

# CHEMICAL CONSTITUENTS IN THE SURFACE SNOW IN MIZUHO PLATEAU

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**Abstract:** Chemical features and profiles of the ice sheet in Mizuho Plateau have been revealed by means of newly developed analytical techniques such as atomic absorption spectrophotometry, neutron activation method and isotope dilution mass spectrometry. The chemical concentration is as low as ppb level even for the major components, Na, K, Mg and Ca, and its distribution is homogeneous in the surface sheet but shows much vertical complexity. Silicate dusts which functioned as the condensation nuclei for the formation of snow crystal in the upper atmosphere and which were captured by snow fall process are poor, while sea salts account for more than 90 per cent of the total weight of components. Annual accumulation of chemical components,  $\mu\text{g}/\text{cm}^2$ , is 0.1 for silicate dusts and 0.40, 0.03, 0.1 and 0.06 for Na, K, Mg and Ca originated from the latter source. Annual accumulation of Hg and Pb is at the level of 0.1 and 1.5  $\text{ng}/\text{cm}^2$  at the present time while 0.02 and 0.3  $\text{ng}/\text{cm}^2$  in ancient times.

## 1. Introduction

The ice sheet in Mizuho Plateau contains the chemical components at the ppb level ( $10^{-6}$  g/kg) which is only  $10^{-2}$ – $10^{-3}$  of the concentration in rain and snow in the middle latitude coastal regions. It is nearly as pure as usually distilled water (Table 1). Sample must receive a high rate preconcentration by techniques such as lyophilization even to determine the major components like Na, K, Mg and Ca. The available sample quantities are usually of the order of

*Table 1. Chemical concentrations in pure water, polar snows and urban rains.*

	Choshi ( $\mu\text{g}/\text{kg}$ )	Mito ( $\mu\text{g}/\text{kg}$ )	Maebashi ( $\mu\text{g}/\text{kg}$ )	Nagoya ( $\mu\text{g}/\text{kg}$ )	Sapporo ( $\mu\text{g}/\text{kg}$ )	Byrd St. ( $\mu\text{g}/\text{kg}$ )	Green- land ( $\mu\text{g}/\text{kg}$ )	Pure water ( $\mu\text{g}/\text{kg}$ )
Na	3840	700	260	440	510	31	20	0.9
K	400	270	50	n.d.	10	1.5	2.4	1.0
Mg	240	50	20	80	190	4.0	5.0	n.d.
Ca	540	960	50	130	100	1.5	5.4	0.4
Cl	6930	1440	430	760	n.d.	60	31	9.2
SO <sub>4</sub>	1320	2160	240	340	n.d.	n.d.	n.d.	n.d.
Analyzed by	Y. MIYAKE			K. SUGAWARA				

several grams to several tens grams when the boring cores are analyzed. Analytical methods with super high sensitivity and accuracy using as little a sample as possible must be developed because these could provide the first key to open the way to the geochemical research of the fine structures of ice sheets. The isotope dilution mass spectrometry using surface ionization techniques is found to be capable of high degree of exploitation in this case.

The concentrations of major components in the surface snow layer of the ice sheet are found to be very uniform over the entire plane while there is a distinct vertical variation in major components. More than 90 per cent of major components is from salts in sea water and Si and Ti show that rock and mineral components which have functioned as condensation nuclei for snow flake formation and which were captured by snow fall process are less than 10 per cent. Furthermore, silicate dry fallout must be present in snow. Concentrations of Hg and Pb in upper layers of snow are higher than those in deeper layers. This comes from the increasing global air pollution with both elements originating in industrial and social activities of the recent age. The annual precipitation rates of chemical components, are 0.4, 0.03, 0.1 and 0.06  $\mu\text{g}/\text{cm}^2$ , for Na, K, Mg and Ca and (0.1–0.02) and (1.5–0.3)  $\text{ng}/\text{cm}^2$  for Hg and Pb.

## 2. Analytical Methods

Chemical components in melt water of snow are analyzed by the newly developed methods (Table 2).

Table 2. Methods applied to polar snow analysis.

Elements	Method I			Method II		
	Method	Sensitivity	Accuracy	Method	Sensitivity	Accuracy
Na	Atomic absorption after freezing concentration	0.5	10	Neutron activation	0.6	10
K	"	1	30	Isotope dilution mass-spectrometry	0.1	3
Mg	"	0.5	10	"	0.1	3
Ca	"	1	30	"	0.1	3
Cl	Colorimetry	50	100	Neutron activation	0.6	10
Si	Emission spectrography	2	30			
Ti	Isotope dilution mass-spectrometry	0.01	3			
Pb	"	0.001	3			
Hg	Atomic absorption	0.0001	5			

Sensitivity in  $\mu\text{g}/\text{kg}$ , accuracy in % error.

### 3. Geochemistry of Snow and Ice

#### 3.1. Concentrations of chemical components

The concentrations of chemical components in the surface snow strata in Mizuho Plateau are listed in Table 3. The chemical characteristic of the region is found to be uniform. In comparison with chemical concentrations of Hokkaido's high mountain snows, those in Mizuho Plateau are about 1/50 of the values in Hokkaido as shown in Table 3. When compared with the middle latitude coastal rainfall, Antarctic snow is at the  $10^{-2}$ – $10^{-3}$  level in chemical concentrations. It may be said that chemical concentrations in Mizuho Plateau are much more dilute than those in its neighboring regions (Table 3), and than those at New Byrd Station, Antarctica and in the northern part of Greenland.

The relationship between the chemical nature of snow flakes and meteorological conditions will be a subject of the future research.

Table 3. Chemical constituents in snow from Mizuho Plateau, West Enderby Land, Antarctica\*.

