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Electrical stratigraphy of polar ice cores: principles, methods, and findings

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Abstract: Electrical methods have now become a routine stratigraphical tool in ice core analysis. As well as providing palaeoclimatic information, they have also given most of the information now available about the relationship between electrical properties and chemical content of ice. In ice cores measured under controlled conditions, real permittivity is controlled by density in shallow ice, and by changes in fabric in deeper ice. Conductivity below the firn layer is determined by the chemical content. The electrical conductivity method (ECM) is the main dc method, responding only to the acidity of the ice. Dielectric profiling (DEP) is the main method at higher frequencies, and responds to chemical concentrations of acid, ammonium, and chloride. Good quantitative relationships can be determined. A combination of Jaccard theory and grain boundary conduction can be used to explain some of the findings, although there remain unanswered questions. A number of instrumental improvements can be envisaged, but the electrical methods can now be considered a mature and indispensable part of the ice core armoury.

1. Introduction

The electrical properties of ice are distinguished by the fact that the charge carriers in ice are protons. The electrical properties have traditionally been studied as an important way of gaining understanding of fundamental properties related to the structure of ice. The results of studies of laboratory-made ice, and the theoretical considerations behind them, are summarised elsewhere [1].

For field glaciologists, an additional motivation is that changes in the electrical properties of ice, particularly changes with depth in an ice sheet or glacier, provide the basis for important and much-used geophysical techniques. For example, the interpretation of radar sounding of ice sheets can be put on a better footing through improved knowledge of the factors determining the electrical properties of ice. Most ice cores drilled in the last two decades have undergone some form of stratigraphic logging, usually including an electrical log. Again, their interpretation requires an understanding of the physical properties and chemical contents that determine the measured parameters.

This paper discusses the methods commonly used to measure the electrical properties of ice cores from the polar

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regions. It presents some of the datasets obtained, describes what we know about the ice properties that control the values measured, and discusses some theoretical insights gained from ice core data. Finally, it will consider the "state of the art" -what new methods or improvements can we expect in the next few years.

2. Parameters controlling electrical properties of ice

The electrical properties most commonly measured in ice cores are the conductivity (which can be simply related to the imaginary permittivity), and the real permittivity. Based on a combination of ice core and laboratory measurements, we can estimate typical variability of these properties for the conditions found in polar

Table 1: Typical dependency of electrical properties to the main variables in polar ice. The values given in the second column indicate typical variations, not the maximum observed range. Unless otherwise stated, standard values apply to ice at −15 °C, 0.1 MPa, 917 kg·m^{-3}, no preferred fabric, and no impurities.

Variable	Typical variation	High-frequency real relative permittivity (ε')	High frequency conductivity (σ_∞ / μS)
Temperature T / °C (ref. 12 and earlier papers)	-15	3.15	9.0
	-50	3.13	0.2
Pressure P / MPa (ref. 39)	0.1	3.15	9.0
	28	no data found	8.7
Density ρ_{firn} / kg m^{-3} (ref. 38)	350	1.67	2.2
	917	3.15	9.0
Fabric (ref. 34)	// c-axis	3.18	9.0
	⊥ c-axis	3.14	9.0
Impurities [H$^+$] / μM (ref. 22)	0	3.15	9.0
	4	3.15	25.0

ice sheets [2]. These values are summarised in Table 1, and indicate the ice sheet parameters one might be able to derive from electrical measurements.

The real permittivity is controlled most strongly by density, so that its measurement is potentially a powerful way of measuring density variations above the firn-ice transition (discussed later). Below that depth, both temperature and fabric variations could be expected to control much smaller variations in permittivity. In the ice sheet itself, both these parameters can vary, but in the laboratory (making measurements on ice cores), it should be possible to control the temperature.

For conductivity, again the temperature is important, but can be controlled in the laboratory. The density is important in the upper layers, but by far the controlling parameter for ice core measurements is the chemical impurity content. Impurity concentrations change dramatically with the season of snowfall, with sporadic events such as volcanic eruptions, and across major climatic changes on the multi-millennial scale, and these changes make conductivity measurement such a powerful tool.

In addition to the changes shown in the table, the permittivity and conductivity of course change with frequency. The static relative permittivity of ice is around 100, while the high frequency value (above a relaxation frequency in the region 1–10 kHz) is 3.2 [1]. The conductivity increases dramatically over the same frequency, reaching a plateau that extends to at least 1 GHz. Most ice core measurements have been aimed at obtaining data either at dc, or at the high frequency plateau, with a few recent data at microwave frequencies.

3. Techniques

3.1. DC conductivity

In early work, dc conductivity of polar ice was studied by making low-frequency ac measurements in a parallel plate capacitor [3], and data have also been obtained using georesistivity surveys in situ [4]. However, the significant breakthrough that made electrical logging of ice cores a possibility was the development of the electrical conductivity measurement (ECM) method by Hammer [5].

In the style of the original ECM, still widely used, a pair of brass electrodes, about 1 cm apart, is scratched along an ice surface (preferably flat and freshly-exposed). A high dc voltage (typically 1200 V) is applied to the electrodes, and the current between them is measured. Although ECM is not a direct measure of the dc conductivity, we can expect a close relationship between them provided the measurement operates on timescales slower than the relaxation frequency (in the kHz region), and faster than the time for space charges to build up and reduce the current (0.1–0.5 s [ref. 5]). With an electrode diameter of 2 mm, and a typical speed of movement of 10 $cm \cdot s^{-1}$, the timescale is of order 20 ms, and meets the above criteria.

