SULPHURIC AND NITRIC ACID CONCENTRATIONS AND SPIKES ALONG A 200 m DEEP ICE CORE AT D 57 (TERRE ADÉLIE, ANTARCTICA)

by

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ABSTRACT

D 57 station in Terre Adélie lies between the coast and the central Antarctic plateau. A 200 m ice core was recovered in summer 1980-81 at this location and analyzed by an electroconductometric method to detect exceptional acid levels linked to fallout from major volcanic eruptions. Several signals were indeed found. The corresponding ice-core sections were then analyzed for mineral acids (H_2SO_4 and HNO_3). We detected several large volcanic events, in particular two eruptions identified as Tambora (1815) and Galunggung (1822). The background concentration of sulphate was found to be relatively low (about 0.5 μeq l^{-1}). On the other hand nitrate values were higher than at coastal or central Antarctic locations (except for the South Pole). Two spikes were found in the nitrate profile at depths of 140 and 148 m. It is thought that they could be either linked to the 1604 and 1572 supernovae Kepler and Tycho or correspond to epochs of particularly high solar activities. With the aid of these sulphate and nitrate exceptional events, a dating of the D 57 ice core can now be proposed which corresponds to a mean snow accumulation rate of 22 cm of ice equivalent per year over the last four centuries.

1. INTRODUCTION

The surface of Terre Adélie can be represented by a continuous and gentle slope from the coast up to the central Antarctic plateau (elevation >3000 m). D 57 station is located at an elevation of 2050 m and at a distance of 200 km from the sea (lat 68°11'S, long 137°33'E). Thus this site occupies an intermediate position between the coastal areas where the snow accumulation rate is high and the plateau where it is very small. The decreasing influence of the marine air masses towards the interior is clearly reflected in the snow chemistry. Glaciochemical studies have already been performed at coastal sites (Aristarain and others 1982, Legrand and Delmas 1985) or at more central Antarctic locations such as the South Pole (Delmas and others 1982, Legrand and Delmas 1984), Dome C (Legrand 1980) or Byrd station (Herron 1982). It was therefore deemed of interest to look at the chemical composition of the trace impurities deposited at locations such as D 57. Drilling to a depth of 200 m was carried out at D 57 during summer 1980-81 and a core recovered for climatic glaciological and glaciochemical studies. In this paper we report on the measurements of H^+, SO_4^{2-} and NO_3^- ions performed on selected sections of the D 57 ice core between 47 and 155 m from the surface.

2. DATING OF THE CORE

As the snow accumulation rate in this region of Terre Adélie is relatively irregular (Young and others 1982), the dating of the D 57 ice core was not accurately known before these studies. The accumulation rate at D 57 was estimated to be about 41 ± 9 g cm^{-2} a^{-1} from stake measurements made over a period of 10 a. The age at the bottom of the core was then calculated to be around AD 1600. Ice-flow and model calculations conducted more recently indicate ages significantly greater than this preliminary estimate (Barnola unpublished). We shall see that a combination of the model with the glaciochemical data reported in this paper allows us to present a new aspect of the dating of this core. Until the discussion of the H_2SO_4 and HNO_3 exceptional

events recorded in this core, the following provisional dates can be given (note that further on in this paper all depth values will be in metres of ice equivalent throughout): AD 1880 at 50 m, AD 1790 at 100 m, and AD 1430 at 150 m.

3. ANALYTICAL METHODS

One of the major primary aims of the glaciological studies at D 57 being the search for past volcanic deposits, continuous conductometric measurements were made in the field according to a method developed by Hammer (1980). A detailed description of the equipment has been given by Zanolini (1983)* and Delmas and others (in press) Several core sections presenting high conductivity levels were detected and selected for further chemical measurements. Moreover a long sequence (6 m at about 50 m depth) was analyzed in order to obtain the background values of the ions studied in the absence of exceptional events.

The determination of trace elements in firn or ice cores necessitates the use of stringent contamination-free techniques. The cores were stored in cold rooms until their analysis in the Grenoble laboratories. The selected sections were cut and recorded following a procedure described by Legrand and others (1984). Only the inner part of each ice (or firn) core was kept for chemical determinations. Acidity was determined by titration to ±0.2 μeq l^{-1} (Legrand and others 1982). Sulphate and nitrate ions were measured (generally ±10% except for lowest concentrations) by ion chromatography with the aid of a Dionex apparatus (Model 10). For acidity measurements, a relatively constant (0.8 to 1.2 μeq l^{-1}) blank value was observed but not subtracted from the acidity data. This blank is not linked to a contamination problem but rather to the titrimetric procedure itself as discussed by Legrand and others (1982).

