報告番号 乙 第 5116 号

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極地氷床コア中の水溶性成分：硫酸塩の時間的・地理的分布

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ABSTRACT

Polar snow contains trace amounts of various atmospheric ionic constituents which are sequentially incorporated during snowfall and deposit. This study describes temporal and spatial variations of water soluble ionic constituents measured over the last millennium in polar ice cores recovered from locations in Antarctica (New Byrd, South Pole and Siple Station) and Greenland (North Central, Camp Century, Milcent, Crete, Dye-2, Dye-3 and South Dome). To obtain a better understanding of the natural sulfur cycle in the polar atmospheres and the ice sheets, discussion was focused on temporal and spatial distributions of concentration levels and deposition fluxes of sulfate and methanesulfonate in snow accumulated in pre-1900 A. D.

A detailed chemical stratigraphy record for the Byrd Station, Antarctica area (NBY89) was made of the temporal variations in ionic concentrations and volcanic events over the last 1360 years. A comparative study was made on the Crete station (CR74), central Greenland ice core for the time period 1130 AD to 1820 AD. The detailed time-scale established for the NBY89 ice core made it possible to trace prominent volcanic index horizons to other Antarctic cores, and finally by cross-dating the results with ice core records from well dated Greenland ice cores.

Temporal and spacial distributions of sulfate are discussed using sodium to trace sea-salt source and methanesulfonate for the marine biogenic dimethylsulfide (DMS) source. Seasonal variations of non-sea-salt sulfate ($nssSO_4^{2-}$) in surface snow at the Byrd station area correlated well with methanesulfonate, suggesting that marine-biogenic sulfur was in fact the dominant source of the non-sea-salt sulfate measured. For the last millennium, background level of sulfate in polar ice cores is nearly constant contributions from sea-salt and background sulfate but disturbed by sporadic volcanic inputs for both polar regions. Eleven prominent bipolar volcanic events were found for the past 1,000 years from a comparison of volcanic event records of the Antarctic and Greenland cores; the 1259 AD event was the most conspicuous bipolar index horizon and was 14 times larger than normal annual sulfate flux at the Byrd station.

As a function of elevation, spatial distribution of $nssSO_4^{2-}$ deposition flux was similar to the $CH_3SO_3^-$ flux distribution in Antarctica but different in Greenland. Deposition fluxes of $nssSO_4^{2-}$ in Greenland were higher than at Antarctic sites at comparable elevation and the $CH_3SO_3^-$ flux. This suggests an additional non-marine biogenic source that is more active in the northern hemisphere. Such an additional source for $nssSO_4^{2-}$ in Greenland ice cores was suggested as mineral dusts containing sulfate and SO_2 from non-erupting volcanic exhalation.

Contents

1. Introduction

1-1. Background

(i) Polar ice cores

Antarctica and Greenland are covered by ice sheets. The ice sheets receive annual snow fall. The inland areas of the ice sheets are a dry snow zone where summer melting rarely occur. In the dry snow area, successive snow fall gradually compresses snow into ice by the overlaying mass of snow accumulation. The transition from air-permeable snow to impermeable glacier ice normally takes place at about 50 to 100-m depth below the surface depending upon temperature and the annual rate of snow accumulation.

Polar snow contains trace amounts of various atmospheric water soluble constituents which are sequentially incorporated during snowfall and deposit. Ice core samples have been measured for their major and trace constituents since soon after successful ice core drilling technology was developed at Site 2 Greenland in 1956 (Langway, 1958). Ice cores obtained from dry snow areas on the polar ice sheets have been used extensively as archives of temporal variations in the past precipitation chemistry (Langway, 1970; see review by Clausen and Langway, 1989; Delmas, 1992a). The results of earlier ionic chemistry investigations of snow and ice in Antarctica (Delmas and Boutron, 1978; Legrand and Delmas, 1984) and in Greenland (Murozumi et al., 1969; Busenberg and Langway, 1979; Herron, 1982) have contributed to a better understanding of the natural geochemical cycles of various constituents in remote pristine area (Galloway, 1985).

Water soluble ionic constituents in polar ice include sea-salts (e.g. Na^+ and Cl^-), mineral salts ($CaCO_3$), organic carbon compounds ($HCOO^-$ and CH_3COO^-), nitrogen compounds (NO_3^- and NH_4^+) and sulfur compounds (SO_4^{2-} and $CH_3SO_3^-$) as discussed in earlier studies (Clausen and Langway, 1989; Delmas, 1992a; Legrand, 1995). Of these natural constituents found in polar snow and ice, sulfur compounds are the major components as revealed by their measured concentration levels. Sources for the sulfur compounds have been attributed to sea-salts, marine biogenic activity and sporadic volcanic eruptions but details of the sulfur cycle in polar regions has not yet been well established (Herron, 1982; Delmas et al., 1982; Clausen and Langway, 1989; Legrand, 1995).

(ii) Sulfate and methanesulfonate in remote atmospheres and polar ice cores

Sulfate is the major water soluble component in the atmospheric aerosol particles and consequently in resulting precipitation. Because of water soluble nature, sulfate containing aerosol particles act as a key constituents in the radiation balance in the atmosphere and in the acidity level of aerosols and precipitation (Charlson and Rodhe, 1982; Warneck, 1988; Charlson et al., 1987). Sulfate in the atmosphere has been identified as the dominant component of cloud condensation nuclei in both remote and polluted settings. Therefore, it is important to obtain a better knowledge of geochemical cycle of sulfate and relating sulfur compounds through the atmosphere because of the potential influence of their change to direct and indirect effects on the earth's radiation budgets and bio-geochemical feedback of interaction between climate and biosphere (Charlson et al., 1987; 1992).

Sulfate is the end product of the oxidation processes from a number of gaseous volatile sulfur compounds in the atmosphere. Major sulfate sources and precursors in tropospheric aerosols and in precipitation have been reported to include (1) a fraction of sea-salt, (2) oxidation of natural reduced sulfur compounds such as dimethylsulfide (DMS), hydrogen sulfide (H_2S) and methyl mercaptan (CH_3SH), (3) oxidation of sulfur dioxide (SO_2) emitted from volcanoes and combustion of fossil fuel, (4) mineral dust containing sulfate such as gypsum (Warneck, 1988; Andreae and Jaeschke, 1992). According to Andreae and Jaeschke (1992), anthropogenic flux (93 ± 15 Tg (S)/yr) of SO_2 is estimated to be nearly equal or slightly larger magnitude of total natural sulfur emission fluxes (65 ± 25 Tg (S)/yr, without sea-salt sulfate) at present.

In the remote southern marine troposphere including the coastal areas of Antarctica, marine biogenic DMS is generally accepted as the steady dominant source of non-sea-salt SO_4^{2-} (nssSO_4^{2-}) in submicron aerosols (Prospero et al., 1991; Savoie et al., 1989; 1992; 1993). DMS is mainly produced biologically in the sea by phytoplankton via biological processes. This biogenic DMS in the ocean diffuses into the atmosphere (Andreae, 1985, 1986, 1990). Unlike nssSO_4^{2-} which has natural non-marine biogenic sources (such as volcanic SO_2), methanesulfonate ($CH_3SO_3^-$, MSA) is an unique oxidation product of marine biogenic DMS in the atmosphere (Hatakeyama et a., 1982; Saltzman et al., 1983; Saltzman, 1995). The greater DMS emissions lead to higher atmospheric concentration levels of nssSO_4^{2-} as well as $CH_3SO_3^-$ in the remote marine atmosphere (Gillett et al., 1993). Elevated concentrations of DMS also have been observed in regions where there is floating sea ice in the Antarctic ocean (Berresheim, 1987; Gibson et al., 1990).

In remote atmospheres, concentration levels of $CH_3SO_3^-$ and ratios of nssSO_4^{2-}/$CH_3SO_3^-$ have been used as a tracer of the relative contribution of nssSO_4^{2-} from the marine biogenic DMS (Savoie et al., 1989; Savoie et al., 1994; Prospero et al., 1995), although the oxidation processes from DMS to end products are not yet fully understood. For example, the ratios for aerosol samples obtained from the marine boundary layer at high-latitudes are lower than those in midto low-latitudes (Bates et al., 1992). But seasonal variation of the ratios of $nssSO_4^{2-}/CH_3SO_3^-$ at Cape Grim, a remote oceanic sampling station in the southern hemisphere, was low in summer and high in winter (Ayers et al., 1991). Although results from laboratory experiments suggest a temperature dependence of the branching ratio in the DMS oxidation with higher $CH_3SO_3^-$ yield for lower temperature (Hynes et al., 1986; Hynes and Wine, 1989; Plane, 1989), the natural latitudinal distribution and the seasonal variation of the ratios is not yet fully explained.

A recent study of coastal Antarctic aerosols (Prospero et al., 1991; Savoie et al., 1993) reported synchronous seasonal variations in $nssSO_4^{2-}$ and $CH_3SO_3^-$ concentration levels associated with oceanic bio-activity, suggesting significant marine biogenic contribution to the sulfur budget over the coastal Antarctic. In Antarctica, $CH_3SO_3^-$ and $nssSO_4^{2-}$ concentrations have also been measured in surface snow and deeper ice core samples (Ivey et al., 1986; Saigne and Legrand, 1987; Legrand et al., 1992a; Kamiyama et al., 1992; Mulvaney et al., 1992; Welch et al., 1993; Udisti et al., 1993; Pasteur et al., 1995). From these measurements, new information is available to more fully understand and interpret the polar $CH_3SO_3^-$ data. For example, it is reported (Mulvaney et al., 1992) that distinct and regular seasonal variations (high in summer and low in winter) exist in the concentration levels of $CH_3SO_3^-$ and $nssSO_4^{2-}$ in snow samples from shallow snow depths but shifting phase-relationship with $nssSO_4^{2-}$ in deeper ice cores. Recent attention has been given to the origin of background $nssSO_4^{2-}$ unrelated with $CH_3SO_3^-$ in snow and aerosols along the coastal Antarctic areas (Udisti et al., 1993, Savoie et al., 1993). On the other hand, sporadic increase of $nssSO_4^{2-}$ concentration levels in vertical core profiles of Antarctic ice are generally attributed to volcanic activity (Delmas and Boutron, 1980; Legrand and Delmas, 1987; Langway et al., 1988).

In Greenland, gradual increase of $nssSO_4^{2-}$ concentration levels was first found at Dye-3, south Greenland (Herron, 1982). This increase in $nssSO_4^{2-}$ concentration levels was found in post-1900 AD ice layers and was attributed to increases of anthropogenic SO_2 emission after the industrial revolution (Herron, 1982; Neftel et al., 1985, Finkel et al., 1986; Clausen and Langway, 1989). The anthropogenic sources have changed not only the magnitude of $nssSO_4^{2-}$ levels in Greenland but also the seasonal pattern of $nssSO_4^{2-}$ concentration levels (Finkel et al., 1986). Volcanic signals in Greenland ice cores were studied in continuous ice core profiles in Holocene and Wisconsin stage deposits by using the Electrical Conductivity Method (Hammer, 1983). The H^+ concentration level in Holocene ice varies with the acid content which is deposited as volcanic H_2SO_4 and HCl. (Herron, 1982). Thus, the prominent acid spikes detected in ice cores represent volcanic events of local, regional, or bi-hemispheric origin (Hammer, 1984). Based on depth-age time scales developed from analysis of oxygen isotopic ratios and dust concentrations , these acid spikes found in Greenland ice cores were correlated with historically recorded volcanic eruptions such as Krakatoa (1883 AD), and Tambora (1815 AD), both in Indonesia, and Laki (1783 AD) in Iceland (Hammer, 1977; 1980; Hammer et al., 1978; 1980). MSA concentrations of Greenland ice cores have also been measured on surface snow and deeper ice core samples (Alley et al., 1990; Hansson and Saltzman, 1993; Whung et al., 1994), but geographical distribution of MSA is not yet obtained.

1-2. Objectives

This study was designed to obtain a better understanding of the atmospheric cycle of sulfur compounds in the remote polar regions. This study describes measured temporal and spacial variations in SO_4^{2-} and $CH_3SO_3^-$ concentration levels and calculated deposition fluxes on deep and shallow ice cores recovered from Antarctica (New Byrd, South Pole and Siple Station) and Greenland (North Central, Camp Century, Milcent, Crete, Dye-2, Dye-3 and South Dome) over the last millennium.

Dating of the core samples, procedures of sample preparation, analytical procedures and data treatment are presented and discussed. Temporal and spacial trends in the concentration levels of SO_4^{2-}, $CH_3SO_3^-$ and other ionic constituents are presented and compared with each other as well as with the oxygen isotopic ratios. General distribution of sulfate deposition rates are estimated and compared with the results from other ice core studies.

The geochemical significance of the SO_4^{2-} and $CH_3SO_3^-$ concentrations in polar ice deposited over the last millennium is discussed in terms of their sources and its variabilities.

1-3. Scope

As mentioned in earlier for ice core studies in Greenland, the anthropogenic influence of SO_4^{2-} concentration levels is expected to Greenland ice layers deposited after 1900 AD. To study the natural undisturbed distributions of sulfate in Greenland, ice layers deposited before 1900 AD are the best sample. This is also important for anthropogenically disturbed species such as NO_3^- and other ionic constituents in Greenland ice cores to interpret. In order to study long-term variability of background average concentration levels, the older end of the study period is extended to the last millennium. The millennium time-scale includes decadal and century scale climatic fluctuations such as the little ice age (between 15th and 19th century, Crowley and North, 1991) which could have changes in natural sulfur cycles. Thus, sampling and study time period is limited to the last millennium but pre-1900 AD ice.

1-4. Approach

Use of pre-1900 AD polar ice cores to investigate the natural distribution of ionic constituents transported and deposited from the atmosphere gives an advantage for eliminating influence of today's human activities, such as SO_4^{2-} and NO_3^- from the combustion of fossil fuel, $HCOO^-$ from motor exhaust and NH_4^+ from use of fertilizer.

For temporal variations, dating of the core samples is critical to compare one to the other. The prime physical and chemical annual cycle indicators should if possible be measured continuously, or over selected long sections of ice cores. For spatial variations, representative chemical data of a given site in a given time period are a key to reveal general aspects of geographical distributions. To obtain meaningful spatial data set, long-term averages of ionic content should be used for discussion to avoid short-term, seasonal and year-to-year variabilities.

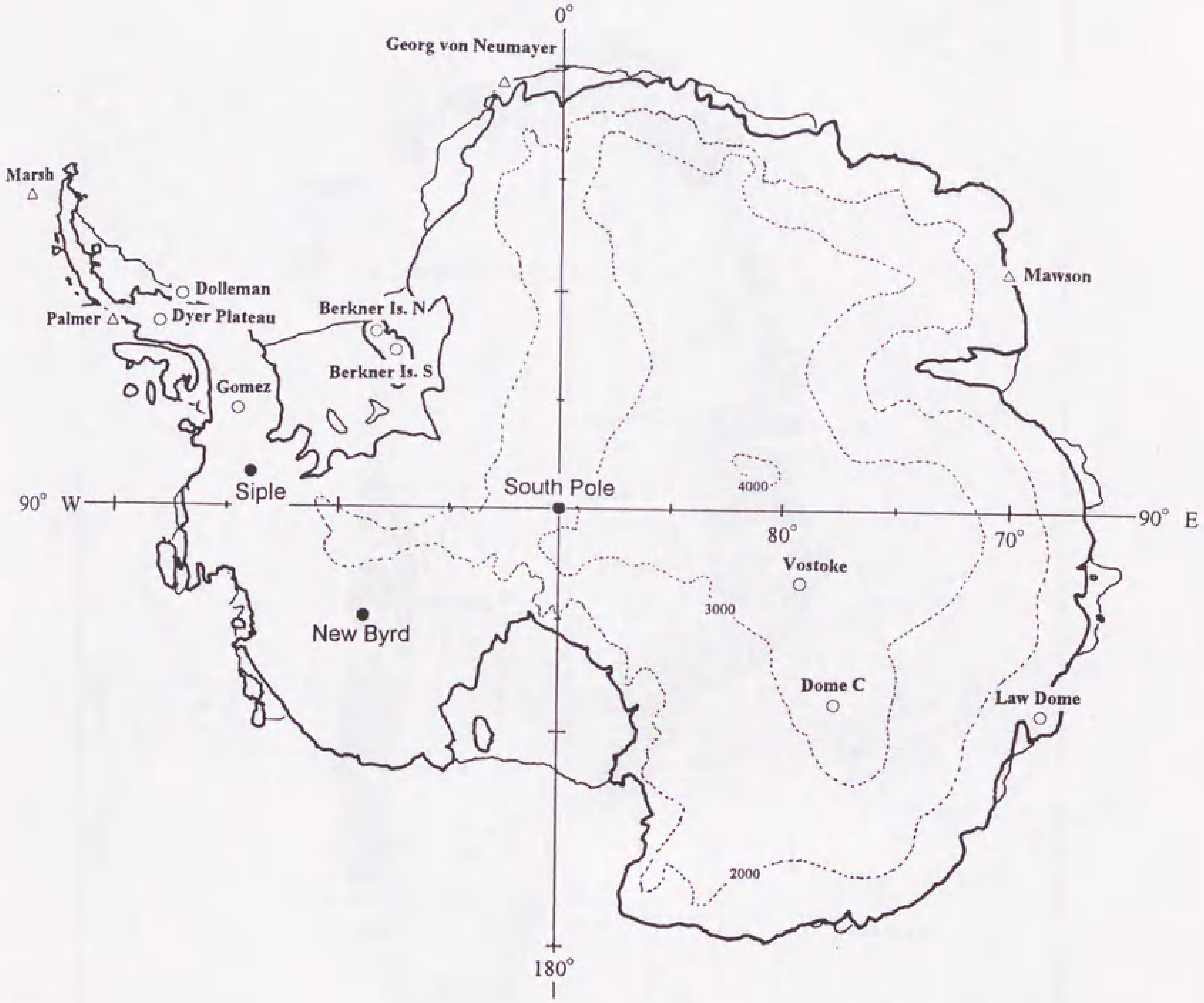
2. Samples and methods

2-1. Introduction

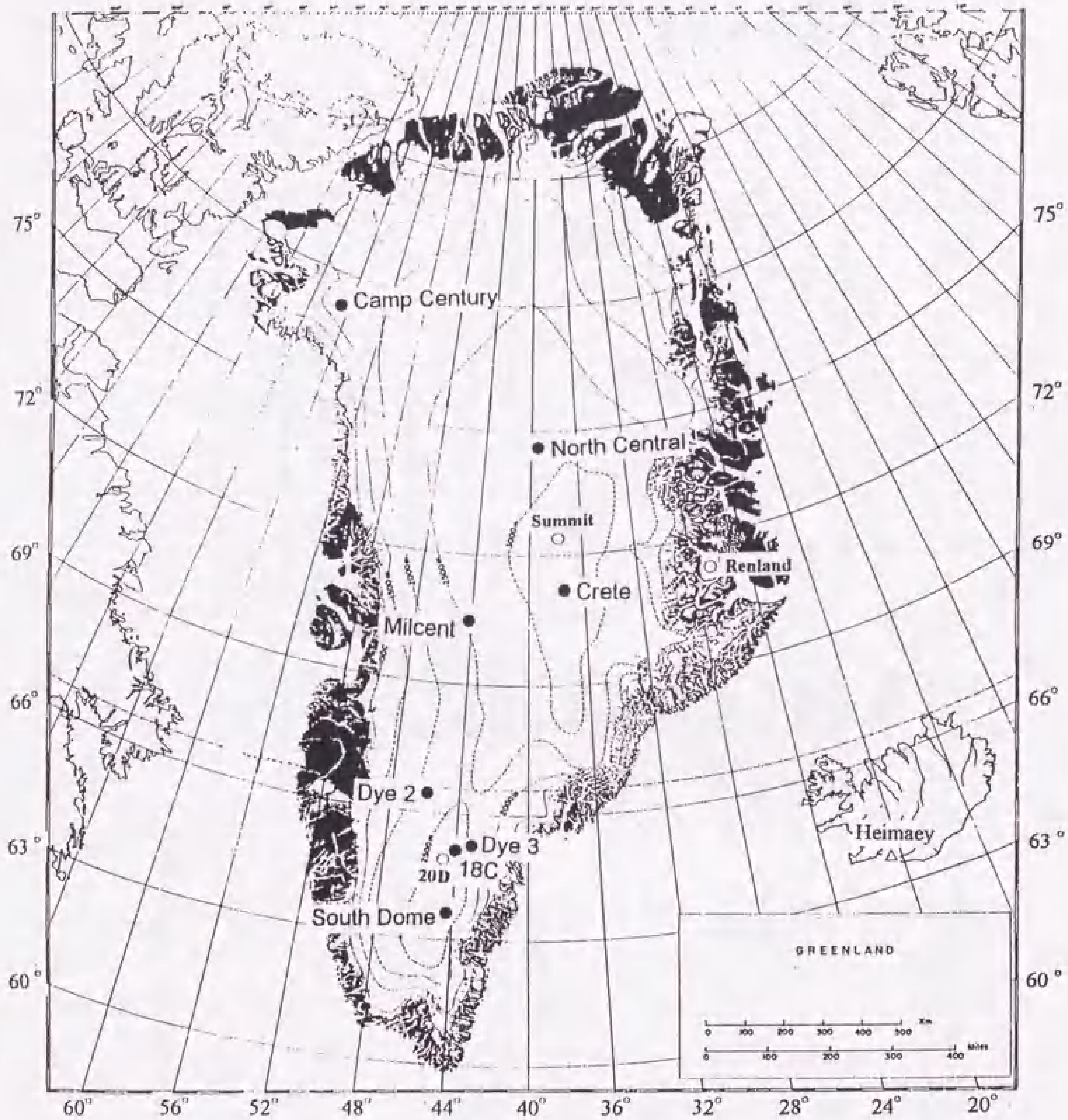
As outlined in the previous section, the selection of core site locations and the depth interval studied are important considerations for this study. The ice cores used for this study were carefully selected from the archives of Ice Core Laboratory, State University of New York at Buffalo. Details of drilling site information and core descriptions are given in Herron and Langway (1980), Langway et al. (1985) and Langway (1992). The specific selection of ice core specimens for this study was based on physical quality, the depth interval of available air-impermiable ice, and the continuity of the core. After appropriate ice cores were selected, the core samples were sectioned into sub-annual or annual layer increments. The surface contaminants were removed before meltings and the measurements following procedures reported in (Langway et al., 1974; Finkel and Langway, 1985, see below).

2-2. Field locations

Ice cores used in this study were obtained from 3 sites in Antarctica (New Byrd, South Pole and Siple Station, as shown in Fig.1) and 8 sites in Greenland (North Central, Camp Century, Milcent, Crete, Dye-2, Dye-3, Dye-3 18C and South Dome as shown in Fig. 2) locations as listed in Table 1. Site and dating information and their references are also given in Table 1. Table 1 includes site location, core length, year drilled, annual mean surface air temperature, annual rate of snow accumulation and references for all site studied. Figures 1 and 2 show core drilling locations used in this study (filled circles) and various sampling locations reported in other studies (open circles for ice cores and triangles for aerosol studies).



Figures 1. Core drilling locations in Antarctica used in this study (filled circles) and various sampling locations reported by other investigators (open circles for ice cores and triangles for aerosol studies). See Table 1 for identification of site codes.



Figures 2. Core drilling locations in Greenland used in this study (filled circles) and various sampling locations reported by other investigators (open circles for ice cores and triangles for aerosol studies). See Table 1 for identification of site codes.

Table 1. Core samples and site Information

(1) Site	(2) Location		(3) Surface Elevation (m)	(4) Average Accumulation rate (gcm^{-2}yr^{-1})	(5) Annual Surface Air Temperature (°C)	(6) Year recovered	(7) Total Depth (m)	(8) References
	Latitude	Longitude						
	Antarctica							
Byrd Station (NB, NBY89)	80°01'	119°31'	1530	101	-28	1989	164	This study
South Pole (SP, SP78)	90°00'		2850	70	-51	1978	111	Langway et al. (1988)
	Greenland							
Camp Century (CC)	77°10'	61°08'	1880	349	-24	1977	102	Herron and Langway (1980)
North Central (NC)	74°37'	39°36'	2930	129	-32	1977	108	Herron and Langway (1980)
Crete (CR, CR74)	71°07'	37°19'	3172	275	-30	1974	404	Dansgaard et al. (1975) Hammer et al. (1980)
Milcent (MC)	70°18'	44°19'	2410	487	-22	1973	398	Hammer et al. (1978)
Dye 2 (D2)	66°29'	46°20'	2100	343	-17	1974	101	Herron and Langway (1980)
Dye 3 (D3, D3 81)	65°11'	43°50'	2486	496	-20	1979-81	2037	Dansgaard et al. (1982)
Dye 3, 18C (D318C)	65°02'	44°23'	2620$^{\#}$	500		1984	113	Dansgaard et al*.
South Dome (SD)	63°33'	44°36'	2831	500	-22	1975	80	Herron and Langway (1980)

#: Gundestrup et al. (1986); *: personal communications

2-3. Sample preparation and chemical analysis

All continuous core increments selected were a few meters long and sectioned into sub-annual or annual thickness of a year's snow accumulation. Depending upon thickness of the annual layer, the NBY89 core was sectioned into 6 to 4 specimens per year, and the SP78 core was sectioned into 3 to 2 specimens per year. All Greenland cores were sectioned into 8 specimens per year, except for some year interval such as the 1832 AD layer of the D3 81 core which was measured as one unit.

