

Electrical Conductivity and pH in Snow and Ice Samples from Various Glacier Areas

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環境の異なる氷河地域における雪氷試料の電気伝導度と pH

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要旨: ネパール・パタゴニア・北極・南極地域からの雪氷試料を用いて、融解後の電気伝導度と pH の値を比較検討した。試料の電気伝導度と pH は地域によって変動の範囲・平均値が異なっている。降雪に含まれる溶存イオン量が小さく電気伝導度の低い場合には、地域に関わりなくほぼ一定の pH 値を示す。しかし、電気伝導度が増加するとともに pH が変動し、そこには地域的特徴が現れる。すなわち南極の海岸付近(昭和基地)・ネパール・パタゴニア地域では、電気伝導度値が増加するのに伴って pH 値も増加しているが、南極の内陸部では逆に pH 値は減少している。原因としては海の直接的影響、土壌圏の中和作用、大気圏上層部での物質の取り込み過程、火山活動、人為的影響などが挙げられる。すなわち、降雪系での物質輸送過程が重要な役割を担っていると考えられる。北極域グリーンランド及びスピッツベルゲン島において採取したコアには、過去の電気伝導度と pH の値が記録されている。グリーンランド試料での値は、南極内陸部と同様な傾向を示す。一方、スピッツベルゲン島の試料では値の変動幅が大きく、さまざまな環境変動の影響を受けてきたことを推測させる。スピッツベルゲン島のコア試料を深さごとに一定間隔で整理することによって、各期間ごとの電気伝導度と pH の変動特性を明らかにした。この変動特性は、コア中の気泡を含んでいない氷の分布と一致していた。このような氷は過去の温暖な時期に形成されるので、変動特性と合わせて物質輸送過程の変動を推定した。

Abstract: Electrical conductivity (EC) and pH of melted snow and ice samples from Nepal, Patagonia, Arctic regions and Antarctica are compared. Most samples showed regional differences in means and ranges of EC and pH values. Low concentrations of dissolved substances, however, were accompanied by low ECs and approximately constant pH values, independent of the regions. Higher values of EC brought about regional pH differences. pH increased with higher EC values in coastal Antarctica (Syowa Station), Nepal and Patagonia. In contrast, pH decreased with the increased EC in snow from inland Antarctica. Ice cores from Greenland and in Spitsbergen provide records of EC and pH in snows of the past. The values of EC and pH in the Greenland samples are similar to those in the inland region of Antarctica. The values in the Spitsbergen samples vary widely,

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implying that they record a variety of past climatic events. A down core fluctuation of characteristics in the EC and pH distributions, is compared to core records in fixed intervals. The fluctuation coincides well with the profile of the clear ice ratio, which records melting events during warmer periods. The periodical variation in the transport process of substances in the precipitation system is estimated from the clear ice ratio and the characteristics of EC and pH.

1. Introduction

The chemical characteristics of glacial snow summarize many of the environmental factors under which the glaciers accumulated. Furthermore, the transportation routes in the atmosphere followed by the moisture prior to its precipitation are important in influencing the chemical characteristics of snow. For example, snow is directly influenced by sea salts, neutralization by soils, acidification by chemical substances in the atmosphere at high altitude, the impacts of human activities as well as volcanic activities. The values of electrical conductivity (EC) and pH are basic measurements for comparing the water samples. After collecting snow and ice core samples from glaciers, allowing them to melt, and placing them in bottles, values of these two can be determined, either *in situ* or in the laboratory.

Over the past decade, we have collected nearly 1400 samples of snow and ice from various glaciers and have discussed some of their characteristics (Table 1). All of the samples obtained in Antarctica are fresh snow. The samples from Nepal and Patagonia are falling snow and ice cores. The samples from Spitsbergen and Greenland are obtained from ice cores. The measurements of EC and pH were conducted *in situ* or in the laboratory as soon as possible after melting.

Table 1. General descriptions of locations providing samples of snow and ice.

