Climatic implications of background acidity and other chemistry derived from electrical studies of the Greenland Ice Core Project ice core

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Abstract. High-resolution continuous profiles were obtained on the Greenland Ice Core Project (GRIP) ice core using two different electrical methods. After correction for temperature and density, the electrical conductivity method (ECM) technique responds only to acidity, while dielectric profiling (DEP) responds to acid, ammonium, and chloride. Detailed chemistry on a section of glacial-age ice allows us to confirm the calibration factor for chloride in DEP. Acidity dominates the DEP variability in the Holocene, Allerod/Bolling, and larger interstadials; ammonium dominates in the Younger Dryas, while chloride is the major contributor in cold periods including smaller interstadials. From the electrical signals plotted on a linear timescale we can deduce the background (nonvolcanic) acidity of the ice, varying from always acidic in the Holocene to always alkaline in the cold periods. In the interstadials, the ice is close to neutral, with most of it acidic in larger interstadials, most of it alkaline in smaller ones, and rapid alternations within interstadials. It is not clear whether neutralization of individual acidic particles occurred in the atmosphere or whether acid and alkaline particles coexisted until deposition in the snowpack. The changes in acidity observed at GRIP apply at least to all of Greenland and probably to much of North America. There would have been ecological effects and important changes in the uptake of some chemicals onto ice. If acidic sulfate particles were neutralized and removed from the atmosphere, which remains uncertain, then there are atmospheric chemistry and radiative effects that require further investigation.

1. Introduction

The two deep ice-core drilling projects at Summit, Greenland, have been breakthroughs not only in the temporal detail with which climate can be observed but also in the range of parameters measured. Thus, in addition to the oxygen isotope ratio (giving temperature information) [*Dansgaard et al.*, 1993; *Grootes et al.*, 1993], data have been published on species such as the greenhouse gas, methane [*Chappellaz et al.*, 1993], and on the major aerosol components [*Fuhrer et al.*, 1993; *Mayewski et al.*, 1993]. These and other physical and chemical measurements, sometimes carried out at subannual resolution over tens of thousands of years, provide the possibility to look at the factors that force climate, as well as at the climate itself. However, difficulties of interpretation mean that for many chemical species, it is not yet possible to unravel changes in source strength, transport, and deposition process efficiency [*Bales and Wolff*, 1995].

Electrical measurements on ice cores provide a rapid way of obtaining continuous measurements that can be interpreted in terms of various aspects of the chemistry of the ice. Notably, electrical measurements have been used frequently to obtain records of volcanic eruption fallout [e.g. *Hammer et al.*, 1980; *Clausen et al.*, 1995]. However, they can also be used to give measurements of background acidity and of some other chemistry in the ice. We have previously published the electrical records from the Greenland Ice Core Project (GRIP) core and discussed how they vary with depth and in comparison to climate changes indicated by the oxygen isotope ratio [*Wolff et al.*, 1995]. The electrical conductivity method (ECM) was also carried out on the Greenland Ice Sheet Project 2 (GISP2) core and is discussed in this special section [*Taylor et al.*, this issue]. In the current paper, we revisit the calibration of the electrical methods, giving new evidence for the effect of chloride at higher frequencies. We present the electrical records plotted for the first time against time. We look briefly at what controls the variability of the records. We then concentrate on the background acidity of the ice and discuss what the record tells us about the acidity of the atmosphere, and we assess the geographical extent of our findings. Finally, we discuss the possible effects of changing acidity on climate, chemistry, and ecosystems.

2. Methods

The 3028-m-long GRIP ice core was drilled at Summit, central Greenland, between 1990 and 1992. Electrical measurements were made on the frozen core in the field. The electrical methods used on the GRIP core were discussed in detail in a previous paper [*Wolff et al.*, 1995], and will only be summarized here.

The electrical conductivity method is effectively a dc method, in which a pair of electrodes are scratched across a freshly planed surface. The current flowing between the electrodes, with an applied voltage of 1250 V, was measured. ECM was carried out on the entire length of the GRIP core, with a resolution of order 1 mm. The temperature-corrected ECM current has been found to respond only to acidity (H^+ concentration) [*Moore et al.*, 1992b, 1994], although the counter anion may have an indirect effect, probably by sequestering H^+ (e.g., in the case of weak acids) and reducing the effective H^+ concentration. The calibration adopted for the GRIP core [*Moore et al.*, 1994] is

$$[H^+] = 0.03 \ I^2 \tag{1}$$

where $[H^+]$ is the acid concentration in micromoles per liter, and I is the current in microamperes. Acidity calculated from this equation is quoted throughout this paper, although the true meaning of the small currents seen even in alkaline ice is unclear. It should be noted that the calibration of ECM instruments depends strongly on the design of the electrodes and the angle and speed of electrode movement. Equation (1) is therefore valid only for the Danish ECM system.