Ice core samples were prepared for chemical analysis using reported procedures (Langway et al., 1974, Finkel and Langway, 1985) with minor modifications. In this study surface contamination was removed by mechanically shaving the outer surface; followed by ultra pure (Millipore, 18 MΩ) water flushes without using the acetone rinse. Porous firn cores were cleaned mechanically (Finkel et al., 1986) but not measured for $HCOO^-$ and NH_4^+ due to the inherent difficulties associated with these measurements when made on porous core samples. After cleaning the outer surface, sample specimens were placed in air tight polyplopylene cups (Falcon) and melted in a microwave oven. All sample handling was done within a clean hood (class <100). Simultaneous measurements of the various anions and cations were made within a clean room (class < 1000), using a two-column ion chromatograph (Dionex 4040i) equipped with HPIC-TAC and -TCC concentrators, AS4A and CS3 separator columns, anion and cation micro-membrane suppressors with recording integrators (Spectra Physics model 4270) and auto-mated samplers (Dionex ASM-2). The step gradient method was used for eluent concentrations: 1 mM $NaHCO_3$ (for separation of $HCOO^-$, $CH_3SO_3^-$ and Cl^-), 1.5 mM $NaHCO_3$ and 2.5 mM Na_2CO_3 (NO_3^- and SO_4^{2-}), 15 mM HCl (Na^+, NH_4^+ and K^+) and 48 mM HCl with 8 mM DAP·HCl (Mg^{2+} and Ca^{2+} separation). Blanks for all procedural checks were made using 18 MΩ, Milli-Q water. Blank values for $HCOO^-$ were below 1 ng/g, values for all other ions were below detection limits (0.4 ng/g for $CH_3SO_3^-$, 2 ng/g for Cl^-, 4 ng/g for NO_3^- and SO_4^{2-}; 1.0 ng/g for Na^+, NH_4^+ and K^+, 0.8 ng/g for Mg^{2+} and 4 ng/g for Ca^{2+}) using an 11 ml sample volume for the anions and a 5.5 ml volume for the cations. Measured concentration levels are not corrected for the blank values. Analytical errors are within 10% of the average concentrations levels measured in the core samples as determined by replicate measurements on diluted working chemical standards made from certified grade pure-salts, except for methanesulfonic acid (>99%, Fluka).

2-4. Dating the cores

Measurements of key chemical and physical parameters are made along continuous and selected long-sections of polar ice cores to provide reliable past snow accumulation rates. The prime accumulation indicators include variations found in the stable isotopes, ionic constituents and acidity concentration levels; and physical changes in the strata and structure. Following this outline, the NBY89 core was dated on an individual year basis using all the multiple cross-correlation techniques. The oxygen isotope and ECM data for the NBY89 core were provided by Drs. Clausen and Hammer, University of Copenhagen. Continuous bulk density data of the NBY89 core were provided by Dr. Shoji, University of Toyama (now at Kitami Institute of Technology). Field and laboratory study programs were summarized in Langway (1992).

For the NBY89 core, the ECM data-series was cross-correlated with the ionic chemistry stratigraphy. Three main prominently defined volcanic horizons: 1884 AD (Krakatoa, 1883 AD), 1816 AD (Tambora, 1815 AD) and 1259 AD (Hammer et al., 1980, unidentified eruption, see Langway et al., 1988; Palais et al., 1992) were established as prime index layers in the NBY89 core using ECM peaks combined with a physical depth-age model. Final dating of the entire NBY89 core from the surface to the bottom was established by multi-parameter time-series analysis. In addition, the density profile (Shoji and Langway, personal communications) and total β curve (Clausen and others, personal communications) were used as reference checks. Dating accuracy for the core is estimated as better than ± 2 years based on clear seasonal ECM peaks and a fine-tuning procedure using both the chemistry and $\delta^{18}O$ curves.

The SP78 core was originally dated using a physical model (Chaing and Langway, 1978) and subsequently adjusted using new acidity (Clausen and others, personal communications) and chemistry measurements made in this study. The results revealed the presence of three key volcanic index horizons which were the key indices for dating this core.

The time-scale finally adopted for SP78 used the summer 1978 snow surface as the datum horizon. From there to the 16.3 m core depth, the level of the chemically identified strong-acid peak (1883 AD Krakatoa eruption), an accumulation rate of 7.5 $gcm^{-2}yr^{-1}$ is obtained. From 16.3 m to the strong-acid peak at 26.2 m (1815 AD, Tambora) a rate of 7.9 $gcm^{-2}yr^{-1}$, and from 26.2 m to the pronounced chemical signal at 87.8 m (the 1259 AD event) the accumulation rate calculates as 7.2 $gcm^{-2}yr^{-1}$. The recognized and early reported sporadic variability in each years snowfall at the South Pole (Gow, 1965) most probably has a real effect on the actual depth and thickness of any annual accumulation layer between the three fixed points representing the volcanic index horizons. Subsequently, the over all dating accuracy for the SP78 is estimated at ±5 to 10 years.

Time-scales for the other Greenland cores were established using the combined results of the $\delta^{18}O$, strong-acid and dust measurements (Hammer et al., 1978) and have an estimated accuracy of ±1 to 3 years (Hammer et al., 1980). All ECM, $\delta^{18}O$ and dating information for

Crete, Milcent, Dye 3 81 and Dye 3 18C are of published or unpublished data from Clausen and Hammer, University of Copenhagen.

All other shallow ice cores used in this study were dated by a snow densification model (Herron and Langway, 1980).

2-5. Data analysis and treatment

The non-sea-salt portion of total Cl^- content (hereafter, $nssCl^-$) of a given sample is calculated as follows:

$$[nssCl^-]=[Cl^-]-1.17[Na^+] \quad \cdots\cdots (1)$$

where $[Cl^-]$ and $[Na^+]$ concentration levels are measured in samples, in neq/g unit, and 1.17 is the Cl^-/Na^+ ratio of average sea water from Wilson (1975). Similarly, non-sea-salt portion of SO_4^{2-} ($nssSO_4^{2-}$) is calculated as follows:

$$[nssSO_4^{2-}]=[SO_4^{2-}]-0.12[Na^+] \quad \cdots\cdots (2)$$

where $[SO_4^{2-}]$ and $[Na^+]$ concentration levels are measured in samples, in neq/g unit, and 0.12 is the SO_4^{2-}/Na^+ ratio of average sea water.

Where exceptionally high concentration levels of $HCOO^-$, $nssSO_4^{2-}$ and NH_4^+ appeared in the profile they were omitted in the calculation for the multi-year average, since short-term sharp peaks are presumed to be caused by non-meteorological events and unusual sources: forest fires for high $HCOO^-$ and NH_4^+ peaks (Legrand et al., 1992b) and volcanic eruptions for high $nssSO_4^{2-}$ peaks (Herron, 1982).

The final value for background concentration levels was calculated as the average of all samples in a few meters of continuous core in the interval selected for the given depth. All short-term sharp peak values were excluded to avoid the spurious influence of rapid increases in the long-term profiles and the geochemical fluxes caused by atypical or non-systematic events.

3. Temporal variations

3-1. Introduction: The last millennium of Antarctic and Greenland ice sheets

Chemical records of ionic constituents in polar ice cores, especially for the time-scale extending up to the last millennium, are not so abundant. Many of them are limited to several hundred years. For example, Delmas and Boutron (1980) reported a vertical profile of sulfate concentration levels in Dome C, Antarctic core for the last hundred years. They suggested that no significant anthropogenic influence was found in Dome C core and that sporadic increases in sulfate concentration levels were attributed to explosive volcanic eruptions. Other studies support their points of view (Legrand and Delmas, 1987; Kirchner and Delmas, 1988; Delmas et al., 1992; Delmas, 1992a) .

For Greenland, Herron (1982) reported vertical profiles of NO_3^- and SO_4^{2-} concentration levels for the last 2000 years at Dye 3, south Greenland. He pointed out that concentration levels of NO_3^- and SO_4^{2-} were nearly constant during the last millennium but increased since about 1900 AD. He also found sporadic high SO_4^{2-} concentration levels of volcanic in origin. Recent studies at south and central Greenland indicate essentially similar profiles (Neftel et al., 1985; Mayewski et al., 1986; Whitlow et al., 1992; Mayewski et al., 1993).

Climate variations as revealed in air temperature and snow accumulation rates show a little fluctuation during the last millennium (for Antarctica: Benoist et al., 1982; Morgan, 1985; for Greenland: Dansgaard et al., 1971; Dansgaard et al., 1975; Clausen et al., 1988). It has been reported (Reeh et al., 1978) for central and southern Greenland that longer term variations in snow accumulation rates at the Crete, Milcent and Dye 3 sites have not significantly changed for the time period covered by this study. Recent study at Summit in Greenland also shows small changes in accumulation rates within 10 % (Meese et al., 1994).

3-2. Antarctica: NBY-89 core

Along with the new 164 m-deep (NBY89) core obtained in November 1989 at a location 1 km upstream from the Byrd surface camp (Langway, 1992), two other 10 m-deep cores were also recovered. These were located at 14 km (NBY-2) and 29 km (NBY-3) upstream from the main core; 2 m-deep pits were hand dug at each drilling location by the field team (Langway, 1992). All cores were augured continuously and recovered in good physical condition.

The Byrd Station is a drilling site of the first Antarctic deep ice core recovered in 1967-68 field season (Ueda and Garfield, 1969). Since snow accumulation rate at the Byrd Station area is sufficiently high, this area is one of the best location in Antarctica to study temporal variations of snow chemistry.

(i) Seasonal variations

Table 2 lists the average ionic concentration levels measured at the three drilling sites for the upper 10 m core profiles and associated snow pits (*1a*, *2a* and *3a*). Figure 3 is a plot of the continuously measured physical and chemical data for the NBY-2 site (14 km upstream from NBY89). For each site the 0 to 2 m depth interval represents approximately 5 years of snow accumulation; the 0 to 10 m depth interval represents from 30 to 40 years of snow deposit. All time-units are referenced to the November 1989 snow surface.

A comparison of the 5- and 10-year ionic averages for the three sites (Table 2) provides a measure of the average short-term vertical and horizontal variations in concentration levels. The average nssSO_4^{2-} and NO_3^- values (columns 7 and 8) show relatively little variability for the same time intervals. The average values for Cl^-, Na^+ and Mg^{2+} (sea-salt components) show some concentration variability but the calculated Cl^-/Na^+ and Mg^{2+}/Na^+ ratios (not shown in Table 1), are consistently close to sea water ratios (1.17 and 0.23 in neq/g, respectively). A comparison of the 40-year averages of the 10 m cores (*1c*, *2c* and *3c*) from the Byrd Station area show slightly higher nssSO_4^{2-} concentration levels at the NBY-89 site, and clearly higher sea-salt concentrations at the NBY-2. Except for these differences all other site data show reasonable good agreement.

Figure 3 shows chemistry and physical properties measurements for the 10 m firn profile at the NBY-2. The $\delta^{18}O$ curve above 2.5 m in Fig. 3 exhibits clear seasonal periodicity with large amplitudes (high in summer and low in winter); below this depth broad shoulders begin to appear on the curve caused by a vapor transfer process which occurs in the upper porous firn (Dansgaard et al., 1973; Johnsen, 1977), complicating the interpretation of annual accumulation layers. In column 2, ice-crusts are absent at several depth-intervals between about 2.6 to 3.8 m; 4.0 to 4.6 m; 6.0 to 6.5 m and 7.6 to 8.0 m. These intervals evolve at about the same time as the $\delta^{18}O$ shoulders appear. The total β curve plotted in column 3 shows a prominent peak, between 8.0 and 8.5 m, which is identified as the well-established 1965/66 nuclear test index horizon also found at other Antarctic locations (Crozaz, 1969).

The upper 2.6 m of the $CH_3SO_3^-$ curve (column 4) indicates clear seasonal cycles with a summer/fall maximum and a winter minimum. As with the $\delta^{18}O$ record, below this depth no apparent seasonality is evident in the $CH_3SO_3^-$ curve. The nssSO_4^{2-} curve (column 5) shows clear seasonal variations with a pronounced summer maximum (ca 1.5 neq/g) and a winter minimum (ca 0.5 neq/g) at the NBY-2 (as well as over the complete 164 m NBY89 core profile). The seasonal variation of $CH_3SO_3^-$ concentrations is correlating well with the nssSO_4^{2-} variations, at least for the upper 2.6 m-depth, suggesting that the dominant source of the nssSO_4^{2-} and $CH_3SO_3^-$ deposited in this region is marine biogenic dimethylsulfide. Diminishing amplitude and seasonality of variation in $CH_3SO_3^-$ profile below this depth may be attributed to smoothing modification of concentration profile, which is probably relating to snow metamorphism as reported for ice cores obtained from other place in Antarctica (Mulvaney et al., 1992).

Table 2. Average ionic concentrations in samples for the upper 10 m profile

(1)	(2) Sample types	(3) Depth interval (m)	(4) Sample thickness (cm)	(5) No. of samples	(6)	(7)	(8) Concentration	(9)	(10)	(11)
					$CH_3SO_3^-$ neq/g	$nssSO_4^{2-}$ neq/g	NO_3^- neq/g	Cl^- neq/g	Na^+ neq/g	Mg^{2+} neq/g
		NBY89 (main site, 1 km upstream from 1989 surface camp)								
1a	snow pit	0-2	5	40	0.11 (0.10)	0.98 (0.52)	0.89 (0.45)	1.58 (0.93)	1.13 (0.74)	0.30 (0.20)
1b	core	0-2	10	19	0.09 (0.08)	1.15 (0.56)	0.89 (0.40)	1.24 (0.87)	0.83 (0.65)	0.22 (0.16)
1c	core	0-10	11	88	0.08 (0.06)	0.98 (0.50)	0.77 (0.29)	1.58 (1.24)	1.22 (0.96)	0.31 (0.25)
		NBY-2 (14 km upstream from main site)								
2a	snow pit	0-2	5	40	0.08 (0.07)	0.63 (0.52)	0.87 (0.52)	2.73 (2.93)	1.91 (2.26)	0.48 (0.53)
2b	core	0-2	7	29	0.06 (0.05)	0.65 (0.52)	0.69 (0.26)	1.92 (1.18)	1.48 (1.04)	0.40 (0.26)
2c	core	0-10	5.5	180	0.07 (0.04)	0.73 (0.56)	0.71 (0.31)	2.23 (2.06)	1.61 (1.65)	0.44 (0.43)
		NBY-3 (29 km upstream from main site)								
3a	snow pit	0-2	5	40	0.09 (0.07)	0.71 (0.44)	0.92 (0.37)	1.58 (0.96)	1.09 (0.74)	0.33 (0.23)
3b	core	0-2	7	28	0.05 (0.05)	0.73 (0.48)	0.84 (0.35)	1.58 (1.07)	1.04 (0.83)	0.27 (0.20)
3c	core	0-10	5.5	184	0.07 (0.05)	0.77 (0.50)	0.71 (0.31)	1.58 (1.21)	1.13 (0.96)	0.30 (0.25)

Column 6 to 11: standard deviation (σ) of the average concentration levels
Column 7: non-sea-salt SO_4^{2-} (see text).

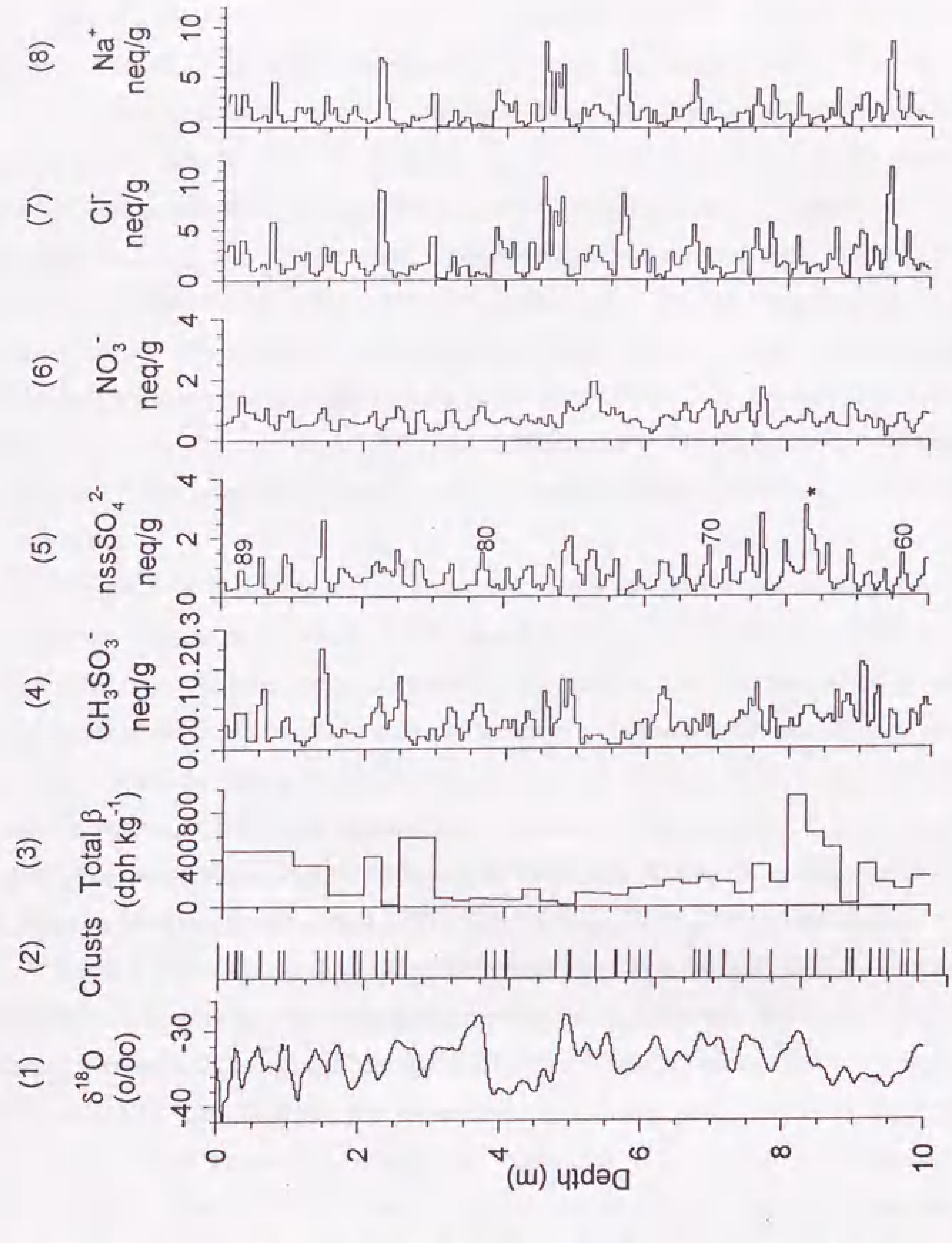


Figure 3. Chemistry and physical properties measurements for the 10 m firn profile at NBY-2. Column 1 is a plot of the $\delta^{18}O$ curve; column 2 shows the distribution of crust layers (as horizontal lines); column 3 shows total β measurements; columns 4 through 8 show curves of various ions. The data plots represent different sample thicknesses for each parameter measured; for $\delta^{18}O$ (10 to 16 samples per year depending on depth); for total β, 25 cm (1.5 to 1 samples per year); and for the ions, 5.5 cm (5 to 7 samples per year). Different horizontal scales are used for each column.

The correlation between $nssSO_4^{2-}$ seasonal peaks and ECM seasonal peaks is strong over the entire NBY89 core as will be discussed later in detail. In column 5, years shown by tick marks are determined by counting $nssSO_4^{2-}$ summer maxima with subsequent refinement when needed by fine-tuning using the $\delta^{18}O$ and ECM curves. The $nssSO_4^{2-}$ curve (column 5) shows the 1966 and 1965 AD accumulation layers are between the 8.2 to 8.4 m depths (designated by an asterisk). The high total-β horizon also correlates well with the age established using the $nssSO_4^{2-}$ (column 3). The 1966/65 interval turns out to be a prime index horizon for dating the near surface stratigraphic layers in this study. The increase in $nssSO_4^{2-}$ appears in both the winter and summer accumulation presumably because of the sustained period of $nssSO_4^{2-}$ deposition from Mt. Agung eruption (8.3°S, 115.5°E) which occurred in March 1963 AD. This relatively broad and high sulfate peak in the 1966 and 1965 layers is found in other Antarctic studies (Legrand and Delmas, 1984; 1987).

The seasonal variations in NO_3^- concentrations in this profile (column 6) show periodicity with summer maxima clearly above 4 m (9 years). The sea-salt components plotted in columns 7 and 8 show large variability and non-systematically spaced winter maximum when compared with peak cycles of $\delta^{18}O$ and $nssSO_4^{2-}$. No clear trends are observed in the sea-salt concentrations at the NBY-2 nor do they correlate closely with the NBY89 and NBY-3 curves. The seasonal variability and magnitude of the measured ionic constituents shown in Fig. 3 agree favorably with results of the atmospheric studies made at both Neumayer Station (Wagenbach et al., 1988) and at Mawson Station (Prospero et al., 1991; Savoie et al., 1992; 1993), Antarctica.

Figure 4 shows plots of the ionic measurements made on the NBY89 main core at a deeper interval including a key acid spike horizon deposited in 1259 AD. The interval was originally selected because it contained the calculated ages of volcanic eruptions. The exact position of the layer was first identified by the measured high strong-acid concentration peaks (ECM measurements) as representing the layers containing the eruption of 1259 AD horizon. Concentration profile of $CH_3SO_3^-$ (column 1) does not show steady cyclic variation and does not correlate with $nssSO_4^{2-}$ variation in column (2). The $nssSO_4^{2-}$ curve (column 2) shows steady cyclic seasonal signals with large amplitude but other acid components in this plot (columns 3 and 4) reveal periodicity to a much lesser degree. All the $nssSO_4^{2-}$ peaks identified by asterisks (*) in Fig. 4, column 2, are taken to represent volcanic eruptions. Except for the large and spurious $nssCl^-$ peak at 95.6 m (column 4), both the NO_3^- and $nssCl^-$ curves do not correlate with volcanic peaks identified in the $nssSO_4^{2-}$ curve.

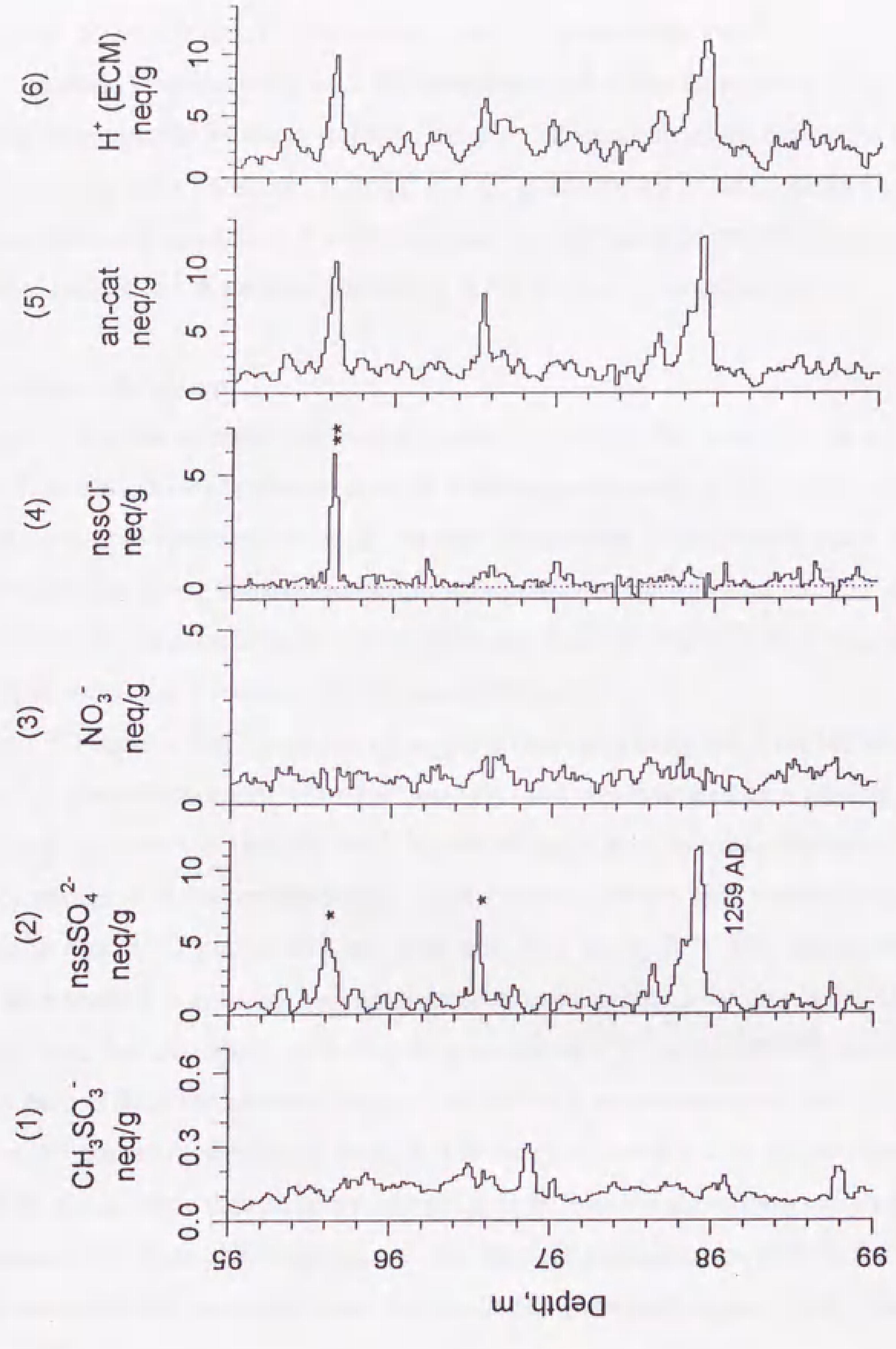


Figure 4. Variations in various acid concentration levels (neq/g) for an interval containing the 1259 AD event and unknown volcanic events (*). Double asterisk is the largest $nssCl^-$ peak in 1346 year chronology associated with $nssSO_4^{2-}$ peak. Column 5 represent $\Sigma(CH_3SO_3^-+Cl^-+NO_3^-+SO_4^{2-})-\Sigma(Na^++Mg^{2+})$ concentration levels. Column 6 shows H^+ concentration levels estimated from ECM (Hammer, 1983).