Region	Altitude (m a.s.l.)	Distance from sea (km)	Sampling (year)	Sample type	References
Nepal	5000	1000	1981-2	Snow cover ice core	WATANABE <i>et al.</i> (1984)
Patagonia	1300	50	1985	Fresh snow ice core	YAMADA (1987)
Coastal region Antarctica	5	0.05	1985	Fresh snow	KAMIYAMA <i>et al.</i> (1987)
Inland region Antarctica	2400-3800	300-800	1985	Fresh snow	KAMIYAMA <i>et al.</i> (1987)
Spitsbergen	1200	20	1987	Ice core	KAMIYAMA <i>et al.</i> (1989b)
Greenland	2100	200	1989	Ice core	FUJII <i>et al.</i> (in preparation)

2. Electrical Conductivity and pH in Snow and Ice Samples

We summarize here the values of EC and pH of the samples we analyzed and make clear the regional characteristics of each glacier. The values of EC and pH reflect water quality of the samples and give information on the origins of substances contained in them. The path through which the sampled water has moved in the environments affects the relationships between EC and pH.

Table 2. Electrical conductivity ($\mu\text{S}/\text{cm}$) of snow and ice samples from each locality.

Region	Number of samples	Average	Maximum	Minimum	Standard deviation
Nepal	195	2.27	7.2	0.6	1.34
Patagonia	97	5.21	20	1.4	10.5
Coastal region*	17	1300	6250	15	1590
Inland region*	102	3.13	9.8	1.4	1.44
(above 3600 m)*	(34)	(4.25)	(9.8)	(2.1)	(1.54)
(below 3600 m)*	(68)	(2.56)	(6.8)	(1.4)	(0.99)
Spitsbergen	818	2.22	26	0.58	1.93
Greenland	167	1.52	3.5	0.94	0.42

* indicates regions in Antarctica.

Table 3. Values of pH of snow and ice samples from each locality.

Region	Number of samples	Average	Maximum	Minimum	Standard deviation
Nepal	181	4.82	6.80	4.70	0.24
Patagonia	99	5.87	7.50	5.27	0.39
Coastal region*	17	6.08	6.76	5.31	0.43
Inland region*	68	5.14	6.05	4.60	0.25
(above 3600 m)*	(34)	(5.02)	(5.43)	(4.60)	(0.17)
(below 3600 m)*	(34)	(5.25)	(6.05)	(4.78)	(0.26)
Spitsbergen	818	5.54	8.30	4.46	0.24
Greenland	167	5.27	5.70	4.69	0.13

* indicates regions in Antarctica.

Tables 2 and 3 show the means and ranges of EC and pH values, respectively, with their standard deviations. The results for the samples in the inland region of Antarctica are given as total values and as values, in parentheses, for the region divided into two areas by altitude. Snow obtained at Syowa Station (SS) beside the sea contains much salts and shows the highest EC. The samples from Greenland have the narrowest range of EC and pH values and show the lowest mean value of EC among these glaciers. The samples from Patagonia have high mean values of EC and pH except the SS samples. The samples from Spitsbergen have the widest range of pH values, with the highest and the lowest values.

3. Regional Characteristics of EC and pH

Here we will present a more detailed discussion on the regional characteristics of EC and pH values. The samples from Antarctica reflect the present characteristics, because we deal only with fresh snow. The samples from Nepal and Patagonia reflect comparatively recent ones, because of the shallower depths of ice cores about 50 and 30 m, respectively, with larger accumulation rates.

3.1. Antarctic region

The results of our measurement of EC and pH values of the snow obtained at SS

and in the inland area of East Queen Maud Land, Antarctica are discussed in detail by KAMIYAMA *et al.* (1987). The snow at the coastal SS location contains sea salts derived unchanged from the sea probably as aerosols. The value of pH in snow samples increases as the value of EC increases, depending on the intrusion rate of sea salts. In contrast, in the inland East Queen Maud Land, the value of pH decreases as the EC values increase. In this area, the higher value of EC occurs near the inland of highest elevation, which is the farthest area from coastline.

We have also presented a discussion of the chemical analyses for the samples from the inland region of Antarctica (KAMIYAMA *et al.*, 1989a). Around the dome area in East Queen Maud Land, the snow obtained above the altitude of 3600 m a.s.l. differs chemically from the snow from below 3600 m a.s.l. The snow from higher elevations reflects more strongly the chemical reactions occurring in the stratosphere than the snow from lower elevations. The surface structure of the glaciers, which reflects the sedimentary conditions, also changes above the altitude of 3600 m a.s.l. (AGETA *et al.*, 1989). The discussion also considers the values of EC and pH. We distinguish the altitude differences in Tables 2 and 3 in the parentheses. Figure 1 shows the frequency distribution of pH relative to altitude in inland Antarctica. The distribution of pH values clearly shows the local characteristics of the snow in the inland region. The profile of whole snow samples shows the normal distribution. Similarly the profiles of snow samples in both regions above and below 3600 m a.s.l. also show the normal distributions respectively, although the mean values differ from each other.

