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D.C. CONDUCTIVITY OF ANTARCTIC ICE IN RELATION TO ITS CHEMISTRY

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191104 Leningrad, USSR***RESUME**

La conductivité électrique de la glace naturelle varie en général avec l'acidité de l'eau de fusion. Cette méthode a été utilisée avec succès par Hammer (1) pour détecter les empreintes d'éruptions volcaniques dans la glace du Groënland.

Dans ce papier plusieurs profils de conductivité sont présentés pour deux sites antarctiques (Vostok et Pôle Sud) en liaison avec une étude globale des impuretés solubles. Nos profils mettent en évidence un important "double pic" de conductivité et d'acide sulfurique dans la neige déposée durant les "années Tambora (1815)", ce qui nous sert d'horizon repère.

Parmi les trois acides habituellement présents dans la glace (H_2SO_4 , HCl et HNO_3) HCl et HNO_3 semblent jouer un rôle prépondérant sur les niveaux de conductivité. Par ailleurs un effet négatif des aluminosilicates est mis en évidence. Ces résultats suggèrent que des impuretés dans la glace seraient localisées aux joints de grains où le pH pourrait atteindre de très basses valeurs. Cette hypothèse est en accord avec le modèle de conduction antérieurement proposé par Wolff et Paren (2).

ABSTRACT

The D.C. conductivity of natural ice generally shows a strong correlation with the acidity of the meltwater sample. This method was successfully applied by Hammer (1) to detect debris of volcanic eruptions recorded in Greenland ice cores.

In this paper we study several conductivity profiles for antarctic ice cores (Vostok and South Pole stations) in relation with a comprehensive study of soluble species. Our profiles revealed an important "double spike" on both conductivity and sulfuric acid record for snow deposited during the "Tambora years (1815)" which is used as a stratigraphic marker.

Among the three acids (H_2SO_4 , HCl and HNO_3) usually present in the ice HCl and HNO_3 seem to be more effective than H_2SO_4 on the conductivity background. In addition it is suggested a negative effect of aluminosilicates. These results suggest that impurities are located at grain boundaries where the pH can reach very low values. This assumption is in agreement with the conductivity model previously proposed by Wolff and Paren (2).

INTRODUCTION

Deep ice cores in Greenland and Antarctic ice sheets provide continuous records of climate and atmospheric content over periods as long as 100 kyears or more. Many features of past environments may be reconstructed, including their historical volcanism. In relation to this topic, Hammer (1) has shown that electrical conductivity measurements (E.C.M.) on Greenland ice core samples are essentially dependent on the acidity of the meltwater, and he proposes a volcanism reconstruction covering the last 10,000 years.

Similar studies have been performed on Antarctic ice (Maccagnan et al (3), Maccagnan and Duval (4), Schwander (5)). However their results deal with certain phenomenological and physical aspects of the DC conductivity and no calibration curve was established for this ice, often different from Greenland ice with respect to impurity content.

Zanolini (6) has examined twelve conductivity spikes observed on a continuous E.C.M. profile from a 200 m deep ice core at D 57 (Terre Adélie) in a more comprehensive chemical study (H^+ , NO_3^- , and SO_4^{--} measurements). Ten peaks were found to be positively correlated with increases of HNO_3 or H_2SO_4 , and two had no correlation. For similar increases in H^+ content, this E.C.M. record suggests that HNO_3 may be more related to conductivity than H_2SO_4 . If true, the interpretation of conductivity profiles in term of volcanism becomes questionable if not checked by chemical analysis, since HNO_3 is not assumed to be of volcanic origin. The two "ghost peaks", unexplained by chemical analysis, cast doubt on the results obtained for D 57 since the E.C.M. signal is temperature dependent and the core temperature was not monitored during E.C.M. measurements.

In addition to the search for optimal conditions to obtain reliable E.C.M. profiles, the objective of this study is to quantify the influence of each acid (H_2SO_4 , HNO_3 and HCl) on the DC conductivity using a comprehensive study of soluble species present in Antarctic ice.

EXPERIMENTAL STRATEGY AND METHODS

E.C.M. was performed using a pair of sharp electrodes (10 mm apart) pushed a few millimetres into the core and moved by a sledge over a plane surface cut parallel to the core axis. The applied voltage was 1000 V and the temperature of the sample (around $-15^\circ C$) was carefully monitored. A 10 mm thick of outer layer of the core was first removed in order to avoid possible ageing effects on stored cores.