It has also been shown that, for a typical ECM setup, volume conduction dominates over surface conduction. This was demonstrated by measuring ice of different thickness [6], and applies at least at temperatures of −15 °C and below. Thus, it seems that ECM is closely related to the dc conductivity of ice, although factors such as the uncertain electrode contact area make it difficult to use a quantitative relationship, so that ECM is generally reported simply as a current, with relevance

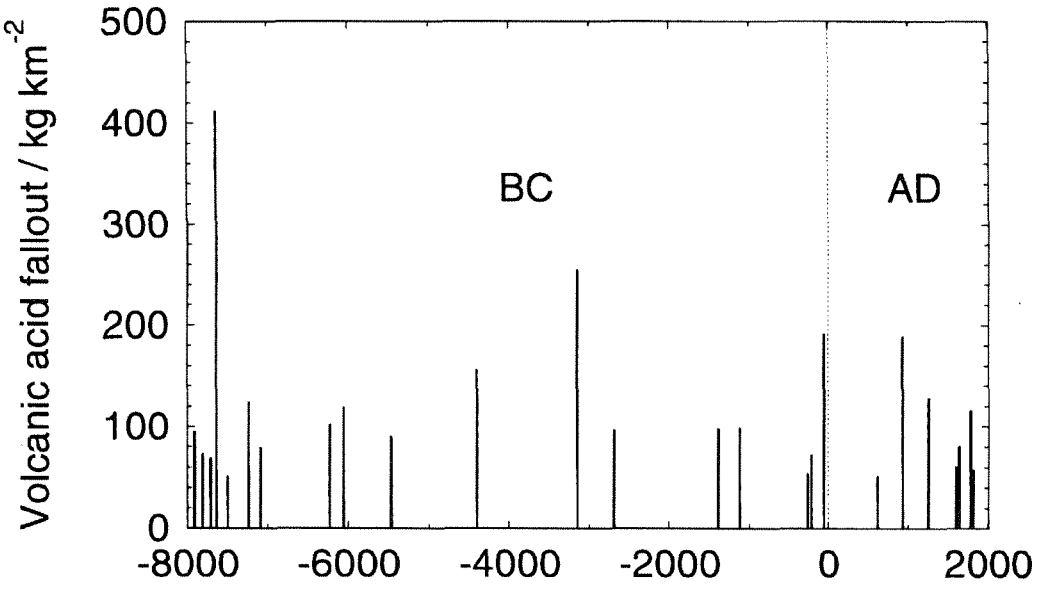

Figure 1: Volcanic stratigraphy of the last 10000 years from the Greenland Crete and Camp Century ice cores. Acid fallout was calculated from size of ECM peaks; based on Table 1 of ref. 7.

only for a particular set of electrodes and operating conditions.

Early on, it was proposed that ECM was effectively a measure of the acidity of ice [5]; I discuss the chemical calibration of ECM later. The original assumption has stood the test of time; the technique has been widely used on most ice cores drilled in the last two decades. The method has been spectacularly successful particularly in revealing a stratigraphy of volcanic eruptions (Fig. 1) that can be used to date ice cores [7], and as a simple way of showing annual layers in many cores to estimate the snow accumulation rate.

3.2. AC conductivity

As with dc studies, early data were obtained with time-consuming measurements between guarded parallel plates [3]. This field was again revolutionised by the development of the dielectric profiling method (DEP) by Moore and Paren [8]. In this technique, whole ice cores are placed between curved electrodes, made of (preferably) anodised aluminium. The bottom electrode is continuous for the length of the core, subtends an angle typically 100–140°, and is connected to the high voltage side of a measuring device. The top electrode is similar, but is sectioned along the length into separate electrodes, which in recent versions might be 2 cm long each. One of these electrodes is connected to the low voltage side of the measuring device while the remaining ones are connected to earth, and therefore act as guards to confine the field to be parallel in one direction. Typical measuring devices (LCR meters) apply 1 V to the electrodes, and then measure the capacitance and conductance at a range of frequencies up to 1 MHz. In one version of the DEP, a switching device allows each top electrode in turn to be the measuring one, so that measurements are made at typically 2 cm

resolution [9]. In other instruments, a single electrode with surrounding guards is moved mechanically along the core [10], and measurements are made at discrete distances.

From the measured parameters, it is possible to derive the high frequency limit of the permittivity and conductivity (which is generally very close to the 100 kHz value). Because the measurements are made across a system that includes ice, air, and sometimes a plastic bag, it has not been possible to derive reliable low frequency (near dc) data from the DEP, although a relaxation frequency (which may be related to the particular chemical impurity causing a signal) can be obtained. The conditions needed to measure permittivity with the accuracy required to be useful are discussed later. The DEP has principally been used to determine the high-frequency conductivity, which turns out to be related to the acidity (as ECM) but also to other chemicals in the ice. The geometry of the DEP is not as simple as that of a parallel plate capacitor, but it can provide quantitative conductivity data, and indeed has provided huge amounts of it [9]. DEP has the major advantage that it can be carried out on whole (uncut) cores, even on those that are still in plastic sleeving.

Recently, a few ice core samples have been measured at microwave frequencies [11], supplementing work on doped ice carried out previously [12]. An advantage of having data both from standard dielectric measurements and microwave ones is that they bracket the frequencies used by most ice radars.

4. Relationship between electrical conductivity and chemistry of ice

The main impurities in polar ice consist of the following important classes: a) Sea salt ions, especially Na^+ and Cl^-. These are of most importance at coastal sites; b) Acids, including sporadic volcanic eruption peaks (usually consisting mainly of sulfuric acid), background sulfuric acid (of marine biogenic origin), background nitric acid (of uncertain origin, but a major impurity), and pollution acids in recent snow and ice; c) Ammonium and organic acid ions, principally derived from vegetation, which are significant in Greenland snow and ice, but less so in Antarctica; d) Terrestrial dust and the ions derived from it, such as Ca^{2+}; these are generally at low concentrations in present day ice from polar regions, but show high concentrations in the last glacial period, particularly in Greenland.

