

Electrical response of the Summit-Greenland ice core to ammonium, sulphuric acid, and hydrochloric acid

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Abstract. Electrical and chemical analysis of the GRIP ice core from Summit in central Greenland confirms that the ECM current is controlled solely by acids in the ice, though there could be different responses for different acids. The dielectric conductivity is dependent on strong acid, on sea salt chloride, and also on ammonium concentrations in the ice. The response to NH_4^+ is similar to that of sea salt chloride, as they both conduct only at AC frequencies, but NH_4^+ is approximately twice as conductive per mole. The response to the strong acids shows results consistent with earlier work, with similar responses throughout the length of the core. It seems as if all the thousands of electrical peaks in the GRIP core may be explained by the response to just three chemical species: acidity, ammonium salts, and a third component which is probably chloride.

Introduction

It has become apparent that changes in chemical impurity concentration are responsible for most of the variability of both the DC and LF conductivity of polar ice [Moore et al., 1992a], although other ice properties may be relevant, particularly above the firn-ice transition. The DC conductivity, effectively measured by the ECM (electrical conductivity measurement) method [Hammer, 1980] is controlled by the acidity of the ice; very high salt concentrations have no effect. At higher frequencies (as measured by the dielectric profiling (DEP) method [Moore and Paren, 1987]), previous work showed that both acids and some component (probably chloride) of sea salt [Moore et al., 1992b] contribute.

The 3028 m GRIP (Greenland Ice Core Project) core spans at least the last complete climatic cycle [GRIP Project Members, 1993] and presents the opportunity to study both the DC and LF properties of natural ice containing a wide range of chemical impurities. This paper shows additional evidence of the

importance of impurities, and introduces a quantitative description of the electrical effect of a further chemical species, ammonium.

The LF electrical properties of the ice were measured at 2 cm resolution with an updated version of the AC dielectric profiling technique (DEP) [Moore and Paren, 1987]. The conductance and capacitance were measured at a range of frequencies from 120 Hz to 300 kHz for each 2 cm section. From a range of properties that can be derived, σ_∞ (the high-frequency limit of the conductivity) has proved to be the most useful, and is reported throughout this paper. Measurements were carried out on the entire core from 138 m down in the field at a range of temperatures between -25 and -10°C. The data have been normalized to a reference temperature of -15°C, using an activation energy of 0.5 eV (48 kJ mol⁻¹) to correct the background part of the conductivity that is due to pure ice, and 0.22 eV (the average for salt and acid from previous studies) to correct everything above this background level [Moore et al., 1992b]. There were some difficulties with this correction because at some depths the temperature of the ice was sometimes still equilibrating when our measurements were made, so that the ice temperature is poorly known.

In ECM, a high DC voltage (1250 V) is applied between two electrodes that are run along a fresh, flat surface, and the current flowing between them is measured [Hammer, 1980]. ECM was carried out at a resolution of a few mm, and data were corrected to -14°C using an activation energy of 0.23 eV. Current data have been converted to H^+ concentrations using the calibration discussed later. Chemical analyses for a range of ions (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , F^- , Cl^- , NO_3^- , SO_4^{2-} , HCOO^- (formate), CH_3COO^- (acetate), CH_3SO_3^- (methanesulphonate), and $\text{C}_2\text{O}_4^{2-}$ (oxalate)) were done by ion chromatography on discrete samples, typically 5 cm in length. At present only a small fraction of the core has been chemically analysed. The main species not directly measured was H^+ , but we can use the ECM technique which is only sensitive to acidity [Moore et al., 1992a], to derive this electrically important species. Ammonia was measured continuously in the field at a few mm resolution by a continuous flow technique [Fuhrer et al., 1993]. Suitable depth-averaging allows direct comparisons between the various records.

Both the ECM and DEP σ_∞ records show many individual peaks (often representing less than a year's snowfall)

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superimposed on a background that varies with climate. The ECM background is high in acidic ice, and low in alkaline ice. The small ECM signal in alkaline ice decreases still further as the ice becomes more alkaline, and this will be discussed elsewhere. Peaks in ECM are normally due to volcanic sulphuric acid, but sometimes HCl is also present. For DEP, there is a conductivity (expected to be $9 \mu\text{S m}^{-1}$ at -15°C) due to pure ice. On top of that is again a background that varies with climate, and peaks that are due to volcanic and other input. All large peaks and trends in ECM can be seen in the DEP, but additional ones due to other components (discussed later) are also present.

