PAST 30-YEAR pH RECORD IN A FIRN CORE FROM THE BRUNT ICE SHELF, ANTARCTICA, AND ITS RELATIONSHIP TO VOLCANIC EVENTS

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Abstract: A pH profile along a well-dated firn core from the Brunt Ice Shelf near Halley Base, Antarctica, was obtained spanning the last 30 years, from 1951/1952 to the present. Especial emphasis is paid to the summer decrease in the seasonal variation and to the extremely low pH values in some summers between 1955/1956 and 1970/1971, and in 1980/1981. Comparison with Lamb's volcanic dust veil indices up to 1968 and to major volcanic events after 1969 suggests that the significant decrease of pH in some summers is linked with major volcanic eruptions in the equatorial zone and to major and even minor ones in the Southern Hemisphere.

1. Introduction

Because the Antarctic ice sheet is completely remote from the other continents, it contains the Southern Hemispheric and even the global palaeo-environmental records for several tens of thousand years.

Recent studies on ice cores from Antarctica have revealed some evidences for palaeo-volcanism which may have affected the global climate. From the analysis of a 2164 m Byrd core, GOW and WILLIAMSON's (1971) studies showed a good correspondence between increased visible volcanic ash and dust bands with the more negative $\delta^{18}O$ periods of the last ice age. THOMPSON (1977), THOMPSON and MOSLEY-THOMPSON (1981) and THOMPSON *et al.* (1981) showed microparticle records of some Antarctic ice cores and suggested the tentative correlations with major eruptive events. HAMMER (1977, 1980) developed a new method of obtaining a continuous acidity profile by measuring the static electrical conductivity of an ice core surface and compared the acidity profile with historically well-known eruptions. DELMAS *et al.* (1982) measured the concentration of sulfate (SO_4) and nitrate (NO_3) in the Dome C ice core, and examined the probable origin of these gas-derived aerosols in Antarctica. They concluded that global volcanic activity strongly affects the sulfate concentration in the core.

The purpose of this paper is (1) to present the seasonal cycle and 30-year profile of pH in surface firn layers from the Brunt Ice Shelf, near the British Halley Base (75°31′S, 25°56′W), (2) to compare the pH profile with historically well-known volcanic eruptions and (3) to show that the pH profile of an Antarctic ice core is a good index of past volcanism.

2. Pit Work, Shallow Coring and Analytical Procedures

The new Halley Base site, about 13 km away from the Base of 1982, was selected as the site for my glaciological pit work and shallow coring. The site is an ideal place being well away, in the direction of the prevailing wind, from the source of artificial pollution at the Base, while being close enough to the Base from the viewpoint of the use of its recent climatological data.

The field work was done from 14 to 23 January 1982 by the author who participated in the British Antarctic Survey. The preliminary glaciological results are reported by FUJII (1983a).

Glaciological pit work was carried out to reveal the detailed stratigraphic features and to obtain snow samples from each layer to clarify the seasonal variation of pH and other elements.

A 21.83 m core was recovered with an electro-mechanical drill especially designed by Prof. Y. SUZUKI of the Institute of Low Temperature Science, Hokkaido University. Coring was followed by stratigraphic observation, density measurements at about 50 to 100 cm interval and sub-sampling for home analysis of pH, microparticle concentration and electrical conductivity at about 15 cm interval, and $\delta^{18}O$ at about 20 cm.

Sub-sampling from the inner part of core was done at the drilling site, as it is considered to be natural clean-air space. Clean polyethylene overgloves were worn and samples were obtained using a stainless steel knife and forceps, which had been pre-cleaned by leaching with 1: 10 nitric acid, followed by soaking in ultra-pure water obtained from a Millipore 'Milli-Q' system supplied with deionized and distilled water. Samples were placed in 70 ml polyethylene containers which had been pre-cleaned in 1: 10 nitric acid, followed by repeated rinsing with ultra-pure water. They were sealed with vinyl tape, numbered, packed in plastic boxes and transported to Japan, not being kept frozen.