The chemical content varies with hemisphere, location, season, and climate (interglacial or glacial). I now present evidence to show which impurities have the major effect on electrical conductivity.

4.1. ECM

From the earliest ECM measurements, it has been apparent that the main influence on the ECM signal of ice is the acid content, with particularly high peaks corresponding to years with fallout of volcanic eruption acid. Hammer [5] derived a relationship for a Greenland ice core:

$$[H^+] = 0.045\, I^{1.73} \quad \text{at } -14\ ^\circ\text{C} \qquad (1)$$

where $[H^+]$ is the acid concentration in μM ($\mu mol \cdot L^{-1}$), and I is current in μA. The large scatter in the data mean that there is

considerable uncertainty on the published constants in equation 1. The constant (0.045 $mol \cdot L^{-1} \cdot A^{-1.73}$) has no special significance, and will vary depending on the electrodes from instrument to instrument, and in some cases, between operators. Additionally, lower currents will be seen in less dense firn than in solid ice. The exponent probably is significant, although it also shows some variation from core to core, and values approaching 2.5 have been reported [13, 14]. The ECM current is temperature dependent, with a reported activation energy of 22 $kJ \cdot mol^{-1}$ [ref. 15].

A typical calibration plot (Fig. 2) shows considerable scatter, and this may be for a number of reasons: (a) Errors in the measurement of H^+. Because of the time-consuming nature of precise acid titration measurements, H^+ is often estimated from pH measurements, or from calculations of acidity as the difference between other measured anions and cations. These procedures lead to large uncertainties in acidity; (b) The ECM measurement itself is prone to uncertainty; although newer instruments try to reduce uncertainty by automating parts of the procedure [16, 17], ECM can be very dependent on factors such as core quality; (c) There also appears to be a real effect whereby, for a given amount of acidity, a stronger response is found for HCl and HNO_3 than for H_2SO_4 [14, 18]. This finding could imply that H_2SO_4 behaves as if it contained only one proton, with the second one undissociated in the ice. Whatever the reason, the effect contributes to the observed scatter, and because sulfuric acid dominates the peaks, but nitric acid often dominates the background, it may

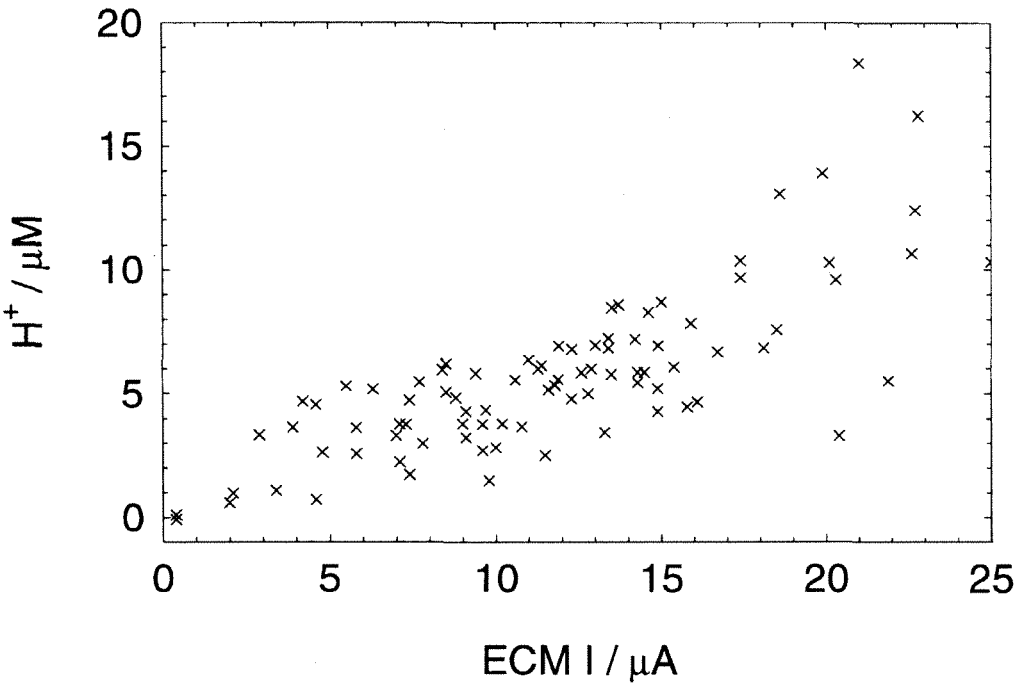

Figure 2: Calibration of acidity against ECM current for an ice core from Dolleman Island, Antarctica (for the same section of ice shown in Fig. 3).

partly explain the observed curvature of ECM calibrations.

Apart from the above secondary effect of the counter-anion, there is no convincing evidence of an ECM response to any other ion apart from acidity. For example, Fig. 3 shows a section of core where the ECM closely follows H^+; in the middle of the section, H^+ is close to zero, but sea salt concentrations (Na^+, Cl^-) soar to very high levels, seen only rarely and at coastal Antarctic sites: no ECM response is seen. This and other examples make it clear that sea salt can be neglected as a contributor to

