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Holocene electrical and chemical measurements from the EPICA–Dome C ice core

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ABSTRACT. The comparison between electric (electric-conductivity measurement (ECM) and dielectric profiling (DEP)) and chemical (sulphate and chloride) depth profiles along the first 400 m of the EPICA-Dome C ice core revealed a very good fit, especially for peaks related to volcanic emissions. From the comparison between these profiles, a dominant contribution of sulphuric acid to the ionic balance of Antarctic ice for the Holocene was confirmed. A progressive increase with depth was observed for chloride concentrations, showing a change of relative contribution between sulphate and chloride. A higher increase of chloride was evident between 270 and 360 m depth, probably due to a change in source or transport processes or to an increase of the annual snow-accumulation rate. The DEP, ECM and sulphate ice signatures of Tambora (AD 1816) and El Chichon (?) (AD 1259) eruptions are described in detail. A characteristic peak series, due to HCl deposition, was identified at 103–109 m depth from the ECM, DEP and chloride profiles.

1. INTRODUCTION

In recent years, ice-core operations have been revolutionized by the ability to make many measurements in the field. This enables scientists to detect events and examine background trends very rapidly and to adjust their sampling in the field accordingly. Electric-profiling methods have become well-established (Hammer and others, 1980; Wolff and others, 1995).

Electric-conductivity measurements (ECM) and dielectric profiling (DEP) are fast, inexpensive, non-destructive techniques, performed in situ directly on the solid ice, able to give useful, but non-specific, information about the ionic content of the ice. In fact, the ECM (Hammer and others, 1980) and a large part of the DEP signal are related to the electrical mobility of H^+, but they do not distinguish between the different anions associated with the H^+ ion. In addition, other conductive species (chloride and ammonium), also present in the ice as salts, give significant DEP signals (Moore and others, 1992, 1994; Wolff and others, 1997). For this reason, the ability to carry out some chemical analyses in the field constitutes a complementary method. Continuous chemical analysis (continuous flow analysis (CFA)) applied to ice-core processing is a more recent innovation (Fuhrer and others, 1993) and the number of chemical species that can be analysed rapidly in the field has been growing.

Recently, a semi-continuous method, based on flow-analysis ion-chromatographic-hyphenated techniques, has been set up for the fast, in situ, determination of chloride, nitrate and sulphate (Udisti and others, in preparation). This method was applied for analysis of the ice core drilled at Dome Concordia (Dome C: 75°06′06″ S, 123°23′42″ E; 3233 m a.s.l.), within the European Project for Ice Coring in Antarctica (EPICA).

The site is expected to yield a climate record of the last 500 000 years. In the shallower parts of the core, the unprecedented range of measurements and their depth resolution will lead to new understanding of climate and biogeochemical variability on short (annual and greater) time-scales. During the 1997/98 and 1998/99 Dome C campaigns, the drilling reached a depth of about 780 m, of which about 600 m has undergone processing, including several analyses in the field. In this paper, we compare results from the top 400 m of ice from electrical measurements (mainly giving an indication of acidity), and chemical measurements (with an emphasis on sulphate). The 400 m depth was chosen as being near the limit between the Holocene and the Last Glacial period, based on earlier data, including that from the "old" Dome C (74°39′ S, 124°10′ E; 3240 m a.s.l.) ice core drilled during the 1977/78 field season (Lorius and others, 1979); about 65 km north of the new one.

For Holocene ice in central Antarctica, by far the largest component of the ionic budget of ice is made up of acids and sulphate (Legrand and Delmas, 1988; Legrand and others, 1996), for the cations and anions respectively, with much smaller components from sea-salt cations, from nitrate and chloride and other ions. High-resolution continuous records of sulphate and acidity are therefore of particular interest. Apart from the background trends over thousands of years, sporadic events, lasting only one or a few years, are of great interest for a number of studies. Where they result from volcanic eruptions, events normally (though not exclusively) consist largely of sulphuric acid. Previously, such events have been identified from continuous electrical measurements for acidity (e.g. Clausen and others, 1997) or from sulphate analyses (Zielinski and others, 1996), although rarely have both been compared at high resolution.

The aim of this paper is to compare the electrical measurements (ECM and DEP) with the concentration–depth profiles of sulphate and chloride, which make a significant contribution to snow acidity and which constitute, together with nitrate, the most plentiful anions in the ionic budget in Dome C ice (Legrand and Delmas, 1988). In particular, some in-phase peaks of ECM, DEP and sulphate were observed in detail to obtain information about some volcanic emissions in the Holocene period. On the other hand, particular ECM and DEP peaks were not related to sulphate content and can be explained by the presence of other snow components, especially chloride. The identification of the chemical species contributing to the increase of the ionic content will make it possible to evaluate the temporal change of different source contributions to the atmospheric aerosol.