This anomalously high concentration level of nssCl^- is correlated with nssSO_4^{2-} peak at 1278 AD and presumed to be volcanic HCl in origin. A similar relationship was first reported for high Cl^- peaks in Greenland ice cores (Herron, 1982) associated with volcanic eruption. The acid character of this peak is supported by the correlation between H^+ concentrations calculated (column 5) as total anion minus cation contents in neq/g and H^+ measured by ECM (column 6). On the other hand, a comparison of columns 1, 5 and 6 suggests that the cause of cyclic ECM signal variations is attributed mainly to the seasonal variations in the nssSO_4^{2-} concentration.

(ii) The last millennium

Figure 5 is a plot of multi-year ionic averages measured in the main core over the entire 164 m depth. The data points represent average measurements made at 74 distinct depth-levels on continuous multiple specimens from a 1 m core increments. Each plotted point represents the average of between 10 to 50 individual sample measurements. Background nssSO_4^{2-} concentration levels (column 3) are calculated from measurements made on samples from non-volcanic time-periods in an individual 1 m core interval (see section 2-5).

The $\delta^{18}O$ curve in Fig. 5 (column 1) suggests that a warming trend started about 400 years B.P., reached a broad maximum about 150 years ago and was followed by a general, but variable, cooling trend; however this trend in the $\delta^{18}O$ record could also be caused by local differences of isotopic composition of the deposited snow. A relatively cooler but also variable period of change is shown in the $\delta^{18}O$ curve between 500 and 900 years B.P. Measurements of $HCOO^-$ concentration levels in porous firn samples have an inherent problem for contamination of gaseous formic acid from the laboratory air during ice core storage. Thus, the $HCOO^-$ profile (column 2) presented here is from the close-off depth at about 60 m to the bottom of the NBY89 core and shows almost constant concentration levels at 0.04 neq/g in average with variation range between 0.02 to 0.06 neq/g. Note that no sporadic high peak is found in short-term variations of $HCOO^-$ concentration levels through the entire core. The $HCOO^-$ concentration level in the NBY89 core is comparable with other published Antarctic results (Legrand and Saigne, 1988; Legrand and De Angelis, 1995).

The $CH_3SO_3^-$ curve (column 3) is characterized by a clear depression at about 350 to 150 years B.P. which is in reverse phase with the $\delta^{18}O$ curve. The nssSO_4^{2-} curve (column 6) shows a very slight increasing trend between 300 to 100 years B.P. but no indication of anthropogenic increase is evident in the profile.

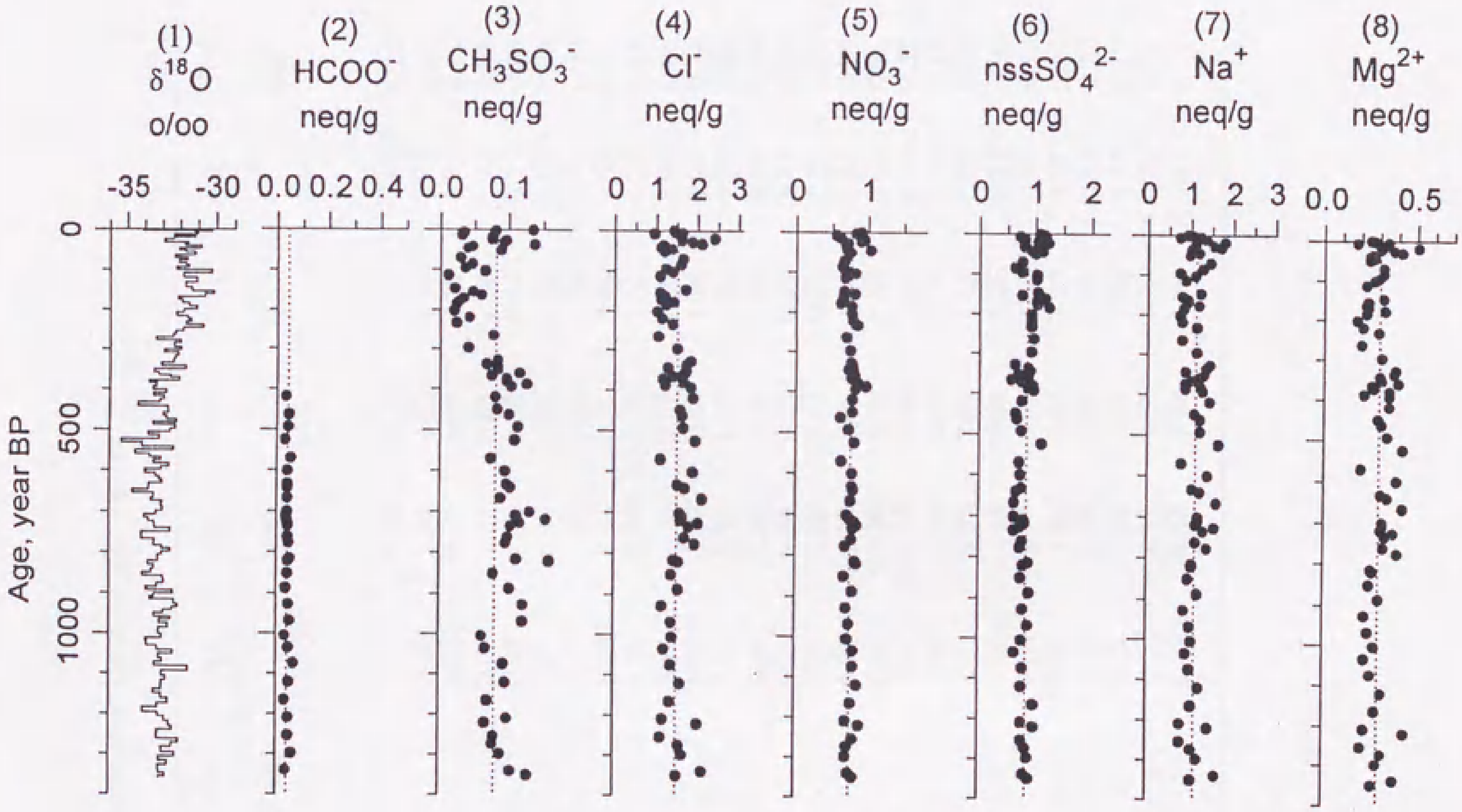


Figure 5. Stable isotope curve (column 1) and average multi-year ionic concentration levels (columns 2-7) as a function of age before 1989 for the 164 m NBY89 core. Data points represent average values for 1 m core increments.

Table 3. Summary of multi-year average ionic concentration levels of the NBY89 core

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
No. of sample	Sample size (cm)	Sample Age (BP)	(AD)	Depth range from (m)	to (m)	Concentration (neq/g) $HCOO^-$	$CH_3SO_3^-$	Cl^-	NO_3^-	SO_4^{2-}	Na^+	Mg^{2+}	$nssSO_4^{2-}$	ssSO4 (nmol/g)	$nssSO_4^{2-}$ $+CH_3SO_3^-$ (nmol/g)	SMR
10	5	1	1989	0.0	1.0	-	0.13	1.41	0.89	1.17	0.91	0.25	1.06	0.05	0.66	4.0
10	5	3	1988	1.0	2.0	-	0.08	1.44	0.82	1.33	1.04	0.27	1.10	0.06	0.63	6.9
8	12	7	1985	2.0	3.0	-	0.03	0.93	0.55	0.79	0.74	0.17	0.71	0.04	0.39	10.9
9	11	6	1983	3.0	4.0	-	0.08	1.61	0.85	1.28	1.22	0.34	1.15	0.07	0.65	7.4
9	11	14	1979	4.0	5.0	-	0.03	1.58	0.60	0.94	1.35	0.33	0.79	0.08	0.43	13.0
8	11	19	1975	5.0	6.0	-	0.07	2.40	0.94	1.23	1.78	0.50	1.02	0.11	0.59	6.8
8	11	24	1971	6.0	7.0	-	0.07	1.61	0.89	1.34	1.09	0.30	1.21	0.07	0.68	8.1
9	11	28	1966	7.0	8.0	-	0.09	1.86	0.71	0.96	1.52	0.37	0.79	0.09	0.49	4.2
10	11	32	1961	8.0	9.0	-	0.09	2.09	0.68	1.00	1.70	0.41	0.79	0.10	0.49	4.3
9	11	37	1956	9.0	10.0	-	0.14	1.16	0.69	1.20	1.00	0.26	1.08	0.06	0.68	4.0
11	11	42	1952	10.0	11.0	-	0.05	1.10	0.69	1.04	1.00	0.24	0.92	0.06	0.50	10.1
5	10	46	1948	11.0	12.0	-	0.04	1.35	1.02	1.10	1.17	0.26	1.10	0.07	0.59	14.2
31	3	51	1943	12.0	12.5	-	0.09	1.18	0.74	1.14	0.96	0.24	0.98	0.06	0.58	5.6
11	9	71	1923	15.0	16.0	-	0.03	1.64	0.66	0.93	1.43	0.31	0.75	0.09	0.40	13.2
10	10	86	1904	18.0	19.0	-	0.05	1.58	0.63	0.77	1.26	0.31	0.63	0.08	0.36	6.9
31	3	96	1893	20.0	21.0	-	0.03	1.21	0.68	1.09	0.74	0.29	0.75	0.04	0.41	10.8
31	3	103	1886	21.0	22.0	-	0.06	1.38	0.81	1.50	1.09	0.26	1.00	0.07	0.56	7.8
32	3	114	1875	22.0	23.0	-	0.01	1.07	0.68	1.10	0.87	0.22	1.00	0.05	0.51	47.5
9	11	147	1842	25.0	26.0	-	0.02	1.69	0.66	1.17	1.22	0.31	1.02	0.07	0.53	25.5
32	3	155	1834	26.0	27.0	-	0.05	1.07	0.81	1.48	0.78	0.23	0.75	0.05	0.42	8.1
31	3	163	1826	27.0	28.0	-	0.06	1.18	0.65	1.26	0.91	0.22	1.15	0.05	0.63	9.7
38	2.5	171	1818	28.0	29.0	-	0.03	1.10	0.65	1.80	0.91	0.23	1.00	0.05	0.53	15.3
38	2.5	178	1811	29.0	30.0	-	0.03	1.41	0.61	1.42	1.17	0.32	1.02	0.07	0.54	18.6
31	3	185	1804	30.0	31.0	-	0.02	1.24	0.76	1.33	0.83	0.22	1.23	0.05	0.64	26.5
9	10	203	1786	32.0	33.0	-	0.02	1.02	0.76	1.00	0.74	0.17	0.92	0.04	0.48	24.2
31	3	220	1769	34.0	35.0	-	0.04	1.13	0.77	1.21	0.78	0.21	0.92	0.05	0.50	11.2
9	10	234	1755	36.0	37.0	-	0.02	1.38	0.84	1.04	1.13	0.29	0.92	0.07	0.48	19.8

Table 3. Summary of multi-year average ionic concentration levels of the NBY89 core (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
No. of sample	Sample size (cm)	Sample Age (BP)	(AD)	Depth range from (m)	to (m)	Concentration (neq/g) $HCOO^-$	$CH_3SO_3^-$	Cl^-	NO_3^-	SO_4^{2-}	Na^+	Mg^{2+}	$nssSO_4^{2-}$	ssSO4 (nmol/g)	$nssSO_4^{2-}$ $+CH_3SO_3^-$ (nmol/g)	SMR
39	3	265	1724	40.0	41.0	-	0.08	1.04	0.69	1.06	0.78	0.20	0.96	0.05	0.56	6.2
10	10	298	1691	44.0	45.0	-	0.04	1.50	0.74	1.06	1.13	0.30	0.92	0.07	0.50	11.5
10	10	329	1660	48.0	49.0	-	0.08	1.83	0.76	0.78	1.43	0.38	0.63	0.09	0.40	3.8
31	3	339	1650	49.0	50.0	-	0.07	1.72	0.77	1.23	1.35	0.37	0.85	0.08	0.49	6.3
31	3	345	1644	50.0	51.0	-	0.08	1.27	0.73	1.00	0.87	0.30	0.90	0.05	0.53	5.4
10	10	354	1635	51.0	52.0	-	0.08	1.72	0.79	0.90	1.30	0.30	0.69	0.08	0.43	4.1
31	3	361	1628	52.0	53.0	-	0.11	1.66	0.81	1.24	1.17	0.40	0.85	0.07	0.54	3.7
32	3	367	1622	53.0	54.0	-	0.07	1.41	0.76	0.69	1.04	0.26	0.56	0.06	0.36	3.8
31	3	374	1615	54.0	55.0	-	0.10	1.16	0.82	0.85	0.87	0.26	0.75	0.05	0.47	3.9
33	3	381	1608	55.0	56.0	-	0.10	1.66	0.85	1.60	1.22	0.35	0.94	0.07	0.56	4.9
34	3	388	1601	56.0	57.0	-	0.13	1.21	0.97	1.15	0.87	0.21	0.85	0.05	0.55	3.4
38	2.5	394	1592	57.0	58.0	-	0.10	1.83	0.82	1.06	1.26	0.35	0.96	0.08	0.58	4.6
10	10	420	1569	60.0	61.0	0.03	0.08	1.89	0.77	0.92	1.43	0.35	0.75	0.09	0.46	4.7
32	3	450	1539	63.5	64.5	-	0.08	1.58	0.77	0.91	1.09	0.29	0.65	0.07	0.41	3.9
11	10	464	1525	65.0	66.0	0.04	0.10	1.64	0.61	0.82	1.22	0.30	0.67	0.07	0.43	3.3
11	10	494	1495	69.0	70.0	0.04	0.11	1.66	0.73	0.92	1.22	0.34	0.75	0.07	0.49	3.3
48	2	526	1463	73.0	74.0	0.03	0.11	1.95	0.81	2.16	1.65	0.42	1.10	0.10	0.66	5.1
11	10	571	1418	78.0	79.0	0.05	0.07	1.10	0.63	0.80	0.78	0.20	0.71	0.05	0.43	4.8
10	10	602	1387	82.0	83.0	0.04	0.09	1.89	0.77	1.33	1.39	0.39	0.73	0.08	0.46	3.8
10	10	634	1355	86.0	87.0	0.04	0.10	1.52	0.77	0.80	1.04	0.30	0.75	0.06	0.47	3.9
48	2	642	1347	87.0	88.0	0.04	0.10	1.69	0.79	1.24	1.22	0.34	0.67	0.07	0.44	3.3
9	10	668	1321	90.0	91.0	0.04	0.09	2.12	0.76	0.81	1.61	0.42	0.63	0.10	0.40	3.5
48	2	702	1287	94.0	95.0	0.04	0.13	1.58	0.71	1.16	1.17	0.31	0.63	0.07	0.44	2.4
47	2	710	1279	95.0	96.0	0.04	0.11	1.64	0.74	1.37	1.17	0.31	0.79	0.07	0.51	3.6
51	2	719	1270	96.0	97.0	0.04	0.15	1.61	0.81	1.23	1.13	0.30	0.81	0.07	0.56	2.6
47	2	727	1262	97.0	98.0	0.04	0.12	2.03	0.84	2.32	1.57	0.37	0.73	0.09	0.48	3.1
46	2	735	1254	98.0	99.0	0.04	0.10	1.81	0.79	0.79	1.30	0.33	0.63	0.08	0.42	3.0
48	2	762	1227	101.0	102.0	0.04	0.10	1.69	0.77	1.23	1.13	0.32	0.77	0.07	0.48	3.9

Table 3. Summary of multi-year average ionic concentration levels of the NBY89 core (continued)

(1) No. of sample	(2) Sample size (cm)	(3) Sample Age (BP)	(4) (AD)	(5) Depth range from (m)	(6) to (m)	(7) Concentration (neq/g) $HCOO^-$	(8) $CH_3SO_3^-$	(9) Cl^-	(10) NO_3^-	(11) SO_4^{2-}	(12) Na^+	(13) Mg^{2+}	(14) $nssSO_4^{2-}$	(15) ssSO4 (nmol/g)	(16) $nssSO_4^{2-}$ $+CH_3SO_3^-$ (nmol/g)	(17) SMR
10	10	777	1212	103.0	104.0	0.05	0.10	1.95	0.69	0.89	1.39	0.40	0.73	0.08	0.46	3.8
10	10	816	1173	108.0	109.0	0.05	0.11	1.44	0.82	1.31	1.04	0.26	0.88	0.06	0.55	3.9
41	2	821	1168	109.0	109.7	0.04	0.16	1.55	0.84	1.43	1.04	0.26	0.79	0.06	0.55	2.5
10	10	852	1137	112.0	113.0	0.04	0.08	1.38	0.68	0.86	0.96	0.25	0.75	0.06	0.45	4.8
46	2	888	1101	116.0	117.0	0.04	0.10	1.55	0.79	1.02	1.17	0.30	0.90	0.07	0.55	4.4
9	10	928	1061	121.0	122.0	0.05	0.12	1.16	0.71	0.90	0.87	0.22	0.79	0.05	0.52	3.3
10	10	969	1020	126.0	127.0	0.05	0.12	1.38	0.74	1.00	1.00	0.24	0.88	0.06	0.56	3.6
42	2	1006	983	130.0	131.0	0.03	0.06	1.41	0.73	0.90	1.04	0.27	0.77	0.06	0.45	6.2
10	10	1036	953	133.0	134.0	0.05	0.07	1.21	0.81	0.75	0.91	0.22	0.65	0.05	0.39	4.8
10	10	1075	914	137.0	138.0	0.07	0.09	1.38	0.81	0.90	1.00	0.26	0.79	0.06	0.49	4.2
18	5	1121	868	141.0	142.0	0.05	0.10	1.61	0.85	1.30	1.22	0.31	0.77	0.07	0.48	4.0
49	2	1165	824	145.0	146.0	0.03	0.07	1.35	0.77	1.10	1.04	0.28	0.98	0.06	0.56	6.9
8	10	1209	780	149.0	150.0	0.05	0.10	1.18	0.71	0.87	0.78	0.22	0.77	0.05	0.48	3.9
29	2	1221	768	150.0	150.6	-	0.07	2.03	0.89	1.14	1.43	0.44	0.98	0.09	0.56	7.3
10	10	1254	735	153.0	154.0	0.05	0.08	1.13	0.81	0.86	0.78	0.21	0.77	0.05	0.47	4.8
40	2	1274	715	155.0	156.0	-	0.08	1.58	0.73	0.96	1.04	0.31	0.83	0.06	0.49	5.3
9	10	1299	690	157.0	158.0	0.06	0.09	1.66	0.71	1.01	1.17	0.29	0.88	0.07	0.53	4.9
43	2	1341	648	161.0	162.0	0.04	0.10	2.14	0.74	1.01	1.61	0.38	0.81	0.10	0.51	3.9
35	2	1351	638	162.0	162.7	-	0.13	1.52	0.81	1.02	1.04	0.26	0.90	0.06	0.58	3.5
		Mean				0.04	0.08	1.51	0.76	1.11	1.13	0.30	0.85	0.07	0.51	7.4
		Minimum				0.03	0.01	0.93	0.55	0.69	0.74	0.17	0.56	0.04	0.36	2.4
		Maximum				0.07	0.16	2.40	1.02	2.32	1.78	0.50	1.23	0.11	0.68	47.5
		STD				0.01	0.03	0.31	0.08	0.29	0.25	0.07	0.15	0.01	0.08	7.0

The NO_3^- curve (5) is relatively flat with 1σ of 0.08 neq/g over the entire core profile. This suggests a constant source/sink processes during the last millennium at this site. The variations in sea-salt components (columns 4, 7 and 8) show nearly coincident variations. On average, the sea-salts have ionic ratios close to sea water. The overall average concentration values for the ionic constituents shown in Fig. 5 are :$HCOO^-$, 0.04 (below the close-off depth of 60 m); $CH_3SO_3^-$, 0.08; SO_4^{2-}, 1.10 (non-volcanic $nssSO_4^{2-}$, 0.85); NO_3^-, 0.76; Cl^-, 1.52; Na^+, 1.13; and Mg^{2+}, 0.30 in neq/g units. Measurements of NH_4^+, K^+ and Ca^{2+} were mostly below instrument detection levels.

(iii) Non-volcanic sulfur budget

Earlier investigations (e.g. Herron, 1982; Delmas et al., 1982) reported sea-salts, marine biogenic activity and sporadic volcanic events as the main sulfur sources for Antarctic snow deposits. Figure 6 shows the $\delta^{18}O$ (column 1), the amount of sea-salt SO_4^{2-} (column 2) estimated from Na^+ content and the SO_4^{2-}/Na ratio in sea water, total amount of background $nssSO_4^{2-}$ plus $CH_3SO_3^-$ concentrations (column 3, hereafter Total Background Sulfur, TBS) in nmol/g units, and sulfur molar ratio (SMR) of $nssSO_4^{2-}$ / $CH_3SO_3^-$ (column 4). The sulfur contributions from sea-salts (column 2) to have provided a fairly constant flux over the last 13 centuries and to have an average contributed only 12% of the total non-volcanic sulfur (background $SO_4^{2-} + CH_3SO_3^-$).

Column 3, Fig. 6, shows the variations of TBS concentration levels and column 4 shows the SMR for the NBY89 core. The TBS curve shows no significant trend. As discussed in previous section, the depression of $CH_3SO_3^-$ concentration at about 200 years B.P. was compensated by unti-correlating slight increase of $nssSO_4^{2-}$ in the profile of TBS. This suggests the same source for the TBS as well as $CH_3SO_3^-$ but different sink processes may be involved. The average TBS content is 0.51 nmol/g (16 ng-S/g), and represents 88% of the total non-volcanic sulfur budget measured in this core, suggesting biogenic sulfur constantly contributed a major portion of the background sulfur cycle at Byrd station during the last millennium.

The sulfur molar ratios (SMR, column 4) for the entire core range from 2.4 to 48 and the mean value is 7.4 calculated by using individual 1 m multi-year average value. The SMR profile shows constant values (about 4) from 1400 to 300 years B.P. and suddenly higher ratios (>15) around 200 years B.P. The constant molar ratio at about 4 is very close but slightly higher than the results from aerosol studies at high latitude oceanic region (Savoie et al., 1993).

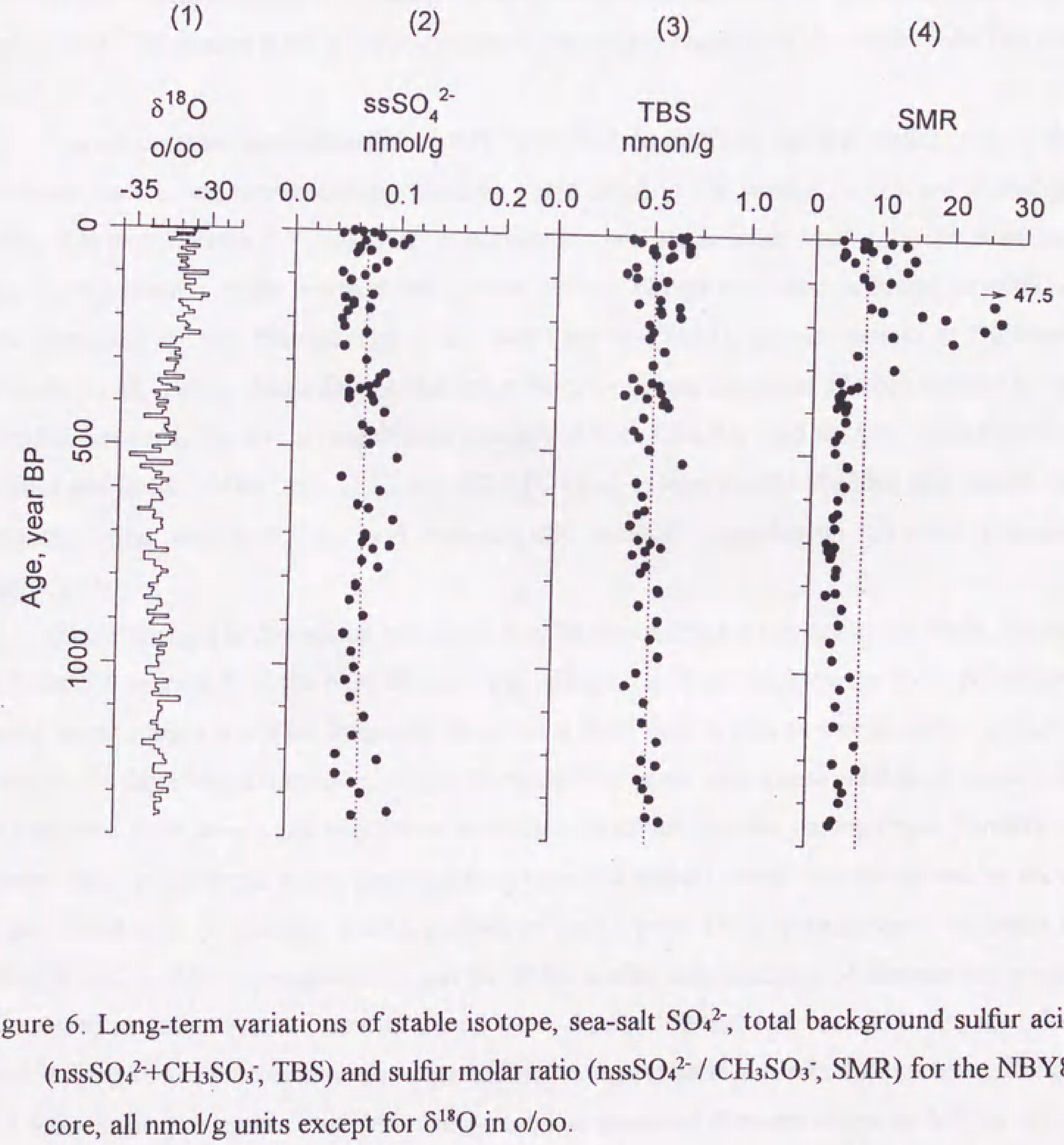


Figure 6. Long-term variations of stable isotope, sea-salt SO_4^{2-}, total background sulfur acids ($nssSO_4^{2-}$+$CH_3SO_3^-$, TBS) and sulfur molar ratio ($nssSO_4^{2-}$ / $CH_3SO_3^-$, SMR) for the NBY89 core, all nmol/g units except for δ^{18}O in o/oo.