Ammonium

Legrand et al. [1992] report the occurrence of occasional large peaks (up to $20 \mu\text{M}$ concentrations) in ammonium formate during the Holocene part of the GRIP core. There are also smaller annual peaks in ammonium concentration. Large ammonium peaks give drops in the ECM current, and peaks in the DEP conductivity (Figure 1). The ECM drop implies that the acidity falls, or that the ice may even be alkaline, as is verified by detailed chemical ion balances on a few of the ammonium peaks. Although NH_4^+ has previously been included in a statistical analysis of the ECM response to chemistry [Taylor et al., 1992], we find no evidence that it has any effect other than that of neutralising the acid that would otherwise be present.

Continuous ammonium data are available but their quantitative accuracy is not yet fully verified. In the Younger Dryas period, where acidity is low due to neutralisation by carbonate dust, ammonium is clearly the main cause of peaks in the DEP σ_∞ (Figure 2). From analysis of the few peaks measured by ion-chromatography, σ_∞ (S m^{-1}) appears linearly related to $[\text{NH}_4^+]$ (molar concentration) by:

$$\sigma_\infty = 1.0 [\text{NH}_4^+] \quad (1)$$

at -15°C assuming that the activation energy of 0.22 eV used for σ_∞ applies also to NH_4^+ signals. However, the coarse chemical sampling procedure makes precise calibration difficult and the variability in the coefficient between different events is about 20%.

We must explain how the ammonium salts can produce a change in σ_∞ while leaving the ECM current and therefore the

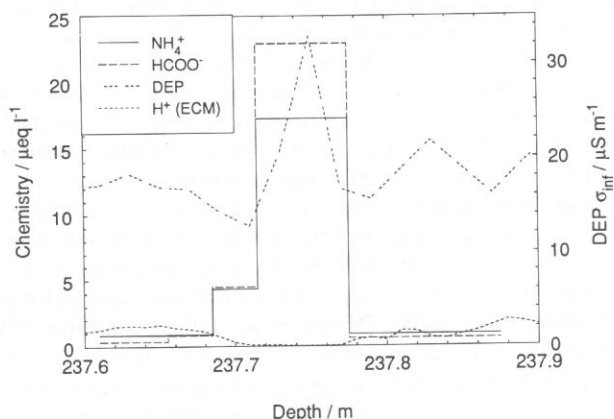


Figure 1. DEP and ECM profile over an ammonium formate peak at 237.7 m. The ECM signal drops as DEP rises.

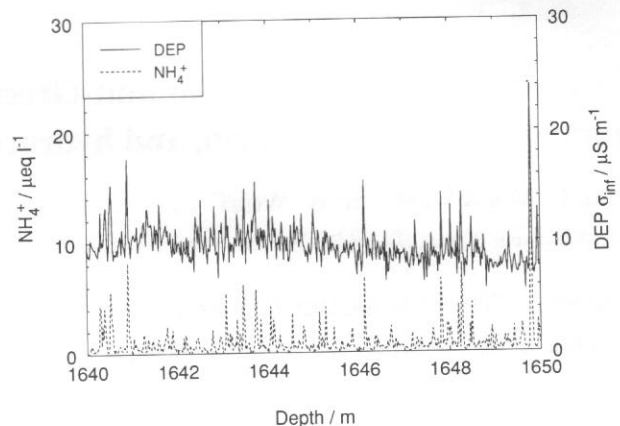


Figure 2. DEP and ammonium (by continuous flow) profiles for a 10 m section of the Younger Dryas ice.