2. SAMPLING AND METHODS

2.1. Sampling station

As part of the EPICA project, Dome C was chosen for an ice core >3000 m long, able to provide paleo-environmental information on the last 500 000 years. The exact location of the drilling site, on top of the topographic dome, was established by geodetic, topographic and radar surveys (Tabacco and others, 1998). Some details of the site and the first year of drilling have been presented previously (Wolff and others, 1999).

2.2. Ice-core treatment

At Dome C cores were cut into lengths of 2.2 m and passed to a purpose-built insulated laboratory (made of cold-room sections) adjacent to the drilling tent. Most of this laboratory was maintained at a temperature of -19°C; despite the low ambient air temperatures (generally below -30°C), the room tended to warm so it was necessary to ventilate it with cold air taken from a trench below the snow surface. A separate room for chemical analyses was maintained close to 18°C by heating.

Cores were allowed to equilibrate to the laboratory temperature and then passed through a processing line that included: two electrical measurements (DEP and ECM); sectioning of ice for analyses to be made in Europe; chemical measurements by CFA; and semi-continuous ion-chromatographic (IC) analysis.

2.3. DEP measurements

The DEP method used at Dome C is described in detail elsewhere (Wolff and others, 1999). Measurements of capacitance and conductivity were made on the whole (uncut) core; the value used here is the 100 kHz conductivity, which is very close (1–2%) to the high-frequency limit of the conductivity (σ_∞), which has been presented in earlier papers. Measurements were made every 20 mm, and have been corrected to -15°C using an activation energy of 48 kJ mol^{-1} (0.50 eV) for the pure ice part of the conductivity, and 21 kJ mol^{-1} for the part controlled by chemical content (Wolff and others, 1995). Sections containing core breaks have, in general, not been removed from the DEP record presented, but are normally recognized easily as dips in the value of σ_∞ below 9 μS m^{-1} (the expected value for pure ice after densification, shallower firn having lower background values).

DEP conductivity responds to acidity, ammonium, and chloride (Moore and others, 1992, 1994; Wolff and others, 1997), and the electrode system used at Dome C was previously calibrated for Greenland ice. Based on the chemical concentrations measured on the previous Dome C core drilled in the late 1970s (Legrand and Delmas, 1988), we would expect the signal in Holocene ice to be dominated by the acidity, and therefore to be very similar to the ECM signal (Wolff and others, 1999).

2.4. ECM measurements

Electric-conductivity measurement (ECM) is mainly a measure of DC conductivity, traditionally carried out by dragging a pair of electrodes with a high voltage between them along a core and measuring the current between the electrodes (Hammer and others, 1980; Neftel and others, 1985). At Dome C a new system, developed at the University of Bern, was used. The system will be described in detail elsewhere and has been summarized by Wolff and others (1999). An assembly of seven electrodes (8 mm apart), made of a carbon-doped silicon rubber, was lowered onto a flat surface of the ice core and 350 V were applied across each adjacent pair of electrodes in turn. The current between them was sampled at regular intervals after a settling time and averaged. The electrodes were lifted and moved 1 mm along the core and the measurement repeated. The data presented here are given as conductances averaged to 10 mm and corrected to -15°C, using an activation energy of 22 kJ mol^{-1} (0.23 eV).

2.5. Semi-continuous IC measurements

The determinations of chloride, nitrate and sulphate have been carried out by a semi-continuous method achieved by coupling ion-chromatographic separation with a flow-analysis method for direct and continuous sample injection (Udisti and others, in preparation). The sample was produced by a continuous melter (Sigg and others, 1994) able to decontaminate a 1.1 m ice-core segment (about 32×34 mm section) with a constant speed (typically, 40 mm min^{-1}), during the melting. The IC system allows one determination every minute, therefore the typical resolution was one measurement every 40 mm of ice. The method detection limits are below 0.5 μg L^{-1} for all species by using a pre-concentrator loaded with 0.75 mL of sample. The reproducibility was better than 2% for sulphate and nitrate, and better than 4% for chloride, in the range 5–50 μg L^{-1}. The method was initially designed for the determination of sulphate only, so that chloride and nitrate measurements carried out in the first Dome C campaign (1997/98) can only be used as approximate values, especially for concentrations below 20 μg L^{-1} (chloride) and 5 μg L^{-1} (nitrate), because of the closeness of their chromatographic peaks to the baseline water dip. An optimization of the working conditions permitted a better separation among the three analysed components and, especially, a sufficient time between the retention time of chloride peak and the one of the water dip. Figure 1 shows a typical chromatogram carried out on a section of the Dome C ice core. The scale expansion shows the complete separation of the three components and the ability to determine the chloride peak out of the water dip. Sulphate and nitrate can be measured without interference from other components (such as bromide and phosphate) that may be present in the sample. In addition, bromide and phosphate are likely not present at significant levels in Antarctic ice cores, given the quasi-perfect ionic balance between anions and cations observed by Legrand (1987) in Dome C snow. Carboxylic