The increase of SMR around 200 years B.P. could be attributed to one or all of the following causes: (1) changes in air temperature at the source region, (2) increase in non-biogenic $nssSO_4^{2-}$ contribution and (3) changes in transport system from source region or deposition processes. First, air temperature at the source region might be warmed up as inferred from the warming trend in the $\delta^{18}O$ curve around 200 years B.P. instead of ice flow effect mentioned in previous section. According to the laboratory experiments (Hynes et al., 1986), warmer air temperature may introduce the higher oxidation branching ratio from DMS to SO_2. This may lead higher molar ratio of $nssSO_4^{2-}$ / $CH_3SO_3^-$ in aerosols at the source area. However, assuming changes in the $\delta^{18}O$ profile (from -34 o/oo to -31 o/oo) are solely derived from temperature, only small air temperature (about 3 °C) change would be expected from the $\delta^{18}O$ profile (Dansgaard et al., 1973). This change is too small to introduce the sudden big shift of the SMR in the NBY89 core.

Second, increase in non-biogenic $nssSO_4^{2-}$ contribution might be another explanation. If the unknown source was active and significantly contributed to the west Antarctic sulfur budget during 350 to 150 years B.P., $nssSO_4^{2-}$ concentration profiles at other west Antarctic sites may also show a similar slight increase during this period. No such a trend is found in $nssSO_4^{2-}$ concentrations at Dyer Plateau (Dai et al., 1995) nor in $CH_3SO_3^-$ concentrations at Dolleman (Pasteur et al., 1995). According to the result from Dolleman and Dyer Plateau located in the Weddell Sea area, there is no significant changes in both $CH_3SO_3^-$ and $nssSO_4^{2-}$ concentration profiles and in the SMRs from 1652 to 1992 AD. Thus, at least for the Weddell Sea sector, the biogenic sulfur source activity and non-biogenic $nssSO_4^{2-}$ contribution have not changed significantly.

Finally, changes in deposition processes may be the reason for the significant SMR change at about 200 years B.P. in the NBY89 core. For example, drifting and blowing snow conditions due to strong surface winds are frequently observed at Byrd Station area as well as other Antarctic stations (Budd, 1966; Dalrymple, 1966). Such drifting snow may cause mixing of seasonally accumulated snow layers and may cause redistribution of snow under the lee slope. Summer to winter ratio of seasonal snow accumulation rate and annual mean concentrations in snow accumulated may be changed during periods of high winds. To fit with observed changes in $CH_3SO_3^-$ and $nssSO_4^{2-}$ concentrations and the SMR profile, accumulation of summer snow may be reduced by some reasons, such as strong wind, during 300 and 150 years B.P. On the other hand, drifting snow particles may scavenge additional atmospheric aerosols during their saltation and suspension processes. This will change original chemical concentrations in drifting snow particles. This could make additional changes in $CH_3SO_3^-$ and $nssSO_4^{2-}$ concentrations during frequent drifting snow periods, thus frequency of drifting snow (strong wind) could be different during this period.

(iv) Volcanic events

Figure 7 is a time-series plot of the volcanic H_2SO_4 fluxes (kg/km^2) calculated for the NBY89 core. The fluxes are estimated by subtracting the average non-volcanic nssSO_4^{2-} from the SO_4^{2-} measurements following the procedures in Langway et al. (1988) and Clausen and Hammer (1988). The variability of natural background flux of 5 kg/km^{2}yr at 2σ is estimated from averaging vertical and lateral variances in annual H_2SO_4 fluxes (ca. 4 kg/km^{2}yr on average) obtained at the three drilling locations in Byrd station area. The vertical dotted line in Fig. 7 is the upper 2σ limit of background noise level. A H_2SO_4 signal which has a flux greater than 2σ threshold value is considered a volcanic event. The initial identification of a volcanic event layer is made by analysis of strong-acid spikes in the ECM curve. Final annual accumulation layer thickness are corrected for thinning by Nye's approximation (Nye, 1963) for calculating volcanic H_2SO_4 flux at the snow surface. Because of relatively low snow accumulation rates at NBY89, a fixed sample cutting length of 2 cm of ice (about 3 cm of snow) was used for individual chemistry specimens.

A total of 25 volcanic signals greater than 2σ are found in the NBY89 sulfate data. Among those signals, 17 have H_2SO_4 fluxes greater than 10 kg/km^2; the largest flux found in the NBY89 core was 54 kg/km^2, measured at the 1259 AD volcanic index horizon which has been found at other locations in both Antarctica and Greenland (Hammer et al., 1980; Langway et al., 1988; Legrand and Kirchner, 1990; Moor et al., 1991; Palais et al., 1992; Delmas et al., 1992; Zielinski et al., 1994). Figure 7 also implies that volcanic H_2SO_4 signals in the NBY89 core is not distributed at uniform in time intervals: frequent periods from about 800 to 700 years B.P., 400-350 years B.P, around 170 and 100 years B.P. and infrequent period in between.

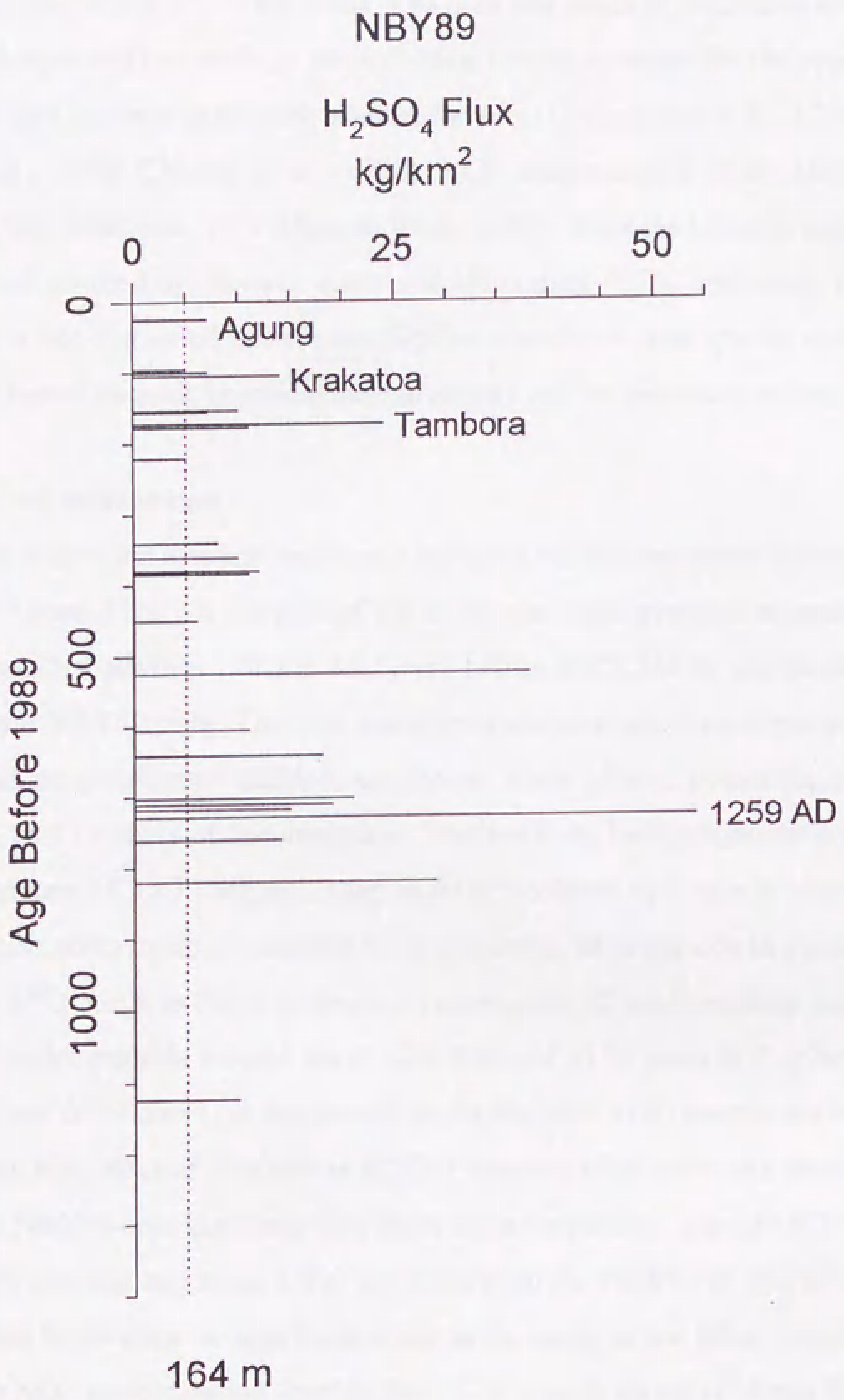


Figure 7. Distribution of volcanic H_2SO_4 fluxes in the NBY89 core as a function of age before 1989. Vertical dotted line on NBY89 curve indicates 2σ background level for average non-volcanic H_2SO_4 fluxes (see text).

3-3. Greenland: Crete-74 core

The 404 m-deep, 12 cm diameter ice core (CR74), was obtained in 1974 at Crete in central Greenland (Langway et al., 1985). The CR74 core was augured continuously by using the thermal drilling technique and recovered in good physical condition except for the upper porous firn layers. The CR74 core has been extensively studied for $\delta^{18}O$ (Dansgaard et al., 1975), accumulation rate (Reeh et al., 1978; Clausen et al., 1988), NO_3^- concentration levels (Risbo et al., 1981) and volcanic events (Hammer, 1977; Hammer et al., 1980). Since the volcanic record in the CR74 core has been well studied by Hammer and co-workers using ECM technique, the volcanic record in the CR74 is not discussed in here but bipolar correlation and spacial variability of the H_2SO_4 deposition based on ionic chemical measurements will be discussed in later section 4-2.

(i) The last millennium

Table 4 lists the average multi-year background concentration levels of ionic constituents in the CR74 core. Figure 8 is a plot of the multi-year ionic averages measured in the CR74 core samples deposited between 170 and 860 years before 1989 AD for comparative purposes for the results of the NBY89 core. The data point represent average measurements made at 13 distinct depth-levels on continuous multiple specimens. Each plotted points represents the average of between 4 and 12 years of accumulation. Similar to the background estimation for the NBY89 core, background $HCOO^-$ (column 2) and $nssSO_4^{2-}$ (column 6) concentration levels are calculated from measurements made on samples from non-event time-periods in a sampling interval.

The $\delta^{18}O$ curve in Fig. 8 (column 1) represents 30 years running mean values and shows relatively cooler periods around about 600, 800 and 1150 years B.P. (Dansgaard et al., 1975). Except for the $\delta^{18}O$ curve, all horizontal scales for each ionic species are the same as plotted in Fig. 5 for the NBY89 core. The plot of $HCOO^-$ concentration levels are about 8 times higher than those in the NBY89 core in average and show large variability. The $CH_3SO_3^-$ concentration levels are relatively constant and about 1/3 of the result from the NBY89 in average. The profile of NO_3^- concentration levels show no significant trend as the same as the other constituents shown in Fig. 5. Average NO_3^- concentration level in the CR74 core is about 1.5 times higher than that in the NBY89 core, whereas average $nssSO_4^{2-}$ concentration level in the CR74 core is about 1.3 time lower than that in the NBY89 core. Theses differences in the average concentration levels are much lesser than the average $HCOO^-$ and $CH_3SO_3^-$ concentration levels, suggesting more abundant source activities in both hemisphere and longer atmospheric lifetime for NO_3^- and $nssSO_4^{2-}$.

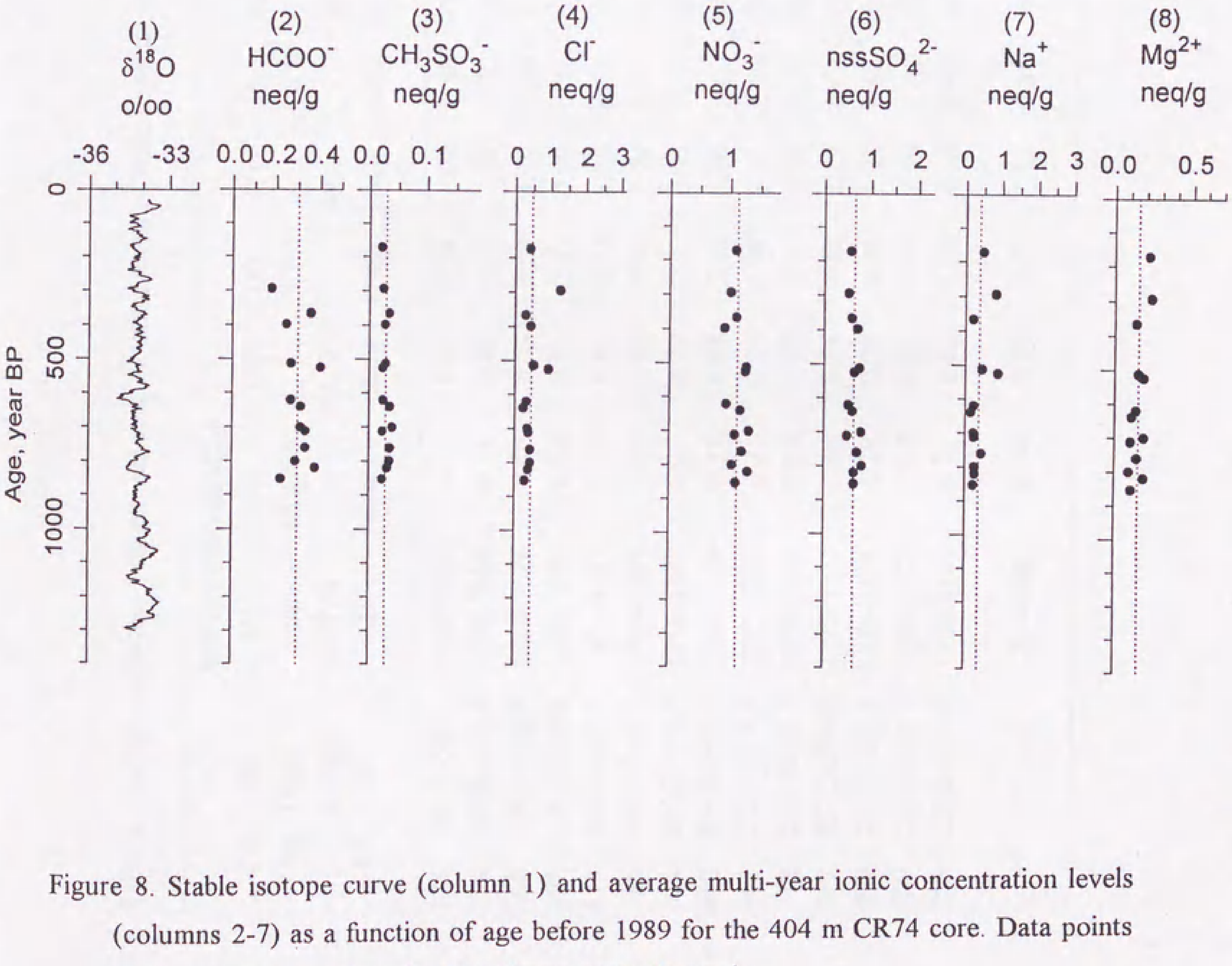


Figure 8. Stable isotope curve (column 1) and average multi-year ionic concentration levels (columns 2-7) as a function of age before 1989 for the 404 m CR74 core. Data points represent average values for 4 to 12 years core intervals.

Table 4. Average multi-year background concentration levels of ionic constituents in the Crete74 core

		Average concentration											
(1) Year BP	(2) Depth Range m	(3) Year Interval AD	(4) $HCOO^-$ neq/g	(5) $CH_3SO_3^-$ neq/g	(6) Cl^- neq/g	(7) NO_3^- neq/g	(8) $nssSO_4^{2-}$ neq/g	(9) Na^+ neq/g	(10) NH_4^+ neq/g	(11) Mg^{2+} neq/g	(12) $ssSO_4^{2-}$ nmol/g	(13) $nssSO_4^{2-}$ $+CH_3SO_3^-$ nmol/g	(14) SMR
173	63.4- 67.7	1809-1820	-	0.02	0.39	1.08	0.56	0.48	-	0.21	0.03	0.30	14.1
294	100.6-101.4	1696-1694	0.18	0.02	1.27	1.00	0.52	0.83	0.22	0.23	0.05	0.28	11.2
366	120.7-122.5	1619-1626	0.36	0.03	0.28	1.10	0.58	0.21	0.21	0.13	0.01	0.33	8.7
398	128.4-131.4	1586-1596	0.24	0.03	0.42	0.90	0.71	-	-	-	0.02	0.38	13.5
513	160.1-162.9	1471-1482	0.27	0.03	0.51	1.26	0.75	0.46	0.27	0.15	0.03	0.40	13.7
525	163.9-166.2	1459-1469	0.40	0.02	0.93	1.24	0.65	0.90	0.36	0.18	0.05	0.35	14.6
621	190.7-191.7	1366-1370	0.27	0.02	0.31	0.96	0.52	0.23	0.27	0.13	0.01	0.28	11.2
640	196.0-198.1	1344-1354	0.31	0.03	0.23	1.16	0.60	0.16	0.27	0.11	0.01	0.37	8.7
701	212.5-213.7	1285-1291	0.31	0.04	0.34	1.31	0.79	0.24	0.34	0.18	0.01	0.43	10.2
712	214.7-216.7	1273-1281	0.33	0.02	0.37	1.08	0.50	0.24	0.34	0.10	0.01	0.27	11.3
761	227.5-229.0	1225-1231	0.33	0.04	0.42	1.19	0.71	0.45	0.26	0.14	0.03	0.39	9.9
800	237.1-239.6	1184-1193	0.29	0.03	0.42	1.03	0.81	0.27	0.35	0.09	0.02	0.44	11.7
820	243.0-244.5	1166-1171	0.38	0.03	0.37	1.29	0.65	0.27	0.29	0.18	0.02	0.35	10.6
853	251.3-254.0	1131-1141	0.22	0.02	0.28	1.10	0.65	0.23	0.23	0.11	0.01	0.35	14.6
		Average	0.30	0.03	0.47	1.12	0.64	0.38	0.28	0.15	0.02	0.35	11.7

The variations in sea-salt components (columns 4, 7 and 8) show nearly coincident variations. On average, the sea-salts have ionic ratios close to sea water with some variabilities. Concentration levels of sea-salts in the CR74 core are about 1/3 of those in the NBY. These differences in average concentration levels between the NBY and the CR74 will be discussed later with geographical distribution of concentration levels of ionic constituents and deposition fluxes.

(ii) Non-volcanic sulfur budget

Figure 9 shows the $\delta^{18}O$ (column 1), the amount of sea-salt SO_4^{2-} (column 2) estimated from Na^+ content and the SO_4^{2-}/Na ratio in sea water. The sulfur contributions from sea-salts (column 2) have an average contribution of only 6% of the total non-volcanic sulfur (background $SO_4^{2-} + CH_3SO_3^-$) with minor long-term changes in concentration levels. Column 3, Fig. 9, shows the variations of total background non-sea-salt sulfur (TBS) concentration levels and column 4 shows the sulfur molar ratio (SMR) of $nssSO_4^{2-} / CH_3SO_3^-$ for the CR74 core. The TBS curve shows no significant trend. The average TBS content is 0.35 nmol/g (11 ng-S/g), and represents 94% of the non-volcanic total sulfur budget measured in this core, suggesting sulfur other than sea-salt fraction constantly contributed to a major portion of the background sulfur cycle at Crete station during the last millennium. The SMR (column 4) for the entire core is 11.7 in average with the variation range from 8.7 to 14.6. The SMR profile shows no significant trend over the profile. A fairly constant SMR at about 12 is a factor of 4 larger than those in aerosol studies at the present Icelandic clean air (Prospero et al., 1995). The increase of the SMR for ice layers deposited after the industrial revolution was reported for a south Greenland ice core (Whung et al., 1994) due to increase of anthropogenic contribution of background $nssSO_4^{2-}$. Since the study period in the CR74 core does not extent to post-industrial revolution period, a discussion of the anthropogenic contribution is not in the scope of this study.

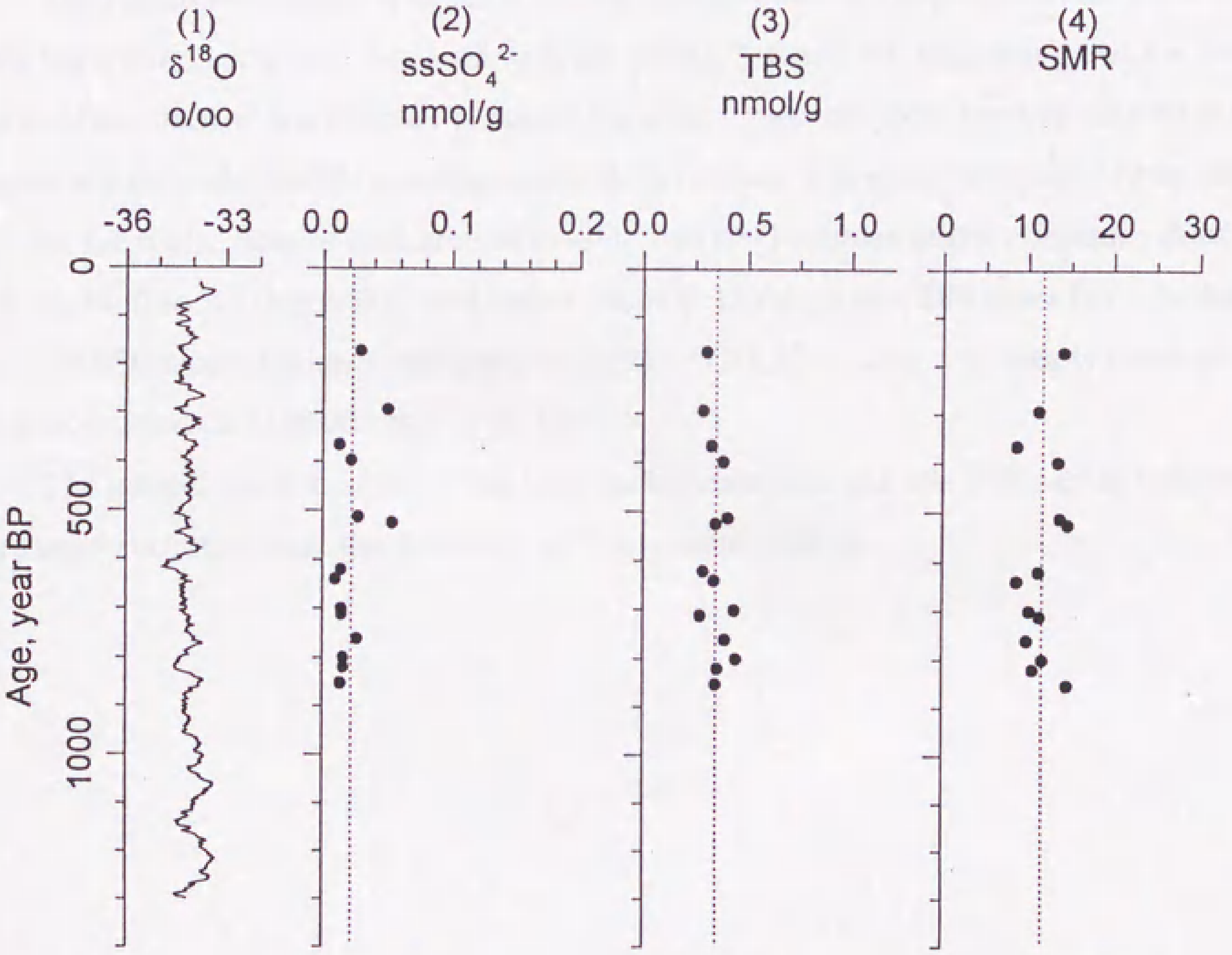


Figure 9. Long-term variations of stable isotope, sea-salt SO_4^{2-}, total background sulfur acids ($nssSO_4^{2-}$+$CH_3SO_3^-$, TBS) and sulfur molar ratio ($nssSO_4^{2-}$ / $CH_3SO_3^-$, SMR) for the CR74 core, all nmol/g units except for $\delta^{18}O$.

3-4. Chapter summary

In this chapter, a detailed record for the Byrd Station Antarctica area was presented for the temporal variations of ionic concentrations and volcanic events between 629 A.D. and 1989 A.D. A comparative study was made with the Crete station, central Greenland between 1130 A.D. and 1820 A.D.

The SO_4^{2-} results show that the west Antarctic total sulfur budget is significantly increased by the 25 major volcanic eruptions identified in the NBY89 core. The largest volcanic contribution over the last millennium in the NBY89 core is found on samples deposited in the 1259 AD horizon with a magnitude 14 times larger than the normal annual background $nssSO_4^{2-}$ flux in the Byrd station area.

The seasonal variations of $CH_3SO_3^-$ concentrations in snow samples from the shallow depth at the Byrd station area correlate well with the $nssSO_4^{2-}$ variations, suggesting that the dominant source of the $nssSO_4^{2-}$ and $CH_3SO_3^-$ is marine biogenic dimethylsulfide. For the NBY89 core, the biogenically derived $CH_3SO_3^-$ concentrations shows a clear depression at about 350 to 150 years B.P and the molar ratio of background $nssSO_4^{2}$ / $CH_3SO_3^-$ shows nearly constant values (about 4) from 1400 to 300 years B.P. and higher ratios (>15) at around 200 years B.P. In the CR74 core, $CH_3SO_3^-$ concentration levels and the $nssSO_4^{2}$ / $CH_3SO_3^-$ ratios were nearly constant during the period between 1130 AD and 1820 AD.

