THE ANTHROPOGENIC IMPACT ON SNOW CHEMISTRY
AT COLLE GNIFETTI, SWISS ALPS

by

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ABSTRACT

By chemical analysis of the upper 40 m of a 124 m ice core from a high-altitude Alpine glacier (Colle Gnifetti, Swiss Alps; 4450 m a.s.l.), records of mineral dust, pH, melt-water conductivity, nitrate and sulfate are obtained. The characteristics of the drilling site are discussed, as derived from glacio-meteorological and chemical analysis. As a consequence of high snow-erosion rates (usually during the winter months), annual snow accumulation is dominated by summer precipitation. Clean-air conditions prevail even during summer; however, they are frequently interrupted by polluted air masses or by air masses which are heavily loaded with desert dust.

Absolutely dated reference horizons for Saharan dust, together with the position of the broad nuclear-weapon tritium peak, provide the time-scale for the following statements:

(1) Since at least the turn of the century the background melt-water conductivity has been rising steadily, as has the mean snow acidity. The trend of increasing background conductivity at Colle Gnifetti (1.9 μS/cm around the beginning of this century, and at present 3.4 μS/cm) is found to be comparable with the records of mean melt-water conductivity reported from ice cores from the Canadian High Arctic.

(2) Sulfate and nitrate concentrations are higher by a factor of 4–5 than they were at the beginning of the century. This is to be compared with the two- to three-fold rise in the concentrations in south Greenland during about the same time span.

INTRODUCTION

Glaciochemical records in the polar ice sheets mainly reflect past environmental changes in geochemical cycles and/or atmospheric circulation on a hemispheric or even global scale (Langway and others 1985, De Angelis and others 1984). The chemistry of a mid-latitude glacier, however, is most likely to be related to its local or regional environment, thus providing very direct information on the history of man's impact on his immediate environment. The aim of the present study is to assess to what extent the chemistry of a high-altitude Alpine glacier (Colle Gnifetti, 4450 m a.s.l., hereafter referred to as CG) may have been affected by anthropogenic activities during approximately the last 100 years.

For this purpose an aliquot of the 124 m ice core which was drilled in 1982 to bedrock (Oeschger and others 1978, Schotterer and others 1985) was analyzed for pH, electrolytical conductivity, mineral dust, sulfate and nitrate.

Due to the extreme exposure and the small scale of the sampling site, reliable evaluation of the temporal trends of these chemical parameters is only possible if the actual receptivity conditions of the snow field are well known.

Therefore basic information is given about the present clean-air status and the prevailing pattern of snow and aerosol deposition of the CG site.

SAMPLING SITE

Forming the uppermost catchment area of the Grenzgletscher (Monte Rosa), the CG drilling site is situated 4450 m a.s.l., close to the Swiss−Italian border. Descriptions of drilling activities, ice-core dating and glaciological surveys are given elsewhere (Oeschger and others 1978, Gäggeler and others 1983, Haeberli and others 1983, Alean and others 1983). Therefore only a brief illustration of the glacio-meteorological conditions at the drilling site (partly derived from an automatic weather station in the saddle (Beck, in preparation) is given. Due to the relatively high 10 m firn temperature of about −15 °C, melt layers and thin ice layers or ice lenses, typically 2–10 mm thick, are frequently found at CG, but conditions leading to the percolation of large amounts of melt water are rare, so vertical ice-glands covering more than about one-half of the mean annual snow accumulation have not been observed in the core. Following Haeberli (Alean and others 1983), the ice core was drilled at the boundary between the infiltration−recrystallization zone and the cold infiltration zone, which is situated up-stream of the bore hole. It is assumed, therefore, that post-depositional formation of melt water has not significantly altered the glaciochemical records presented here.

