

PRELIMINARY REPORT ON ANALYSES OF MELTED DOME FUJI ICE CORE OBTAINED IN 1993

Okitsugu WATANABE¹, Kokichi KAMIYAMA¹, Hideaki MOTOYAMA¹, Makoto IGARASHI¹,
Sumito MATOBA¹, Takayuki SHIRAIWA², Tomomi YAMADA²,
Hitoshi SHOJI³, Satoru KANAMORI⁴, Nobuko KANAMORI⁴,
Masayoshi NAKAWO⁴, Yutaka AGETA⁴,
Seiji KOGA⁵ and Kazuhide SATOW⁶

¹*National Institute of Polar Research, 9-10, Kaga 1-chome, Itabashi-ku, Tokyo 173*

²*Institute of Low Temperature Science, Hokkaido University,
Kita-19, Nishi-8, Kita-ku, Sapporo 060*

³*Kitami Institute of Technology, 165 Koencho, Kitami 090*

⁴*Institute for Hydrospheric and Atmospheric Sciences, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-01*

⁵*National Institute for Resources and Environment, 16-3, Onogawa, Tsukuba 305*

⁶*Nagaoka National College of Technology, Nishi-kataikai-machi, Nagaoka 940*

Abstract: An ice core from the glacier surface down to 112.59 m depth was obtained in 1993 at Dome Fuji Station. The ice core was divided vertically in the home cold laboratory and various analyses were carried out for the solid and liquid phases of core samples. The measurements of numbers of microparticles, electrical conductivity, pH, oxygen isotopic ratio and chemical constituents were carried out for the melted ice core samples.

In this report, the procedures and the methods for the measurements are introduced with results obtained. The results open preliminary step on ice core research at Dome Fuji Station, which should be useful to evaluate the environments at the dome in the comparison with core analyses at various sites. The vertical distributions for the some of the values obtained are presented to facilitate further discussion of the past climate and environments.

1. Introduction

Snow, which deposits onto an ice sheet surface, is compacted into snow layers. The continuous snow layers can be recovered as an ice core and contain information on the environment at the time of deposition. This information is detected as chemical and physical signals recorded in ice cores. Some of the signals are useful for understanding climatic change. For example, methanesulfonic acid (MSA), biogenic aerosols in the atmosphere, signals have a close relationship to biogenic activity in the sea and also the occurrence of atmospheric clouds (LEGRAND and FENIET-SAIGNE, 1991). Some of the light carboxylic acids are useful indicators for past environments (LEGRAND and ANGELIS, 1995).

An ice core of 112.59 m length was obtained at Dome Fuji Station in 1993. For detection of the signals recorded in the cores, several measurements were carried out for the solid ice core and the melted one. Here we would like to discuss the analytical method

and the values of electrical conductivity (LEC), pH, numbers of microparticles, oxygen isotopic ratio and chemical constituents. The discussion will give us basic information for snow and ice chemistry at Dome Fuji Station and also give us a chance to make clear the local and periodical fluctuations. The methods for ice core analyses were introduced by FUMI *et al.* (1989) and we would like to introduce here the additional methods newly used with the results obtained for the ice core samples.

2. Method and Materials with the Results

The first shallow coring at Dome Fuji Station was carried out in 1993 down to 112.59 m with a dry mechanical drilling system to make a pilot bore hole. The core was carried to cold storage at NIPR in 1994 for processing. The diameter of the core is 10 cm, larger than that of a deep core and each core length is about 50 cm. All of the core samples were cut vertically and some of them were restored for the next analyses (WATANABE *et al.*, 1997). About 100 segments of half cut cores, obtained every 50 cm intervals, were melted to be analyzed for preliminary results.

2.1. Core cutting and decontamination

Core samples for the analyses were treated in a cold laboratory.

