

# 1000 years of explosive volcanism recorded at the South Pole

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## ABSTRACT

Cataclysmic volcanic eruptions generally disturb the global atmosphere markedly for around 2 years. During that time, long-life volcanic products (mainly H<sub>2</sub>SO<sub>4</sub>), stored in the stratosphere gradually return to the troposphere. Antarctic snow may be subsequently contaminated and acid signals recorded. The recovery of these signals along Antarctic ice cores provides a history of past volcanic events, most often of global, but sometimes of just regional, significance. Several physical and chemical techniques have been used to analyse a 1000-year ice core drilled near Amundsen-Scott Base. Acid and ultrafine ash deposits of volcanic origin have been carefully investigated. 23 major volcanic eruptions have been detected, dated and tentatively identified. The results have been compared with similar Antarctic and Greenland records. The amount of volcanic sulfate deposited in Antarctic snow, calculated and averaged over the last millennium, is, however, minor (13% of the total sulfate) in comparison with that of the marine biogenic source. The 19th century was the period of the millennium most seriously disturbed by global explosive volcanic activity. The chlorine cycle, as recorded in Antarctic ice, seems to be little affected even by such a large event as Tambora, 1815.

## 1. Introduction

A few times per century, an explosive volcanic eruption injects ash and gases into the stratosphere. Atmospheric chemistry and global climate can then be perturbed for up to 2 or 3 years. Hammer (1977) was the first to find records of these major volcanic events in polar ice sheets in the form of sulfuric acid layers. Several publications have confirmed that ice cores can play an important role in documenting the link between climate and volcanism (Hammer et al., 1980; Gilliland, 1982; Angell and Korshover, 1985; Self and Rampino, 1988; Mass and Portman, 1989). Volcanologists are interested in knowing the frequency and location of large eruptions of the past and glaciologists hope to date their ice cores using well known volcanic horizons (Hammer, 1989). Delmas et al. (1985) discussed the transport, deposition and methods of detecting volcanic deposits in Antarctic snow and ice. Zanolini et al.

(1985) and Legrand and Delmas (1987) reported two volcanic records (spanning about 800 and 220 yr, respectively) in East Antarctic ice. In this paper, we extend the Antarctic volcanic record back to the turn of the last millennium.

Sulfuric acid is clearly the most important compound serving to volcanic deposits. Explosive eruptions are capable of emitting several Tg (1 Tg = 10<sup>6</sup> Tons) of sulfur, generally in the form of SO<sub>2</sub> which is transformed into H<sub>2</sub>SO<sub>4</sub> in the atmosphere and deposited in this form along with the snow. However background aerosol is also constituted mainly of H<sub>2</sub>SO<sub>4</sub> (derived from marine biogenic activity) which makes it difficult to identify unambiguously the volcanic sulfate contribution with respect to this natural fluctuating sulfate background. The safest method for reconstructing the chronology of large volcanic eruptions recorded in the ice is the continuous chemical analysis of the ice core not only for the sulfate ion but also for all major ions such as H<sup>+</sup>,

Na<sup>+</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>. With the aid of the ion balance of the precipitation, it is possible to fully interpret the nature of the signals detected and to check whether other gaseous acid species were emitted by the eruption (Legrand and Delmas, 1984 and 1987). However this method is extremely time consuming and can be used only for limited sections of ice cores. The electroconductometric method (ECM) first developed by Hammer (1980) is by far the most rapid way of detecting volcanic signals along several tens or hundreds of meters of ice cores. Delmas et al. (1985) have discussed the chemical analyses which can be used as a complement to ECM in order to improve the quality of the interpretations. As for the D 57 ice core (Zanolini et al., 1985), a combination of several methods was used. (1) Major volcanic events were searched for along the whole ice core by ECM. (2) Every signal was analysed for major ions. (3) A few longer sequences were also measured in detail in order to check the validity of ECM results. (4) The chemical composition of insoluble volcanic microparticles found in the ice for several volcanic levels was determined for an attempt to identify the eruption responsible for the acid signal (Palais et al., 1990). (5) The ice record was compared with other proxy records covering the same time period, in particular frost rings in trees (La Marche and Hirschboeck, 1984).

## 2. Sample preparation and analysis

This study deals with glaciochemical measurements at the South Pole (elevation 2850 m, mean annual temperature -50.7°C). 22 electromechanical drillings were performed around the Amundsen Scott Base during the summer season 1983-84 in order to investigate the spatial variations of snow deposition at this location. Continuous electroconductometric measurements were made on several of the ice cores in the field using the method developed by Hammer and equipment constructed in our laboratory. The record obtained by this method exhibits peaks which are assumed to correspond to volcanic acid layers.

The two ice cores PS1 (127.55 m long) and PS14 (30.4 m long) drilled 1 km west and 4 km east, respectively, of the Dome were more specifically

used for this study. Along these cores, we selected by ECM the levels for the study of past explosive volcanic activity. Another set of 42 samples (0.4 m long) selected for snow chemistry studies in non-volcanic periods was also analysed: the results are reported elsewhere (Kirchner and Delmas, 1988). We report in Table 1 the various samples which were analyzed on the PS1 and PS14 ice cores.

The ice core sections were sub-sampled following the procedure described by Legrand et al. (1984). In particular, stringent precautions were taken in order to minimize contamination problems. Tools and flasks were pre-washed thoroughly with double deionized water before use. Only the inner part of the ice samples was kept for chemical determinations. All these operations were carried out in a clean air bench installed in a cold room at -15°C. After preparation, the samples placed in double-sealed polyethylene bags, were stored frozen at -15°C until melted at room temperature for chemical analyses. The major soluble ions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>, Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup>) were determined by ion chromatography using a Dionex unit, model 2010i, equipped with preconcentration columns. Cation and anion measurements were each made on 3 ml aliquots.

Excess-sulfate (SO<sub>4</sub><sup>\*</sup>) was calculated from Na according to equation:

$$[\text{SO}_4^*] = [\text{SO}_4] - 0.25[\text{Na}] \quad (1)$$

Table 1. *Samples selected and analyzed along the PS1 (634 samples) and PS14 (775 samples) ice cores*

	Depths (m)	Sampling	Time scale
PS1	0-50.1	0.4 m* every 3 m	1984-~1625
	50.1-69.42	0.05 m, continuous	~1625-~1445
	69.42-111.41	0.4 m* every 3 m	~1445-~1010
* Subsampled every 0.05 m (8 samples), for a total length of 31.3 m			
PS14	0-6.65	every 0.025 m	1984-1953
	6.65-14.40	every 0.05 m	1953-1910
	14.40-16.45	every 0.025 m	1910-1897
	16.45-26.62	every 0.05 m	1897-1827
	26.62-29.58	every 0.025 m	1827-1807
	29.58-30.42	every 0.05 m	1807-1800

Similarly excess-chloride ( $\text{Cl}^*$ ) was obtained by equation (2):

$$[\text{Cl}^*] = [\text{Cl}] - 1.8[\text{Na}] \quad (2)$$

(All concentrations in  $\text{ng} \cdot \text{g}^{-1}$ ).

Analytical uncertainties were calculated from the linear regression coefficients of the calibration curves obtained from standard solution measurements. The degree of contamination was regularly controlled with the aid of blanks included amongst the samples. A total of 634 samples from PS1 and 775 samples from PS14 were analysed.

