

# Factors Controlling the Electrical Conductivity of Ice from the Polar Regions—A Summary

Eric W. Wolff,\*<sup>†</sup> William D. Miners,<sup>†</sup> John C. Moore,<sup>‡</sup> and Julian G. Paren<sup>†</sup>

British Antarctic Survey, Natural Environment Research Council, High Cross, Madingley Road, Cambridge CB3 0ET, U.K., and Arctic Centre, University of Lapland, Box 122, SF96101 Rovaniemi, Finland

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Data on the relationship between the electrical conductivity and the chemistry of ice cores from the polar regions are summarized. The electrical conductivity measurement is used as a proxy for dc conductivity, while dielectric profiling gives high-frequency conductivity. The dc conductivity seems to be controlled entirely by the acidity of the ice, with a secondary effect of the accompanying anion. There is no positive response when huge excesses of sea salt, ammonium, or calcium are present, except in ice where brine is present. The high-frequency conductivity is controlled by acidity, ammonium, and chloride. This finding can be accommodated within Jaccard theory, but the relative response at high frequency to the three ions seems puzzling. The possibility that dc conduction may be through grain boundaries can also not be discounted.

## 1. Introduction

The electrical properties of ice have been studied in many reports over several decades. Current theoretical understanding and the laboratory measurements of pure and doped ice samples have been summarized recently by Petrenko.<sup>1</sup> While such studies are often valued for the insights they give into the structure of ice, an additional motivation for field glaciologists is the importance of the electrical properties for geophysical measurements. In particular, they are the basis for some stratigraphical measurement techniques used on ice cores and for the understanding of data from radar surveys of ice sheets.

In recent years, the amount of data on the electrical conductivity of ice from the polar regions has increased by a huge factor, mainly due to techniques used on ice cores. These measurements have been related particularly to the chemical impurity content of the ice.<sup>2–7</sup> Considerable progress has been made in relating the chemical content to the electrical conductivity of the ice, but the new data have not yet been fully integrated into the theoretical framework derived from laboratory measurements. In this paper, we summarize what is now known about the dc and high-frequency conductivity of ice from Antarctica and Greenland. We do not consider here the density and temperature dependence, which certainly exist, but concentrate on the relationship between conductivity and chemical content. We set this in the context of the existing theories with the aim of starting a debate that will incorporate these data.

## 2. Experimental Techniques

**2.1. dc Conductivity.** dc conductivities have been inferred from three main data sources. A small amount of data are available from extrapolations of low-frequency ac measurements (using parallel plates) of samples from polar ice cores.<sup>8</sup> dc conductivities can be estimated from georesistivity surveys carried out on the polar ice sheets,<sup>9,10</sup> although it is not possible to obtain unique solutions, and it is therefore difficult to make comparisons with chemistry. By far the largest potential data source has been the use of the electrical conductivity measurement (ECM) method on polar ice cores. In this method, a pair

of electrodes with high voltage between them (of order 1200 V) is run across the fresh surface of a core and the current between them is measured. This method was developed two decades ago<sup>2,11</sup> and has become a routine method for the study of ice cores.<sup>3,12–15</sup> ECM data exist, often at millimeter resolution, for most of the thousands of meters of ice cores that have been drilled at both polar regions. ECM is not strictly a dc method but records some transient signals as the electrodes move along the core. However, the speed of movement in relation to the resolution of the method means that the time scale for measurement at any place along the core is of order 0.1 s: large enough for ac effects to be unimportant but small enough that space charge buildup<sup>2</sup> is also not important. It is hard to translate ECM currents into any quantitative measure of conductivity, and indeed the results are very dependent on the electrode design and operator. Nonetheless, arguments have been presented to suggest that ECM does give an indication of the volume dc conductivity,<sup>16</sup> and this has generally been assumed.

