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New chemical stratigraphy over the last millennium for Byrd Station, Antarctica

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ABSTRACT

A 164 m-deep, 10 cm diameter, ice core was obtained at Byrd Station surface camp (NBY89), West Antarctica in November 1989. In addition, two 10-m shallow cores were recovered at 14 km and 29 km distances upstream from the main core; 2 m-deep pits were dug at each drilling location. Over 2300 individual samples were analyzed for ionic concentration levels in continuous but selected depth-intervals. Results of study provided a continuous 1360-year chronology for the 164-m core based on multiple cross-correlations of $\delta^{18}O$, ECM and ionic chemistry data combined with megascopic stratigraphy and physical properties. Average ionic concentration values over the entire core profile are $CH_3SO_3^-$, 0.08; Cl^-, 1.52; NO_3^-, 0.76; SO_4^{2-}, 1.10; Na^+, 1.13 and Mg^{2+}, 0.30 in μeq kg^{-1}. Between 60 m to 164 m, the average $HCOO^-$ concentration level is 0.04 μeq kg^{-1}. Measurements of NH_4^+, K^+ and Ca^{2+} were mostly below instrument detection levels. Except for $CH_3SO_3^-$, the chemistry curves show no significant trends with time. Excess SO_4^{2-} reveals distinct seasonal cyclicity over the entire 164 m core but $CH_3SO_3^-$ and NO_3^- concentrations also show seasonal variations, most clearly over the top 2 to 4 m. 25 excess SO_4^{2-} peaks greater than 5 kg km^{-2} are identified as volcanic in origin. 5 prominent excess SO_4^{2-} volcanic peaks below 90 m are laterally traced to the same time-unit events near the top of the Byrd Station deep core recovered in 1968, thereby establishing a reliable chronological connection between the new NBY89 core data with the older ice core records which extends back to Early Wisconsin age.

1. Introduction

A 2164 m-deep ice core (BS68) was drilled at Byrd Station, West Antarctica (80°01′S, 119°31′W; 1530 m elevation), during the 1967–68 field seasons (Ueda and Garfield, 1969). Subsequent laboratory investigations made on this first long core to completely penetrate the Antarctic ice sheet provided valuable long-term environmental records dating back to the beginning of the Wisconsin Ice Age (see summaries and extensive reference list of previous work contained in Mackinnon, 1980; Brennan and Barry, 1989). However, all earlier studies reported for BS68 began 88.4 m below the 1967/68 AD snow surface (ca. 1340 AD), where continuous core recovery first began due to limitations in the then existing drilling technology. Consequently, a main goal of this study was to obtain a new core to provide a continuous chronology from today's surface to tie into and overlap the deep ice core records of BS68 and fill-in the approximately seven century gap existing until now in the continuous paleoenvironmental history of the area.

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2. Samples

The new 164 m-deep, 10 cm diameter ice core (NBY89), was obtained in November 1989 at a location 1 km upstream from the temporary Byrd surface camp operated by the US Navy (Langway, 1992). Two 10 m-deep cores were also recovered 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. All cores were augured continuously and recovered in good physical condition. They were then logged and the megascopic stratigraphy carefully recorded. Continuous bulk density measurements, sample cutting for the oxygen isotope study and the acidity measurements (ECM, Hammer, 1980) were also made in the field.

Our initial dating of the entire BS68 deep ice core was made in 1980 and 1982 using the Electrical Conductivity Method (ECM) (Hammer, 1980, 1983). All cores contained within the 2088 1-m core containers were measured in the freezer storage facility in Buffalo N.Y. over a $3\frac{1}{2}$-month period. Age was determined by counting the seasonal variations as in Hammer 1980 and 1983. For the NBY89 core investigation, an updated ECM apparatus was used. The NBY89 ECM dataseries was cross-correlated with the ionic chemistry stratigraphy (this study). 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 and total β curve were also 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 complete time-scale, $\delta^{18}O$ and acidity measurements will be reported elsewhere.