Dielectric profiling (DEP) is an ac technique in which conductance and capacitance are measured on whole (uncut) cores at a range of frequencies between dc and, in this case, 100 kHz. DEP was carried out on the entire core from 138-m depth to the bed, at 2-cm resolution. A range of electrical properties can be derived. We have found that the most useful is σ_∞, the high-frequency limit of the conductivity. This parameter, normalized to -15°C, has been used here [*Wolff et al.*, 1995]. Previous work [*Moore et al.*, 1989, 1992a, 1994] has shown that σ_∞ values depend on acidity, on ammonium concentrations, and on a component of sea salt (probably chloride). This will be discussed further in the next section.

Further measurements were made with a second, high-resolution, DEP (HRDEP) [*Moore*, 1993]. This instrument was used on selected cores after planing the ice surface. It measures the capacitance and conductance at a single frequency. In this case, we chose 50 kHz, which represents a satisfactory compromise between the need to be well above the relaxation frequency of the ice and avoiding the region of reduced instrument accuracy at high frequency. The results cannot be considered quantitative but give a qualitative estimate of σ_∞ variations at 2-mm resolution.

3. DEP Calibration

The DEP σ_∞ appears to be controlled by four components: a pure ice part and concentration dependent parts due to acidity, ammonium, and sea salt (presumably chloride). The calibration has been discussed before [*Moore et al.*, 1992a, b, 1994], but the sea salt calibration has relied until now only on statistical presentations. We have taken a section of core from the last glacial maximum, in which acidity (as determined by ECM) is negligible and ammonium concentrations are also low, but where chloride concentrations are high, so that sea salt is expected to be the main influence on σ_∞. We carried out HRDEP on this section and also carried out high-resolution (2-mm resolution) chemical analysis (using a microtome cutting and low-volume ion-chromatography technique).
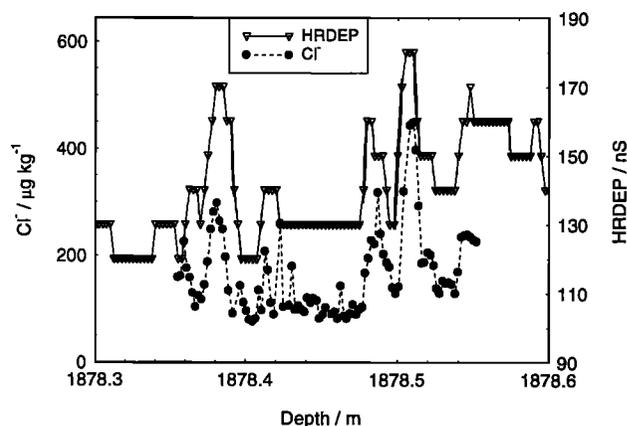

Figure 1. The high-resolution dielectric profiling (HRDEP) and chloride signal in a short section of ice from approximately 18,000 years B.P. from the GRIP core.

The result of the comparison of HRDEP with detailed chemistry is shown in Figure 1. Chloride and the HRDEP conductance follow each other very closely (nitrate and sulfate give much less correspondence with HRDEP), confirming that sea salt is the main influence in this cold-period ice. HRDEP, as used at GRIP, was not designed to be fully quantitative. Nonetheless, by smoothing the signal and comparing it to the normal DEP signal, we were able to estimate an HRDEP/DEP relationship for this section of core (this relationship will vary from core to core, since the pieces of core used in HRDEP were of variable cross section and the HRDEP temperature was not controlled). Using this, the best fit between chloride and HRDEP is obtained by assuming that the DEP/Cl⁻ coefficient at -15°C is 0.5 S m⁻¹ M⁻¹ (where M is the symbol for moles per liter), with a large uncertainty. This is in good agreement with the coefficient of 0.55 S m⁻¹ M⁻¹ at -15°C deduced from earlier work [*Moore et al.*, 1992a].

This discussion confirms that the best calibration for σ_∞ at -15°C, as previously suggested [*Wolff et al.*, 1995], is

$$\sigma_\infty = 9 + 4 \ [H^+] + 1 \ [NH_4^+] + 0.55 \ [Cl^-] \tag{2}$$

where σ_∞ is in microsiemens per meter and chemical concentrations are in micromoles per liter. The constant (9) in this equation is the conductivity of pure ice at -15°C.

