Sea Salt Dependent Electrical Conduction in Polar Ice

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A 45 m length of ice core from Doleman Island, Antarctic Peninsula has been dielectrically analysed at 5 cm resolution using the dielectric profiling (DEP) technique. The core has also been chemically analysed for major ionic impurities. A statistical analysis of the measurements shows that the LF (low frequency) conductivity is determined both by neutral salt and acid concentrations. The statistical relationships have been compared with results from laboratory experiments on ice doped with HF (hydrogen fluoride). Salts (probably dispersed throughout the ice fabric) determine the dielectric conductivity. The salt conduction mechanism is probably due to Bjerrum L defects alone, created by the incorporation of chloride ions in the lattice. Samples of ice from beneath the Filchner-Ronne Ice Shelf were also measured and display a similar conduction mechanism below a solubility limit of about 400 μM of chloride. The temperature dependence of the neutral salt, acid and pure ice contributions to the LF conductivity of natural ice between -70°C and 0°C is discussed. These results allow a comprehensive comparison of dielectric and chemical data from natural ice.

1. INTRODUCTION

Most dielectric studies of natural ice (reviewed by Reynolds [1985]) have not included comprehensive chemical analysis of the ice. Early dielectric studies were very time consuming allowing only a small number of samples to be measured. Ice has been the subject of detailed dielectric study since Auty and Cole [1952] showed that pure ice exhibits the simplest form of dielectric response expected from the classical theory of dipolar relaxation. The response in audio to low frequency range is approximated by a Debye dispersion (see Hobbs [1974] or Glen and Paren [1975]), which has a maximum dielectric loss at a frequency called the relaxation frequency, f_r . At frequencies, $f \ll f_r$, the permittivity is about 90, similar to the value for water. When $f \gg f_r$ the molecular dipolar polarization is negligible, and the permittivity is about 3.2. The d.c. conductivity of pure ice is very low, and the conductivity increases through the relaxation region reaching a limiting value at high frequencies, σ_∞ . For pure ice at -22°C , $f_r = 650 \text{ Hz}$ and $\sigma_\infty = 4.7 \mu\text{S m}^{-1}$ [Reynolds, 1985]. The existence of a Debye relaxation spectrum and the high polarization of ice at low frequencies is surprising for a crystalline substance, since it implies that all the water molecules in the ice lattice are constantly changing their orientations. The long established explanation of the mechanism through which this occurs was first suggested by Bjerrum [1951] and relies on two types of imperfections being present within an ice crystal. Firstly, ionic defects formed from the weak ionization of H_2O into H_3O^+ and OH^- . Secondly 'Bjerrum' defects formed by imperfect bonding between molecules; an oxygen-oxygen (O-O) bond with an extra hydrogen is called a Bjerrum D defect and one with no hydrogens is a Bjerrum L defect. Movement of Bjerrum defects occurs when a water molecule rotates about the oxygen atom. The ionic and Bjerrum defects are both necessary to transport protons as a direct current; they act in series and the d.c. conductivity is

determined by the weaker of the ionic and Bjerrum defect conductivities. Both defect currents can act in parallel at frequencies higher than the relaxation frequency; they then determine the value of σ_∞ . As the frequency of the exciting field increases, the ability of water molecules to preferentially align with it decreases, causing the observed relaxation process to occur. The theory was developed independently by Jaccard [1959, 1964, 1965] and Onsager and Dupuis [1960, 1962] and Onsager [1969]. It predicted a variation of permittivity with frequency governed by a simple Debye type dispersion. The parameters involved are determined by the mobilities, effective charges and concentrations of the Bjerrum and ionic defects. These data can be found by experiments on doped single crystals of ice. In addition estimates of the mobilities can be made from experiments on proton injection [Petrenko *et al.*, 1983] or on the surface conductivity of ice [Petrenko and Maeno, 1987].

The behaviour of ice has been found to change considerably when it is doped with small amounts of impurities. The earliest work was done using HF as a dopant since it has a similar molecular size to H_2O and was thought to be easily incorporated into the crystal lattice [Jaccard, 1959]. Probably the most reliable and self-consistent HF-doped ice dielectric data are that of Camplin *et al.* [1978]. Many other dopants have also been studied. Gross *et al.*, [1978] separate these into two classes: the conductivity enhancing solutes (HCl, HF, NaCl, KF, NH_4F) and the conductivity depressing solutes (NH_4OH , NH_4Cl , NH_5CO_3 , NaHCO_3). Different impurities in each group behave in remarkably similar ways which is surprising since they are very different in size and chemical structure. What is not clear is where the impurities are located in the ice samples (crystal lattice, localized in the grain boundary, triple junctions, etc), and hence how they interact with the water molecules in the ice, affecting the concentrations of Bjerrum and ionic defects. For example, the rate of freezing strongly affects incorporation of impurities and very little of the impurity in the solution can be incorporated in the crystal lattice. Ice made in the laboratory is unlikely to reproduce the processes which occur during the natural growth of ice in the atmosphere or the subsequent diagenesis in an ice sheet.

Recently, interest in the mechanisms that cause the Antarctic spring ozone depletion has prompted research into the processes that occur on atmospheric ice particles. Wolff *et al.* [1989], and Hanson and Mauersberger [1990] suggest that under stratospheric conditions, HCl is present as a concentrated acid on the surface of polar stratospheric cloud particles or in liquid droplets, and not incorporated significantly in the bulk of the ice crystals.