3. Laboratory

Preparation of core samples for chemical analyses followed published procedures (Langway et al., 1974; Finkel et al., 1986). The anions and cations are simultaneously measured in a Class-100 clean-room, using a two-column ion chromatograph (Dionex 4040i) equipped with HPIC-TAC and -TCC concentrators, AS4A and CS3 separator columns, anion and cation micromembrane suppressors with recording integrators (Spectra Physics model 4270) and auto-mated samplers (Dionex ASM-2). Step gradient methods are 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 are made from 18 MΩ Milli-Q water. Blank values for $HCOO^-$ are below 1 ng g^{-1} and below detection limits for other ions (0.4 ng g^{-1} for $CH_3SO_3^-$, 2 ng g^{-1} for Cl^-, 4 ng g^{-1} for NO_3^- and SO_4^{2-}, 1 ng g^{-1} for Na^+, NH_4^+ and K^+, 0.8 ng g^{-1} for Mg^{2+} and 4 ng g^{-1} for Ca^{2+}). Sample volumes for anions are 11 ml and 5.5 ml for cations. Measurements for NH_4^+, K^+ and Ca^{2+} were mostly below the detection limits of our instrument. 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). A total of 2300 ionic measurements were made on various samples for this study.

4. Results and discussion

4.1. Top 10 m

Table 1 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). Fig. 1 is a plot of the continuously measured physical and chemical data for the NBY-2 site only (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 3 sites (Table 1) provides a measure of the average short-term vertical and

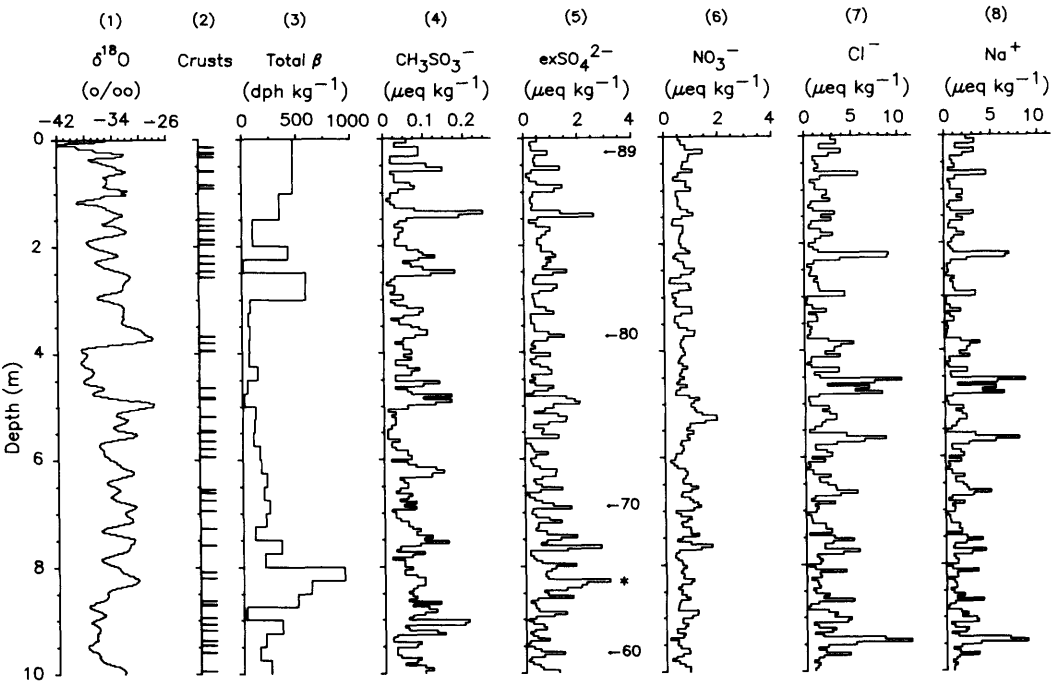

Fig. 1. Chemistry and physical properties measurements for the 10 m firn profile at NBY-2. Column 1 is a plot of the $\delta^{18}O$ curve; column 2 shows the distribution of crust layers (as horizontal lines); column 3 shows total β measurements; columns 4 through 8 show curves of various ions. The data plots represent different sample thicknesses for each parameter measured; for $\delta^{18}O$, 2.5 cm (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.

horizontal variations in concentration levels. The average $exSO_4^{2-}$ and NO_3^- values (columns 7 and 8) show relatively little variability for the same time intervals. The concentration of $exSO_4^{2-}$ represents the non-sea-salt portion of total SO_4^{2-} as calculated by subtracting the average sea water ratio of SO_4^{2-}/Na^+ (0.12) from the measured values. 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 $\mu eq\ kg^{-1}$, 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 $exSO_4^{2-}$ concentration levels at the NBY-89 site, and clearly higher sea-salt concentrations at NBY-2. Except for these differences all other site data show reasonable good agreement.