**2.2. High-Frequency Conductivity.** In the past, a few laboratory measurements of ice from the polar regions were made with parallel plate capacitors.<sup>8</sup> In recent years, the vast majority of measurements have come from the dielectric profiling technique (DEP).<sup>4,17</sup> As for parallel plate capacitors, DEP uses a bridge to measure the conductance and capacitance of ice at various frequencies up to 300 kHz (well above the relaxation frequency of ice); from these the high-frequency limit of the conductivity ( $\sigma_{\infty}$ ) can be determined. The DEP uses curved electrodes on whole ice cores, and by switching electrodes in sequence, the properties (including  $\sigma_{\infty}$ ) can be profiled along the length of the core. Although the geometry is less ideal than with a parallel plate system, good, repeatable, and apparently quantitative results can be obtained. Notably, DEP has been used at 2 cm resolution on the 3028 m long GRIP ice core from Greenland.<sup>6,15,18</sup> DEP is now becoming a routine analysis method for ice-coring projects.

**2.3. Chemical Data.** There are now large amounts of chemical data from polar ice, mainly from ion-chromatographic analysis. The main ionic impurities found in polar ice are (1) sea salt ions (e.g. Na, Cl<sup>-</sup>); (2) acids—across volcanic eruption peaks, the main acid is sulfuric, but there is also a background of mainly nitric and sulfuric acids; (3) ammonium and organic anions are occasionally found in relatively high concentrations in Greenland ice but are present in much lower concentrations

\* E-mail for correspondence: e.wolff@bas.ac.uk.

<sup>†</sup> Natural Environment Research Council.

<sup>‡</sup> University of Lapland.

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in Antarctica; (4) terrestrial dust and ions derived from it are at rather low concentrations in present day snow but are found at high concentrations in ice from the last ice age, especially in Greenland.

The concentrations of the different impurities of course vary with hemisphere, location (e.g. distance from the coast), season, and climatic period.

### 3. Relationship between ECM Current and Chemistry

**3.1. Effect of Acidity.** The initial paper on the ECM technique<sup>2</sup> found that the primary control on ECM currents was the acidity of the ice, with particularly large peaks at depths where fallout from volcanic eruptions had occurred. On the basis of a number of measurements of the  $H^+$  content of melted ice, a calibration was suggested for ice at  $-14^\circ C$

$$[H^+] = 0.045I^{1.73} \quad (1)$$

where  $[H^+]$  is the concentration in  $\mu M$  ( $\mu mol L^{-1}$ ), and  $I$  is the current in  $\mu A$ . Although the form of this equation is of interest, the multiplying factor has no particular significance since it will depend strongly on factors such as the area of the electrode in contact with the ice, which will differ from instrument to instrument and (in older, more manual instruments) from operator to operator. Additionally, it has been found that the best fit calibration varies somewhat from site to site, even with the same instrument, with exponents up to 2.43 or higher.<sup>5,14</sup> There is considerable scatter in the calibration curves, and this can arise from a number of factors:

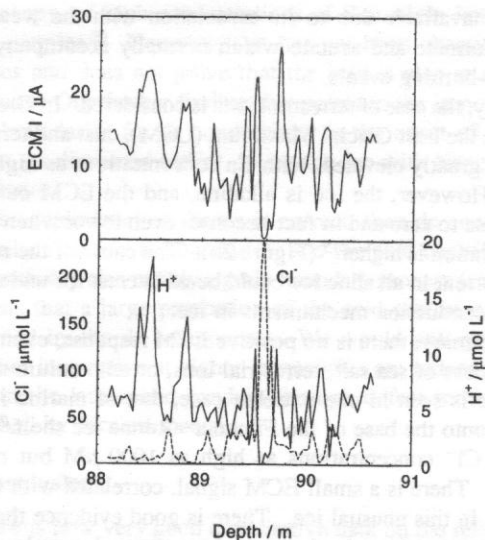
(1) Direct measurements of  $H^+$ , carried out for instance by acid titration, are time consuming, so acidity is often estimated from pH measurements or from measurements of other ions, with  $H^+$  calculated as the difference between anions and cations. These procedures inevitably lead to a large uncertainty in the acidity.

(2) The ECM measurement itself has an uncertainty because of the nature of the method. Some newer instruments have aimed to reduce uncertainty by automating aspects of the procedure, but they may be strongly affected by factors such as core quality.

