DIELECTRIC STRATIGRAPHY OF ICE: A NEW TECHNIQUE FOR DETERMINING TOTAL IONIC CONCENTRATIONS IN POLAR ICE CORES

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Abstract. A 133 m deep Antarctic ice core from Dolleman Island, Antarctic Peninsula, has been profiled by dielectric measurements in the AF-LF (20 Hz - 100 kHz) frequency range. This has revealed large variations in dielectric relaxation and conductivity down the core. A comparison with the chemical stratigraphy along 45 m of the core demonstrates for the first time the decisive role played by acids and salts in determining the electrical behaviour of natural ice. The total ionic concentration along the ice core can be deduced from the dielectric response. This technique may be applied rapidly in the field and, as it requires no contact between ice core and electrodes, the core is maintained in pristine condition for later chemical analysis.

Introduction

The discovery, whilst sounding ice sheets by radar, of internal reflections deep within the ice [Robin et al., 1969; Harrison, 1973; Gudmandsen, 1975] is evidence of natural dielectric variability [Paren and Robin, 1975; Millar, 1981]. Furthermore, Reynolds [1985] found marked differences in dielectric behaviour between ice recovered from the cold interiors of polar regions and ice from warmer coastal areas. A chemical explanation of these variations is possible, since trace levels of impurities in ice grown from dilute solutions in the laboratory have been shown to affect the dielectric behaviour [Camplin et al., 1978; Gross et al., 1978; Takei and Maeno, 1987]. To date no similar evidence exists for natural ice. The only technique so far developed to characterise changes in the chemical content of ice without melting it, is the electrical conductivity measurement (ECM) developed by Hammer [1980]. This powerful stratigraphic technique has identified the deposition of acid following volcanic events, and also annual cycles in Greenland precipitation. A freshly cut ice surface is required, along which two electrodes (1.5 mm²) a few cm apart are drawn, with a high (~kV) voltage applied to the electrodes. The current flowing between the electrodes is related to the acid content and the thermal history of the ice, but is independent of the salt concentration [Hammer, 1980; Maccagnan et al., 1981]. For repeatable current measurements a new surface must be prepared.

A dielectric profiling (DEP) technique developed by Moore and Paren [Moore and Paren, 1987; Moore, 1988a; Moore, 1988b] has practical advantages over ECM profiling. The technique requires no direct contact between ice and electrodes so the core can be maintained in pristine condition within a polythene sleeve. The method is totally non-destructive and gives repeatable measurements, with an applied voltage of 1V. Measurements of the dielectric response of the core with polythene sleeve are made every 5 cm down the core using a microprocessor controlled bridge sweeping the AF-LF frequency range. A 1 m length of core can be analysed in 20 minutes. The composite system (ice and polythene) displays a dominant Debye dispersion,

with the thin sleeve acting as an electrical blocking layer. At LF, 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 frequency range [Glen and Paren, 1975]. We designate this conductivity, σ_∞ , the subscript denoting a frequency much higher than the relaxation frequency, f_r , of the dominant dispersion of the composite. We find that σ_∞ and f_r display a strong chemical signal despite the "noise" in the response due to varying contact between electrode, polythene and ice.

Observations

Dielectric measurements have been made in a cold room at -22°C on a 133 m core from Dolleman Island, Antarctic Peninsula (70°35'S, 60°55'W, elevation 400 m, mean annual

Fig. 1. A comparison of sodium (Na^+), excess sulphate (XSO_4^{2-}), marine cation (salt), and acidity with the LF conductivity (σ_∞) and relaxation frequency (f_r) for a 15 m length of Dolleman Island core. Peaks in σ_∞ and f_r appear at peaks in the chemical parameters. For example, the large peaks in Na^+ and salt at 27.5 m, 34.5 m, and 40.2 m are associated with large peaks in both dielectric parameters. These can be compared with the peaks in XSO_4^{2-} and acid between 29.5 m and 31 m during a period when salt concentrations were low; these produce significant peaks in σ_∞ , but much smaller effects in f_r .