Fig. 1 shows chemistry and physical properties measurements for the 10 m firn profile at NBY-2. The $\delta^{18}O$ curve above 2.5 m in Fig. 1 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 we see 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 where ice-crusts are absent. 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 we identify 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

Table 1. *Average ionic concentrations in samples from all study sites 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)	(9)	(10)	(11)
					Concentrations (μeq kg^{-1})					
					$CH_3SO_3^-$	$exSO_4^{2-}$	NO_3^-	Cl^-	Na^+	Mg^{2+}
			NBY89 (main site, 1 km upstream from 1989 surface camp)							
1a	snow pit	0–2	5	40	0.11	0.98	0.89	1.58	1.13	0.30
					(0.10)	(0.52)	(0.45)	(0.93)	(0.74)	(0.20)
1b	core	0–2	10	19	0.09	1.15	0.89	1.24	0.83	0.22
					(0.08)	(0.56)	(0.40)	(0.87)	(0.65)	(0.16)
1c	core	0–10	11	88	0.08	0.98	0.77	1.58	1.22	0.31
					(0.06)	(0.50)	(0.29)	(1.24)	(0.96)	(0.25)
			NBY-2 (14 km upstream from main site)							
2a	snow pit	0–2	5	40	0.08	0.63	0.87	2.73	1.91	0.48
					(0.07)	(0.52)	(0.52)	(2.93)	(2.26)	(0.53)
2b	core	0–2	7	29	0.06	0.65	0.69	1.92	1.48	0.40
					(0.05)	(0.52)	(0.26)	(1.18)	(1.04)	(0.26)
2c	core	0–10	5.5	180	0.07	0.73	0.71	2.23	1.61	0.44
					(0.04)	(0.56)	(0.31)	(2.06)	(1.65)	(0.43)
			NBY-3 (29 km upstream from main site)							
3a	snow pit	0–2	5	40	0.09	0.71	0.92	1.58	1.09	0.33
					(0.07)	(0.44)	(0.37)	(0.96)	(0.74)	(0.23)
3b	core	0–2	7	28	0.05	0.73	0.84	1.58	1.04	0.27
					(0.05)	(0.48)	(0.35)	(1.07)	(0.83)	(0.20)
3c	core	0–10	5.5	184	0.07	0.77	0.71	1.58	1.13	0.30
					(0.05)	(0.50)	(0.31)	(1.21)	(0.96)	(0.25)

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

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 $exSO_4^{2-}$ curve (column 5) shows clear seasonal variations with a pronounced summer maximum (ca. 1.5 μeq kg^{-1}) and a winter minimum (ca. 0.5 μeq kg^{-1}) at NBY-2 (as well as over the complete 164 m NBY89 core profile). The correlation between $exSO_4^{2-}$ seasonal peaks and ECM seasonal peaks is strong over the entire NBY89 core. In column 5, years shown by tick marks are determined by counting $exSO_4^{2-}$ summer maxima with subsequent refinement when needed by fine-tuning using the $\delta^{18}O$ and ECM curves. The $exSO_4^{2-}$ 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 $exSO_4^{2-}$ (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 $exSO_4^{2-}$ appears in both the winter and summer accumulation presumably because of the sustained period of $exSO_4^{2-}$ 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 $exSO_4^{2-}$. No clear trends are observed in the sea-salt concentrations at 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. 1 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), Antarctica.

4.2. Selected deeper sequences

Fig. 2 is a plot of the ionic measurements made on the NBY89 main core at three chosen depth-intervals. The intervals were originally selected because they contained the calculated ages of historically recorded volcanic eruptions. The exact position of the layers were first identified by measured high strong-acid concentration peaks (ECM measurements) as representing the layers containing the eruptions of Krakatoa, 1884, (Fig. 2a), Tambora, 1816 (Fig. 2b) and the 1259 AD horizon (Fig. 2c). The $exSO_4^{2-}$ curve (column 1) shows seasonal cycles with large amplitude but other acid components in this plot (columns 2 and 3) reveal periodicity to a much lesser degree. All the $exSO_4^{2-}$ peaks identified by asterisks (*) in Fig. 2, column 1, are taken to represent volcanic eruptions of either unknown or historically recorded events. The excess chloride ($exCl^-$) curve (column 3) shows the amount of non-sea salt Cl^- present after subtracting the sea-water ratio contribution from the measured total values. Except for the large and spurious $exCl^-$ peak at 95.6 m, both the NO_3^- and $exCl^-$ curves do not correlate with volcanic peaks identified in the $exSO_4^{2-}$ curve. This anomalously high concentration level of $exCl^-$ is correlated with $exSO_4^{2-}$ peak at 1278 AD and presumed to be volcanic HCl in origin. The acid character of this peak is supported by the ECM profile (not shown here). A similar relationship was first reported for high Cl^- peaks in Greenland ice cores (Herron, 1982) associated with volcanic eruption.