We carried out two series of measurements on ice cores drilled at two Antarctic stations : South Pole ($90^\circ S$, 2800 m elevation a.s.l) and Vostok ($78^\circ S$, $107^\circ E$, 3600 m a.s.l). First, we selected ice samples corresponding in time to the huge eruption of Tambora in 1815 which was followed by a large input of H_2SO_4 . This event can be easily identified on a continuous record (Fig. 1) since it is preceded by another eruption, seven years earlier of an unknown volcano (no historical record) (Legrand and Delmas (7)). This "twin" peak was identified at South Pole in seven cores drilled in a 10 km radius around the station, and in 3 different cores at Vostok. The depth of the Tambora event is consistent with the accumulation rate deduced from total Beta radioactivity measurements at each location. The Tambora

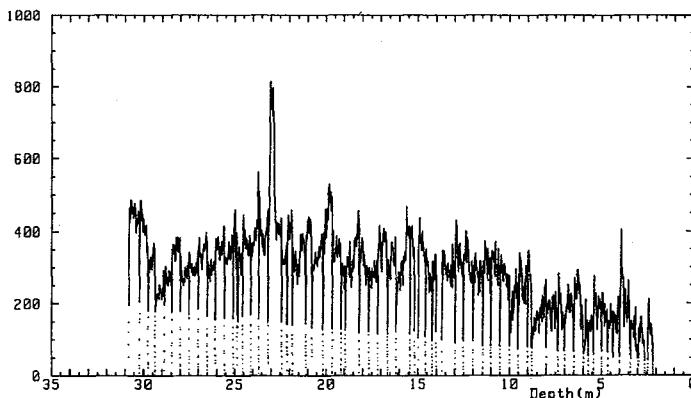
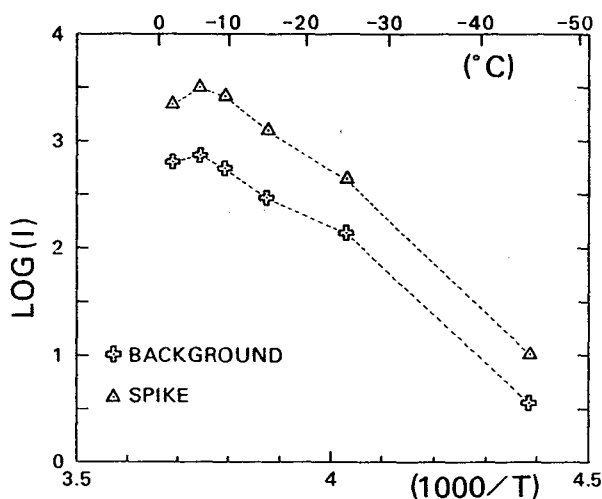


Fig. 1 : Continuous E.C.M. profile obtained at South Pole Station. The highest peak, at 23 m depth, corresponds to the Tambora eruption, preceded by another volcanic eruption. A peak at 4 m depth corresponds to the Mt Agung eruption in 1963 (not studied in this paper).

layer is found at a depth of 23 m at South Pole and 15 m at Vostok. This double spike is also seen on other profiles covering this time period performed at various locations (at Dome C, Legrand (8) ; at Siple, Schwander (5) and at D 57 Zanolini (6)). These two peaks, seven years apart and the largest of the two last centuries recorded anywhere in Antarctica, are a valuable aid in the dating of snow layers. For example, these two volcanic reference layers were used by Zanolini et al. (9) to establish the chronology of a 200 m deep ice core from D 57 where dating is very difficult in relation to an irregular accumulation variation and glaciological parameters (ice flow).

From Fig. 1, the E.C.M. signal tends to increase with depth from the surface down to 30 m, attributable to the increased contact between firn and electrodes due to firn hardening as well as the increase in the conductivity of firn as its density increases. In order to calibrate the Vostok E.C.M. signal to a depth of about 25 m we applied a correction factor of 1.4 to these data, representing approximately the ratio between 23 and 15 m signals on Fig. 1.

The second set of measurements was made on samples from the 2083 m Vostok core, retrograded in Grenoble. These samples cover the last 150 kyrs and have been used in stable isotope studies to reconstruct the last climatic cycle (Lorius et al. (10)). Note that during glacial climate, the ice shows a drastic enhancement of insoluble and soluble compounds (Legrand et al., to be published). The E.C.M. signal is temperature dependent. Fig. 2 represents the signal from the core before and during the Tambora spike versus the reciprocal of temperature.