4. The Electrical Records From GRIP

The agreement between GRIP and GISP2 ice core records of oxygen isotopes, ECM, and other measurements is very good to a depth corresponding to about 100,000 years, but there are significant differences below that [*Grootes et al.*, 1993; *Taylor et al.*, 1993a]. Measurements of gases in the cores [*Chappellaz et al.*, this issue] suggest that disturbed stratigraphy may occur in both cores, and investigations of visual stratigraphy and crystal fabrics cannot rule this out [*Alley et al.*, 1995]. For this reason, we present here the electrical records only in the section to 100 kyr, where the dating and stratigraphic order of the core are reasonably secure. This is the first presentation of the electrical records on a linear time axis (Figure 2). The profiles presented here have been smoothed and resampled to a 100-year interval in order to give comparable variance through the core.

The records, at high depth resolution, and their relationship with the oxygen isotope signal and calcium signal were discussed in detail before [*Wolff et al.*, 1995]. On the 100-kyr scale, the DEP signal mirrors the ECM signal very closely, reflecting the dominant influence of acidity in the calibration (equation (2)). The apparent
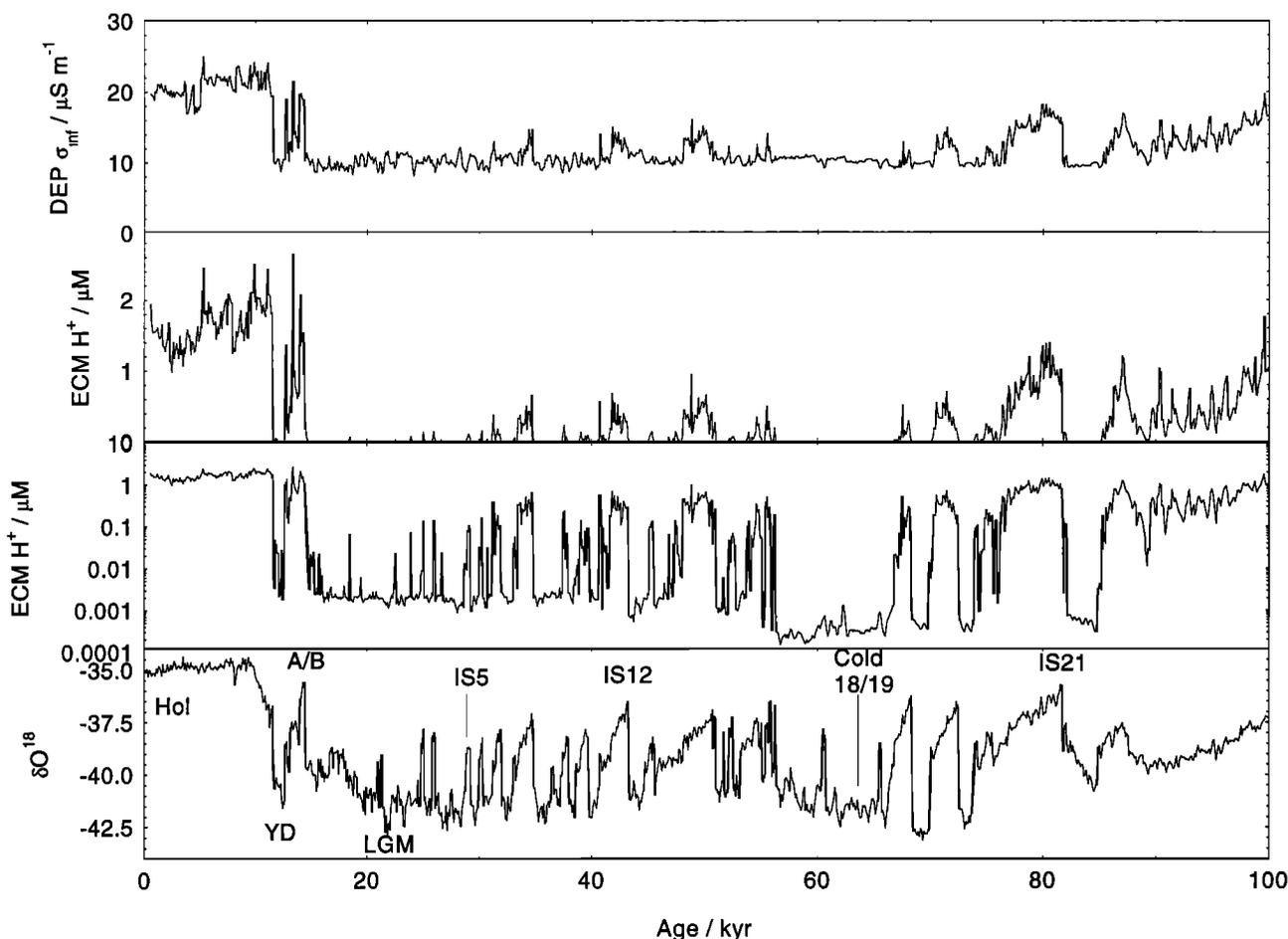
Figure 2. The electrical records, and the oxygen isotope record, of the last 100 kyr from the GRIP core. From the top panel, dielectric profiling (DEP) signal, electrical conductivity method (ECM) on a linear scale, ECM on a logarithmic scale, and oxygen isotope signal are shown. Some climatic periods are marked: Hol, Holocene; YD, Younger Dryas; A/B, Allerod/Bolling; IS, interstadial; Cold 18/19, cold period between IS 18 and 19. The apparent level changes in the DEP around 4 kyr B.P. are probably due to difficulties with the temperature correction in this section [*Wolff et al.*, 1995].