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temperature -17°C) [Moore, 1988b]. A continuous 45 m of this core, from between 26 m and 71 m depth, has been chemically analysed for Na^+ , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^- . This has provided 807 sets of chemical and dielectric data. All sections of the core have been subject to the same thermal history since drilling. The temporal resolution of the chemical and dielectric data is equivalent to one month's snowfall.

Figure 1 shows measurements on 15 m of core (~ 270 data sets). Na^+ is almost totally derived from sea salt at this near coastal site. The salt parameter, representing the total marine cation concentration, was calculated from the chemical measurements, assuming marine ratios for the cations

$$[\text{salt}] = 1.05 ([\text{Na}^+] + [\text{Mg}^{2+}]) \quad (1)$$

XSO_4 is the excess sulphate: that is the sulphate concentration above that expected if the salt and sulphate ions were in normal sea salt ratios. Negative excess sulphates were observed from time to time: this phenomenon has been noted elsewhere and is the subject of some debate [Wagenbach et al., 1988]. Excess sulphate is essentially sulphuric acid, which is the main acidic component of the ice. The strong acid content of the ice core has been calculated from the chemical measurements by

$$[\text{acid}] = [\text{Cl}^-] + [\text{SO}_4^{2-}] + [\text{NO}_3^-] - 1.05 ([\text{Na}^+] + [\text{Mg}^{2+}]) \quad (2)$$

which assumes no other ions are present in significant quantities, (i.e. there are no terrestrial sources or NH_3 , see for example Legrand et al., 1988), and acids are present as HCl , HNO_3 , and H_2SO_4 . The approach was checked by directly measuring $[\text{H}^+]$ by acid titration on 63 samples and found to be in very good agreement. A full discussion of the chemical time series will appear elsewhere. The plotted values of σ_{∞} have been corrected for density (see Glen and Paren [1975]). Figure 1 clearly shows that peaks in both acid and salt concentrations affect σ_{∞} and f_r .

The relationships between salt and acid and the two dielectric parameters have been derived using non-linear

regression analyses. In both cases the exponents for acid and salt were not significantly different from unity. This contrasts with observations linking currents measured during ECM profiling and acidity where exponents of 0.58 were found by Hammer [1980] for acidity in Greenland ice, and exponents of 0.63 and 0.40 by Legrand et al. [1987] for two Antarctic sites. For DEP the linear responses at -22°C were

$$\sigma_{\infty} = (0.39 \pm 0.01) [\text{salt}] + (1.43 \pm 0.05) [\text{acid}] + (12.7 \pm 0.3) \quad (3)$$

which accounts for 76.6% of variance,

$$f_r = (440 \pm 11) [\text{salt}] + (612 \pm 65) [\text{acid}] + (8200 \pm 400) \quad (4)$$

which accounts for 68.4% of variance. The units of σ_{∞} are $\mu\text{S m}^{-1}$, f_r are Hz, and $[\text{salt}]$ and $[\text{acid}]$ are $\mu\text{Eq l}^{-1}$. No significant trend with depth and hence age has been found: the age range of the data is 100 years.

The total ionic concentration of the ice core is strongly linked to the dielectric parameters. A non-linear regression between the total anion concentration ($[\text{Cl}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}]$) and the dielectric parameters gives

$$[\text{anions}] = [\text{salt}] + [\text{acid}] = 0.022 \sigma_{\infty}^{1.89} + 1.0 \times 10^{-6} f_r^{1.61} - 0.2 \quad (5)$$

where the units of $[\text{anions}]$ are $\mu\text{Eq l}^{-1}$. This model accounts for 86.7% of the variance. Figure 2 shows the agreement between the measured total anion concentrations and values calculated from the model: it demonstrates the power of the DEP technique to respond to both neutral salts and acids in the ice, and thus complements the ECM technique which reacts to acids alone.