4. RESULTS AND DISCUSSIONS

The electrical conductivity of the ice core was first measured in the field and then confirmed in Grenoble in the cold rooms (−15°C). A nearly continuous record was obtained from a depth of 40 to 155 m, the firn cores being unsuitable for measuring with our equipment.

All conductometric profiles are reported elsewhere (Zanolini 1983). They exhibit large variations and peaks. These peaks were assumed to be linked to rapid increases of the acidity of the ice. Twelve of them (listed in Table I) were particularly pronounced and were analyzed chemically after recoring. It is worth noting that their length is generally from 1 to 2 a. The results of the chemical measurements are plotted as a function of depth (Figs 1, 2 and 3). It was not always possible to obtain continuous profiles, either because portions of the ice cores were broken or missing or because a few meltwater samples were lost or contaminated during laboratory work. As an example, all alkaline samples were considered as definitely contaminated (this point is explained in Legrand and others 1982).

It has already been discussed and demonstrated elsewhere (Aristarain and others 1982, Delmas and others 1982, Legrand

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* In this report the depths were erroneously given in metres of ice equivalent. They must be read as metres below the surface.

TABLE I. THE PEAKS OF CONDUCTIVITY SELECTED FOR CHEMICAL STUDIES ALONG THE D 57 ICE CORE). The mean current (averaged over segments 0.2 m long) obtained from conductometric measurements gives an indication of the strength of the signal. The background variability of the current was in the range from 0.5 to 1 μA.)

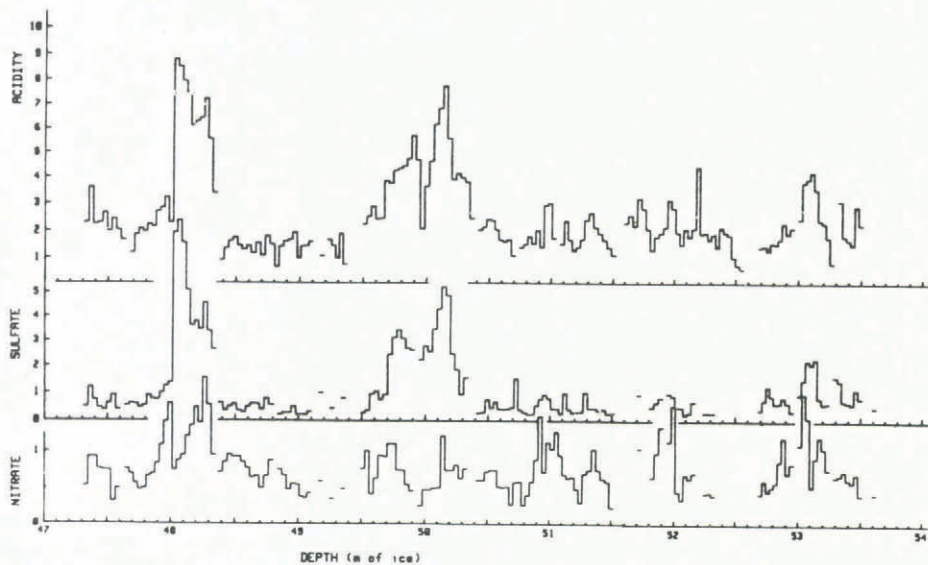| Peak no	1	2*	3	4	5	6	7	8	9	10	11	12
Depth interval (m)	48.00	49.49	52.80	82.57	88.67	101.26	110.09	111.69	117.76	120.25	126.44	153.99
	48.37	50.41	53.02	83.11	89.99	101.56	110.76	111.96	118.47	120.49	126.63	155.26
Mean current (μA)	2.5	3.0	2.5	2.5	2.0	1.3	1.6	1.9	2.5	2.5	1.5	2.7

*Double peak

Fig.1. D 57 station. Acidity, sulphate and nitrate profiles (in μeq l^{-1}) from 47.3 to 53.6 m (metres below the surface) deep.