level changes in the DEP around 4 kyr B.P. are probably due to difficulties with the temperature correction in this section [*Wolff et al.*, 1995]. Table 1 shows the typical contributions of each chemical component to the σ_∞ signal in various climate stages [*Dansgaard et al.*, 1993]. This is based on the ECM signal presented here, on continuously-measured ammonium concentrations [*Fuhrer et al.*, 1996], and on discontinuous chloride measurements [*de Angelis et al.*, this issue]. The major contributor for each period is marked with an asterisk in Table 1. Interstadial (IS) numbering corresponds to that given in earlier papers [*Dansgaard et al.*, 1993]. IS5 has been chosen as typical of many "smaller" late glacial interstadials (e.g., IS 2-7, 9-11), while IS12 seems typical of many of the larger (and longer) interstadials (e.g., 8, 14) which begin the longer-term cycles of cooling often called Bond cycles [*Bond et al.*, 1993]. IS21 has been identified with marine isotope stage 5a [*Greenland Ice Core Project Members*, 1993]. In each case, the chemical signal is superimposed on the (presumed) constant pure ice background signal. Acidity is certainly the most important part of the DEP signal in the Holocene, the Allerod/Bolling, and larger interstadials. At high (annual) resolution, ammonium can make a noticeable contribution in the Holocene (especially during events believed to be due to biomass burning input [*Legrand et al.*, 1992]) and probably the Allerod/Bolling. Ammonium is the major contributor to the DEP

signal in the Younger Dryas. Chloride seems to be the main contributor in DEP in cold periods, including smaller interstadials. In each case, the chemical components show quite a strong short-term (especially seasonal) variability when sufficient resolution is reached (see, for example, Figure 1 for Cl⁻), and therefore the major contributor is also expected to control the short-term variability in the DEP signal.

Both ECM and DEP were essential in the field for identifying chemically interesting sections of core for more detailed study. The DEP signal provides the electrical information that will be needed to make comparisons with profiles of radar returns. The ECM signal is the primary source of acidity data for the GRIP core (discussed in the next section). It would also be possible, using ECM and DEP together, to distinguish between major peaks in H⁺, NH₄⁺, and Cl⁻: acid gives peaks in both methods, large ammonium spikes give peaks in DEP but often appear as troughs in ECM, and large chloride spikes give peaks in DEP but no signal in ECM. However, since a nearly continuous record of ammonium, directly measured, is available for the GRIP core [*Fuhrer et al.*, 1996], and a discontinuous record is also available [*de Angelis et al.*, this issue] for chloride (whose weak DEP signal means that only large peaks can be identified), it has not been necessary to use DEP for these purposes at GRIP.

The ECM signal is plotted on both a linear and logarithmic scale

Table 1. Average Contributions of Chemical Species to the DEP Signal in Different Climatic Stages.

Period	Age / kyr	DEP contributions / μS m^{-1}		
		H$^+$	NH$_4^+$	Cl$^-$
Holocene	0-11.5	6*	0.5	0.2
YD	11.5-12.7	0	1.5*	1
A/B	12.7-14.5	4*	0.9	0.5
LGM (min δ)	22	0	0.5	1.6*
IS5	29	0.4	0.3†	0.9*
IS12	43	1.5*	0.3	0.5
Cold (18/19)	63	0	0.3	1.4*
IS21	80	4*	0.7	0.3

Abbreviations are YD, Younger Dryas; A/B Allerod/Bolling; LGM, late glacial maximum (defined here as the oxygen isotope minimum); IS, interstadial; Cold (18/19), cold stage between IS18 and IS19.

* The major contributor for this period.