All the core samples were cut vertically; half of each was prepared for melting. As a preliminary investigation, some of core portions were separated as the samples for the determination; approximately 10 cm long and the weight of 50 g samples were cut off by a band saw in every one meter of half core samples. The surface of each sample was scribed by a ceramic knife on a clean bench in the cold laboratory and about 5 mm thickness was removed from the surface as being possibly contaminated. The inner parts were stored in bottles pre-cleaned for the melting.

2.2. Melting

Samples were melted in the bottle packed in the cold laboratory at a temperature of 5 degrees to keep the chemical constituents well preserved. Within about 2 days, each melted sample was divided into 3 types of bottles: for microparticles, LEC and pH; for ion chromatography (IC); and for oxygen isotopic ratio. Down to 30 m depth, the samples were also divided into other bottles for hydrogen peroxide (H_2O_2).

2.3. Determination of number of microparticles

Numbers of microparticles with various diameters were counted in the liquid phase by a laser particle counter (Met One, Sensor Type: 211-H.C.). Samples of volume 10 ml were introduced to a measuring cell through a flow line with a perister pump. The laser light in the cell is scattered by microparticles. The intensity of the scattering is detected by a photo sensor to generate electric pulses. The counts and diameters of every particles are detected as pulses and their strength, respectively. The system can distinguish microparticles of diameter 0.5–25 μm . The pulses with strength were obtained during the measurement. The result for each sample is a matrix of diameters and numbers. We classify the particle diameters into ten grades as listed in Table 1 for preliminary discussion. The distribution of the numbers in each grades is given in Table 2 and some of the results

Table 1. Classification for diameters of microparticles.

Grade	From (μm)	To (μm)	Grade	From (μm)	To (μm)
A		0.65	F	2.75	4.25
B	0.65	0.90	G	4.25	6.25
C	0.90	1.25	H	6.25	8.75
D	1.25	1.75	I	8.75	15.00
E	1.75	2.75	G	15.00	

Table 2. Distribution for numbers of microparticles of every diameter. The number of samples is 106.

Grade (ID)	Maximum	Minimum	Average	Median	Standard deviation
	(counts/ <i>l</i>)				
A	17000	2700	6200	6100	1700
B	14000	3200	6200	5700	2100
C	8400	950	3000	2500	1500
D	2600	0	710	590	470
E	1200	0	380	300	270
F	950	0	300	220	230
G	890	0	260	190	210
H	350	0	80	37	89
I	310	0	65	27	75
G	210	0	41	18	48

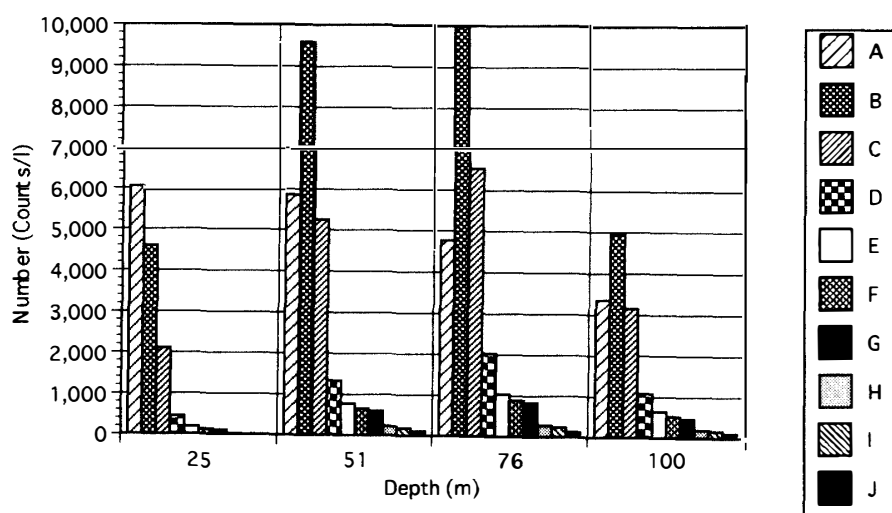


Fig. 1. Four examples for the determination of number of particles in each diameter range listed in Table 1.

are shown in Fig. 1. The number of particles has a wider range in grade A (the smallest diameter) than in grade B (the second smallest diameter) as shown in Table 1; the largest count for some samples occurs in grade B. The numbers of microparticles larger than grade D become smaller in all samples.