As a consequence of the extreme exposure of the small-scale CG site, net snow accumulation in the saddle area is controlled mainly by wind erosion of the snow surface. Note that the vertical ice cliff, about 100 m east of the drilling site, acts as a perfect sink for drifting snow particles. Automatic snow-gauge readings and δ^{18}O profiles from snow pits dug each year clearly demonstrate that snow erosion mainly affects winter precipitation and newly fallen snow. As a result, the impurity content of the CG ice-core samples may mainly reflect the air and precipitation chemistry of the summer seasons. Due to the preferential remobilization of new snow, dry deposition plays an important role in delivering the impurities to the snow surface throughout the year. From these findings and from our knowledge of frequent Saharan dust deposition at CG (Wagenbach unpublished), it becomes evident that straightforward estimation of air-concentration level from the average impurity content found in CG snow samples would lead to over-estimating the former. Indeed, summer aerosol concentrations on CG were found to be much lower when compared with those observed by the Swiss clean-air station at Jungfraujoch, 3500 m a.s.l. Crustal material (*c.* 1 μg/m^3 at CG) is lower by a factor of 5; partly anthropogenic trace elements like S, Se, Sb, As and Zn are lower by up to a factor of 10 (Wagenbach and others
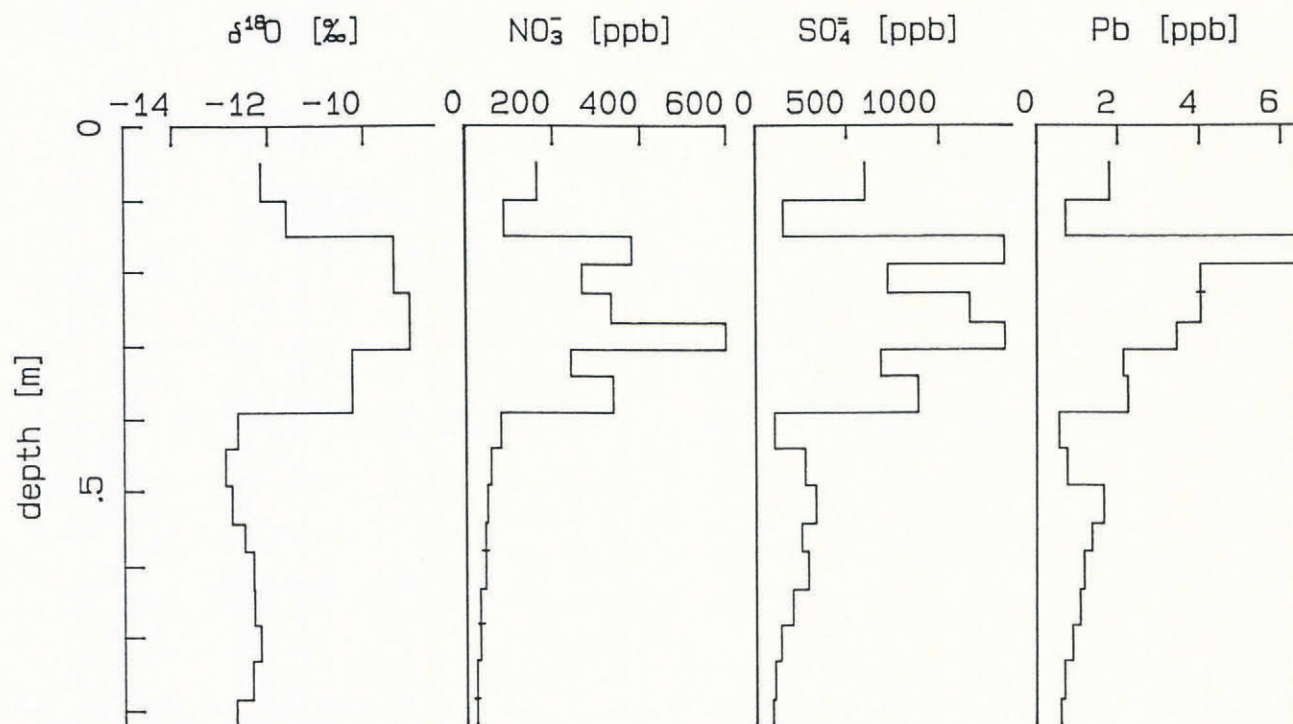
Fig.1. Profiles of $\delta^{18}O$, NO_3^-, SO_4^{2-} and Pb with depth in a shallow snow pit at Colle Gnifetti. The snow surface represents July 1982.