DC conductivity unaltered. The coefficient in (1) is approximately twice the coefficient (0.55 at -15°C) found for sea-salt Cl [Moore et al., 1992b], which also affects only the AC conductivity of ice. Moore et al. [1992b] interpret the electrical effect of sea-salt Cl using the Jaccard theory (see for example Petrenko [1993]) of electrical conduction in ice. The Cl^- ions are incorporated into the ice lattice with the production of Bjerrum L defects. Bjerrum defects are the majority electrical charge carriers in ice at temperatures encountered in natural ice sheets, and consequently determine only the AC conductivity. The expression for the AC conductivity (σ_∞) in Jaccard theory is

$$\sigma_\infty = n_L \mu_L |e_L| + n_D \mu_D |e_D| \quad (2)$$

where the subscripts L and D refer to the Bjerrum L and D defects respectively, n is the concentration of the species, e its charge, and μ its mobility.

In the larger NH_4^+ spikes, NH_4^+ seems to be present as ammonium formate, although other anions could be important in the more frequent smaller peaks. No laboratory data exist on the electrical properties of ice doped with ammonium formate, though the behaviour of ice containing NH_4^+ has been studied [Gross et al., 1978]. Ammonium formate will be dissociated in water to the very polar ions NH_4^+ and HCOO^- . The covalent radius of N is close to that of O and it is expected that either NH_3 or NH_4^+ may be substitutionally incorporated into the ice lattice for an H_2O . The one or two excess protons introduced would then behave as 1 or 2 D defects in the lattice; depending on the affinity of the protons for the N centre, NH_4^+ might also lead to the formation of an ionisation defect, but the lack of a DC signal suggests this is not significant. It is possible to imagine the relatively small HCOO^- ion fitting within the ice lattice and causing L defect propagation, but this requires further investigation.

We therefore could have up to 2 D defects (and perhaps 1 L defect) produced for each ammonium in the ice. Jaccard theory requires that $e_L = -e_D$, and experimental measurements suggest $e_D/e = 0.37$ [Petrenko, 1993] (e is $1.6 \times 10^{-19} \text{ C}$). From measurements on ice doped with HF impurity, at -15°C , $\mu_L = 1.8 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ [average of Camplin et al., 1978 and Jaccard, 1959]. No values for μ_D are reported in the literature, though it

has been shown that $\mu_D \leq \mu_L$ [Petrenko, 1993]. From equation (2) we can obtain a value for k in an equation of the form:

$$\sigma_\infty = k [\text{NH}_4^+] = (k_L N_L + k_D N_D) [\text{NH}_4^+] \quad (3)$$

where N_L and N_D are the number of L and D defects introduced per ammonium ion present, and the other units are as in equation (1). From equation (2), $k_L = 0.66$, while $k_D \leq 0.66$.

The observed coefficient (1) for the GRIP core at -15°C is 1.0. With this coefficient we appear to need at least the formation of 2 D defects (with $> 75\%$ efficiency of defect generation). Moore et al., [1992b] found that L defects were generated by Cl^- ions at an efficiency of about 70%. Because of the uncertainty in the value of μ_D , it may be that only D defects are produced, but we cannot exclude the possibility that the anion (HCOO^- in larger peaks) is incorporated in the lattice. If $\mu_D \ll \mu_L$, then L defect formation would certainly be required.

Acids

Ion balance calculations of the measured anions and cations were used to give an estimate of $[\text{H}^+]$. In general, the background acidity in Holocene Greenland ice is mainly HNO_3 , with large peaks due mainly to volcanic eruptions which usually deposit mostly H_2SO_4 , but occasionally are dominated by HCl . The original ECM calibration ($[\text{H}^+] = 0.045I^{1.73}$) [Hammer, 1980] is not good for ice cores taken recently from the central areas of Greenland, and Moore et al. [1992a] published a different calibration based on a short section of Greenland ice core containing the Laki large volcanic signal. Comparisons of the ECM and chemical data across volcanic peaks in the GRIP core shows that they fit poorly to the original calibration [Hammer, 1980]. In Figure 3, we have plotted the ECM current against acidity for 11 volcanic events where chemical data at suitable resolution exist, and for the Laki event at Site G [Moore et al., 1992a]. For the Site G Laki data, H^+ was measured directly by acid titration. To calculate H^+ for the GRIP data, we used either the total ion balance, or the sum of acidic anions. Past experience suggests that, used with care, these parameters give a good agreement with H^+ measured directly.