2.4. Determinations for liquid electrical conductivity (LEC) and pH

LEC and pH were measured by flow cell type sensors. The flow line is connected to the sensor for microparticle counting. The samples are introduced by the perister pump first to the sensor for microparticle counting, then to the one for LEC and finally for pH. The flow rate is controlled with the same perister pump for the particle counting. The apparatus for the measurement are listed in Table 3 and the distributions for the values in Table 4. Ionic concentrations are small considering the LEC values; slight acidification is observed for many samples. Some samples became more neutral relative to the equilibrium values of carbon dioxide in the atmosphere.

The relationship between LEC and pH is shown in Fig. 2. The values of LEC and pH in various snow and ice samples were discussed by KAMIYAMA *et al.* (1990). Lower LEC and higher pH values were observed in the core samples than in snow samples in the inland region of Antarctica. There possibly exist two causes, the different characteristics between ice core and fresh snow samples and the different measuring systems. There was limited sampling duration for in situ snow samples and further discussion is needed for evaluate the results.

Table 3. Apparatus for the measurement of liquid electrical conductivity (LEC) and pH.

Sensor	Type	Cell constant	Cell volume
LEC	Flow cell (TOA CG-90005PL)	0.05 cm ⁻¹	6.28 ml
pH	Flow cell (TOA GS-80B)		0.25 ml

Table 4. Distribution for the values of electrical conductivity (LEC) and pH together with the modified values as H concentration expressed by mol. The number of samples is 102.

		Maximum	Minimum	Average	Median	Standard deviation
EC	($\mu\text{S}/\text{cm}$)	3.28	1.79	2.51	2.41	0.30
pH		6.54	4.70	5.53	5.52	0.34
H	($\mu\text{mol}/\text{l}$)	2.0E-5	2.9E-7	3.9E-6	3.1E-6	3.5E-6

2.5. Determination of oxygen isotopic ratio

Five ml of each liquid sample was taken for the measurement of oxygen isotopic ratio ($\delta^{18}\text{O}$). The ratio was determined by a mass spectrometer (Finnigan-MAT Delta-E) on CO_2 equilibrated with samples. The distribution is listed in Table 5. The oxygen isotopic ratio of the Vostok ice core during the Holocene was about -56‰ , reported by JOUZEL *et al.* (1993), similar to the average value of the 112 m depth ice core at Dome Fuji Station. On the other hand, the average oxygen isotopic ratio during the Holocene in the ice core at Summit, Greenland, reported by DANSGAARD *et al.* (1993), was larger than that

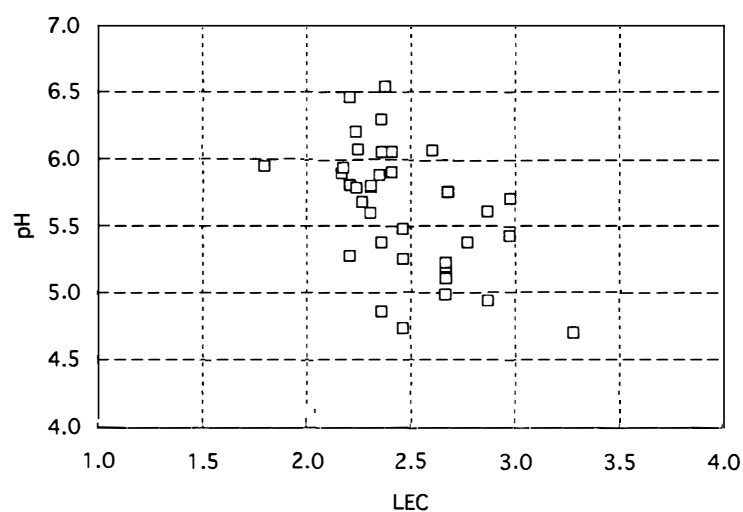


Fig. 2. The relationship between LEC and pH.