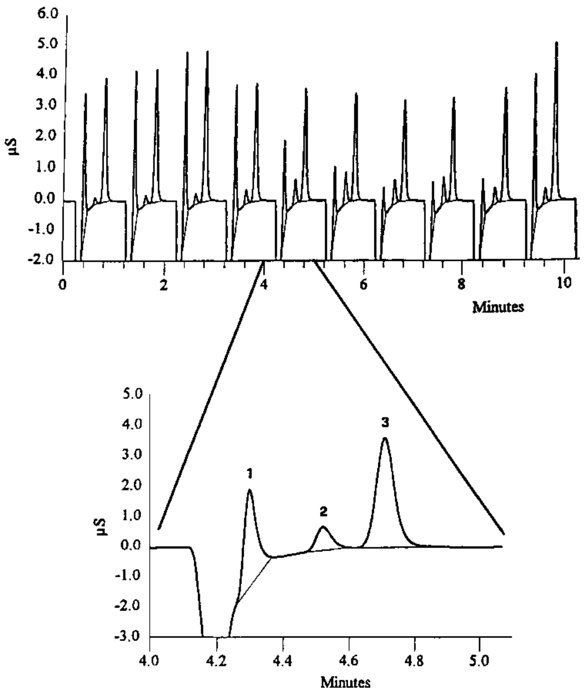

Fig. 1. Semi-continuous (1 measurement every minute) ion chromatogram of a section of EPICA–Dome C ice core. Expanded figure shows separation between chloride (1), nitrate (2) and sulphate (3) peaks.

acids (especially acetate and formate) and methanesulphonic acid (MSA) peaks may be partially superimposed on the chloride peak. By considering the higher detector response (conductometric detector with conductivity suppressor) to chloride concentration, with respect to that obtained for organic acids at the same concentration, an error $<10\%$ is estimated for the determination of chloride when its concentration is $>10\ \mu\text{g L}^{-1}$ and the cumulative concentration of organic acids is $<20\ \mu\text{g L}^{-1}$. In fact, at Dome C, the expected levels of carboxylates are close to $1\ \mu\text{g L}^{-1}$ or less (Legrand and Saigne, 1988) and the levels of MSA are close to $5\ \mu\text{g L}^{-1}$ during the Holocene (Saigne and Legrand, 1987).

3. RESULTS AND DISCUSSION

3.1. Data discussion

From a general point of view, there is a very close relationship among the different parameters in the whole 0–400 m depth interval, especially for events characterized by a fast increase of the signals with respect to the background level, such as the volcanic inputs. The 400 m depth was set as an approximate limit between the Holocene and the interglacial–glacial transition.

As an example of the common trend, Figure 2 shows the profiles of ECM (a), DEP (b) and sulphate (c) in the 100–200 m depth range. The three profiles fit very well, with peaks in-phase between them. In particular, we can point out the close correlation between DEP and sulphate profiles, where almost all spikes coincide and often exhibit the same shape and relative height. This is particularly true for the series of peaks around 130–135, 140–145 and 153–165 m and for the peak at about 170 m. The depth with the three highest sulphate and DEP peaks (at about 131, 145 and 170 m), does not have similar ECM signals. On the other hand, at about 180 m depth, where the ECM profile shows the highest peak, the DEP and sulphate profiles show rather lower spikes. The different pattern may be due to the different efficiency of HCl with respect to sulphuric acid on the ECM response (Legrand and others, 1987). The IC analysis of discontinuous samples collected in these depth intervals will clarify the different pattern of the ECM profile by determining the acidic and non-acidic species content.

In spite of some particular exceptions, the similarity between ECM (more selective towards the H^+ content) and

