

Anthropogenic versus natural sources of atmospheric sulphate from an Alpine ice core

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ABSTRACT

Opposite to greenhouse gases, sulphate aerosol particles are expected to cause climate cooling, but uncertainties exist about source variability and strength. We analysed an ice core from a European glacier to quantify source strengths of aerosol-borne sulphate over a 200-year period. Sulphate from emissions of SO₂ increased by more than an order of magnitude during this century. This anthropogenic source is responsible for about 80% of total sulphate in the industrial period, and reflects emissions of west European countries. In the pre-industrial period mineral dust was the dominant contributor, followed by sulphate from SO₂ emissions with volcanoes or biomass burning as possible sources.

1. Introduction

Sulphate aerosol particles originating from anthropogenically emitted SO₂ may have a negative climate forcing which might be sufficient to reduce significantly the positive forcing by anthropogenic greenhouse gases on a regional scale, especially in the Northern Hemisphere (Charlson et al., 1991, 1992; Langner and Rodhe, 1991; Kiel and Briegleb, 1993; Taylor and Penner, 1994; Charlson and Heintzenberg, 1995; Mitchell et al., 1995; IPCC, 1996). Since SO₄²⁻ aerosols have a relatively short atmospheric lifetime of the order of days (Langner and Rodhe, 1991), they are not uniformly mixed throughout the troposphere. To estimate radiative forcing effects, regional information on sulphate aerosol sources and concentrations are therefore required, especially in industrialised regions with rapidly changing rates of emissions during this century.

Strong evidence for a large-scale increase in the atmospheric burden of anthropogenic aerosols has been obtained from Greenland ice cores. For non-sea-salt sulphate a pronounced concentration increase over the past century was found (Neftel et al., 1985; Mayewski et al., 1990). Similar data from Antarctica show no such increase (Legrand and Delmas, 1987), emphasising the strong regional inhomogeneity of aerosol concentrations. Historical records of aerosol related species from non-polar regions are therefore desirable in order to identify concentration trends, to quantify source strengths and to provide input data for models of the atmospheric aerosol burden and its effects.

In this study, we performed a detailed analysis of palaeochemistry records from a high-elevated glacier in the Swiss Alps (Colle Gnifetti, Monte Rosa massif, Swiss Alps, 4450 m asl, 7°51'52"E, 45°53'33"N) covering the time period 1756–1982. The purpose of the analysis was to identify different sources of aerosol SO₄²⁻ from the ice core record and to quantify their contributions to the observed concentration trend using selected source

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tracers. The approach is based on palaeochemistry records extending back over time to the pre-industrialised period (1756–1870) in order to establish the natural background. Previous studies have shown that the Colle Gnifetti glacier is very suited as an archive for the history of air pollution in Europe (Fig. 1) since it is located in the European Alps, which are surrounded by highly populated and industrialised countries (Oeschger et al., 1977; Schotterer et al., 1985; Wagenbach et al., 1988; Wagenbach, 1989; Döscher et al., 1995a, 1996; Maupetit et al., 1995; Wagenbach et al., 1997; Schwikowski, 1997). The site has been glaciologically characterised and meets the requirements of an environmental and climate archive (Oeschger et al., 1977; Alean et al., 1983; Haeberli et al., 1983; Haeberli et al., 1988; Haeberli and Funk, 1991). Studies focusing on the period of industrialisation revealed that several aerosol related species show a marked concentration increase in the ice during this century: NH_4^+ (Döscher et al., 1996), NO_3^- and SO_4^{2-} (Wagenbach et al., 1988; Döscher et al., 1995a), lead (Schwikowski, 1997), and black carbon (Lavanchy et al., 1999).

2. Acquisition of the core, chemical analysis and dating

In 1982 two ice cores were recovered from the Colle Gnifetti, located between the two summits

Signalkuppe and Zumsteinspitze of Monte Rosa (Schotterer et al., 1985). One ice core reached bedrock, revealing a glacier thickness of 124 m, and the second 109 m, of which the top 70 m have been investigated for this study. A borehole temperature of -14°C at 10 m below the surface indicates that this part of the glacier belongs to the cold infiltration zone, where meltwater percolation is negligible. Thus, disturbance of the chemical stratigraphy by meltwater is assumed to be zero, which is a prerequisite for the interpretation of palaeochemistry records. For further details of this site and the glaciochemical studies previously performed there we refer to Oeschger et al. (1977), Haeberli et al. (1983), Alean et al., (1983), Schotterer et al., (1985), Wagenbach et al. (1988), Wagenbach (1989), Wagenbach and Geis (1989), Maupetit et al. (1995), Döscher et al. (1995a), (1996), Wagenbach et al. (1996), and Wagenbach et al. (1997).

Core sections of 0.5 m length and 7.8 cm diameter were sealed at the drilling site in polyethylene bags and kept frozen at -30°C until the processing started. In a cold room, the core sections were cut further into 2.5 to 5.0 cm long samples using a band saw. To reduce surface contamination 0.5 cm of the outer part of the core was removed mechanically by chiselling. The samples were melted only prior to the analysis. All vials and tools were carefully pre-cleaned with ultrapure water (18 $\text{M}\Omega\text{ cm}$ quality) in the

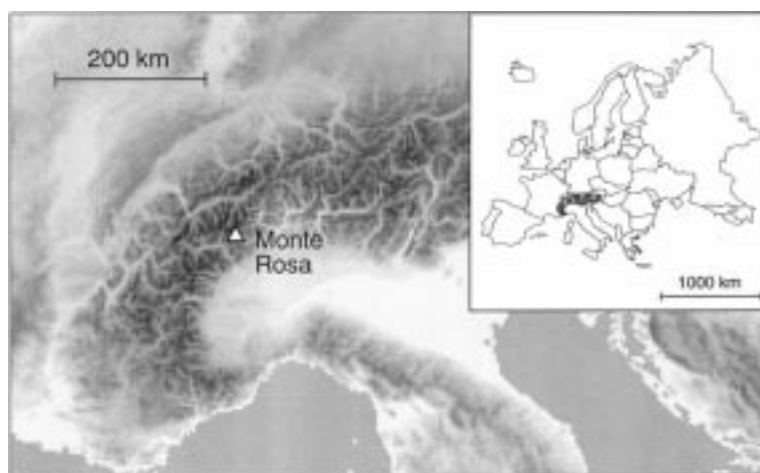


Fig. 1. Topographic map of the Alps showing the location of the Colle Gnifetti. The top panel gives a map of Europe where the Alps are indicated.

laboratory before use. Concentrations of the main water-soluble ionic species Ca^{2+} , Cl^- , K^+ , Mg^{2+} , Na^+ , NH_4^+ , NO_3^- , and SO_4^{2-} were determined by ion chromatography with conductivity detection (Döscher et al., 1995a; Döscher et al., 1995b; Döscher et al., 1996). In selected samples also the total (soluble and insoluble) concentrations of Ca^{2+} , K^+ , Mg^{2+} , and Na^+ were analysed by optical emission spectrometry, and the observed insoluble fraction was negligible (Döscher et al., 1995b). In some samples methane sulphonate (MSA) was also analysed.