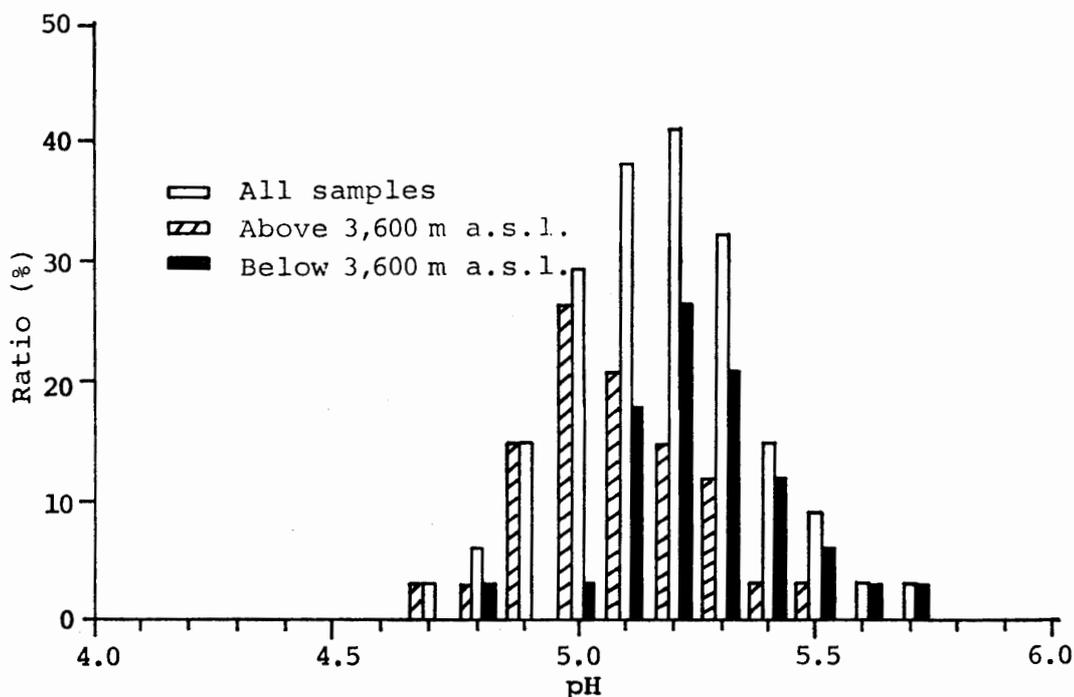


Fig. 1. Frequency distribution diagram of pH in snow over the inland high region around the dome in East Queen Maud Land, Antarctica. Each distribution corresponds to the snow samples from the whole sampling area, in the regions above and below 3600 m a.s.l., respectively.

3.2. Comparison of EC and pH in snow and ice samples among various regions

Figure 2 shows the relationships between EC and pH in samples of the glaciers in Nepal and Patagonia with those of snow samples in the inland and the coastal regions (SS) of Antarctica. The samples with low EC values show approximately constant pH values, near the equilibrium value of carbon dioxide in distilled water at atmospheric pressure. The higher values of EC are accompanied by distinctive regional fluctuations of pH values. In samples from Nepal and Patagonia, the increase in the value of pH occurs with the increase in the values of EC; the rate of increase is almost the same. A similar case exists in the coastal region of Antarctica, although the rate of increase is smaller. In the inland region of Antarctica, however, the decrease occurs as the values of EC increase. There is no clear difference in the rate of decrease between the samples above and below 3600 m a.s.l., although the lower pH values often occur in the samples above 3600 m a.s.l. as is clearly shown in Fig. 1.

Modern precipitation appears to be affected significantly by human activities, namely acid rain. Figure 3 shows the relationship between the values of EC and pH in rainwater collected at Beppu in the northeastern region of Kyushu, Japan. These values are scattered in low pH range comparable to the extended values for the inland region of Antarctica. Figure 4 shows the relationship between the values of EC and the concentration of sulfate in the rainwater. Sulfuric acid, produced mainly by combustion of fossil fuels and industrial processes, increased EC and decreased pH values in the precipitation.