1985). We assume, therefore, that even during summer the CG site is on average well separated from the polluted mixing layer underneath. Exceptions can be attributed to (a) the long-range transport of Saharan air masses or of air masses from polluted areas, (b) very intense vertical mixing, e.g. during summer thunderstorms.

In the following, two illustrations of the effects of such episodic pollution on the snow chemistry of CG are presented. First, sulfate concentrations in newly fallen summer snow (assumed to be the most representative of actual air concentration) range from values as low as 57 ppb during clean-air conditions to 2300 ppb during the advection of Saharan air masses. In addition, sulfate in sleet precipitation from thunderstorm clouds has been measured at concentrations up to 4700 ppb (which are comparable to concentrations at ground level). Secondly, in a snow pit from summer 1982 (Fig.1), concentrations of the "anthropogenic" aerosol species SO_4^{2-}, NO_3^- and Pb show a pronounced peak in the upper part, coincident with very high $\delta^{18}O$ values (where the high $\delta^{18}O$ level probably indicates rapid vertical motion of non-precipitating air masses). The concentrations in the lower part of the pit may reflect true continental background conditions.

ICE CORE
Experimental techniques
Space-charge conductivity (SC) was measured continuously along the core immediately after drilling. For this purpose the core was cut into two parallel sections, the smaller of which was afterwards cut into samples 5–12 cm long. The space-charge signal served as a crude guide for the location of the individual cuts (Schotterer and others 1985). To reduce surface contamination, 5–10 mm of the outer part of the core was removed beforehand by a microtome knife. The samples were melted, and pH was measured by a fast-response glass electrode which had been calibrated in a strong ionic-strength buffer solution. The insoluble residue was analyzed for titanium by X-ray fluorescence spectroscopy (Wagenbach and others 1985) in order to determine the mineral-dust content. Sulfate and nitrate were measured by ion chromatography (IC).

Real laboratory blanks are below 10%, even for the lowest SO_4^{2-} and NO_3^- concentrations observed in the core. The ice-core aliquot was, however, too small to check the

efficiency of the surface-decontamination procedure. Therefore no blank correction has been made so far, and all IC data from the 1982 core are considered as upper concentration limits. Since counting the annual layers is not possible within the CG cores, the upper 40 m of the core were dated by the 1963 nuclear-weapon tritium horizon and, in more detail, by well-documented Saharan dust falls (see Fig.2).

RESULTS AND DISCUSSION
Depth profiles of the chemical bulk parameters pH, melt-water conductivity and mineral dust are presented in Figure 2. The mineral-dust concentration record of approximately the last 100 years is presented on a coarse scale only, to show up the extremely large dust falls used for dating the ice core. The pH and conductivity records are dominated by the highly variable input of crustal material and of acid-related aerosol. Saharan dust layers, for instance, bring the pH up to above 6 and the conductivity up to 23 μS/cm. The pH data given here should not be taken as true H^+ concentrations. It would be difficult to determine the representative pH of the snow samples by the technique used here, in view of the low ionic-strength melt water (in the absence of dust) and, more importantly, also where relatively large amounts of steadily dissolving crustal material are present. Nevertheless it would be easy to identify samples heavily influenced by crustal material or by mineral acids if one used the information from both the pH and the conductivity data. Beyond this, one finds from the pH record that the mean acidity of CG snow has increased markedly since the beginning of this century, and reached its maximum in the mid-seventies. The latter feature is also visible in the space-charge data (Schotterer and others 1985).