The dating of the ice core was established by using well known horizons of Saharan dust events (identified by yellowish layers accompanied by high concentrations of calcium), nuclear weapons testing in 1963 (identified by high tritium concentrations), and volcanic eruptions (identified by high sulphate concentrations together with high sulphate to calcium ratios). In order to obtain a continuous time scale the stratigraphic markers were used to fit the accumulation rate of a simplified ice flow model allowing for the thinning of the ice (Johnsen et al., 1972), as detailed by Döscher et al. (1996), revealing that the 70 m ice

core covers the time period 1756–1982. The resulting time scale was corroborated by continuous measurements of ^{210}Pb (back to 1900). Between the surface and 44 m depth (period 1883–1982) the uncertainty of dating is assumed to be 2 years, and further down (period 1756–1882) 5 years.

3. Data basis and definition of industrial and pre-industrial time period

Concentration records consist of 1451 analysed samples for the 70 m ice core, representing 52.9 m water equivalent (weq). The time resolution ranges between 14 samples per year in the upper part to 4 samples per year in the lower part due to the increasing density and thinning of the ice with depth. In order to maintain a resolution of 4 samples per year, sample size was reduced from 5 to 2.5 cm slices at a depth of 44 m weq. Basic concentration records of SO_4^{2-} , NO_3^- , NH_4^+ , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and Cl^- are shown in Fig. 2. They illustrate the large concentration fluctuations typical for high-alpine snow, which are caused by

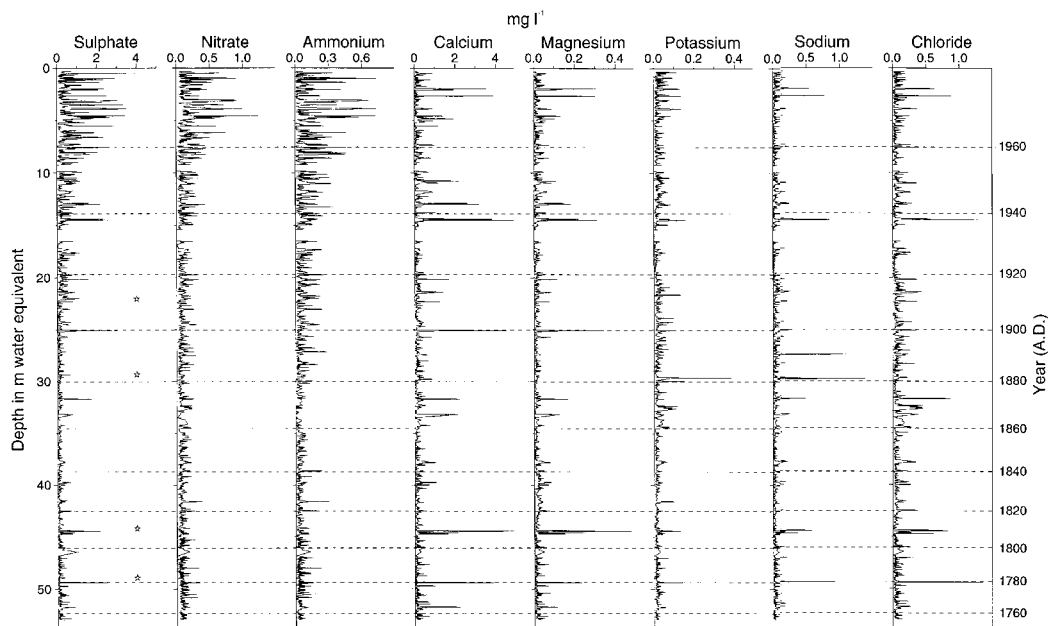


Fig. 2. Concentration records versus depth and time from the Colle Gnifetti ice core. Stars mark the horizons of the volcanic eruptions of Katmai (1912), Krakatau (1883), Tambora (1815), and Laki (1783), however, one has to keep in mind that they were identified by high sulphate to calcium ratios together with high sulphate concentrations.

the strong seasonality of atmospheric transport. During winter, high-alpine sites are decoupled from regional aerosol sources due to strong atmospheric stability (Baltensperger et al., 1997; Lugauer et al., 1998) resulting in low concentrations of aerosol-borne impurities in winter snow. In summer an enhanced vertical transport caused by convection is reflected in higher concentrations of the respective species in the deposited snow (Döscher et al., 1995a, 1996; Nickus et al., 1997).

In order to investigate the industrial and a pre-industrial impurity inventory of snow precipitation, two time periods were selected: 1963–1981 (industrial, 265 samples) and 1756–1870 (pre-industrial, 572 samples). The industrial period represents the maximum in the SO_4^{2-} concentration record, whereas the definition of the pre-industrial period was based on the findings that the concentrations of SO_4^{2-} began to increase significantly at about 1880 (Döscher et al., 1995a; Döscher et al., 1996). In addition, samples were classified into two sub-groups: (1) samples with $[\text{Ca}^{2+}] > 20 \mu\text{eq l}^{-1}$, representing samples dominated by Saharan dust, and (2) samples with $[\text{Ca}^{2+}] < 20 \mu\text{eq l}^{-1}$, representing normal conditions. This classification accounts for the particular situation of Alpine glaciers, where Saharan dust depositions are an annual phenomenon, but showing great variation in intensity (De Angelis and

Gaudichet, 1991). Since Saharan dust deposits are not only characterised by high Ca^{2+} concentrations and alkalinity, but also often by increased levels of most chemical species it is justified to consider these sub-groups separately. It seems that the enhanced concentrations are due to a very efficient scavenging occurring in the warm and moist air masses carrying Saharan dust (Schwikowski et al., 1995). The threshold value of $[\text{Ca}^{2+}] > 20 \mu\text{eq l}^{-1}$ was selected in line with mean Ca^{2+} concentrations of $24 \mu\text{eq l}^{-1}$ determined in alkaline snow samples from the French Alps by Maupetit and Delmas (1994). In the following the samples with $[\text{Ca}^{2+}] > 20 \mu\text{eq l}^{-1}$ are referred to as Ca-rich-industrial and Ca-rich-pre-industrial, whereas those with $[\text{Ca}^{2+}] < 20 \mu\text{eq l}^{-1}$ are referred to as Ca-poor-industrial and Ca-poor-pre-industrial.

25th-quantile, median, and 75th-quantile of the concentrations of chemical species are summarised in Table 1 for all samples of the two time periods, whereas in Tables 2 and 3, the corresponding values for the Ca-rich and Ca-poor samples are given. Generally, concentrations of all species are enhanced in the Ca-rich samples. A significant concentration increase from the pre-industrial to the industrial level is observed for NO_3^- , SO_4^{2-} , and NH_4^+ , reflecting the enhanced anthropogenic emissions (Döscher et al., 1995a, 1996), whereas

Table 1. Characteristic values of the concentrations of chemical species for the industrial (1963–1981, $n = 267$) and pre-industrial time period (1756–1870, $n = 572$) ($\mu\text{eq l}^{-1}$)

		Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
industrial	25th-quantile	0.74	1.39	4.98	0.69	1.28	0.26	0.47	2.35
	median	1.23	2.45	8.79	1.12	3.06	0.43	0.83	4.08
	75th-quantile	2.26	4.5	17.40	1.97	7.5	0.75	1.73	10.03
pre-industrial	25th-quantile	0.71	0.77	0.93	0.57	0.83	0.21	0.54	2.13
	median	1.18	1.17	1.60	0.96	1.61	0.30	0.90	3.89
	75th-quantile	1.96	1.66	2.80	1.65	2.56	0.46	1.55	8.06

Table 2. Same as Table 1, but for the Ca-rich samples ($\mu\text{eq l}^{-1}$)

		Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
industrial ($n = 34$)	25th-quantile	3.54	3.58	16.63	2.8	7.61	0.75	3.66	26.63
	median	4.56	5.73	29.81	4.26	10.83	1.22	4.41	30.98
	75th-quantile	5.74	8.42	43.25	6.30	16.11	1.37	7.03	58
pre-industrial ($n = 44$)	25th-quantile	3.36	1.27	5.52	3.43	2.44	0.63	3.47	26.5
	median	5.45	1.92	7.46	5.13	3.47	0.85	4.29	33.5
	75th-quantile	7.87	2.58	14.2	7.94	4.40	1.24	7.43	53.3

Table 3. Same as Table 1, but for the Ca-poor sample ($\mu\text{eq l}^{-1}$)

		Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
industrial ($n = 233$)	25th-quantile	0.71	1.29	4.60	0.65	1.17	0.25	0.45	2.15
	median	1.06	2.05	7.75	1.02	2.5	0.37	0.72	3.61
	75th-quantile	1.80	3.81	13.48	1.63	6.28	0.61	1.24	6.81
pre-industrial ($n = 219$)	25th-quantile	0.71	0.77	0.91	0.56	0.83	0.21	0.53	2.10
	median	1.11	1.11	1.45	0.89	1.51	0.28	0.82	3.63
	75th-quantile	1.74	1.63	2.49	1.43	2.44	0.42	1.43	6.85

the concentrations of Cl^- , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} remained constant as discussed in the following.

4. Reconstruction of sulphate sources

4.1. Natural sources: sea-spray

For quantifying the contribution of sea-spray to the sulphate concentrations, both Na^+ and Cl^- were tested as possible sea-spray tracers. A correlation analysis between the two species gave: $[\text{Cl}^-] = 0.96[\text{Na}^+] + 0.19$ ($r^2 = 0.97$, industrial period; concentrations in $\mu\text{eq l}^{-1}$) and $[\text{Cl}^-] = 0.98[\text{Na}^+] + 0.37$ ($r^2 = 0.87$, pre-industrial period). The high correlation coefficients indicate a common, predominate source of Na^+ and Cl^- which was independent of the time period. The slopes can be directly interpreted as ratios since the intercepts are near zero. The estimated Cl^- to Na^+ ratio is slightly smaller than the sea-spray molar ratio 1.16. This could either be caused by a loss of Cl^- due to release of HCl from sea-salt particles by reaction with strong mineral acids like H_2SO_4 or HNO_3 (Hitchcock et al., 1980; Clegg and Brimblecombe, 1985) or by an additional source of Na^+ , e.g., mineral dust. The loss of Cl^- during transport seems unlikely since no long-term change in Cl^- concentrations was observed (Döscher et al., 1995a) as it would be expected due to the increase of SO_4^{2-} and NO_3^- concentrations.

An additional source of Na^+ has already been proposed for snow from the French Alps (Maupetit and Delmas, 1994), and our data support their explanation. This source is most likely mineral dust since many minerals have a lower Cl^- to Na^+ ratio than sea-salt (Horn and Adams, 1966), e.g., 0.5 for carbonate minerals which represent an important water soluble fraction of

Saharan dust. Other minerals like clay and sandstone have even lower ratios of only 0.023 and 0.0025 (Horn and Adams, 1966), thus already a small contribution would significantly influence the Cl^- to Na^+ ratio in the snow. Hence, we conclude that long-range transported sea-salt particles are the predominant source of Cl^- and Na^+ in the Colle Gnifetti ice core since 1750. Since the precision of the Na^+ analyses is higher than those of the Cl^- analyses Na^+ was selected as sea-salt tracer in order to estimate the sea-salt contributions to the SO_4^{2-} concentrations, taking a SO_4^{2-} to Na^+ molar ratio of 0.12. There is a possibility that by using Na^+ the actual contribution is slightly overestimated. For the industrial period a contribution of $0.23 \mu\text{eq l}^{-1}$ (2%) of sea-salt SO_4^{2-} to the total SO_4^{2-} was obtained, whereas for the pre-industrial time the contribution amounted to $0.20 \mu\text{eq l}^{-1}$ (7%). Thus, no change in the absolute contribution of sea-salt SO_4^{2-} was observed from pre-industrial to industrial times, reflecting the concentration record of Na^+ which does not show a trend over the studied time period, as illustrated in Fig. 3 by looking at the concentrations plotted on a logarithmic scale. The difference in the percentage is caused by the increased SO_4^{2-} concentrations during the industrial period. Such a small portion of sea-salt SO_4^{2-} is in good agreement with results from snow sampling in the French Alps, where it represented less than 5% of the total SO_4^{2-} (Maupetit and Delmas, 1994). These samples were collected from 1989 to 1991 and are therefore representative for the industrialised time.

4.2. Natural sources: mineral dust

Mineral dust aerosols, particularly those originating from the Sahara, play an important role for the chemical inventories of Alpine glaciers, since

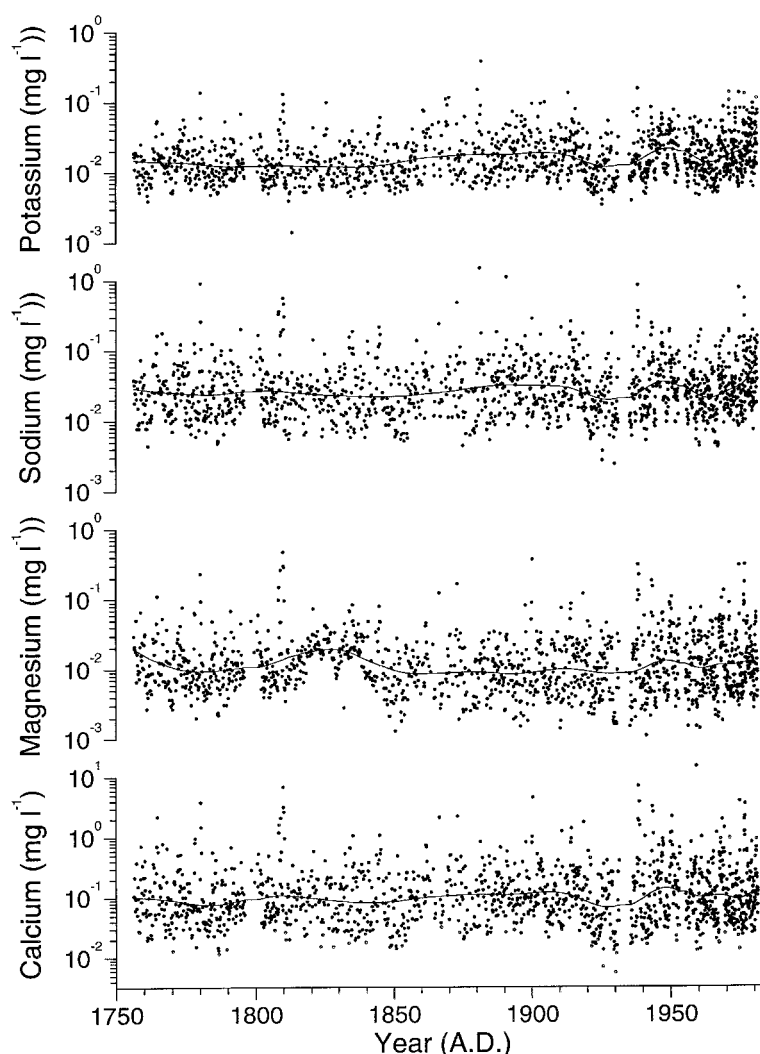


Fig. 3. Concentrations of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ plotted on a logarithmic scale. The solid lines showing smoothed values are to guide the eye.