The acid substances in the precipitation induce the increase in EC and the decrease in pH. The substances produced from industrial origins will make the precipitation cause these changes. The acidity in the precipitation can also be produced by reactions in the atmosphere during the transport process (LEGRAND and DELMAS, 1988). The intrusion of substances occurring in the stratosphere of high altitude, such as HNO_3 ,

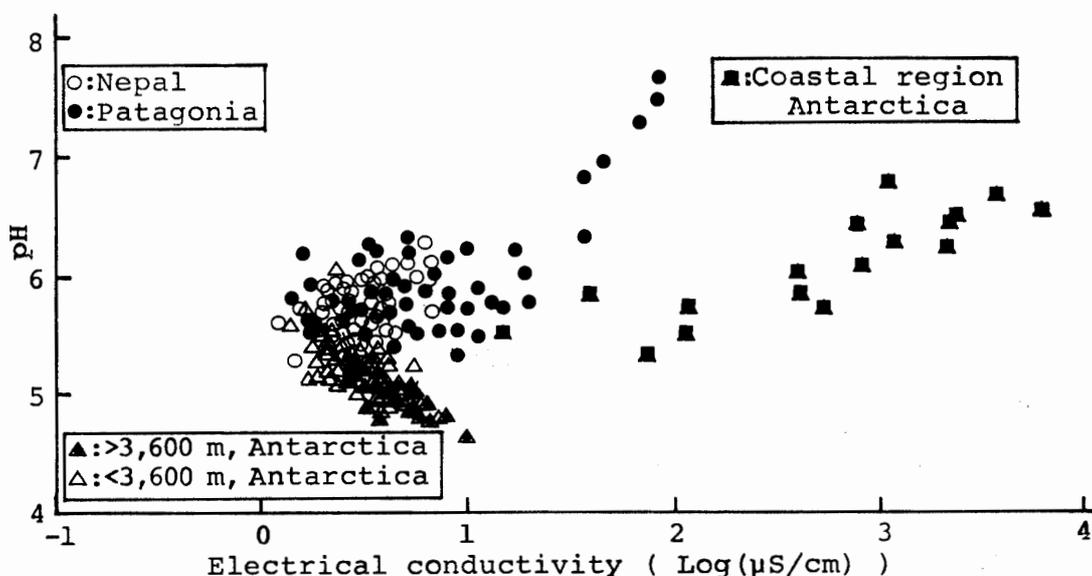


Fig. 2. Relationships between EC and pH in samples of the glaciers (Nepal and Patagonia), and of snow in Antarctica (the inland and coastal regions). The values of electrical conductivity are expressed as $\mu\text{S}/\text{cm}$ in logarithmic scale.

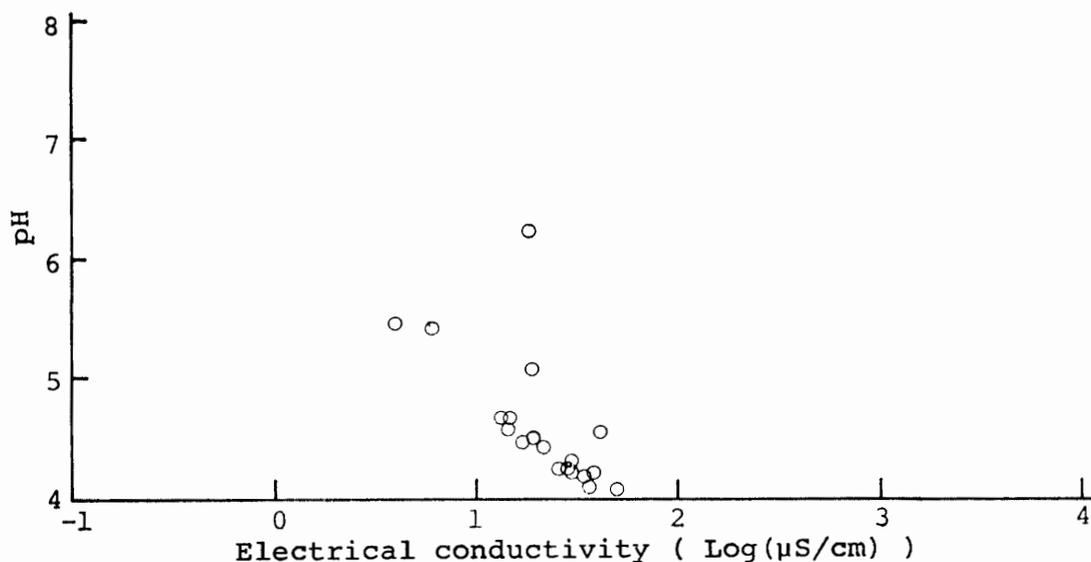


Fig. 3. Relationship between EC and pH in rainfall at Beppu in the northeastern region of Kyushu, Japan. The values of electrical conductivity are expressed as $\mu\text{S}/\text{cm}$ in logarithmic scale.