4.3. The entire curve

Fig. 3 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 $exSO_4^{2-}$ concentration levels (column 3) are calculated from measurements made on samples from non-volcanic time-periods in an individual 1 m core interval.

The $\delta^{18}O$ curve in Fig. 3 (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. The $CH_3SO_3^-$ curve (column 2) 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 $exSO_4^{2-}$ curve (column 3) shows a very slight increasing trend between 300 to 100 years B.P. This suggests that a simple relationship between $CH_3SO_3^-$ and $exSO_4^{2-}$ does not exist.

The NO_3^- curve (4) is relatively flat with a σ of 0.08 μeq kg^{-1} over the entire core profile. This suggests a constant and wide spacial source. The variations in sea-salt components (columns 5, 6 and 7) show nearly coincident variations. On average, the sea-salts have ionic ratios close to sea water. Below the pore close-off zone (about 52 m), the $HCOO^-$ concentration levels (not plotted in Fig. 3) range between 0.02 to 0.06 μeq kg^{-1}, comparable with other published Antarctic results (Legrand and Saigne, 1988). The overall average concentration values for the ionic constituents shown in Fig. 3 are: $CH_3SO_3^-$, 0.08; SO_4^{2-}, 1.10 (non-volcanic $exSO_4^{2-}$, 0.85); NO_3^-, 0.76; Cl^-, 1.52; Na^+, 1.13; and Mg^{2+}, 0.30 in μeq kg^{-1} units.

4.4. Non-volcanic sulfur

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. In this study we find the sulfur contributions from sea-salts 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. We also found only minor long-