There is clearly much scatter, some of which is certainly induced by the method of calculating the chemistry; a more precise calibration must await direct measurements of H^+ . The two Cl-rich volcanoes (xs $\text{Cl}^- > 50\%$ of total acidity) fall well away from the other data. Curves of various forms will fit the data, but Moore et al., [1992a] found a calibration curve of the form $[\text{H}^+] = aI^b + c$, where I is ECM current. However, with a positive value of c , a poor fit is obtained at low currents and the relationship does not explain the low but significant ECM signal in the alkaline (and therefore negative H^+) Wisconsin ice. We have tried to reduce these difficulties by forcing c to be zero. With the data that we have at present, more complicated calibrations are not justified. Regressions including different volcanic peaks show that the values of a and b are very sensitive, with b values between about 1.6 and 2.7 for various central Greenland datasets. The choice of equation affects mainly the calculated H^+ values for the very largest volcanic peaks, and the different regressions predict fairly similar H^+ at typical values of $0.5\text{--}5\ \mu\text{M}$. Throughout this paper we use:

$$[\text{H}^+] = 0.03 I^2 \quad (4)$$

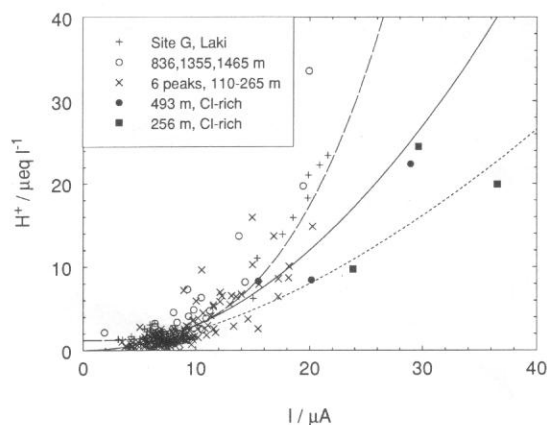


Figure 3. ECM calibration plot. Solid squares and circles show data from volcanic signals where Cl^- was a major component. Open circles represent data analysed at Summit, crosses show data analysed in Copenhagen from ice above 300 m depth. The short-dashed curve represents the Hammer [1980] ECM calibration, the long-dashed curve is the Site G calibration of Moore et al. [1992a], and the solid line is that produced by (4).

Data from the two Cl-rich peaks fit close to the Hammer [1980] calibration. It has already been suggested [Legrand et al., 1987, Moore et al., 1992a] that HCl and HNO_3 may lead to larger ECM signals than an equivalent H^+ from H_2SO_4 , and this would help to explain both the discrepancy, and some part of the curvature of the main calibration. For the remainder of this paper we will use the calibration (4) to calculate H^+ . Note that we do not yet know the meaning of the relationship seen in alkaline ice (calculated H^+ values below about $0.1\ \mu\text{M}$).

We will now use (4) to investigate the response of the AC conductivity, σ_∞ to acidity. We show in Figure 4 four sections covering different climatic regions of the core, and different ranges of acidity. The scatterplots show some curvature at low acidity, reflecting in part our ignorance of the calibration in alkali ice. The lines shown are linear regressions of all data above $0.3\ \mu\text{M}$. The coefficient relating a linear fit of σ_∞ to $[\text{H}^+]$ is similar for all four sections (3.74, 5.25, 4.51 and 4.67). The differences between sections are partly due to the different ranges of acidity involved, but are also due largely to differences in values at the low acidity end, where the temperature correction becomes particularly critical because the correction to the pure ice part becomes dominant. At an acidity of $3\ \mu\text{M}$, the regressions for all four sections predict σ_∞ between 25.3 and $26.5\ \mu\text{S m}^{-1}$. Moore et al., [1992a] found a coefficient of 1.8 for the Laki H_2SO_4 eruption (Site G) at -22°C , corresponding to a coefficient of 2.4 at -15°C . The coefficient found for the Laki signal is lower than that for the GRIP core here. However, if we take the original ECM data for the Laki core and convert it to H^+ by (4), the σ_∞/H^+ coefficient becomes 3.9 at -15°C . This shows that the σ_∞ -ECM relationship is in good agreement between cores, but that apparent discrepancies arise from the imprecise nature of the calibration of ECM against measured chemistry.