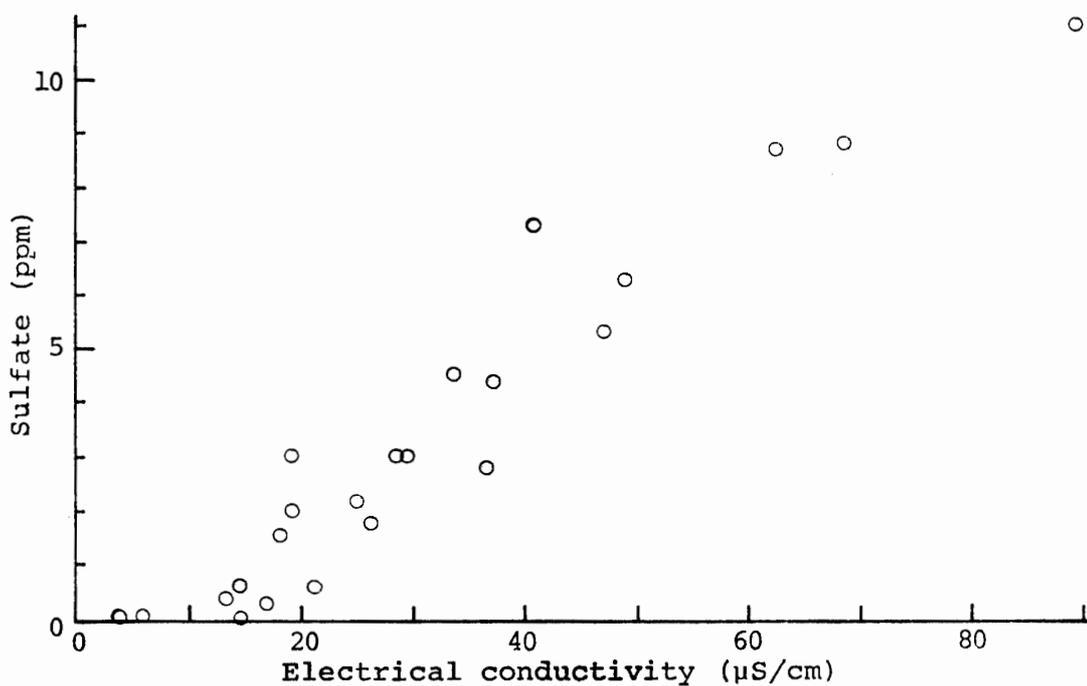


Fig. 4. Relationship between EC and concentration of sulfate in rainfall at Beppu in the northeastern region of Kyushu, Japan. The values of electrical conductivity are expressed as $\mu\text{S}/\text{cm}$, and the concentration is expressed in ppm.

also converts the precipitation into a more acid condition (KAMIYAMA *et al.*, 1989a).

In contrast, alkaline substances and salts occurring in soils and seawater will maintain the pH of precipitation at high values. Snow which accumulates in the glaciers of a small size has so many chances to interact with alkaline substances from

Table 4. Relationship between EC and pH and characteristics of local environments.

Region	pH increase with the value of EC	Type of sedimentary environments
Nepal Patagonia	++	Under the effect of soil region
Coastal region*	+	Under the effect of sea salts
Inland region below 3600 m* above 3600 m*	—	Under the effect of atmosphere at high altitude
(Beppu, Japan)	—	Acid rain Human activities

* indicates regions in Antarctica.

the surrounding soils and the vegetation. This is possibly the case for the glaciers in Nepal and Patagonia. The direct intrusion of sea salts into the precipitation will increase their values of EC and pH, as is the case for the precipitation at SS in the coastal region, Antarctica (KAMIYAMA *et al.*, 1987).

The relationships between EC and pH values in the precipitation are, therefore, related to the local atmospheric and sedimentary environments, as compiled in Table 4.