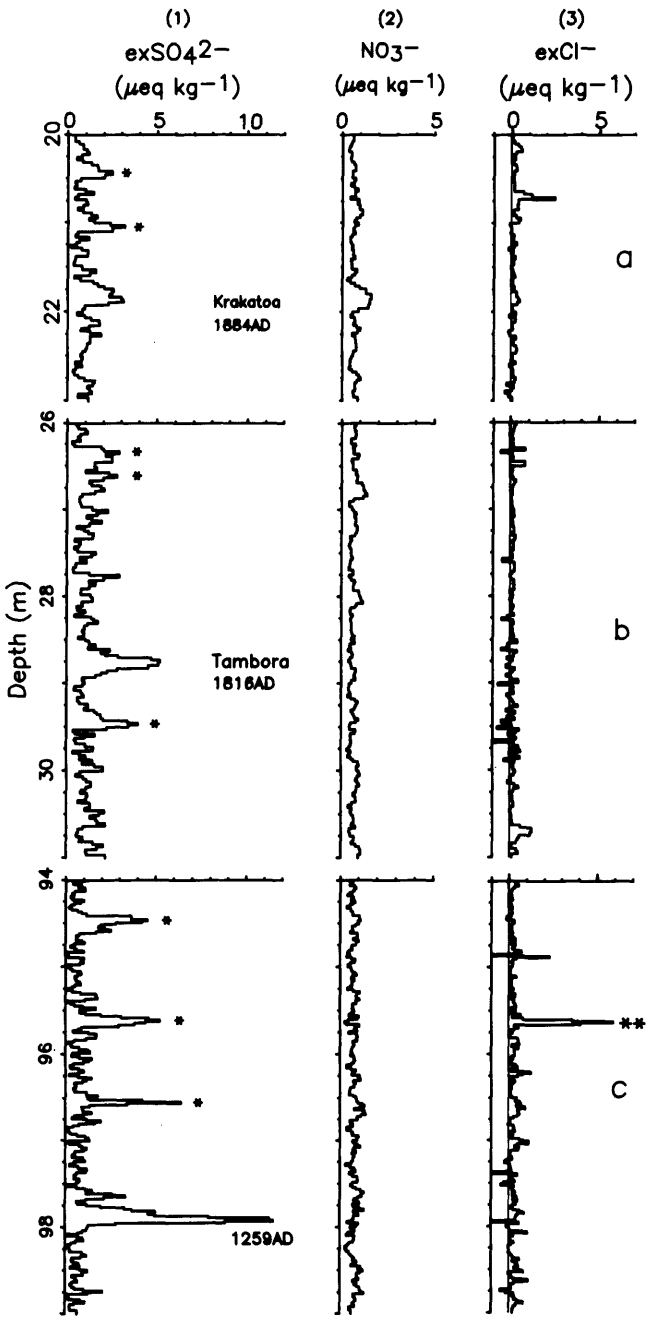

Fig. 2. Variations in major acid ion concentration levels for selected NBY89 core intervals containing an identified volcanic eruption: (a) Krakatoa; (b) Tambora; (c) the 1259 AD event and unknown volcanic events (*). Double asterisk (**) largest $exCl^-$ peak in 1364 year chronology associated with $exSO_4^{2-}$ peak.

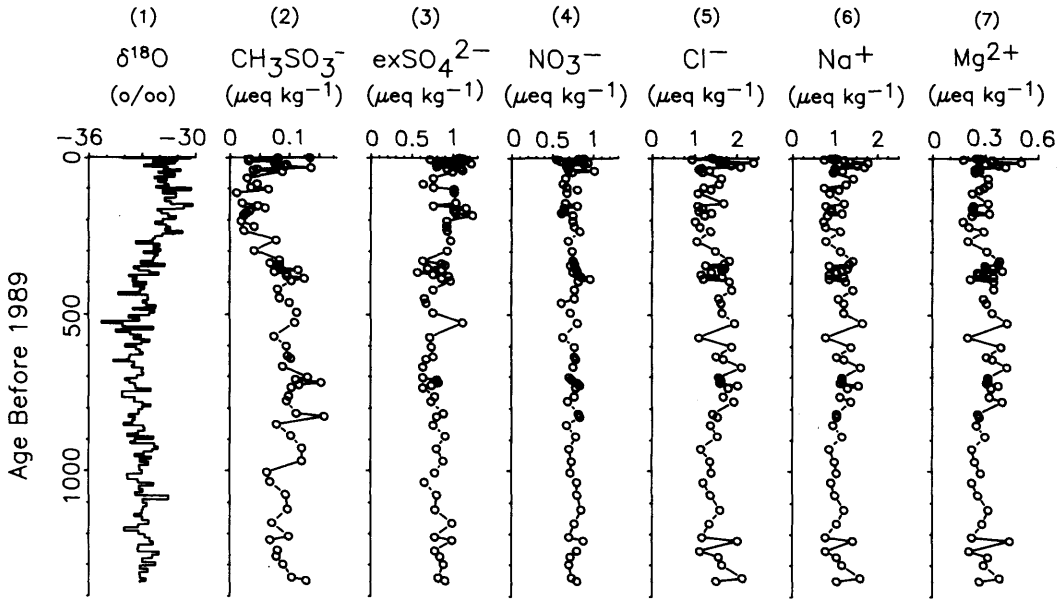

Fig. 3. Stable isotope curve (column 1) and average multi-year ion concentration levels as a function of age (column 2–7) for 164 m NBY89 core. Data points represent average values for 1 m core increments.