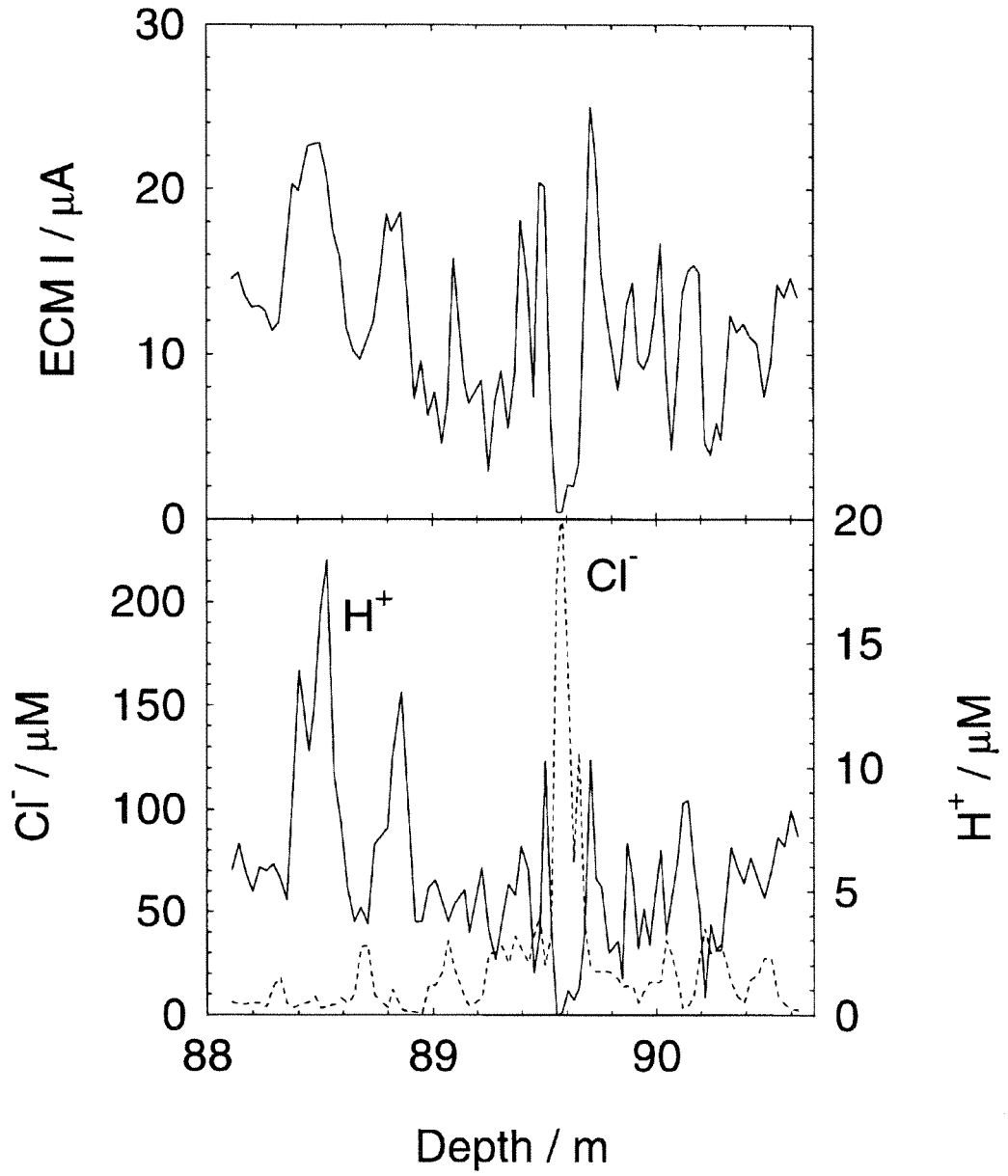

Figure 3: H^+, Cl^- and ECM across a section of core from Dolleman Island, Antarctica [13].

ECM for all meteoric ice in the polar regions.

Ammonium can also reach quite high levels during biomass burning events reaching Greenland, but the ECM response is usually to reduce [19], rather than to increase (Fig. 4). Although this might be seen as a response (albeit negative) to ammonium, a more likely explanation is that the weak acid ions (formate and acetate) which normally accompany these events have partially associated with the acidity, making it unavailable.

Ca (and other terrestrial ion) concentrations can be very high (20 μM) in Greenland ice from the last glacial maximum. The ice is in fact alkaline, and the ECM current is very close to zero, becoming even lower when the Ca concentration is higher [9]. This indicates that Ca and other ions associated with input of terrestrial dust cannot cause any significant ECM current. In summary, ECM shows no positive response, even in the presence of the largest excesses observed in polar ice of the major ionic impurities, sea salt, terrestrial ions or ammonium. Apart from acidity, a response has been observed in only one exceptional case, that of ice that freezes from sea water onto the underside of Filchner-Ronne Ice Shelf [20]. This ice contains no acid, but Cl^- up to 1000 μM; the small ECM signal is correlated with the salt content in this ice. The Cl^- content of this ice is above the estimated solubility limit of 400 μM, and there is direct evidence that there is free brine in this concentrated ice [21]; ECM is probably conducting through the liquid phase in this case.