The Dolleman Island core displays a wide range of acidities and marine salt concentrations, typical of coastal Antarctica. Mean and maximum values are given in Table 1. Sea salt dominates acid concentrations in most of the core. The major acid, H_2SO_4 , is mainly produced by the photochemical oxidation of sulphurous gases derived from biogenic sources [Delmas, 1982], and shows a clear annual cycle, (Figure 1). Peaks in salt and acid are out of phase since acid peaks at mid-summer whereas sea salt peaks in

Fig. 2. A comparison of the measured total anion ($\text{Cl}^- + \text{SO}_4^{2-} + \text{NO}_3^-$) concentrations (thin line) and that predicted from the modelling of the dielectric (σ_{∞} and f_r) parameters (thick line) for the Dolleman Island core between 26 m and 71 m core depths.

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 $[\text{acid}] = [\text{anions}] - [\text{salt}]$

autumn [Mulvaney and Peel, 1988]. By contrast in central polar regions there are much lower salt concentrations and most of the acid present is from volcanic sources [Herron, 1982; Legrand and Delmas, 1987]. Typical volcanic acid peaks have concentrations of $5 \mu\text{Eq l}^{-1}$ and should be easily detectable by the DEP technique.

Discussion

A knowledge of impurity locations within the ice fabric is required to understand ice electrical conduction mechanisms. Mulvaney et al. [1988] and Wolff et al. [1988] have used a scanning electron microscope (SEM) to study sections of the Dolleman Island core and have shown that sulphate (chiefly H_2SO_4) is concentrated at the triple junctions, whilst marine chloride could not be detected. The sulphuric acid is sufficiently concentrated to remain liquid at temperatures above -70°C , and forms an interconnecting network of veins throughout the ice. These observations support the theoretical model of the d.c. conductivity of polar ice developed by Wolff and Paren [1984]. The model predicts $\sigma_\infty = P[\text{acid}] + \text{other terms}$, where P is a constant of proportionality dependent on the relative concentration of each acid. At -22°C , for H_2SO_4 alone $P = 1.41$, for HNO_3 alone $P = 2.42$, and for HCl alone $P = 2.30$, where the units of $[\text{acid}]$ are $\mu\text{Eq l}^{-1}$, and the units of σ_∞ are $\mu\text{S m}^{-1}$. For the Dolleman Island ice we find $\sigma_\infty = 1.43[\text{acid}] + \text{other terms}$. The value of P is closer to that for sulphuric acid alone than might be expected from the relative acid concentrations in Table 1. We associate the acid term primarily with the d.c. conductivity, since acids are detected by ECM (a pseudo-d.c. conductivity), and no dielectric dispersion is predicted for acid veins in the AF-LF frequency range. The nature of the dielectric dependence on salt concentration is consistent with one Bjerrum L defect being generated for each one to two salt ions present in the ice [Moore 1988a]. This would indicate that a large fraction of the neutral salt impurity was incorporated into the ice lattice, which would explain why marine chloride was not detected by the SEM.

An important implication for the dependence of σ_∞ on both acid and salt concentrations is the possibility that some internal reflection horizons seen in the ice sheet during radar sounding may be caused by highly salty or acidic precipitation. The large concentrations of sea salts

found near coastal areas [eg. Herron, 1982] would considerably increase the radar absorption of the ice and may explain the difficulty in obtaining radar returns from these areas.

Conclusion

We have demonstrated that the DEP technique is sensitive to sea salt concentrations in ice cores allowing rapid identification of the periods of major storms and open seas. Such knowledge is as important to climate research as the identification of volcanic eruptions, a major success of the earlier ECM electrical profiling technique.