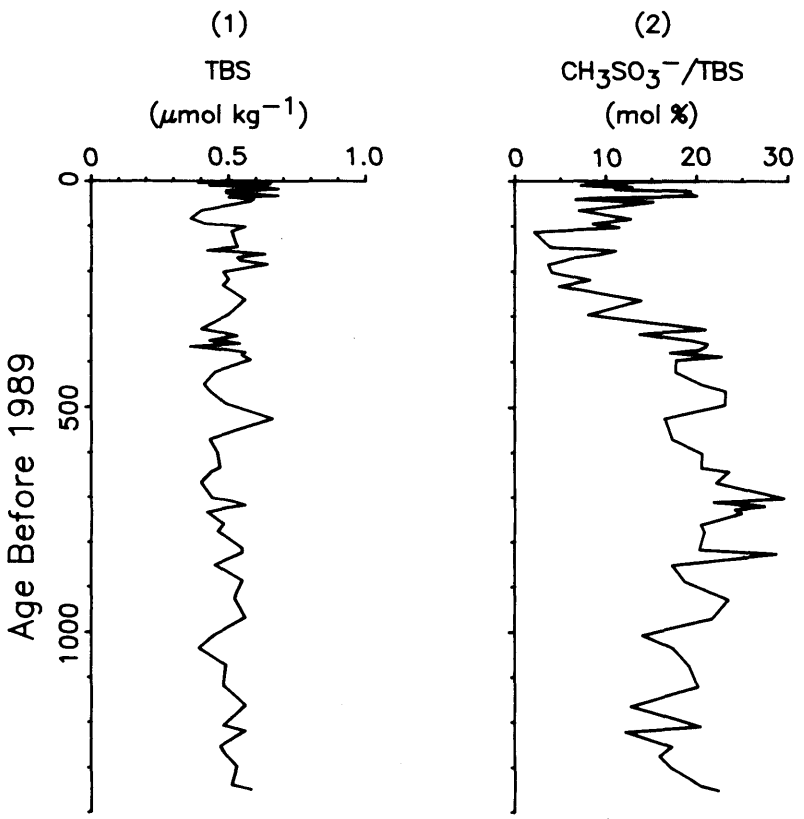

Fig. 4. Long-term variations of total biogenic sulfur, TBS concentration levels (μmol kg^{-1}) and molar ratio of $CH_3SO_3^-$ to TBS in % as a function of age. Data used are from Fig. 3.

term changes in concentration levels of other sea salt components. A recent study of Antarctic aerosols (Prospero et al., 1991) reported synchronous seasonal variations in non-sea-salt SO_4^{2-} and $CH_3SO_3^-$ concentration levels associated with oceanic bio-activity, suggesting significant marine biogenic contribution to the Antarctic sulfur budget. Although the oxidation transformation processes from dimethylsulfide (DMS) to SO_4^{2-} and $CH_3SO_3^-$ are not well understood (Plane, 1989) and the ratio between the two compounds is variable with temperature (Hynes et al., 1986), both ions are considered to be the major oxidation end-products resulting from a gaseous biogenic DMS produced and emitted by the ocean.

Fig. 4 shows the variations of the total biogenic sulfur (TBS) concentration levels (column 1) and the molar ratio of $CH_3SO_3^-$/TBS in % (column 2) for the NBY89 core. TBS is calculated as total $CH_3SO_3^-$ plus the non-volcanic $exSO_4^{2-}$ content in μmol kg^{-1}. The TBS curve shows no significant trend. The average TBS content is 0.51 μmol kg^{-1} (16 ng-S g^{-1}), and represents 88% of the non-volcanic total sulfur budget measured in this core,