Huber *et al.*, [1973] inferred from backscattering of He from ice monocrystals that had been in contact with HCl solution that Cl was substitutionally incorporated into the ice lattice at a surprisingly high concentration. This experiment appears to contradict much of the other evidence on impurity incorporation into ice, where impurities are generally incorporated at much lower levels; however the physical process involved is solid-state diffusion rather than crystal growth. The experimental technique does not appear to have been used on other impurities despite its usefulness in determining if an impurity is incorporated interstitially or substitutionally. Studies of impurity locations in natural polar ice using scanning electron microscopy (SEM) with an X-ray fluorescence detector [Mulvaney *et al.*, 1988, Wolff *et al.*, 1988] have shown that sulphur is often concentrated at triple grain junctions, probably as concentrated H_2SO_4 . Cl has not been detected in any of the meteoric ice samples studied using this technique (R. Mulvaney, personal communication).

The present understanding of the electrical behaviour of ice may be briefly summarized. Pure and HF-doped ice have a dielectric behaviour determined by Bjerrum and ionic defects as described by the 'classical' theories of Jaccard. Other impurities incorporated within the lattice are also likely to generate point defects leading to similar electrical behaviour, however impurity concentrations above the solubility limit of the impurity in ice will be excluded from the lattice and forced to grain boundaries or interstitial spaces. There is strong evidence that the d.c. conductivity of natural polar ice is determined by acids, perhaps in liquid form at triple grain boundaries. There is laboratory evidence on the dielectric behaviour of artificial ice, usually monocrystals, doped with impurities which show rather ambiguous and variable results.

2. STATISTICAL ANALYSIS OF THE DIELECTRIC AND CHEMICAL DATA

This study describes results from ice between the depths of 26 m and 71 m of a 130 m ice core from Doleman Island (70°35'S, 60°55'W; elevation 400 m, mean annual temperature -17°C, 400 $\text{kg m}^{-2} \text{yr}^{-1}$ accumulation rate). Also discussed are samples from a German ice core through the Filchner-Ronne Ice Shelf at site B13 (76°59'S, 52°16'W); the samples come from the part of the core that formed by the freezing of sea water to the base of the ice shelf [Oerter *et al.*, 1992]. These samples have much lower salinity than typical sea ice, but much higher than normal polar ice. SEM analysis (to be described elsewhere) suggests that at least part of the salt is excluded from the lattice in the B13 samples, with concentrated brine pockets present in the higher salinity samples. Doleman Island is an ice rise on the edge of the Larsen Ice Shelf within 15 km of the Weddell Sea. The proximity of the ice rise to the sea results in large concentrations of marine salt in the ice core. The sea salt shows annual cycles that peak in early winter when sea ice extent is a minimum and storms are common. The unusually large (for an Antarctic ice core) range of sea salt concentrations in the Doleman core, and the even higher levels of sea salt in the B13 core make these samples very

suitable for investigating the variation of electrical properties with salt concentration.

2.1 Dielectric Analysis

A dielectric profiling (DEP) technique has been fully described by Moore and Paren [1987] and Moore and Maeno [1991]. The technique requires no contact between ice and electrode so that the core can be maintained in pristine condition within a protecting polythene sleeve. Measurements of the dielectric response of the 10 cm diameter core with 5 cm wide electrodes are made quickly every 5 cm down the core using a microprocessor controlled bridge sweeping the 20 Hz-300 kHz frequency range. The electrodes were guarded at the ends to prevent loss of spatial resolution due to fringing fields. The composite system (ice and polythene) displays a dominant Debye dispersion, with the thin sleeve acting as an electrical blocking layer. Inversion formulae are available [Gross *et al.*, 1980] for extracting the intrinsic ice behaviour from that of the ice-polythene sandwich, but a critical parameter, the size of the variable gap between electrode and ice is not known in practice. We have found that the dielectric parameters of the composite system alone relate satisfactorily to the chemical stratigraphy. At the highest frequencies, the conductivity of the composite is within a few percent of that intrinsic to the ice, and approximates well to the conductivity of ice in the HF-VHF range. This conductivity must be corrected for density effects [Glen and Paren, 1975],

$$\sigma_{\infty} = \sigma_{\infty f} / [\nu (0.68 + 0.32 \nu)^2] \quad (1)$$

where ν is the ratio of firm density to solid ice density (0.917 Mg m^{-3}), $\sigma_{\infty f}$ is the firm conductivity, and σ_{∞} is the solid ice conductivity value, the subscript denoting a frequency much higher than the relaxation frequency, f_r of the dominant dispersion. Figure 1 shows the frequency dependence of the conductivity for the four Doleman Island samples at -22°C,

Fig. 1. The frequency response of the conductivity of four samples of Doleman Island ice at -22°C. The relaxation frequency (f_r) of the dominant dispersion is marked by a line drawn from the curve at the relaxation frequency to the sample name.

showing one dominant dispersion with a marked f_T . We find that σ_∞ and f_T display a strong and reproducible signal along the core, related to the chemistry, despite the "noise" in the response due to varying thickness of the polythene and air blocking layer between electrode and ice. Understandably, f_T cannot be directly compared with intrinsic ice values. The main dielectric data set used was a set of measurements at -22°C . This provided a set of 806 values of each parameter. A further set of 278 dielectric measurements were obtained at -9°C . In addition four samples from Dolleman Island and three samples of ice from beneath the Filchner-Ronne ice shelf were dielectrically analysed at temperatures between -70°C and 0°C .