Bulk meltwater samples (50–100 ml) from 9 major volcanic horizons selected along the PS1 and PS14 ice cores (1816, 1809, 1795, 1641, 1621, 1600, 1596, 1450 and 1259 AD ( $\pm 5$  years) eruptions) were filtered on Nuclepore filters (porosity  $0.45 \mu\text{m}$ ), each sample covering 4 to 9 years (0.5–1.0 m of ice). The insoluble volcanic shards were then examined and analysed by scanning electron microscope (SEM) and energy-dispersive X-ray (EDAX) analysis.

### 3. Dating of the ice cores

The two ice cores used in this study were dated step by step as follows.

(1) A preliminary age-depth profile was first calculated from the values of the snow accumulations obtained at South Pole by previous studies (Jouzel et al., 1983). However the range of these values being relatively large:  $6.6\text{--}12.5 \text{ g cm}^{-2} \text{ a}^{-1}$ , this dating is very inaccurate.

(2) A recent stratigraphical study of a 202 m ice core drilled 50 m from PS1 gives a mean accumulation of  $8 \text{ g cm}^{-2} \text{ a}^{-1}$  for the last  $2000 \pm 60$  years (Gow, personal communication). Using this value the age of the bottom of the PS1 profile is 1080 AD with an uncertainty [ $+400$ ,  $-150$  years], corresponding to an accumulation varying in the range  $6\text{--}10 \text{ g cm}^{-2} \text{ a}^{-1}$ . (Kirchner and Delmas, 1988).

(3) Langway et al. (1988) discovered an inter-hemispheric volcanic time-marker dated 1259 AD in ice cores from Greenland and Antarctica. It is the largest acid signal of the last 1000 years. At South Pole, in their ice core collected in 1978, it was found at a depth of 87.8 m. In PS1 (collected 5 years later) a very strong acid signal

corresponding to the highest sulfate level of the whole ice core was detected at 87.9 m. We have therefore taken this peak as being the 1259 signal. With this time marker, the mean accumulation at our drilling site is then adjusted to  $7.5 \text{ g cm}^{-2} \text{ a}^{-1}$  over the last 724 years.

(4) The continuous chemical study over the 30.42 m of the PS14 firn core made it possible to refine the chronology since 1800 AD by identifying most major volcanic acid layers one after the other, beginning from the surface.

(5) Between 1259 and 1800 AD (540 years), the age uncertainty, estimated at around  $\pm 10$  years, has been tentatively improved with the aid of a few volcanic events (see below). In conclusion, the chronology of our ice cores may be considered to be established to within  $\pm 2$  years for the time period 1790–1983 and probably  $\pm 10$  years, before except for some time periods where accumulation rate could have changed drastically. The key reference horizons are Tambora (1816) and overall the unknown 1259 volcanic signal. Consequently, if the 1259 signal would be erroneously dated or identified, all the following discussions would have to be changed significantly.

## 4. Results and discussion

### 4.1. Introduction

The background sulfate depth profile reported for PS1 by Kirchner and Delmas (1988) is assumed to be linked to the transport of marine biogenic sulfate in the Antarctic troposphere. It exhibits fluctuations which can be attributed either to source strength variations (possible changes in the marine biogenic activity in the surrounding oceans) or to transport phenomena.

From time to time, volcanic eruptions disturb the background sulfate level. During 1 to 2 years the concentration of sulfate in the snow is then markedly higher than the "normal" variations of the background values ( $55.0 \pm 11.6 \text{ ng g}^{-1}$ , Kirchner and Delmas, 1988). Exceptionally, the acid spikes detected by ECM may be due to an acid other than  $\text{H}_2\text{SO}_4$  (for instance HCl, see below). Generally only sulfate levels of  $+11.6 \text{ ng g}^{-1}$  above the background and having a duration of at least 1 yr were considered as volcanic.

The volcanic spikes detected and discussed for

the last 1100 years are reported in Table 2. Depths are given both in actual meters (m) and in meters of water-equivalent (m w.e.).

Over the 115.4 meters (76.3 m w.e.) of the ice core analysed in this study we have calculated that the volcanic signals have a total length of 3.65 m w.e., which represents 4.8% of the length of the ice core. In other words, the time periods disturbed by explosive volcanic eruptions would represent roughly 5% of the 10 centuries of the study.

In the following, we will comment in detail on

the volcanic events reported in Table 2. Let us discuss first the last 200 years which had already been studied elsewhere, particularly at Dome C (Legrand and Delmas, 1987). We identify the Tambora eruption (1815, the first depositional marker appearing in 1816 in Antarctica), which is the key horizon for this period. Thereafter, we jump straight to the second key horizon of our profile: the 1259 event and comment on the volcanic events around and before this date. Between 1259 and 1800, we then discuss in more detail the time period 1380–1460 with a large

Table 2. *Volcanic events detected along the PS1 and PS14 ice cores*

Volcano	Dating of the signal A.D.	Depth (m) firn or ice	water equiv.	Deposition flux $\Phi$ ( $\text{mg m}^{-2}$ )	$\text{SO}_4^{2-}$ climax ( $\text{ng g}^{-1}$ )	Duration (years)	Eruption
PS14							
1	1964	4.72	1.89	9.1	146	1.7	Agung
2	1887	18.02	8.30	6.0	107	1.7	Tarawera
3	1884	18.48	8.55	8.2	168	3.0	Krakatoa
4	1880	19.12	8.89	4.4	102	1.7	Cotopaxi
5	1836	25.33	12.37	9.2	150	1.9	Coseguina
6	1831	25.95	12.73	3.6	86	1.3	?
7	1816	28.15	14.00	72.3	766	2.5	Tambora
8	1809	29.01	14.56	29.8	332	2.2	?
PS1							
2	1886	16.93	7.71	13.5	176	2.2	Tarawera
3	1884	17.19	7.85	9.4	152	2.7	Krakatoa
5	1836	24.18	11.72	12.2	182	2.4	Coseguina
7	1816	27.10	13.39	67.6	614	3.3	Tambora
8	1809	27.89	13.85	32.0	365	2.1	?
9	1795	29.78	14.96	6.5	101	2.1	Sub Antarct.
10	1641	48.8	26.73	19.7	224	2.9	Deception?
11	1621	51.19	28.29	10.2	177	1.6	Sub Antarct.
12	1601	53.51	29.82	22.5	184	3.4	Huaynaputina
13	1596	53.96	30.11	21.5	152	3.2	Ruiz
14	1450	68.85	40.35	74.4	569	3.9	?
15	1340	80.05	48.46	19.0	187	2.7	?
16	1279	86.06	52.98	87.3	818	3.1	?
17	1269	86.91	53.62	10.5	242	1.0	?
18	1259	87.94	54.39	135.7	1220	3.6	El Chichon?
19	1191	94.54	59.49	12.1	153	3.0	?
20	1177	95.88	60.54	19.5	293	1.9	?
21	1118	101.5	64.98	10.2	173	2.7	Tarawera?
22	1047	107.9	70.15	2.2	166	1.8	?
23	970	115.01	76.02	13.8	142	2.9	?

Information includes the dating of the acid signal, its depth (in actual meters and meters of water equivalent), the corresponding deposition flux, the maximum value of the sulfate peak, its duration and a tentative identification of the eruption.

eruption around 1450, and, proceeding back progressively to recent centuries, we show that the volcanically quiet 16th century was followed by several strong signals from 1590 to 1650. Finally we look at the scarce eruptions recorded from 1650 to 1800.

This order of commenting the data is dictated by the necessity of having firm chronological horizons for identifying each volcanic eruption one after the other.