Assuming that current (i) is a function of temperature (T) according to an Arrhenius law ($i = i_0 \exp -E/RT$), an activation energy of 0.25 eV is found in the -25 to -9°C temperature range. For temperatures higher than -6°C the signal decreases. This may be due to weaker contact between the electrodes and the ice crystals since the firn becomes too soft for good contact. Another possibility is a drastic modification of the conduction process. In the -25 to -9°C temperature range, our activation energy is consistent with previous studies (Hammer (11), Neftel et al. (12), Reynolds and Paren (13)) and we use this value in normalizing all data to a temperature of -15°C .

Fig. 2 : The conductivity signal as a function of temperature : triangles refer to the Tambora signal and crosses to an undisturbed level (sample from South Pole Station).

We have measured major ions (i.e. Na^+ , NH_4^+ , K^+ , Ca^{++} , Mg^{++} , H^+ , Cl^- , NO_3^- and SO_4^{--}) on the corresponding samples. H^+ content was measured by an acid titration method which rules-out the influence of CO_2 (Legrand et al. (14)). All other ions were determined by ion chromatography using stringent contamination free techniques (Legrand et al. (15)). As already discussed, (see, for example, Legrand and Delmas (16)), such a comprehensive study can be used to identify the origin of each ion. In this way, we have demonstrated that the proton present in ice comes from HNO_3 , H_2SO_4 and sometimes HCl (calculations of each contribution are detailed in this volume ; see Legrand (17)).

THE INFLUENCE OF THE PROTON ORIGIN

Fig. 3 shows the E.C.M. record of the Tambora eruption for Vostok and South Pole ice cores with results for each origin of acidity. The HCl concentration is very low ($\approx 0.2 \mu\text{Eq. l}^{-1}$) and is assumed to have a behaviour similar to that of HNO_3 . The sum of $\text{HCl} + \text{HNO}_3$ is therefore reported. The E.C.M. signal (i) is plotted versus total acidity ($[\text{H}^+]^3$) in Fig. 4.

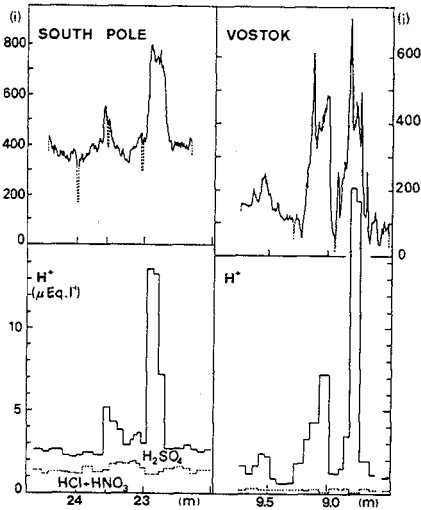
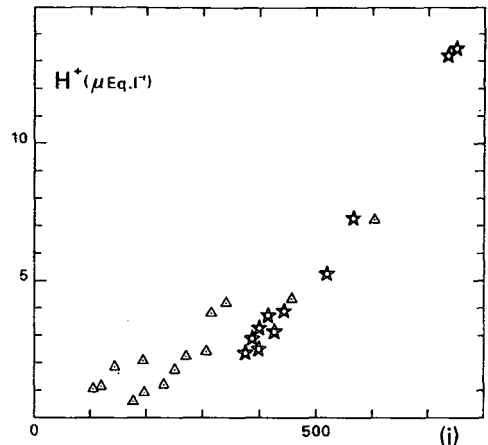


Fig. 3 : Tambora eruption as recorded by E.C.M. and by acid reconstitution from chemistry at South Pole and Vostok. For acids, the upper curve refers to the sums of $\text{HNO}_3 + \text{HCl} + \text{H}_2\text{SO}_4$ contributions and the broken line to the sum of HNO_3 and HCl.

Fig. 4 : Total acidity H^+ as a function of E.C.M. signal for South Pole (stars) and Vostok (triangles) data from Fig. 3.



Data are fitted by a regression function $i^\alpha = a [\text{H}^+]^b$, where α and a are estimated by the least squares method. The values for α and a are $1.1 \cdot 10^{-6}$ (relative units) and 2.48 for South Pole data and $9.5 \cdot 10^{-4}$ and 1.58 for Vostok respectively. For low acidity, around $2 \mu\text{Eq. l}^{-1}$ the conductivity signal appears significantly higher at South Pole than at Vostok.