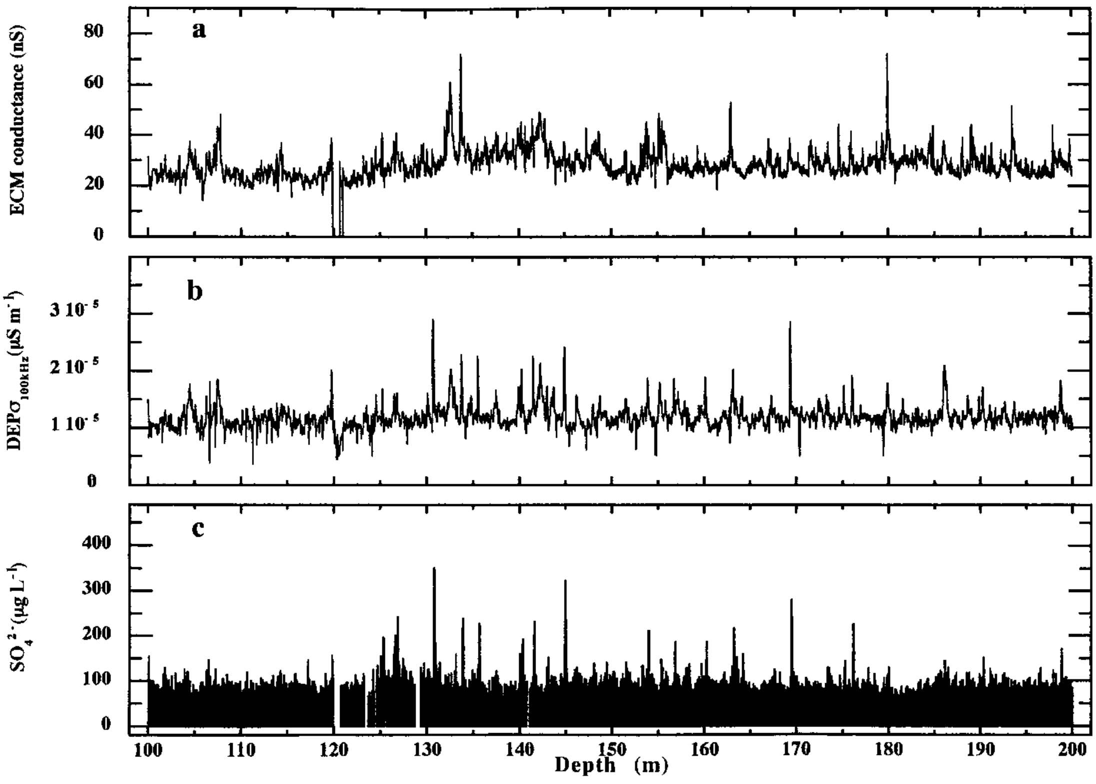

Fig. 2. Depth profiles of (a) ECM, (b) DEP and (c) sulphate determinations in Dome C ice core at 100–200 m depth.

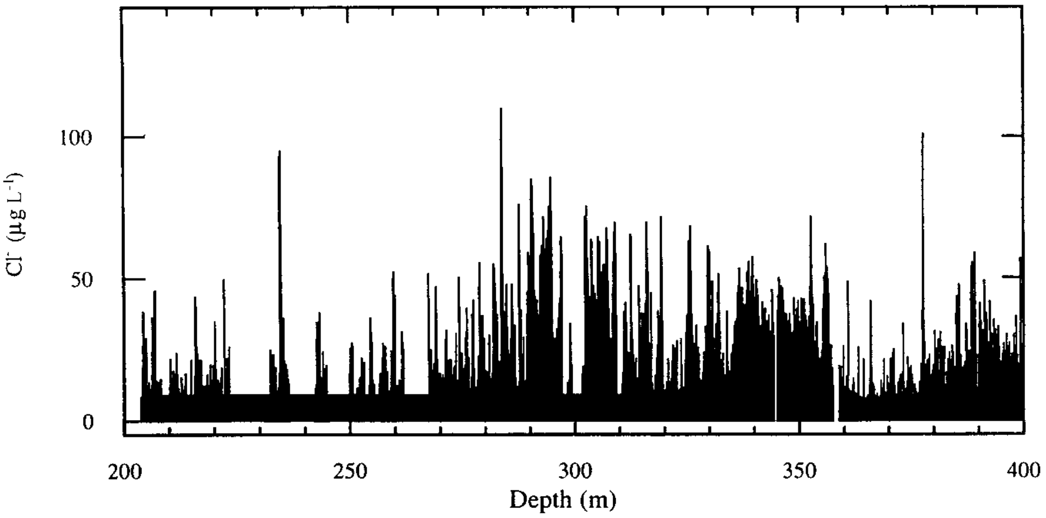

Fig. 3. Depth–concentration profile of chloride in Dome C ice core at 200–400 m depth.

DEP (whose signals are related also to other conductive species) profiles confirms the dominance of acidity in the ionic balance of the Holocene ice (Wolff and others, 1999). A similar pattern was shown by the ECM and DEP profiles of the Greenland Icecore Project (GRIP) ice core (Wolff and others, 1995) in the Holocene period (0–1623 m, 0–11 550 years), where most of the volcanic signals occurred. In some GRIP Holocene sections, an in-phase periodicity of the ECM and DEP peaks seems to indicate annual cycles in acidity, probably due to the seasonal pattern of nitrate, the main acidic species at Summit, Greenland (Wolff and others, 1995, and references therein). For the Dome C ice core, a seasonality of the ECM and DEP profiles is not seen because of the too-low annual accumulation rate. In addition, the acidity at Dome C is dominated by sulphuric acid rather than nitric acid, as demonstrated by the ratio 4.2 (eq/eq) between H_2SO_4 and HNO_3, found by Legrand and Delmas (1988) in the Holocene period. The good correlation between the conductivity properties and the sulphate-concentration–depth profile at Dome C confirms that the Antarctic Holocene firn and ice is strongly dominated by inputs of sulphuric acid. This is especially true for the most obvious peaks, usually related to volcanic inputs.