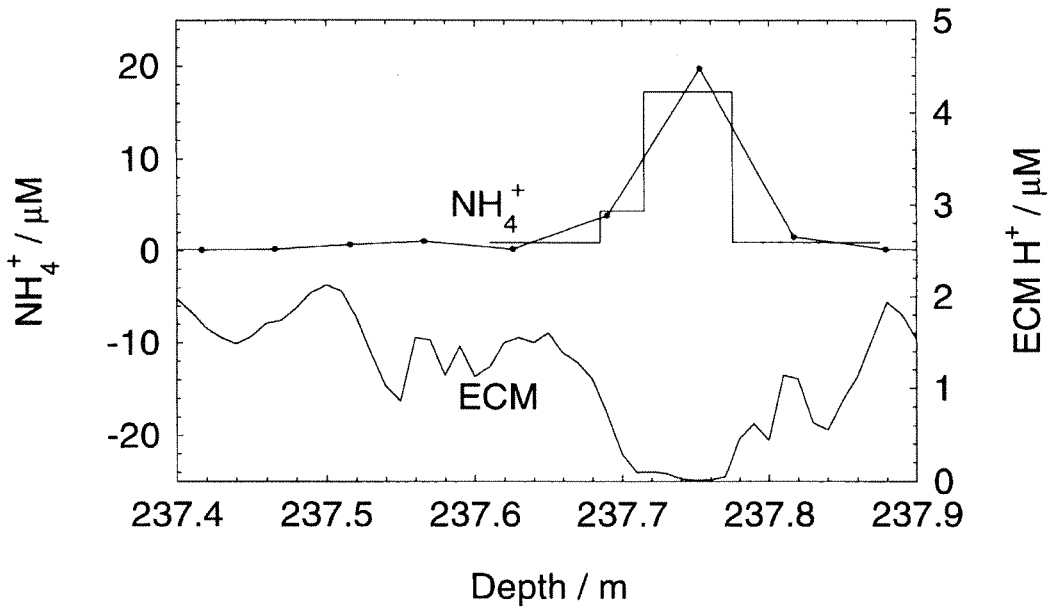

Figure 4: ECM response to a large ammonium peak in the Summit, Greenland, ice core [22]. The ammonium was measured by continuous flow analysis at University of Bern (continuous line), and by ion chromatography at LGGE (short section).

4.2. DEP

Although the DEP conductivity responds strongly to acidity, it has also been shown that it responds (less strongly) to ammonium and to chloride [22]. In contrast to the dc conductivity, pure ice has a significant high frequency conductivity, which is seen as a background when few impurities are present. There is no evidence so far of any significant effect of depth, age of ice, or crystal size. The DEP signal is temperature dependent (see below). In this section, the dependency of conductivity on each of the three impurities is illustrated by choosing sections of the GRIP ice core where one of them dominates over the other two.

In the Holocene period, acid dominates; chloride is generally low, and ammonium is only sporadically high. In this period, the DEP signal looks very similar to the ECM signal (Fig. 5). The ECM closely represents the acidity. In the Younger Dryas time period (~ 12 kyr B.P.), acidity was very low, but ammonium concentrations remained rather high. As a result, the DEP conductivity follows the ammonium concentration very closely (Fig. 6). A further illustration of the dependency on ammonium has come with analysis of the debris-laden basal ice of the GRIP core. Over the bottom few metres, the DEP signal increases towards the bed, and this turns out to be almost entirely due to increasing ammonium concentrations (ascribed to biota in the growing ice sheet) [23]. The constant of proportionality between σ_∞ and ammonium is almost identical to that derived from the Younger Dryas ice.

In the last glacial maximum, both acidity and ammonium were low in GRIP ice, but there remains a DEP signal variability when viewed at high resolution.

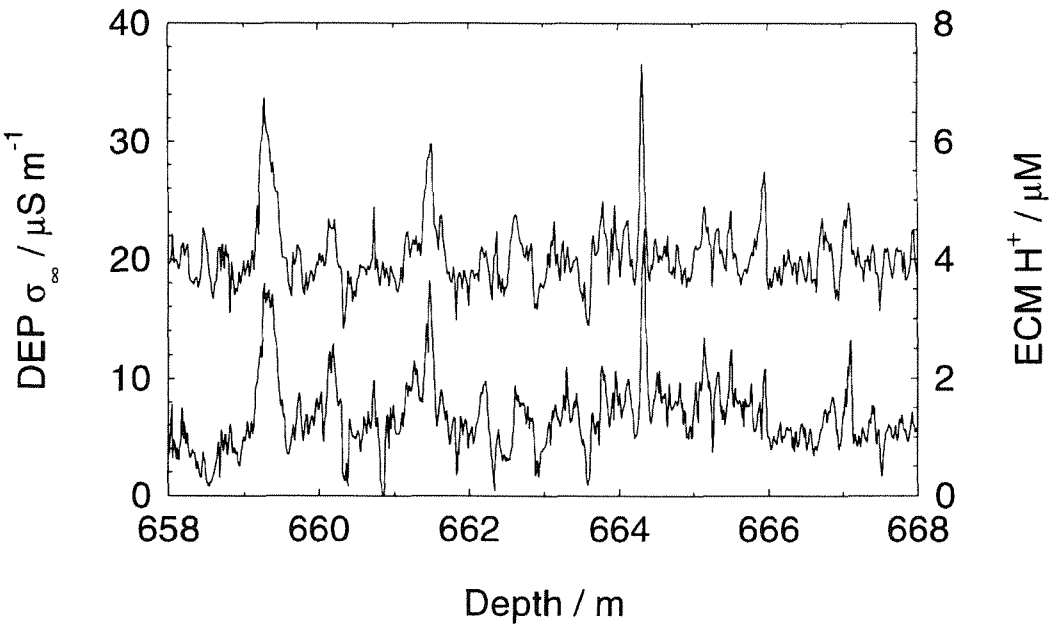

Figure 5: ECM current (lower line, converted to acidity using a simple calibration) and DEP σ_∞ (upper line) in a section of ice (~3300 years old) from the Holocene in the GRIP ice core, Greenland.