A long-term conductivity trend shows up most clearly in the relative minima of the curve. The base-line conductivity has increased steadily over the last 100 years. This is consistent with the general trend observed in the pH curve. No systematic long-term trend is found in the mineral-dust record (except the relatively high input around 1947). Consequently the increase in base-line melt-water conductivity from 1.9 μS/cm at the beginning of the century to about 3.4 μS/cm today may be taken as the net signal due to the anthropogenic impact on the ionic composition
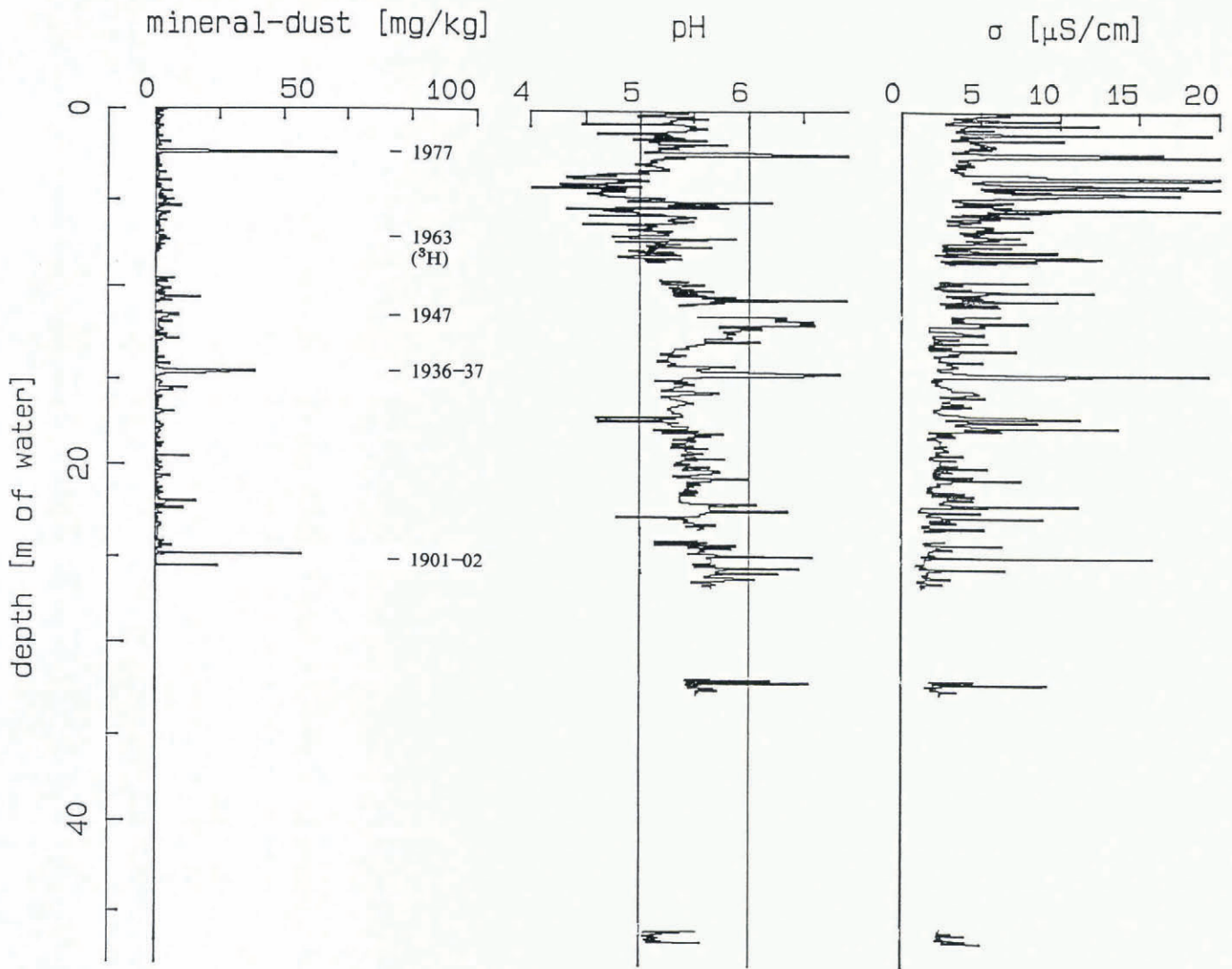
Fig.2. Colle Gnifetti records of mineral dust, pH and melt-water conductivity measured in 5–12 cm sub-samples from the 1982 core. Reference horizons used for core dating are displayed in the mineral-dust profile.