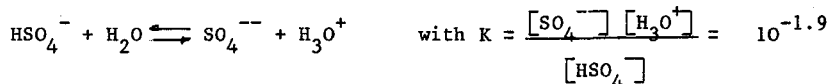
The chemical analysis shows that H_2SO_4 represents the predominant contribution of the acidity background for Vostok ($1.1 \mu\text{Eq. l}^{-1}$ or 81%), HNO_3 being minor ($0.26 \mu\text{Eq. l}^{-1}$ or 19%) and HCl not present at all. On the contrary, for South Pole, only 45% of the acidity is due to the presence of H_2SO_4 ($1 \mu\text{Eq. l}^{-1}$) and 55% is due to HNO_3 and HCl ($1.5 \mu\text{Eq. l}^{-1}$). In order to estimate the specific effect of other components, $[\text{HNO}_3 + \text{HCl}]$ on one hand, $[\text{H}_2\text{SO}_4]$ on the other, we assume that the E.C.M. signal is a function of an effective acidity (H_{eff}) according to the equation: $i^\alpha = a (\text{H}_{\text{eff}})^b$, where this effective acidity is a linear combination of three main components:

$$\text{H}_{\text{eff}} = [\text{HNO}_3 + \text{HCl}] + b [\text{H}_2\text{SO}_4] \quad \text{eq: 1}$$

HCl and HNO_3 are assumed to have a similar behavior with respect to H_{eff} . The best fit of the 30 data points in Fig. 3 gives 1.8 for α , 3.98 for a and 0.95 for b . The regression coefficient is 0.98. We tested the sensitivity of the result to α and b in two cases : i) when we remove the highest 3 values (where H^+ is greater than $7 \mu\text{Eq. l}^{-1}$) and ii) when the calibration coefficient used to compensate for the

varying densification effect between the two locations is reduced to 1.2. In both cases, α and b decrease toward 1.3 and 0.4 respectively, representing extreme values.

These data suggest that the influence of HNO_3 and HCl on the conductivity background is more important than H_2SO_4 . This can be explained considering the model proposed by Wolff and Paren (2). Indeed HCl , HNO_3 and H_2SO_4 (at least for the first dissociation) are strong acids, but the second dissociation of H_2SO_4 is an equilibrium reaction which depends on the pH :



For several reasons already developed (Legrand, 17) we agree with the idea (previously proposed by Maccagnan (18), Wolff and Paren (2)) that sulfuric acid is mainly in the ice at the grain boundaries. In this case, the pH of the liquid vein can reach low values (i.e. $\text{pH} \approx 2.5$ when $b = 0.7$ and $\text{pH} \approx 1$ when $b = 0.4$).

A value of 0.4 for b would suggest that a small fraction of HCl or HNO_3 is located at grain boundaries. This assumption is not overly surprising. Indeed, for the opposite case of H_2SO_4 , Legrand (17) concludes that only a small fraction of HNO_3 is deposited directly at the snow surface. So the incorporation into the ice would be better for HNO_3 than H_2SO_4 (at least during the deposition step). This conclusion needs to be checked by other experiments on natural ice and doped laboratory-grown crystals.

It is also important to note that our present results do not question the calibration curve established by Hammer on Greenland ice cores (1). Indeed this curve was performed using cores from Crête, Dye 3 and Camp Century and the nitrate contents at these locations are very similar (about $1 \mu\text{Eq. l}^{-1}$ Herron (19)) and the HCl content is probably insignificant (Hammer et al. (20)).

POSSIBLE EFFECT OF OTHER IMPURITIES

The E.C.M. results of the 56 ice sections (20 cm long) and taken roughly every 40 meters from the 2083 m Vostok core are reported in Fig. 6, plotted versus their corresponding total acidity. For 47 samples, the acid components were identified, but for the remaining nine , the high level of the total ionic load (up to $30 \mu\text{Eq. l}^{-1}$) prevents accurate estimation of HNO_3 and HCl contributions. In the 47 samples, H_2SO_4 contributions to the total acidity are preponderant (60 to 90 %) and the variations are in the range of 0.4 to $4.5 \mu\text{Eq. l}^{-1}$. HNO_3 and HCl vary in the range of 0.16 to $0.48 \mu\text{Eq. l}^{-1}$ and their contributions are so small that the calculation of the α and b coefficients of the calibration curve is not significant. However if we adopt the calibration curve we obtained here above, the correlation coefficient is 0.91 for these 47 values.