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References

- Camplin, G.C., J.W. Glen and J.G. Paren, Theoretical models for interpreting the dielectric behaviour of HF-doped ice, *J. Glaciol.*, **21**, 123-142, 1978.
- Delmas, R.J., Antarctic sulphate budget, *Nature*, **299**, 677-678, 1982.
- Glen, J.W. and J.G. Paren, The electrical properties of snow and ice, *J. Glaciol.*, **15**, 15-38, 1975.
- Gross, G.W., I. Cox Hayslip, and R.N. Hoy, Electrical conductivity and relaxation in ice crystals with known impurity content, *J. Glaciol.*, **21**, 143-159, 1978.
- Gudmandsen, P., Layer echoes in polar ice sheets, *J. Glaciol.*, **15**, 95-101, 1975.
- Hammer, C.U., Acidity of polar ice cores in relation to absolute dating, past volcanism and radio echoes, *J. Glaciol.*, **25**, 359-372, 1980.
- Harrison, C.H., Radio echo sounding of horizontal layers in ice, *J. Glaciol.*, **12**, 383-397, 1973.
- Herron, M.M., Impurity sources of F^- , Cl^- , NO_3^- and SO_4^{2-} in Greenland and Antarctic precipitation, *J. Geophys. Res.*, **87**, 3052-3060, 1982.
- Legrand, M. and R.J. Delmas, A 220-year continuous record of volcanic H_2SO_4 in the Antarctic ice sheet, *Nature*, **327**, 671-676, 1987.
- Legrand, M., J.R. Petit, and Y.S. Korotkevich, D.C. conductivity of Antarctic ice in relation to its chemistry, *J. Phys., Paris*, **48** (C1)605-611, 1987.
- Legrand, M., C. Lorius, N.I. Barkov, and V.N. Petrov, Vostok (Antarctica) ice core: atmospheric chemistry changes over the last climatic cycle (160,000 years), *Atmos. Envir.*, **22**, 317-331, 1988.
- Maccagnan, M., J.M. Barnola, R. Delmas, and P. Duval, Static electrical conductivity as an indicator of the sulphate content of polar ice cores, *Geophys. Res. Lett.*, **8**, 970-972, 1981.
- Miller, D.H.M., Radio-echo layering in polar ice sheets and past volcanic activity, *Nature*, **292**, 441-443, 1981.
- Moore, J.C., Geophysical aspects of ice core drilling in Antarctica, *Thesis, Council for National Academic Awards (UK)*, 1988.
- Moore, J.C., Dielectric variability of a 133 m ice core: implications for radar sounding, *Ann. Glaciol.*, **11**, 95-99, 1988.
- Moore, J.C. and J.G. Paren, A new technique for dielectric logging of Antarctic ice cores, *J. Phys., Paris*, **48** (C1), 155-160, 1987.
- Mulvaney, R. and D.A. Peel, Anions and cations in ice cores from Dolleman Island and the Palmer Land plateau, *Ann. Glaciol.*, **10**, 121-125, 1988.
- Mulvaney, R., E.W. Wolff, and K. Oates, Sulphuric acid at

- grain boundaries in Antarctic ice, *Nature*, **331**, 247-249, 1988.
- Paren, J.G. and G. de Q. Robin, Internal reflections in polar ice sheets, *J. Glaciol.*, **14**, 251-259, 1975.
- Reynolds, J.M., Dielectric behaviour of firn and ice from the Antarctic Peninsula, *J. Glaciol.*, **31**, 253-262, 1985.
- Robin G. de Q., S. Evans, and J.T. Bailey, Interpretation of radio echo sounding in polar ice sheets, *Phil. Trans. R. Soc.*, **265**, 437-505, 1969.
- Takei, I., and N. Maeno, Electrical characteristics of point defects in HCl doped ice, *J. Phys., Paris*, **48** (C1), 121-126, 1987.
- Wagenbach, D., U. Gorlach, K. Moser, and K.O. Munnich, Coastal Antarctic aerosol: the seasonal pattern of its chemical composition and radionuclide content, *Tellus*, **40**, 426-436, 1988.
- Wolff, E.W. and J.G. Paren, A two phase model of electrical conduction in polar ice sheets, *J. Geophys. Res.*, **89**, 9433-9438, 1984.
- Wolff, E.W., R. Mulvaney, and K. Oates, The location of impurities in Antarctic ice, *Ann. Glaciol.*, **11**, 194-197, 1988.
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