The sea-salt fraction of SO_4^{2-} and total background non-sea-salt sulfur acids concentration were nearly constant over the Antarctic and Greenland profiles.

4. Prominent bipolar volcanic events

4-1. Introduction

In this chapter, the results of a multi-parameter investigations made on five ice cores (NBY89, SP78, CR74, D3 81 and D3 18C) from Greenland and Antarctic locations are discussed. The main emphasis is on the chemical stratigraphy and volcanic-acid records of these cores in an attempt to horizontally trace the prominent volcanic layers identified in the Antarctic cores with other ice cores from Greenland. This bipolar comparison of volcanic signals in polar ice cores may provide a view of volcanic disturbance in sulfur budget occurring in interhemispheric scale.

4-2. Bipolar record

The prominent acid spikes detected in ice cores by electrical and chemical measurements are mainly a representation of variations in H_2SO_4 (and in a few cases HCl and HF) concentration levels associated with major gaseous volcanic eruptions (Hammer, 1977, 1980, 1983; Hammer et al., 1978, 1980, 1994; Delmas and Boutron, 1978, 1980; Clausen and Hammer, 1988; Clausen and Langway, 1989; Legrand and Delmas, 1987; Lyons et al., 1990; Moore et al., 1991; Delmas et al., 1992; Zielinski et al., 1994) and may represent volcanic events of local, regional or bi-hemispheric origin (Hammer, 1984). At lower concentration levels, continuous systematic and sequential seasonal variations in acidity are also identified to great depths in ice cores. The annual signals are mainly attributed to factors related to seasonal changes in the sources of the acids (Hammer, 1983; Hammer et al., 1994, see also section 3-2, Figure 4).

Figure 10 shows the continuous acidity (estimated from ECM) and $\delta^{18}O$ curves for the 164 m long NBY89 core. Similar curves exist for all cores used in this study. All ECM and $\delta^{18}O$ data are from University of Copenhagen (Table 1). The annual H^+ (ECM) time-series curve for the NBY89 shown in Fig. 10a may be used as a general "volcanic" activity nomograph. Layers that show high H^+ concentration levels above 2σ threshold value (3.3 neq/g) from the average (1.96 neq/g) are candidates for finding a volcanic signature in ionic chemistry.

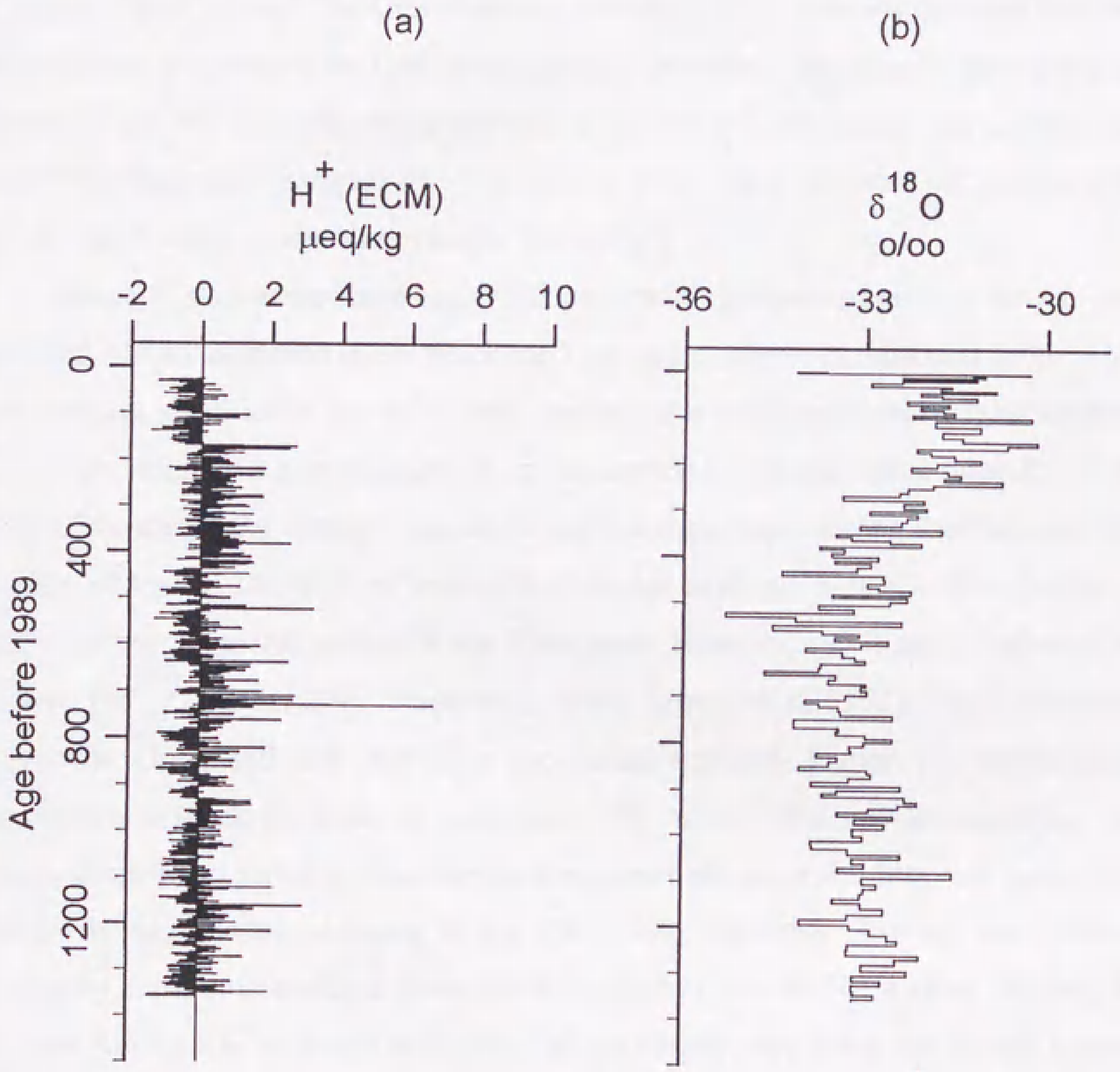


Figure 10. The continuously measured results from the ECM and δ^{18}O studies on the NBY89 core. The results shown in Fig. 10a is a plot of departures from the mean ECM value of 1.96 neq/g. Figure 10b shows the complete δ^{18}O curve plotted in 1-m averages. These data were compiled from 8 to 5 samples per year measurements for dating purposes over the top 25 m.

Figures 11 through 15 show plots of the $nssSO_4^{2-}$ measured in the various cores at selected depths (ages). The ages shown are estimated from time-scales developed for each core (section 2-4). Of special interest in Fig. 11 is the nearly equal concentration level maxima of the $nssSO_4^{2-}$ content in both hemispheres from the Krakatoa event. The main eruptive violence of Krakatoa (6°S, 105°E) occurred on August 26, 1883 (Simkin, et al., 1981; Newhall and Self, 1982). In an earlier analysis of the Crete core Hammer (1977) concluded it took about one-year for the Krakatoa signal to reach the Greenland ice sheet and about a two-year period for the maximum concentration to appear in the Crete area in central Greenland. The signal first appears in the south Greenland D3 18C core after only a one-year delay, but still shows a strong residual SO_4^{2-} deposit for the following year. (samples of 1884 AD and 1885 AD strata were not available from the D3 81 and CR74 cores to measure ions for this study.)

Figure 12 shows maximum $nssSO_4^{2-}$ concentration horizons at bi-polar sites in the 1835 AD and 1832 AD accumulation layers which are 3 to 5 times above background levels. The 1832 AD layer was not identified in the SP78 core, possibly due to the relatively low accumulation rate at South Pole. Figure 12 is an example of an "unidentified" volcanic event often found in ice cores. Figure 13a shows the chemical signals in various cores representing the Tambora (8°S, 118°E) eruption of April 5, 1815 and an "unidentified" marker at about 1810 AD. This doublet of volcanic events has been reported earlier for the Crete core (Hammer, 1977) and by others (Legrand and Delmas, 1987; Dai et al., 1991; Moore et al., 1991; Delmas et al, 1992). The Tambora signal peak appears in Greenland one year after the actual eruption. Figure 13b shows high $nssSO_4^{2-}$ concentration levels between the indicated 1450 AD to 1464 AD accumulation layers in the various cores. Most probably these signals all represent the same real time-unit period of 1459 AD due to the high dating accuracy of the CR74; the variations observed are likely due to the uncertainty in the time-scales at these depth, particularly for the SP78 core. Of note, however, is the 1464 AD horizon measured in the NBY89 core which represents the second highest $nssSO_4^{2-}$ concentration peak measured in that entire core.

Figure 14 shows correlative volcanic layers at 1339 AD to 1348 AD (row a) at about the same $nssSO_4^{2-}$ concentration levels in each core. Although samples of the D3 81 core were no longer available for ionic measurement a strong-acid peak at 1346 AD was originally identified in the core by Hammer. The several peak volcanic layers identified in the remaining stratigraphic horizons shown in Fig. 14 (row b and c) are taken to represent the 1287, 1278, 1270, 1259 and 1228 AD accumulation horizons, respectively. The triplet of strong-acid peaks at about 1287 AD, 1278 AD and 1270 AD are found in both Antarctic cores, however, no ECM strong-acid peak was measured in the vicinity of the 1270 AD layer in the CR74 core and SO_4^{2-} was not measured. Similarly a strong-acid ECM peak exists at 1229 AD in the D3 81 core but SO_4^{2-} was not measured. The 1259 AD layer has the most conspicuously high $nssSO_4^{2-}$ peak concentration levels shown in Fig. 5 and is the highest SO_4^{2-} value measured in the entire NBY89 core. It turns out that the 1259 AD layer is the most ubiquitous volcanic event yet observed in polar ice cores (Langway et al., 1988) and apparently represents a major eruptive occurrence which was globally transported from a source area yet to be established (Palais et al., 1992). Figure 15 shows a major $nssSO_4^{2-}$ peak in the layers represented which we tentatively establish as the 1168 AD reference horizon and attribute the variability in dates indicated in the Figure to time-scale uncertainties. It should be noted that all mentioned $nssSO_4^{2-}$ peaks in the CR74 record are identified in the ECM record of the new Central Greenland ice core from GRIP (Clausen et al., 1995) with ages corresponding to the CR74 ages, except for the 1287 and 1228 events where the new GRIP dating deviates -1 and +1 years from the CR74 dating, respectively.

The results of the time-scale analysis of the 164 m-deep NBY89 core provides a continuous yearly record of accumulation, and data on rate changes, for the past 1360 years (to 629 AD) with an overall estimated accuracy of better than ±2 to 5 years. The deeper layers have the greater uncertainty. Using the various time-scales the age at the bottom of the 111 m-deep SP78 core is 980 AD ±10 years; at the bottom of the 113 m-deep D3 18C core 1776 AD ±1 year (208 annual layers from the 1984 AD surface, Langway and Azuma, 1988); at the bottom of the 404 m-deep CR74 core, 553 AD ±3 years (1421 annual layers from 1974 AD surface, Hammer et al., 1980).

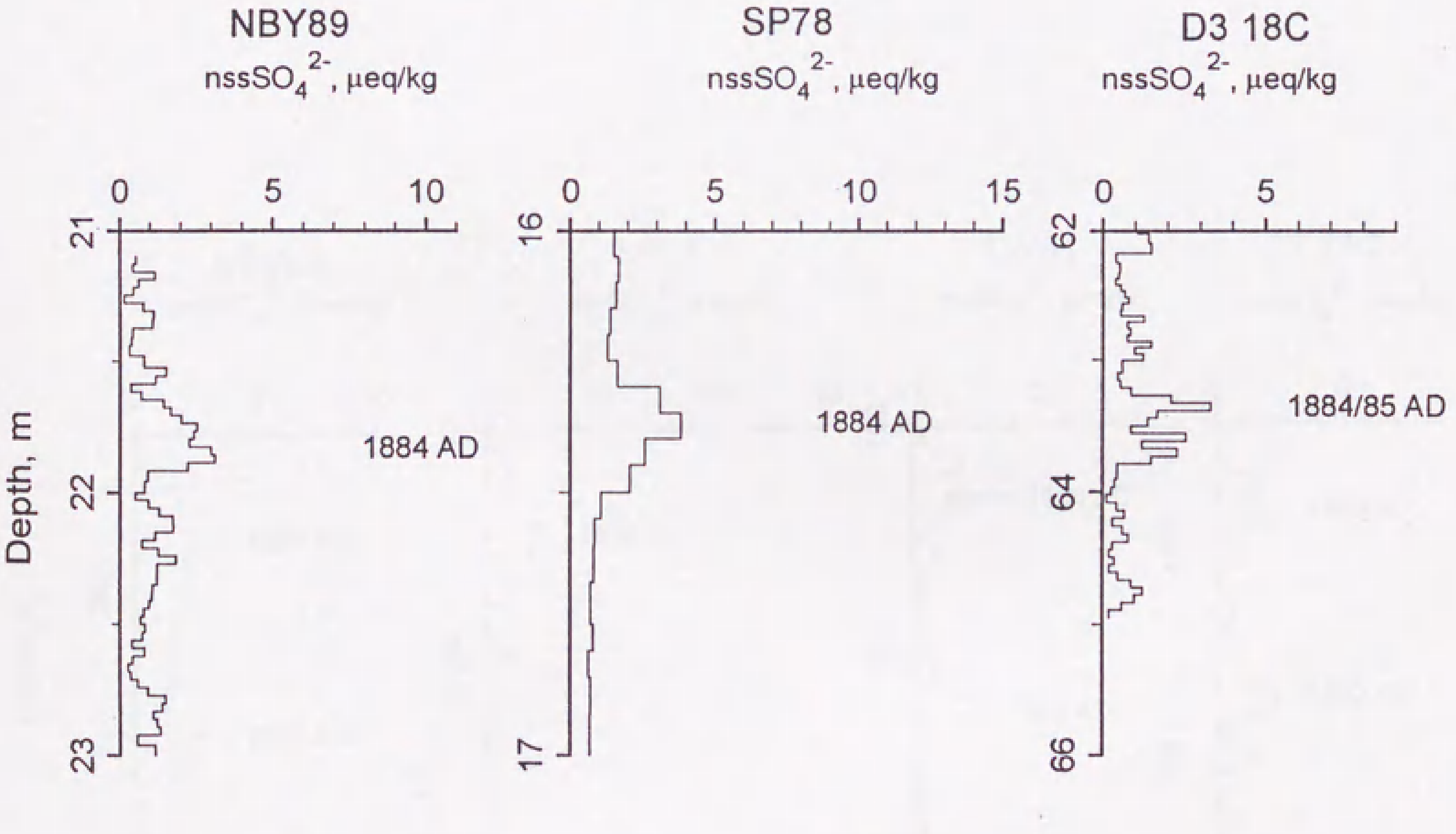


Figure 11. The $nssSO_4^{2-}$ results from three bi-polar cores sampled from around the time of the Krakatoa eruption (1883 AD) level in ice cores from bi-hemispheric locations.

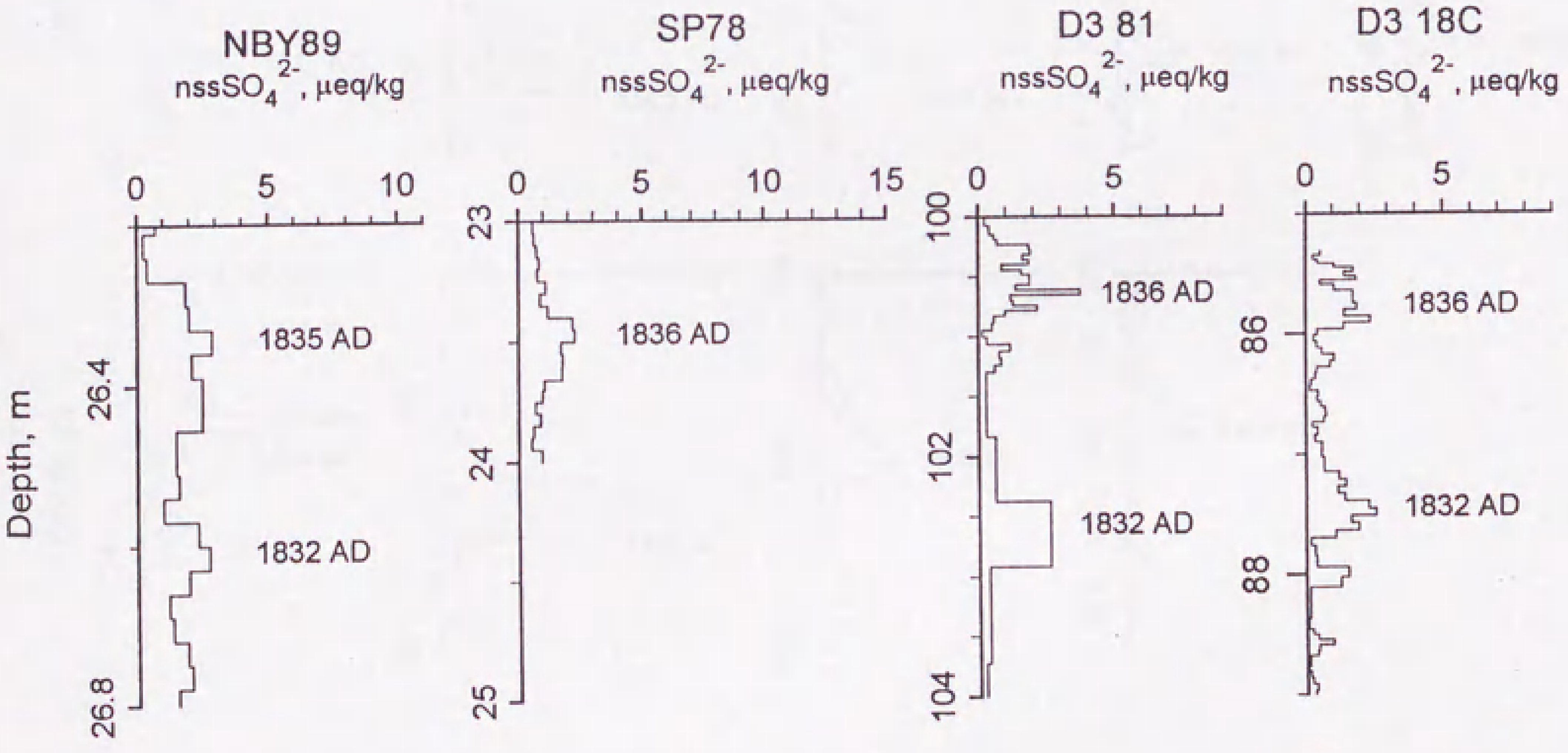


Figure 12. The nssSO$_4^{2-}$ results at two "unidentified" volcanic layers at 1836 AD and 1832 AD found in both polar regions.

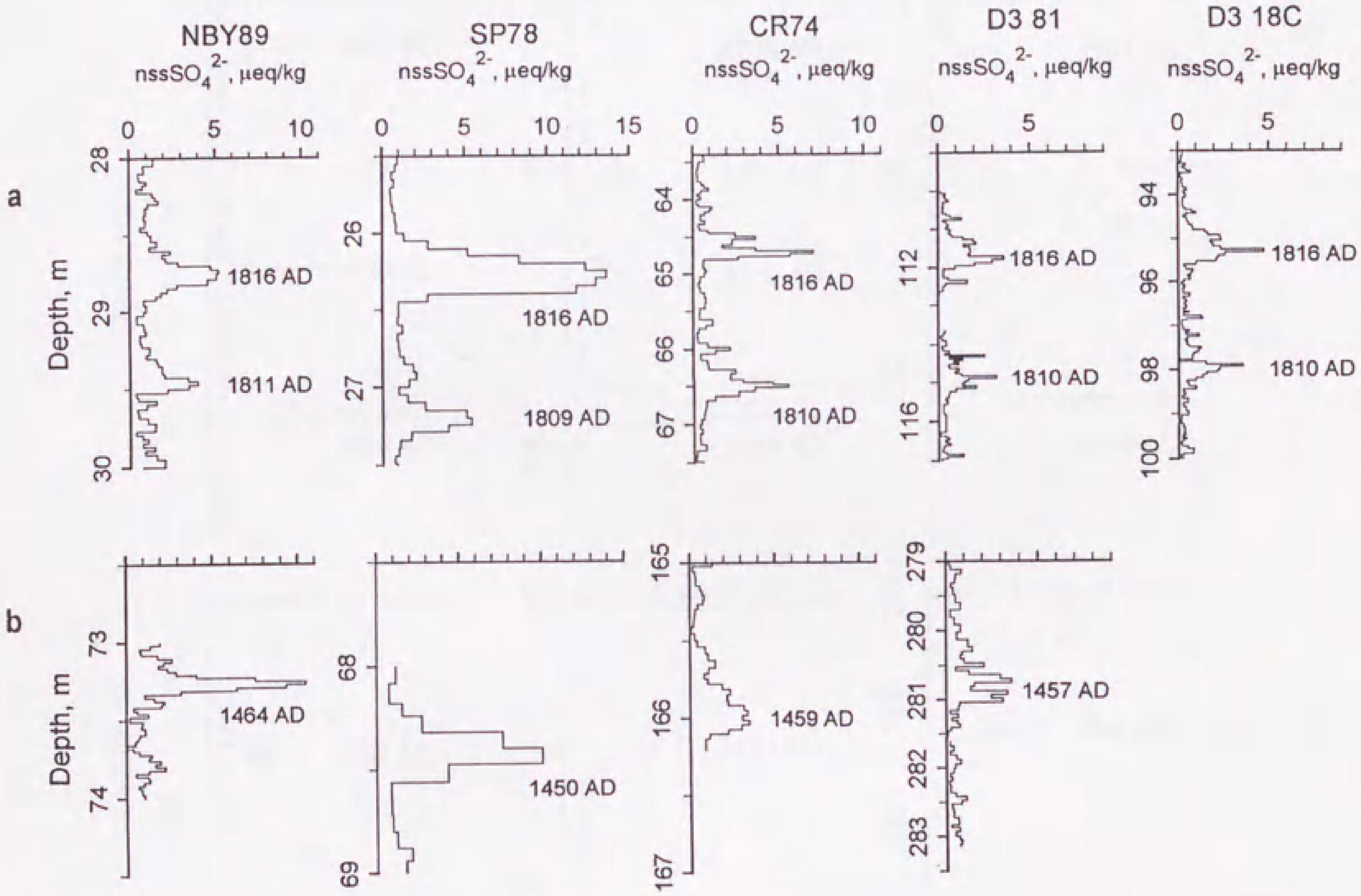


Figure 13. The nssSO$_4^{2-}$ results from five bi-polar cores sampled from depths. a) around the time of the Tambora eruption (1815AD), b) an "unidentified" volcanic event at 1809/11 AD and c) an "unidentified" volcanic event at 1450/1464 AD. Variations in ages shown are likely the result of time-scale uncertainties. The SP78 core has the greatest error in dating.

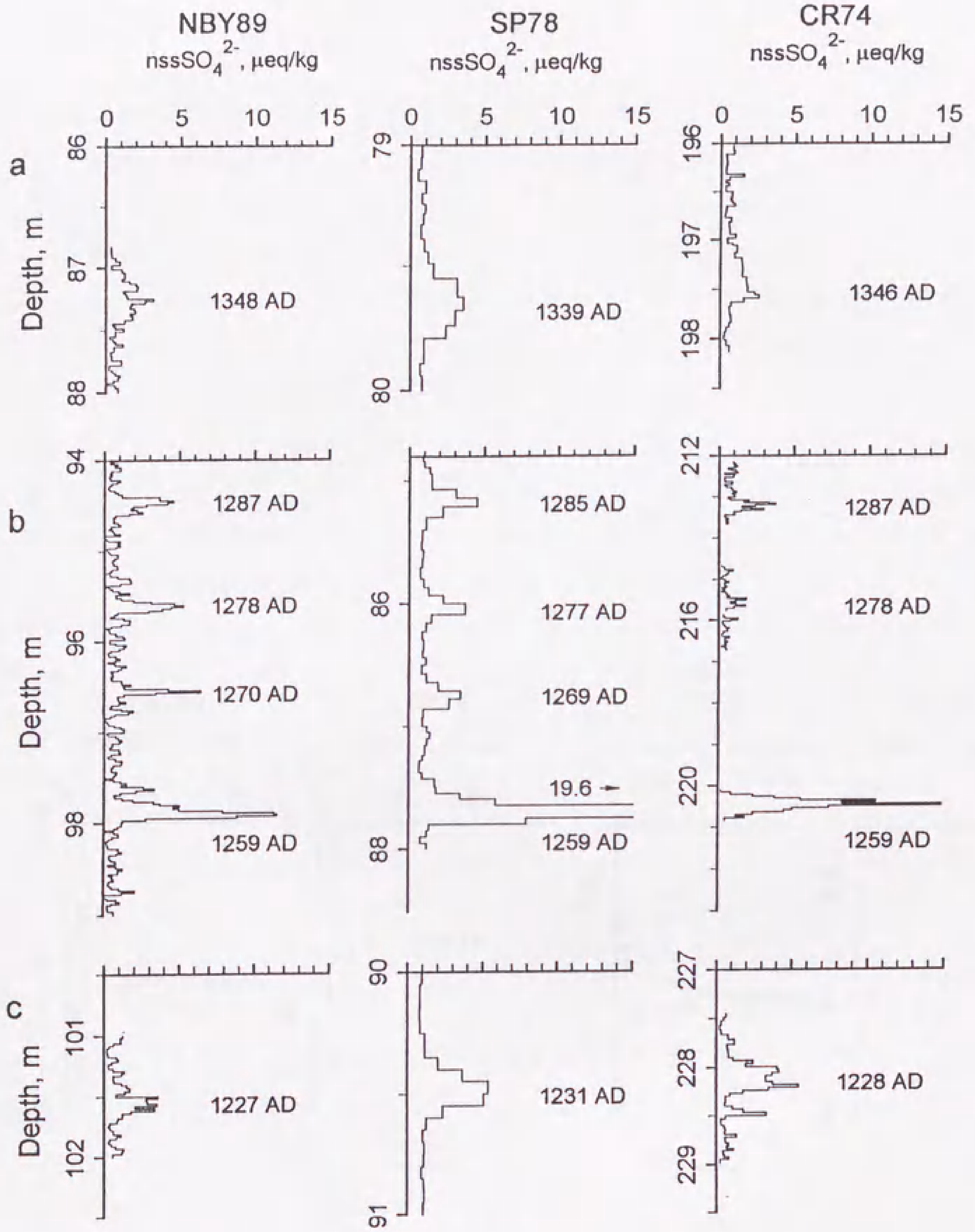


Figure 14. The nssSO$_4^{2-}$ results from three bi-polar cores sampled at various depth levels. a) an "unidentified" volcanic event between 1339/46 AD, b) a triplet of "unidentified" volcanic events above the most prominent "unidentified" volcanic event at 1259 AD, c) an "unidentified" volcanic event at 1227/31 AD which is registered in each bi-polar core.