Saharan dust depositions occur almost annually, but with great variation in intensity (De Angelis and Gaudichet, 1991). As well as typical mineral dust tracers such as Ca^{2+} and Mg^{2+} , they often also significantly contribute to the input of various other chemical species, e.g., SO_4^{2-} , NO_3^- , NH_4^+ , carbonates, organic acids (Schwikowski et al., 1995; Nickus et al., 1997; Wagenbach et al., 1997). Major Saharan dust depositions can easily be identified in the Ca^{2+} and Mg^{2+} concentration records as spikes, and this was utilised for the

dating of the ice core by historically well known events (1977, 1936/37, 1901/02, see Döschner et al., 1996). For some of the Saharan dust events equally pronounced concentration maxima of Na^+ and K^+ were observed. These spikes dominate the concentration records of the respective species. However, by looking at the data on a logarithmic scale no concentration trends of the cations Ca^{2+} , Mg^{2+} , Na^+ , and K^+ are obvious, as already discussed for Na^+ (Fig. 3), neither in the high values nor in the background values. The most

critical point in deducing background concentrations from the records is the discrimination of the Saharan dust contribution. By choosing a logarithmic scale the influence of Saharan dust dominated samples with high concentrations was minimised, and thus a classification of the samples was not necessary in order to look at concentration trends (Fig. 3). We conclude from the constant low and high concentrations of the cation records that the source strengths and the atmospheric concentrations have not changed during the investigated time period assuming constant transport patterns and deposition processes. This is in contrast to a decline of the cation concentrations reported from several precipitation chemistry records in Northern Europe for the time period 1970–1989 (Hedin et al., 1994). These records were based on data from networks in the Netherlands and in Sweden, where the concentration of mineral dust tracers in precipitation are lower than in the southern part of Europe due to the reduced importance of Saharan dust transport (Semb et al., 1995). Thus, in these areas point-source emissions from fuel combustion and industrial processes, as well as open-source emissions, e.g., from traffic on unpaved roads, might have made a larger relative contribution to the total emissions of base cations. In addition, the atmospheric transport of such coarse aerosol constituents up to the high altitude of the glaciers is limited, suggesting that the ice core record rather reflects a natural European background of cations than local or regional emissions. Opposite findings were reported by Wagenbach et al. (1996) from an ice core drilled on the northern slope of Colle Gnifetti close to the drilling site of this study. They stratified their data set into a Saharan dust and a background dominated record. The latter revealed an unexplained long-term change of the Ca^{2+} background level. The increase started in the second half of the 19th century and resulted in a twofold higher level in recent times. However, their raw Ca^{2+} record does not reveal an obvious long-term trend in the dust layer frequency or in the mean Ca^{2+} level and their average concentrations of Ca^{2+} (industrial: 9.5, pre-industrial: 7 $\mu\text{eq l}^{-1}$) are in good agreement with the values presented here (industrial: 11, pre-industrial: 8 $\mu\text{eq l}^{-1}$). Thus, it seems that their trend in the Ca^{2+} background level is induced by the stratification procedure.

Although Ca^{2+} and Mg^{2+} are only minor con-

stituents of mineral dust aerosols, which are in the case of Saharan dust dominated by quartz or calcite (Schütz and Seibert, 1987), both are highly correlated, corroborating a common source. Characteristic values of the regression analysis, performed with non sea-salt Ca^{2+} (nssCa^{2+}) and non sea-salt Mg^{2+} (nssMg^{2+}), which were obtained by correction for the sea-salt contribution, taking Na^+ as tracer with a $\text{Mg}^{2+}/\text{Na}^+$ ratio of 0.227 and a $\text{Ca}^{2+}/\text{Na}^+$ ratio of 0.044 (molar ratios), are: $[\text{nssCa}^{2+}] = 12.3[\text{nssMg}^{2+}] - 3.2$ ($r^2 = 0.78$, industrial period) and $[\text{nssCa}^{2+}] = 8.6[\text{nssMg}^{2+}] - 1.3$ ($r^2 = 0.85$, pre-industrial period). The sea-salt contribution amounted to 1% for Ca^{2+} and 30% for Mg^{2+} , independent of the time period. The slopes of the regression analysis interpreted as $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios are comparable for the industrial and pre-industrial time, indicating a constant dust composition over the last 2 centuries with respect to these tracers. Thus, they can indeed be used in order to quantify the terrestrial source of SO_4^{2-} . However, in contrast to sea-salt, no universal $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ratio exists for mineral dust. In the industrial period, the $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ratio is significantly higher for the samples with high concentrations of Ca^{2+} . This is certainly an effect of higher atmospheric concentrations of SO_2 and SO_4^{2-} , but it is not clear whether SO_4^{2-} is truly enriched in the mineral dust due to heterogeneous reactions or whether an increased scavenging during snow formation erroneously suggests such an enrichment (Schwikowski et al., 1995). The latter seems more likely since an increased ratio is also observed for NH_4^+ . Accordingly, a good correlation between non sea-salt SO_4^{2-} (nssSO_4^{2-}) and nssCa^{2+} was only observed for the pre-industrial period ($[\text{nssSO}_4^{2-}] = 0.175[\text{nssCa}^{2+}]$, $r^2 = 0.68$, concentrations in $\mu\text{eq l}^{-1}$; see Fig. 4). The linear correlation is determined by samples with high concentrations of nssCa^{2+} , indicating the presence of a significant amount of mineral dust. On the other hand, most samples with low nssCa^{2+} show values which scatter above the regression line, hinting to an additional source of nssSO_4^{2-} . Thus, the observed slope of 0.175 is interpreted as the pre-industrial $\text{nssSO}_4^{2-}/\text{nssCa}^{2+}$ ratio of mineral dust in snow at the Colle Gnifetti glacier, which is close to the $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ratio of 0.13 in aerosol samples collected in the Negev desert, Israel, since 1995 (W. Maenhaut, University of Ghent, personal

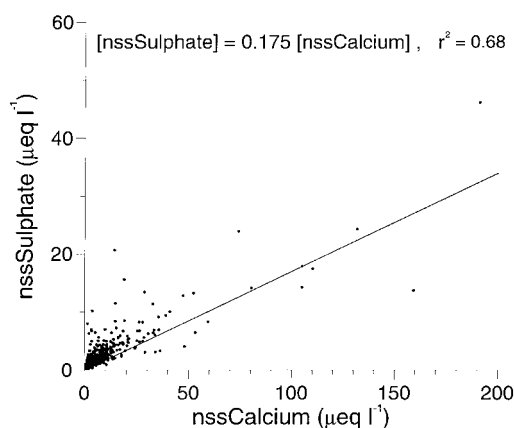


Fig. 4. Scatter plot of pre-industrial nssSO_4^{2-} and nssCa^{2+} concentrations along with the obtained linear regression line. Regression line was forced through zero.

communication), but higher than the 0.08 observed in soils (Vinogradov, 1959). For glacial ice from Summit, Greenland, a higher $\text{nssSO}_4^{2-}/\text{Ca}^{2+}$ ratio of about 0.25 was reported (Legrand et al., 1997). Assuming that the transport patterns and source regions have not changed during the last 2 centuries, the terrestrial SO_4^{2-} contribution can now be estimated for the entire time period by using the pre-industrial $\text{nssSO}_4^{2-}/\text{nssCa}^{2+}$ ratio. For the industrial period mineral dust SO_4^{2-} amounted to 13%, and in the pre-industrial period to 57% of the total SO_4^{2-} , thus being the dominating contributor in this period. The contributions of the different sources to the total concentration of SO_4^{2-} for the two time periods are summarised in Table 4, with exSO_4^{2-} being the SO_4^{2-} concentration after correction for the sea-salt and the terrestrial contribution.