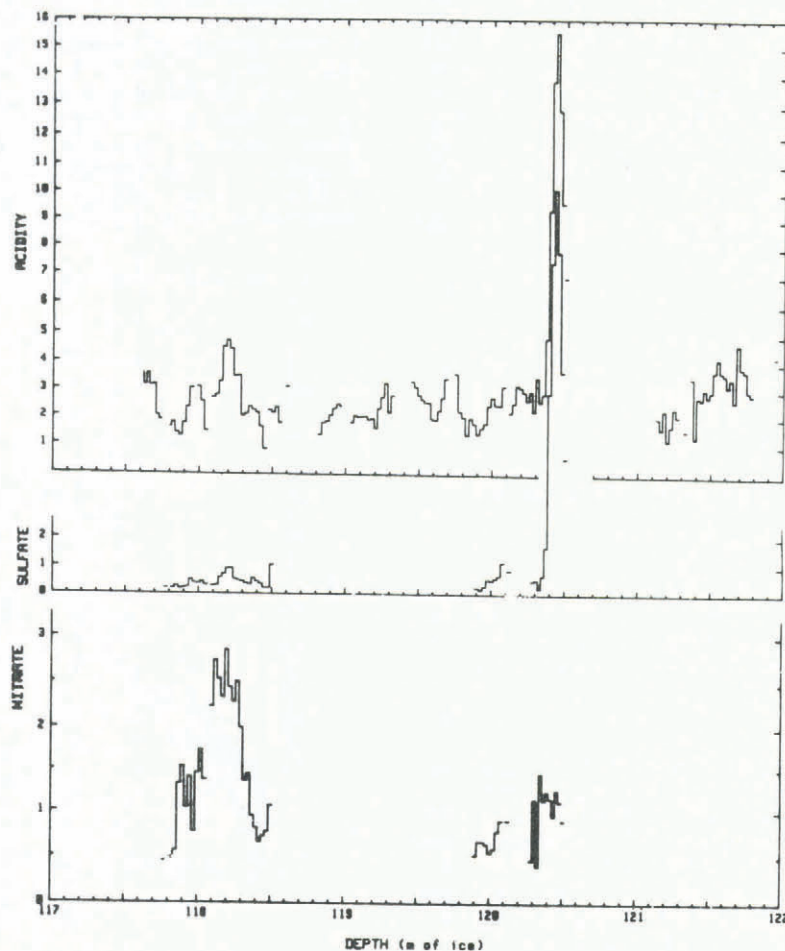Fig.2. D 57 station. Acidity, sulphate and nitrate profiles (in μeq l^{-1}) between 117.7 and 121.8 m (metres below the surface) deep.

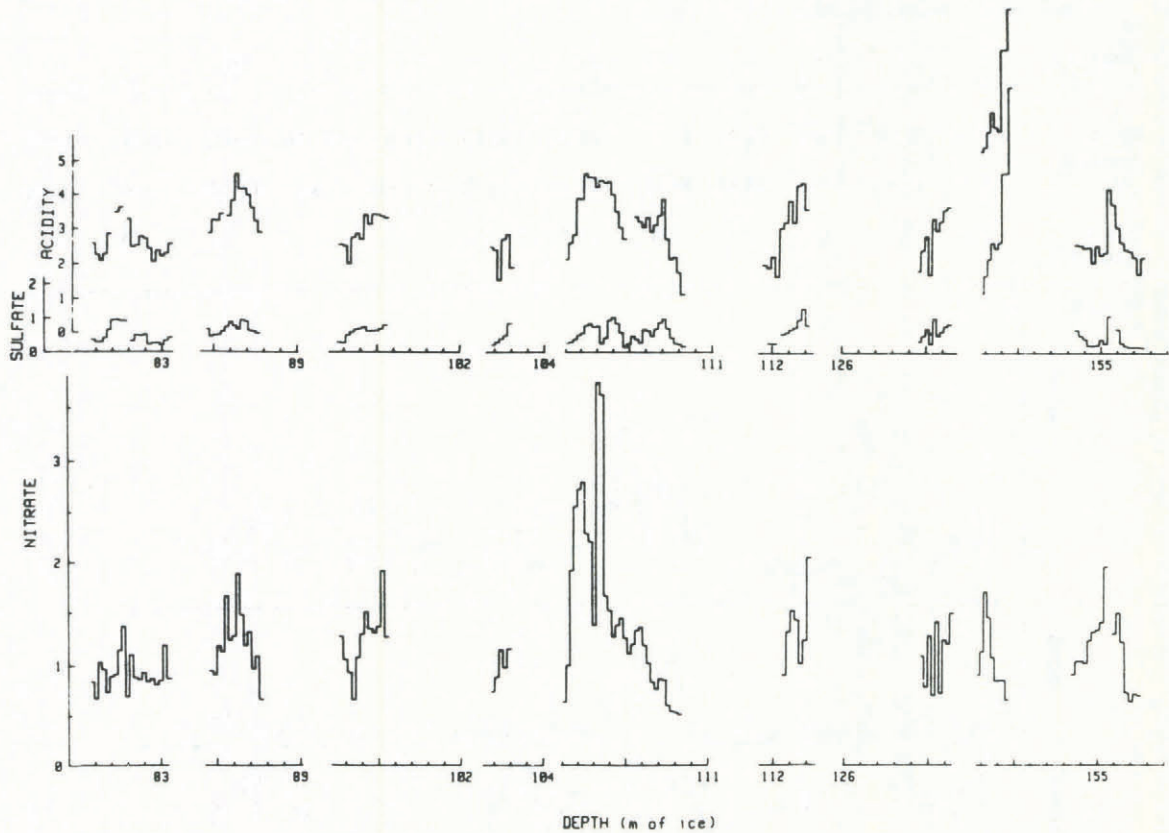https://doi.org/10.3189/S0260305500005930 Published online by Cambridge University Press