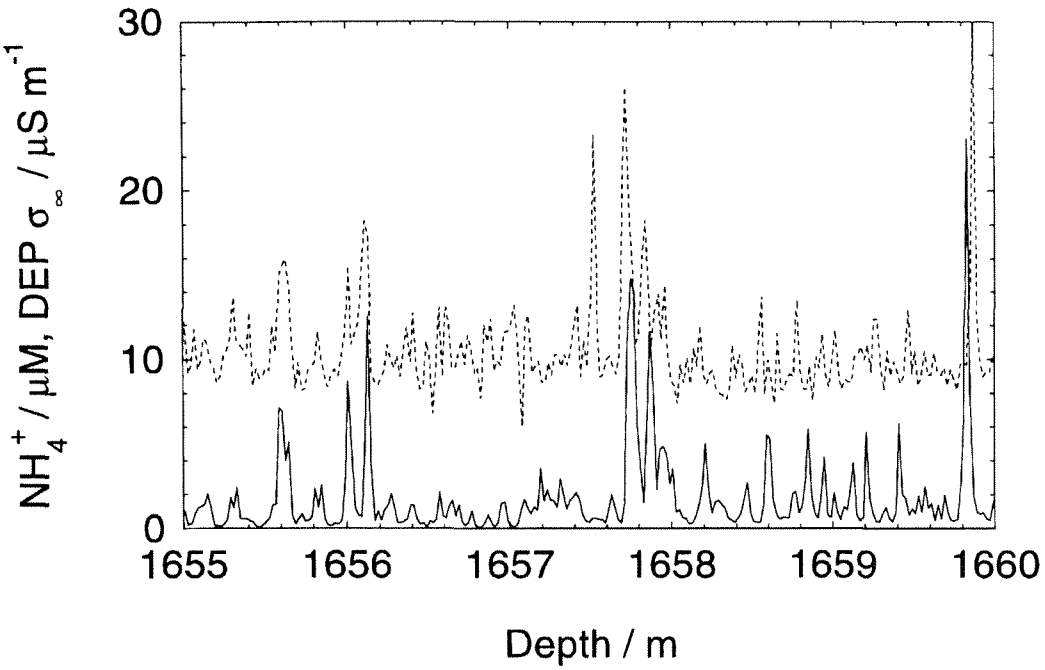

Figure 6: DEP σ_∞ (dashed line) and ammonium concentration (solid line) in part of the Younger Dryas period in the GRIP ice core, Greenland [9]. There is an ECM peak at 1657.52 m, indicating that the corresponding DEP peak there is due to acidity. Uncertainty in the relative depth measurements by 1–2 cm explains the slight offset between ammonium and DEP peaks.

This variability corresponds closely to that of chloride, but not to any of the other major ions measured. This confirms a result already found from coastal Antarctic ice cores [24], where sea salt concentrations are also high.

Based on the above data, and statistical analyses for coastal Antarctica and especially for the GRIP core, the calibration often used for the DEP conductivity of solid ice at −15 °C is:

$$\sigma_\infty = 9 + 4[H^+] + 1[NH_4^+] \text{ or} \quad (2)$$

$$\sigma_\infty = 9 + 4[H^+] + 0.55[Cl^-] \quad (3)$$

where σ_∞ is in $\mu S \cdot m^{-1}$, and chemical concentrations are in $\mu mol \cdot L^{-1}$. Which equation to use depends on which of chloride and ammonium is present. It is not strictly correct to add the contributions from these species, as was done in a previous paper [25], because the defects they each produce would be mutually destructive (see later section on conduction mechanisms). In practice, cores in which both components are present in significant amounts are rare. The constants in equations 2 and 3 have significant uncertainties. It was estimated that the ammonium coefficient varied by about 20 % between different events in the GRIP ice core, while the coefficient for acidity differed also by about 20 % when calculated from different depth intervals of the same core [22]. The other two constants were pinned down to only a few percent

from single cores [24], but also show considerable scatter for individual data values.

The above equations are based mainly on the GRIP core, where they appear able to explain all significant peaks, but more data from other cores are needed. The different parts of the equations above have different temperature dependencies. The pure ice part (9 $\mu S \cdot m^{-1}$) has a recommended literature activation energy of 0.58 eV (56 $kJ \cdot mol^{-1}$) [26], but slightly lower values (0.5 eV) seem to give a better result for Antarctic and Greenland ice [9, 24]. For the acid and chloride parts of the conductivity, 0.22 eV has been used, based on measurements of Antarctic ice at different temperatures [24]. No measurements of the activation energy for the ammonium part have been made, but the assumption might be that it is similar to that for chloride.

By combining ECM and DEP data, it should in theory be possible to determine acidity and either chloride or ammonium solely from electrical data. In practice however, in most acidic ice, the DEP value is dominated by the acidic component, and the statistics of the equations (1–3) are not defined well enough to make the separation. There are sites in the coastal regions of Antarctica which have high acidity in summer and high salt content in winter, where such a separation may be possible; glacial period ice from central Antarctica may also be amenable to such a treatment.

5. Conduction mechanisms

There are now large amounts of data, much of it quantitative, on electrical conduction in well-characterised polar ice. These data certainly exceed many fold those available from laboratory studies on artificial ice. It is therefore timely to assess how well the findings from polar ice fit to the conventional theories about conduction mechanisms in ice.

The principal findings that need to be accommodated are: a) ECM (representing the dc conductivity) responds only to acidity, and not at all to other anions or cations; b) ECM appears to have a non-linear relationship to acidity, although this may be partly due to the interesting observation that it responds more strongly to a quantity of acid associated with chloride or nitrate than to one associated with sulphate; c) DEP (representing high-frequency conductivity) responds to acidity, ammonium, and chloride, with a strength of response as shown above; d) The temperature responses of the ECM and DEP signals need also to be accommodated.

Electrical conduction in ice has generally been discussed in the framework of Jaccard theory [1]. However, there is also evidence that the dc conductivity of impure ice may be controlled by a grain boundary process [27]. I now discuss the data in terms of each of these possibilities.