Table 5. Distribution for oxygen isotopic ratio ($\delta^{18}O$). The number of samples is 106.

Maximum	Minimum	Average	Median	Standard deviation
(‰)				
−50.80	−59.54	−54.76	−54.77	1.384

of Dome Fuji Station. The average values reasonably reflect the atmospheric temperatures at the coring sites.

2.6. Determination of concentrations of cations and anions

The concentrations of cations and anions were determined by the ion chromatography (Dionex DX-500). Samples of 3 ml was prepared into the pre-cleaned polyethylene bottles for cations and anions available for setting up to automatic sample changers. Measuring systems for cations and anions are shown in Table 6 and the gradient conditions for anion determination in Table 7. The systems are able to determine Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} as cations and F^- , Cl^- , SO_4^{2-} , NO_2^- , NO_3^- , $HCOO^-$, CH_3COO^- , $C_2O_4^{2-}$ and $CH_3SO_3^-$ as anions with the retention time listed in Table 8. The statistic values for the distribution of all ions with the detection limits are listed in Table 9. The concentration of chemical species in the snow and air in these years at Summit, Greenland, was reported by DIBB *et al.* (1994, 1996), which shows that concentration level was more smaller at Dome Fuji Station in Antarctica than at Summit in Greenland possibly depending upon the distance from the human activities. Input of some chemical species including $CH_3SO_3^-$ into the South Pole and Vostok snow in these years were discussed by LEGRAND *et al.* (1992) and LEGRAND (1995). The concentration of $CH_3SO_3^-$ was also smaller at Dome Fuji core than at South Pole and Vostok cores. The concentration of NO_3^- in South Pole ice core at various depths are listed by LEGRAND and KIRCHNER (1990),

Table 6. Measuring systems of cations and anions set up for ion chromatography.

	Cation	Anion
Pump system	IP20 isocratic pump	GP 40 gradient pump
Eluent	0.7 mM CH ₃ SO ₃ H	E1: ultra pure water E2: 5 mM NaOH E3: 100 mM NaOH
Flow-rate	1.0 ml/min	2.0 ml/min
Separator column	CS14	AS11
Guard column	CG14	AG11
Suppressor	CSRS-I (Auto Suppression Recycle Mode)	ASRS-I (Auto Suppression External Mode)
Sample loop volume	0.5 ml	1.0 ml

Table 7. Working gradient conditions used for anion determination.

Time (min)	E1	E2 (%)	E3	Concentration of eluent (mM NaOH)
0.1	90	10	0	0.50
1.5	90	10	0	0.50
4.0	0	100	0	5.00
6.0	0	100	0	5.00
13.0	0	65	35	38.25
14.9	0	65	35	38.25
15.0	90	10	0	0.50

Table 8. Retention time of cations and anions detected.

Cation	Time (min)	Anion	Time (min)	Anion	Time (min)
Na	4.05	F	2.91	NO ₂	5.99
NH ₄	4.63	CH ₃ COO	3.14	NO ₃	7.82
K	5.61	HCOO	4.01	SO ₄	10.95
Mg	8.46	CH ₃ CO ₃	4.39	C ₂ O ₄	11.35
Ca	9.69	Cl	5.57	PO ₄	13.81

where the values are higher than Dome Fuji core. The more discussion is needed for the local distributions of the concentration levels.

3. Discussion

3.1. Ionic balance

The ionic balance in an ice core is useful and basic information on snow chemistry. An average electric equivalent for the chemical constituents obtained by ion chromatography and hydrogen ions calculated from pH by the glass electrode method are shown in Fig.

Table 9. Distribution of concentrations of chemical constituents obtained by ion chromatography. The number of samples is 106.