2.2 Chemical Analysis

The Dolleman core was stored at -20°C in sealed polythene sleeves for about 6 months and then chemically analysed for major anions and cations between depths of 26 m and 71 m. Table 1 summarizes the chemical results. The full chemical time series will be published elsewhere. The anions were measured using a Dionex 2010i ion chromatograph; the instrument has an accuracy of 5%. Cations were analysed by flame atomic absorption spectrometry using a Pye Unicam SP9; precision is about 3%. Such accuracy was achieved over the full range of concentrations discussed in this paper. The chemical data were obtained at a higher resolution than the dielectric data, so the chemical series were interpolated to fit the dielectric data. This was done by fitting a spline function to each chemical series, and then averaging the function over the length covered by the electrode in each dielectric measurement. The average chemical concentration was then assigned to the electrode mid-point position. This procedure has the effect of slightly blurring sharp chemical spikes.

2.3 Investigating the Chemical and Dielectric Response

Various combinations of the parameters listed in Table 1 were tried in statistical analyses to obtain their relationships with σ_∞ and f_T for the Dolleman data. The simplest and most useful combination was with the two terms, salt and acid. The salt concentration was defined as the sum of the marine cations, which

using the sea water ratios of Davis [1977, p.172] is given by

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

where the concentrations are in $\mu\text{eq L}^{-1}$.

The acid concentration was defined as the difference between the concentration of marine anions and cations:

$$[\text{acid}] = [\text{Cl}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}] - [\text{salt}] \quad (3)$$

using only the values where $[\text{acid}] > 0$. This was true for 801 out of the 806 values. Many other chemical parameters were also investigated; in particular it was found that Na and Mg gave regressions with the same gradients and did not improve the statistical fit when treated separately, and so were treated as the single variable (salt). Separating the acid component into the three strong acids HNO_3 , HCl and H_2SO_4 also led to no significant improvement in statistical fit. While we use salt as our indicator of marine ions, we believe that it is the chloride ions associated with the salt parameter that determine the electrical effects in ice. However, because of the presence of large amounts of HCl in the Dolleman ice, we chose not to model with measured Cl directly. The response of HCl is likely to be different to that of neutralized Cl , since the acid may be not incorporated in the lattice [Moore et al., 1989], and any HCl in the lattice would introduce ionic H_3O^+ defects in addition to defects produced by the Cl^- ion. The marine chloride level can be calculated from the sea water ratios as $0.91[\text{salt}]$.

Table 2 shows the fits obtained to σ_∞ and f_T by various models involving salt and acid. In general, multiple non-linear regression analyses were used, but a simple linear time series model with autocorrelated errors was also tested. The best fitted powers of both acid and salt are all within two standard errors of unity (model 1). It is therefore reasonable to accept models 2 and 5 which have linear coefficients.

Possibly the most surprising result was the lack of any significant relationship between the DEP parameters and depth. Nor was there any significant difference in the regression coefficients found when the data in 10 m long sections was analysed separately. The lack of such a variation apparently rules out any conductivity contribution that depends simply on the ice grain surface area, since the grain size increases with the age of the ice at a rate dependent on temperature [Gow, 1969]. The depth range between 26 m (the 1945 horizon) and 71 m (1845) corresponds to a time period of 100 ± 3 years (D. Peel, personal communication). This should be a sufficiently long period at a temperature near -17°C if any simple change in electrical properties with time were to exist. Since there is no evidence of any change, this calls into doubt the existence of the natural 'ageing' effect in electrical behaviour discussed by Reynolds [1985]. The electrical effects associated with annealing of ice at temperatures very close to the melting point or the effects of storage in a laboratory environment [Schwander et al., 1983] were not investigated by this study.

The better fits shown in Table 2, model 4, obtained by a time series analysis technique demonstrates that adjacent data cannot be treated as strictly independent. The time series technique makes use of the serial correlation inherent in the data to define the error structure for the model. At present only a simple analysis of this has been attempted. One possible explanation is the occurrence of a natural separation of chemical impurities during snowfall with different elements being precipitated at different rates, (R. Mulvaney, personal communication). This would result in local enrichments and depletions of these elements in the ice core, thus violating the assumption that marine salts

TABLE 1. Chemical Composition of the Dolleman Island Core (26-71 m Depths)

Species	Mean, $\mu\text{eq L}^{-1}$	Maximum, $\mu\text{eq L}^{-1}$
Na^+	11.20	110.85
Mg^{2+}	2.70	12.92
Cl^-	14.64	124.95
SO_4^{2-}	4.76	21.79
NO_3^-	0.55	1.86
XSO_4^{2-} ^a	3.40	20.26
XCl^- ^b	1.44	15.50
[anions] ^c	19.95	128.77
[salt] ^d	14.59	121.09
[acid] ^e	5.36	20.45

^a Calculated as $[\text{XSO}_4^{2-}] = [\text{SO}_4^{2-}] - 0.0982 ([\text{Na}^+] + [\text{Mg}^{2+}])$.

^b Calculated as $[\text{XCl}^-] = [\text{Cl}^-] - 0.95 ([\text{Na}^+] + [\text{Mg}^{2+}])$.

^c Calculated as $[\text{anions}] = [\text{Cl}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}]$.

^d Calculated as $[\text{salt}] = 1.05 ([\text{Na}^+] + [\text{Mg}^{2+}])$.

^e Calculated as $[\text{acid}] = [\text{anions}] - [\text{salt}]$.