Fig.3. D 57 station. Acidity, sulphate and nitrate concentrations (in μeq l^{-1}) in different core sections.

and Delmas 1984) that, except at the coast, sulphate and nitrate are mainly present in Antarctic precipitation as H_2SO_4 ("excess sulphate") and HNO_3, respectively. Another possible acid is HCl ("excess chloride"), which has not been measured systematically in this study but has been estimated on a few chromatograms. It appears that its contribution is always weak in this geographical region as confirmed by the glaciochemical studies reported by Legrand and Delmas (1985) in Terre Adélie.

We can therefore write the following equation (the concentrations in square brackets are in μeq l^{-1})

$$[H^+] = [SO_4^{2-}] + [NO_3] + b, \qquad (1)$$

where b is the blank value (see section 3). Acidity may be slightly neutralized by ammonia (Legrand and Delmas 1984) and neutral salt formed. In this case we would have

$$[H^+] < [SO_4^{2-}] + [NO_3] + b. \qquad (2)$$

On the other hand, the presence of HCl would lead to

$$[H^+] > [SO_4^{2-}] + [NO_3] + b. \qquad (3)$$

In order to check out these two last eventualities, all acidity, sulphate and nitrate data were analyzed mathematically. A multiple correlation coefficient of 0.948 was obtained for the multiple regression of Equation (4)

$$[H^+] = s [SO_4^{2-}] + n [NO_3] + b. \qquad (4)$$

The calculation gave s = 1.00, n = 0.95, and b = 0.97. This demonstrates that generally we have unneutralized H_2SO_4 and HNO_3 in snow, (in particular in the sulphate and nitrate "peaks"), the variance of the acidity being explained almost completely by the sum of these two acids. The term b = 0.97 falls within the observed fluctuations of the experimental blank. This also means that the HCl content is generally very low. These results are plotted in Figure 4 (acidity as a function of sulphate + nitrate). The observed scattering may be explained partly by the sum of the analytical errors in

the determination of ions (which increases at low concentrations), and partly by the presence of NH_4^+ or HCl in small amounts as explained earlier (Equations (2) and (3), respectively).

