VOLCANIC RECORDS AND DATING OF THE UPPER HALF OF THE H15 ICE CORE FROM MIZUHO PLATEAU, EAST ANTARCTICA

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Abstract: Two closely-spaced peaks of electrical conductivity were found at depths between 45 and 50 m of the 120-m long ice core drilled at site H15 in Antarctica by the 32nd Japanese Antarctic Research Expedition in 1991. Chemical analysis of the core containing these peaks revealed that the ice layers were characterized by high acidity and high sulfate concentration suggesting volcanic signals. In order to identify these characteristics, the core was dated using two methods: (1) counting the number of high electrical conductivity peaks resulting from seasonal variations of SO_4^{2-} and NO_3^-, and (2) an empirical model of firn densification. The dating results suggest that the high conductivity is related to deposition of acidic aerosols from the volcanic eruptions of Tambora in 1815 A. D. and of an unknown volcano in 1809 A. D.

1. Introduction

Ice sheets of the Arctic and Antarctic regions contain atmospheric aerosols of volcanic, marine and artificial origin which are deposited as dry fall-out and wash-out. They occur as aggregates in snow particles. Ice cores drilled from ice sheets, therefore, include records of past volcanic activities, climatic and environmental changes.

A huge amount of volcanic gases and dust is emitted to the atmosphere at the time of an explosive volcanic eruption. These volcanic products, especially volcanic sulfur gases, are oxidized to form aerosols of sulfuric acid droplets in the stratosphere. Such aerosols stay in the stratosphere for several years after the eruption and reduce the insolation to the troposphere. Lowering of atmospheric temperature may follow the explosive eruption, lasting for several years (Lamb, 1970; Stothers, 1984; Rampino and Self, 1982; Rampino *et al.*, 1988; Sigurdsson, 1990). The amount of volcanic sulfur added to the atmosphere by a volcanic eruption is important to assess its effect on the earth's atmospheric environment.

The amounts of volatile emission by explosive volcanic activity in the past have been estimated by two methods: the petrologic method (Devine *et al.*, 1984; Palais and Sigurdsson, 1989; Kohno, 1992) and the chemical method based on hydrogen ion concentration of ice core under the assumption that the global distribution pattern of the volcanic sulfuric acid aerosols and that of bomb-produced total β activity are the same (Hammer, 1977; Hammer *et al.*, 1980; Clausen and Hammer, 1988; Langway *et al.*, 1988). Global acid fallout by past large volcanic eruptions in the northern hemisphere has been estimated from the analysis of acidity of Greenlandic ice core samples from Crete (71°12'

N, 37°32' W) for the last 1500 years and Camp Century (71°17' N, 61°13' W) for 10000 years (HAMMER et al., 1980). For example, the amounts of sulfuric acid emitted by volcanic eruptions of Laki (1783 A. D., Iceland, 64°42' N, 17°33' W) and of Tambora (1815 A. D., Indonesia, 8°25' S, 118°00' E) were both estimated to be ca. 300 Mt (CLAUSEN and HAMMER, 1988). The ice cores from Dome C (74°40' S, 125°10' E) and Vostok (78°28' S, 106°48' E) in East Antarctica, Siple (75°55' S, 85°55' W) in West Antarctica and South Pole contain records of several major volcanic events that took place in the southern hemisphere in the last 220 years. They are the Tambora 1815, Krakatoa 1883 (Indonesia) and Agung 1963 (Indonesia) eruptions with the relative proportion of acid emission by these eruptions being approximately 5 : 1 : 1 (LEGRAND and DELMAS, 1987). Prominent bipolar excess H_2SO_4 signals found in ice cores from Byrd Station (80°01' S, 119°31' W) and South Pole in Antarctica and from Crete and Dye 3 (65°18' N, 43°49' W) in Greenland in the last 1000 years were recorded in layers whose ages are 1885, 1836,
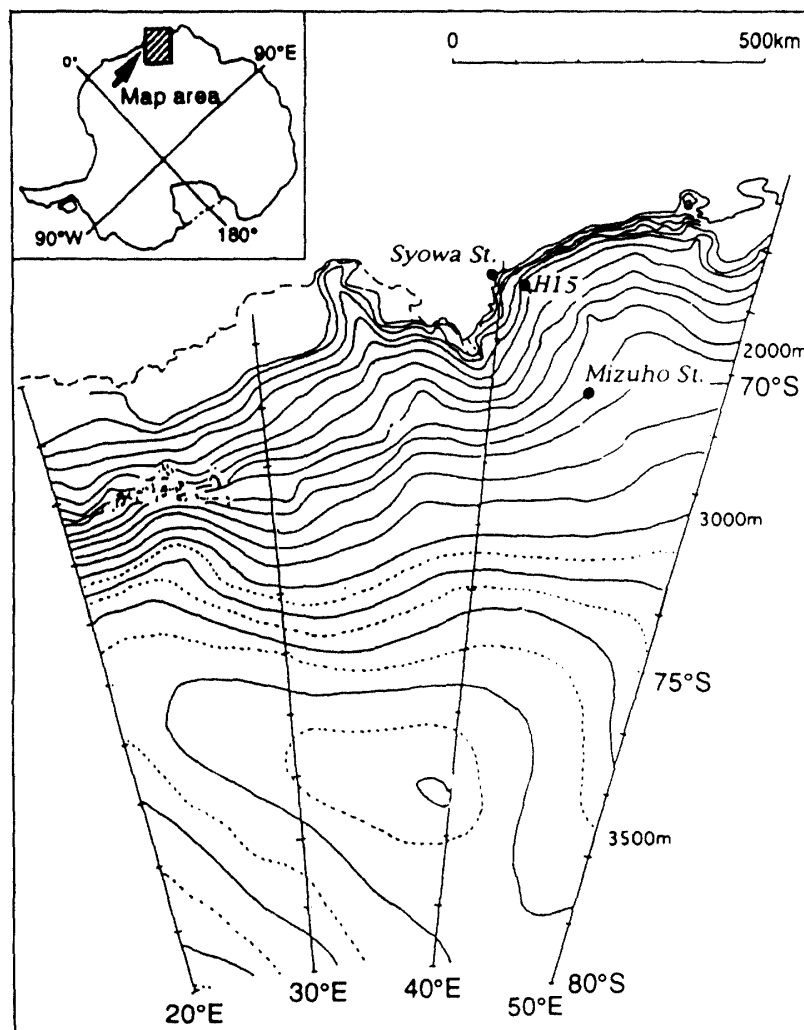

Fig. 1.   Map showing the location of the drilling site of the H15 ice core in
Dronning Maud Land, East Antarctica.

1816, 1810, 1459, 1346, 1287, 1278, 1259, 1228 and 1168 A. D. The excess H_2SO_4 signals in the layers dated in 1885, 1836 and 1816 A. D. were identified to originate from volcanic eruptions of Krakatoa 1883, Coseguina 1835 (Nicaragua) and Tambora 1815. The other signals were regarded to be due to aerosols released from volcanoes at low latitude (Langway et al., 1995).