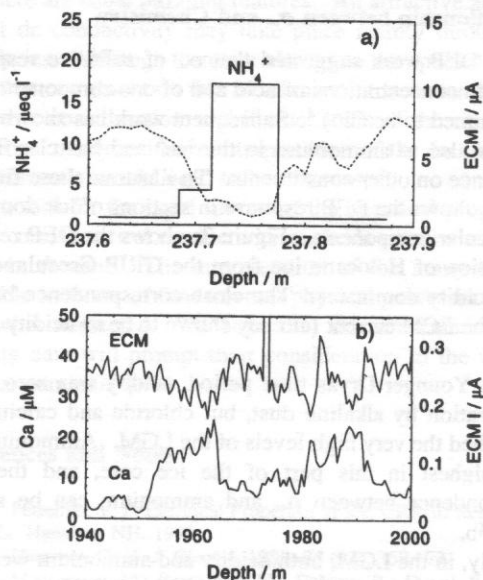
(3) There seems to be a genuine effect where the identity of the anions associated with the  $H^+$  may affect the strength of the response. For a given amount of acidity, a stronger response was found for HCl and  $HNO_3$  than for  $H_2SO_4$ .<sup>7</sup> A similar result was found in another study, with volcanoes containing HCl giving a stronger response than those containing only  $H_2SO_4$ .<sup>14</sup> This finding could be due to some of the  $H^+$  being unavailable, perhaps because the second proton of  $H_2SO_4$  is not fully dissociated. Whatever the cause, it will lead to scatter in acidity/current plots. In addition, since the background acidity has a large nitrate component, whereas most of the large volcanic peaks are dominated by sulfuric acid, it would be expected to lead to a curvature in the plots that may be unrelated to the conduction mechanism.

**3.2. Effect of Other Ions.** Although the secondary effect of the counteranion must be considered, there has been no evidence of any ECM response to any species present in polar ice other than  $H^+$ , with one specialized exception presented at the end of this section. To illustrate this, we present data from two cores (Figure 1).

In Figure 1, the close correspondence between the acidity peaks (measured by an acid titration method) and the ECM current can be seen. At a very large sea salt peak (containing high concentrations of Na and  $Cl^-$ ) at 89.6 m, the acidity virtually disappears and the ECM current also approaches zero.<sup>5</sup>



**Figure 1.** The ECM current (top), and the  $H^+$  (measured by acid titration) and  $Cl^-$  concentrations (dashed) (bottom) recorded on a section of core from Dolleman Island, Antarctica.<sup>5</sup>



**Figure 2.** (a)  $NH_4^+$  and ECM current across a section of the GRIP core from Summit, Greenland.<sup>6</sup> This section covers a high-ammonium event that has been ascribed to the arrival of a biomass-burning plume at the site. (b) ECM current and Ca concentration across a section of GRIP core from the Last Glacial period.<sup>15</sup> Note the amplified ECM scale compared to the previous figures.

The sea salt concentration over this peak is at least 10 times higher than that of the largest acidity peak in the record shown, and yet there is no ECM response. At other sites near the coast of Antarctica, also with very high sea salt concentrations ( $Cl^-$  up to  $100 \mu M$ ), winter peaks of sea salt are accompanied by a near-zero ECM current.<sup>19,20</sup> If there is any response to sea salt ions, it is extremely weak and can be neglected for even the most concentrated samples of meteoric ice seen in the polar regions.

The case of ammonium is illustrated in Figure 2a. Large ammonium peaks, corresponding to biomass-burning events, are found in Greenland snow and ice. The ECM signal is generally reduced across the peaks.<sup>21</sup> In some of the peaks, the acidity may have been reduced through partial neutralization, but there does seem to be some residual acidity across some of the large peaks (M. Legrand, personal communication). Although this might be seen as a response (albeit negative) to the presence of ammonium, a more likely explanation is that the  $H^+$  is again



partly unavailable due to its association with the weak acid anions formate and acetate which normally accompany these biomass-burning events.

Finally, the case of terrestrial ions is considered. In Greenland ice from the Last Glacial Maximum (LGM), dust and terrestrial ions are greatly elevated, with Ca concentrations as high as 20  $\mu\text{M}$ .<sup>22</sup> However, the ice is alkaline, and the ECM current is very close to zero and in fact becomes even lower when the Ca concentration is higher<sup>15</sup> (Figure 2b). The cause of the residual small current in alkaline ice could be of interest for understanding the conduction mechanisms in ice.