	Maximum	Minimum	Average	Median	Standard deviation	Detection limit
	(μmol/l)					(μmol/l)
a) Cation						
Na	7.404	0.310	1.626	3.857	0.836	0.051
NH ₄	2.772	0.003	0.478	1.388	0.426	0.327
Ca	1.358	0.053	0.411	0.705	0.211	0.023
Mg	0.461	0.032	0.189	0.246	0.069	0.002
K	0.855	0.007	0.145	0.431	0.120	0.031
b) Anion						
Cl	8.198	0.970	1.960	4.115	0.767	0.033
SO ₄	3.019	0.456	1.192	1.515	0.358	0.011
NO ₃	1.327	0.000	0.359	0.682	0.148	0.037
HCOO	0.642	0.033	0.190	0.341	0.119	0.039
F	0.654	0.004	0.093	0.359	0.102	0.064
CH ₃ COO	0.330	0.000	0.041	0.181	0.051	0.031
CH ₃ SO ₃	0.143	0.000	0.032	0.077	0.029	0.012
NO ₂	0.154	0.000	0.023	0.089	0.024	0.023
PO ₄	0.146	0.000	0.003	0.107	0.018	0.069
C ₂ O ₄	0.065	0.000	0.002	0.039	0.011	0.012

3. The order of cations and anions in each legend is the same in the bar graphs. The difference between anions and cations depends possibly upon the bicarbonate ions, determined by the equilibrium for carbon dioxide in the atmosphere. Pure water containing no dissolved substances should have a pH of 7, while pure water becomes moderately acidic with a pH of 5.7 as a result of the solution of atmospheric carbon dioxide to equilibrium (BERNER and BERNER, 1996). The estimated values of bicarbonate ions are similar to the missing value for the average pH 5.53 with small amounts of chemical constituents as shown in Table 7.

The ratio of $\text{Ca}^{2+}/\text{Na}^{+}$ in the Dome Fuji core is similar to the one in the South Pole core in Antarctica and lower than that in Summit core in Greenland during the Holocene reported by WHITLOW *et al.* (1992). The ratio possibly depends upon the influence of not the sea but the earth. The mean ionic compositions in the present climate and in the Glacial Age at Vostok in Antarctica and at Summit Greenland were discussed by LEGRAND (1995). In the present climate, the Mg ratio at Dome Fuji Station is similar to the one at the South Pole and higher at Vostok. More investigation is needed to verify the local distributions in ice core samples.

3.2. Vertical distributions of some components in the core

The vertical distributions of the elements in the ice core discussed above are shown in Fig. 4; $\delta^{18}\text{O}$, H^{+} , Na^{+} , NH_4^{+} , Ca^{2+} , Mg^{2+} , K^{+} , Cl^{-} , SO_4^{2-} , NO_3^{-} and HCOO^{-} . In spite