An ice core was drilled at site H15 (69°04'46" S, 40°46'54" E, 1050 m a.s.l.) to a depth of 120.2 m using an electromechanical drill by the 32nd Japanese Antarctic Research Expedition in September to October, 1991 (Fujii et al., 1992, Fig. 1). Electrical conductivity measurements (ECM), a measure of acidity of ice core, were made at Syowa Station soon after the core recovery. They indicate that two remarkably high peaks first appear at depths between 45 and 50 m. We have determined the chemical composition and oxygen isotopic variations of the ice core samples between 43 and 50 m to find the causes for the high ECM peaks. We also attempted to date the ice core in order to obtain chronological information on the upper part of this core using two independent methods: (1) counting the number of peaks resulting from seasonal variations of SO_4^{2-} and NO_3^-, and (2) an empirical model of firn densification of Herron and Langway (1980).

2. H15 Ice Core

The site H15 is located near the Sôya Coast, Dronning Maud Land, East Antarctica (Fig. 1), where a high annual snow accumulation gives a high time resolution of the

Table 1.   The annual accumulation rate of snow between 1971 and 1991.

Period	Annual accumulation rate	
	Snow depth* cm/yr	Water equiv. depth** g/cm²/yr
Apr.1971–Apr. 1972	51.0	21.6
Jan. 1977–Feb. 1978	127.0	53.8
Jan. 1978–Jan. 1979	72.0	30.5
Jan. 1980–Jan. 1981	63.0	26.7
Jan. 1981–Jan. 1982	108.0	45.8
Jan. 1982–Jan. 1983	87.5	37.1
Jan. 1983–Dec.1983	74.3	31.5
Dec.1983–Jan. 1985	60.0	25.4
Jan. 1985–Jan. 1986	89.0	37.7
Jan. 1986–Jan. 1987	89.0	37.7
Jan. 1987–Jan. 1988	25.0	10.6
Jan. 1988–Dec.1988	35.0	14.8
Dec.1988–Jan. 1990	75.0	31.8
Jan. 1990–Jan. 1991	87.0	36.9
Jan. 1991–Oct. 1991	78.5	33.3
Jan. 1993–Jan. 1994	87.0	36.9
Average	75.5	32.0
Std dev.	25.4	10.8

* Data compiled from JARE Data Report (1972–1995).
** The accumulation rate of water was calculated using mean surface snow
    density of 0.42 g/cm³ measured along Route S29 to H54 (Nishio, 1984).

core. It is situated along the route S-H-Z from Syowa Station to Mizuho Plateau.

Table 1 summarizes the surface mass balance of snow observed at site H15 (SHIMIZU, 1975; FUJII, 1979; WADA *et al.*, 1981; KOBAYASHI *et al.*, 1982; SATOW *et al.*, 1983; NAKAWO *et al.*, 1984; NISHIO, 1984; FUJII *et al.*, 1986, 1992; NISHIO *et al.*, 1986, 1988; AGETA *et al.*, 1987; NISHIO and OHMAE, 1989; WATANABE *et al.*, 1990; MOTOYAMA *et al.*, 1995). The observation has been continued since April 1971. The 1972–76, 1979 and 1992 data are lacking. The mean annual accumulation rate since 1971 is 32.0±10.8 g/cm²/year. In this period, snow accumulated every year without hiatus. The mean annual accumulation rate of snow there suggests that the whole core represents the records of the last 300 years.

Bulk density of the core was measured and ice structures such as the melt layers were described soon after recovery at the Syowa Station (FUJII, 1992). The site H15 is located above the dry snow line. The mean annual atmospheric temperature is −21°C. However, ten distinct melt layers, which indicates presence of the hiatus of snow deposition, thicker than 3 mm were observed in the snow and firn layers down to 60 m below the surface. Three thick melt layers out of the 10 melt layers were observed at depths of 15.3 m, 19.1 m and 26.0 m (water equivalent depth), their thicknesses being 8 mm, 7 mm and 25 mm (water equivalent), respectively. The melt layers were formed during warm summer periods in the past. Existence of the melt layers may suggest that the atmospheric temperature was warmer than that at present.

3. Sample Preparation and Analytical Procedures

The core, 70 mm in diameter, was cut in half along the direction of depth after recovery, and has been preserved in a low-temperature room (−20°C) at the National Institute of Polar Research. The core was sliced into a wafer (7–10 cm thick) which covers a period of 4–6 months. Surface 5–10 mm of the ice core was removed using a grater in order to eliminate contaminants on the surface.

Water samples after melting the ice wafers were used for measurements of the pH, major chemical composition and oxygen isotopic ratios ($^{18}O/^{16}O$ ratio). The core samples were melted in a microwave oven in a Teflon beaker that had been cleaned with ultrapure water, and filtered with 0.2 μm filter paper (Nuclepore polycarbonate membrane, Corning Costar Corp.) in a clean room (class-1000) at the National Institute of Polar Research. The residue on filter paper was preserved for observation of solid residue.

Acidity, which is an index of acidic aerosols accumulated in snow, was measured using a pH meter (HM-60S, TOA Electronics Ltd.). The pH meter consists of a glass electrode separated from a comparative reference electrode (FAR-101, TOA Electronics Ltd.), because melt water of ice cores had a small buffer capacity due to very low ionic concentration (FUJII *et al.*, 1989). Concentrations of major anions (Cl⁻, NO_3^- and SO_4^{2-}) and cations (Na⁺, K⁺, Mg^{2+} and Ca^{2+}) were measured with ion chromatography using a Dionex ion chromatograph (model 2000i) equipped with HIPC-AG4A and -CG3 concentrators, AS4A and CS3 separator columns, and anion and cation micro membrane suppressors to concentrate the ionic species that are dissolved in a ~100 ppb level. Replicate measurements of standard solutions prepared from analytical grade reagents (NaCl, $NaNO_3$, K_2SO_4 and KCl, Mg and Ca 1000 ppm standard solutions) indicated the relative

analytical error of 5% of a measured value. The $^{18}O/^{16}O$ ratio ($\delta^{18}O$) of samples was measured with a stable isotope mass spectrometer (MAT-262) using the H_2O-CO_2 exchange technique of Epstein and Mayeda (1957), and reported in a conventional $\delta^{18}O$ expression with respect to SMOW.

4. Dating of the H15 Core

Dating methods of ice cores proposed so far include (1) the stake method (annual accumulation rate), (2) the empirical model for firn densification (Herron and Langway, 1980), (3) the stratigraphical method based on seasonal variations of $\delta^{18}O$, particle concentration, chemical composition, pH and ECM profiles (Epstein et al., 1965; Hammer et al., 1978; Fujii, 1981; Thompson et al., 1981; Legrand and Delmas, 1984; Watanabe et al., 1988), (4) detection of key volcanic signals such as tephra and high SO_4^{2-} concentration from volcanic eruption of a known date (Hammer, 1977; Hammer et al, 1980), and (5) the ^{210}Pb method (Crozaz and Langway, 1966; Masuda and Harada, 1986). Since the mean annual accumulation rate of snow at site H15 from 1971 to 1993 varies as much as ±30% (Table 1), it is difficult to use the mean accumulation rate for accurate dating of the H15 core. In this study, we thus adopted the stratigraphical method, i.e., counting the number of ECM peaks due to seasonal variations in snow chemistry, and the snow densification model proposed by Herron and Langway (1980) for the core dating.