Measurements of pH of the melted samples were carefully made with a Denki Kagaku Keiki COM-10 pH meter, reading the pH value at least 15 minutes after immersing the probe in the sample. The meter was calibrated with standard pH-4 and pH-7 liquids twice a day, before and after the sample measurements. Prior to starting a day's measurements, one or two samples measured on the previous day were remeasured and the pH values of both days were compared to confirm the reliability of the measurement. The accuracy is about ± 0.05.

3. Core Chronology

Glaciological pit observations and the analysis of samples from pit walls indicate that there are no great difficulties in determining annual layers, and thus in obtaining a year-by-year dating of the core. Figure 1 shows the results of the pit work. Figure 2 shows the stratigraphic symbols used in Fig. 1.

The profile of oxygen stable isotope composition ($\delta^{18}O$) shows a typical seasonal variation, ranging from $-14 \sim -16‰$ in isotopic summer to $-26 \sim -28‰$ in isotopic winter. A seasonal variation is also seen in the pH profile. The highest acidities

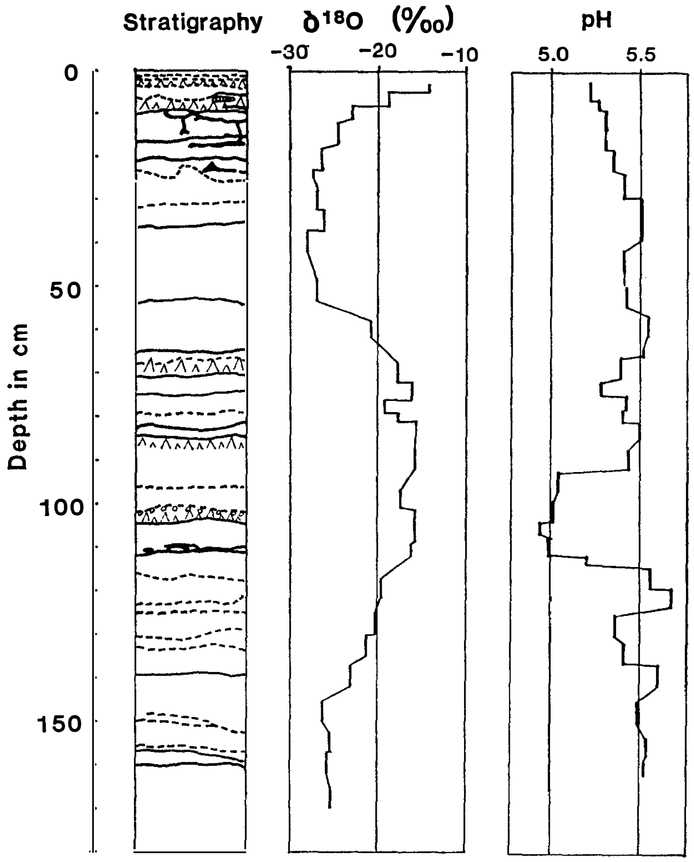

Fig. 1. Stratigraphy of a 1.75 m deep snow pit near Halley Base, Antarctica showing good correspondence between depth of thick ice layers, the minimum values of pH and the maximum of $\delta^{18}O$.

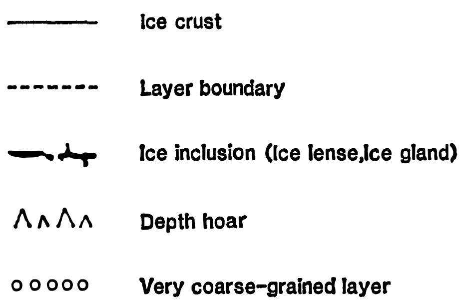

Fig. 2. Descriptive legend of snow stratigraphy.

correlate with the maxima in the δ^{18}O profile.

At this site ice lenses or thick ice layers are the best stratigraphic criteria to judge summer surfaces. Coarse-grained granular snow layers are also a good indicator of summer layers.