In summary, there is no positive ECM response, even with a huge excess of sea salt, terrestrial ions, or ammonium salts. A response is seen in one extreme case, that of marine ice that freezes onto the base of the Filchner–Ronne ice shelf.<sup>23</sup> This ice has  $\text{Cl}^-$  concentrations as high as 1000  $\mu\text{M}$  but no acid content. There is a small ECM signal, correlated with the salt content, in this unusual ice. There is good evidence that there is free brine present in the more concentrated samples of this ice,<sup>24</sup> and it is likely that the ECM conduction is actually through the liquid phase in this case.

#### 4. Relationship between $\sigma_{\infty}$ and Chemistry

Early DEP work suggested that  $\sigma_{\infty}$  of solid ice responded linearly to concentrations of acid and of one component of sea salt (assumed to be  $\text{Cl}^-$ ).<sup>4</sup> Subsequent work has shown that it responds also to ammonium in the ice<sup>6</sup> and has clarified the dependence on other constituents. To illustrate these findings, Figure 3 shows the DEP response in sections of ice dominated by particular components. Figure 3a shows the DEP response in a section of Holocene ice from the GRIP Greenland core, where acidity dominates. The close correspondence between  $\sigma_{\infty}$  and the ECM current (already shown to be an acidity signal) is seen.

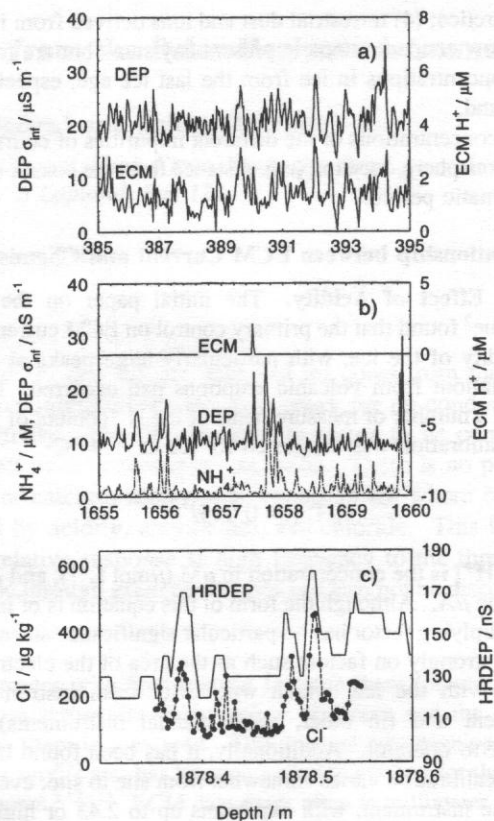
In the Younger Dryas time period, acidity was zero due to neutralization by alkaline dust, but chloride and calcium had not reached the very high levels of the LGM. Ammonium was at its highest in this part of the ice core, and the close correspondence between  $\sigma_{\infty}$  and ammonium can be seen in Figure 3b.

Finally, in the LGM, both acidity and ammonium were very low in the core, but there was still a residual DEP signal when viewed at high resolution. Its variability corresponds closely to the  $\text{Cl}^-$  content of the ice (Figure 3c). There is no similar correspondence with calcium or with sulfate or nitrate. Ice from Antarctica also shows a strong dependence of  $\sigma_{\infty}$  on chloride content.<sup>25</sup> In the extreme case of the marine ice frozen onto the underside of an ice shelf, the constant of proportionality reduces above about 400  $\mu\text{M}$ , estimated as the solubility limit for  $\text{Cl}^-$ . We interpret this again as being due to some of the chloride being present in brine, where it cannot contribute to intracrystalline DEP conduction.