†NH$_4^+$ data not available for IS5, estimated from similar core sections.

in Figure 2 (the linear plot shows the acidity most clearly, while the logarithmic plot shows structure in the signal even in the alkaline ice). We can identify four different types of period as far as acidity (deduced from ECM) is concerned: (1) Holocene, in which ice remains acidic more or less throughout; (2) large interstadials, including the Allerod/Bolling and IS21 in which ice is generally acidic but goes neutral or alkaline at times when seen at high resolution; (3) small interstadials, in which ice is generally alkaline or neutral but may occasionally become slightly acidic; and (4) cold periods, in which ice is alkaline. For this purpose, we assume that ECM values calculated as 0.1 μM and below in fact represent alkaline ice. The four categories correspond to progressively increasing concentrations of calcium and dust, and it appears that neutralization by carbonate dusts is responsible for the change from acidic to alkaline ice [*Wolff et al.*, 1995]. We note in passing that categories (2) and (3) are those where acidic ice and alkaline ice may be in close proximity, allowing the possibility of reactions leading to CO_2 evolution, as has been hypothesized to explain unusual CO_2 levels in some Greenland ice [*Delmas*, 1993; *Anklin et al.*, 1995].

Although there may be stratigraphic disorder in ice older than 100 kyr, the isotopically warm ice below this almost certainly is from the last (Eemian) interglacial. This ice is again consistently acidic (although slightly less so than Holocene ice), suggesting that acidic ice is a general feature of interglacials.

5. What Spatial Scale Does the Acidity Record Represent?

We have clearly shown that the acidity of the ice changes quite dramatically over the last 100 kyr. We now need (1) to show whether this represents changes in atmospheric acidity and (2) to deduce what portion of the globe was affected.

5.1. Where Did Neutralization Occur?

Acidity in ice during the warm periods arises from a number of sources. In preindustrial period Holocene ice from Summit, the dominant acids (except in sporadic volcanic eruption peaks) were nitric, followed by sulfuric [*Whitlow et al.*, 1992; *Legrand et al.*, 1996]. Nitrate peaked in summer, while non-sea-salt sulfate peaked in spring [*Whitlow et al.*, 1992]. Nitric acid is derived from

NO_x, but the sources leading to nitric acid in Greenland are not clear: tropical lightning, stratospheric production, and possibly soil exhalation are considered to be the main ones [*Wolff*, 1995]. Non-sea-salt sulfate in preindustrial times is derived mainly from marine DMS emissions and from noneruptive volcanic degassing [*Legrand*, 1995]. Although DMS emissions and soil exhalation could have been strongly affected by climate changes, the other sources would be expected to remain at similar magnitude through the climatic cycle. In other words, we expect that acidic species were still being produced in at least comparable amounts throughout the climatic cycle. Our finding that the ice in cold periods is alkaline means that this acid was neutralized either (1) at source, (2) in transport, or (3) in the ice. Which of these is correct determines what proportion of the globe was affected by the acidity change.

The neutralizing agent in cold periods appears to be alkaline dusts. The soluble fraction present in the ice in the last glacial is mainly calcium carbonates and calcium sulfate [*Mayewski et al.*, 1994; *Legrand et al.*, 1996; *Biscaye et al.*, this issue]. The origin of these dusts is not yet established, but evidence from mineralogy, and Sr/Nd isotope analysis, suggests an Asian origin [*Biscaye et al.*, this issue].

On the basis of this information, neutralization could not occur at source, since the source regions were almost certainly different. The dust, if it originated in Asian deserts, was carried to Greenland in the strong westerly circulation of the glacial period [*Webb et al.*, 1993]. The acidic sources are mainly from above (in the case of lightning, stratospheric NO_x and at least eruptive volcanism) or the ocean (dimethylsulfide), volcanic areas, and soils.

It is harder to judge whether neutralization occurred en route in the atmosphere, in the snowpack during metamorphosis of the snow, or even deeper in the ice. In the latter two cases, we would envisage acidic particles and gases coexisting with alkaline dust particles in the atmosphere until deposition. Precipitation would on average be alkaline, but acidic particles (which currently act as efficient cloud condensation nuclei) would still be present in the atmosphere. In the former case, acidic particles would not be present. Which of these scenarios is correct depends on how well mixed the acidic and alkaline air masses were and on factors such as the size distribution of particles and the age of the air mass [*Winchester and Wang*, 1989]. At an extreme, it is possible that alternating snowfalls with different air mass origins could have been acidic or alkaline. In that case, neutralization would be impossible in the atmosphere and could only have happened in the snowpack or ice. Studies are underway to identify the season of deposition of different species at different climate periods, which may help to resolve this question. It is further confused by the fact that for acidic gases (including nitric acid), recent studies on the air/snow relationship suggest that the concentration seen in the ice is significantly affected by postdepositional losses as well as by initial uptake [*Bales and Wolff*, 1995; *Legrand et al.*, 1996].