Considering the background values, the mean sulphate concentration does not change significantly from the surface (0–100 m; 106.0 ± 43.5 μg L^{-1}; $n = 1611$) to the ice-core bottom (300–400 m; 98.50 ± 35.9 μg L^{-1}; $n = 2648$). So, the all-Holocene mean value is very similar (95.4 ± 34.5 μg L^{-1}; $n = 9690$), with a relatively low standard deviation, confirming the homogeneity of the background level. This value is a little higher than the mean value reported by Legrand and Delmas (1988) in the 1970s Dome C ice core (about 76 μg L^{-1} in the Holocene period), but this difference may be due to the different resolution: in this paper we report a continuous sulphate record (9690 samples with a resolution of 40 mm for approximately 1.3 years), while Legrand and Delmas analysed 55 sections, selected along the ice core, each of them covering approximately 5 years. Part of the sulphate background difference may also be due to a different accumulation rate between the new and the old Dome C drilling sites. In fact, for the new site, Wolff and others (1999) evaluated an accumulation rate about 10% less than the old one.

The chloride concentration, on the contrary, shows a progressive increase with depth. The chloride mean concentration of the last 100 m range (300–400 m; 23.3 ± 14.7 μg L^{-1}; $n = 2517$) is about 1.8 times higher than in the first interval (0–100 m; 12.6 ± 10.4 μg L^{-1}; $n = 1587$). Therefore, there appears to be a progressive increase of the chloride contribution to the ionic balance with increasing depth in the Holocene period. Superimposed on this general trend, there is a faster increase of chloride starting at around 270 m depth (Fig. 3). The chloride concentration values remain higher than the background up to around 360 m. In this interval, the chloride profile shows concentration peaks 4–5 times higher than the background local value (around 13 μg L^{-1}). A similar pattern of the chloride concentration in the same depth range was observed by Legrand and Delmas (1988) in the 1970s Dome C ice core, where the mean concentration value for 215–360 m (33.3 μg L^{-1}) was about 2 times higher than the mean value in the 0–215 m interval (14.9 μg L^{-1}). These values are in good agreement with our mean Cl^- concentrations (13.5 ± 12.0 μg L^{-1} from 0–200 m and 27.9 ± 16.1 μg L^{-1} in the 270–360 m range) confirming that even the Cl^- measurement performed in the 1997–98 Dome C campaign are reliable, in spite of the poor separation between the chromatographic peaks of Cl and of some organic acids (see section 2). The general trend of chloride in this section corresponds to the trend in background of the electrical records.

The interpretation of this behaviour is very difficult in the absence of other chemical or isotopic markers, so we can give only some preliminary guess as to the cause of the higher chloride values:

(1) a real increase of the chloride deposition as HCl and/or NaCl;

(2) a changed HCl/NaCl ratio in the atmospheric aerosol. The NaCl species is better retained than HCl (Legrand and others, 1996) in the snow layers; and

(3) a lower re-emission into the atmosphere of HCl by post-depositional loss, perhaps implying an increased snow-accumulation rate (Legrand and others, 1996).

Further chemical and stratigraphic data are necessary to understand the chloride behaviour.

3.2. Special events

In a preliminary way, we report some examples of a detailed comparison between the electrical and chemical profiles, for

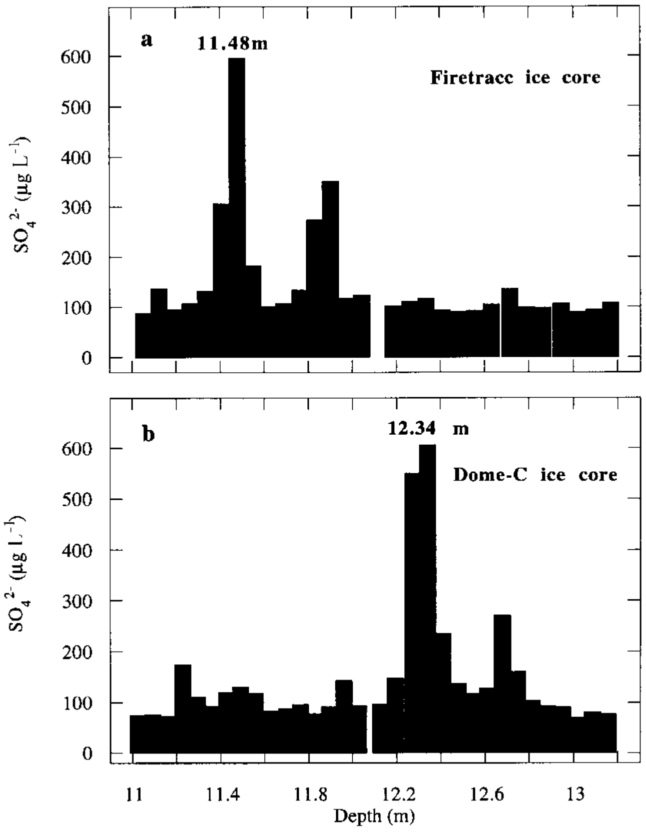

Fig. 4. Dephasing between the Tambora records in the sulphate profiles from the (a) Firetracc and (b) Dome C ice cores.

peaks characterized by particular height and/or shape. We chose two volcanic events from the first 40 m depth, because their characteristic signals are recorded in all polar ice cores (Hammer and others, 1980; Herron, 1982; Legrand and Delmas, 1987; Delmas and others, 1992; Zielinsky, 1995; Zielinsky and others, 1996; Clausen and others, 1997) and their dating is well known. In Antarctica, the years of these signatures have been set by Delmas and others (1992) from the sulphate profile of a 1000 year ice core drilled near Amundsen–Scott Station (South Pole). On the other hand, the third event was characterized by a particular pattern for chloride.