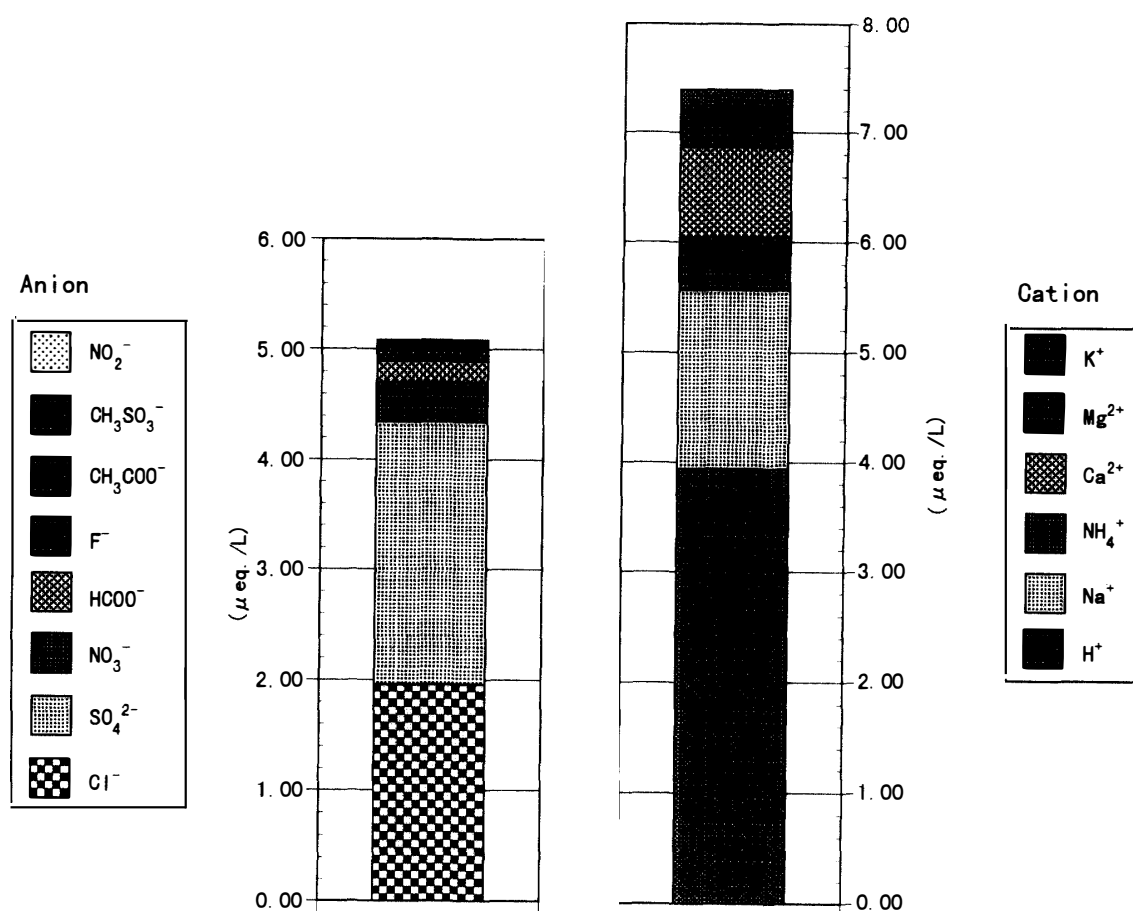


Fig. 3. The average electric equivalent for the elements obtained by ion chromatography and hydrogen ion obtained by glass electrode.

of the sampling interval of about 1 m of ice core, it is interesting that the values fluctuate continuously as shown in close circles of higher values of Na⁺, Cl⁻, NH₄⁺, Ca²⁺ and should be checked again.

However we omitted the distributions of microparticles. We obtained the number of microparticles in every diameters. Nevertheless we should discuss the classification method for diameter more effective on the target for analyses; for example, climatic change. And the LEC distribution is clearer in the distribution of each chemical constituent.

We obtained the concentrations of 15 chemical elements with ion chromatography as listed in Table 9. The vertical distributions of some elements, the average values are about five times larger than each detection limits, are shown in Fig. 4. We should discuss the vertical distributions more carefully for the chemical constituents the concentrations of which are near the detection limits.

In the core from the top down to 30 m depth, the concentration of H₂O₂ was found to be under the detection limit ($<10^{-8}$ mol/l). A strong decrease with depth in the surface snow at the South Pole was reported by McCONNELL and BALES (1996). We also found that the decrease of H₂O₂ was strong in the surface several ten centimeters depth in snow pits around the Dome Fuji area, and H₂O₂ disappeared at 3 m, as will be discussed