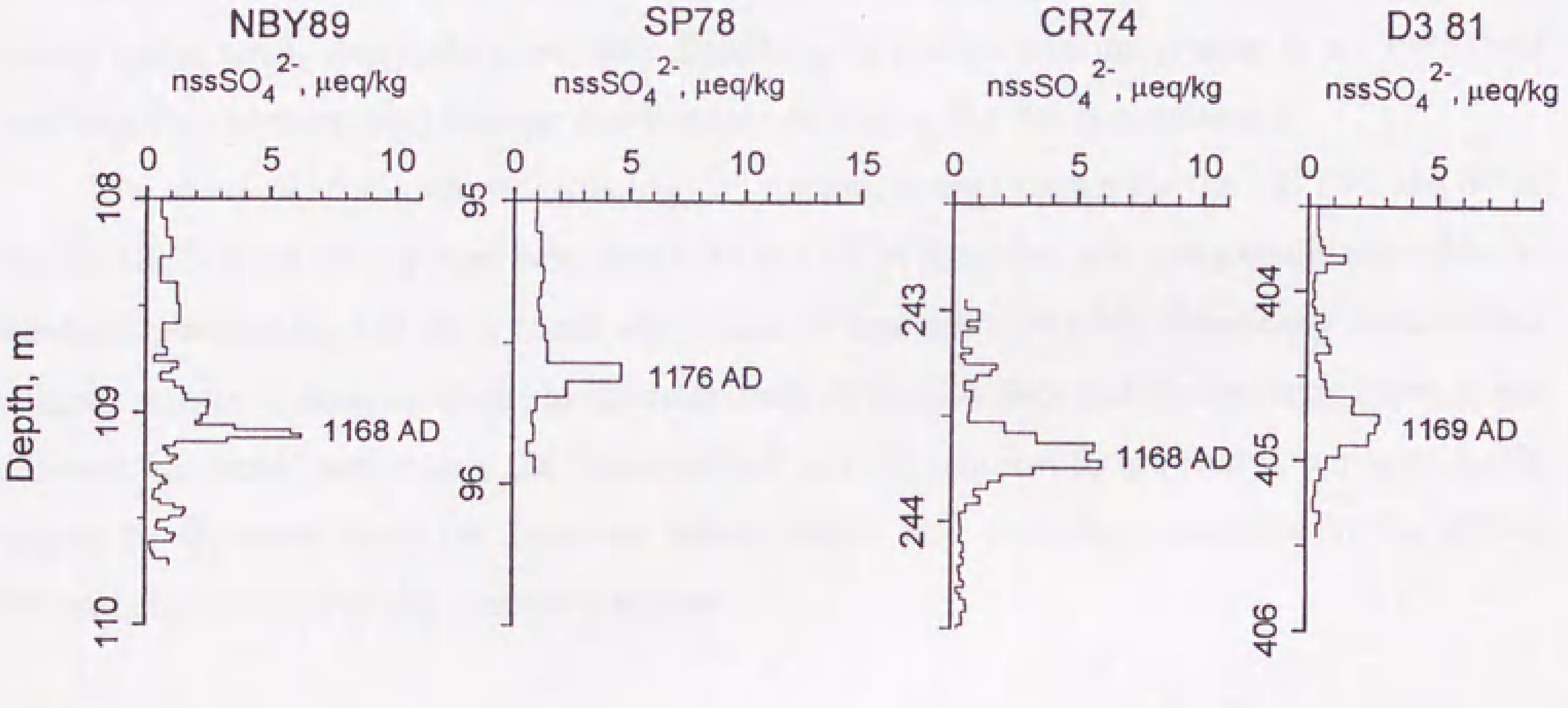


Figure 15. The $nssSO_4^{2-}$ results from four bi-polar cores of an "unidentified" volcanic event sampled at various depth/age levels showing a prominent peak at a horizon between 1168/1169 AD, except at SP78 where it may be appearing in the layer designated as 1176 AD.

Figure 16 is a composite plot of prominent bi-polar volcanic signals measured in the cores over about the last 1000 years calculated as total acid fluxes. These data are for each prominent peak identified at each site. Because of the absence of core material to make new measurements, the H_2SO_4 fluxes for the CR74 core plotted with asterisks are estimates calculated from ECM values (Hammer et al., 1980). Final accumulation layer thicknesses were corrected using a thinning of layers approximation developed by Nye (1963). For this figure the time-scales for all cores are adjusted to the November 1989 reference surface of the NBY89 core. The dotted vertical line shown for the NBY89 in Fig. 16 is the 2σ threshold (5 kg/km^{2}yr) used to indicate the calculated average background levels for the variation of the mean annual flux (4 kg/km^{2}yr$^-$) at the Byrd Station area. The maximum H_2SO_4 fluxes found in this bi-polar study exist in samples measured from the 1259 AD layers.

In general all flux variations measured in each core for a given event are within about a factor 2, with the sole exception of the Tambora eruption (1816 AD) in the Antarctic cores. The variability of fluxes is expected to be greater in Antarctica and lower in Greenland. This may be explained as due to the commonly observed more severe surface wind conditions that mixes the usually sparse newly deposited snow fall, disturbing its natural layering (Fisher et al., 1985) and affecting the chemistry and isotope distributions as well as the net accumulation.

The chemical stratigraphy chronology of volcanic events shown for the NBY89; the SP78 and the CR74 cores are coherent with their $\delta^{18}O$ and ECM data sets, are horizontally traceable on a bi-hemispheric scale, and show consistency back-in-time with available historically documented volcanic activity. Lateral variability in the magnitude of the flux deposits for the same event at the different locations, particularly the "unidentified" events, requires future study , but is probably related to distances from the eruption source areas, and unknown variations in the global atmospheric circulation and transport system.

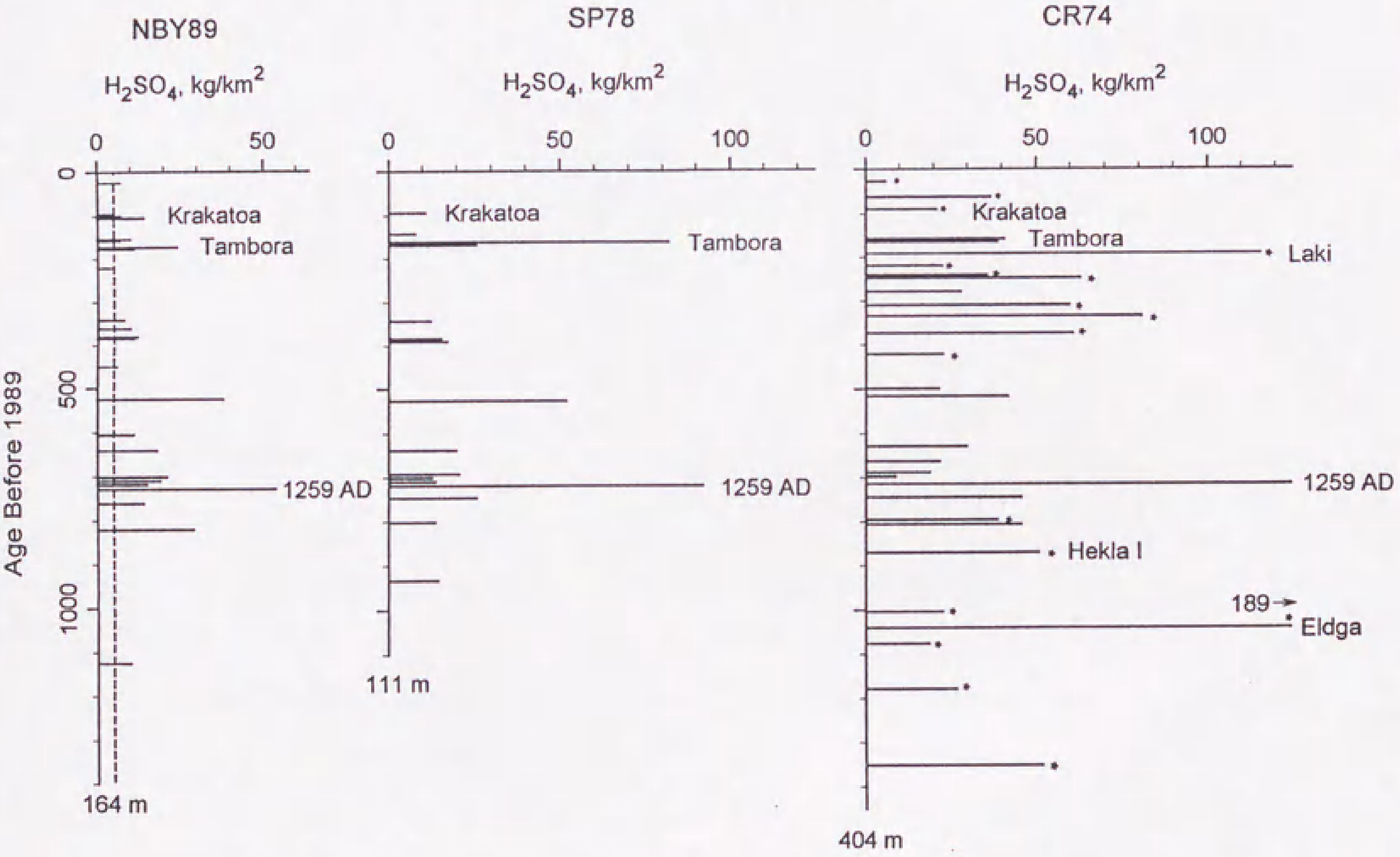


Figure 16. A summary of the prominent volcanic signals identified in the three bi-polar cores. These data are calculated as total sulfuric acid flux using measured values of $nssSO_4^{2-}$ except for the fluxes plotted on the CR74 curve having asterisks which are estimates calculated from ECM values from Hammer et al. (1980). The CR74 core samples were not available for ionic measurements at the asterisk depths.

4-3. Chapter summary

The key element in this chapter was determining a reliable time-scale for the NBY89 ice core and thereafter tracing prominent volcanic index horizons to the other Antarctic cores, and finally cross-dating the Antarctic results with ice core records from Greenland.

A bi-hemispheric comparison of high non-sea-salt SO_4^{2-} peaks showed strong correlation at: 1885, 1836, 1816, 1810, 1459, 1346, 1287, 1278, 1259, 1228 and 1168, in AD units at time of snow deposit. A number of volcanic events in the Greenland CR74 core records are larger than those in the Antarctic NBY89 and SP78 cores. The prominent 1259 AD volcanic signal appears to be a significant bi-polar ice core index horizon. These events contributed sporadic and huge deposits of sulfate in both polar region and significantly disturbed the normal sulfur budget.

5. Spatial variations

5-1. Introduction: Regional and interhemispheric variations

Recent investigations on Greenland ice cores have included measurements of organic acids such as $CH_3SO_3^-$ and $HCOO^-$ (Whung et al., 1994; Alley et al., 1990; Suzuki et al., 1991; Legrand et al., 1992a; Kawamura et al., 1991, 1992; Hansson, 1994; Jafferazo et al., 1994; Legrand and De Angelis, 1995) and ammonium (Busenberg and Langway, 1979; Mayewski et al., 1990; Whitlow et al., 1992; Legrand et al., 1992b; Legrand and De Angelis, 1995). Most of previous studies included only a few limited sites or time-intervals. This chapter describes results of a systematic glaciochemical study of the spatial distribution of $CH_3SO_3^-$, SO_4^{2-} and other ionic constituents in ice cores deposited before the industrial period. These data provide insights into major sources and possible atmospheric pathways of various ionic constituents in ice cores.

In this chapter, spatial distributions of ionic constituents are discussed first as a function of the average accumulation rate to obtain a better knowledge of deposition processes and to see any relationship with moisture flux from the surrounding ocean.

5-2. Spatial distribution of concentration

(i) Antarctica

To investigate the spatial distribution of ionic species in Antarctica, the NBY89 data in Table 3 and similar data sets for other Antarctic locations reported in the available literatures are used, as summarized in Table 5. All data in Table 5 are average multi-year concentration levels in neq/g units. Data sets having both $CH_3SO_3^-$ and $nssSO_4^{2-}$ are chosen as prime ionic species. Annual accumulation rates of sites listed in Table 5 range widely from 22 to 880 kg/m^2yr. In general, sites located near the coast have large annual accumulation rates.

Figure 17 shows scatter plots of average multi-year concentration levels (neq/g) as a function of average accumulation rate (kg/km^2yr). There are few data available for $HCOO^-$ and NH_4^+ in Antarctica. Available data show very low concentration levels for both ions.

The spacial distribution pattern of $CH_3SO_3^-$ is similar to that of $nssSO_4^{2-}$ except for interior Antarctica (Vostok, Dome C and South Pole): higher contents at Berkners Island and Dolleman, and nearly uniform at sites having accumulation larger than 400 kg/km^2yr. The spatial distribution pattern of NO_3^- concentrations is nearly constant at levels of about 0.5 neq/g, except for the highest concentration level at South Pole. No simple relationship between average multi-year concentration levels of various ionic constituents and accumulation rate is found in the Antarctic data sets.

Table 5. Average multi-year concentration levels (neq/g) of ionic constituents in Antarctic ice cores reported by other investigators

(1) Site	(2) Year interval (AD)	(3) Elevation (m)	(4) Average accumulation rate (kg/m^{2}yr)	(5) Temp. (°C)	(6) HCOO$^-$	(7) $CH_3SO_3^-$	(8) Cl^-	(9) NO_3^-	(10) $nssSO_4^{2-}$	(11) Na^+	(12) NH_4^+	(13) Mg^{2+}	(14) SMR	(15) References
Siple (SI)	1800's	1000	400	-24	0.10	0.05	2.34	0.45	0.50	-	-	-	5	1,2
Dome C (DC)	Holocene	3240	34	-54	-	0.03	0.42	0.31	1.46	0.93	0.04	0.18	24	3,4
Vostok (VK)	Holocene	3480	22	-57	-	0.05	0.51	0.26	2.13	1.20	0.10	0.30	21	4,5
South Pole (SP)	1922-84#	2850	73	-51	-	0.06	0.88	1.67	1.04	0.48	0.03	-	9	6,7
Gomez (GZ)	1942-80	1130	880	-17	-	0.11	2.35	0.40	0.60	-	-	-	3	8,9
Dyer Plateau (DP)		1900	480	-22	-	0.09	1.40	0.38	0.56	-	-	-	3	8,10,11
Dolleman (DN)	1652-1992	398	340	-17	-	0.69	11.8	0.60	3.17	-	-	-	2	8,11
Law Dome (LD)	1920's	1375	523	-22	-	0.08	6.08	0.48	0.39	5.82	-	1.02	2	12
Berkner Is, North (BN)	1969-90	730	174	-23	-	0.20	29.6	0.52	2.33	-	-	-	6	13
Berkner Is, South (BS)	1961-90	940	226	-25	-	0.17	16.1	0.55	1.75	-	-	-	5	13

Column 2: # last 1000 years except for $CH_3SO_3^-$ and $nssSO_4^{2-}$

Column 5: mean surface air temperature

Column 14: sulfur molar ratio ($nssSO_4^{2-}/CH_3SO_3^-$)

Column 15: 1, Herron (1982); 2, unpublished data; 3, Legrand and Delmas, 1988; 4, Legrand et al., 1991; 5, Legrand et al., 1988; 6, Legrand and Saigne, 1991; 7, Kirchner and Delmas, 1988; 8, Mulvaney et al, 1992; 9, Mulvaney and Peel, 1988; 10, Dai et al., 1995; 11, Pasteur et al., 1995; 12, Ivey et al., 1986; 13, Wagenbach et al., 1994.

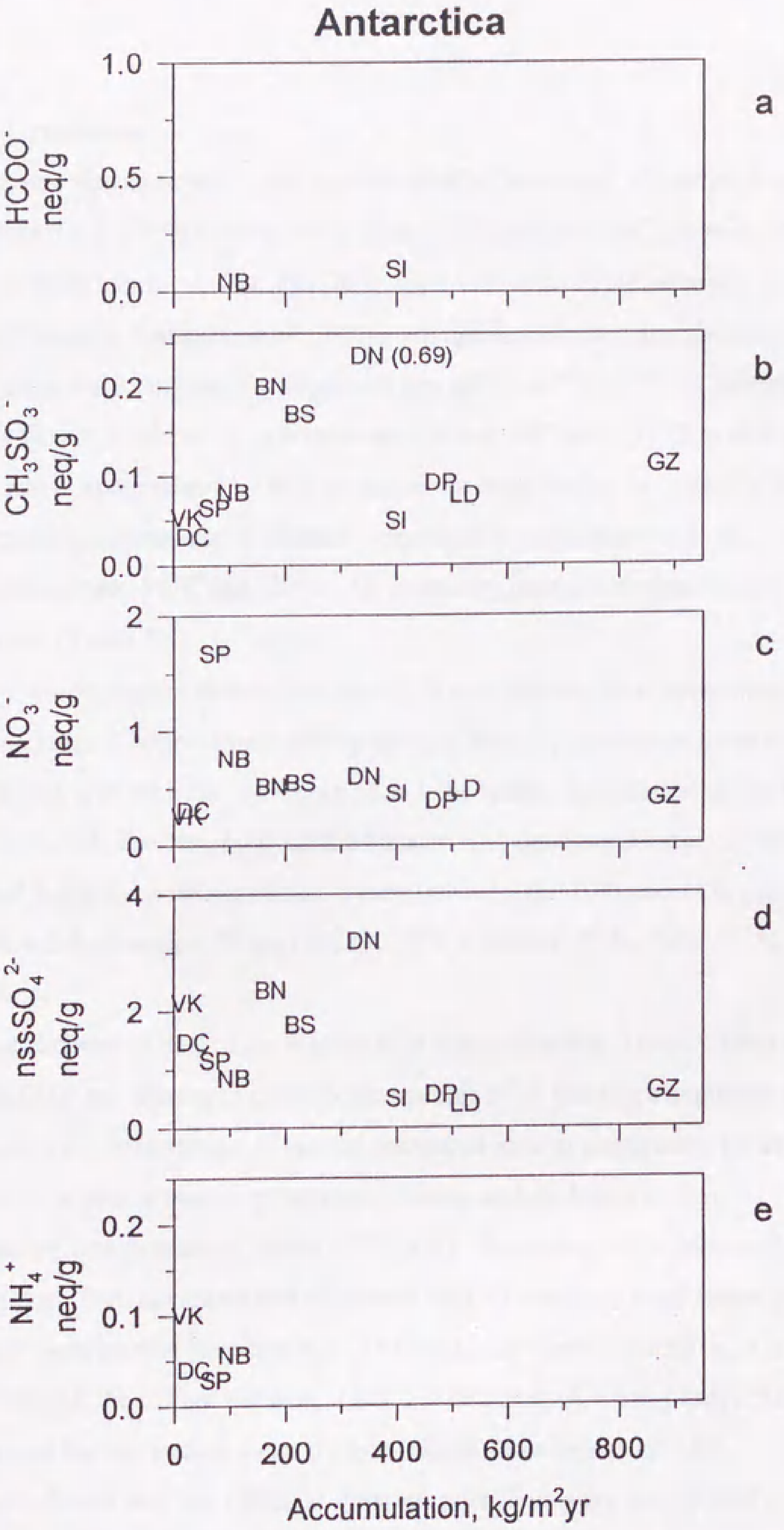


Figure 17. Average multi-year background concentration levels of ionic constituents (neq/g units) for Antarctic sites as a function of annual rate of accumulation (kg/m^{2}yr). See Table 1 and 5 for site identification codes.

(ii) Greenland

For the spatial distribution of ionic constituents in Greenland, ice cores were selected from the Camp Century (CC), North Central (NC), Crete (CR), Milcent (MC), Dye-2 (D2), Dye-3 (D3) and South Dome (SD) locations (Fig. 2). These ice cores were obtained at the GISP sites during the 1971-81 field seasons (Langway et al., 1985). All specimens used are identified in Table 4 and 6. All drilling sites are inland and located between about 64°N to 77°N latitude and 37°W to 61°W longitude (Table 1 column 2). Altitudes range from 1880 m to 3172 m above sea level. The recent annual snow accumulation rates at the seven sites varies by about a factor of 4. The maximum and minimum mean annual surface temperatures (as measured at the 10 m depth in the bore hole) varies between -17°C and -32°C. All chemistry data are summarized in Table 6 except for the CR74 core (Table 4).

In Table 6, chronological time-units (column 2) vary somewhat at some sites. At three sites, Crete, Milcent and Dye 3 approximate stratigraphic continuity exists in a general way during the 19th, 16th, 15th and 12th centuries (see section 3-3 for temporal variation in the CR74 core). As discussed in section 3-3, the variability of the background concentration levels for all species are within a factor of 2 and show no significant trends between the 19th and 12th centuries. At Crete the relative standard deviations in % are $HCOO^-$, 18%; $CH_3SO_3^-$, 23%; NO_3^-, 11%; $nssSO_4^{2-}$, 15% and NH_4^+, 13%.

Other spatial chemical data in the literatures is summarized in Table 7. Data set having both $CH_3SO_3^-$ and $nssSO_4^{2-}$ are chosen as prime ionic species from literature available. Figure 18 plots the average multi-year background values of measured ions in neq/g units (from Table 4, 6 and 7) as a function of the recent annual mean rate of snow accumulation in kg/m^2yr (Table 1 and 7). Figure 18a shows concentration levels of $HCOO^-$ increasing with increasing annual snow accumulation rates. The maximum and minimum $HCOO^-$ concentration levels show agreement with the core site mean surface temperatures. At Dye 2, the warmest location, it is at a high of 36 ng/g; at North Central, the coldest location, it is a low of 6 ng/g. A weak positive linear correlation r^2=0.65 is obtained for the annual mean surface temperature versus $HCOO^-$.

Figure 18b shows that the $CH_3SO_3^-$ concentration levels are not related to the amount of annual snow accumulation. On the other hand, NO_3^- and $nssSO_4^{2-}$ concentration levels shown in Fig. 18c and 18d decrease with increasing annual snow accumulation rates except for Renland. This relationship previously has been referred to as the "dilution effect" (Junge, 1977; Herron, 1982). Excluding data from Renland, negative liner correlations exist in both Fig. 18c and 18d as follows:

$$C[NO_3^-]=1.47-0.0014\lambda,\ r^2=0.63 \cdots\cdots \quad (3)$$

$$C[nssSO_4^{2-}]=1.00-0.0010\lambda,\ r^2=0.78 \cdots\cdots \quad (4)$$

where C is the background concentration levels, in neq/g, and λ is the mean annual rate of snow accumulation, in kg/m^{2}yr, and r is a correlation coefficient. It is obvious that correlations in Greenland are different from those in Antarctica, which suggest that a simple and an uniform source/sink process is dominantly acting for these constituents at Greenland. For the Renland data, deviation from these relationships suggests that a different atmospheric source/sink process exists in coastal Greenland areas.

The distribution pattern of the $nssSO_4^{2-}$ concentration decreases with higher snow accumulation which differs from the $CH_3SO_3^-$, even though major portions of $CH_3SO_3^-$ and some portions of $nssSO_4^{2-}$ are presumed to be derived from marine biogenic DMS (Saltzman et al., 1983; 1995). This difference in the distribution pattern for ionic sulfur compounds is most likely a consequence of the differences in the size distribution of aerosols containing $CH_3SO_3^-$ and $nssSO_4^{2-}$ (Berresheim et al., 1990; Pszenny, 1992) or significant contribution from $nssSO_4^{2-}$ source which is not relating to $CH_3SO_3^-$, in other words, non-DMS contribution, in this region.

The plot of NH_4^+ concentration levels versus snow accumulation shown in Fig. 18e indicates a nearly uniform distribution of NH_4^+ with the amount of accumulation. The highest concentration level of NH_4^+ is found at Dye 2, which is also the location for maximum value of $HCOO^-$.