For the 0–100 m depth range, ECM measurements are shifted about 0.9 m with respect to the other parameters. In fact, the 0–100 m ECM profile was measured on a parallel ice core (Firetracc ice core), drilled during the 1998/99 campaign very close to the main Dome C ice core, for which the ECM profile was not measured. The Tambora eruption signal, described below, was used to estimate the depth shift between the two Dome C drillings (Firetracc and main Dome C ice core). Figure 4 shows the Tambora sulphate peak in the two ice cores. We can observe a close correlation between the two profiles, within the limits of the sample resolution (40 mm), but the Tambora peak is recorded in the Dome C ice core 0.86 m deeper than in the Firetracc ice core (comparison of DEP profiles for the two cores confirms this difference, also to within 40 mm).

Tambora signature

Figure 5 shows the ECM (a), DEP (b) and sulphate (c) profiles related to the unambiguous signal of the Tambora (Indonesia) eruption, recorded at 12.34 m in the sulphate and DEP profiles. This eruption is dated to AD 1815 and the signature in Antarctic firn is set at 1816 by Delmas and others (1992) in the South Pole core.

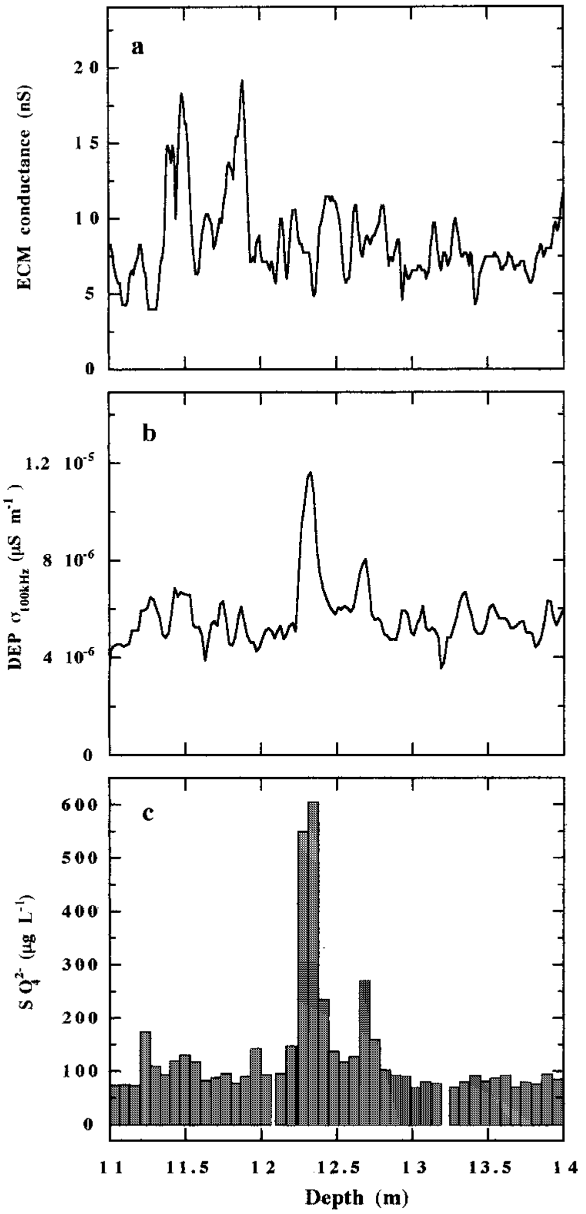

Fig. 5. Signatures of the Tambora eruption (AD 1816) in (a) ECM, (b) DEP and (c) sulphate profiles. The ECM profile is from the Firetracc ice core. The DEP and sulphate profiles were measured on the Dome C ice core.

The sulphate concentration reaches 606 µg L^{-1}, about 7.5 times higher than the local background value (around 80 µg L^{-1}). The second peak, that characterizes the Tambora period, is at 12.68 m and its height is about 270 µg L^{-1}. The sulphate ratio between the two peaks is 2.24. The DEP profile is coincident in depth and peak shape with that of sulphate, with a similar ratio between the two peaks, if they are measured with respect to the background values of about 5×10^{-6} µS m^{-1}. The ECM peaks are shifted by about 0.9 m (coming from the Firetracc ice core, see above) and do not have the same relative heights as the DEP and sulphate peaks. We can observe that the two peaks have approximately the same height. In general, the ECM profile shows a higher background noise, with respect to the DEP, in the first 100 m section. Therefore, the ECM Tambora peak becomes less evident than in the DEP and, above all, in the sulphate profile.