TABLE 2. Statistical Analysis of the Dolleman Island Core (26-71 m Depths)

-22°C data					
Model 1: $\sigma_{\infty} = A \text{ salt}^p + B \text{ acid}^q + \text{const} + E$			$f_t = A \text{ salt}^p + B \text{ acid}^q + \text{const} + E$		
Parameter	Value	S.E.	Parameter	Value	S.E.
p	0.99	0.05	p	1.095	0.05
q	1.03	0.1	q	0.981	0.28
A	0.407		A	295	
B	1.32		B	642	
const	12.87		const	8880	
variance accounted for 76.6%			variance accounted for 68.4%		
Model 2: $\sigma_{\infty} = A \text{ salt} + B \text{ acid} + \text{const} + E$			$f_t = A \text{ salt} + B \text{ acid} + \text{const} + E$		
Parameter	Value	S.E.	Parameter	Value	S.E.
A	0.393	0.009	A	442	11
B	1.425	0.05	B	612	64
const	12.73	0.34	const	8210	405
variance accounted for 76.6%			variance accounted for 68.3%		
Model 3: $\sigma_{\infty} = A \text{ salt} + \text{const} + E$			$f_t = A \text{ salt} + \text{const} + E$		
Parameter	Value	S.E.	Parameter	Value	S.E.
A	0.41	0.01	A	450	12
const	20.1	0.26	const	11400	245
variance accounted for 55.8%			variance accounted for 64.6%		
Time series models with autocorrelated errors					
Model 4: $\sigma_{\infty} = A \text{ salt} + B \text{ acid} + \text{const} + AE$			$f_t = A \text{ salt} + B \text{ acid} + \text{const} + AE$		
Parameter	Value	S.E.	Parameter	Value	S.E.
A	0.360	0.01	A	430	13
B	1.228	0.057	B	590	66
const	14.3	0.4	const	8510	520
variance accounted for 84.4%			variance accounted for 79.8%		
Best linear regression for -9°C data					
Model 5: $\sigma_{\infty} = A \text{ salt} + B \text{ acid} + \text{const} + E$			$f_t = A \text{ salt} + B \text{ acid} + \text{const} + E$ ($f_t < 80 \text{ kHz}$)		
Parameter	Value	S.E.	Parameter	Value	S.E.
A	0.60	0.03	A	405	40
B	2.58	0.17	B	870	250
const	24.8	1.1	const	15500	1600
variance accounted for 72.3%			variance accounted for 31.6%		

σ_{∞} ($\mu\text{S m}^{-1}$); f_t (Hz); salt; acid ($\mu\text{eq L}^{-1}$); E, random error; AE, autocorrelated error.

would be precipitated in sea salt ratios. The enrichment would probably change gradually and cyclically along the core leading to an apparently varying set of electrical parameters. Such behaviour may lead to the type of time series response actually observed. Until a more detailed analysis is complete the parameter estimates from the best least squares regression (models 2 and 5) will be accepted.

Figure 2 shows the relationship between Cl concentration and σ_{∞} after removing the contributions from acid and constant terms. Substituting Cl for salt, using sea water ratios [Davis, 1977], in the linear fits for σ_{∞} and f_t described in Table 2, gives

$$\sigma_{\infty} = 12.7 + 0.43 [\text{Cl}] + 1.43 [\text{acid}] \quad (4a)$$

$$f_t = 8200 + 490 [\text{Cl}] + 612 [\text{acid}] \quad (4b)$$

Equation (4a) is represented by the line in Figure 2. There is large scatter about the line at low Cl concentrations, because samples with low Cl concentrations usually had a higher conductivity due to acid than salt, resulting in a large correction to σ_{∞} and a relatively small residual conductivity due to Cl. As can be seen the two samples from the B13 core with the lowest salinity fit well on the Dolleman regression line. The two higher concentration samples have conductivities lower than expected.

2.4. Temperature Dependence of Conductivity

The temperature dependence of σ_{∞} for samples with various impurity concentrations was investigated using a parallel plate electrode apparatus (Figure 3). Eight samples were studied, four from Dolleman Island, three B13 samples, and one sample made

Fig. 2. Logarithmic plot of σ_{∞} corrected for the effects of acid and 'constant' terms using equation (4a) at -22°C versus chlorine concentration for Dolleman Island and the Filchner-Ronne B13 core samples. The straight line is the linear regression relation between marine chloride and σ_{∞} for the Dolleman Island samples.

from double distilled de-ionized water representing pure ice behaviour. A fourth B13 sample (FR262) was only measured at -22°C . The samples were roughly 1 cm thick cross-sections of core, except for the artificial sample. The solid ice B13 and pure ice samples were microtomed to produce flat and parallel surfaces. The Dolleman firm samples were simply cut on a band saw. The samples were measured with a polythene sheet between the ice and electrodes to produce a blocking layer capacitor as was used in the DEP measurements on the whole Dolleman core. Since the pure ice sample was to be used as a baseline for investigating the effects of impurities in the ice, a bubbly,

polycrystalline specimen was made by freezing water in a plastic beaker at -22°C . The frozen sample contained bubbles and appeared polycrystalline when viewed under crossed polarisers.

The samples were placed in the electrodes at -22°C then cooled slowly to -70°C in a freezer. After equilibrating overnight, the electrodes were allowed to warm slowly at a rate of $2.5^{\circ}\text{C}/\text{hour}$. The temperature of the electrodes was measured by a platinum resistance thermometer (PRT) above the electrodes. Complete dielectric spectra were measured at resolutions of between 0.1°C and 0.5°C (higher resolution at warmer temperatures). The PRT temperature was not the average ice temperature because of the thermal inertia of the electrodes. The ice temperature was calculated from a calibration experiment using a thermistor embedded within an artificial ice sample. The sample was warmed in an identical fashion to the real samples. It was found that temperature differences between the thermistor and the PRT reading was typically 4°C at rapid warming rates, becoming only 0.2°C as the warming rate became very low at 0°C . The thermistor temperature was modelled by the PRT reading using a fifth order polynomial which accounted for 99.995% of the variance. The uncertainty in the ice temperature was probably mainly due to temperature gradients across the sample, estimated to be $< 1^{\circ}\text{C}$. The temperatures used in the rest of this section are the derived ice temperatures. The Dolleman samples were only warmed to -15°C to preserve the samples for further study, the other samples were warmed until they had clearly started to melt, generally at a derived temperature within 0.2°C of 0°C . A small volume of ice removed from the top and bottom surfaces of the samples during sample preparation was chemically analysed, (Table 3). The samples themselves were not analysed because of possible contamination introduced during the partial melting at the end of the experiment. Comparison of values of σ_{∞} and f_r expected from the statistical relationships with the measured values, shows that for the Dolleman samples, there is a likelihood that the chemistry of the bulk samples was different to the small volume collected for chemical analysis. Figure 4 shows the Arrhenius plots for the samples.