#### 4.2. The two last centuries

Fig. 1 was plotted using the continuous sulfate measurements obtained from PS14. Exceptional spikes, assumed to be due to volcanic eruptions were removed from the data set. A spline function was calculated for the values representative of the sulfate background, then volcanic levels were reintroduced in the profile.

In their previous glaciological study at Dome C, Legrand and Delmas (1987) presented a detailed description of the explosive volcanic activity recorded for the last 220 years. However the dating

of their ice core was not accurate enough to definitively identify the two large events (one of them being Tambora) responsible for the double acid signal observed in several Antarctic ice cores at the beginning of the 19th century. The time lag between the two spikes of the doublet was about 7 years, as we find also at South Pole. The issue was therefore to determine which of these two peaks corresponded to Tambora and to tentatively identify the eruption responsible for the other one. The catalogue of Simkin et al. (1981) on past volcanic eruptions indicates a large event in 1822 (Galunggung) but none around 1810. Zanolini et al. (1985) concluded therefore that the deepest signal was Tambora. The absence of glass shards with a composition corresponding to that of Tambora cast doubt on this first conclusion (De Angelis et al., 1985). Legrand and Delmas (1987) recognized that no firm conclusion was possible.

The two large acid signals of the doublet were found at 28.15 and 29.01 m depth for PS14 and at 27.10 and 27.9 m for PS1. Fig. 2 shows that the

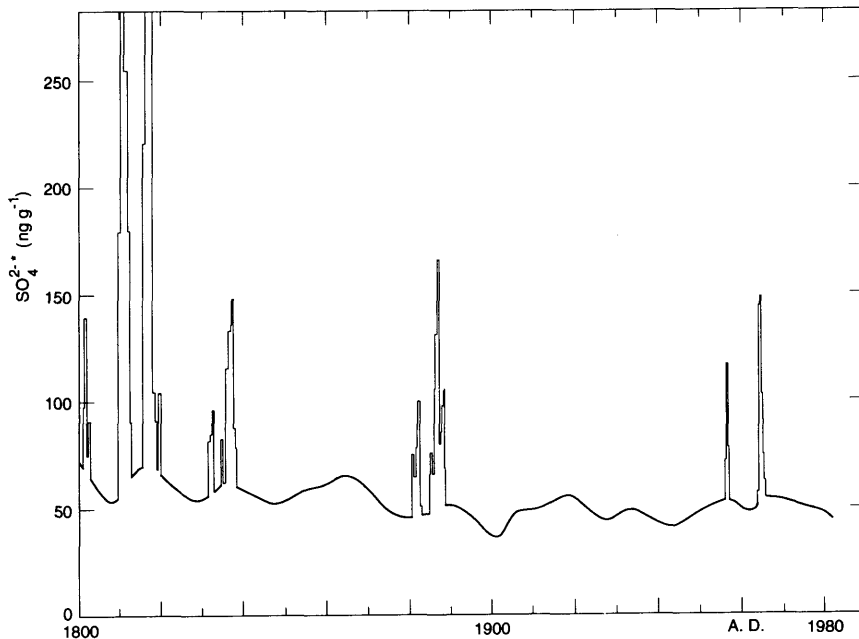


Fig. 1. Excess-sulfate profile at South Pole (PS14 ice core) over the last 180 years. Volcanic levels are superimposed on the fluctuating biogenic sulfate background. Two very strong eruptions (the doublet) are recorded in 1809-10 (unknown eruption) and 1816-17 (Tambora). Coseguina (1836), Krakatoa + Tarawera (1885-87) and Agung (1965) are the other most salient recorded eruptions (see text).

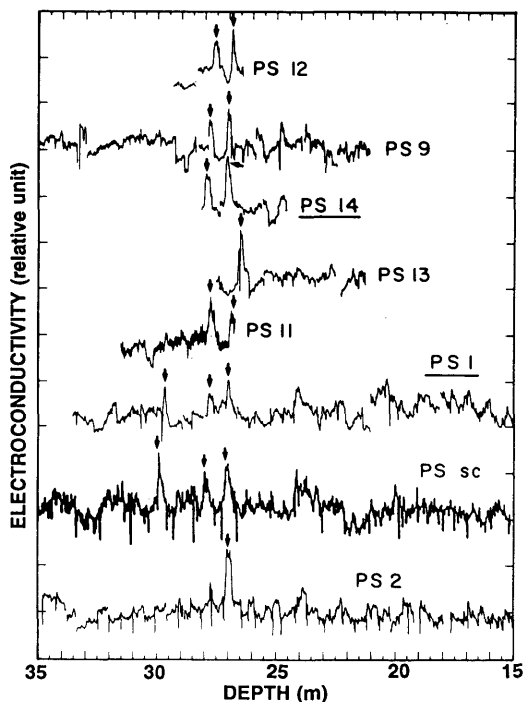


Fig. 2. ECM (Electroconductometric measurements) data on 8 firn cores obtained by M. Legrand and J. R. Petit (PS1, 2, 9, 11, 12, 13 and 14) and J. Schwander (PSsc) at South Pole for the time period of the doublet (beginning of the 19th Century). The most recent peak (arrow) corresponds to Tambora. Sometimes a third spike is visible, in relation to a Cl-event dated 1796.

doublet was detected in most of the firn cores studied by ECM around South Pole but the interpretation of the records is not always straightforward since some spikes were occasionally missing (see for instance the case of PS2). The profiles of major ions were obtained continuously for the upper part of the PS14 core where, occasionally, other volcanic events were detected and identified. This work allowed a relatively accurate dating up to the first part of the 19th century. The detail of the snow chemistry for the "Tambora years" is reported in Figs. 3a and 3b.

The conundrum was solved by the use of SEM (Scanning Electron Microscopy) and EDAX (Energy-Dispersive X-ray Analysis) techniques applied to the glass shard particles found in the deposits obtained by filtering bulk meltwater samples from the two major volcanic levels suspected to correspond to Tambora in PS14. The details of

the measurements are given by Palais et al. (1990). It is shown that the chemical composition of the glass shards collected in the upper acid layer of the doublet is very similar to the results given by a microprobe analysis of glass particles collected in the plinian deposits from the 1815 Tambora eruption. Particles extracted from the other acid peak have a different composition which allows us to conclude that this signal is not that of Tambora. A similar conclusion was formulated by De Angelis et al. (1985) on the basis of the SEM/EDAX analysis of glass shards detected in the lowest acid layer of the doublet in the Dome C ice core. In this case, the second volcanic event of the doublet has to be dated 1809 and could correspond, according to the chemical composition of the ash and due to the lack of a marked signal in Greenland snow at this time (Hammer et al., 1980), to an unknown eruption in the Southern Hemisphere.

The fixing of the Tambora level at 27.1 and 28.15 m depth for PS1 and PS14, respectively leads to mean accumulation rates of 7.97 and 8.33  $\text{g cm}^{-2} \text{a}^{-1}$  between the surface and 1816. We will see that the identification of the volcanic eruptions recorded for the 19th and 20th centuries is in agreement with this dating.