5.1. Jaccard theory

In Jaccard theory, conduction is through movement of defects within the ice crystals. It is assumed that the dc conductivity is controlled by the minority charge carriers (ionic H_3O^+ defects), while at high frequencies the majority carriers (Bjerrum L- and D-defects) would be most important. If this is the mechanism for conduction in polar ice, then we can draw a number of conclusions: a) Of the impurities in polar ice, only H^+, NH_4^+ (or NH_3), and Cl^- (or HCl) are entering the ice lattice and creating defects. This appears reasonable

since N and Cl have a similar covalent radius to O, and can probably replace it in the lattice (we might expect F^- to do the same, but as it is always a minor ion in polar ice, such ice cannot be used to test the hypothesis). It is not surprising that large anions such as NO_3^- and SO_4^{2-} do not enter the lattice, and play no role, and we would not expect cations such as Na or Ca to play an explicit role; b) Again assuming Jaccard theory alone describes the conduction process, then the ECM data suggest that only H^+ is creating ionic defects in the ice; c) Jaccard theory allows calculation of the expected conductivity based on the number of defects. If we assume that the Cl^- part of the conductivity is due to L-defects only, then for that part of σ_∞ only,

$$\sigma_{\infty Cl} = n_L \mu_L |e_L| \quad (4)$$

where n_L is the concentration of L-defects, e_L is the charge on an L-defect and μ_L is its mobility. We could write a similar equation for D-defects assuming that they are solely responsible for the NH_4^+ part of σ_∞.

From the literature, $-e_L = e_D = 0.37e$ [ref. 1], where $e = 1.6 \times 10^{-19}$ C. μ_L is given as 1.5–2.4 x 10^{-8} $m^2 \cdot V^{-1} \cdot s^{-1}$ at −15 °C [ref. 1]. Cl^- can enter the lattice as HCl (giving one L-defect and one ionisation (H_3O^+) defect [28]) or as Cl^- (giving two L-defects, and implying that the cation is incorporated interstitially or at grain boundaries); the latter seems more likely in alkaline ice where the ECM current is low. Comparing equation 3 (Cl^- coefficient) with equation 4, the ratio of L-defects to Cl^- ions is $n_L/n_{Cl} = 0.55/(1000 * N_A \mu_L |e_L|)$, where N_A is Avogadro's number, so that $1000 * N_A$ converts from mol L^{-1} to molecules m^{-3}. This ratio is then calculated as 0.7–1.0, suggesting the possibility either that not all Cl^- ions are in the lattice or that not all the possible L-defects are mobile.

For NH_4^+, we can use similar arguments; we can expect two D-defects if NH_4^+ is incorporated (with the anion interstitial or at grain boundaries), or one D-defect and one OH^- ionisation defect if NH_3 or NH_4OH is incorporated [28]. Using equation 2 and the D-defect analogy of equation 4, we would estimate the ratio of D-defects to NH_4^+ ions to be in the range 1.3–2.0 even if we assumed that $\mu_D = \mu_L$. In fact, the literature suggests that $\mu_D < \mu_L$. Thus in this case, the polar ice data require that defects are formed more efficiently from NH_4^+ than from Cl^-, and that the mobility of D-defects is at least as high as that of L-defects; this conflicts with the current view based on laboratory data.

For the acidity, we note that the charge from an ionisation defect is 0.63e (almost double that of the Bjerrum defects), and the mobility may be similar [1]; based on this, we could accept that σ_∞ responds more strongly to acidity than to the other two ions. However, the activation energy for ECM and for acidic ice in DEP [15, 24] is clearly positive (about 20 $kJ \cdot mol^{-1}$), whereas the literature gives zero activation energies for ionisation defect mobilities [1]. For HF, dc conductivity is predicted to have a square root dependence on HF concentration at high concentration, and we do indeed see something close to a square root dependence in most calibrations of ECM against acidity. However, where the acid anion is not incorporated into the lattice (as in the case of sulfate), it is not clear that this should apply, and there may be other reasons (including the lower response when sulfate is the anion) to explain the curvature.

5.2. Grain boundary conduction

It has been proposed that dc conductivity could occur through a network of connected liquid veins at the triple junctions in ice [27]. If the impurities do sit at the triple junctions, such veins could remain liquid down to the eutectic point of the impurity mixture with water and ice (which is −73 °C for H_2SO_4 and ice). The magnitude and temperature dependence of the dc conductivity is well predicted by calculations based on this model. It would also predict the lower conductivity when sulfate is the anion, since the second proton of sulfuric acid would be undissociated at the high concentrations in the veins. However, the grain boundary model predicts a linear relationship between conductivity and acidity (in contrast to what is observed in ECM, see Fig. 2), and cannot easily explain why ECM conductivity persists even in single large crystals in deep ice [C. Hammer, pers. comm., 1992] (unless we assume that the acidic liquid is spread over the entire surface in this case). A similar modification would be needed to explain how ECM conductivity persists in firn, as seen by numerous studies, even though in firn the concept of a triple junction cannot exist.

In doped laboratory ice, there is excellent evidence that conduction is through a liquid phase; in microwave frequency experiments, the conductivity of ice doped with both acids and salt showed a strong step reduction at exactly the relevant eutectic temperature where the liquid could no longer exist [12]. There is also recent evidence [32] that currents are higher in the vicinity of grain boundaries than in the middle of crystals, again for doped ice. For natural polar ice, the grain boundary mechanism is supported by direct observations (using scanning electron microscopy with X-ray detection of S atoms) that S is present in high (molar) concentrations at triple junctions in some samples [29]; unfortunately further observations to confirm this in more samples remain lacking. For one sample of Antarctic ice, Raman spectra taken at triple junctions contain peaks due to bisulfate (HSO_4^-) and nitrate ions in liquid [30], while nothing was seen in the bulk ice; a second sample gave a more equivocal result, and again further data are needed.

5.3. Conduction mechanisms summarised

If the grain boundary mechanism is correct, then the dc conduction, and probably the acid part at ac, take place through the boundaries. The other ions active at higher frequency are indeed incorporated into the lattice, and conduction is through defect movement as described by Jaccard theory. However, before this combination can be fully accepted, a number of questions must be answered: a) are the acidic impurities indeed found at triple junctions in most samples? - this requires many further analyses by methods such as the SEM or Raman experiments; b) how would the theory be modified for firn where the connectivity of the conducting material is clearly a factor?; c) how would we explain the ECM currents seen in large single crystals from deep ice, where there are no triple junctions?; d) can the defect mobilities estimated from polar ice be reconciled with those deduced in the laboratory?