AD 1259 eruption

Figure 6 shows an interesting series of peaks in the 36–42 m

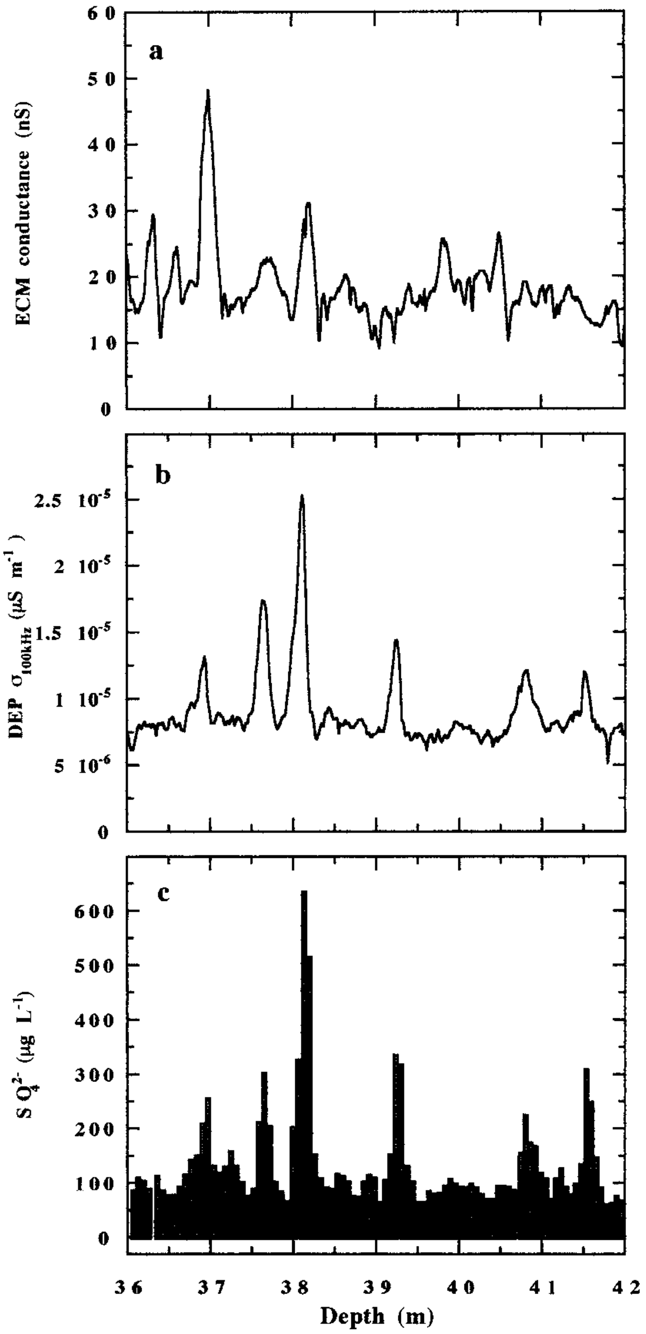

Fig. 6. AD *1259 eruption (El Chichon?) signature and adjacent peaks in (a) ECM (b) DEP and (c) sulphate profiles. The ECM profile is from the Firetracc ice core. The DEP and sulphate profiles were measured on Dome C ice core.*