Concentration of excess sulfate (or non sea-salt sulfate) of aerosols in the atmosphere at Mawson (67°36' S, 62°53' E) in East Antarctica is highest in January and relatively low from May to September (Prospero et al., 1991). The atmospheric excess SO_4^{2-} concentration is governed by the oxidation of biogenic dimethylsulfide (DMS) to SO_2 and methanesulfonic acid. The extent of oxidation varies with atmospheric temperature (Hynes et al., 1986; Koga et al., 1990). The sulfur dioxide of DMS origin is oxidized to form sulfuric acid in the atmosphere (Hatakeyama et al., 1985) and then accumulates in snow by wash-out. Seasonal variations of SO_4^{2-} and NO_3^- concentrations in drifting snow which collected at Mizuho Station during February to December in 1986 increased significantly in summer (Osada et al., 1989; Osada, 1994), and the pH values of drifting snow samples indicate that snow in summer is more acidic than that in the other seasons (Fujii, 1989). Therefore, it is conceivable that an ECM peak reflects summer acidity of snow, and that an ice core can be dated by counting the ECM peaks.

When DC voltage is applied across a piece of ice through electrodes, a weak electric current is induced. The current depends on the concentration of mobile ions, their mobility and efficiency of charge exchange at the electrodes. Since the mobility of H_3O^+ ions is much greater than that of OH^- and other ions, the initial current is proportional to the H_3O^+ concentration or acidity. This is the principle of ECM (Hammer, 1980, 1983). Figure 2 shows the ECM profile down to 50 m. The core depth has been converted to the water equivalent depth based on the density profile shown in Fig. 3. The profile represents the ECM values after taking a running average over every 10 cm interval. Above 50 m, we find two high ECM peaks at depths of 46.7 m and 48.3 m (Fig. 2).

Figure 4a compares the ECM profile of the top 4 m of the H15 core with the dates of
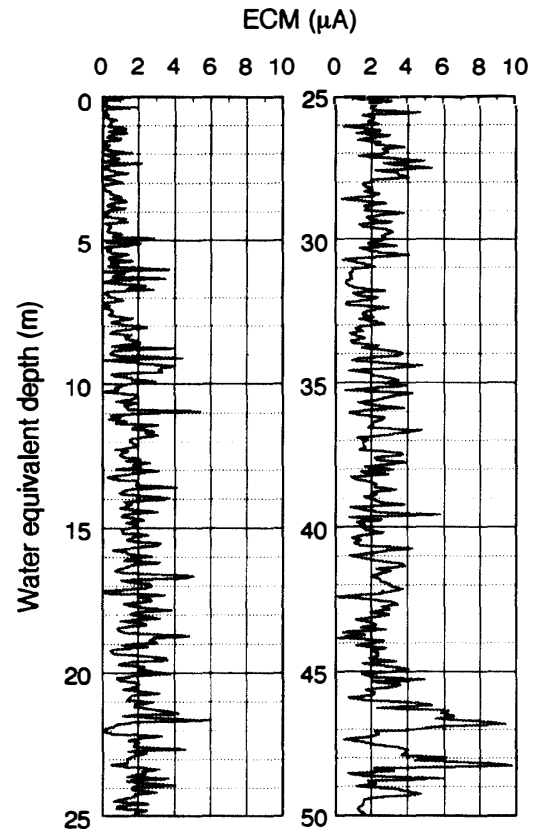
ECM (μA)

Fig. 2. ECM profile of the upper 50 m of the H15 core.
The profile was obtained by taking a running average
over every 10 cm interval. The core depth was con-
verted to water equivalent depth based on the measured
density of firn.
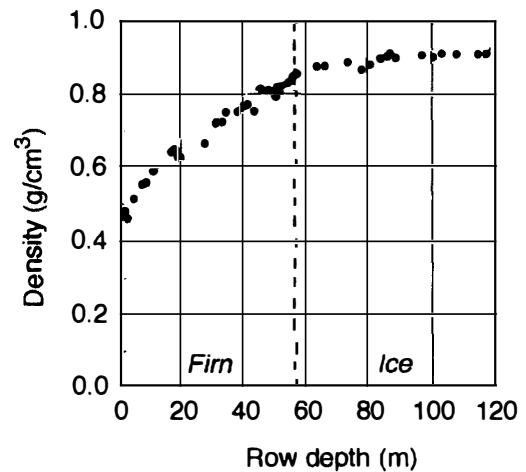
Fig. 3. Density profile of the upper part of the H15 core.
The density was measured for about 30 samples from
firn layers and 10 samples from ice layers.

firn given by stake observations (Table 1). We have assigned high ECM peaks to sum-
mer of an appropriate year based on the stake observations. Summer peaks are generally
indicated by a number assigned to the high ECM peaks, although there are a few excep-
tions. It should be noted that the highest ECM peak is found between the two ECM
peaks assigned to the 1983 and 1984 summers. Excess SO_4^{2-} concentrations shown in
Fig. 4b were calculated using the following equation assuming that Na^+ ions are entirely
derived from seaspray.

Fig. 4. (a) ECM profile from the surface to 4.0 m depth (reproduced from Fig. 2). Dates of snow from the stake observations are indicated on the top scale. ECM peaks have been assigned to appropriate dates based on th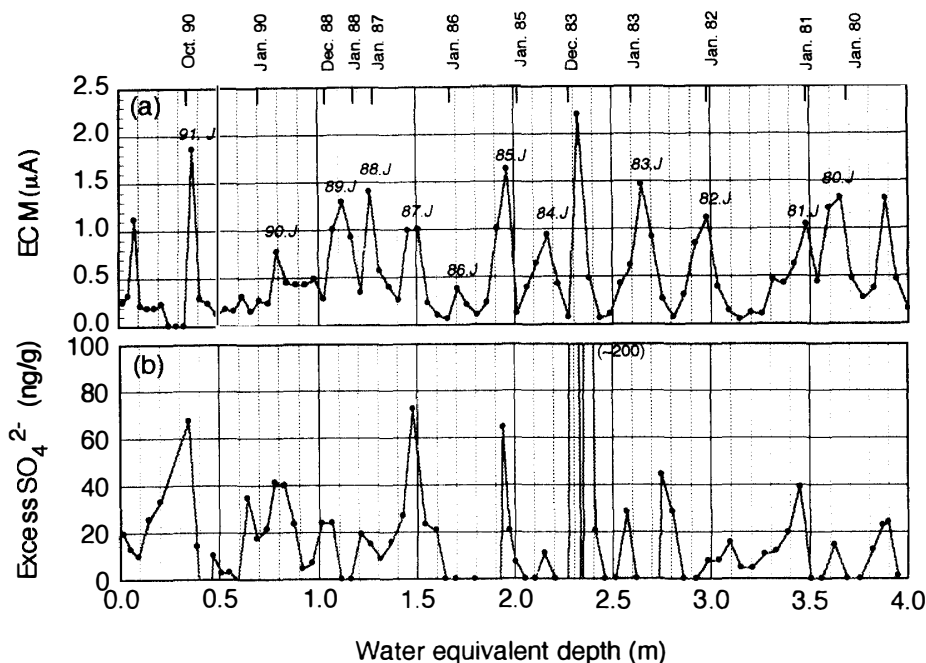e annual accumulation rate from the stake data. (b) Excess sulfate concentration profile from the surface to 4.0 m depth.