The dating given by Schwander (1984) on the basis of his ECM record (PSsc in Fig. 2) has been corrected in order to fit with all our results, and particularly with those of PS1 since PSsc and PS1 were drilled only 50 m apart. The upper 6.5 m of PS14 have been accurately dated ( $\pm 1$  year) and chemically analysed in great detail. The acid fallout of Agung, already discussed in other papers (Legrand and Delmas, 1984, 1987) culminates at  $146 \text{ ng} \cdot \text{g}^{-1}$  of  $\text{nssSO}_4$  at 4.7 m depth. This signal will not be further discussed here. The minor sulfate spike at 6 m depth could be tentatively attributed to the Nilahue volcano, which erupted violently ( $\text{VEI} = 4$ ) on July 1955 in Chile ( $40^\circ 35' \text{S}$ ). The first half of the twentieth century was remarkably quiet and no unambiguous sulfate signal is recorded (for instance Rabaul eruption,  $\text{VEI} = 4$ , in 1937 or Cerro Azul eruption,  $\text{VEI} = 5$ , in 1932, Simkin et al., 1981). The first years of the century appear to have low sulfate levels, the Santa Maria, Soufrière and Montagne Pelée eruptions (1902–03) being not clearly recorded in the sulfate profile, whereas at Dome C (Legrand and Delmas, 1987) the sulfate signals corresponding to these events were rather well identified. This suggests

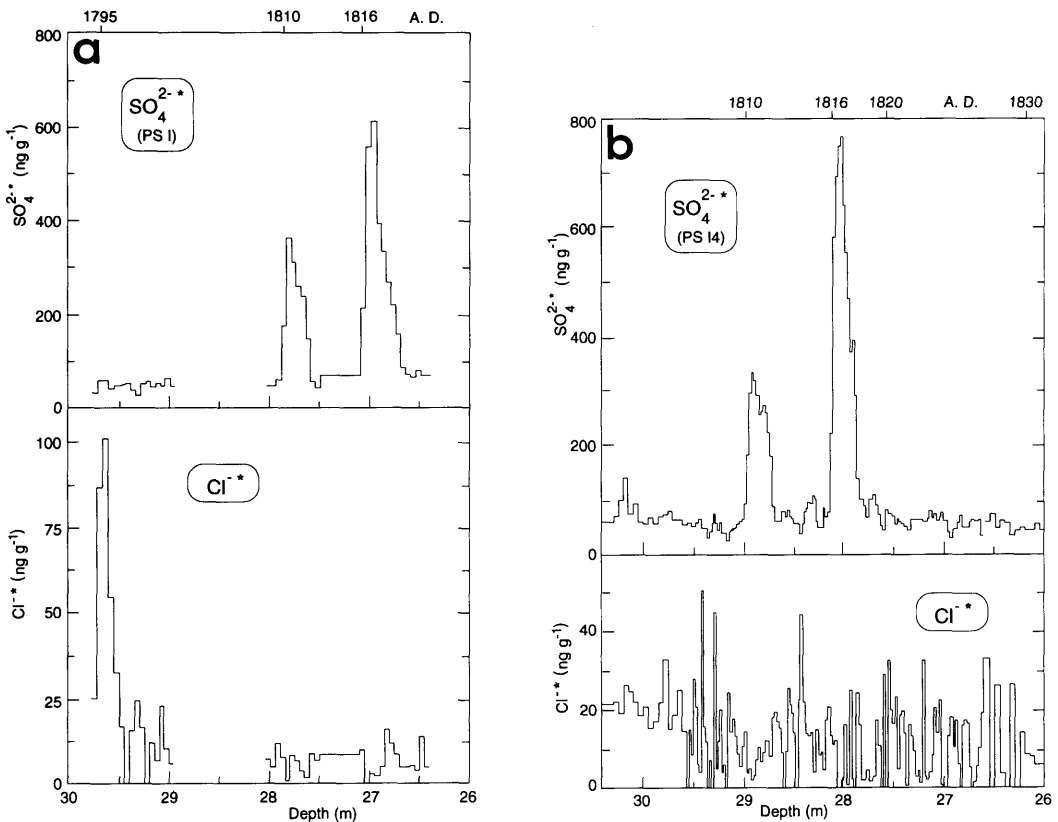


Fig. 3. Excess-sulfate ( $\text{SO}_4^{2-}$ ) and excess-chloride ( $\text{Cl}^-$ ) concentrations for the end of the 18th and the beginning of the 19th centuries. (a) PS1, (b) PS14.

that additional minor eruptions could be better detected at sites of lower accumulation rates, as earlier emphasized (Delmas et al., 1985).

The next volcanic sequence to examine is the Krakatoa period (Fig. 4) which is located around 17–18 m depth in PS1 and PS14. Even if the shape of the signal is not exactly the same in both profiles, a relatively long volcanic sequence is obvious and confirms previous publications (Delmas and Boutron, 1980; Delmas et al., 1985; Legrand and Delmas, 1987). It is generally accepted that Tarawera's fallout (June 1886) followed immediately that of Krakatoa (August 1883). The recent DEP (high frequency dielectric profiling) reported by Moore et al. (1991) for Mizuho Station (East Dronning Maud Land) clearly exhibits two distinct volcanic signals at this time. In Greenland the high acidity levels also last from 1884 to 1887 (Hammer, 1977) but the

eruptions which caused this phenomenon could be different in the two hemispheres, except for the case of Krakatoa which is universally recognized as being an event of global significance. For PS14, an additional eruption (not identified, Cotopaxi, 1877?) seems to be recorded a few years before Krakatoa.

Let us examine now the time period corresponding to the depths 24–27 m in PS14 and 23–25 m in PS1 (1830–1840 years, see Fig. 5). It includes the famous eruption of Coseguina ( $13^\circ\text{N}$ ) in Nicaragua in 1835. Even if this event seems to be well recorded at Dome C (Legrand and Delmas, 1987), its strength was strongly overestimated in the past, as already pointed out by Self et al. (1981, 1989). In the continuously analysed PS14 core, there are clearly 2 volcanic events recorded within a few years of each other. The more recent and also the strongest (culminating at  $150 \text{ ng g}^{-1}$  of sulfate)

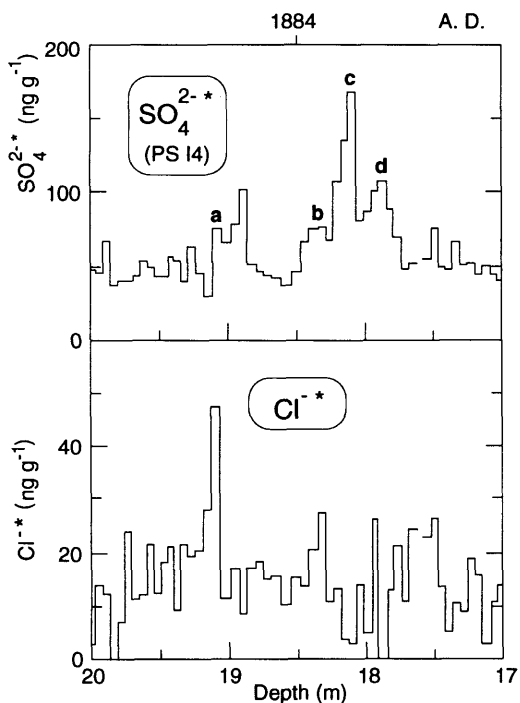


Fig. 4. Excess-sulfate ( $\text{SO}_4^{2-*}$ ) and excess-chloride ( $\text{Cl}^{-*}$ ) concentrations for a time period centered on 1884 (PS14 ice core). (b) and (c) peaks are most likely linked to Krakatoa, (d)-peak to Tarawera (New-Zealand). (a)-peak is due to an unknown eruption.

is dated  $1836 \pm 2$  and is likely Coseguina whereas the second (maximum sulfate level  $100 \text{ ng g}^{-1}$ ) could correspond to the Babuyan eruption in the Philippines ( $19^\circ \text{N}$ ) in 1831 as discussed by Lamb (1970). La Marche and Hirschboeck (1984) mention frost rings in 1831 in the Northern Hemisphere. We conclude that the Coseguina eruption is most probably recorded at South Pole, but that it was a moderate event. The values of the accumulation rate for PS14 and PS1 assuming the Coseguina eruption is at 25.33 and 24.18 m depth, respectively, are compatible with the dating of both ice cores as already proposed.