In conclusion, although both air masses and precipitation were certainly on average neutral or alkaline through most of the last glacial, it is not possible to be certain that acidic particles and gases were not also present. This is an important uncertainty. We will discuss some effects where the average acidity (or alkalinity) of the snow itself, or of the meltwater, is important. However, there is also a range of effects that depends on the presence or absence of small acidic particles in the atmosphere, irrespective of whether the air was on average neutral.

5.2. Geographical Extent of Acidity Changes

Antarctic ice remains acidic even in the last glaciation [*Delmas and Legrand*, 1989]. A number of previous ECM records for northern hemisphere ice sheets extending back into the last glaciation exist that can be used for comparison with the Summit
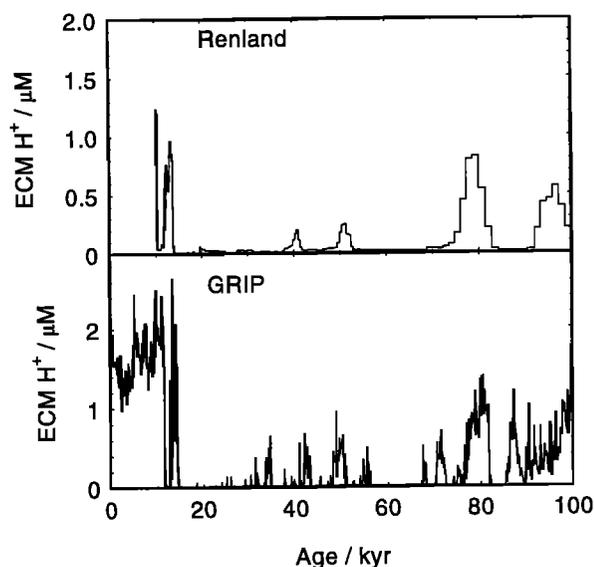
Figure 3. The electrical conductivity method (ECM) signal from GRIP and from Renland in east Greenland [*Hansson*, 1994].

record. First, on the very local scale, there is excellent qualitative agreement over the last 100 kyr, even at the decade to century scale, between the GRIP core and the GISP2 core, sited 30 km apart [*Taylor et al.*, 1993a]. The alkaline (low ECM) nature of most of the last glaciation has been reported for cores from Camp Century, north Greenland [*Hammer*, 1980], and from Dye 3, south Greenland [*Hammer et al.*, 1985]. Detailed records have not been presented, but the good agreement between the oxygen isotope profile at Dye 3, Camp Century, and Summit [*Johnsen et al.*, 1992], and the similar increases in dust concentrations [*Hammer et al.*, 1985] observed at the sites lead us to expect that the acidity profiles would look quite similar. Ice-core records from Ellesmere Island and Devon Island in northern Canada [*Fisher*, 1987], and from Penny Ice Cap, Baffin Island (D. Fisher, personal communication, 1996), also show a generally "dead" ECM signal in the pre-Holocene ice. Finally, the ECM record for Renland, east Greenland, has been presented on a linear timescale [*Hansson*, 1994] and is compared to the GRIP record in Figure 3. The Renland record is poorly resolved in time, but it is clear that the major features seen in the GRIP record are present.

On the basis of the evidence above, it seems likely that most of the changes between acidic and alkaline ice occurred over at least the entire Greenland landmass and northeastern Canada. Since there would have been no major sources of acidic or alkaline material to the west over the ice-covered Laurentide, it seems that the zone of alkaline air must have extended across the North American continent also. We can only speculate on whether the zone also extended further eastward across the Atlantic or whether extra sources of acidity, and deposition of the alkaline dusts, were able to exhaust the supply of neutralizing material. We can also only speculate on how far south the dusty, alkaline zone spread. Consideration of dust in marine sediments [*Rea*, 1994], and modeling studies of transport pathways, would be needed to investigate this. In summary, neutral or alkaline air and precipitation must have occurred over at least a large part of North America and the North Atlantic region.

Transitions from alkaline to acidic occurred very rapidly, with transitions complete in decades [*Wolff et al.*, 1995] and still faster "flickers" [*Taylor et al.*, 1993b] occurring. In the next section, we will discuss some of the consequences of an alkaline atmosphere and of the rapid changes.