$$(SO_4^{2-})_{excess} = (SO_4^{2-}) - (SO_4^{2-} / Na^+)_{seawater} \cdot (Na^+), \tag{1}$$

where (SO_4^{2-}) and (Na^+) are the observed SO_4^{2-} and Na^+ concentrations of ice core samples (Table 2) and $(SO_4^{2-}/Na^+)_{seawater}$ is the ratio of SO_4^{2-} to Na^+ concentration in seawater, which is 0.25 (weight ratio). The excess SO_4^{2-} concentration generally varies between 0 and 70 ppb (Fig. 4b). High excess SO_4^{2-} peaks roughly agree stratigraphically with high ECM summer peaks. However, there are a few sporadic negative peaks (not shown in Fig. 4b), which suggests the existence of excess Na^+ for unknown reasons. There is a layer that contains very high excess SO_4^{2-} concentration at 2.3 m depth. Deposition of this excess SO_4^{2-} occurred in the latter half of 1983, and is likely to reflect deposition of sulfuric acid aerosols originated from an explosive volcanic eruption of El Chichon 1982 (Mexico, 17°36' N, 93°23' W) as will be discussed later. From the foregoing, counting the summer peaks in the ECM profile is certainly a usable method of dating the ice core.

The high ECM peaks shown in Fig. 2 were counted from the surface to 50 m depth. Above 50 m, there are two remarkably high peaks at 46.7 m and 48.3 m depths. They correspond to ~1826 A. D. (~165 B. P.) and ~1821 A. D. (~170 B. P.), respectively, although this dating method may involve errors due to counting of non-summer ECM peaks such as a volcanic signal at 2.3 m depth (El Chichon 1982) or under-counting of small summer peaks and undetected summer peaks caused by melting of snow as observed at depths of 15.3 m, 19.1 m and 26.0 m (water equivalent depth).

An empirical model of firn densification was proposed by HERRON and LANGWAY (1980). This model is based on the principle that air space in the firn is linearly related

Table 2. *H+ concentration, chemical composition and δ18O from surface to 4 m depth of H15 core.*

Water equiv. depth m	H+ n mol/g	Cl- ppb	NO3- ppb	SO42- ppb	Na+ ppb	K+ ppb	Mg2+ ppb	Ca2+ ppb	δ18O ‰
0.02	3.09	318	0	65	183	5	–	–	−24.7
0.05	3.72	301	11	55	170	5	–	–	−24.8
0.10	2.75	–	0	56	187	8	–	–	−27.3
0.14	3.31	566	0	106	322	17	–	–	−25.1
0.20	4.47	344	21	82	195	14	–	–	−22.9
0.35	5.62	178	93	90	93	3	–	–	−21.7
0.39	4.68	721	56	111	387	15	–	–	−25.8
0.43	3.98	884	14	83	505	20	–	–	−29.8
0.47	3.98	298	22	36	104	2	–	–	−25.1
0.51	3.89	309	12	30	109	2	–	–	−24.7
0.55	3.98	192	13	19	65	0	–	–	−24.2
0.60	3.63	404	13	29	119	2	–	–	−26.3
0.64	3.80	656	10	121	343	8	–	–	−20.6
0.69	3.63	453	8	56	156	0	–	–	−20.0
0.74	3.72	628	8	85	253	6	–	–	−19.5
0.78	3.89	89	30	53	48	0	–	–	−20.4
0.83	4.37	47	32	48	31	0	–	–	−23.5
0.87	3.55	87	1	34	44	0	–	–	−27.2
0.92	3.89	294	16	28	96	0	–	–	−29.9
0.96	3.63	299	1	32	101	0	–	–	−27.8
1.01	3.98	350	0	55	124	0	–	–	−24.0
1.06	3.47	78	27	35	–	–	–	–	−23.8
1.11	3.72	–	–	–	–	–	–	–	−22.1
1.16	3.47	–	–	–	–	–	–	–	−23.1
1.21	3.47	339	22	66	–	–	–	–	−26.8
1.26	3.89	220	40	41	103	2	12	9	−31.7
1.31	3.55	180	23	32	95	2	9	8	−29.6
1.37	2.88	146	58	36	81	1	9	15	−23.6
1.43	3.55	238	14	63	144	26	15	12	−20.9
1.48	4.68	213	47	101	116	2	12	6	−21.2
1.54	3.63	69	24	32	35	4	4	5	−22.8
1.60	3.72	148	10	41	–	–	–	–	−22.7
1.65	3.09	–	–	–	–	–	–	–	−23.1
1.70	3.72	–	–	–	–	–	–	–	−23.5
1.75	3.24	277	11	24	–	–	–	–	−24.3
1.80	3.09	–	–	–	–	–	–	–	−24.5
1.85	2.88	237	7	67	846	–	10	–	−24.3
1.89	3.16	122	5	42	816	–	6	–	−25.5
1.94	3.89	256	14	100	–	–	–	–	–
1.97	3.02	419	4	79	–	–	–	–	−28.1
2.00	2.88	380	13	60	–	–	–	–	−27.6
2.06	3.16	–	–	–	–	–	–	–	−28.0
2.11	2.95	–	–	–	–	–	–	–	−27.5
2.15	3.02	107	9	25	–	–	–	–	−25.1
2.21	3.24	–	–	–	–	–	–	–	−22.0
2.26	3.24	2452	68	180	–	–	–	–	−18.3
2.31	3.09	2442	17	438	–	–	–	–	–
2.34	3.55	104	9	99	813	–	6	–	−22.1

(continued)

Table 2.　(continued)