On the basis of above-mentioned stratigraphic features, that is, the seasonal variation of δ^{18}O and the existence of ice lenses or thick ice layers, the 22-m firn core was dated.

Figure 3 shows the stratigraphic diagram for the core, the profiles of δ^{18}O and pH, and the determined annual layer boundaries. The stratigraphic symbols are shown in Fig. 2. As shown in this figure, in a few places cold summers or irregular variations in the δ^{18}O and pH profiles make the judgement of annual layer boundaries difficult. The suggested chronology may have an error of ± 2 years; it gives the age of the core bottom as the 1951/1952 summer.

4. Variation in the pH Profile Since the 1951/1952 Summer

There are significant variations in the pH profile for the last 30 years as is shown

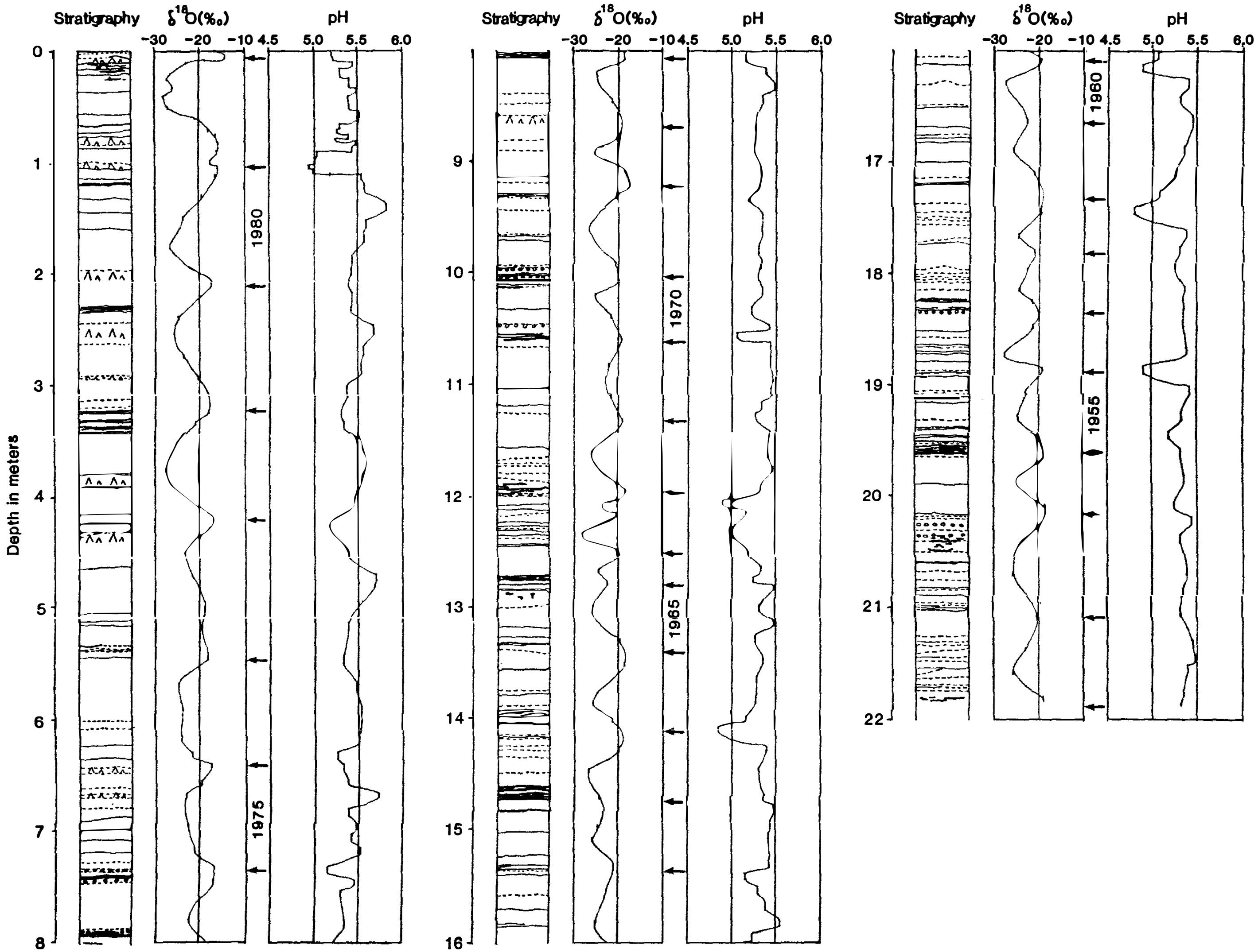

Fig. 3. Stratigraphic diagram and profiles of $\delta^{18}O$ and pH of the 22-m firn core. Arrows indicate annual layer boundaries, judged from stratigraphic features and $\delta^{18}O$ variations.

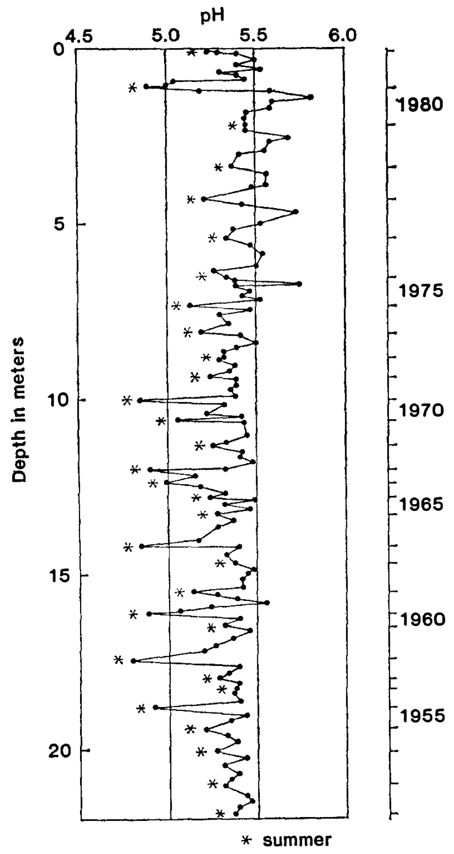

Fig. 4. The pH profile from 1951/1952 to 1981/1982 summer. Individual summers are marked with stars.

in Fig. 4. Stars in this figure mark annual layer boundaries, determined by the $\delta^{18}O$ and stratigraphic methods, described previously. The variation of pH between successive stars, therefore, indicates the seasonal variation for that year, being a minimum in summer and a maximum in winter.

A gradual decrease of summer pH from 5.35 in 1951/1952 summer is followed in 1955/1956 summer by a significant drop to a pH of 4.92. Since then significant decreases of summer pH occurred frequently up to the 1970/1971 summer. pH values lower than 5.0 are noted in the summers of 1955/1956, 1958/1959, 1963/1964, 1966/1967, 1967/1968 and 1970/1971.

During the decade beginning in 1970, pH in summer snow layers tended to increase gradually, but the summers in 1973/1974, 1974/1975 and 1977/1978 were minor exceptions, showing decreased values. High values of pH ranging from 5.6 to 5.8 in the six successive winters of 1975–1980 are also worth a mention.

A drastic decrease of pH in summer appears again in 1980/1981, and is followed by a moderate pH value in the 1981/1982 summer, when the present field work was carried out.

Table 1 shows the pH values of summer minimum, annual mean and five year-mean.

Table 1. pH values of summer minimum, annual mean and 5-year mean.