Table 6. Average multi-year concentration levels (neq/g) of ionic constituents in Greenland ice cores other than listed in table 4

(1) Site	(2) Year interval (AD)	(3) Elevation (m)	(4) Average accumulation rate (kg/m^{2}yr)	(5) Temp. (°C)	(6) No. of sample	(7) $HCOO^-$	(8) $CH_3SO_3^-$	(9) Cl^-	(10) NO_3^-	(11) $nssSO_4^{2-}$	(12) Na^+	(13) NH_4^+	(14) Mg^{2+}	(15) SMR
Camp Century (CC)	1770's	1880	349	-24	35	0.44	0.01	1.07	0.74	0.63	0.83	0.33	0.33	32
North Central (NC)	1380's	2930	129	-32	31	0.13	0.01	0.42	1.34	0.90	0.32	0.36	0.20	45
Milcent (MC)	1588-1598	2410	487	-22	80	0.51	0.02	0.38	0.84	0.67	0.47	0.32	0.13	17
	1471-1481				81	0.56	0.02	0.46	1.10	0.65	0.40	0.40	0.22	16
	1178-1188				84	0.50	0.03	0.57	1.08	0.52	0.75	0.37	0.16	9
			Average			0.52	0.02	0.47	1.00	0.59	0.54	0.36	0.17	15
Dye-2 (D2)	1760's	2100	343	-17	77	0.80	0.02	0.59	1.08	0.67	0.39	0.56	0.19	17
Dye-3 (D3)	1846-1860	2486	496	-20	15	0.36	0.02	0.59	0.68	0.50*	ND	ND	ND	13
	1462-1452				83	0.35	0.03	0.90	1.06	0.48	0.70	0.24	0.25	8
	1169-1173				28	0.34	0.04	0.57	0.84	0.54	0.39	0.39	0.17	7
			Average			0.35	0.03	0.69	0.85	0.50	0.54	0.32	0.21	8
South Dome (SD)	1830's	2821	500	-22	70	0.42	0.01	0.71	0.60	0.40	0.65	0.28	0.14	20

ND: not determined

Column 5: Mean surface air temperature

Column 11: * estimated from Cl^- content using SO_4^{2-}/Cl^- ratio (0.107) in sea water

Column 15: Sulfur molar ratio ($nssSO_4^{2-}/CH_3SO_3^-$)

Table 7. Average multi-year concentration levels (neq/g) of ionic constituents in Greenland ice cores reported by other investigators

(1) Site	(2) Year interval (AD)	(3) Elevation (m)	(4) Average accumulation rate (kg/m²yr)	(5) Temp. (°C)	(6) $HCOO^-$	(7) $CH_3SO_3^-$	(8) Cl^-	(9) NO_3^-	(10) $nssSO_4^{2-}$	(11) Na^+	(12) NH_4^+	(13) Mg^{2+}	(14) SMR	(15) References
Renland (RN)	Holocene	2340	455	-18	-	0.03	1.09	1.34	1.03	1.01	0.45	0.50	17	1
Summit GISP II (SM)	700-1989*	3208	220	-31	0.24#	0.04	0.37	1.14	0.74	0.25	0.34	0.11	9	2,3
Dye 3 20D (2D)	1767-1984**	2615	410	-20	-	0.04	-	0.89$	0.63$	-	-	-	11	4,5

Column 2: *, 1259-1900 except for $CH_3SO_3^-$ and $nssSO_4^{2-}$; * *, 1869-1900 for $nssSO_4^{2-}$, 1869-1955 for NO_3^-

Column 5: mean surface air temperature

Column 6: #, data from Legrand and De Angelis (1994)

Columns 9 and 10: $, data from Mayewski et al. (1986)

Column 14: Sulfur molar ratio ($nssSO_4^{2-}/CH_3SO_3^-$)

Column 15: 1, Hansson, 1994; 2, Saltzman and Whung, 1991; 3, Whitlow et al., 1992; 4, Whung et al., 1994; 5, Mayewski et al., 1986

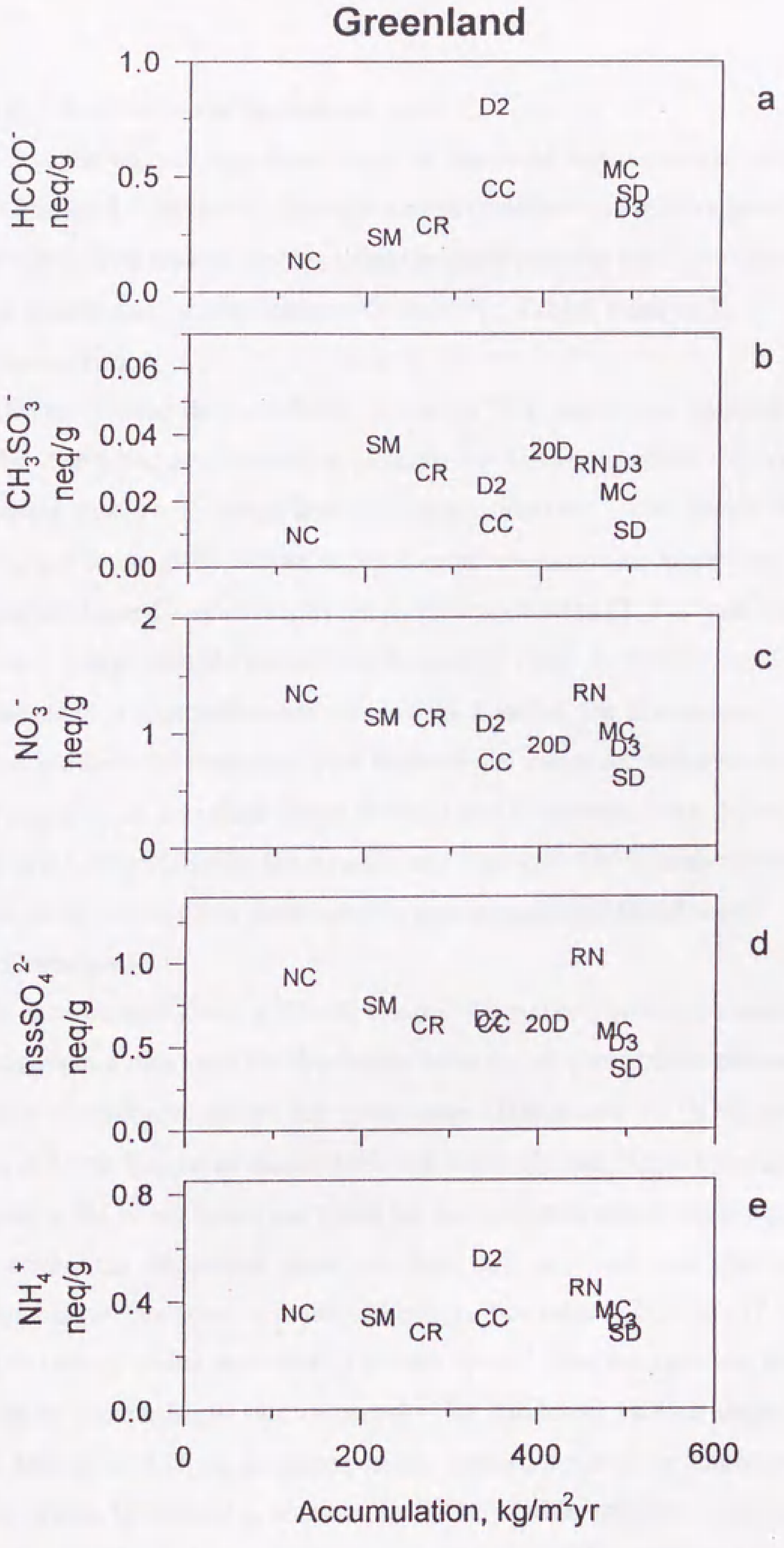


Figure 18. Average multi-year background concentration levels of ionic constituents (neq/g units) for Greenland sites as a function of annual rate of accumulation (kg/m^{2}yr). See Table 1 and 7 for site identification codes.

5-3. Spatial distribution of deposition rate

Table 8 lists the annual deposition rates for the ionic species measured at each site in Antarctica and Greenland. The annual deposition rates (mol/km^{2}yr) are calculated by multiplying the background concentration level (nmol/g, using the multi-year average from Table 3, 4, 5, 6 and 7) by the recent annual mean accumulation rate (kg/m^{2}yr, Tables 1 and 5, 7).

(i) Antarctica

There are very limited data available for the $HCOO^-$ and cation concentration levels in Antarctic ice. For other ionic constituents, in general, low elevation coastal region receives more chemical deposition fluxes with a high annual accumulation rate. Exceptionally high deposition rates of $CH_3SO_3^-$ are found at Dolleman; about 2 order of magnitude larger than high elevation inland sites such as Dome C and Vostok. Sea-salt components (Cl^-, Na^+ and Mg^{2+}), NO_3^- and $nssSO_4^{2-}$ also show a large spatial variability in deposition rates. At Vostok and Dome C, where the annual mean snow accumulation rate is below 40 kg/m^{2}yr, the deposition rates for all ionic species measured are also at a minimum. Post depositional losses for some acids (such as HNO_3 and HCOOH) might be an important factor (Neuber and Heumann, 1988; Neftel, 1991; Wolff, 1995; Silvente and Legrand, 1995; De Angelis and Legrand, 1995) at the interior location in Antarctica because of the very low accumulation rate of snow-fall found there.

(ii) Greenland

As is the case in Antarctica, at North Central, Greenland, where the annual mean snow accumulation rate is at a minimum the deposition rates for all constituents measured are also at a minimum. Post depositional losses for some acids (HNO_3 and HCOOH, etc.) may be an important factor at North Central because of the low accumulation rate as mentioned previously. On the other hand, at the South Dome site which has the maximum annual snow accumulation rate found in this study, the deposition rates are high but vary with ion species. The largest geographical variability in Greenland is found in the deposition rates of $HCOO^-$ (12 times different) and $CH_3SO_3^-$ (14 times), which represents a greater spread than the variation that exists in the annual mean snow accumulation rate (4 times). The maximum $HCOO^-$ deposition rates are obtained at the Milcent and Dye 2 locations on the western slope of the Greenland ice sheet. A lesser variability within Greenland is obtained for NO_3^-, $nssSO_4^{2-}$ and the NH_4^+ deposition rates (about 2 to 3 times). These data suggest a more geographically uniform deposit and longer atmospheric residence time for these ions. The sea-salt components (Cl^- and Na^+) show larger depositional rates at Camp Century and South Dome. Sea-salts show a strong relationship between the deposition rates and distance to the coast as well as with the elevation of the site (Herron, 1982).

Sources for $HCOO^-$ in the remote troposphere are not well established but possible sources for the ion or it's precursors may evolve from the degradation of volatile hydrocarbons and aldehydes associated with the vegetation growth on continents and to a lesser extent, from marine biogenic sources (Keen and Galloway, 1986; 1988; Arlander et al., 1990) and methane oxidation in atmosphere (Legrand and De Angelis, 1995). In our study, sites on the western slope (Dye 2 and Milcent) give a maximum $HCOO^-$ deposition rate, suggesting a stronger contribution from continental sources. This hypothesis is supported by the existence of the predominant atmospheric circulation pattern trajectories over Greenland (Ohmura and Reeh, 1991). The predominant air flow appears to arrive from the southwest, where a large regional ice-free area exists between the west Greenland ice margin and the North American continent. The significant decrease in the $HCOO^-$ deposition rate from Dye 2 to Crete and North Central sites implies a short atmospheric residence time for $HCOO^-$ as suggested by Keen and Galloway (1988). Antarctic ice core data are spatially limited (NBY89 and Siple cores) but very low concentration levels in Antarctica also support dominant source from remote continents and rapid removal before reaching the interior Antarctic.

Sources for NH_4^+ are also enigmatic. Contribution sources are not well established but include possible emanations from soils and bacterial decomposition of animal droppings (Warneck, 1988). To a lesser extent a marine origin has been suggested for the NH_3 source (Quinn et al., 1988) as well as sporadic natural burning of biomasses (Warneck, 1988; Legrand et al., 1992b). In short NH_4^+ closely parallels $HCOO^-$ in its depositional pattern on the ice sheet and probably mainly originates from a continental source but may have a possibly small oceanic component. The distribution of NH_4^+ deposition rates and very low concentration levels in Antarctic ice cores are consistent with this.

Table 8. Background deposition rates (mol/km^{2}yr) of ionic constituents at each site

(1) Site	(2) $HCOO^-$	(3) $CH_3SO_3^-$	(4) Cl^-	(5) NO_3^-	(6) $nssSO_4^{2-}$	(7) Na^+	(8) NH_4^+	(9) Mg^{2+}	(10) References
Antarctica									
NBY89	4	9	161	80	45	120	6	16	
Siple	38	19	937	181	100	-	-	-	1
Dome C	-	1	14	10	25	32	1	3	2,3
Vostok	-	1	11	6	23	26	2	3	3,4
South Pole	-	5	64	122	38	35	2	-	5,6
Gomez	-	97	2068	352	264	-	-	-	7,8
Dyer Plateau	-	43	67	182	134	-	-	-	7,9,10
Dolleman	-	235	4012	204	539	-	-	-	7,10
Law Dome	-	42	3180	251	102	3044	-	267	11
Berkner Is N	-	35	5150	90	203	-	-	-	12
Berkner Is S	-	38	3639	124	198	-	-	-	12
Greenland									
Crete	79	8	109	310	86	97	78	20	
Camp Century	155	4	374	259	109	288	116	57	
North Central	17	1	55	173	58	41	46	13	
Milcent	255	11	228	489	147	265	176	42	
Dye 3	176	15	336	424	127	270	157	52	
Dye 2	274	8	203	371	114	134	191	32	
South Dome	211	5	353	298	99	326	139	35	
Summit (GISPII)	53*	9	81	251	82	55	75	12	13,14
Renland	-	14	496	610	234	460	205	114	15
20D Dye-3	-	16	-	365	129	-	-	-	16,17

Column 2: *, Legrand and De Angelis, 1995

Column 10: 1, Herron, 1982 and unpublished data, 2, Legrand and Delmas, 1988; 3, Legrand et al., 1991; 4, Legrand et al., 1988; 5, Kirchner and Delmas, 1988; 6, Legrand and Saigne, 1991; 7, Mulvaney et al, 1992; 8, Mulvaney and Peel, 1988 ; 9, Dai et al., 1995; 10, Paeteur et al., 1995; 11, Ivey et al., 1986; 12, Wagenbach et al., 1994; 13; Saltzman and Whung, 1991; 14, Whitlow et al., 1992; 15, Hansson, 1994; 16, Whung et al., 1994; 17, Mayewski et al., 1986.

5-4. Sulfate and methanesulfonate in polar ice

Discussion of this section is focused on spatial distributions of $nssSO_4^{2-}$ and $CH_3SO_3^-$ measured on polar ice. Spatial distribution of $nssSO_4^{2-}$ is compared with that of $CH_3SO_3^-$ which is considered to be a tracer of the marine biogenic DMS.

The SMR (sulfur molar ratio, $nssSO_4^{2-}$ / $CH_3SO_3^-$) has been widely used to estimate contributions of marine biogenic DMS precursors and other precursors to the $nssSO_4^{2-}$ content to the aerosols (see Saltzman et al., 1986, 1995; Savoie et al., 1989, 1993, 1994; Prospero et al., 1995). There is a lack of significant anthropogenic $nssSO_4^{2-}$ sources to the aerosols and consequently the snow chemistry of Antarctica and pre-1900 AD ice in Greenland (Clausen and Langway, 1989; Delmas, 1992). It is further assumed that the atmospheric oxidation pathway of DMS will result in a relatively constant ratio of the components and that deviations from this ratio for a given environment in remote atmosphere may be attributed to contribution of natural (if no anthropogenic sources exists) $nssSO_4^{2-}$ from other sources (Prospero et al., 1995).

Figure 19 shows SMR (from Table 3, 4, 5, 6, and 7) as a function of site elevation (m above sea level) for Antarctic (Fig. 19a) and Greenland (Fig. 19b) sites. In Antarctica, the SMRs are nearly constant at 4 in average below 2000 m elevation, whereas the SMRs increase with increasing elevations above this. Spatial distribution of the SMRs in aerosols at the coastal area of Antarctica shows nearly constant ratios at about 2 to 3 (Savoie et al., 1993). Note that the SMRs are about 4 in the NBY89 profile for the most of the study period and that this value is the same as the average SMR below 2000 m elevation in Antarctica.

Some hypotheses for the spatial distribution of the SMRs over Antarctica have been proposed. First, higher SMRs over the high interior Antarctica could result from a larger relative amount of $nssSO_4^{2-}$ from sources other than DMS oxidation. Because of the very low $CH_3SO_3^-$ and $nssSO_4^{2-}$ concentrations in ice cores, even a small addition of $nssSO_4^{2-}$ from other sources could have substantial impact on the overall ratio. According to the results of aerosol study at Mawson and Palmer (Savoie et al., 1993), significant quantities of non-biogenic $nssSO_4^{2-}$ occur at both locations and may be derived from continental sources. However, as mentioned in chapter 3-2, there is no significant amount of non-sea-salt Ca^{2+} which is potentially related to terrestrial $nssSO_4^{2-}$ for making the dust mineral of $CaSO_4$. The other non-biogenic $nssSO_4^{2-}$ source could be the stratospheric background sulfuric aerosols. Delmas (1992) and Legrand (1995) were suggested that stratospheric contribution of sulfur budget in the interior Antarctic is small (<10 to 20% of total sulfate deposition) but not negligible. Based on the analysis of ^7Be in aerosols as a stratospheric tracer at the South Pole, Cunnigham and Zoller (1981) suggested that the stratospheric contribution of sulfate to the Antarctic tropospheric sulfur budget seems to be smaller than about 10 %. No similar measurement of ^7Be has been made for Dome C and Vostok stations.

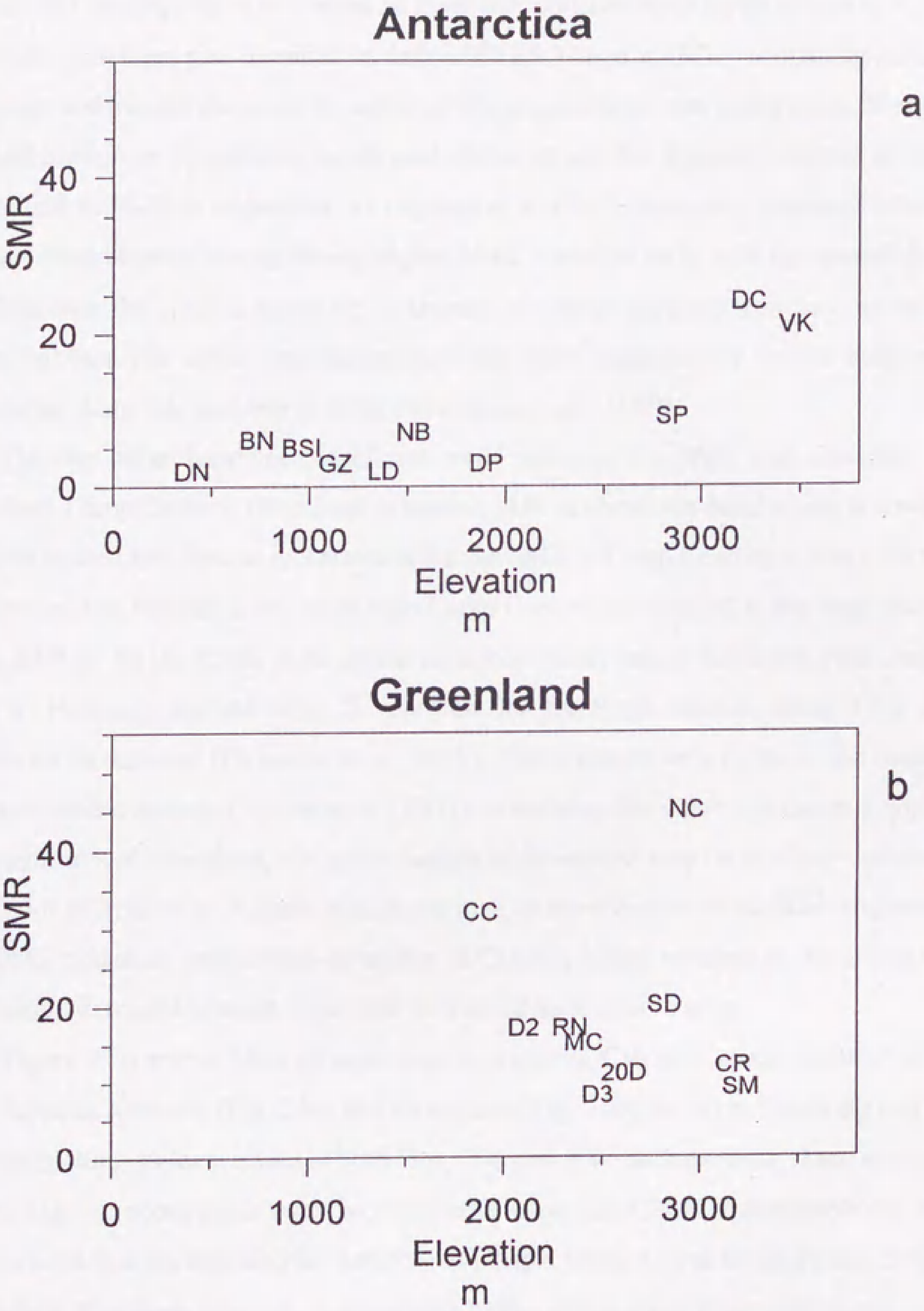


Figure 19. Sulfur molar ratio (SMR, nssSO_4^{2-} / $CH_3SO_3^-$) as a function of site elevation (m a. s. l.): **a** for Antarctica and **b** for Greenland.

Another potential hypothesis is the differences in the mass median diameter between aerosols containing $CH_3SO_3^-$ and $nssSO_4^{2-}$ (Pszenny, 1992; Saltzman et al., 1983; Berresheim et al., 1990). The larger $CH_3SO_3^-$ containing aerosols could be more rapidly removed from the atmosphere by both dry and wet deposition processes, as if sea-salt concentration levels decrease with increasing elevation. However, size-distribution data of $CH_3SO_3^-$ and $nssSO_4^{2-}$ containing aerosols are still too sparse and transfer functions to snow for these species are not well known. If any hypothesis or combination of hypotheses mentioned above is not the dominant reason to reveal spatial distribution of SMR in Antarctica, as Legrand et al. (1992) assumed, transport from a low- to a mid-latitudinal biogenic source having higher SMR is needed to fit with the spatial distribution of the SMR over the interior Antarctic. Transport of aerosol particles from low- to mid-latitudinal region to Antarctic upper troposphere has also been suggested by a case study of trajectory analysis for Antarctic summer in 1983 (Yamazaki et al., 1989).

On the other hand, no significant trend between the SMR and elevation is found in Greenland. Camp Century, Greenland, is located 1880 m above sea-level which is almost the same elevation as the Dyer Plateau in Antarctica but the SMR at Camp Century is about 10 times higher than that in Dyer Plateau. Sites other than Camp Century are located at the high-inland locations above 2000 m. All the SMRs show similar or higher values than at the South Pole. Recent aerosol study at Heimaey, Iceland (Fig. 2), reported that the SMR ratios is about 3 for the clean air conditions in summer (Prospero et a., 1995). This value is very close to the results from the Antarctic coastal stations (Savoie et al., 1993). Assuming this value represents a typical ratio for the coastal area of Greenland, the sulfur budget in Greenland may be similarly distorted as it is in the interior of Antarctica. Namely, the causes include contribution of $nssSO_4^{2-}$ sources from other than DMS oxidation, preferential deposition of $CH_3SO_3^-$ before reaching at the interior Greenland, or $CH_3SO_3^-$ aerosol transport from mid- to low-latitude source area.

Figure 20 is scatter plots of multi-year averages of $CH_3SO_3^-$ versus $nssSO_4^{2-}$ concentration levels found in Antarctic (Fig. 20a) and Greenland (Fig. 20b) ice cores in nmol/g units. Note that the same plotting scales are used in both Figs. 20a and 20b. In Antarctica, there is a general trend that $nssSO_4^{2-}$ concentration levels increase with increasing $CH_3SO_3^-$ concentration levels except for sites located in the high interior Antarctica (Vostok, Dome C and South Pole). Excluding these high-inland sites from calculation, remaining 8 sites give a weak liner correlation:

$$[nssSO_4^{2-}]=0.24+2.14 \cdot [CH_3SO_3^-],\ r^2=0.76 \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (5)$$

where $[nssSO_4^{2-}]$ and $[CH_3SO_3^-]$ are average multi-year concentration levels in nmol/g unit and the r is a correlation coefficient. The slope is about half of the simple average value of the SMRs in Table 5 because both concentrations of ionic sulfur compounds at Dolleman are exceptionally high and the SMR for Dolleman is very low. Relatively constant SMRs in Fig. 19a and the weak but positive correlation in Fig. 20a without high inland sites suggest that dominant source of $nssSO_4^{2-}$ deposited in the coastal Antarctic area is the marine biogenic DMS as well as the $CH_3SO_3^-$, at least for the sites near the coast and elevation below 2000 m.

According to airborne measurements of DMS, SO_2, $CH_3SO_3^-$ and $nssSO_4^{2-}$ near Tasmania, Australia, vertical profiles of SMR showed higher values in free troposphere (about above 2 km) than those in marine boundary layer (Berresheim et al., 1990). The vertical profiles of SMR in aerosols over the coastal and the interior Antarctic are not yet known but the airborne results near Tasmania appear to be consistent with the Antarctic SMR distribution of an increasing trend with increasing elevation above 2000 m.

In contrast to Antarctica, both $nssSO_4^{2-}$ and $CH_3SO_3^-$ concentration levels distribute within narrow range and show no significant trend in Greenland as shown in Fig. 20b. The inserted figure magnifies the rectangle part of the Fig. 20b at the left corner. The lack of a simple relationship between $nssSO_4^{2-}$ and $CH_3SO_3^-$ and higher SMRs suggest that no simple aspect exists in the Greenland sulfur budget even in pre-1900 AD ice.