When looking at the depth profiles in Figure 1, it can be seen that both sulphate and nitrate exhibit fluctuations which resemble seasonal variations. However there is apparently no link between the two. Sulphate profiles are relatively regular but are sporadically disturbed by strong perturbations of a duration of 1 to 2 a. Such observations
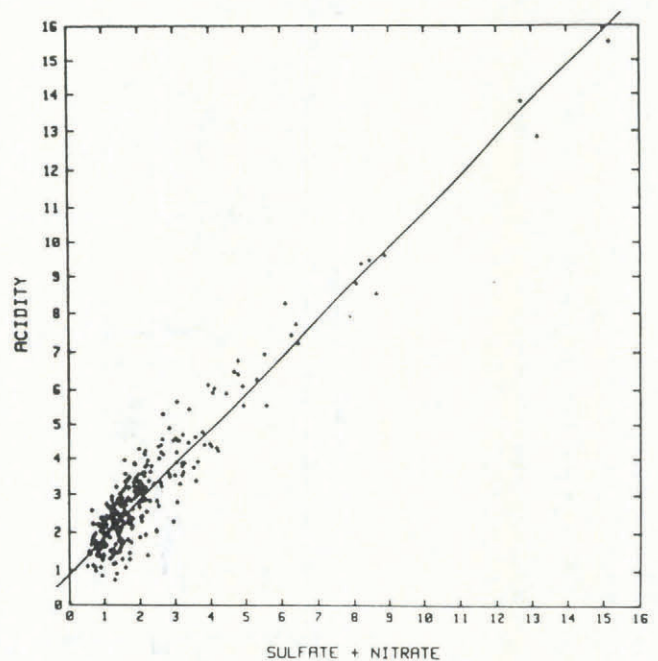

Fig.4. Acidity as a function of sulphate plus nitrate (in μeq l^{-1}).

were made at other Antarctic locations. At the South Pole, the seasonal variations of sulphate (with a maximum during summer) are relatively well-defined (Legrand and Delmas 1984). On James Ross Island the summer maximum is even greater (Aristarain and others 1982). Moreover it is now established that the sporadic sulphate increases in Antarctic snow are due to large explosive eruptions in the southern hemisphere (Delmas and Boutron 1980, Delmas and others in press).

Nitrate appears to be more variable than sulphate from one year to another (Fig.1) and shows no clear seasonal trend. At other Antarctic locations the seasonal effect is sometimes observed (e.g. South Pole), sometimes not (e.g. James Ross Island). The influence of the solar cycle of 11 a, as suggested from nitrate profiles at the South Pole (Zeller and Parker 1981), is not detected on the nitrate profile of Figure 1 which encompasses about 30 a.

Let us compare the values of sulphate and nitrate in the upper continuous sequence (from 47.3 to 53.6 m depth). This time period, situated in the nineteenth century, is apparently marked by two important volcanic events which will be discussed later. In order to obtain the background values of SO_4^{2-} and NO_3^- concentrations at this time, we have made two histograms (Figs.5 and 6) of the data reported in Figure 1. SO_4^{2-} concentrations higher than 2 µeq l^{-1} are related to volcanic events. The background values of sulphate and nitrate are found in the ranges of 0.4 to 0.5 and 0.5 to 0.7 µeq l^{-1}, respectively. This is about half the present-day values at the South Pole (1.5 and 1.44 µeq l^{-1}, respectively (Legrand and Delmas 1984)). At Dome C (located at a higher elevation) nitrate concentrations are still lower, but sulphate concentrations are higher (Delmas and others 1982). On James Ross Island, the histograms of excess sulphate and
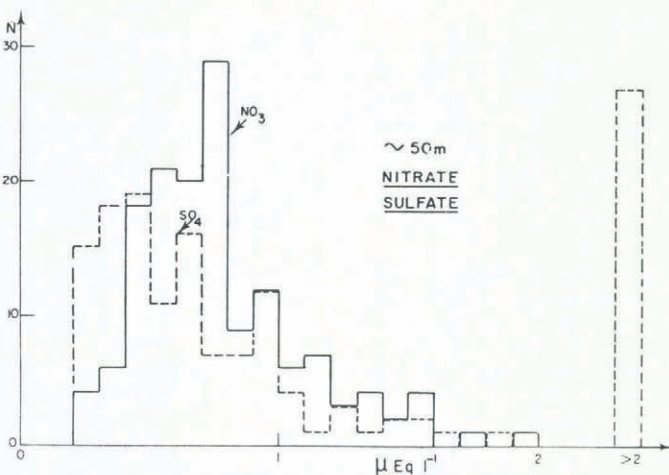
nitrate had very different shapes: flat for the former, narrow for the latter, which is not the case at D 57. Our conclusion is, therefore, that the air chemistry is probably quite different at D 57 (elevation 2050 m) and on Dalinger Dome of James Ross Island (elevation 1660 m).