Water equiv. depth m	H^+ n mol/g	Cl^- ppb	NO_3^- ppb	SO_4^{2-} ppb	Na^+ ppb	K^+ ppb	Mg^{2+} ppb	Ca^{2+} ppb	$\delta^{18}O$ ‰
2.37	3.02	–	14	490	–	–	–	–	–21.7
2.41	3.39	603	7	104	–	–	–	–	–20.3
2.46	1.26	–	–	–	–	–	–	–	–20.4
2.52	2.57	–	–	–	–	–	–	–	–21.0
2.57	3.02	170	5	52	–	–	–	–	–20.3
2.62	3.16	–	–	–	–	–	–	–	–20.8
2.66	3.72	85	29	89	815	–	3	15	–22.6
2.70	3.24	96	21	86	908	–	4	23	–26.1
2.75	3.24	205	16	73	–	–	–	–	–
2.81	2.95	224	13	60	–	–	–	–	–23.4
2.87	3.31	–	–	–	–	–	–	–	–20.9
2.93	3.55	–	–	–	–	–	–	–	–21.3
2.98	3.55	161	11	30	89	2	10	6	–24.3
3.04	3.55	99	6	22	60	1	6	4	–26.2
3.10	3.80	98	30	30	59	1	6	7	–25.5
3.15	3.39	134	33	24	78	1	8	8	–22.8
3.21	3.80	262	4	44	158	2	17	8	–19.9
3.27	3.16	330	4	56	184	4	20	8	–19.2
3.33	3.39	170	6	36	98	2	11	5	–19.2
3.39	3.39	51	12	26	28	0	4	3	–19.4
3.45	3.63	132	21	57	–	–	–	–	–21.1
3.51	3.39	–	–	–	–	–	–	–	–24.2
3.56	3.31	–	–	–	–	–	–	–	–27.9
3.62	3.55	213	34	44	–	–	–	–	–27.1
3.69	3.47	–	–	–	–	–	–	–	–23.3
3.75	3.31	–	–	–	–	–	–	–	–22.3
3.82	3.55	220	11	43	–	–	–	–	–21.6
3.87	3.31	147	1	59	144	–	10	7	–21.6
3.90	3.63	187	14	68	175	–	12	8	–
3.95	3.39	195	7	28	–	–	–	–	–21.9

–: not determined

to stresses resulting from the weight of overlying snow. According to HERRON and LANGWAY (1980), there is a linear relationship between the depth of firn and ln $(\rho/(\rho_i-\rho))$, where ρ_i is a constant density of ice (0.917 g/cm³) and ρ is the density of the firn layer at a given depth. The plot of ln $(\rho/(\rho_i-\rho))$ versus depth relationship is divided into two segments based on the densification rate. The first segment is for $\rho < 0.55$ g/cm³ and the second segment is for $0.55 < \rho < 0.82-0.84$ g/cm³. These segments correspond to the stages where settling and packing of snow grains and further compaction take place. Since "pore close-off" will occur at densities greater than 0.82–0.84 g/cm³, the above model cannot be applied for ice whose density is greater than 0.84 g/cm³. The relationship between ln $(\rho/(\rho_i-\rho))$ and raw depth that has been converted from the density profile (Fig. 3) is shown in Fig. 5. HERRON and LANGWAY (1980) related the annual accumulation rate A to the slope C of the ln $(\rho/(\rho_i-\rho))$ versus depth relationship as,
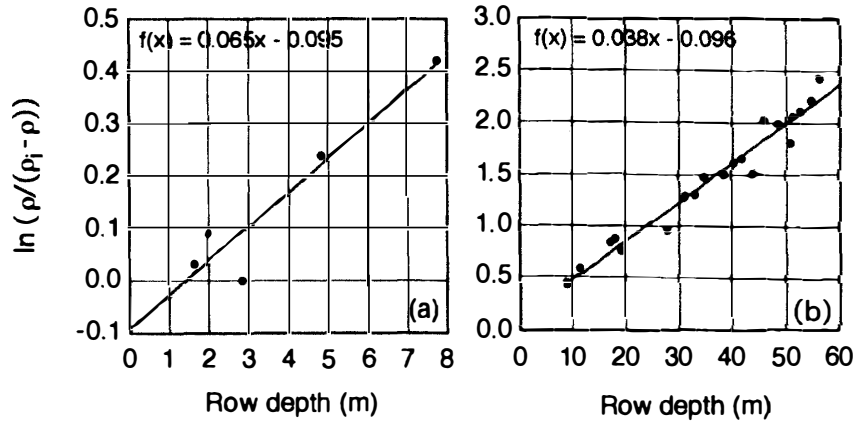
Fig. 5. Relationship between ln $(\rho/(\rho_i-\rho))$ and depth of the H15 core. (a) The first stage: $\rho < 0.55$ g/cm³, (b) The second stage: $0.55 < \rho < 0.84$ g/cm³.

$$A = (\rho_i \cdot k_1 / C)^2,\qquad(2)$$

where k_1 is a constant related to the densification rate. The value of k_1 is a function of the mean atmospheric temperature and is given in HERRON and LANGWAY (1980). Taking the mean atmospheric temperature of $-21°C$ at site H15 and the slope C of regression lines of the first and second stages in Fig. 5 to be 6.5×10^{-2} and 3.8×10^{-2}, respectively, the accumulation rate A is calculated to be 145 and 51 cm/year for the first and second stages, respectively. The time necessary for snow to attain the maximum density of the first stage ($\rho = 0.55$ g/cm³; 6.2 m in raw depth or 2.9 m in water equivalent depth) is calculated to be 2 years by dividing 2.9 m by the accumulation rate. Indeed, the density of 0.55 g/cm³ is found at 7.8 m (Fig. 3). Similarly, the time required to attain the maximum density of the second stage ($\rho = 0.84$ g/cm³; 58.8 m in raw depth or 42.9 m in water equivalent depth) is calculated to be 148 ± 12 years. The bottom of the firn in the second stage was thus deposited ~150 years ago, corresponding to 1841 ± 12 A. D. The error arises from the regression of the ln $(\rho/(\rho_i-\rho))$ versus depth relationship. As mentioned earlier, there are two high ECM peaks at 46.8 and 48.3 m (water equivalent depth, Fig. 2). The dates of these peaks should, therefore, be older than 1841 ± 12 A. D., and are roughly estimated to correspond to 1822–1828 (± 12) A. D., assuming a constant accumulation rate below the layer with $\rho = 0.84$ g/cm³.

5. Acidity, SO₄²⁻ Concentration and $\delta^{18}O$ Measurements

Acidity, chemical composition and $\delta^{18}O$ of the H15 core samples were measured from the surface to 50 m depth. As stated previously, the ECM and excess SO_4^{2-} peaks at 2.3 m depth are present between 1983 and 1984 (Fig. 4) and are likely to be related to deposition of stratospheric aerosols released by the volcanic eruption of El Chichon in 1982. Other possible explosive volcanic activities prior to 1984 are the eruptions of Galunggung 1982 (Java, 7°03' N, 108°01' E) and Colo 1983 (Indonesia, 0°02' N, 121°06' E) whose Volcanic Explosivity Indices (VEI) are both 4 (SIMKIN and SIEBERT, 1994). Of these explosive eruptions, that of El Chichon in April, 1982 (VEI=5) is most likely to be