On the basis of the statistical analysis of data from sections such as those above, the calibration currently preferred for the DEP conductivity of solid ice<sup>15</sup> at  $-15\text{ }^{\circ}\text{C}$  is

$$\sigma_{\infty} = 9 + 4[\text{H}^+] + 1[\text{NH}_4^+] + 0.55[\text{Cl}^-] \quad (2)$$

where  $\sigma_{\infty}$  is in  $\mu\text{S m}^{-1}$ , and chemical concentrations are in  $\mu\text{M}$ . Note the constant, which is close to the estimate of pure ice conductivity at this temperature.<sup>1</sup> It should be recognized that this equation is based mainly on data from the GRIP ice core in Greenland and that data from other sites are required to confirm it. In the GRIP core, it seems possible to explain all of the thousands of peaks in the core and the major trends, on



**Figure 3.** (a) DEP  $\sigma_{\infty}$  and acidity (estimated from ECM current) for a section of ice ( $\sim 1800$  years old) from Summit, Greenland.<sup>15</sup> (b)  $\text{NH}_4^+$ , DEP  $\sigma_{\infty}$ , and acidity (estimated from ECM current) for a section of GRIP core<sup>15</sup> from the Younger Dryas period (12 kyr before present). Apart from one acidity peak, the DEP signal is dominated by ammonium in this section. (c)  $\text{Cl}^-$  concentration (dashed) and high-resolution DEP (HRDEP) signal from a section of GRIP core from the Last Glacial period,<sup>18</sup> where both acid and ammonium have very low values. HRDEP<sup>30</sup> is a rapid method that gives 2 mm resolution at a single frequency, but variable core geometry and poor temperature control prohibits the use of a single formula for quantitative conversion to conductivity.

the basis of these three chemical components. There is no evidence for any change in response with depth, age of ice, crystal size, or other parameters.

#### 5. Conduction Mechanisms

On the basis of mainly ECM and DEP data, we have now amassed a large amount of quantitative and qualitative data that should be used to test theories of electrical conduction applying to naturally-occurring ice from the polar regions. In particular, any theory must explain (1) why ECM responds only to  $\text{H}^+$  and not at all to other ions; (2) the form of the ECM dependence on acidity; (3) the relative strength of the high-frequency response to  $\text{H}^+$ ,  $\text{NH}_4^+$ , and  $\text{Cl}^-$ ; and (4) the temperature dependence of the responses (not discussed here).

Most theoretical discussions of the electrical properties of ice begin with Jaccard theory,<sup>1</sup> and we will discuss the findings in that context first. However, there is also some evidence that the dc conductivity of impure ice may be controlled by a grain boundary process,<sup>26</sup> and we discuss this possibility also.

**5.1. Jaccard Theory.** In Jaccard theory, it is assumed that intracrystalline conductivity dominates. The dc conductivity would be controlled by the minority charge carriers (ionic  $\text{H}_3\text{O}^+$  defects), while at higher frequencies, the majority carriers (Bjerrum L- and D-defects) would be more important. If this does describe the processes we are observing in polar ice, then it leads to a number of implications. (1) Only  $\text{H}^+$ ,  $\text{NH}_4^+$  (or

NH<sub>3</sub>), and Cl<sup>-</sup> (or HCl) are able to enter the ice lattice. This is reasonable, since they are able to replace existing atoms because the covalent radius for N and Cl is similar to that of O atoms. If F<sup>-</sup> was ever a significant ion in polar ice, we would expect it also to show a response, but we would not expect large anions such as NO<sub>3</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup> to play any role nor would we expect cations such as Na or Ca to have an effect. (2) Only H<sup>+</sup> creates ionic defects in the ice. (3) In Jaccard theory, considering only Bjerrum defects:

$$\sigma_{\infty} = n_L \mu_L |e_L| + n_D \mu_D |e_D| \quad (3)$$

where L and D refer to the Bjerrum L- and D-defects, respectively,  $n$  is the concentration of the defect,  $e$  its charge, and  $\mu$  its mobility.  $e_L = -e_D$ , and experiments suggest  $e_D/e = 0.37$ ,<sup>1</sup> where  $e = 1.6 \times 10^{-19}$  C. From the literature,<sup>1</sup>  $\mu_L$  at  $-15$  °C is  $1.5\text{--}2.4 \times 10^{-8}$  m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. If Cl<sup>-</sup> enters the lattice as HCl, we expect the formation of one L-defect and one ionization (H<sub>3</sub>O<sup>+</sup>) defect,<sup>27</sup> whereas if Cl<sup>-</sup> enters the lattice alone with the cation incorporated interstitially or at grain boundaries, we could expect two L-defects. Comparing the coefficient for Cl<sup>-</sup> in eq 2 with the L-defect calculation in eq 3, it appears that the ratio of L-defects to the Cl<sup>-</sup> concentration would have to be in the range 0.7–1 (leaving the possibility that either some Cl<sup>-</sup> ions are not in the lattice, or not all Cl<sup>-</sup> ions create L-defects). (4) Similar arguments can be applied to the conductivity from NH<sub>4</sub><sup>+</sup>. In this case, we expect two D-defects (incorporation of NH<sub>4</sub><sup>+</sup>, with anion interstitial or at grain boundaries) or one D-defect and one OH<sup>-</sup> ionization defect (incorporation of NH<sub>3</sub> or NH<sub>4</sub>OH).<sup>27</sup> The literature suggests that  $\mu_D < \mu_L$ . Even if we assume  $\mu_D = \mu_L$ , the ratio of D-defects to NH<sub>4</sub><sup>+</sup> would have to be in the range 1.3–2.

It is currently difficult to understand the greater efficiency of defect formation from ammonium compared to that from chloride and the simultaneous requirement for high D-defect mobility. Because the charge from an ionization defect is higher than that from Bjerrum defects and the mobility may be similar,<sup>1</sup> we can understand that  $\sigma_{\infty}$  responds more strongly to acid than to either of the other ions. However, the activation energy in ECM and for acidic ice in DEP<sup>25,28</sup> is not consistent with the zero activation energies for the ionization defect mobilities that are in the literature.<sup>1</sup> For HF, a square root dependence of dc conductivity on HF concentration is predicted at high concentrations, as observed in some calibrations of ECM current against acidity. However, where the acid anion is not expected to be incorporated into the lattice, it is not clear that this should apply, and there may be other explanations (including the influence of sulfate in reducing conductivity) for the apparent curvature of the calibrations.

**5.2. Grain Boundary Conduction.** It has been suggested that dc conductivity could take place through a network of connected liquid veins at triple junctions in the ice.<sup>26</sup> These veins would be present down to the eutectic point of the impurity mixture with ice and water ( $-73$  °C for H<sub>2</sub>SO<sub>4</sub>/water/ice). The magnitude and temperature dependence of the dc conductivity fit well with calculations based on this model. It also explains well the lower conductivity of the acid associated with sulfate, since the second proton of sulfuric acid would indeed be undissociated at the high acidities that would be found in the liquid veins. It cannot by itself explain any curvature of ECM calibrations but instead predicts a linear relationship. It also cannot easily account for the findings that ECM conductivity persists even in single large crystals in deep ice (although any acidic liquid might be expected to be present over the entire surface in this case). In favor of this grain boundary conduction mechanism is the direct observation, using scanning electron

microscopy, of high concentrations of S at triple junctions in some samples.<sup>29</sup> However, this has not been observed in all samples and does not prove that the acid is also at the triple junctions. One further finding that points to the importance of grain boundaries for dc conductivity is the onset of an ECM current, as discussed earlier, in marine ice with brine at grain boundaries.

If the triple junction theory is correct, then dc conductivity takes place mainly at boundaries, and the acid contribution to  $\sigma_{\infty}$  is probably also mainly a grain boundary process (calculation suggests that a large proportion of the acid part of  $\sigma_{\infty}$  can be explained by the dc component). We would still expect that the other ions active at higher frequencies are indeed incorporated in the lattice and conduct through defect movement as described by Jaccard theory.

## 6. Conclusion

There is now very good quantitative data on the relationship between electrical conductivity and chemical concentrations in ice. The data can mainly be explained in terms of Jaccard theory but have not yet been incorporated into it in a quantitative way, and there are some puzzling features. An attractive alternative is that dc conductivity may take place mainly through grain boundaries. Although there are also some unexpected observations that cast doubt on this mechanism, it is certainly worthy of further consideration, and if true, some of the experiments that led to the quantitative interpretation of the Jaccard theory used currently would need to be reassessed.

As a tool for the rapid survey of the chemical properties of an ice core, electrical conductivity methods are now mature and much in demand. The interpretation of the many data now available in terms of fundamental physical processes has been somewhat neglected. We hope that this presentation of the existing data will prompt their consideration in the wider ice physics community.

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