Year	Summer minimum	Annual mean	Number of samples	5-year mean
1982				
	5.21			
1981		5.34	20	
	4.94			5.38
1980		5.42	9	
	5.44			
1979		5.51	7	
	5.36			
1978		5.50	4	
	5.21			
1977		5.45	5	5.47
	5.34			
1976		5.47	4	
	5.26			
1975		5.44	8	
	5.13			
1974		5.31	4	
	5.19			
1973		5.36	5	
	5.30			
1972		5.34	4	5.31
	5.24			
1971		5.35	5	
	4.85			
1970		5.21	4	
	5.06			
1969		5.34	5	
	5.27			
1968		5.40	4	
	4.90			
1967		5.10	4	5.30
	4.99			
1966		5.26	2	
	5.23			
1965		5.38	4	
	5.28			
1964		5.28	5	
	4.85			
1963		5.19	3	
	5.31			
1962		5.43	5	5.28
	5.15			
1961		5.28	6	
	4.89			
1960		5.21	3	
	5.32			
1959		5.33	4	
	4.80			
1958		5.18	3	
	5.28			
1957		5.35	3	5.29
	5.37			
1956		5.38	3	
	4.92			
1955		5.23	4	
	5.21			
1954		5.36	2	
	5.27			
1953		5.35	5	5.37
	5.32			
1952		5.41	4	

5. Discussion

In snow deposited in summers the pH values in the Halley Base firn core, as well as the pH of the surface snow drift at Mizuho Station (70°42′S, 44°20′E, 2230 m a.s.l.), as described by FUJII (1983b), drops to an annual minimum. Sulfuric acid droplets are the dominant aerosols in summer, not only in the stratosphere but also in the low troposphere, as observed at McMurdo by CADLE *et al.* (1968), at South Pole by MAENHAUT *et al.* (1979), and at Syowa Station by ITO (1980).

Sulfur gases such as SO_2 and H_2S are oxidized to H_2SO_4 vapor which, in turn, is transformed into sulfuric acid droplets. Since these processes are photo-chemical ones which occur in both troposphere and stratosphere, the sulfuric acid aerosols increase in summer.

Since, to a first approximation, the trace-element compositions in snow and in air are related as was shown at Dome C by BOUTRON and LORIUS (1979), the decrease of pH in the Halley Base firn core in summers, and the year-by-year variations may be attributed to variations of the sulfuric acid droplets in the atmosphere.