responsible for the high peaks because of its large magnitude. Its maximum column height is estimated to have reached 32 km (CAREY and SIGURDSSON, 1986), high enough to have global impact. The eruption injected a large amount of sulfur into the stratosphere, an estimate being 3.3–10 Mt by the total ozone mapping spectrometer on the Nimbus 7 satellite (EVANS and KERR, 1983; KRUEGER, 1983). The aerosols spread over the globe at latitude 20°N for about 20 days and further to higher latitude following the general atmospheric circulation. The solar radiation into the atmosphere observed at Syowa Station started to decrease from November, 1982, and was obviously low in January, 1983 (YAMAUCHI and SHIMURA, 1984). A time lag of over 1 year between the eruption (April, 1982) and the date (mid-1983) when the high excess SO_4^{2-} peak in Fig. 4b was observed is explained by the long residence time of volcanic aerosols in the stratosphere. This is consistent with the fact that the stratospheric aerosols were present for about 2 years after the explosive volcanic eruption of Mt. Pinatubo (Philippines, 15°13' N, 120°35' E) in June 1991 (MCCORMICK et al., 1995). The PS1 and PS14 ice cores drilled at the South Pole in 1983–1984 summers do not contain a prominent volcanic signal of the 1982 El Chichon eruption (DELMAS et al., 1992). It may have taken longer for the volcanic aerosols to reach the South Pole compared to the site of H15 since the latitude of the South Pole is higher than that of H15, and the aerosols may not have been deposited yet at the South Pole when the ice cores were drilled in the 1983–1984 summers.

The H^+, excess SO_4^{2-} and $\delta^{18}O$ variations were measured in detail for depths from 43 m to 50 m in order to determine the causes for the two high ECM peaks at 46.7 and 48.3 m depths (Fig. 2). The results are shown in Table 3 and Fig. 6. It is obvious that the two high ECM peaks are accompanied by H^+ (Fig. 6b) and excess SO_4^{2-} peaks (Fig. 6c). The excess SO_4^{2-} concentrations of 350 ng/g at 46.7 m and 200 ng/g at 48.3 m correspond to 7 and 4 μ equiv. H^+/kg, respectively, assuming that the excess SO_4^{2-} was deposited as sulfuric acid. These values are in reasonable agreement with the directly measured H^+ concentrations at corresponding depths (Fig. 6b). This is a good indication that excess SO_4^{2-} originates from acid fallout as sulfuric acid. From the dating, the layers containing these high acidity peaks correspond to the beginning of the 19th century. Two significant sulfate peaks have been found in the ice cores drilled at Stations Dome C and Vostok (LEGRAND and DELMAS, 1987) in East Antarctica, Siple (DAI et al., 1991) and Byrd (LANGWAY et al., 1994, 1995) in West Antarctica and South Pole (DELMAS et al., 1992; LANGWAY et al., 1995). The two high SO_4^{2-} peaks in the Dome C core are considered to have originated from the unknown 1809 eruption and Tambora 1815 eruption (MOORE et al., 1991; DAI et al., 1991; DELMAS et al., 1992; LANGWAY et al., 1995). High SO_4^{2-} layers are observed in ice cores in a similar age range at Siple and Byrd in West Antarctica and South Pole and Site A (70°38' N, 35°49' W), Site T (72°35' N, 38°27' W), Dye 3 and Crete in Greenland. A comparison of the SO_4^{2-} concentrations of these cores indicates that an explosive volcanic eruption occurred in 1809 or earlier at the low latitude and the amount of stratospheric aerosol emission was about half that of Tambora in 1815, although a volcanic event in 1809 has not been described in the historical literature (DAI et al., 1991; LANGWAY et al., 1995). Of these cores, the hydrogen ion concentration of a layer containing aerosols from the Tambora eruption is higher than that from the 1809 unknown eruption by a factor of 1.5–2 except at Dome C (LEGRAND and DELMAS,

Table 3.   H⁺ concentration, chemical composition and δ¹⁸O at a depth between 43 and 50 m of H15 core.

Water equiv. depth m	H⁺ n mol/g	Cl⁻ ppb	NO₃⁻ ppb	SO₄²⁻ ppb	Na⁺ ppb	K⁺ ppb	Mg²⁺ ppb	Ca²⁺ ppb	δ¹⁸O ‰
42.98	2.95	78	6	15	37	0	3	1	−24.3
43.07	3.55	168	20	38	91	2	7	2	−23.3
43.16	3.09	133	10	16	70	0	5	1	−23.1
43.25	3.89	−	−	−	−	−	−	−	−
43.34	3.89	−	−	−	−	−	−	−	−
43.43	3.89	−	−	−	−	−	−	−	−
43.52	3.80	−	−	−	−	−	−	−	−
43.60	4.17	−	−	−	−	−	−	−	−
43.68	3.31	153	23	33	92	0	−	−	−26.4
43.76	3.31	587	21	63	324	10	−	−	−26.9
43.84	3.55	281	26	45	158	3	−	−	−26.4
43.91	3.47	30	38	12	16	0	−	−	−24.3
43.98	3.31	66	20	17	39	0	−	−	−22.6
44.05	3.63	199	14	45	129	3	−	−	−21.8
44.12	3.63	497	16	115	295	8	−	−	−22.0
44.19	3.72	126	39	66	76	0	−	−	−23.7
44.27	3.47	224	14	25	116	2	−	−	−24.9
44.35	3.39	523	18	95	18	6	−	−	−24.9
44.42	3.72	358	25	98	211	4	−	−	−24.7
44.49	3.55	108	22	47	70	0	−	−	−24.7
44.56	3.55	101	24	22	45	0	−	−	−24.4
44.63	3.72	17	55	46	6	0	−	−	−23.4
44.71	3.24	183	18	35	102	0	−	−	−23.9
44.78	3.09	356	13	71	171	0	−	−	−24.8
44.85	3.72	64	31	71	35	0	−	−	−24.4
44.92	3.89	147	40	87	73	0	−	−	−23.4
44.99	3.39	136	29	54	80	0	−	−	−22.8
45.07	2.95	63	12	23	36	0	−	−	−22.9
45.14	2.95	68	13	19	38	−	−	−	−22.1
45.22	4.68	77	14	47	40	0	3	1	−21.5
45.31	4.90	109	19	70	59	0	6	2	−21.6
45.40	4.79	50	25	50	−	0	2	1	−22.6
45.49	3.09	381	16	68	208	−	19	10	−24.3
45.57	3.09	152	17	40	34	−	14	8	−24.2
45.65	3.89	−	−	−	−	−	−	−	−
45.74	3.72	−	−	−	−	−	−	−	−
45.82	3.80	−	−	−	−	−	−	−	−
45.90	3.55	−	−	−	−	−	−	−	−
45.99	3.47	−	−	−	−	−	−	−	−
46.06	4.47	108	30	53	137	−	5	3	−23.4
46.13	5.13	208	52	104	114	−	15	8	−23.3
46.20	4.57	118	26	52	66	−	7	3	−23.3
46.27	4.27	176	14	49	90	−	12	4	−22.7
46.33	5.25	254	23	94	92	−	44	4	−23.6
46.40	4.17	1413	32	114	866	−	34	39	−25.2
46.46	5.62	328	17	167	255	−	38	6	−27.2
46.52	5.75	130	47	86	146	−	6	3	−27.2
46.58	5.37	424	22	147	240	−	34	10	−25.2
46.64	5.89	505	32	207	368	−	37	13	−23.4