Finally we emphasize that no other noticeable sulfate spike is observed between Coseguina and 1877, except for a questionable signal around 1863.

#### 4.3. The large eruption of 1259 and the time period 970–1280

The 1259 eruption was first pointed out and commented by Langway et al. (1988) in a

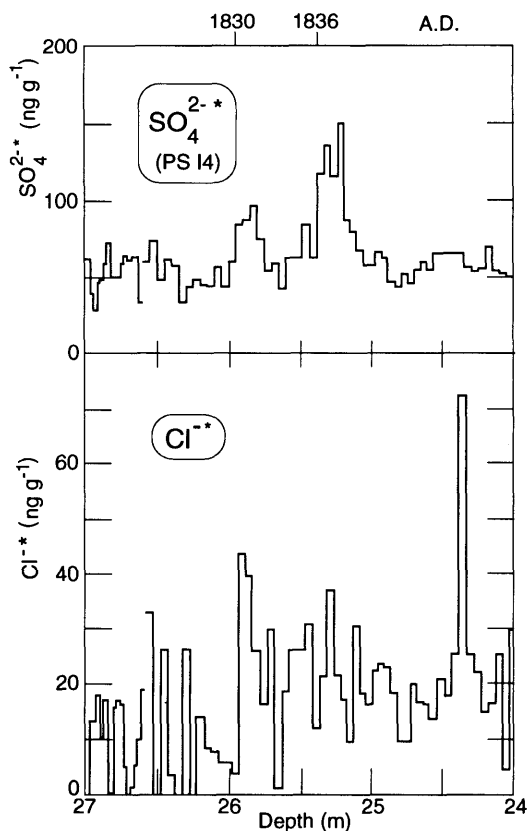


Fig. 5. Excess-sulfate ( $\text{SO}_4^{2-*}$ ) and excess-chloride ( $\text{Cl}^{-*}$ ) concentrations for a time period encompassing the eruption of Coseguina (1835). (PS14 ice core).

glaciochemical study at several locations in both Greenland and Antarctica. It is situated in our profile between 87.94 (54.40 m w.e.) and 87.59 m depth (54.18 m w.e.) and covers therefore 35 cm of firn (i.e., about 2.5 yr) (Fig. 6). The highest sulfate value is  $1220 \text{ ng g}^{-1}$ , which is nearly double the Tambora signal. It is clearly recorded by Schwander (1984) at 88.5 m depth. This global event, the strongest of the last millennium, has not been identified positively but the chemical composition of fine ash particles reported by Palais et al. (1990) suggests strongly that it is an early eruption of the volcano El Chichon in Yucatan (Mexico). Around the date of this major eruption, a series of other significant eruptions took place between 1177 and 1272. Some of them have also been detected at Crête in Greenland (Hammer



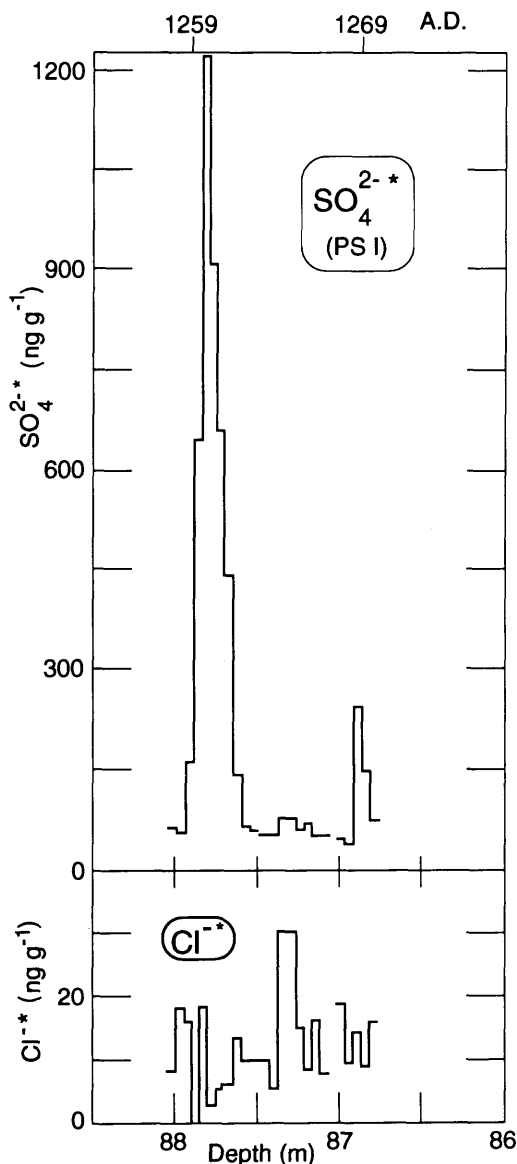


Fig. 6. Excess-sulfate ( $\text{SO}_4^{2-*}$ ) and excess-chloride ( $\text{Cl}^-$ ) concentrations in PS1 for the time of the huge 1259 volcanic eruption. Note the absence of any significant perturbation on the chloride profile at the time of the sulfate peak.

et al., 1980), which allows, by comparison, an accurate dating of our own profile at South Pole up to 1178 AD.

The most recent eruption (at 53 m w.e.) of this series is dated 1279 AD by us and 1276 on

Schwander's profile, but it does not appear unambiguously in Greenland profiles, even though its ECM climax at South Pole is higher than Tambora. It could be an eruption confined to the Southern Hemisphere.

Between 86.76 and 86.91 m depth (53.62 m w.e.) an eruption of mid strength ( $242 \text{ ng g}^{-1}$  of  $\text{SO}_4^*$ ) has been detected at South Pole (both by us and Schwander) and dated 1269. This eruption of short duration ( $< 2$  years) is not seen in the Crête profile and therefore also occurred most probably at mid or high southern latitudes.

Schwander's profile exhibits a strong signal (not found by us) around 1230. It corresponds satisfactorily with the strong signal found by Hammer et al., at Crête in 1228 (but not identified) and to frost rings dated 1227 AD by La Marche et al. (1984). Between 94.54 m (59.50 m w.e.) and 94.25 m is found a moderate signal (maximum value  $152 \text{ ng g}^{-1}$ ) dated 1191 at South Pole in our profile and 1196 by Schwander in his profile. No signal is observed at this time in Greenland.

Finally we find a sulfate peak ( $292 \text{ ng g}^{-1}$ ) between 95.70 and 95.88 m (60.54 m w.e.) (dated 1177 AD). Its duration ( $< 2$  years) first suggests that the event could be located at high southern latitudes. However a very sharp signal is found by Hammer in 1178 at Crête, which indicates a mid or low latitude for this eruption.

The deepest part of the South Pole ice core has not been studied exhaustively. We find 3 major events between 100 and 116 m: at 101.5 m (1118 AD), 107.9 m (1047 AD) and 115 m (970 AD). The 101.5 m peak, assessed by the conductometric method, but not chemically studied, is not recorded at Crête. It could be linked to a large eruption of Tarawera (New-Zealand) which occurred around this date (Simkin et al., 1981). The 1047 event (climax  $165 \text{ ng g}^{-1}$  of sulfate) is also not recorded in Greenland. On the other hand, the 970 AD eruption (maximum  $141 \text{ ng g}^{-1}$  of sulfate) seems to be recorded also in Greenland at the same date.