4.3. Natural sources: volcanic emissions

Four horizons were identified in the ice core, attributed to eruptions of the volcanoes Katmai, Alaska (1912), Krakatau, Indonesia (1883), Tambora, Indonesia (1815), and Laki, Iceland (1783) (Döscher et al., 1996; see Fig. 2). In the industrial period, detection of volcanic layers was not possible since the identification criterion (high sulphate concentrations together with high sulphate to calcium ratios) could not be applied due to the enhanced sulphate concentrations from anthropogenic emissions. With the conservative assumption that the entire exSO_4^{2-} detected in the volcanic horizons is of volcanic origin, their contributions to the total exSO_4^{2-} deposition in the respective 5-years period amounted to 35% (Katmai), 59% (Krakatau), 41% (Tambora), and 44% (Laki). Thus, in the pre-industrial period SO_4^{2-} from volcanic eruptions might be a significant source of exSO_4^{2-} . However its impact is restricted to periods of a few years only.

Quiescent degassing from volcanoes and moderate or small eruptions have also been discussed as important natural contributions to the atmospheric sulphur budget (Graf et al., 1997; Simpson et al., 1999). Based on a global model, a relation of the volcanic to the anthropogenic SO_4^{2-} burden in Europe of 47% in summer and 37% in winter was reported (Graf et al., 1998). In that study global volcanic SO_2 emissions were considered including continuous degassing from Mt. Etna in Sicily, which emits sulphur amounts comparable to anthropogenic sources in industrialised Central Europe.

Since no tracer for volcanic degassing was analysed in the ice, its contribution to the SO_4^{2-} inventory can only be indirectly estimated

Table 4. Average concentrations of SO_4^{2-} (mg l^{-1}) from different sources and their percentage contribution to the total SO_4^{2-} for the industrial and pre-industrial time period

	Total SO_4^{2-}	Sea-salt SO_4^{2-}	Mineral dust SO_4^{2-}	Natural ^a	exSO_4^{2-} Anthropogenic ^a
industrial	0.707	0.011 (2%)	0.092 (13%)	0.047 (6%)	0.555 (79%)
pre-industrial	0.131	0.009 (7%)	0.074 (57%)	0.047 (36%)	0

^a Estimation of anthropogenic exSO_4^{2-} is based on the conservative assumption that the pre-industrial exSO_4^{2-} was purely of natural origin and that this natural contribution remained constant over the entire time period.

from the pre-industrial exSO_4^{2-} concentration. Assuming a constant degassing behaviour over the entire time period and the pre-industrial exSO_4^{2-} originating exclusively from the volcanic source, an upper limit of the volcanic contribution of 0.047 mg l^{-1} of SO_4^{2-} would be obtained. Strongly contradicting the model estimates, this represents only 8% of the exSO_4^{2-} in the industrial period, all the more since the pre-industrial exSO_4^{2-} certainly also includes a significant contribution from biomass burning (see below). Although the volcanic source is of minor importance for the sulphur burden in the industrial period, it might have been more significant in pre-industrial times.

4.4. Natural sources: dimethylsulphide (DMS) oxidation

Oxidation of DMS emitted from the oceans is an important source of SO_2 and subsequently SO_4^{2-} on a global scale. However, very low DMS concentrations were observed on a cruise in the North and South Atlantic from 50°N as far as 58°S (Davison et al., 1996a, 1996b), indicating that for continental Europe this source is probably of minor importance due to the long distance from the productive ocean regions. This is in line with the rather small contribution of sea-salt sulphate in the ice core (7% in the pre-industrial period, Table 4). Although determinations of methanesulphonate (MSA) concentrations, an oxidation product of DMS, in the ice were not routinely performed, a few analysis results for pre-industrial ice exist. 80% (282 samples) of the analysis revealed values below the detection limit of 0.001 mg l^{-1} , whereas the remaining samples showed an average concentration of 0.003 mg l^{-1} . Thus, pre-industrial concentrations of MSA in alpine ice are significantly lower than the 0.0029 mg l^{-1} found in interglacial Greenland ice (Legrand et al., 1997), indicating that DMS oxidation is an unimportant source of SO_4^{2-} in Europe, as expected.

4.5. Anthropogenic sources

We assume that the exSO_4^{2-} , which remains after correction for the sea-salt and the terrestrial contribution, originated exclusively from oxidation of SO_2 in the atmosphere. This SO_2 was

emitted either from anthropogenic or natural sources. Temporal changes in SO_2 emissions can thus be deduced from the exSO_4^{2-} record. During the industrial period exSO_4^{2-} constituted the major portion, i.e. 85% of the total SO_4^{2-} , whereas in pre-industrial time it accounted only for 36% (Table 4). In Fig. 5 the historical development of exSO_4^{2-} concentrations is illustrated, revealing a strong increase from 1870 until about 1970, which we interpret directly as a record of anthropogenic SO_2 emissions. ExSO_4^{2-} increased from 0.047 mg l^{-1} in the pre-industrial to 0.602 mg l^{-1} in the industrial time period, equivalent to a factor of 13. The record exhibits interesting details, i.e. the collapse of the 5-years averages after World Wars I and II as well as the extremely steep increase after 1950, presumably due to the enhanced combustion of liquid fuels replacing coal. After 1970 a pronounced downward trend is observed, likely reflecting air pollution control measures and possibly also the economic downturn at that time.

Between 1756 and 1870, no concentration trend of exSO_4^{2-} could be observed. Since the black carbon concentration shows a similar behaviour in this period (Lavanchy et al., 1999; correlation coefficient $r^2 = 0.36$), we assume that a significant portion of the exSO_4^{2-} originated from wood combustion for domestic heating. However, since no universal black carbon/ SO_2 emission ratio can

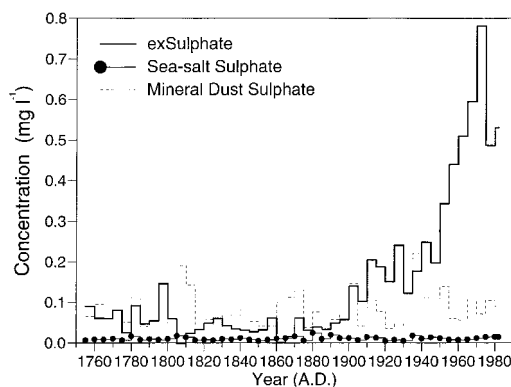


Fig. 5. Record of 5-years averages of exSO_4^{2-} obtained by applying the following formula to each sample: $[\text{exSO}_4^{2-}] = [\text{SO}_4^{2-}] - 0.12[\text{Na}^+] - 0.175[\text{nssCa}^{2+}]$ (concentrations in $\mu\text{eq l}^{-1}$), along with the corresponding records of sea-salt and mineral dust derived SO_4^{2-} .

be applied, a quantification of the contribution of this source was not possible.