Table 3.   (continued)

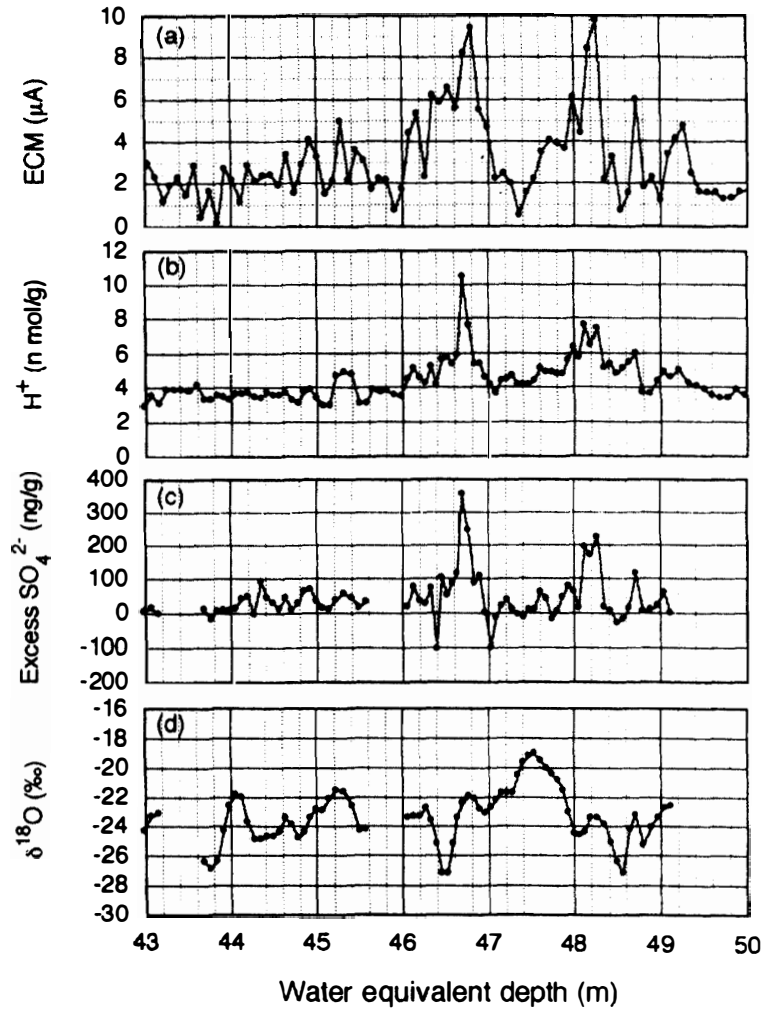| Water equiv. depth m	H⁺ n mol/g	Cl⁻ ppb	NO₃⁻ ppb	SO₄²⁻ ppb	Na⁺ ppb	K⁺ ppb	Mg²⁺ ppb	Ca²⁺ ppb	δ¹⁸O ‰
46.70	10.47	166	68	397	167	–	6	4	–22.4
46.76	7.59	84	40	257	45	–	6	2	–21.9
46.83	5.37	174	9	108	85	–	11	3	–22.1
46.90	5.37	217	16	163	219	–	15	6	–22.8
46.96	4.57	229	18	68	271	–	23	5	–23.1
47.02	4.17	1304	15	112	844	–	36	41	–22.7
47.09	3.63	763	9	90	409	–	54	17	–22.2
47.15	4.37	226	12	50	119	–	23	4	–21.7
47.21	4.47	432	14	112	293	–	29	10	–21.7
47.28	4.68	304	9	44	134	–	33	6	–21.7
47.34	4.17	1001	19	156	634	–	39	29	–20.5
47.40	4.17	265	8	42	225	–	27	5	–19.6
47.47	4.17	187	10	36	111	–	14	8	–19.2
47.54	4.37	413	10	66	222	–	24	10	–19.0
47.60	5.13	357	13	109	199	–	29	8	–19.5
47.67	4.90	164	26	62	87	–	10	4	–20.0
47.74	4.90	48	64	18	144	–	3	0	–20.4
47.81	4.79	137	26	23	77	–	5	4	–20.8
47.87	4.79	94	15	58	55	–	–	–	–21.5
47.93	5.62	114	24	97	74	–	–	–	–23.0
48.00	6.31	167	49	107	181	–	–	–	–24.5
48.06	5.75	200	41	93	315	–	–	–	–24.6
48.12	7.59	483	35	262	–	–	–	–	–24.4
48.19	6.46	264	41	204	139	–	–	–	–23.4
48.27	7.41	158	50	243	73	–	–	–	–23.4
48.35	5.13	42	28	51	136	–	–	–	–23.9
48.42	5.37	81	49	53	185	–	–	–	–25.1
48.49	4.79	246	30	43	283	–	–	–	–26.4
48.57	5.13	274	16	34	208	–	–	–	–27.2
48.64	5.50	174	42	77	251	–	–	–	–24.2
48.71	6.03	203	43	139	92	–	–	–	–23.2
48.80	3.72	197	12	32	112	1	12	4	–25.3
48.89	3.63	229	13	42	132	3	11	3	–24.1
48.97	4.37	396	17	75	216	5	8	3	–23.4
49.04	4.90	200	20	83	96	1	23	4	–22.7
49.12	4.57	525	26	72	289	6	17	12	–22.6
49.22	5.01	–	–	–	–	–	–	–	–
49.33	4.27	–	–	–	–	–	–	–	–
49.43	4.07	–	–	–	–	–	–	–	–
49.52	3.89	–	–	–	–	–	–	–	–
49.60	3.55	–	–	–	–	–	–	–	–
49.70	3.39	–	–	–	–	–	–	–	–
49.79	3.39	–	–	–	–	–	–	–	–
49.88	3.89	–	–	–	–	–	–	–	–
49.98	3.55	–	–	–	–	–	–	–	–

–: not determined.

Fig. 6. Profiles of (a) ECM (reproduced from Fig. 2), (b) H⁺ concen-
tration, (c) excess SO_4^{2-} concentration and (d) $\delta^{18}O$ of the H15
core from 43 m to 50 m depth.

1987; MOORE et al., 1991; DAI et al., 1991; DELMAS et al., 1992; LANGWAY et al., 1995).
At H15, the total amounts of H_2SO_4 deposition were calculated by integrating the areas
of the H⁺ peaks at 46.7 m from 46.46 to 46.90 m and at 48.3 m from 48.12 to 48.27 m,
respectively (Fig. 6). The amounts of H_2SO_4 were calculated to be 68 kg/km² at 46.7 m
and 44 kg/km² at 48.3 m with the ratio of 1.5. This fact, together with the observations
at the other sites that the Tambora 1815 eruption emitted more acid than the unknown
1809 eruption by a factor of 1.5–2, suggests strongly that the 46.7 m peak corresponds
to the Tambora 1815 eruption and the 48.3 m peak corresponds to the unknown 1809
eruption.