On the other hand the ratios of SO_4^{2-} and NO_3^- at the South Pole and D 57 are not very different (~1 and ~0.8, respectively) which could indicate that the atmospheric conditions prevailing at both locations are relatively similar (Note however that the time periods compared are not the same). In the deeper part of the ice core, the background value of sulphate appears to remain the same as is clearly shown by comparing the histograms of this compound at depths of ~50 and 102 to 120 m (Fig.7). However, the case of nitrate appears to be different, the deeper concentrations being significantly higher (up to ~1 µeq l^{-1}) than those in the upper sequence studied. Since the origin of this compound in the Antarctic is still uncertain, we can formulate no explanation for this observation.

Fig.7. A comparison of the histograms of nitrate at depth of 50 and from 102 to 120 m. N is the number of events.

Let us now examine the few exceptional levels of sulphate and nitrate that were detected by electroconductometric measurements. Two large sulphate events (volcanic eruptions) are recorded at depths of 48 and 50 m. The heights of the signals show us that they were very powerful. The identification of these events was made difficult by the uncertainty of the dating of this core (see section 2). The two known major eruptions of the last century (Krakatoa in 1883 and Tambora in 1815) are the two most plausible candidates to explain one of these signals which are only a few (5 to 10) years apart. The similar pattern found at the South Pole (Legrand personal communication) where the firn layers are much better dated than at D 57 and the uncertain record of the Krakatoa eruption at Antarctic sites where the snow-accumulation rate is relatively high (such as D 57) are discussed elsewhere (Legrand and Delmas 1985, Delmas and others in press). In this case the first eruption would appear to be Tambora and the second (at 48 m depth) most probably Galunggung (in Indonesia in 1822). The atmospheric effect of these eruptions, as recorded in the D 57 ice core, lasted apparently two years (1816 and 1817 for Tambora, 1823 and 1824 for Galunggung). It is remarkable that Galunggung appears here to have been as powerful as Tambora (at least for sulphate compound emissions), a surprising conclusion in the light of published data (Newhall and Self 1982).

The conductivity record (Zanolini 1983) exhibited two other large volcanic events at a depth of 120.5 and 154.4 m. The great intensity of the 120.5 m event (an increase of more than 12 µeq l^{-1} of sulphate over the background value) and the rapid decrease of the peak strongly suggest that the eruption could have occurred in Antarctic or sub-Antarctic areas (Delmas and others in press). On the other hand, the acid signal at a depth of 154.4 m could be related to a very powerful eruption (even more so than Tambora) of global concern, in the southern hemisphere some six centuries ago.

Fig.5. Histograms of sulphate and nitrate around a depth of 50 m. Sulphate values higher than 2 µeq l^{-1} correspond to volcanic events. N is the number of events.
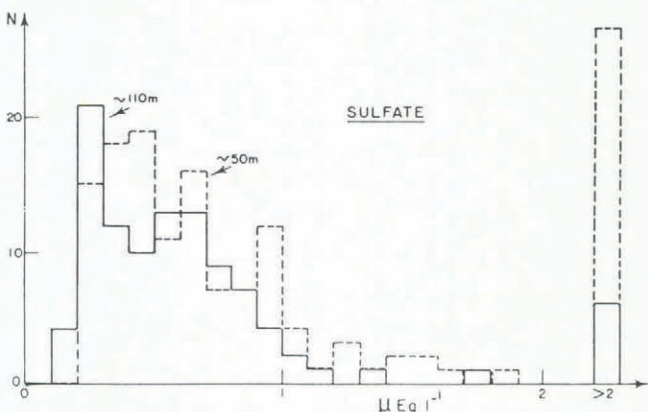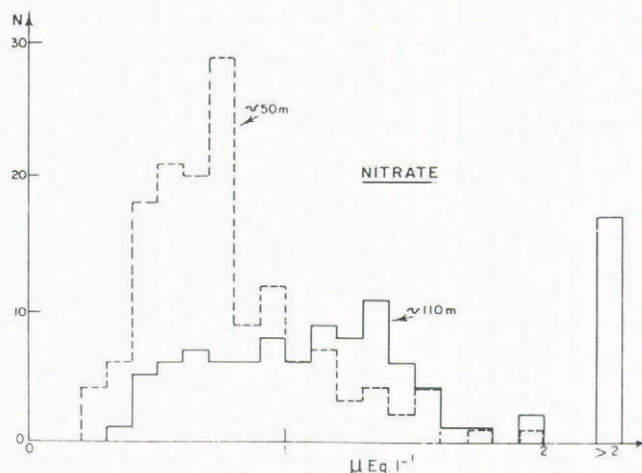

Fig.6. A comparison of the histograms of sulphate at depths of 50 and from 102 to 120 m. N is the number of events.