In Fig. 5, the set of nine values is obviously different with respect to the calibration curve. For a given H^+ concentration, a reduction of the E.C.M. signal is observed for those samples containing high impurity concentrations (see calcium content reported Fig. 5).

These nine cores are from the glacial age and moreover reveal the highest salt content of our profile (10^{-9} g.g^{-1}). As developed by Legrand (17) (this volume), during glacial conditions, the ice contains large amount of sea salt (mainly NaCl and some K^+ , Ca^{++} , Mg^{++} , SO_4^{--}) terrestrial salts (mainly CaSO_4) and insoluble species (various aluminosilicates, Petit et al. (21)). Sea salt would not significantly influence the current (Hammer (1)). Furthermore, as demonstrated by Legrand (17), (8), it is important to note that calcium is present in Antarctic ice during the coldest time period in the form of CaSO_4 . This is not the case for Greenland ice cores in which Hammer (1) pointed out high calcium contents associated with alcalic ice ($\text{pH} = 7$). The explanation for this phenomenon therefore does not seem to be linked to the soluble species.

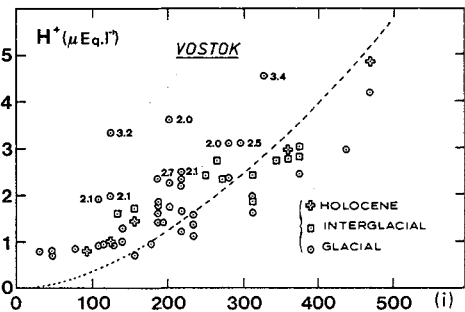
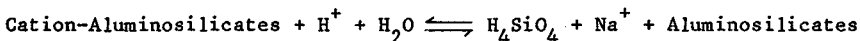


Fig. 5 : Total acidity $[H^+]$ as a function of E.C.M. signal for samples of different climatic periods from the 2083 m Vostok core. Dots with numbers refer to samples from the glacial age (with calcium concentrations higher than $2 \mu\text{Eq. l}^{-1}$ as indicated by the number). The broken line is a mean calibration curve calculated from eq. (1) assuming a constant contribution of $\text{HNO}_3 + \text{HCl}$ equal to $0.3 \mu\text{Eq. l}^{-1}$ would be excepted for value of H^+ near zero.

High calcium content is associated with high aluminosilicate content (as suggested by the strong correlation between Al and Ca^{++} contents obtained by Legrand (8)). Aluminosilicates are insoluble in water (at $\text{pH} = 5$, see Legrand (8)) but sodium present in these compounds is easily exchanged with proton at $\text{pH} = 2.3$ according to the reversible reaction (Stumm and Morgan (22)) :



As previously discussed by Wolff and Paren (2), both H_2SO_4 and insoluble particles are probably located in the ice at grain boundaries. In this case, at grain boundaries, the pH is probably close to one and aluminosilicates can partly exchange cations with protons. When we melt the ice, the pH decreases and the preceding reaction shifts completely to the left. Therefore, the exchange between acid and aluminosilicates can explain the decrease of the E.C.M. signal when both are present at the grain boundaries.

CONCLUSION

In addition to the glaciological interest of the detection of a "twin" peak at various Antarctic locations, this study shows that the E.C.M. is well correlated with the H^+ content of the meltwater (at least at one location). However, HNO_3 and HCl appear to be more effective (by a factor 1.5 to 2.0) than H_2SO_4 on the DC conductivity of ice. Our results therefore suggest that the H_2SO_4 acts as a monoacid in the ice. This would be compatible with a high concentration at the location of this impurity in ice (possibly at the grain boundary). The effect of insoluble impurities is negligible, but becomes more sensitive at high concentration levels as found in Ice-Age layers. This is not due to the reaction of acid with carbonate, as observed in Greenland, but rather to the reaction with aluminosilicates found in Antarctic ice. The resulting effect is also a weaker correlation between acidity of meltwater and DC conductivity.

Finally, for Antarctic ice, because HCl and HNO_3 contents vary greatly for different geographical locations, the interpretation of E.C.M. profiles in terms of volcanic input requires confirmation by comprehensive chemical studies. Further work (electrical and chemical measurements) may also provide valuable aid in locating impurities within the lattice.

ACKNOWLEDGEMENTS

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