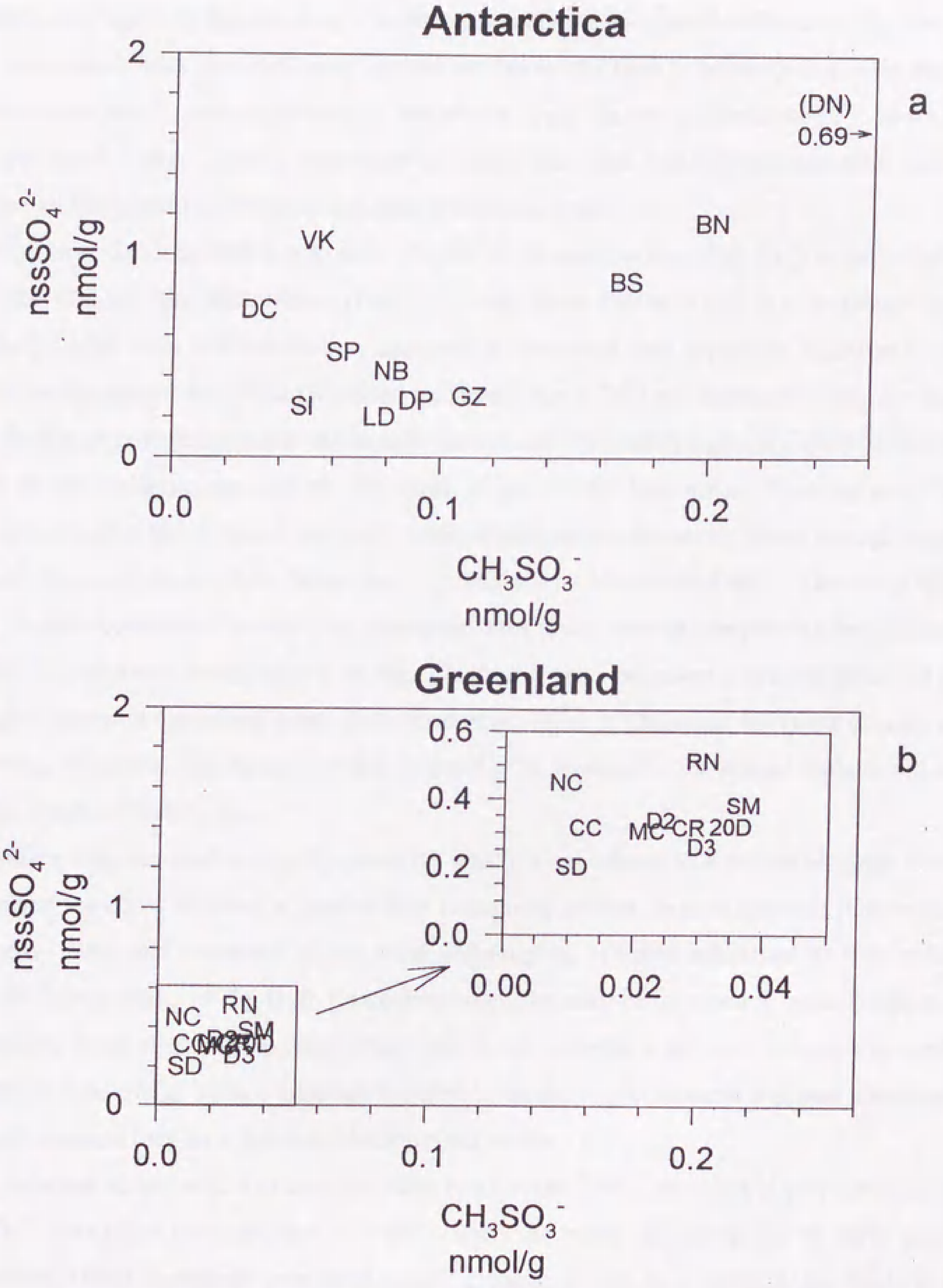


Figure 20. Scatter plot between $CH_3SO_3^-$ and $nssSO_4^{2-}$ concentration levels (nmol/g): **a** for Antarctica and **b** for Greenland. Figure inserted in **b** magnifies rectangle range at the left axis.

On the other hand, deposition fluxes of $CH_3SO_3^-$ and $nssSO_4^{2-}$ in Table 8 are plotted in Figure 21 as a function of elevation. Figure 21a ($CH_3SO_3^-$) and 21b ($nssSO_4^{2-}$) are the plots for Antarctic sites and both figures show a similar general decreasing trend with increasing elevation with some variabilities near the coast. Deposition fluxes of $CH_3SO_3^-$ of the coastal sites show all higher values than the sites in the interior Antarctica. Dyer Plateau is located at 1900 m a.s.l. but receives much higher $CH_3SO_3^-$ and $nssSO_4^{2-}$ fluxes than Siple and Byrd station area, probably because of closeness to surrounding highly productive ocean.

In Greenland, spatial distribution of $nssSO_4^{2-}$ deposition flux (Fig. 21d) is quite different from the $CH_3SO_3^-$ flux distribution (Fig. 21c). Deposition fluxes of $CH_3SO_3^-$ in Greenland are generally higher than in Antarctica at comparable elevations, and especially higher at the sites located on the eastern side of the Greenland ice sheet (Dye 3, 20D and Renland). This is in accord with the marine production in the ocean near Iceland and associated high $CH_3SO_3^-$ concentration levels in the Icelandic atmosphere (Prospero et al., 1995). Deposition fluxes of $nssSO_4^{2-}$ in Greenland are also higher than at Antarctic sites of comparable elevation, which strongly suggest a source that is more active in the northern hemisphere as first pointed out by Herron (1982).

Higher deposition of $nssSO_4^{2-}$ at Greenland sites is also seen at comparable deposition flux of $CH_3SO_3^-$ in Antarctica as shown in Fig. 22. Open circles represent Antarctic sites and filled triangles represent Greenland sites. Both deposition fluxes at Dolleman (DN) are exceptionally high, thus, off scales. The deposition flux of $nssSO_4^{2-}$ at Renland is the second highest and show a much smaller $CH_3SO_3^-$ flux.

Such a background source for $nssSO_4^{2-}$ which is not related to a marine biogenic DMS in Greenland ice cores includes a mineral dust containing sulfate, such as gypsum (Glaccum and Prospero, 1980) and oxidation of SO_2 from non-erupting volcanic exhalation at high northern latitude (Bates et al., 1992). Both possible sources also may be involved in contributing to the background levels of $nssSO_4^{2-}$ in the free troposphere. Considering a stronger influence in northern hemisphere where large surface areas are covered by landmass, the mineral dust and non-eruptive volcanic material may be a dominant background source.

Seasonal variation of dust concentration in ice cores from Crete area is very similar to that of SO_4^{2-}, maximum concentration of SO_4^{2-} and dust occur during spring to early summer (Steffensen, 1988). Significant amount of $nssCa^{2+}$ associated with dust particles was found in Dye 3, Milcent and Crete ice cores (Langway et al., 1977). On the other hand, gypsum ($CaSO_4$) is a minor but an important mineral often found in atmospheric dust particles(Glaccum and Prospero, 1980; Okada et al., 1990). Because of the very low $CH_3SO_3^-$ and $nssSO_4^{2-}$ concentrations in Greenland ice cores, even a small addition of $nssSO_4^{2-}$ from gypsum could have substantial impact on the overall ratio. For example, average multi-year concentration levels of nss Ca^{2+} at Crete is 0.34 neq/g. As a very simple estimation, assuming all the nssCa^{2+} is derived from gypsum dust, an equivalent amount of SO_4^{2-} is about 55% of the total nssSO_4^{2-} measured. The amount of nssSO_4^{2-} other than the fraction derived from gypsum is about 0.28 neq/g, which is calculated as total nssSO_4^{2-} (0.62 neq/g) minus SO_4^{2-} derived from gypsum(0.34 neq/g). Assuming this amount of nssSO_4^{2-} is a true marine biogenic SO_4^{2-}, the SMR becomes 5 (0.28/2/0.03) at the Crete, which is about half of the initial SMR value (12) at Crete. The calculated SMR about 5 is an "order estimation" but close to the value of the aerosol study performed at Iceland.

Non-eruptive volcanic exhalations appear to be major natural sources of sulfur budget in northern hemispheric troposphere, especially latitude between 50 to 80°N (Bates et al., 1992). Non-eruptive volcanic sources are good candidates for making longer-term background nssSO_4^{2-} concentration in Greenland. As discussed in Chapter 4, a volcanic event in a nssSO_4^{2-} profile can only be identified when it is abnormal; concentration levels increase abruptly and the peak concentration level is significantly different from normal variability. Thus, depending on the amount of SO_2 released, non-eruptive and small eruption could not be detected as an "outlier" in nssSO_4^{2-} profile found in ice cores. For Greenland deposits, the Icelandic volcanoes could be the background source for nssSO_4^{2-}. The high deposition flux of nssSO_4^{2-} at Renland may be attributed partly to the non-eruptive volcanic source for nssSO_4^{2-}

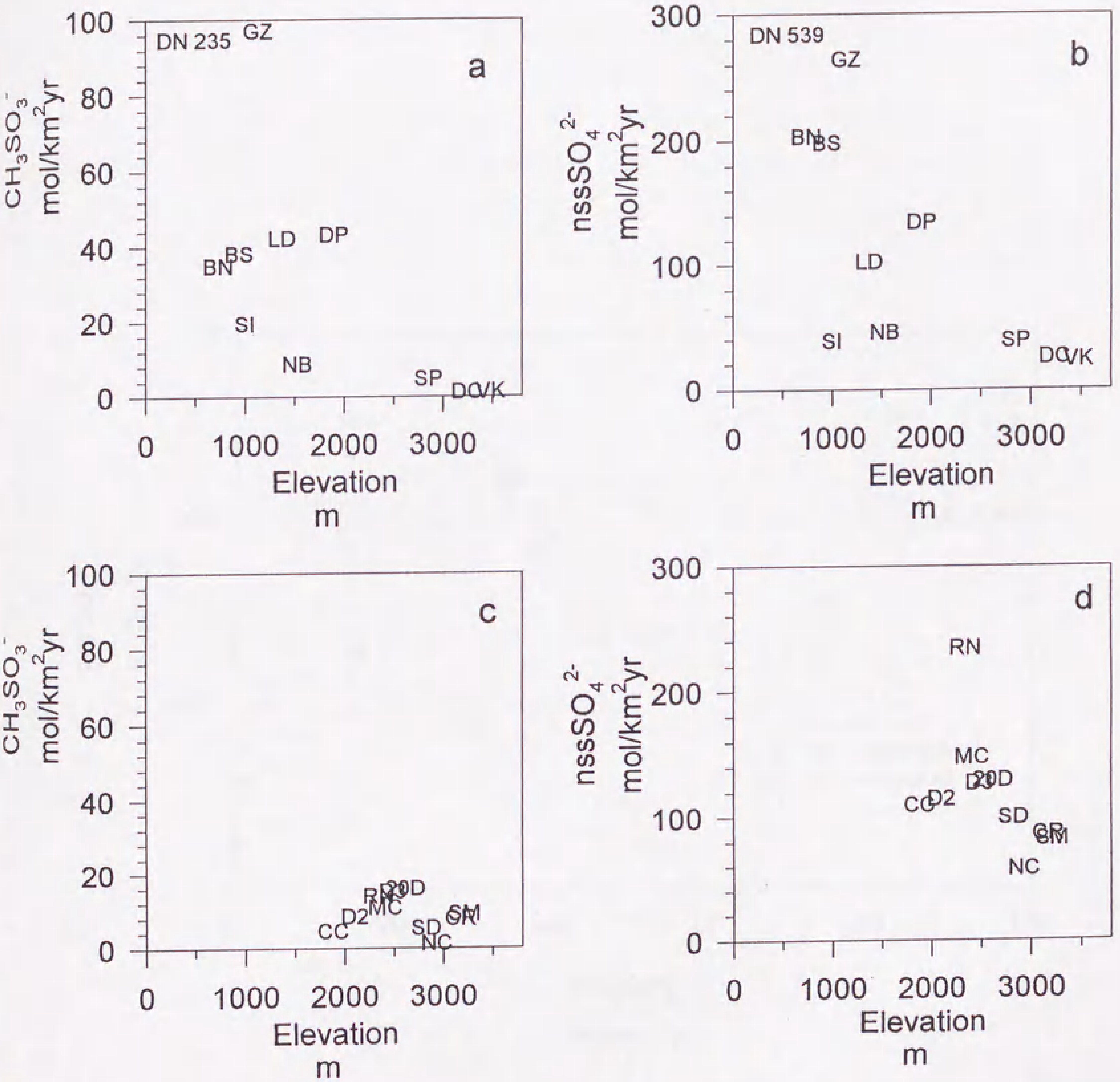


Figure 21. Deposition fluxes (mol/km^{2}yr) of $CH_3SO_3^-$ and $nssSO_4^{2-}$ as a function of elevation (m a.s.l.): **a** and **b** for Antarctica, **c** and **d** for Greenland sites.

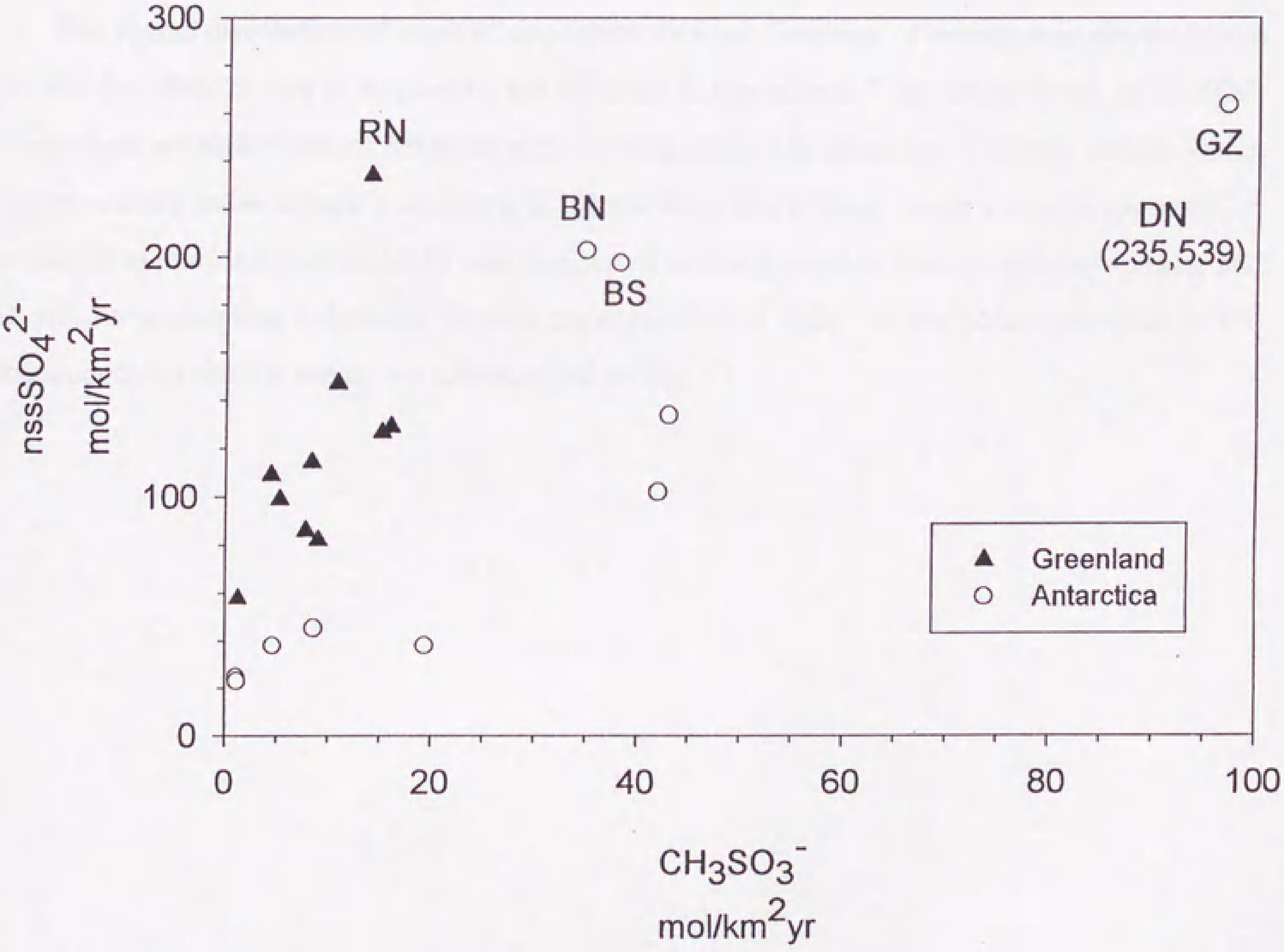


Figure 22. Scatter plot between $CH_3SO_3^-$ and $nssSO_4^{2-}$ deposition fluxes (mol/km^{2}yr). Open circles represent values from Antarctica and filled triangle represent for Greenland.

5-5. Chapter summary

In this Chapter, the results of measuring the multi-year background concentration levels of $HCOO^-$, $CH_3SO_3^-$, NO_3^-, $nssSO_4^{2-}$ and NH_4^+ in Antarctic and Greenland ice cores were discussed. The background concentration levels of the ionic species measured vary somewhat with time but noticeably more on a regional basis. The spatial distributions of $nssSO_4^{2-}$ and $CH_3SO_3^-$ in polar regions were discussed using available data in the literature.

Low and nearly constant spatial distribution of sulfur molar ratios (SMRs) with a weak correlation between $CH_3SO_3^-$ and $nssSO_4^{2-}$ concentration levels suggests that dominant source of $nssSO_4^{2-}$ deposited in the coastal Antarctica is the marine biogenic DMS as well as the $CH_3SO_3^-$, at least for the sites near the coast and elevation below 2000 m. The lack of simple relationship between $nssSO_4^{2-}$ and $CH_3SO_3^-$ and higher SMRs suggest that part of $nssSO_4^{2-}$ in Greenland ice is originated from some other source not related to marine DMS, even before anthropogenically polluted 20th century.

The spatial distribution of $nssSO_4^{2-}$ deposition flux as a function of elevation is similar to the $CH_3SO_3^-$ flux distribution in Antarctica but different in Greenland. Deposition fluxes of $nssSO_4^{2-}$ in Greenland are higher than at Antarctic sites of comparable elevation and $CH_3SO_3^-$ fluxes, which suggests a more active source is operating in the northern hemisphere. Such a source for $nssSO_4^{2-}$ not related to marine biogenic DMS was suggested as being mineral dust containing sulfate, and SO_2 from non-erupting volcanoes. Source contributions of SO_4^{2-} to the polar atmospheres and subsequently to the ice sheets are schematized in Fig. 23.

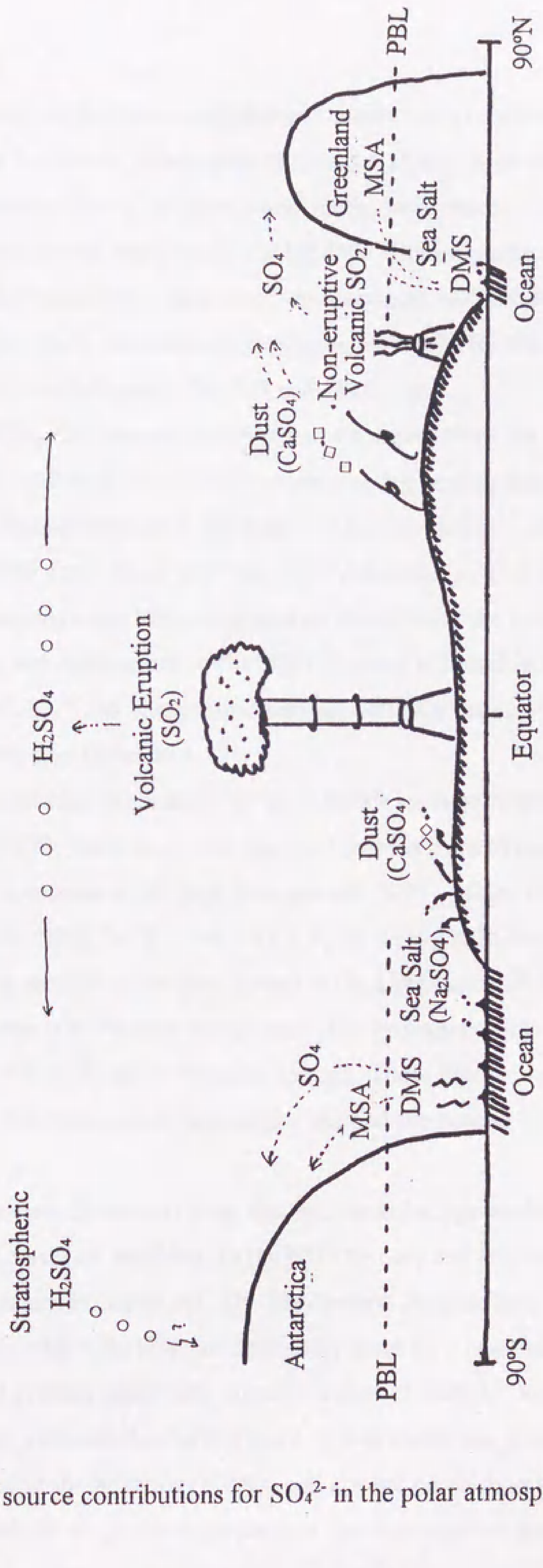


Figure 23. Schematic diagram of source contributions for SO_4^{2-} in the polar atmospheres and the ice sheets based on this study.

6. Summary and conclusions

This study investigated some of the water soluble ionic constituents contained in polar ice cores. Of prime interest was to obtain information on temporal and spatial variations of concentration levels and deposition fluxes of sulfate and methanesulfonate. First, a detailed paleoenvironmental and chemical stratigraphy study for the Byrd Station Antarctica area was discussed to establish the time-unit variations in ionic concentrations and volcanic events over the last millennium. Next, comparative study was made of the chemistry results for the Crete station, central Greenland for the time period between 1130 AD and 1820 AD.

The seasonal variation of $CH_3SO_3^-$ concentrations in snow samples from the shallow depth at the Byrd station area correlates well with the $nssSO_4^{2-}$ variations, suggesting that the dominant source of the $nssSO_4^{2-}$ and $CH_3SO_3^-$ deposited in this region is marine biogenic dimethylsulfide. The SO_4^{2-} results of the NBY89 core show that the west Antarctic total sulfur budget is significantly increased by the numerous major volcanic eruptions identified in the core. The largest volcanic contribution over the last millennium in the NBY89 core is found in the 1259 AD horizon. The sea-salt fraction of SO_4^{2-} and background non-sea-salt SO_4^{2-} concentrations levels are nearly constant over Antarctic and Greenland.

Second, a reliable time-scale was established for the NBY89 ice core to trace prominent volcanic index horizons to the SP78, Antarctica, with ice core records from Crete and Dye 3 in Greenland. A bi-hemispheric comparison of high non-sea-salt SO_4^{2-} peaks showed strong correlation at: 1885, 1836, 1816, 1810, 1459, 1346, 1287, 1278, 1259, 1228 and 1168, in AD units at time of snow deposit. The number of volcanic events in the Greenland CR74 core record is larger than that in the Antarctic NBY89 and SP78 cores. The prominent 1259 AD volcanic signal appears to be a significant bi-polar ice core index horizon. These bipolar volcanic events contributed sporadic deposition of sulfate, and significantly disturbed the normal sulfur budget in both polar regions.

Finally, spatial distributions were discussed using the multi-year background concentration levels of $HCOO^-$, $CH_3SO_3^-$, NO_3^-, $nssSO_4^{2-}$ and NH_4^+ in the NBY89 core and in pre-1900 AD ice layers from 7 different drilling locations in Greenland. The background concentration levels of the ionic species measured vary somewhat with time but noticeably more on a regional basis.

The spatial distribution of average multi-year concentrations of $nssSO_4^{2-}$ and $CH_3SO_3^-$ in polar regions was discussed with available data in literature. It was found that a low and nearly constant spatial distribution of sulfur molar ratios (SMRs) and a weak correlation with $CH_3SO_3^-$ and $nssSO_4^{2-}$ concentration levels in ice cores suggests that the dominant source of $nssSO_4^{2-}$

deposited in Antarctica is from marine biogenic DMS as well as $CH_3SO_3^-$, at least for coastal sites with elevations below 2000 m. The lack of a simple relationship between $nssSO_4^{2-}$ and $CH_3SO_3^-$ and higher SMRs suggests that part of background $nssSO_4^{2-}$ in Greenland ice originates from a source not related to the marine DMS, even in pre-1900 AD ice layers.

The spatial distribution of $nssSO_4^{2-}$ deposition flux as a function of elevation is similar to the $CH_3SO_3^-$ flux distribution in Antarctica but different in Greenland. Deposition fluxes of $nssSO_4^{2-}$ in Greenland are higher than at Antarctic sites at comparable elevations as well as the $CH_3SO_3^-$ flux, which suggest a more active source in the northern hemisphere. Such a source for $nssSO_4^{2-}$ not related to marine biogenic DMS was suggested as mineral dust containing sulfate and SO_2 from non-erupting volcanic in origin.

7. Acknowledgements

I am grateful to Professors Chester C. Langway, Jr. and Hitoshi Shoji for providing me with the opportunity to study the ice cores at the Ice Core Laboratory, State University of New York at Buffalo during the 2 1/2 years spent there and for the valuable guidance and helpful advice since then. I am also grateful to Dr. Henrik. B. Clausen for extended discussions and suggestions and thank many other colleagues at the Geophysical Isotope Laboratory, University of Copenhagen for sharing their oxygen isotope and ECM dating and volcanic signal information. I wish to thank Ms. G. Sokalski who performed some of the chemical analyses and Messrs M. Lukich and T. Langway for assistance in ice core sample preparation at ICL/SUNY at Buffalo. I also wish to thank members of field teams of ice core drilling at New Byrd station, South Pole, Siple and GISP sites. I would like to thank Dr. K. Azuma for useful advice of daily living at Buffalo.

I am grateful to Professors K. Higuchi and Y. Ageta for valuable discussions during very early stage of this study. I am also grateful to Professor Y. Iwasaka, Drs. Matsunaga and T. Shibata, and Mr. M. Hayashi for many helpful discussions, valuable guidance and academic supports.

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副論文

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