The anthropogenic sulphate source in the industrial period can now be estimated having contributed 79% of the total sulphate, thus being the most dominant source (Table 4). This is a conservative estimation based on the assumption that exSO_4^{2-} in the pre-industrial period was purely of natural origin and that this natural contribution remained constant over the entire time period.

In order to determine possible source regions of exSO_4^{2-} in the ice, its development was compared with estimated SO_2 emissions based on the SO_2 emission inventory compiled for each country in Europe from 1880 to 1990 using energy and industry statistics (Mylona, 1993). For the comparison, countries in the vicinity of the Colle Gnifetti were selected (Switzerland, Italy, West Germany, East Germany, France, and total Europe excluding emissions from USSR and Turkey) and their estimated SO_2 emissions were normalised to 100 at the respective maximum value on account of the significant differences of the absolute emissions of the individual countries (Fig. 6). The SO_2 emissions were normalised to their maximum value since the statistics are more reliable in recent times. Only the trends were compared. The historical development of exSO_4^{2-} is similar to the evolution of SO_2 emissions in Switzerland, France, and West Germany, where the maximum was reached in 1965–1975. This indicates that precipitation at the Colle Gnifetti reflects conditions of countries north-west to west of the site, which is consistent with the prevailing air mass transport direction in Europe. Surprisingly, no resemblance with the trend of the Italian emissions occurred, although the Colle Gnifetti is located at the Swiss–Italian border. This is again explained by the main transport directions, and is in agreement with results from trajectory analyses studying the transport from the Po valley, the major source area in Italy, to high-alpine sites (Seibert et al., 1998). The SO_2 emissions in total Europe do not show a downward trend until 1985, due to the impact of eastern European countries (e.g., East Germany, see Fig. 6), where emission control strategies have not been implemented. However, as discussed above, emissions from eastern European countries are not significantly recorded in the Colle Gnifetti ice core.

5. Conclusions

An ice core from the high-altitude Alpine glacier Colle Gnifetti was analysed in order to reconstruct the history of aerosol SO_4^{2-} concentrations in Europe. From the core, high-resolution chemistry records over the time period 1756–1982 could be deduced. A significant increase from the pre-industrial (1755–1870) to the industrial period (1963–1982) was observed for concentrations of NO_3^- , SO_4^{2-} , and NH_4^+ , reflecting the enhanced anthropogenic emissions. Sea-spray and mineral dust tracers Cl^- , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} showed, on the contrary, no concentration trend. Furthermore, in the case of the mineral dust tracers no trend was even detected considering background and Saharan dust concentrations separately.

The following natural SO_4^{2-} sources were considered: sea-spray, mineral dust, volcanic emissions, and DMS oxidation. The sea-spray contribution quantified by using Na^+ as tracer amounted to 0.23 and 0.20 $\mu\text{eq l}^{-1}$ in the industrial and pre-industrial period, representing 2% and 7% of the total SO_4^{2-} . The mineral dust contribution was determined from the pre-industrial nssSO_4^{2-} to nssCa^{2+} ratio, revealing that in pre-industrial times mineral dust was the dominating SO_4^{2-} source, contributing 57% of the total. The mineral dust contribution became less important in the industrial period with only 13%. For volcanoes, eruptive and quiescent emissions were distinguished. Major eruptions like those from Katmai, Krakatau, and Tambora significantly influenced the SO_4^{2-} budget only over a restricted 5-year period in the pre-industrial time, possibly increasing the concentration by about 60% at the most. Quiescent degassing was a minor source during the industrial period, contributing at most 0.047 mg l^{-1} , or 7% of the total. This 7% represent an upper limit. Nevertheless, in pre-industrial times they may have amounted to a significant 38% of the SO_4^{2-} burden. The contribution of DMS oxidation could not be exactly quantified. However, since MSA concentrations were low, we assume that this is an unimportant source.

ExSO_4^{2-} , remaining after correction for sea-salt and mineral dust SO_4^{2-} , was assumed to originate exclusively from oxidation of naturally or anthropogenically emitted SO_2 . The concentration record revealed a large increase of a factor of 13

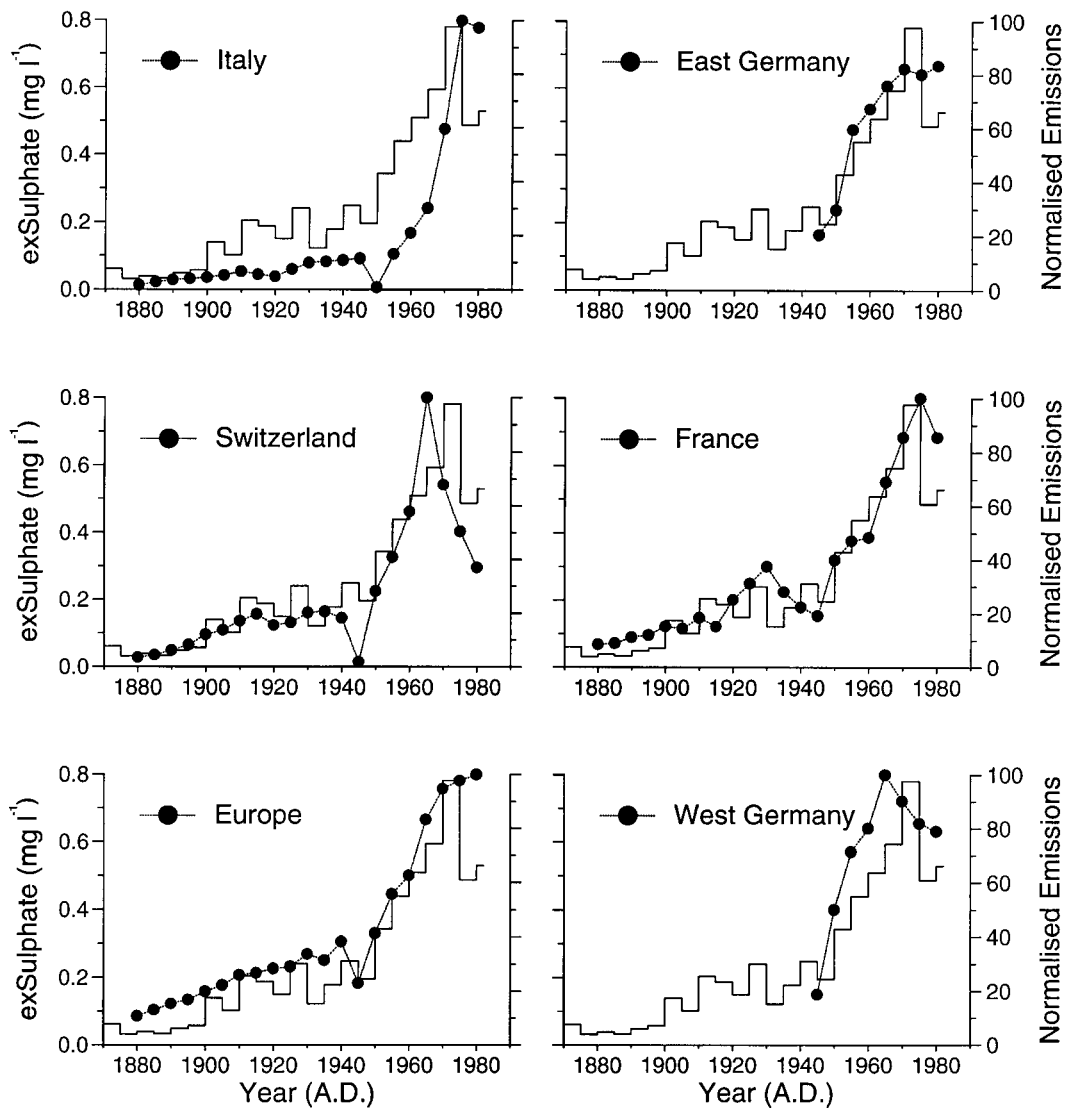


Fig. 6. 5-year averages of exSO_4^{2-} from the Colle Gnifetti ice core (solid step) compared to 5-years estimates of SO_2 emissions in Switzerland, Italy, West Germany, East Germany, France, and total Europe excluding emissions from USSR and Turkey (dashed line, circles), compiled from Mylona (1993). The historical SO_2 emissions are normalised to 100 at their maximum value (in thousand tonnes SO_2 : Switzerland: 330, Italy: 3900, West Germany: 4100, East Germany: 5200, France: 3800, total Europe excluding USSR and Turkey: 42000).