of the continental background aerosol in mid-latitude. The base-line conductivities at CG appear to be consistent with the *mean* values reported by Barrie and others (1985) for the High Arctic Agassiz Ice Cap and Oxford Glacier. The same holds true if the temporal trends are compared.

In order to substantiate the picture presented by the chemical bulk parameters, including SC, nearly all the available sub-samples have been analyzed for sulfate and nitrate by IC. The time variation of mean NO_3^- and SO_4^{2-} found in the individual core samples is shown in Figure 3. In this diagram, mean values of the individual ice-core samples which are represented by four to ten sub-samples have been plotted. These mean values represent a time interval of about 1 year in the upper part of the core section and of about 2 years in the lower part. In order to reduce the contribution by terrigenic sulfate (e.g. gypsum), which is frequently associated with desert dust, all sub-samples with a pH above 6, and those leaving a reddish-brown colour in the filter residue, were discarded. The natural 1σ scatter from sub-sample to sub-sample is about ±70% for sulfate and ±65% for nitrate in the upper part of the core, and ±55% and ±45% respectively in the lower part.

As already suggested by reference to the pH and the base-line conductivity records, the average concentrations of SO_4^{2-} and NO_3^- in CG have increased significantly during the present century. The spline smoothing of the points in Figure 3 clearly emphasizes the general trend.

The large scatter in the records may be attributed primarily to the extreme fluctuations in local glacio-

meteorological conditions on CG, as discussed in the previous section. Direct contamination at the drilling site also cannot be excluded altogether. In the case of sulfate, furthermore, part of the scatter is due to the fact that only the most prominent Saharan dust events have been eliminated from the data. This also leads to a general over-estimation of the anthropogenic sulfate level. From the total amount of Saharan dust, it would be difficult to estimate the amount of terrigenic sulfate which has been deposited, since the sulfate (as well as the calcium) content of various Saharan dust falls differs by more than one order of magnitude (most probably depending on the source region). The same is true for the insoluble sulfate fraction remaining in the corresponding glacial melt water.

Note further that two effects may to some extent have shifted the trends in the direction observed: (a) contamination of the drilling site by increasing tourist activities (e.g. helicopter skiing), and (b) the increasing efficiency, with increasing impermeability (age) of the firn samples, of the decontamination procedures applied. Since surface-snow samples which had obviously not been affected by tourist-borne contamination were found to be not significantly lower in sulfate and nitrate concentration when compared with the uppermost part of the ice-core and the snow-pit samples, and since most helicopter activities were cancelled about 8 years ago, we feel that the long-term increase in local Alpine tourist traffic did not influence to any substantial extent the trends of the ionic impurities which have been observed. Effect (b) is presumably not very large, since the sulfur record presented by Wagenbach and
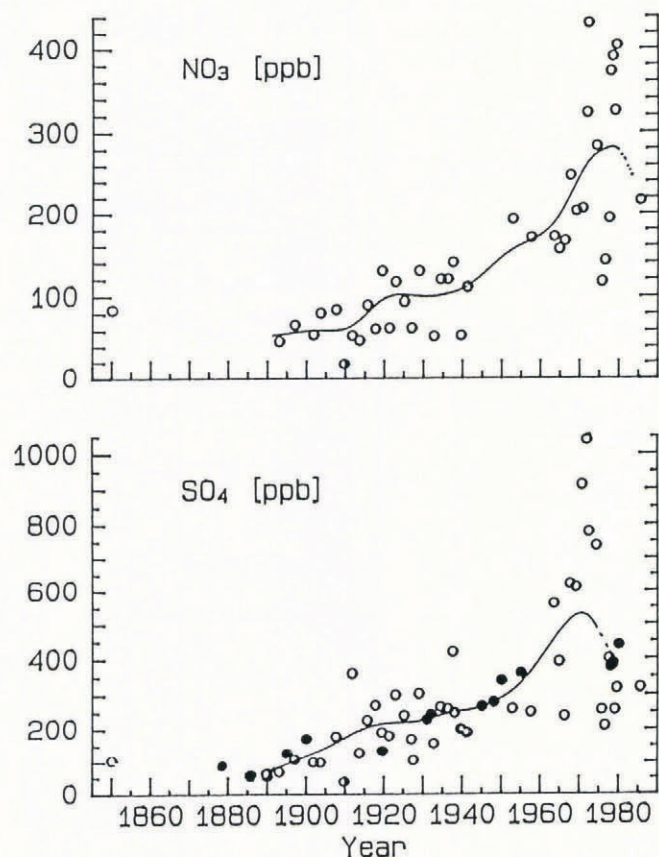
Fig.3. Temporal trends of the concentration of NO_3^- and SO_4^{2-} in melted glacial ice of the Colle Gnifetti cores (open circles represent the 1982 core, solid circles represent the 1977 core). The period of each data point is approximately 1—2 years. For the time-scale, see the reference horizons shown in Figure 2. The most recent data point represents the net snow accumulation between August 1985 and August 1986. Smoothing is by natural cubic spline functions.