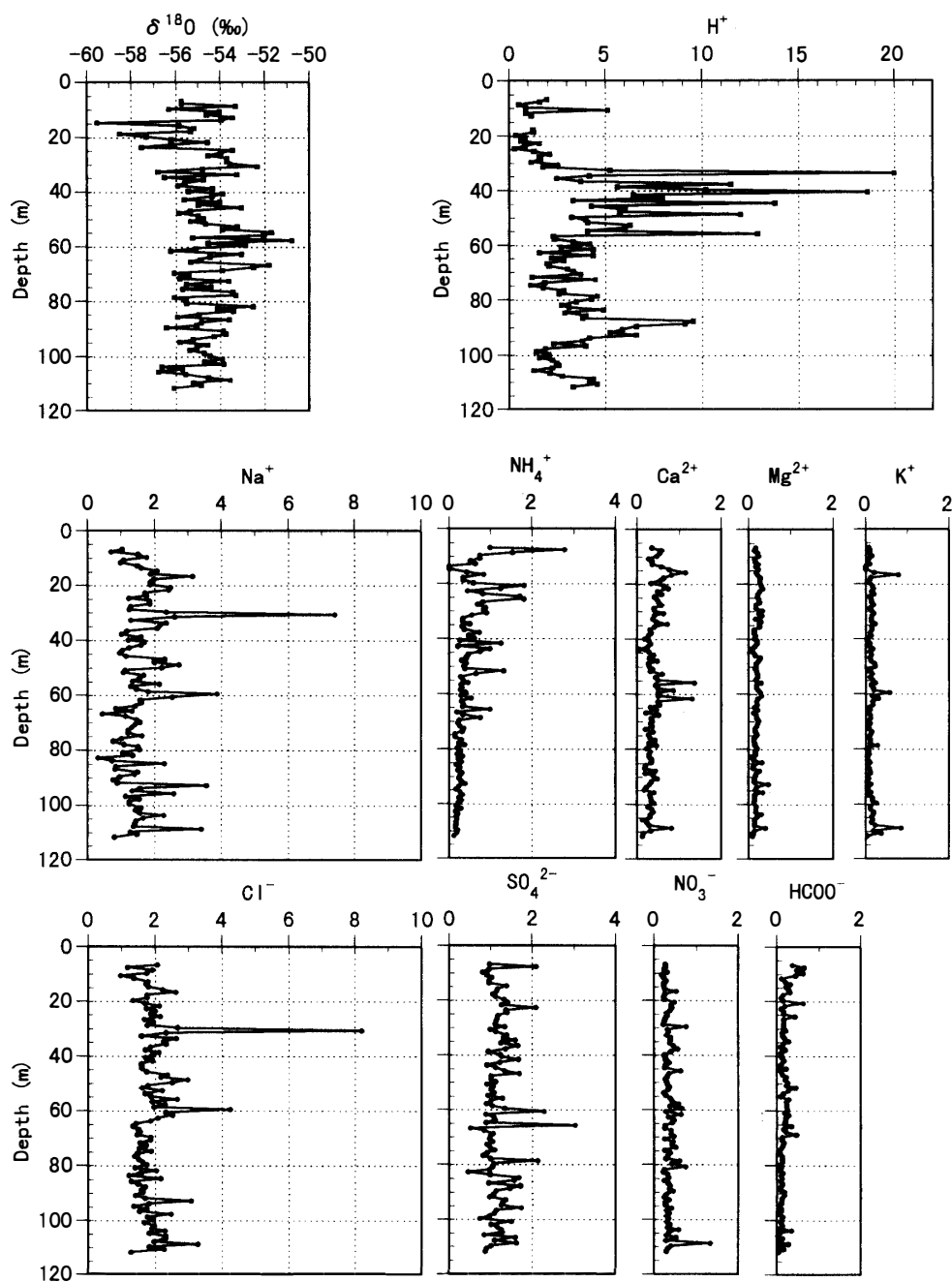


Fig. 4. The vertical distributions of the elements in the discussion. Unit of concentration is $\mu\text{mol/l}$.

in another paper.

The evolution process of the chemical composition in firn layers of snow, investigated by ANGELIS and LEGRAND (1995), suggested that the signals detected from the ice core originate from both signal flux from the atmosphere and a modification process in the firn. In considering the core profiles, transfer functions of substances between atmosphere and snow and also between snow and deep ice through firn should be made clear.

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(Received May 13, 1997; Revised manuscript accepted June 9, 1997)