between the pre-industrial and industrial period, starting at about 1870. This increase reflects anthropogenic emissions of SO_2 , constituting 80% of total sulphate in the industrial period. After 1970, a pronounced decline in exSO_4^{2-} concentration was observed due to air pollution control measures. In the pre-industrial period, a correla-

tion between exSO_4^{2-} and black carbon suggests that anthropogenic sources, e.g., wood combustion, were already of importance. A comparison of the general trends of the exSO_4^{2-} record and SO_2 emission estimates for different European countries showed that the Colle Gnifetti ice core reflects emission conditions of west European

countries, which is consistent with the prevailing air mass transport direction in Europe.

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REFERENCES

- Alean, J., Haeberli, W. and Schädler, B. 1983. Snow accumulation, firn temperature and solar radiation in the area of the Colle Gnifetti core drilling site (Monte Rosa, Swiss Alps): distribution patterns and interrelationships. *Zeitschrift für Gletscherkunde und Glazialgeologie* **19**, 131–147.
- Baltensperger, U., Gäggeler, H. W., Jost, D. T., Lugauer, M., Schwikowski, M. and Seibert, P. 1997. Aerosol climatology at the high-alpine site Jungfraujoch, Switzerland. *J. Geophys. Res.* **102**, D16, 19707–19715.
- Charlson, R. J., Langner, J., Rodhe, H., Leovy, C. B. and Warren, S. G. 1991. Perturbation of the northern hemisphere radiative balance by backscattering from anthropogenic sulfate aerosols. *Tellus* **43A**, 152–163.
- Charlson, R. J., Schwartz, S. E., Hales, J. M., Cess, R. D., Coakley, J. A., Hansen, J. E. and Hofman, D. J. 1992. Climate forcing by anthropogenic aerosols. *Science* **255**, 422–430.
- Charlson, R. J. and Heintzenberg, J. 1995. Aerosol forcing of climate. *Proc. Dahlem Workshop*, 20–29 April 1994, J. Wiley & Sons, Berlin.
- Clegg, S. L. and Brimblecombe, P. 1985. Potential degassing of hydrogen chloride from acidified sodium chloride droplets. *Atmos. Environ.* **19**, 465–470.
- Davison, B., O'Dowd, C., Hewitt, C. N., Smith, M. H., Harrison, R. M., Peel, D. A., Wolf, E., Mulvaney, R., Schwikowski, M. and Baltensperger, U. 1996a. Dimethyl sulfide and its oxidation products in the atmosphere of the Atlantic and Southern oceans. *Atmos. Environ.* **30**, 1895–1906.
- Davison, B., Hewitt, C. N., O'Dowd, C., Lowe, J. A., Smith, M. H., Schwikowski, M., Baltensperger, U. and Harrison, R. M. 1996b. Dimethyl sulfide, methane sulfonic acid and physico-chemical aerosol properties in Atlantic air from the United Kingdom to Halley Bay. *J. Geophys. Res.* **101**, 22855–22875.
- De Angelis, M. and Gaudichet, A. 1991. Saharan dust deposition over Mont Blanc (French Alps) during the last 30 years. *Tellus* **43B**, 61–75.
- Döscher, A., Gäggeler, H. W., Schotterer, U. and Schwikowski, M. 1995a. A 130 years deposition record of sulfate, nitrate and chloride from a high-alpine glacier. *Water, Air and Soil Pollution* **85**, 603–609.
- Döscher, A., Schwikowski, M. and Gäggeler, H. W. 1995b. Cation trace analysis of snow and firn samples from high-alpine sites by ion chromatography. *J. Chromatogr. A* **706**, 249–252.
- Döscher, A., Gäggeler, H. W., Schotterer, U. and Schwikowski, M. 1996. A historical record of ammonium concentrations from a glacier in the Alps. *Geophys. Res. Lett.* **23**, 2741–2744.
- Graf, H.-F., Feichter, J. and Langmann, B. 1997. Volcanic sulfur emissions: estimates of source strength and its contribution to the global sulfate distribution. *J. Geophys. Res.* **102**(D9), 10727–10738.
- Graf, H.-F., Langmann, B. and Feichter, J. 1998. The contribution of Earth degassing to the atmospheric sulfur budget. *Chem. Geology* **147**, 131–145.
- Haeberli, W., Schotterer, U., Wagenbach, D., Haeberli-Schwitzer, H. and Bortenschlager, S. 1983. Accumulation characteristics on a cold, high-alpine firn saddle from a snow-pit study at Colle Gnifetti, Monte Rosa, Swiss Alps. *Journal of Glaciology* **29**, 260–271.
- Haeberli, W., Schmid, W. and Wagenbach, D. 1988. On the geometry, flow and age of firn and ice at the Colle Gnifetti core drilling site (Monte Rosa, Swiss Alps). *Zeitschrift für Gletscherkunde und Glazialgeologie* **24**, 1–19.
- Haeberli, W. and Funk, M. 1991. Borehole temperatures at the Colle Gnifetti core-drilling site (Monte Rosa, Swiss Alps). *Journal of Glaciology* **37**, 37–46.
- Hedin, L. O., Granat, L., Likens, G. E., Buishand, T. A., Galloway, J. N., Butler, T. J. and Rodhe, H. 1994. Steep declines in atmospheric base cations in regions of Europe and North America. *Nature* **367**, 351–354.
- Hitchcock, D. R., Spiller, L. L. and Wilson, W. E. 1980. Sulfuric acid aerosols and HCl release in coastal atmospheres: evidence of rapid formation of sulfuric acid particulates. *Atmos. Environ.* **14**, 165–182.
- Horn, M. K. and Adams, A. S. 1966. Computer-derived geochemical balances and element abundances. *Geochim. Cosmochim. Acta* **30**, 279–297.
- IPCC (Intergovernmental Panel on Climate Change), 1996. Climate change 1995. *The science of climate change*. Contribution of Working Group I to the Second Assessment Report of the Intergovernmental Panel on Climate Change (eds. J. T. Houghton, L. G. Meira Filho, B. A. Callander, N. Harris, A. Kattenberg and K. Maskell), Cambridge University Press, Cambridge, UK.
- Johnsen, S. J., Dansgaard, W., Clausen, H. B. and