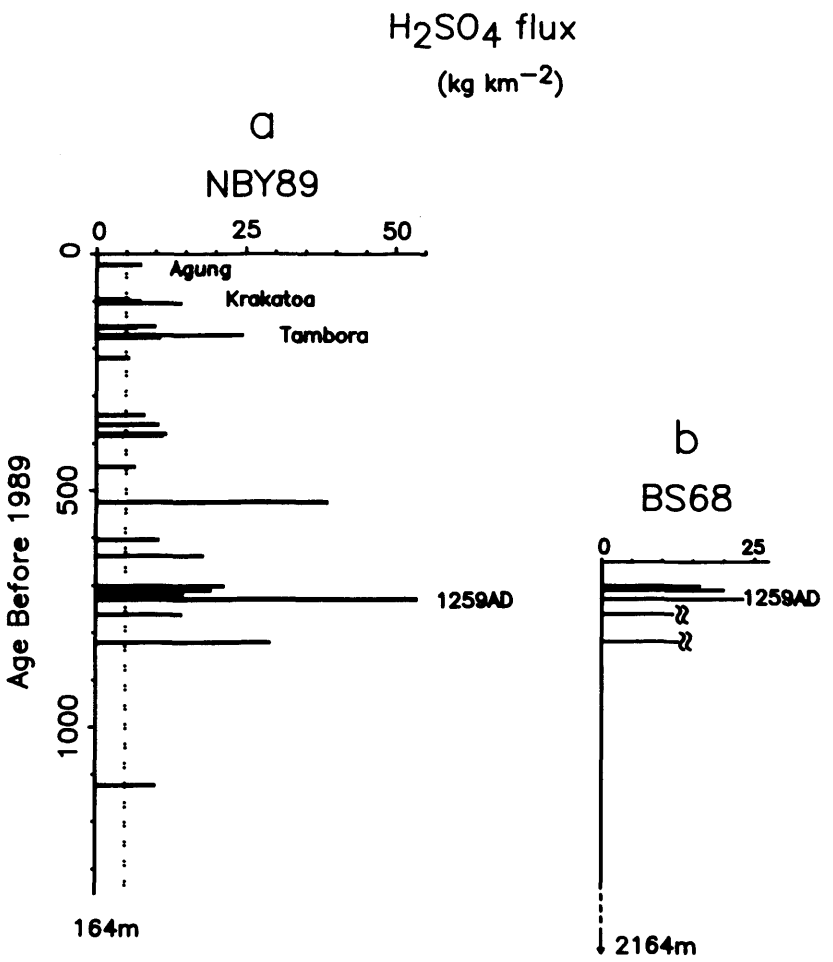

Fig. 5. Distributions of volcanic H_2SO_4 fluxes in NBY89 core and Byrd Station deep ice core (BS68) recovered in 1968, as a function of age from 1989 AD surface. Vertical dotted line on NBY89 curve indicates 2σ background level for average non-volcanic H_2SO_4 flux (see text). Flux value at 1259 AD layer for BS68 core was from Langway et al. (1988) but corrected for the annual layer thinning. BS68 curve with wave lines for maximum flux values are estimated from ECM data.

suggesting biogenic sulfur constantly contributed a major portion of the background sulfur cycle at Byrd station during the last millennium. The $CH_3SO_3^-$ concentration level represents approximately 16% of the average TBS concentration. The curve in Fig. 4 (column 2) shows a maximum percentage of 29% around 700 years B.P. and a minimum of 4% around 110 years B.P.

4.5. *Volcanic events*

Fig. 5 is a time-series plot of the volcanic H_2SO_4 fluxes (kg km^{-2}) calculated for (a) the NBY89 core and (b) the upper portion of the BS68 deep core. The fluxes are estimated by subtracting the average non-volcanic $exSO_4^{2-}$ from the SO_4^{2-} measurements following published procedures (Langway et al., 1988; Clausen and Hammer, 1988). The variability of natural background flux of 5 kg km^{-2} yr^{-1} at 2σ is estimated from averaging vertical and lateral variances in annual H_2SO_4 fluxes (ca. 4 kg km^{-2} yr^{-1} on average) obtained at the three drilling locations. The vertical dotted line for NBY89 data (Fig. 5) is the upper 2σ limit background noise level. A H_2SO_4 signal which

Table 2. *Volcanic H_2SO_4 fluxes, NBY89 main core*

(1)	(2) Year of deposition (AD)	(3) Depth interval top — bottom (m)	(4) Volc. H_2SO_4 index (kg km^{-2})	(5) Identified volcano (Date, AD)	(6) Ref.
#	1965	8.25 — 8.55	7	Agung (1963)	(1–3, 6, 8, 10)
	1893	20.31 — 20.45	5		
	1889	20.90 — 21.06	7		
*	1884	21.65 — 21.89	14	Krakatoa (1883)	(1–4, 6, 8, 10)
	1835	26.27 — 26.51	10	Coseguina (1835)	(3, 6, 10)
	1832	26.57 — 26.78	7		(10)
*	1816	28.50 — 28.90	24	Tambora (1815)	(1–8, 10)
	1811	29.30 — 29.50	11		(1–3, 6, 7, 8, 10)
	1768	34.56 — 34.67	5	Cotopaxi (1768)	(3)
	1648	49.69 — 49.93	8		(2)
	1628	52.45 — 52.66	10		
	1609	55.19 — 55.40	12		
	1607	55.57 — 55.73	5		
	1605	55.80 — 56.13	11		(2)
	1539	63.96 — 64.07	6		
	1464	73.08 — 73.33	38		(2, 6, 8, 10)
	1384	82.87 — 82.96	11		
	1348	87.11 — 87.45	18		(2, 10)
	1287	94.38 — 91.64	21		(2)
	1278	95.52 — 95.68	19		(2, 10)
	1270	96.43 — 96.60	15		(10)
*	1259	97.73 — 97.99	54		(2, 4, 6, 8, 9, 10)
	1227	101.50 — 101.68	14		(2, 10)
	1168	108.85 — 109.16	29		(2, 10)
	865	141.70 — 141.79	10		