As observed by many authors [e.g., Glen and Paren, 1975, Camplin et al., 1978], the pure ice sample exhibits a much higher activation energy of conduction (0.55 eV), than samples

Fig. 3. Elevation view of parallel plate electrodes and their enclosure. Samples of ice about 1 cm thick were used in the experiment.

TABLE 3. Dielectric Analysis at -22°C of the Dolleman Island Core (D Prefix) and Filchner-Ronne B 13 (FR Prefix) Samples That Were Temperature Cycled

Sample	Depth, m	Density, Mg m ⁻³	Marine Cl, µeq L ⁻¹	Acid, µeq L ⁻¹	Measured σ_{∞} , $\mu\text{S m}^{-1}$	Predicted σ_{∞} , $\mu\text{S m}^{-1}$	Measured f_t , kHz	Predicted f_t , kHz
D1024	23.13	0.629	13.64	1.7	30.7	22	10.0	16
D1076	67.1	0.751	90.8	1.6	73.2	55	84.0	54
D1083	73.3	0.773	8.12	7.7	25.6	32	20.0	17
D1093	80.6	0.826	37.12	0.5	48.6	30	17.2	26
FR252	154.36	0.917	1135	0	211	500	103	560
*FR262	159.96	0.917	811	0	192	360	100	405
FR294	179.01	0.917	405	0	167	187	69	206
FR322	196.94	0.917	355	0	156	165	75	182

Acid concentration found using equation (2). Marine [Cl] = $0.95([\text{Na}^+] + [\text{Mg}^{2+}])$. Sample conductivities corrected to solid ice density using equation (1). Predicted values of σ and f_t based on equations (4a) and (4b).

* Sample FR252 measured only at -22°C.

containing impurities. *Camplin and Glen* [1973] report an activation energy of 0.61 eV for a pure single crystal, the highest value in the literature. Other values reviewed by *Glen and Paren* [1975] vary between 0.6 eV and 0.56 eV for laboratory grown

single crystals. The Dolleman samples (about 0.19 eV) and the B13 samples (0.26 eV) show lower activation energies. All the samples appear to be well characterized by a single activation energy over the whole temperature range. This contrasts with the

Fig. 4. Arrhenius plot showing the temperature dependence of σ_{∞} for the four cross section samples of Dolleman Island core, three of the four samples from the Filchner-Ronne B13 core, and a 'pure ice' sample made from double distilled de-ionized water. Details of the dielectric and chemical properties can be found in Table 3.

behaviour generally seen in polycrystalline natural ice [Glen and Paren, 1975; Reynolds, 1985] which exhibit a rise in activation energy as the melting point is reached until the activation energy is close to that of pure ice. Even pure ice monocrystals have lower activation energies at temperatures below -55°C [Glen and Paren, 1975]. The pure ice sample in Figure 4 shows a slight decrease in activation energy at low temperatures, however this is less pronounced than for many of the pure samples reported by Glen and Paren [1975].

Activation energies for permeable polar ice are around 0.21 eV [Reynolds, 1985], in good agreement with the Dolleman samples. Deep (therefore denser) polar ice typically has higher activation energies around 0.24 eV [Reynolds, 1985] again in good agreement with the B13 samples. Sample D1083, having the highest acidity shows some evidence of higher activation energy at warmer temperatures (0.28 eV between -22°C and -15°C). Sample FR252 shows much variability at warm temperatures, probably due to the very high relaxation frequency (over 100 kHz). Addison [1975] observed discontinuities at certain temperatures in the dielectric properties of sea ice associated with the eutectic points of several major brine components. No discontinuities are evident in Figure 4 for the B13 samples. This is perhaps expected considering the low brine volumes present in even the most saline of the samples.

The statistical analysis of Dolleman Island σ_{∞} data at -9°C and -22°C for 278 samples gives the activation energies, E , for the salt, acid and constant terms as

$$E_{\text{salt}} = 0.19 \pm 0.02 \text{ eV} \quad (5a)$$

$$E_{\text{acid}} = 0.26 \pm 0.03 \text{ eV} \quad (5b)$$

$$E_{\text{const}} = 0.30 \pm 0.02 \text{ eV} \quad (5c)$$

The constant term seems likely to be made up of a pure ice component with behaviour similar to that of the artificial sample in Figure 4, together with an extra component representing other factors. The factors may be ice fabric dependent, or caused by chemical species that vary independently of those measured. Since the pure ice sample in Figure 4 was polycrystalline and contained bubbles, and shows behaviour similar to that of bubble free single crystals, we feel that unmeasured chemical species may be the correct explanation. Possible species include CO_2 , likely to be fairly constant in concentration along the core, or organic acids, which on Dolleman Island vary in concentration and seasonality relative to the species considered in the statistical models in Table 2 [Mulvaney et al., Submitted to Tellus]. Table 2 model 2 gives a constant of $12.7 \mu\text{S m}^{-1}$ at -22°C, model 5 gives a constant $24.8 \mu\text{S m}^{-1}$ at -9°C. If we represent the pure ice behaviour as having a σ_{∞} of $4.7 \mu\text{S m}^{-1}$ at -22°C and $16.5 \mu\text{S m}^{-1}$ at -9°C corresponding to an activation energy, E_{pure} of 0.55 eV, we can separate (5c) to give the activation energy for the unknown factors E_x ; this turns out to be 0.0 ± 0.1 eV.