- Langway, C. C. Jr. 1972. Oxygen isotope profiles through the Antarctic and Greenland ice sheets. *Nature* **235**, 429–434.
- Kiehl, J. T. and Briegleb, B. P. 1993. The relative roles of sulfate aerosols and greenhouse gases in climate forcing. *Science* **260**, 311–314.
- Langner, J. and Rodhe, H. 1991. A global three-dimensional model of tropospheric sulfur cycle. *Journal of Atmospheric Chemistry* **13**, 225–263.
- Lavanchy, V. M. H., Gäggeler, H. W., Schotterer, U., Schwikowski, M. and Baltensperger, U. 1999. Historical record of carbonaceous particle concentrations from a European high-alpine glacier (Colle Gnifetti, Switzerland). *J. Geophys. Res.*, in press.
- Legrand, M. and Delmas, R. 1987. A 220 yr continuous record of volcanic H₂SO₄ in the Antarctic Ice Sheet. *Nature* **327**, 671–676.
- Legrand, M., Hammer, C., De Angelis, M., Savarino, J., Delmas, R., Clausen, H. and Johnsen, S. J. 1997. Sulfur-containing species (methanesulfonate and SO₄) over the last climatic cycle in the Greenland Ice Core Project (central Greenland) ice core. *J. Geophys. Res.* **102(C12)**, 26663–26679.
- Lugauer, M., Baltensperger, U., Furger, M., Gäggeler, H. W., Jost, D. T., Schwikowski, M. and Wanner, H. 1998. Aerosol transport to the high Alpine sites Jungfrauoch (3454 m asl) and Colle Gnifetti (4452 m asl). *Tellus* **50B**, 76–92.
- Maupetit, F. and Delmas, R. J. 1994. Snow chemistry of high altitude glaciers in the French Alps. *Tellus* **46B**, 304–324.
- Maupetit, F., Wagenbach, D., Weddeling, P. and Delmas, R. J. 1995. Seasonal fluxes of major ions to a high altitude cold alpine glacier. *Atmos. Environ.* **29**, 1–9.
- Mayewski, P. A., Lyons, W. B., Spencer, M. J., Twickler, M., Buck, C. F. and Whitlow, S. 1990. An ice core record of atmospheric response to atmospheric sulphate and nitrate. *Nature* **346**, 554–556.
- Mitchell, J. F. B., Johns, T. C., Gregory, J. M. and Twett, S. F. B. 1995. Climate response to increasing levels of greenhouse gases and sulfate aerosols. *Nature* **376**, 501–504.
- Mylona, S. 1993. *Trends of sulphur dioxide emissions, air concentrations and depositions of sulphur in Europe since 1880*. EMEP/MSC-W Report 2/93. Meteorological Synthesizing Centre-West, The Norwegian Meteorological Institute, PO Box 43-Blindern, N-0313 Oslo 3, Norway.
- Neftel, A., Beer, J., Oeschger, H., Zürcher, F. and Finkel, R. C. 1985. Sulphate and nitrate concentrations in snow from South Greenland 1895–1978. *Nature* **314**, 611–613.
- Nickus, U., Kuhn, M., Pichlmayer, F., Baltensperger, U., Delmas, R., Gäggeler, H. W., Kasper, A., Kromp-Kolb, H., Maupetit, F., Novo, A., Preunkert, S., Puxbaum, H., Rossi, G., Schöner, W., Schwikowski, M., Seibert, P., Staudinger, M., Trockner, V. and Wagenbach, D. 1997. SNO₃P: ion deposition and concentration in high alpine snow packs. *Tellus* **49B**, 56–71.
- Oeschger, H., Schotterer, U., Stauffer, B., Haeblerli, W. and Röthlisberger, H. 1977. First results from alpine core drilling projects. *Zeitschrift für Gletscherkunde und Glazialgeologie* **13**, 193–208.
- Schotterer, U., Oeschger, H., Wagenbach, D. and Münnich, K. O. 1985. Information on paleo-precipitation on a high-altitude glacier Monte Rosa, Switzerland. *Zeitschrift für Gletscherkunde und Glazialgeologie* **21**, 379–388.
- Schütz, L. and Seibert, M. 1987. Mineral aerosols and source identification. *J. Aerosol Science* **18**, 1–10.
- Schwikowski, M., Seibert, P., Baltensperger, U. and Gäggeler, H. W. 1995. A study of an outstanding Saharan dust event at the high-alpine site Jungfrauoch, Switzerland. *Atmos. Environ.* **29**, 1829–1842.
- Schwikowski, M. 1997. Analytical chemistry in high-alpine environmental research. *Chimia* **51**, 8–13.
- Seibert, P., Kromp-Kolb, H., Kasper, A., Kalina, M., Puxbaum, H., Jost, D. T., Schwikowski, M. and Baltensperger, U. 1998. Transport of polluted boundary layer from the Po Valley to high-alpine sites. *Atmos. Environ.* **32**, 3953–3965.
- Semb, A., Hanssen, J. E., Francois, F., Maenhaut, W. and Pacyna, J. M. 1995. Long range transport and deposition of mineral matter as a source for base cations. *Water, Air and Soil Pollution* **85**, 1933–1940.
- Simpson, D., Winiwarter, W., Börjesson, G., Cinderby, S., Ferreira, A., Guenther, A., Hewitt, C. N., Janson, R., Khalil, M. A. K., Owen, S., Pierce, T. E., Puxbaum, H., Shearer, M., Steinbrecher, R., Svennson, B. H., Tarrason, L. and Öquist, M. G. 1999. Inventorying emissions from nature in Europe. *J. Geophys. Res.* **104**, 8113–8152.
- Taylor, K. E. and Penner, J. E. 1994. Response of the climate system to atmospheric aerosols and greenhouse gases. *Nature* **369**, 734–737.
- Vinogradov, A. N. 1959. *The geochemistry of rare and dispersed chemical elements in soils*, 2nd edition, Consult. Bur., New York, p. 231.
- Wagenbach, D., Münnich, K. O., Schotterer, U. and Oeschger, H. 1988. The anthropogenic impact on snow chemistry at Colle Gnifetti, Swiss Alps. *Annals of Glaciology* **10**, 183–187.
- Wagenbach, D. and Geis, K. 1989. The mineral dust record in a high altitude glacier (Colle Gnifetti, Swiss Alps). In: *Paleoclimatology and paleometeorology: modern and past patterns of global atmospheric transport* (eds. M. Leinen and M. Sarnthein). Kluwer Academic Publishers, Dordrecht, 543–564.
- Wagenbach, D. 1989. Environmental records in Alpine glaciers. In: *The environmental record in glaciers and ice sheets* (eds. H. Oeschger, and C. C. Langway Jr.). John Wiley and Sons, Chichester, 69–83.
- Wagenbach, D., Preunkert, S., Schäfer, J., Jung, W. and Tomadin, L. 1996. Northward transport of Saharan dust recorded in a deep alpine ice core. In: *The impact of desert dust across the Mediterranean* (eds. S. Guerzoni and R. Chester). Kluwer Academic Publishers, The Netherlands, 291–300.
- Wagenbach, D., Geis, K., Hebestreit, K., Preunkert, S., Schäfer, J., Schajor, R., Ulshöfer, V. and Weddeling,

- P. 1997. Retrospective and present state of anthropogenic aerosol deposition at a high altitude alpine glacier (Colle Gnifetti, 4450 m a.s.l.). In: *Cloud multi-phase processes and high Alpine air and snow chemistry* (eds. S. Fuzzi and D. Wagenbach). Springer-Verlag, Berlin Heidelberg, Germany, 223–233.