#### 4.4. The "1450 event" and the time period 1380–1460

The 1450 volcanic event lasts from 68.85 (40.35 m w.e.) to 68.48 m (40.13 m w.e.). From the thickness of the acid layer (22 cm w.e.), we deduce that the atmospheric effects were significant for nearly 3 years. Considering this duration and the

strength of the sulfate signal, (culminating at  $570 \text{ ng g}^{-1}$  of  $\text{SO}_4^*$ ; Fig. 7), this event was likely of global significance. In addition two small eruptions (maximum  $100 \text{ ng g}^{-1}$  of sulfate) occurred 3 years before and 4.5 years after this very strong eruption. The "1450 event" is also clearly recorded in the conductivity profiles of Schwander (1984) and Moore et al. (1991), as well as in the sulfate and ECM profiles of Zanolini et al. (1985) (at 120.5 m of ice with a climax equal to the value found at South Pole). In the Northern Hemisphere, there are some traces of this eruption: a relatively modest acid spike at Crête, central Greenland, found by Hammer et al. (1980) in 1453 and a major frost ring dated 1453 in Western USA

by La Marche et al. (1984). At this point of the discussion, it may be concluded that there was in 1452 AD a large eruption in the Southern Hemisphere with noticeable effects in the Northern Hemisphere.

The microparticle profile obtained by Mosley-Thompson and Thompson (1982) for the South Pole is most interesting. At 35.5–36 m depth (m w.e.) in an ice core collected in 1974, these authors detected one of the four largest concentration levels of particles (more than  $10^5$  particles/g of water). The perturbation, lasting about 15 years, was dated 1450–1470 AD. Taking into account the spatial variability of the snow accumulation rates around the Amundsen Scott base and the uncertainties in the dating (Kirchner, 1988), we believe that the "1450 event" found by us fits satisfactorily the period of the exceptional microparticle signal detected in the 1974 ice core. This indicates that the eruption was located at high or mid southern latitudes since such particles are tracers of regional eruptions. We have no chemical analysis of microparticles from this depth. It is therefore impossible to conclude on the exact location of the volcano. We suggest Deception Island or the Sandwich Islands as tentative candidates. The chemical signature recorded in Greenland ice was low but the climatic perturbation, which was probably very severe in the Southern Hemisphere, affected the entire globe, which explains the frost rings mentioned by La Marche and Hirschboeck (1984). From the microparticle profile we learn that the paroxysmal eruption was part of a long series of minor events covering one to two decades. Using the publication of La Marche and Hirschboeck and our own dating scale, the "1450 volcanic event" is re-dated 1452 AD.

In the 14th century, only one large signal is observed, dated around 1340 AD (80 m depth). At this date we measure a sulfate peak culminating at  $187 \text{ ng g}^{-1}$  and lasting at least 2 years. It has also been observed by Schwander (1984) and by Hammer et al. (1980) in Greenland (in 1345) which shows that the eruption was of global significance and probably located at low latitudes. However no frost rings were found around this date by La Marche and Hirschboeck.

#### 4.5. The time period 1460–1800

For more than the first hundred years (1460–1590) volcanic activity recorded at South

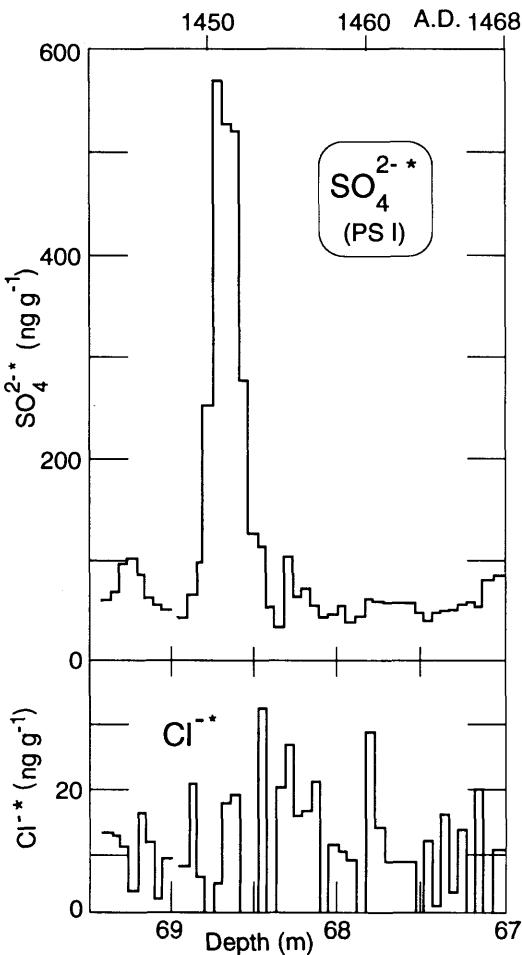


Fig. 7. Excess-sulfate ( $\text{SO}_4^{2-*}$ ) and excess-chloride ( $\text{Cl}^-$ ) concentrations around 1450 AD (PS1 ice core).

Pole appears to be very low, with the first remarkable signal ( $\text{SO}_4^{2-} \sim 100 \text{ ng g}^{-1}$ ) being located at 55.00 m depth (30.70 of water) corresponding to a moderate eruption in 1588 (Kelut  $8^\circ\text{S}$  in 1586?).

In the following years, 3 more noticeable events are recorded at 54.0, 53.51 and 51.19 m depth (30.2, 29.82 and 28.29 m w.e.). They culminate at 152, 184 and 177  $\text{ng g}^{-1}$  of sulfate, respectively (Fig. 8). The chemical composition of the few ash particles found (Palais et al., 1990) indicates that the first event could correspond to Ruiz ( $4^\circ 88'\text{N}$ ). An eruption is indeed documented by Simkin et al. (1981) in March 1595 with a VEI = 4. Note that in the Greenland ice core, Hammer et al. (1980) do not observe a clear signal at this date and furthermore no frost ring is recorded in trees, showing that the eruption concerned mainly the Southern Hemisphere (however Moore et al., 1991, found no signal recorded at this time in East Antarctica). The second eruption at 53.5 m depth may well be the large eruption of Huaynaputina if we rely on the chemical signature of ash particles (Palais et al., 1990). Huaynaputina, located in the Peruvian Andes at  $16^\circ 58'\text{S}$  is well documented in the book written by friar Vasquez de Espinosa (Bullard, 1962). Several arguments, e.g., the occurrence of a very high signal in Greenland in 1601–1602 (Hammer et al., 1980) and a marked tree ring effect at the same date (La Marche and Hirschboeck, 1984) would rank this eruption as a major eruption.

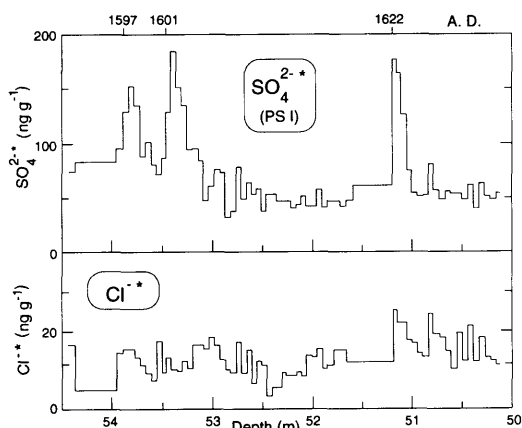


Fig. 8. Excess-sulfate ( $\text{SO}_4^{2-}$ ) and excess-chloride ( $\text{Cl}^-$ ) concentrations from  $\sim 1595$  to 1625 AD, including the Huaynaputina signal (1601), (PS1 ice core).