The layers at 46.7 m and 48.3 m depths were initially dated to 1828 and 1822 A. D.,
respectively, by the empirical densification model (HERRON and LANGWAY, 1980), and to
1826 and 1821 A.D., respectively, by counting the ECM highs. The difference of ~10
years may be ascribed to the presence of an unconformity as indicated by the three dis-
tinct melt layers between 15 m and 26 m (water equivalent depth). MACHIDA et al. (1995)

assumed that the ECM peaks at 46.7 m and 48.3 m depths correspond to the Tambora 1815 and unknown 1809 eruptions in their estimation of the annual accumulation rate of 26.0 g/cm²/year. The present study supports their assumption.

Andesitic fine ash was found in layers dated to 1809–1810 and 1816 A. D. in the South Pole and Dome C cores (De Angelis et al., 1985; Palais et al., 1990). Fine ash-like materials (~10 µm) have been found in the corresponding layers of the H15 core. If the materials are proven to be of volcanic origin through chemical analysis, our interpretation will be further strengthened.

Except for the high ECM peaks at 46.7 and 48.3 m, we can see ECM peaks that are significantly higher than the background variations (Fig. 2). Sulfate concentrations were measured for samples of high ECMs (> 2 µA above 15 m depth and > 4 µA below 15 m depth). If the SO_4^{2-} concentration is higher than 100 ng/g (note that the background SO_4^{2-} concentration is about 50 ng/g, see Fig. 4) and if the layer is thicker than 0.1 m (water equivalent), we regard such peaks to represent volcanic signals. There are altogether eight ECM highs satisfying the above conditions. Table 4 lists these eight ECM highs in the H15 ice core, together with the estimated dates, maximum SO_4^{2-} concentration, and duration of the ECM highs. Duration was calculated from the thickness of the SO_4^{2-} concentration peak and the annual accumulation rate of 26.0 g/cm²/year by Machida et al. (1995).

We attempted to relate these ECM highs to possible volcanic eruptions. After 1815, two volcanic eruptions are known to have VEIs greater than 5 (Simkin and Siebert, 1994), and therefore to give large aerosol loading to the atmosphere: Coseguina 1835 (Nicaragua, 12°09' N, 87°05' W) and Krakatoa 1883 (Indonesia, 6°01' S, 105°04' E, Rampino and Self, 1982; Devine et al., 1984; Self et al., 1989). The volcanic signals due to these eruptions have been found in the ice cores from Dome C, Vostok, Siple, Byrd and South Pole (Legrand and Delmas, 1987; Dai et al., 1991; Delmas et al., 1992; Langway et al., 1994, 1995). The ECM highs that are likely due to these eruptions occur at the water equivalent depths of 39.57 and 26.29 m in the H15 core, and have been dated to 1839 and 1890, respectively, based on the stake method using the annual accumulation rate of 26.0 g/cm²/year by Machida et al. (1995). These estimated dates are younger than the

Table 4. Eight ECM highs in the H15 core and their relation to possible volcanic eruptions.

Water equiv. depth	Estimated date	Maximum excees SO_4^{2-}	Duration	Possible volcanic eruption	Δt**
m	A.D.	ng/g	year		year
2.31	1983	186	0.4	El Chichon 1982	−1
9.09	1957	136	1.0	Agung 1963	−6
10.99	1949	134	0.5	Nilahue 1955	−6
26.29	1890	207	0.9	Krakatoa 1883	+7
34.40	1859	140	0.4	?	?
39.57	1840	128	0.5	Coseguina 1835	+5
46.70	1815*	355	1.9	Tambora 1815	−
48.27	1809*	255	0.9	unknown 1809	−

*Fixed date.
**Difference between the actual and estimated dates.

actual dates of the respective eruptions by 5–7 years. This probably arises from the formation of melt layers as will be discussed later.

Since there is no known big volcanic eruption around 1859 which corresponds to 34.4 m in the H15 core, the cause of this ECM high is not clear. The ECM highs at 10.99 m (estimated to be 1949 A.D.) and at 9.09 m (estimated to be 1959 A.D.) may have resulted from the volcanic eruptions of Nilahue 1955 (Chile, 40°04' S, 72°01' W) and Agung 1963 (Indonesia, 8°03' S, 115°05' E), respectively. The difference of 6 years between the actual and estimated dates probably reflects the "unconformity" effect discussed below.

Table 4 are listed the estimated dates of the ECM (and SO_4^{2-}) highs and the dates of the volcanic eruptions that might have caused the ECM highs. It is known that there are three thick melt layers at 15.3, 19.1 and 26.0 m (water equivalent depth), which indicates the presence of a hiatus of snow deposition. If the hiatus did occur, the accumulation rate of 26.0 g/cm^2 by MACHIDA et al. (1995) becomes an underestimate. With this value, the layers above the melt-containing layers would be dated younger than the actual dates, whereas the layers below would be dated older, since the period for the hiatus would have been included in the calculation of dating. The difference between the estimated and actual dates should thus be negative below 26.0 m and positive above this depth. This is quite consistent with the above consideration of the effect of the hiatus on the accumulation rates. Different mean accumulation rates must be used below and above the melt layers.

The $\delta^{18}O$ values of rain and snow vary with the average local atmospheric temperature (DANSGAARD, 1964). Consequently, seasonal changes of atmospheric temperature and long-term climatic changes are reflected in the oxygen isotopic variations of ice cores (JOHNSEN et al., 1972; HAMMER et al., 1980; DAI et al., 1991; DANSGAARD et al., 1993; GREENLAND ICE-CORE PROJECT MEMBERS, 1993). Figure 6d shows the $\delta^{18}O$ variations between 43 and 50 m depths in the core. Unfortunately, we cannot recognize the summer-highs and winter-lows in the $\delta^{18}O$ variations. There is a tendency for the $\delta^{18}O$ values to decrease after Tambora 1815 eruption (46.7 m depth), but this is not the case for the $\delta^{18}O$ values after the unknown 1809 eruption (48.3 m depth). The $\delta^{18}O$ profile of the Siple core indicates that short-term temperature changes after explosive volcanic eruptions such as Tambora 1815 were not recorded in the core (DAI et al., 1991). Thus, interpretation of the $\delta^{18}O$ variations as volcanic signals is not straightforward.

6. Conclusions

Two remarkably high peaks of ECM, acidity and excess SO_4^{2-} concentrations were found at the water equivalent depths of 46.7 m and 48.3 m of the 120-m ice core drilled at site H15 in East Antarctica. These signals are considered to have originated from the volcanic eruptions of Tambora in 1815 A. D. and unknown in 1809 A. D. The dates were estimated by two independent methods by counting the number of ECM peaks, and an empirical model of firn densification. A high SO_4^{2-} peak detected at depth 2.3 m most likely resulted from the volcanic eruption of El Chichon in 1982. There is a possibility that the ECM peaks associated with SO_4^{2-} highs between Tambora 1815 and El Chichon 1982 eruptions may represent the effect of the volcanic eruptions of Coseguina

1835, Krakatoa 1883 and Agung 1963.

Acknowledgments

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