6. Climatic, Chemical and Ecological Consequences of Acid/Alkaline Switches

6.1. Climatic Impact

During the coldest parts of the glacial cycle, changes in concentration of tropospheric aerosol may have made a significant impact on climate. The cooling effect of coarse-mode (continental dust and sea salt) aerosol has been calculated [*Harvey*, 1988], and may represent a positive feedback (more particles in the colder atmosphere enhancing cooling) in the climate system. However, it has also been pointed out by *Anderson and Charlson* [1990] that fine-mode sulfate aerosol has far more effect per unit mass than do the larger crustal and marine particles. These authors suggested that the effect of larger particles, and hence the calculated ice-age cooling, is less than *Harvey* [1988] calculated. This conclusion clearly needs to be tested again in the light of the far more detailed information about the temporal profile and spatial distribution of ice age dust concentrations that is now available.

In section 5.1, we have suggested that acidic aerosol may have been lost both in the coldest periods and at least in parts of the interstadials (but note that this loss remains uncertain, since we do not know if neutralization of individual particles occurs in the atmosphere or in the snowpack). This could imply loss of the fine particle mode (since the likely method of neutralization would be via attachment of acidic aerosol to larger alkaline particles), which would be expected to offset some of the direct radiative cooling effect of larger aerosol. For instance, *Anderson and Charlson* [1990] suggest that the coarse mode currently causes about 15% of aerosol optical depth (τ), with fine-mode sulfate aerosol causing the rest. This implies that, if the fine mode were removed from the column, the coarse mode would have to increase by a factor of 6 just to maintain the same optical depth. In some of the smaller interstadials, the increase of dust over present levels was modest, but enough to neutralize the atmosphere; if fine particles really did disappear, the net effect could have been a reduction of aerosol optical depth in some interstadials compared to the present.

Even if loss of fine particles did occur, it was only over a limited part of the globe, as discussed before. Indeed, although it could have been much more widespread, we have evidence to infer neutralization of the atmosphere convincingly only over the Laurentide Ice Sheet, Greenland, and the North Atlantic. All these areas were ice covered (i.e., with high albedos) in the last glaciation. As a result, at least over these areas, the radiative effect of increased aerosol optical depth may be positive (warming) or neutral.

In summary, we can see that the radiative effect of aerosols in the last glacial is complex; new model experiments, analogous to those recently carried out to study the effect of aerosol on future climate [*Mitchell et al.*, 1995], would be interesting. However, meaningful model runs would require firmer conclusions on two major questions: (1) did the fine particle sulfate aerosol mode disappear (this might be addressed by modeling the likelihood of interactions between dust and acid particles in the atmosphere)? and (2) over what area was the atmosphere neutralized (bring in estimates of dust concentrations from paleorecords outside the polar regions, along with better estimates of acid production areas in the glaciation)?

The above discussion is all concerned with the direct radiative effect of sulfate aerosol. There is also the secondary effect, because sulfate aerosols (sulfuric acid and ammonium sulfate) act as the main source of cloud condensation nuclei (CCN) in the present-day atmosphere. If these small particles are not present, then other particles will have to act as CCN. These would be sea salt and crustal particles: predominantly $CaCO_3$ and $CaSO_4$. The latter two compounds are only very slightly soluble, and larger

supersaturations would be required to activate particles of similar size than would be the case for more soluble sulfate aerosol. However, the particles are predominantly larger, helping to offset this factor. The calculation of secondary effects is very uncertain at the moment but depends on the number of CCN and whether there are many small cloud droplets or a smaller number of large ones. During cold periods, large amounts of sea salt (and relatively insoluble dust) may be able to provide sufficient CCN to take the place of sulfate aerosol. However, if the fine mode is also missing in interstadials, there could have been a shortage of CCN, with effects on radiation and on the probability of precipitation. Finally, in this section, we note that models suggest [*Fisher*, 1991] that cloud supersaturation plays an important role in determining stable isotope and particularly deuterium excess values in precipitation. Possible couplings between acidity and isotope ratios need to be considered.

6.2. Chemical and Ecological Effects

In the atmosphere, many reactions are now known to take place heterogeneously. Some of these are dependent on the *p*H of cloud droplets, and their efficiency will therefore be altered if acidic droplets are not present. One obvious case is the reaction of sea salt with sulfuric acid:

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$$
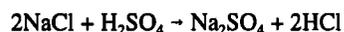
This can lead to the formation of gaseous HCl and is also responsible for departures from seawater ratios of species found in precipitation, including ice cores. Obviously, this reaction could not take place if the sulfuric acid was removed rapidly by neutralization by crustal dust (but if both sea salt and sulfuric acid are formed over the ocean, this reaction might take place before neutralization).