Equations (5a) and (5b) show that activation energies for impurities are much lower than for the pure ice contribution to σ_{∞} . Therefore at low temperatures, impurity contributions to σ_{∞} increase in significance relative to that from pure ice. For example, at -60°C the pure ice contribution to σ_{∞} is $0.05 \mu\text{S m}^{-1}$, (4a), (5a) and (5b) show that $0.3 \mu\text{eq L}^{-1}$ of acid or $0.5 \mu\text{eq L}^{-1}$ of neutral chloride would produce an equal additional contribution to σ_{∞} . This may explain the decrease in activation energy observed in pure ice samples at low temperature [Glen and Paren, 1975]: low levels of impurities in the samples becoming dominant factors in σ_{∞} at low temperatures.

As can be seen from the equations (5a) and (5b), the activation energy for acid is slightly higher than that for salt, at least between -22°C and -9°C. As mentioned above sample D1083 does have higher activation energy than the other samples between -15°C and -22°C, consistent with its higher acidity. The activation energies of the B13 samples are at least as high as the much lower salinity Dolleman samples, not showing the decreasing activation energies with increasing salt content that would be expected from (5a). The behaviour is quantitatively in line with the increase in activation energy with density [Reynolds, 1985]. No realistic value of activation energies for the f_T fits can be found because of the poor fit of the -9°C data.

3. MODELS OF CONDUCTION PROCESSES

3.1 Results from Laboratory Data on Doped Ice

The 'classic' account of the conduction processes and relaxation developed by Jaccard [1959] is relevant for the interior of ice crystals. In order to apply the theory to Antarctic ice it is necessary to determine the lattice concentrations of the impurities and their associated defects. This can only be done by reference to studies of single crystals of HF-doped ice where it is assumed that the impurity is in the ice lattice. Laboratory studies on chloride doped ice with a range of different cations [Gross et al., 1977, 1987] show that although the distribution coefficient of chloride in ice is typically an order of magnitude lower than for fluoride, the dielectric spectra for both species are remarkably similar; this implies a similar incorporation mechanism for chlorides as for fluorides. Studies of ice grown from solutions containing other non-chloride salts and acids common in Antarctic snow are not sufficiently reproducible and well-documented to assist us.

The most complete dielectric data on HF-doped ice is that of Camplin et al., [1978]. Their measurements were made on single crystals following very consistent procedures through the various stages of crystal growth, dielectric measurement, and crystal HF concentration measurement [Camplin and Glen, 1973]. The experimental technique appears not to introduce unknown contamination. With confidence in their experimental procedures we have investigated further the relationships between dielectric parameters and HF concentrations using unpublished data of G.C. Camplin. Linear relationships are found between both σ_{∞} and f_T with HF concentration at -9°C and -22°C. The relationships found at -22°C for the 15 samples with HF concentrations between pure and $51 \mu\text{M}$ are:

$$\sigma_{\infty} = (4.91 \pm 0.74) + (1.73 \pm 0.03) [\text{HF}] \quad (6)$$

which accounts for 99.6% of variance, and

$$f_T = (654 \pm 174) + (165 \pm 7) [\text{HF}] \quad (7)$$

which accounts for 97.1% of variance.

The conductivity relationship at -9°C is

$$\sigma_{\infty} = (15.5 \pm 1.7) + (3.16 \pm 0.07) [\text{HF}] \quad (8)$$

which accounts for 99.3% of variance. The concentrations are in units of $\mu\text{eq L}^{-1}$ of ice, conductivity in $\mu\text{S m}^{-1}$, and frequency in Hz.

Camplin et al., [1978] used the HF dielectric data to deduce the mobilities and charges for the various electrical defects. They made the assumption that in both pure and HF-doped ice the conductivity due to Bjerrum defects, σ_{DL} was dominated by the L defect conductivity. Similarly the ionic conductivity, $\sigma_{\pm}$ was approximated by that due to H_3O^+ , σ_{+} , because the OH^- mobility

is known to be lower than that of H_3O^+ . The mobility, μ_L and charge, j_{Le} of L defects at -22°C were estimated as $1.73 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $0.458e$ where e is the charge of an electron. The mobility, μ_+ and charge, j_{+e} of an H_3O^+ defect at -22°C were $2.88 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $0.702e$. The conductivity due to ionic defects can then be found as

$$\sigma_{\pm} \approx \sigma_+ = [\text{H}_3\text{O}^+] j_{+e} \mu_+ = 1.95 [\text{H}_3\text{O}^+] \quad (9)$$

and that due to Bjerrum defects as

$$\sigma_{DL} \approx \sigma_L = [L] j_{Le} \mu_L = 0.763 [L]. \quad (10)$$

Similarly, the conductivities at -9°C are

$$\sigma_+ = 1.85 [\text{H}_3\text{O}^+] \quad (11)$$

$$\sigma_{DL} = 1.48 [L], \quad (12)$$

where, following our earlier practice, the concentrations are in μM (in ice), and the conductivities in $\mu\text{S m}^{-1}$.