4. Estimation of Paleo-Environments from the Values of EC and pH in the Core Samples in Spitsbergen

The profiles of EC and pH values were reported for the cores in Spitsbergen by KAMIYAMA *et al.* (1989b) and in Greenland by FUJII *et al.* (in preparation). The whole core samples from the surface to the bedrocks at about 86 m depth in Spitsbergen possibly cover the period from the present up to 6000 years ago (FUJII *et al.*, 1990). The 200 m depth of the core in Greenland reaches from the present to 600 years ago (SHOJI *et al.*, in preparation). In the decades during which the accumulation of snow occurs, the sedimentary environments of the glacier possibly change.

The relationships between EC and pH in ice core samples of Greenland and Spitsbergen are shown respectively in Fig. 5. In the Greenland samples, the relationship is simpler and less variable than in the Spitsbergen samples. An increase in EC value often occurs with a decrease in pH value. The values of EC and pH in Greenland samples are distributed similarly to those in the inland region of Antarctica. The human activity and chemical substances in the atmosphere will acidify the precipitation over the Greenland glacier, as will volcanic activities (FUJII *et al.* and NISHIO *et al.*, in preparation). Snow accumulation has proceeded under such conditions in Greenland, although the degree and the process of intrusion have changed with time. The more detailed discussion on the samples in Greenland will be presented later.

In contrast to the Greenland samples, the values from Spitsbergen are distributed widely, and an increase in EC sometimes occurs with the increase of pH value.

We try to consider more precisely the values of EC and pH recorded in the whole core samples in Spitsbergen. Here we discuss the core records in intervals of about 10 m from the surface to the bottom of the glacier. Tables 5 and 6 show the average,