On the basis of Huaynaputina, the third event at 51.19 m depth can be dated accurately 1621 AD. The ash particle composition indicates a great similarity between this eruption and the Cl-event of 1795, which is believed to correspond to a sub antarctic volcano (Sandwich Island?). Contrary to the DEP of Moore et al. (1991), Schwander's ECM profile does not exhibit a clear signal at this depth and no frost ring is observed in the Northern Hemisphere. The volcanic event at 48.80 m depth (26.73 m w.e.) can be dated 1641, using Huaynaputina as a reference date. The chemical composition of the ash particles filtered from this level indicates that this eruption was most probably located on Deception Island. This identification is corroborated by the finding of a thick (0.5 mm) ash layer at a depth corresponding approximately to this date in an ice core drilled in 1981 on James Ross Island (Aristarain, personal communication), located about 250 km from the assumed eruptive center. All these ash particles have very similar chemical compositions. The sulfate signal peaks at  $224 \text{ ng g}^{-1}$  at South Pole and has a duration of 35 cm i.e., 2.5 years. At about the same time, the Crête profile (Hammer et al., 1980) shows a well marked signal that was attributed to Komagatake (Japan, 1640). The Awu volcano (Indonesia), which erupted violently in January 1641 (Simkin et al., 1981), is also a candidate for the signal ( $3.5 \mu\text{Eq} \cdot \text{l}^{-1}$  of  $\text{H}^+$ ) reported at Crête. It is questionable that a volcanic eruption at  $63^\circ\text{S}$  (the latitude of Deception Isl.) could influence so strongly a site located  $71^\circ\text{N}$ . It is more likely that this Deception Island eruption coincided with a low latitude eruption (e.g., Awu) giving a relatively simultaneous acid spike observed in both ice caps. La Marche et al., found a noticeable frost event in 1640 which could be also attributed to the same eruptions.

After 1642, the next eruption detected conductometrically by us is in 1795 (chloride event). However Schwander found 2 volcanic signals around 1695 and 1743 (these dates were calculated by us) and Moore et al. (1991) found a strong signal in 1675–80 and several others around  $1750 \pm 10$  AD. No frost rings nor acid signals in ice are found in the Northern Hemisphere for these years. The second half of the 17th and the entire 18th centuries can therefore be considered as being volcanically quiet, at least for the Southern Hemisphere. We shall finish the discussion of this

period with the exceptional eruption found in the last decade of the 18th century.

#### 4.6. The chloride event of 1795

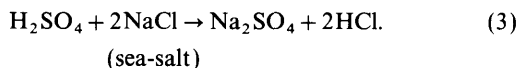
The conductometric profile of PS1 exhibits a marked spike 3 meters below Tambora (Fig. 2). It cannot be confused with the second peak of the doublet since its time lag with Tambora is  $\sim 20$  yr. Its duration is about 2 years and it has never been mentioned in previous studies. Schwander (1984) confused it with the Tambora signal due to an ambiguous ECM record (see Fig. 2). The chemical analyses performed on the 3 conductometric levels removes the ambiguity and allows a clear interpretation of the phenomenon: the 1795 signal is due to an unusual chloride level (up to  $122 \text{ ng g}^{-1}$  found in PS1 at 29.6 m depth) (see Fig. 3).

We have examined whether this event is noticeable in other ice cores from Antarctica. The ECM profile obtained by Zanolini (1982) at D 57 exhibits a strong signal at 30.82 m depth just before the doublet. This conductometric spike cannot be explained by the sulfate and nitrate values which are not exceptional ( $99 \text{ ng g}^{-1}$  and  $33 \text{ ng g}^{-1}$ , respectively). Unfortunately no chloride measurements are available for this level. However the dating of the peak (1796) is a good indication that it corresponds to the same event. At Dome C, the chemical profiles obtained by Legrand (1985) for this time period show that a marked perturbation occurred around 13 m depth (i.e., at the turn of the 18th century) in the chloride content of the snow. Finally the ECM measurements of Schwander (1984) on an ice core retrieved at Siple (Antarctic Peninsula) and dated accurately ( $\pm 1$  year) indicate that a very high conductometric signal is visible for 1794–95 (it was attributed by Schwander to a local volcanic eruption).

Therefore there is evidence that a noticeable event occurred in 1795 in the Antarctic atmosphere even if Moore et al. (1991) observe no corresponding DEP signal at Mizuho Station. A very similar phenomenon has already been reported by Legrand and Delmas (1988) for the Dome C core just one century later. It was attributed to the questionable eruption of Thompson Island at  $54^\circ\text{S}$  in the sub-antarctic ocean.

These authors proposed that this eruption caused a large increase in the tropospheric content in HCl at sub-Antarctic latitudes by the reaction of

$\text{SO}_2$  bubbling from a submarine volcano, rapidly oxidized into  $\text{H}_2\text{SO}_4$  and reacting with sea-salt particles to form HCl according to equation (3):



In the case discussed here, the phenomenon could be similar, but the volcano different since the 1895 event, even if markedly recorded at Dome C, is definitely not visible at South Pole (PS14). The transport of the volcanic gases from the Thompson Island area ( $5^\circ\text{E}$ ) to South Pole is probably less possible than to Dome C. As an explanation for the 1795 event, we favor a submarine volcano located in the Antarctic Peninsula, an area which is known to supply most of the tropospheric aerosol deposited at South Pole (Shaw, 1979) and where active volcanic events at sea level have been discovered (Gonzales-Ferran, 1983).

#### 4.7. Volcanic eruptions and the atmospheric sulfate budget

The mean value for sulfate deposition at South Pole is  $4.2 \text{ mg m}^{-2} \text{ a}^{-1}$  in the absence of volcanic fallout. Table 2 gives the deposition amounts of this compound after large eruptions ( $\Phi$  is in  $\text{ng}$  of sulfate through the full duration of the perturbation). With respect to non-volcanic periods, the increase can be up to about one order of magnitude (in 1259), which would correspond to a pH lowered by about one unit.

Delmas et al. (1985) and Legrand and Delmas (1987) have shown that this deposition depends strongly on the snow accumulation rate (SAR) of the site and for Agung the latter found the following relationship:

$$\Phi = 5.5 + 0.4[\text{SAR}] \quad (4)$$

The sulfate deposition values available for the Agung eruption at Vostok, Dome C, South Pole and D 80 (all central Antarctic locations) lead to relationship 5,

$$\Phi = 6.12 + 0.39[\text{SAR}] \quad (r=0.95), \quad (5)$$

which is very similar to relationship (4). However, such a relationship cannot be obtained for other eruptions like Tambora (including Greenland data) or the 1259 event. Even if this can partly be explained by the uneven distribution of the

volcanic plumes between the two hemispheres (when data of the two ice caps are compared), these results demonstrate that the volcanic deposition patterns are generally relatively inaccurately known.

Taking into account this uncertain estimate of the local sulfate deposition flux, the global deposition (or the source function) of a given volcano has to be calculated with caution. To estimate a latitude correction factor, we have used the method proposed by Langway et al. (1988). These authors based the correction on the deposition patterns of the artificial radioactive debris after the bomb tests of 1954–55 and 1961–62.