6. Future developments

6.1. ECM

ECM remains the primary method for estimating the acidity of ice cores, although there are prospects of fast, continuous-flow methods of chemical measurement which are currently being developed. Traditional systems of the sort developed by Hammer, with two brass electrodes moved by hand continue to be popular. They are fast and simple, and leave the operator the freedom to avoid poor quality ice and to cope with surfaces that are not perfectly flat. A number of recent systems have been automated, with electrodes transported over the ice surface on rails at constant speed and with constant downwards pressure and angle to the ice surface (e.g. [16]). Such systems have the advantage of totally reproducible conditions irrespective of the operator, and need less operator attention when working, but they require more maintenance, and may have difficulty coping with poor quality ice.

Recently, a new system has been used on ice from Dome C, Antarctica. This system, developed at University of Bern [17] [J. Schwander, personal communication, 1998] has 7 carbon-doped silicone rubber electrodes in a line across the core at 8 mm spacing. They use a lower voltage than traditional systems (350 V), and are lowered onto the ice surface every mm; the current is sampled at intervals and averaged, and then the electrodes are lifted again and moved on. This system again has very reproducible conditions, and the multiple electrodes generate 6 parallel traces and can allow correction for stratigraphic layers that are not perpendicular to the core axis. This method is considerably slower than the traditional ECM, but can keep pace with the DEP for example. It may only be suitable for larger projects and research analysis, but certainly offers prospects of more quantitative data for comparison with chemistry.

As a mature method, ECM is well-established, but further efforts to develop calibrations using the best acidity measurements possible would be desirable. Instrumental developments seem to include moves in both directions: more sophisticated instruments (such as the Bern ECM above), and still simpler hand-held portable instruments with all controls incorporated into the electrode holder, that are now commercially available.

6.2. DEP

DEP has also become a mature method, carried out on most major ice cores. It can be used as a totally non-destructive alternative to ECM where acidity dominates, but also responds to Cl^- and NH_4^+, giving a distinctive response in some ice (such as alkaline last glacial Greenland ice, or salty coastal Antarctic ice).

The traditional DEP developed by Moore and Paren has been used most notably at Summit, Greenland (GRIP) and now at Dome C, and has many electrodes (120 in recent versions) with switching between them. It can be made very simple to use, has no moving parts (except relays), and gives conductivity quantitatively, with good proven calibrations against chemistry. However, it has the disadvantage that each electrode is slightly different, which introduces extra uncertainty, and that there is a practical limit to the spatial resolution because of the need to limit the number of switches to a reasonable quantity.

Some laboratories have developed a kind of AC-ECM, with either 2 or 4 point

electrodes moving along the core (e.g. [31, 32]). Such a system can have excellent resolution, and can be combined on a single bench with other profiling instruments. However, data are not simply converted from conductances into absolute conductivities, and it is harder to eliminate surface effects. It has not proven simple until now to obtain good calibrations with such systems, although some are now available [32].

A combination of the two ideas has been to move a plate or curved electrode along the core. This was exploited to obtain high resolution (but less quantitative) data from the GRIP core [33], and more recently in a configuration with improved guarding [10]. In this latter instrument, there is a single top electrode for which the geometry and hence the theoretical permittivity can be calculated precisely. One can envisage with such an instrument a high resolution instrument without an unfeasible number of switches, and it should be possible to produce chemical calibrations with it of similar quality to those already obtained with the static multi-electrode system.

6.3. Other developments

An obvious step that is envisaged but until now not really exploited is to get better low frequency measurements from DEP (or to use DEP and ECM together) to clearly separate the effect of acidity from the other chemical components. In practice there are only limited situations where both acid and other ions are contributing significantly in the same section of ice, but this should be the case in some cores from near-coastal Antarctica (such as Siple Dome and Berkner Island) and these would be examples where this approach would be worthwhile.

In principle, DEP can give precise permittivity data that can be used to derive the density in near-surface firn and ice [10], and that should be controlled by fabrics in deeper ice. However, the difference in permittivity between measurements parallel and perpendicular to the c-axis in single crystals is about 1 % (0.03) [34], and the likely variations in natural ice due to fabric are smaller than that [11]. Permittivity measurements to this precision are possible on precisely cut discrete samples, but are unlikely to be possible in a profiling method on core with slightly varying geometry. For density measurements in firn, the main limitation is likely to be the core quality, which may limit the precision of density estimates to maybe between 3 and 10 %.

A further instrumental development we might anticipate is downhole ECM and DEP instruments which take measurements from the wall of the borehole. Such instruments are possible but technically more challenging, and have the danger that the user may not be aware when contact difficulties or other problems occur. One can envisage uses such as precise relocation of specific layers in the borehole for strain measurements after long intervals, and in cases where the core has been of poor quality.

Finally, a long-term dream is that radar internal layer data might be inverted to give profiles of chemical impurities. In some cases it is possible to match ECM records with radar layers, and attempts are being made to make forward models of the electrical data to produce synthetic radar records [35, 36]. However, in shallower ice, density-controlled variations in permittivity are certainly a major cause of internal reflections, and in some cases it appears

likely that fabric-controlled changes in real permittivity may be a major cause of internal layers [37], making inversion to chemistry in practice impossible. However, if the chemical-electrical link is made firmly on a core or cores, and particularly strong reflectors can be linked to the electrical properties measured on cores, then it could be feasible to infer some chemical concentration and depth information from radar profiles.

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