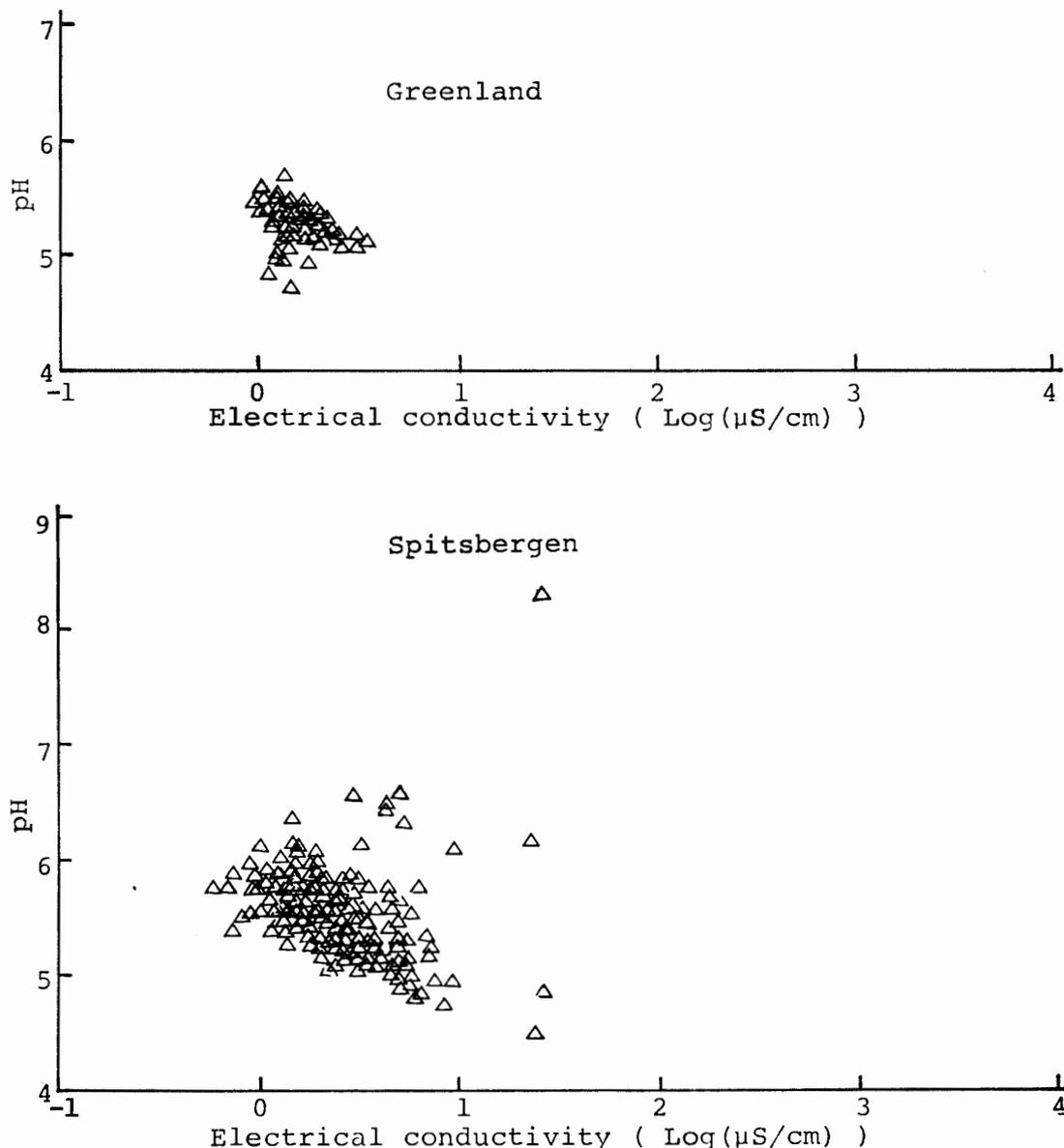


Fig. 5. Relationships between EC and pH in core samples obtained from the glaciers in Greenland and Spitsbergen. The values of electrical conductivity are expressed as $\mu\text{S}/\text{cm}$ in logarithmic scale.

maximum and minimum values of EC and pH in each interval with their standard deviations. The fluctuations of the values are the greatest in the interval from about 30 to 40 m depth, which suggests that there existed vigorous environmental fluctuations during the period corresponding to this core depth.

The climatic events are recorded as the maximum and minimum values of EC and pH profiles in the core. Some appear as the maximum/minimum values of EC at a given depth accompanied by the minimum/maximum values of pH (a negative relationship), and others as the maximum/minimum values of EC accompanying the maximum/minimum values of pH (a positive relationship). Figure 6 shows the numbers of positive and negative relationships. Each number reflects the frequency of environ-

Table 5. Electrical conductivity ($\mu\text{S}/\text{cm}$) in each interval of ice core samples from Spitsbergen.

Interval	Number of samples	Average	Maximum	Minimum	Standard deviation
Surface-10 m	105	2.62	9.1	1.1	1.25
10-20 m	84	1.95	6.2	1.2	0.84
20-30 m	92	2.34	9.3	1.2	1.18
30-40 m	110	3.43	26	0.71	4.42
40-50 m	92	1.98	6.0	0.93	0.90
50-60 m	70	1.47	2.5	0.58	0.33
60-75 m	92	1.98	6.0	0.93	0.90
75-bottom	84	1.86	4.4	1.1	0.64

Table 6. pH in each interval of ice core samples from Spitsbergen.

Interval	Number of samples	Average	Maximum	Minimum	Standard deviation
Surface-10 m	103	5.32	5.68	4.80	0.16
10-20 m	83	5.48	5.77	4.83	0.15
20-30 m	92	5.51	6.48	5.15	0.17
30-40 m	110	5.60	8.30	4.46	0.41
40-50 m	91	5.59	6.34	5.06	0.21
50-60 m	70	5.65	5.85	5.46	0.09
60-75 m	91	5.59	6.34	5.06	0.21
75-bottom	84	5.71	6.54	5.41	0.16

mental events. Also shown is the ratio of positive to negative relationships. From the surface to 10m depth, all the events are negative, possibly implying the modern acidification of the precipitations. The ratio of positive to negative events fluctuates with depth, which reflects the fluctuation of the sedimentary environments, as suggested in Table 4.

The occurrences of sand particles, bacteria and clear ice in the whole core have been recorded *in situ* precisely and compiled (FUJII *et al.*, 1990). These data provide additional climatic information and reveal that there existed repetitions of warm and cold periods during accumulation. The profile of the clear ice ratio in the core, included in Fig. 6, agrees well with the ratio of positive to negative events. The occurrence of melting in the past is preserved as the clear ice in the core strata, and the proportion of clear ice depends on the past climate. Here we can estimate the transport process of substances in the past precipitation system in Spitsbergen. In warmer periods when the melting of the glacier occurs frequently, the glacier is often under effect of environments influenced by soil regions or by sea salts directly. In these periods, the glacier becomes smaller and the sea is often free from sea ice. In colder periods when the melting scarcely occurs, the glacier is often under the environment exposed to the atmosphere, and the chemical reaction in the atmosphere will acidify the precipitation. In these periods, the glacier grows and the area of sea ice expands over the ocean. The volcanic events also increase EC and decrease pH values, and create colder periods by interruption of solar radiation by ash clouds. FUJII *et al.* (1990) estimate some volcanic events in the past from the records of EC and pH profiles in the ice core from Spitsbergen. It