The results of this calculation are reported in Table 3 for some of the studied eruptions of global concern. The term GVI (Global Volcanic Index) was introduced by Legrand and Delmas (1987) to rate the strength of volcanic eruptions by emission rates of sulfuric acid estimated from ice cores.

The source functions found by GVI's are significantly higher than the sulfur emissions calculated by volcanologists from the sulfur content of the ash: for instance Palais and Sigurdsson (1989) obtained the figure of 52.4 Tg for Tambora (we find 307 Tg, see Table 3). This discrepancy can easily be explained if one considers that only a minor part of the sulfur bearing gases are degassed from the magma. In any case Palais and Sigurdsson indicate that their values are minimum values.

We have assessed the relative importance of these volcanic eruptions for the sulfate budget at

South Pole over the last millennium and have mentioned in Section 4–1 that about 5% of the time period can be considered as “volcanically disturbed”. As the atmospheric effects of large eruptions last generally two years, a mean of 2.2 eruptions per century are recorded in the South Pole snow. We have indeed counted and examined in detail in this study 24 eruptions in 11 centuries (plus the “Cl eruption”). Their temporal distribution is very uneven, nearly 2/3 of them having occurred during the 19th century. This figure of 2.2 large eruptions per century is probably a conservative estimate since moderate events may have remained undetected by ECM in the part of the ice core where no continuous chemical study was performed. Furthermore, as the strength of the eruptions considered in the preceding sections may be widely different, the volcanic sulfate fallout, as estimated from our measurements, is highly variable from one century to the other. By rating the eruption by the height of their sulfate climax and taking the 20th century arbitrarily equal to 1, we obtain the sulfate fallout values reported in Table 4.

We find that the mean sulfate concentration in the volcanic peaks is  $137 \text{ ng g}^{-1}$  (the biogenic sulfate background being subtracted). By comparing now the biogenic and the volcanic sulfate contributions, we find that volcanic sulfate represents only 13% of the total sulfate deposition (volcanic + biogenic). A previous rough estimate covering only the last 100 years led to a proportion of 30% (at Dome C, Delmas and Boutron, 1980). The

Table 3. *Glaciological volcanic index (GVI) of some of the major events recorded in the PS1 ice core*

Volcano	Year AD	Latitude	GVI (Tg H <sub>2</sub> SO <sub>4</sub> ) this work	GVI at Dome C <sup>a</sup>	GVI at South Pole <sup>b</sup>
Agung	1963	8° S	40	30	—
Krakatoa	1883	6° S	34	30–38	48
Cotopaxi	1877	0° S	19	17	—
Coseguina	1835	13° N	47	23	—
Tambora	1815	8° S	307	> 150	364
Huaynaputina	1600	16° S	100	—	—
Ruiz?	1595	9° N	33	—	—
?	1259	tropical	600	—	394

<sup>a</sup> Legrand and Delmas, 1987.

<sup>b</sup> Langway et al., 1988.

Table 4. *Volcanic sulfate fallout over the last 11 centuries (in arbitrary units, see text)*

Century	XX	XIX	XVIII	XVII	XVI	XV	XIV	XIII	XII	XI	X
eruption number	1	6	0	3	1	2	1	3	3	1	1
sulfate fallout	1	14	0	4	1	6	1	22	4	1	1

discrepancy is mainly due to the fact that at this time every fluctuation of the sulfate background was interpreted as being caused by an eruption. Moreover the present study is much more detailed and reliable.

Finally, the mean annual volcanic sulfate deposition at South Pole is estimated to be  $\sim 55 \text{ ng/cm}^2$  over the millennium. Extrapolated to the entire Earth ( $5.1 \times 10^{18} \text{ cm}^2$ ), the contribution of explosive volcanos is calculated to be only  $0.28 \text{ Tg a}^{-1}$ . Even if this kind of calculation includes major uncertainties and assumptions, it can be deduced that this sulfur contribution is probably minor in the volcanic sulfur budget (estimated to be  $36 \text{ Tg a}^{-1}$  by Berresheim and Jaeschke, 1983).

#### 4.8. *Volcanic eruptions and the atmospheric chlorine budget*

It is well established that volcanos introduce large amounts of gaseous sulfur species in the stratosphere. The case of halogen gases is much less certain. Various calculations (see for instance Devine et al., 1984 or Palais and Sigurdsson, 1989) made from the content of this element in the magma, predict that huge amounts of Cl are emitted simultaneously with  $\text{SO}_2$  at the time of the eruption and probably injected into the stratosphere. Note that these are just speculations. Nevertheless this question has to be discussed in depth since chlorine is of particular concern in the stratospheric ozone depletion problem. Volcanic halogen injections to the stratosphere, if any, could be used to validate the chemical processes elaborated for explaining the ozone polar destruction by CFCs.

Ice core studies could be of some help in the discussion. The most important halogen to be considered is Cl. We have assessed the amount of

chloride in the ice in the form of HCl ( $\text{Cl}^*$ , see eq. (2)). In the figures giving the  $\text{SO}_4^*$  peaks of individual eruptions, we have also reported the  $\text{Cl}^*$  profiles. It is clear that none of them show a visible increase of  $\text{Cl}^*$  which could be paralleled with the volcanic sulfate increase (except the case of the 1795 signal which is purely due to chloride). Therefore, on the basis of the present data, we are unable to confirm the assumption that cataclysmic volcanic eruptions contaminate the stratosphere with Cl. Let us consider more specifically the case of the Tambora time period (Fig. 4). There the excess chloride background is  $11 \text{ ng g}^{-1}$ . Let us consider that we are able to detect a 50% increase of this background, i.e.,  $5.5 \text{ ng g}^{-1}$  or a deposition of  $\sim 24 \times 5.5 \times 10^{-9} \times 5.1 \times 10^{18} \text{ g}$  of chloride ( $24 \text{ g cm}^{-2}$  is the amount of snow deposited during the Tambora years and  $5.1 \times 10^{18}$  the area for the Earth in  $\text{cm}^2$ ), i.e.,  $\sim 0.7 \text{ Tg}$  on a global scale.

The profile given in Fig. 4 therefore suggests that the increase of the stratospheric chloride burden due to Tambora was less than 0.7 Tg.

The Cl amount generally present in the stratosphere is estimated at 0.5 Tg (Pinto et al., 1989). Devine et al. (1984) calculated that the release of HCl by Tambora could be as high as 220 Tg. However, as discussed by Pinto et al. (1989), only a minor fraction of this HCl is capable of reaching the stratosphere (4.1 Tg is a more reasonable figure) and other phenomena that tend to reduce this amount in the stratosphere after an eruption have to be considered.

In conclusion, even during the strongest cataclysmic eruptions, our data suggest that the chloride content of the stratosphere is not disturbed. Our data, as well as more theoretical considerations, allow the formulation of quantitative limits.

## 5. Conclusion

It has been possible to detect by ECM and study chemically by ion chromatography 23 large volcanic eruptions recorded in a 115 m ice core drilled near Amundsen-Scott Base (South Pole). Even if some major volcanic events may have escaped detection, it can be assumed that this record is well representative of the global volcanic activity over the last millennium. The 19th century appears clearly to have been a time of particularly intense explosive volcanic activity.

This study confirms the usefulness of ice records for reconstructing past volcanic activity. Volcanic microparticle analyses have to be systematically performed on acid levels in order to identify the geographical location of the recorded eruptions. Other such records obtained at various Antarctic and Greenland sites would help to provide a more

precise assessment of the volcanic sulfate deposition patterns on a global scale.

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