A second set of values for the σ_L coefficients is found using the data on HF doped ice of Jaccard [1959]. The value of the coefficient in equation (10) is 0.5, and the coefficient in equation (12) is 0.86. The values of the coefficients in equations (9) and (11) are determined by the proton mobility. Other techniques are available to measure directly proton mobility and a wide range of values have been found. Gosar [1963] deduced a value from theoretical considerations of the quantum mechanical tunnelling process involved. He found that mobility is extremely sensitive to the O-O distance in the lattice; in fact a change of only $0.1 \text{ \AA}$ produces a 100 fold change in value. Neither the experimental parameters nor the theory is sufficiently well defined to predict an accurate value from this theory. Petrenko *et al.*, [1983] state that the best value of proton mobility comes from the work of Eckner *et al.*, [1973] and is about $10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a near zero activation energy, and a similar value of $1.2 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ was found by Kunst and Warman [1983]. Petrenko and Maeno [1987] used a novel method to estimate the mobilities of both types of ionic defects, they found values of 9.2×10^{-8} and $2.7 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for H_3O^+ and OH^- ions at -33°C . It can be seen that the present consensus is for proton mobility (and consequently the coefficient in equation (9)), to be about three to four times higher than that found by Camplin *et al.*, [1978]. As an aside we can say that this disagreement would be reconciled if $2/3 - 3/4$ of the HF molecules in supposedly single crystals did not interact with the other water molecules. In addition, the analysis of Camplin *et al.*, [1978] did not meet the theoretical requirement that $j_{Le} + j_{+e} = e$, which could introduce a discrepancy in to the other derived parameters.

Comparing equations (6) and (8) with equations (9) to (12) it can be seen that the HF coefficient in equation (6) lies between that of L defects and ionic defects at -22°C , the coefficient at -9°C is higher than both that in equation (11) and (12). HF introduces defects of each type into the lattice, affecting both the d.c. conductivity and the relaxation process in the ice. Comparing the coefficients in equations (9) and (11) it can be seen that the ionic conductivity decreases with rising temperature (a consequence of proton quantum mechanical tunnelling), and this is completely at odds with the behaviour of the HF conductivity in equations (6) and (8). These observations support the conclusion that HF introduces mainly L defects into ice. It may be noticed that the effectively zero activation energy of the ionic defects is in agreement with the activation energy of the unknown factors E_x , however since there is no concentration data on the factors

responsible for this conductivity contribution, little further can be said here.

Unfortunately, there are fewer dielectric studies on laboratory ice doped with chlorides, which would be more relevant to the behaviour of natural ice. Gross *et al.*, [1977, 1987] studied NaCl and HCl impurities finding similar dielectric behaviour to fluorides which they interpreted in terms of point defects introduced by substitutional incorporation of chlorides. Takei and Maeno [1987] measured the electrical properties of ice doped with HCl. Only 3 different samples were studied and the HCl concentrations in the ice were not measured, only the concentrations in the solutions from which the ice was grown.

3.2 Acid Conduction Mechanism

A d.c. measure of conductivity is often used to study ice cores [Hammer, 1980]; the technique involves the measurement of the current flowing between two pointed electrodes which are at a potential difference of at least 1 kV and are scratched along a freshly cut ice core surface. This form of analysis (ECM) has been shown to be a very useful tool in the stratigraphic analysis of ice cores. The current flowing between the electrodes depends non-linearly on the acid concentration of the ice core [Hammer, 1983, Legrand *et al.*, 1987] but is independent of marine ion concentrations, even at concentrations of $100 \mu\text{M}$ of NaCl [Moore *et al.*, 1992]. This contrasts with evidence from laboratory grown ice where Gross *et al.*, [1978] found that the d.c. conductivity varied as $[\text{Cl}]^{0.4}$. This discrepancy will be discussed further in the next section.

The σ_{∞} relations found for the Dolleman core (Table 2, model 2) gave coefficients of 0.4 for salt and 1.4 for acid components at -22°C . These coefficients are for concentrations in water; in order that they may be compared with the coefficients in equations (6) to (12), they must be converted to concentrations in ice. The salt coefficient is then 0.43 and the acid coefficient 1.55 at -22°C . If the acid component were to be found in the lattice, it apparently introduces defects in a similar way to HF. However the acid coefficient in the f_T relationship is very different to that in equation (7). In addition, the SEM evidence of Mulvaney *et al.*, [1988] that SO_4 is localized at triple junctions, leads us to believe that most of the acid component in the Dolleman core is not located inside the ice grain. The acid conduction mechanism is discussed further by Moore *et al.*, [1989], and Moore *et al.*, [1992].

3.3 Salt Conduction Mechanism

As mentioned in Section 2.3, we believe that it is the marine chloride that is responsible for the conduction mechanism parameterized by the salt factor. The chloride ionic radius, though 40 % larger than the ionic radii of fluoride and oxygen [G.W. Gross, personal communication] is much closer in size to the oxygen atom and may therefore be substituted into the lattice more easily than the other major anions (SO_4^{2-} and NO_3^-) found in polar ice which are larger. The marine cations, (Na^+ and Mg^{2+}) would have to be substituted for the much smaller H^+ which is unlikely to occur. The salt component has a coefficient of 0.43 in the σ_{∞} relation at -22°C , the factor for marine chloride would be 0.47. Since this is about half the coefficient in equation (10), and also less than the coefficient (0.5) derived from Jaccard's data, it may suggest that one L defect is introduced into the lattice on average for every one to two chloride ions. A similar result holds for a comparison at -9°C . If chloride produces only L defects then the d.c. conductivity of the ice will not be

increased, since the d.c. conductivity is determined by the minority charge carriers which at -9°C and -22°C are ionic defects. This hypothesis is supported by the observation of Hammer [1980] and Moore *et al.*, [1992] that marine ions do not contribute to the ECM current, and evidence from the recent GRIP ice core shows that HCl does produce an ECM (d.c.) current. In laboratory doped ice, HCl and NaCl produce similar electrical effects, which can be explained by the reactions

If (13) does not favour the right hand side of the reaction while (14) does, then NaCl will behave differently at d.c. than HCl. Since NaCl does not affect the d.c. conductivity of polar ice, we conclude that (13) does not go to the right. Instead we believe that the NaCl creates L defects as Cl^- is substituted for oxygen in the lattice.