Legrand and de Angelis [1995] suggest some other examples of reactions that would be affected if cloud droplets became less acidic. At *p*H > 5, formate produced in cloud from formaldehyde is destroyed by further oxidation. And it has been suggested that, at higher *p*H, peroxyacetyl nitrate (PAN) is slightly more soluble in water and can be hydrolyzed to give acetate, along with both nitrite and nitrate [*Legrand and de Angelis*, 1995]. Again, we would require a better understanding of whether acidic droplets are neutralized in the atmosphere and of the geographical extent of this effect before it would be possible to model the likely changes in atmospheric chemistry.

Neutralization in the atmosphere could also affect the deposition mechanisms to snow of both aerosol and gaseous species. This is most likely to have an effect on acidic gases such as nitric acid. If it is neutralized in the atmosphere by reaction with terrestrial particles, then nitrate deposition in cold periods will occur through aerosol deposition mechanisms, rather than through the gaseous uptake that takes place now. Even if nitrate remains acidic in the air, gaseous uptake and retention will be greatly altered by the fact that the snow surface is not acidic in cold periods. Thus great care must be taken in interpreting ice-core records of species where the deposition mechanism may have altered significantly. Carboxylic acids are another group of species whose uptake (either in cloud droplets or at the snow surface) is expected to be affected strongly by the acidity of the droplet or snow. There is evidence (both from recent snow and from volcanic layers) that the concentrations seen in Greenland snow and the relative concentrations of different carboxylic acids are strongly *p*H dependent [*Legrand and de Angelis*, 1995]. A better understanding of current deposition mechanisms is certainly needed before we can interpret records for most acidic gases with any confidence [*Legrand et al.*, 1996].

A final group of effects are the mirrors of those ecological effects generally associated with increased levels of acidity in recent decades. Among these would be the effects on lakes and soils in ice-free areas. The *p*H of liquid precipitation (or snow meltwater) in the Holocene is generally lower than 5.6 (*p*H for CO_2 in equilibrium with water), while for the colder periods, pH would have ranged upward from 5.7 (*p*H for CO_2 at the reduced level of 200 parts per million by volume (ppmv) in equilibrium with water) toward about *p*H 6.8 for the most alkaline water melted from Summit ice (note that, although the carbonate buffer has kept the *p*H just below neutral in meltwater, the true H$^+$ concentration in solid snow and ice is less easily determined and we have frequently referred to carbonate-laden ice as alkaline in this paper). Such changes will affect the species present in lakes and processes such as soil leaching to an extent. The effects are likely to be strongest in areas that are not naturally buffered (e.g., areas with granitic bedrock), and assessments of lake sediment species assemblages need to take account of possible acidity changes as well as changes in other climate variables. Particularly strong effects may have been felt during retreats and final melting of the Laurentide (and assuming the neutralization was more widespread, the Fennoscandian) ice sheets. Depending on the pattern of melt in particular areas, water bodies that received the melt could have experienced periods of near-neutral melt (from glacial period ice) interspersed with periods of acidic melt (arising from interglacial and some interstadial ice) over periods of decades to centuries.

7. Conclusions

Continuous high-resolution electrical measurements on ice cores are an essential tool for identifying interesting changes in ice chemistry during field operations. The changes in both ECM and DEP can be described rather well based on the chemistry of the ice. While three different chemical species control the DEP conductivity, with each dominating in different climate periods, ECM is controlled by acidity alone. Attention has often focused on the acidic spikes from volcanic eruptions, but the background acidity of the ice can also be deduced. There is a striking alternation between acidic ice in the Holocene and neutral or alkaline ice in the cold periods of the last glaciation. Many interstadials fall on the borderline, exhibiting acidity at times.

Some effects of this alternation are clear; in particular, the changing acidity would have affected the uptake of some chemicals by either cloud droplets or the snow surface. This is a very important factor that has to be accounted for in assessing chemical profiles in ice cores. Less certain are the very important effects that could have arisen if acidic cloud droplets were not present. However, it is not yet clear whether neutralization occurred at this scale or only in the snowpack after deposition. It is also not clear over what spatial scale neutralization occurred: it certainly affected the entire Greenland Ice Sheet and almost certainly the ice-covered North American continent. Further work on other paleorecords needs to be integrated into this story to define this spatial scale. Measurements of the seasonal distribution of different chemicals in the ice core record would provide important constraints to understanding where neutralization took place, while microphysical experimental and modeling studies may help with deciding whether neutralization occurred in the atmosphere or on the ground.

shown in Figure 1. We thank the various people who helped with ECM and DEP measurements in the field. We also thank Margareta Hansson for providing the Renland ECM data.

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