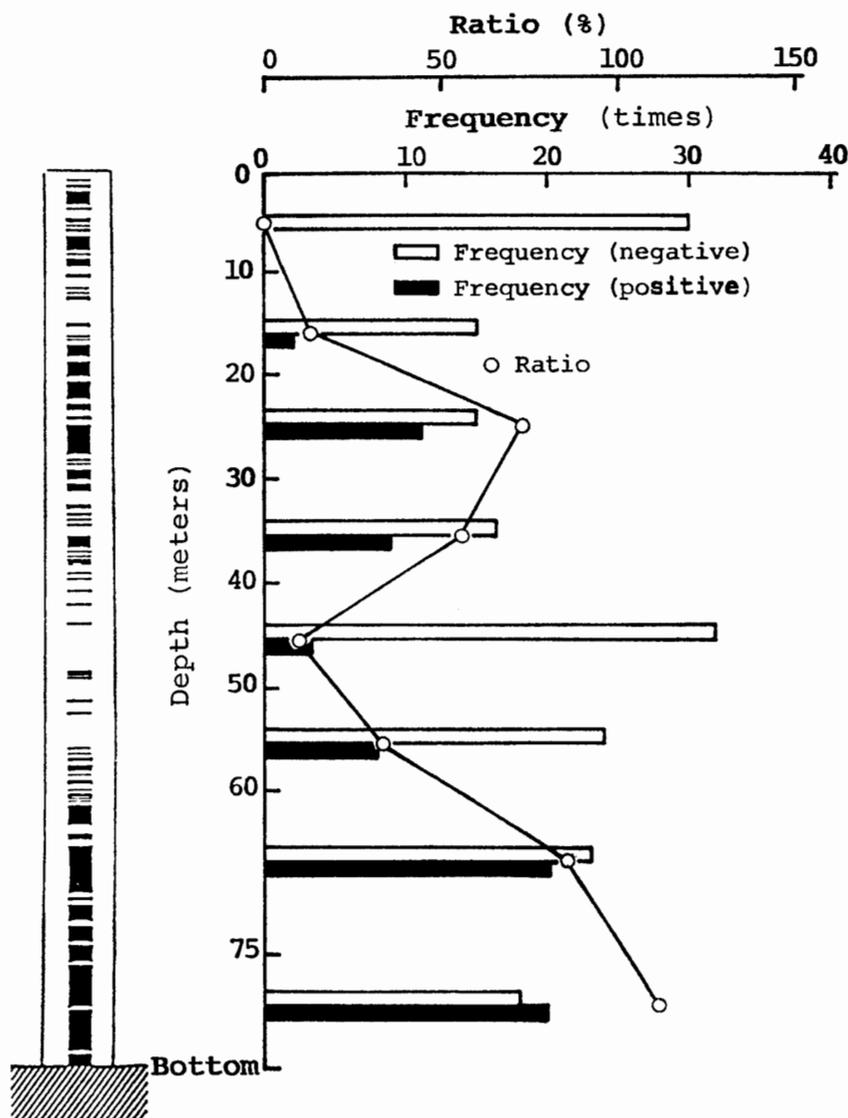


Fig. 6. Occurrence of maximum and minimum values of EC and pH with depth in about 10 m intervals, with the ratio of clear ice in the core (after FUJII et al., 1990). Some maximum/minimum values of EC with depth follow the minimum/maximum values of pH (negative). Other maximum/minimum values of EC with depth follow the maximum/minimum values of pH (positive). The ratio of the positive to negative events is indicated by open circles.

is difficult, however, to distinguish the difference between colder environments and the acidification process affecting the modern precipitations. The events also increase EC and decrease pH values.

5. Summary and Conclusion

The values of EC and pH in the snow and ice samples have unique properties which depend on the local environments. Samples from Nepal, Patagonia, Antarctica and Greenland have regional characteristic values of these parameters.

Using the relationships between electrical conductivity and pH, paleo-environments recorded in the whole core samples in Spitsbergen can be estimated. The impact of modern acid rain appears to be recorded in this ice core, as are fluctuations in warm/cold periods over the past 6000 years.

The values of EC and pH are useful in the first stage of chemical analyses. We are presently trying to establish the chemical characteristics which actually decide the EC and pH values that would reveal the transport process of substances in the precipitation system. We should be able to distinguish the origin of the substances in the precipitations, including volcanic activities.

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