1988) report concentrations of SO₄²⁻ in a short section of core from the same area. Most of the SO₄²⁻ is probably present as H₂SO₄, if salt concentrations are typical of inland polar regions. Peak values of 4-8 μEq l⁻¹ were measured. This is very similar to average levels of acidity in the Dollemann core, and suggests that acidity is the major factor determining σ∞ in the Mizuho core.

Figure 6 shows the σ∞ and fᵣ variations in the core sections measured with the DEP system. The relaxation frequency parameter is generally very well correlated with σ∞ and does not appear to be as independent a parameter as it was in the Dollemann Island data. This is probably due to the chemical composition of the core. Values of fᵣ are not directly comparable to those of ice found by normal dielectric measurements (for example see Reynolds, 1985). This is because of the effect of the blocking layer, which has the general effect of increasing fᵣ by a factor dependent on Q, but which is typically around 5 for the experimental arrangement described here (Gross and Johnson, 1983). A correction to the values of fᵣ found from DEP by a factor of
about 5 would result in values very similar to those reported by MAENO (1978) for samples of the JARE 13 core. The relaxation frequency of polar ice exhibits a rather different behaviour from that of pure ice. Both polar and pure ice have similar relaxation frequencies at temperatures close to the melting point; however, the relaxation frequency of pure ice decreases much more quickly than that of polar ice as the temperature is lowered. At -22°C, pure ice has a relaxation frequency of around 1 kHz, whilst values for polar ice are up to an order of magnitude faster. REYNOLDS (1985) discusses the variability of relaxation frequency between samples from different source areas. He concludes that samples from 'warm' sites with a mean annual temperature of near zero exhibit fast relaxations, whilst those from 'cold' sites (mean annual temperature less than -10°C) have slower relaxations that are only 2 or 3 times quicker than pure ice. However, there are several important exceptions to this rule. In particular, the Mizuho samples studied by MAENO (1978) showed a high relaxation frequency, placing it in the 'warm' group despite its annual mean temperature of -33°C! REYNOLDS (1985) attributes this to annealing caused by the thermal drill used. However, REYNOLDS (1985) also notes that samples from George VI Ice Shelf, where extensive summer melt pools are common, display a 'cold' type of behaviour. It seems unlikely that greater annealing could have occurred during the drilling of the Mizuho core than occurs naturally every summer on George VI Ice Shelf. Therefore another explanation for the rapid relaxations of polar ice must be sought. We believe a better explanation lies in the chemical differences between the samples (MOORE et al., 1990), perhaps in combination with another, 'ageing' factor dependent on the specific surface area of the ice crystals (MACCAGNA and DUVAL, 1982).

Fig. 6. The \( \sigma_m \) (lower curves at each core depth) and \( f_r \) (upper curves) profiles at -22°C of the JARE 13 core. The crosses mark the values of \( \sigma_m \) found by MAENO (1978) at -24°C for the core.
Figure 6 also shows the spot values of $\sigma_\infty$ obtained by Maeno (1978) at $-24^\circ$C. There are no cases where the same core sample was measured in both experiments. However, it is clear that the DEP measurements are considerably lower in magnitude than the earlier set. The DEP measurements (if a correction for density is made, Maeno, 1978) are close to the expected lower limit of conductivity as defined by the conductivity of a single crystal of pure ice. At $-22^\circ$C Camplin et al. (1978) reported a high frequency conductivity of 4.5 $\mu$S m$^{-1}$ for a single pure ice crystal. From the limited and discontinuous measurements it is difficult to draw conclusions about the mechanisms for the decrease in conductivity. There are no consistent shapes for curves of $\sigma_\infty$ or $f_i$ for the individual core lengths which suggests that contamination, which would tend to affect the ends of the core, has not been significant.

There does seem to be a more noticeable decrease in the conductivity of the topmost sections of the core, above about 55 m, than below this depth. 55 m depth corresponds to the pore close-off depth in the core (Narita et al., 1978). It appears that the chemical source of the ice conductivity has disappeared in some way, and the greater disappearance in areas where the ice is more permeable suggests that the grain boundaries or triple junction veins play an important part. It has been observed in ECM studies (Hammer, 1980) that repeatable currents will be measurable only on freshly prepared surfaces. E. W. Wolff (pers. commun.), has described the difficulties of preparing samples for scanning electron microscope studies (Mulvaney et al., 1988; Wolff et al., 1988), that will consistently allow detection of high concentrations of sulphur at triple grain junctions. Only freshly prepared samples are suitable for the work. Liquid acid veins that are responsible for conduction appear to offer an explanation for all these observations, since the liquid will diffuse and evaporate away from exposed surfaces much more quickly than could occur by solid diffusion of impurities. It thus appears possible that the d.c. component of the conductivity caused by acids has decreased dramatically or disappeared. This accounts for the general low values of $\sigma_\infty$ and the behaviour of $f_i$ in Fig. 6. If only a dielectric conductivity remained then $f_i$ would vary in conjunction with $\sigma_\infty$, and therefore would not be an independent parameter.

5. Conclusion

The DEP technique is an important new tool in ice core stratigraphy since it is the only non-destructive method of estimating both the neutral salt and acid concentrations in ice. DEP is sensitive to properties of the bulk of the ice sample being measured. ECM, on the other hand, is a surface phenomenon. Therefore, DEP may be expected to provide results that are less sensitive to actual experimental conditions than the notoriously sensitive ECM. The technique should also provide valuable insights into ice conduction processes and the mechanisms of impurity incorporation in ice.

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References


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