Column 1: # NBY-2 core result. * index horizons.
Column 4: Only fluxes >5 kg km^{-2} listed.
Column 5: Only 5 of the 25 events listed are historically documented eruptions.
Column 6: References: (1) Hammer et al., 1977, Crete, Greenland, (2) Hammer et al., 1980, Crete, Greenland, (3) Legrand and Delmas, 1987, Dome C, Antarctica, (4) Langway et al., 1988, Greenland and Antarctica, (5) Clausen and Hammer, Greenland, 1988, (6) Moore et al., 1991, Antarctica, (7) Dai et al., 1991, Greenland and Antarctica, (8) Legrand and Kirchner, 1990, Antarctica, (9) Palais et al., 1992, Greenland and Antarctica, (10) Delmas et al., 1992, South Pole.

has a flux greater than the 2σ threshold value is considered a volcanic event. The initial identification of a volcanic event layer is made by analysis of strong-acid peaks in the ECM curve. Final annual accumulation layer thicknesses are corrected by using Nye's approximation (Nye, 1963) for calculating volcanic H_2SO_4 flux. 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 this study 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; Moore et al., 1991; Palais et al., 1992; Delmas et al., 1992). Fig. 5 also shows the stratigraphic continuity for 5 other volcanic signals between 90 m to 111 m in both the NBY89 and BS68 deep core for the years 1287, 1278, 1259, 1227 and 1168 AD. These data, however, show differences in the magnitude of the H_2SO_4 fluxes for the same events registered at each site. Some of variance can be attributed to stratigraphic noise probably caused in part by the non-uniform snow accumulation processes and by post-depositional redistribution of snow by surface winds. These same processes may also account for the missing volcanic signals in the BS68 deep core but clearly found in the NBY89 core at 1270 AD and 865 AD.

Table 2 is a summary of the volcanic activity data derived from the NBY89 core compared to published results of volcanic events found in various other Antarctic and Greenland ice cores. If we assume that the normal annual H_2SO_4 flux for the Byrd Station area is 4 kg km^{-2} yr^{-1} in average, the volcanic H_2SO_4 flux rates listed in Table 2, column 4, make a large but sporadic contribution to the total sulfur budget of the area during periods of strong volcanic activity.

The presence of specific unidentified volcanic events recorded in the NBY89 core poses a special problem (as with all Antarctic cores) because of (1) the lack of adequate historical documents or other detailed information related to the as yet unidentified volcanic periodicities and magnitudes in the Southern Hemispheric (Newhall and Shelf, 1982), and (2) the sometimes imprecise dating of an ice core.

5. Summary and conclusions

This study was made to establish a detailed paleoenvironmental and chemical stratigraphy record for the Byrd Station Antarctica area from today's snow surface which would tie into and overlap the long-term climate and environmental records available from the BS68 deep core obtained 24 years earlier. The combined results of the NBY89 core study has provided a detailed chronology of the chemistry/volcanic stratigraphy and physical property changes, and establishes an average accumulation rate of 10.1 g cm^{-2} yr^{-1} for the area during the last 1360 years. Results show that distinct seasonal variation was found in excess SO_4^{2-} concentration levels over the entire core profile whereas other ions exhibit inconsistent periodicity (Cl^-, Na^+ and Mg^{2+}) or limited seasonal variability ($CH_3SO_3^-$ and NO_3^-). A decrease in the $CH_3SO_3^-$ concentration level is observed between 150 years B.P. and 350 years B.P. which correlates slightly with a small increase in the $\delta^{18}O$ values over the same period. The NO_3^-, Cl^-, Na^+ and Mg^{2+} contents show no significant trends over the core profile. The SO_4^{2-} results show that the West Antarctic total sulfur budget is significantly increased by the 25 major volcanic eruptions identified in this core and that the sea-salt and biogenically derived sulfur concentration are nearly constant over the profile. The volcanic strata found in the NBY89 core is horizontally tied into the BS68 deep core chronology allowing the continuous extension to today's surface of all the earlier records which started in the early Wisconsin age and ended ca. 1340 AD. The H_2SO_4 flux chronology from the NBY89 study may prove to be useful as a marker series, particularly for the east Antarctic area where determining annual layers by using the seasonal ECM and $\delta^{18}O$ methods have not yet been well established.

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