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The number of volcanic events recorded in this core is therefore very limited. This observation corresponds with the general discussion of volcanic deposits in Antarctic snow (Delmas and others in press) where it was shown that D 57, due to its relatively high snow-accumulation rate, is not a very suitable site for palaeovolcanic studies. Volcanic signals are probably less clearly recorded here than on the Antarctic plateau (Legrand and Delmas 1985).

By means of electroconductometric measurements we also detected acid events which were found to depend mainly on HNO_3 (Zanolini 1983). The two strongest are located between depths of from 110.2 to 110.4 and from 118.1 to 118.3 m (i.e. durations of about one year). They differ markedly (by nearly 1.5 $\mu eq\ l^{-1}$) from the seasonal variations of nitrate at these depths. The distance between these two prominent events (~7.9 m of ice, i.e. ~35 a) may suggest that they could be linked with the two supernovae Kepler and Tycho which are known to have occurred in AD 1604 and AD 1572. The possible influence of these outbursts on the nitrate fallout in Antarctica was first proposed by Rood and others (1979) who observed two important spikes around these dates in the nitrate profile obtained at the South Pole.

This discovery was strongly questioned by several authors (Stothers 1980, Risbo and others 1981) with theoretical as well as experimental arguments. Stothers proposed an alternative explanation: the influence of giant solar flares on the atmospheric background concentrations of HNO_3. He calculated that the high-energy radiation produced during these events is sufficient to form large amounts of HNO_3. He emphasized that giant solar flares occur preferentially during periods of intense solar activity and that two such periods are known to have occurred between AD 1565-1585 and AD 1605-1630, i.e. in the same epoch as the two supernovae. The next largest solar maxima were in AD 1778-1788 and AD 1947-1959. In the absence of convincing theoretical calculations regarding the possibility of the formation of large amounts of HNO_3 by supernovae and in the absence of finding HNO_3 spikes at the two other epochs of high solar activity, our interpretation concerning the two HNO_3 peaks of our profile at 110.3 and 118.2 m depth cannot be regarded as definitive.

Nevertheless the dating obtained using the dates of the two supernovae presents some very attractive aspects. Together with the signals of Tambora and Galunggung (1815 and 1822), they allow us to propose a new and coherent interpretation for the dating of this ice core. If we consider these four horizons, we can calculate the snow-accumulation rates reported in Table II (the solar flare hypothesis would give similar but less accurate results).

The model proposed by Barnola (unpublished) gave a mean accumulation of 29.4 cm of ice equivalent a^{-1} over four centuries. Our value is nearly 25% lower, just entering in the limits of the results of the model calculations. If we may be relatively confident with our dating until ~ 1800 AD, we must agree that the dating of the lower part of the core is very uncertain either by using references horizons or model estimations. By using this new dating, we can locate the Maunder minimum between depths of 80 and 105 m. Rood and others (1979) assumed that the nitrate levels in polar ice might be reduced during this time period in relation to the particularly low solar activity and claimed they had detected this effect in South Pole snow (see also Parker and others 1982). Our nitrate data from depths around 83, 89

and 102 m (indeed very limited, Fig.3) are not lower than the background value at the beginning of the nineteenth century (50 m). The solar influence on the nitrate level of Antarctic snow is therefore not confirmed, as already observed for cycles of 11 a.

5. CONCLUSION

The detailed chemical study of a deep Antarctic ice core is a very time-consuming task. Here we have used a physico-chemical method to detect the most interesting levels of the D 57 ice core and to analyze a limited set of samples for acidity, sulphate and nitrate. With the aid of these measurements we have obtained interesting features concerning the temporal variability of these compounds in snow over approximately six centuries. A limited number of chemical spikes were found and identified but those of nitrate need to be confirmed by further glaciochemical work at other Antarctic sites.

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TABLE II. ACCUMULATION RATES DEDUCED FROM THE SULPHATE AND NITRATE HORIZONS

Reference levels	Mean accumulation rate (cm of ice equivalent a^{-1})
Surface - Tambora (50.2 m)	18.5
Galunggung (48.2 m) - Tambora	20.0
Surface - Kepler SN (110.3 m)	22.2
Kepler SN - Tycho SN (118.2 m)	23.4

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