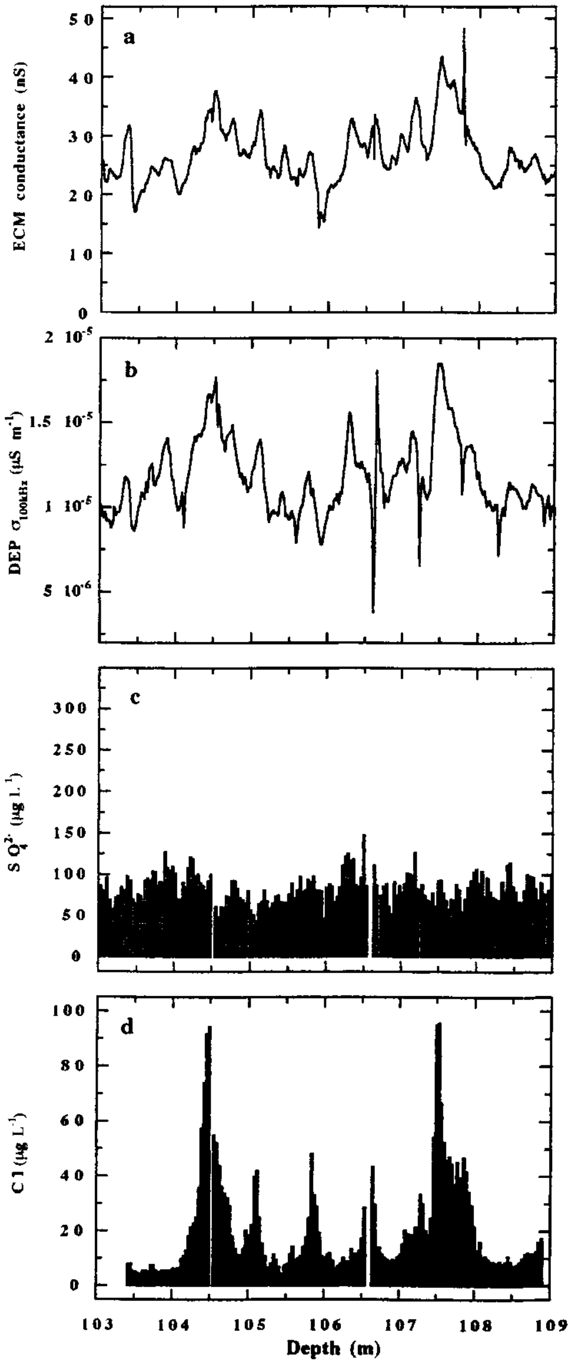

Fig. 7. Depth profiles of (a) ECM, (b) DEP, (c) sulphate and (d) chloride determinations at 103–109 m depth.

depth range. The same series is observed by Clausen and others (1997) in the Dye 3 1980 ice core. We can observe six well-defined sulphate peaks (Fig. 6c) the highest of which is located at 38.12 m, with a sulphate concentration (637 μg L^{-1}) similar to that of the Tambora eruption. This peak is related to an unknown eruption (probably El Chichon in Mexico) whose signal was dated at AD 1259 by Delmas and others (1992).

The DEP profile is surprisingly close to that of sulphate: all peaks are in-phase and the relative ratios between the peak heights are very similar. The ECM profile shows a similar pattern, too, with in-phase peaks (taking into account the shift between the two ice cores) and similar peak shapes, but with a higher background noise and some differences for the peaks to the left of the main peak. The good agreement between ECM, DEP and sulphate peaks demonstrates that all the peaks are caused by sulphuric acid from volcanic emissions.

103–109 m depth

Figure 7 shows a depth range where a particular chloride (Fig. 7d) pattern is recorded. At 104.48 and 107.52 m we can observe two high peaks of chloride reaching 95 μg L^{-1}, about nine times as high as the background value (around 10 μg L^{-1} in this depth range). They are separated by four other lower peaks (about 40 μg L^{-1}) set at similar intervals between them (around 0.7 m). The sulphate values (Fig. 7c) do not show any particular trend, with values close to the background level of about 90 μg L^{-1}. A structure similar to that of chloride is also visible in the DEP and ECM profiles, in spite of the high background noise and some very narrow electrical spikes. In fact, HCl gives a higher ECM response with respect to sulphuric acid (Legrand and others, 1987). For this reason, we infer a dominant contribution of HCl to the electrical pattern of this ice-core section. The periodicity of HCl deposition calls for further study of the chemical composition of this depth interval (when the CFA and the discontinuous IC data are available), to understand the temporal trend of the source (volcanic activity?) and/or of the long-range-transport processes. On the basis of a preliminary time-scale (personal comunication from J. Schwander, 1999), the 104–108 m depth interval corresponds approximately to the time interval 2490–2620 BP.

4. CONCLUSIONS

The ECM and DEP measurements, performed in situ, are able to give fast and continuous records of variations in the ionic content of the ice. By comparing them, it is possible to obtain information on the acidic or non-acidic components, because of the higher selectivity of ECM for H^+. Nevertheless, for determining the dominant acidic species, such electrical measurements have to be followed by chemical analysis. In situ, continuous or fast semi-continuous chemical analysis constitutes, therefore, a complementary method to distinguish sulphuric, hydrochloric or nitric acids and to correlate the ice composition to the different sources and transport processes.

From the electrical and chemical profile for the first 400 m of the EPICA–Dome C ice core, some conclusions can be drawn:

Unlike the Greenland Holocene ice, where nitric acid is dominant, the main acidic species in the Antarctic Plateau is H_2SO_4, but some particular events are characterized by high HCl concentrations;

The ECM, DEP and sulphate profiles match very well, particularly for peaks coming from volcanic activity. Some differences are due to HCl deposition or to ice layers with a dominant contribution of non-acidic ionic species;

An increase with depth in the background values has been observed for chloride. This component also shows a progressive increase of data dispersion, in particular for the 300-400 m range;

Around 270–360 m depth, a further increase in chloride is visible. This trend confirms the previous observation reported by Legrand and Delmas (1988) from the old Dome C ice core. Further work is needed to determine whether this pattern is due to a change in the source or a change in climatic factors (transport or accumulation rate) affecting the amounts or speciation of deposited and retained chloride. In any case, it indicates a significantly different regime in the early Holocene compared to the later period;

Along the sulphate profile, many spikes were found, probably due to volcanic depositions, with concentration maxima up to 900 $\mu g\,L^{-1}$. The shallower large peaks were identified by comparison with Antarctic and Greenland ice cores. When a reliable dating of the Dome C ice core is available, some of the unidentified peaks can be used as temporal horizons because of their characteristic shape or relative height.

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