Following an examination of potential sources of tropospheric sulfate in the

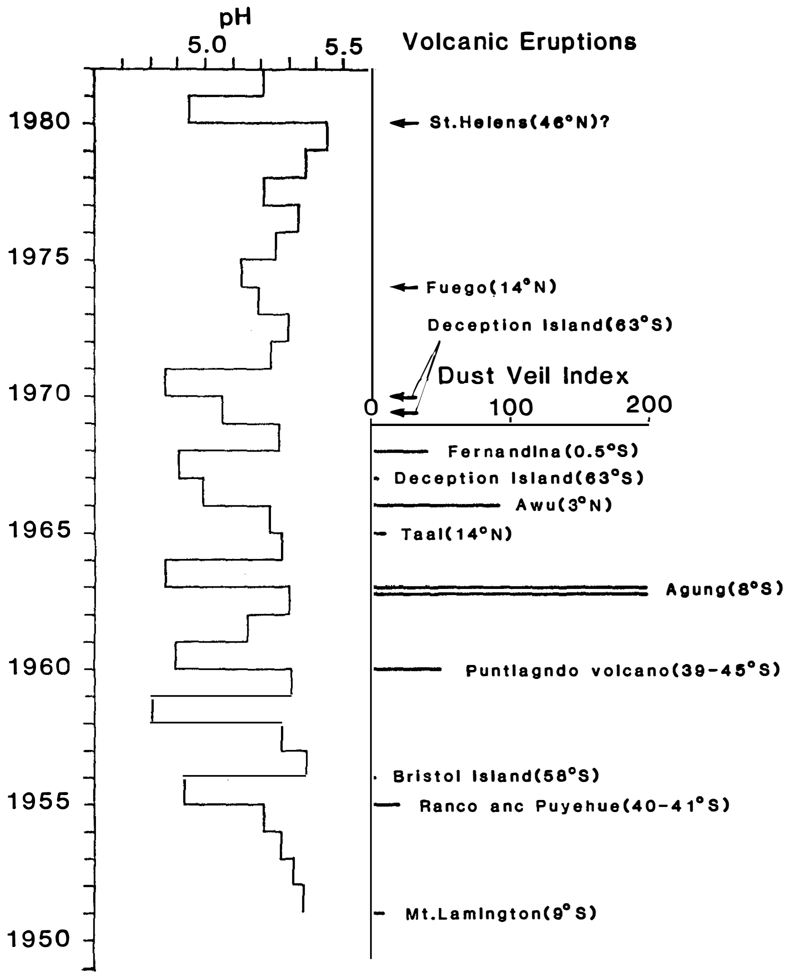

Fig. 5. Variation in minimum pH values of summer snow, with Lamb's dust veil indices (DVI) for the Southern Hemisphere up to 1968 and with major volcanic eruptions.

Antarctic atmosphere, DELMAS and BOUTRON (1980) and DELMAS *et al.* (1982) concluded that marine sulfur-bearing gases can account for the sulfate concentrations observed in Antarctic snows. These tropospheric gas-derived aerosols may represent the "background", but irregular decreases of pH in the Halley Base firn core cannot be explained by this process. It is therefore considered that the significant decreases in the pH profile are mainly, if not entirely, due to the enhancements of stratospheric gas-derived aerosols caused by global and especially Southern Hemispheric volcanic eruptions, which inject great amount of sulfuric gases into the stratosphere.

Figure 5 shows the minimum pH values for the individual summers in the period from 1951/1952 to 1981/1982. The pH data are compared with LAMB's (1970) volcanic dust veil indices (DVI) for the Southern Hemisphere. No correction has been made on his DVI for the different latitudes of the individual eruptions or for the residence time of aerosols in the high-latitude stratosphere. The DVI is given till 1968 and the major eruptions after that are shown with arrows.

As is seen in this figure, extremely low pH values in summer snow layers are quantitatively related with volcanic eruptions. The quantitative correlation however, is not particularly good between summer pH and DVI, especially in both cases of 1958/1959 summer and the Agung (8°S) eruption in 1963. The correction of DVI for eruptions in the equatorial zone such as the eruption of the Agung, (the factor being the multiplication by 0.35 as described by HAMMER *et al.*, 1981), will improve the quantitative correlation between them.

On the other hand, the DVI less than 1 for the eruption of Deception Island (63°S, 60°W) in 1967 seems to be undervalued for its influence on the pH of surface snow at Halley Base (76°S, 27°W), which is about 1500 km away to the southeast, the leeward direction from Deception Island. The 1967 eruption was followed by new ones in 1969 and 1970. The 1970 eruption was more violent than the 1967 or 1969 eruptions. Ash was ejected to a height of several kilometers and 4 mm of ash was recorded at Arturo Port Station, 70 km northeast of Deception Island (ORHEIM, 1971). The low pH values in 1969/1970 and 1970/1971 summers may be due to the series of eruptions.

It is possible that the most recent large decrease of pH, in 1980/1981 summer, is linked with the voilent eruption of Mount St. Helens (46°N, 122°W) in May 1980. According to the data of the NASA orbiting satellite SAGE (Stratospheric Aerosol and Gas Experiment) (MCCORMICK, 1981), the eruption introduced 0.25 to 0.5×10^6 tons of aerosol mass into the stratosphere. However, Mount St. Helens is located in the middle latitudes of the Northern Hemisphere and the ejected mass was two orders of magnitude less than that of Agung in 1963, which is located at 8°S. This leads one to suggest that the decrease of pH in 1980/1981 summer may be more closely linked with minor eruption in the Southern Hemisphere, in middle to high latitudes, such as an eruption of Marion Island (47°S, 38°E) between February and October 1980 (VERWOERD *et al.*, 1981).

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