others (1985) agrees very well with the general trend in the 1982 core (solid circles in Figure 3). The data published previously is from a core drilled in 1977, at a location very close to the 1982 core. The 1977 core had been decontaminated by scraping it in a much more rigorous way.

At this stage a few general conclusions may be drawn from the historical trend of the sulfate and nitrate which has been observed in CG snow samples:
1. The general trend for both constituents appears to be exclusively due to an increase in the anthropogenic chemical species. Volcanic eruptions do not show a pronounced long-term influence, and are obviously not able to produce the general increase with time that has been observed at CG.
2. The mean sulfate level of 110 ± 45 ppb at the turn of the century (*c.* 1890–1910) is more than a factor of 4 lower than in recent snow (*c.* 1970–1986), which has a level of 480 ± 270 ppb. The corresponding nitrate levels have changed by a factor of about 5 (from 60 ± 20 to 280 ± 110 ppb). Mayewski and others (1986) report, on the basis of Greenland (Dye 3) ice cores, an increase by a factor of 3 for non-sea-salt sulfate, and Neftel and others (1985) find an increase of a factor 2.5 for total sulfate over approximately the last 80 years. As pointed out by Mayewski and others (1987), local contamination of the snow surface at Dye 3 by pollutant sulfate from the camp cannot be ruled out totally. In contrast to the five-fold increase in nitrate observed to have taken place at CG since the turn of the century, present-day nitrate at Dye 3 was found to be higher by only a factor of 2 when compared with snow samples from 1900 (Neftel and others 1985). According to Mayewski and others (1986) Dye 3 nitrate has doubled since the mid-fifties.

Future work

1. For the evaluation of the true anthropogenic influence, the pre-industrial levels of SO_4^- and of NO_3^- at CG still need to be defined more reliably. When this is achieved, comparison with model results, particularly with emission data, will be feasible. Finkel and others (1986), in their review of pre-industrial south Greenland snow sulfate and nitrate data, found average concentrations of 24 and 52 ppb respectively. These values are lower by more than a factor of 4 in sulfate but only slightly lower in nitrate than shown by CG snow from the beginning of the period of continuous measurements (i.e. from about 1890).
2. Further work (detailed snow-pit studies) is needed to investigate the evolution since the mid-seventies of acid-related species on CG.
3. Due to the fact that the increase with time of anthropogenic pollution is clearly visible at CG, it seems possible that even records of those aerosol species (e.g. heavy metals) which are usually plagued by serious contamination problems may be reconstructed if adequate decontamination of the firn cores can be achieved.

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