It is encouraging that the vast majority of the data points are above the minimum expected conductivity at -15°C of $9\ \mu\text{S m}^{-1}$, the conductivity of pure ice single crystals [Camplin et al., 1978]. The intercept for the Holocene data set is somewhat higher than expected when the relatively low concentrations of chloride and ammonium in the ice are considered. This may be partly due to

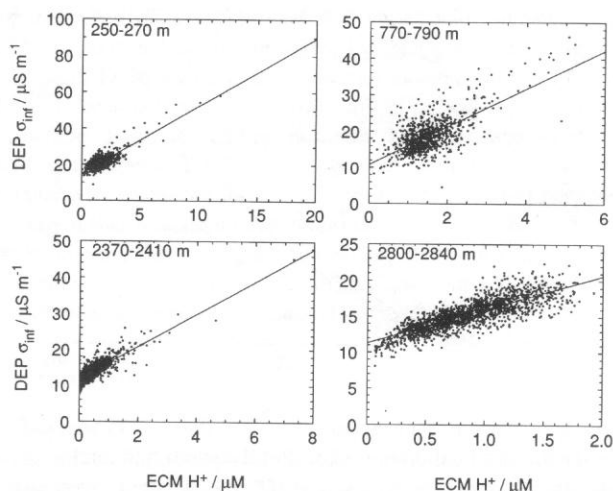


Figure 4. Scattergrams of four separate core sections showing the σ_{∞} - acidity relationship. The acidity was calculated from the ECM data using (4). In each case the lines are the best fits for data above $0.3 \mu\text{M}$ from ECM. The upper two core sections are Holocene ice, the section 2370-2410 m is a warm interstadial in Wisconsin-age ice, and the 2800-2840 m section is from ice identified as being in the Eemian interglacial.

problems with the temperature correction (as discussed above), and partly due to some genuine curvature because of the change from mainly HNO_3 to H_2SO_4 dominance at higher acidities; another possibility is that our chosen ECM calibration is still poor for estimating H^+ at low acidities.

$[\text{H}^+]$ from HCl in the two peaks investigated produces a stronger response in ECM, but not in DEP, than does an equivalent $[\text{H}^+]$ from H_2SO_4 . The ECM result implies less efficient dissociation of the H_2SO_4 than HCl. Possible mechanisms of acid conduction are discussed by Moore et al., [1992a], where the two hypotheses of conduction via a Jaccard mechanism and via concentrated liquid acid at grain boundaries are evaluated. The different response of ECM and DEP is not easy to explain at this stage.

The third component

Detailed examination shows some peaks in the record that appear to be significant, are not due to acid or ammonia, but seem to be related to peaks in calcium. Since many chemical components in the ice increase more or less in phase with calcium, it is not yet possible to be sure which is responsible for the DEP signal. However, previous work shows that Cl^- causes a DEP signal, and it seems probable that this will turn out to be the third factor responsible for DEP signals in the GRIP core. More detailed chemistry will be needed before this can be confirmed.

Conclusion

Despite the huge quantities of electrical data now available for the GRIP core, more high-resolution chemical data is needed to provide a final quantitative description of the electrical-chemical relationship. However, the evidence here confirms that the ECM (DC) response is controlled by acidity alone, although there remains work to be done to substantiate the suggestion that there is a different response to different acids. This first, and clear, evidence of an AC only signal due to ammonium in natural ice

should stimulate theoretical work on the defect formation responsible for the signal. In the GRIP core most of the thousands of DEP σ_{∞} peaks are explained simply by a response to acid, to ammonium salts, and to one of the other species (probably chloride) that varies in phase with Ca in glacial age ice. This confirms the potential of using the two electrical methods together as a very powerful way of surveying rapidly the general chemical properties of long ice cores, to indicate the form both of the acidity profile and of the variations in other impurities.

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