Using the values of μ_L found by Jaccard [1959] and Camplin *et al.*, [1978] and the corresponding activation energies of (0.235 - 0.29) eV allows the calculation to be made of the L defect concentration in pure ice [Hobbs, 1974]. The value found at -22°C lies between 4-10 μM , if the D defect conductivity is assumed to be negligible, and the corresponding σ_{∞} is 4.7 $\mu\text{S m}^{-1}$. In pure ice, with negligible d.c. conductivity, σ_{∞} and f_T would double if the concentration of defects in the ice doubled. For the Dolleman core, σ_{∞} has an extrapolated value of 12.7 $\mu\text{S m}^{-1}$ at -22°C for ice with no acid or salt; to increase this value by 4.7 $\mu\text{S m}^{-1}$ (the pure ice conductivity) requires 12 $\mu\text{eq L}^{-1}$ of salt. To double f_T requires 18 $\mu\text{eq L}^{-1}$ of salt. These calculations show that salt concentrations in the range 12-18 $\mu\text{eq L}^{-1}$ effectively create 4-10 μM of L defects. Earlier it was argued that one L defect could be created in the lattice for each one to two chloride ions: here the ratio turns out nearer 1:2. The same calculations for -9°C data lead to an L defect concentration in pure ice of 8-21 μM with a σ_{∞} of 17.5 $\mu\text{S m}^{-1}$. To increase σ_{∞} of Dolleman Island ice by this amount requires 29 $\mu\text{eq L}^{-1}$ of salt. As with the -22°C data, the ratio of L defects to chloride ions is about 1:2. Either all the chloride is in the lattice, producing one L defect for two ions, or 50% of the chloride is in the lattice (minimum 30%, maximum 70%) creating one L defect for each ion in the grain. In the latter case 30%-70% will be located outside the grain. Since no Na or Cl has been found in the SEM observations of the Dolleman ice, we must assume that the remainder of the NaCl is not localized, or is at least localized in areas too small to be detected with the SEM. This is supported by SEM observations of the B13 Filchner-Ronne samples (paper in preparation); the lower salt concentration samples showed some evidence of Cl at grain boundaries, however the higher concentration samples show large inclusions or pockets of Cl and other brine impurities, together with large amounts at grain boundaries.

Gross *et al.* [1977] work on laboratory grown ice suggested a solubility limit existed for NaCl which represented the maximum concentration that could be incorporated into the crystal lattice. The limit was 100-200 μM , which also agreed with earlier measurements by Seidensticker [1972]. The σ_{∞} of the two lower concentration B13 samples fall very close to the expected value using the relations found for Dolleman Island, while the two higher concentrated samples have much lower values of σ_{∞} than expected. This is consistent with a solubility limit around 400 μM below which there is a linear dependence of σ_{∞} on Cl concentration. This is also consistent with the SEM observations

showing much less Cl in the lower concentration samples than the levels expected if all the Cl had been localized at grain boundaries.

The B13 samples formed in solution at -2°C , then gradually cooling to about -12°C over a period of several hundred years. The Dolleman ice originally formed in the atmosphere, was deposited at temperatures between -40°C and -2°C , then spent many years at -17°C in the ice sheet. This could lead to very different impurity incorporation mechanisms for the two ices. The agreement between the extrapolated Dolleman behaviour and the lower salinity B13 samples (Figure 2), may be coincidental. However, the B13 samples were effectively formed from essentially pure ice surrounded by trapped concentrated brine at grain boundaries and inclusions for many years. The NaCl in the Dolleman ice was initially a solid particle, probably the nucleating particle for the ice crystal. SEM observations of the Dolleman ice have never detected these particles and it is unlikely that they are present in such a form in the ice. In the Dolleman Island ice sheet, NaCl was in contact with practically pure ice at temperatures above the NaCl eutectic point (-21°C), for many years. Therefore it seems that the NaCl would form a solution of concentrated NaCl and ice, creating similar conditions to those that led to the formation of the B13 ice. The two types of ice may be comparable in terms of chloride incorporation in the lattice and therefore electrical properties.

4. CONCLUSIONS

The contribution from marine salts, probably the chloride ions, to electrical conduction in ice from Dolleman Island and from beneath the Filchner-Ronne Ice Shelf can be explained in terms of the Jaccard theory of conduction. Comparison with laboratory data on HF-doped ice implies that chloride ions introduce L Bjerrum defects into the lattice at a rate of one L defect for every one to two ions. If the dependence of dielectric parameters on the chloride concentration is compared to pure ice, it appears that about half the ions present in the ice are in the lattice. If salt (that is chloride ions) introduce only L defects in the lattice, then marine ions should not affect the d.c. conductivity of ice. There appears to be a solubility limit of about 400 μM below which the relationships found are valid; above this concentration the excess chloride is localized in inclusions in the ice, and conductivity increases more slowly with increasing chloride concentration.

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