Sampling station	Latitude and longitude	Date of sampling	Concentration ( $\mu\text{g}/\text{kg}$ )					
			Na	K	Mg	Ca	Ti	Silicate dusts
S122	70°01.2'S 43°09.4'E	Jan. 18, 1971	53	2.1	13	3.18	0.04	8
Mizuho Camp	40°41.9'S 44°19.9'E	Nov. 17, 1970	14	1.2	2.1	2.78	0.01	2
Mizuho Camp	70°41.9'S 44°19.9'E	Jan. 9, 1971	14	0.88	2.4	1.89	0.00	0
Y135	71°26.8'S 47°21.8'E	Nov. 24, 1970	12	1.0	3.0	1.81	0.06	12
Y200	71°46.2'S 48°56.0'E	Nov. 27, 1970	14	1.0	2.3	3.76	0.03	6
Y300	70°54.9'S 49°52.9'E	Dec. 4, 1970	11	0.56	1.7	1.93	0.04	8

\* Collected by Hiromu SHIMIZU, The Institute of Low Temperature Science, Hokkaido University.

#### 3.2. Silicate dusts in snow crystals

The Ti concentration in snow and ice is at the level of  $10^{-2}$   $\mu\text{g}/\text{kg}$  (Table 4).

Table 4. Determination of Ti and silicate dusts in snow ice.

Sampling station	Sample taken (g)	Ti measured ( $\mu\text{g}$ )	Ti ( $\mu\text{g}/\text{kg}$ )	Silicates ( $\mu\text{g}/\text{kg}$ )	Ti/Na
S122	106	0.0046	0.04	8	0.0007
Mizuho	203	0.0012	0.005	2	0.0051
Y135	100	0.0059	0.06	12	0.005
Byrd Station	100	0.002	0.02	4	0.0006
Camp Century	100	0.010	0.10	20	0.005
Tokachidake	27.4	0.012	0.44	90	0.0006
Asahidake	24.4	0.012	0.51	100	0.0009

As for the origin of Ti, the Ti/Na ratios in sea water are of the order of  $10^{-7}$ , while those of snow and ice in Mizuho Plateau are of  $10^{-3}$ – $10^{-4}$  and those of rocks and minerals are of  $10^{-1}$ – $10^{-2}$ . It is thought that most of Na in snow has originated from sea water. Furthermore, it is reasonable to conclude that Ti comes mainly from silicate dusts and minerals but not from sea water.

To obtain the amount of silicate dust in snow and ice, Ti quantity is multiplied by 200. Silicate dust contents of snow in Mizuho Plateau are close to each other and to that of Byrd Station, Antarctica, but are  $10^{-1}$  less than that of Camp Century, Greenland.

This may be due to the uneven distribution of land masses that are the source of silicate dusts, and to the complex atmospheric circulation in the northern and southern hemispheres.

The contents of Na, K, Mg and Ca in silicate dusts are calculated and given in the third column of Table 5. These values are only  $10^{-1}$  to  $10^{-2}$  of the total amounts in the fourth column of the table. The difference in value between the two columns must be attributed to the component originating in sea water, if

Table 5. Amounts of silicate dusts in polar snow.

Sampling station	Silicate dusts ( $\mu\text{g}/\text{kg}$ )	Elements in silicate dusts				Total amounts of elements in snow ice				
		Na ( $\mu\text{g}/\text{kg}$ )	K ( $\mu\text{g}/\text{kg}$ )	Mg ( $\mu\text{g}/\text{kg}$ )	Ca ( $\mu\text{g}/\text{kg}$ )	Na ( $\mu\text{g}/\text{kg}$ )	K ( $\mu\text{g}/\text{kg}$ )	Mg ( $\mu\text{g}/\text{kg}$ )	Ca ( $\mu\text{g}/\text{kg}$ )	
S122	8	0.2	0.2	0.2	0.3	53	2.1	13	3.18	
Y200	6	0.1	0.1	0.1	0.21	14	1.0	2.3	3.76	
Mizuho Camp	Mizuho Plateau	2	0.02	0.01	0.002	0.04	14	1.2	2.1	2.78
Y300		8	0.2	0.15	0.2	0.3	11	0.56	1.7	1.93
Y135		12	0.3	0.2	0.3	0.42	12	1.0	3.0	1.81
Byrd Station	4	0.1	0.1	0.1	0.1	31	1.5	4.0	1.3	
Camp Century	20	0.5	0.5	0.5	0.7	21	3.1	8.0	6.4	
Tokachidake	90	2	2	2	3	750	50	200	100	
Asahidake	100	2	2	2	4	590	40	100	130	

Table 6. Amounts of sea salt contained in Enderby Land snow.

Station No.	Na (ppb)	K (ppb)	Mg (ppb)	Ca (ppb)
S122	53	1.8 (0.036)	12.8(0.24)	2.9(0.055)
Mizuho-1	14	1.2 (0.086)	2.1(0.15)	2.7(0.20)
Mizuho-2	14	0.88(0.063)	2.4(0.17)	1.9(0.14)
Y135	12	0.80(0.068)	2.7(0.23)	1.4(0.12)
Y200	14	0.90(0.065)	2.2(0.16)	3.6(0.26)
Y300	11	0.41(0.038)	1.5(0.14)	1.6(0.15)

contributions of other sources are neglected. The difference with regard to Na, K, Mg and Ca is listed in Table 6, in which the values in parentheses are the fraction of each difference with respect to Na difference. The values of K/Na, Mg/Na and Ca/Na in sea water are 0.038, 0.120 and 0.038 by weight respectively. Snow values in Table 6 are close to values in sea water except for Ca.

Table 7. Chloride and sodium concentrations in polar snows.

Sample date	Cl concn. ( $\mu\text{g}/\text{kg}$ )	Na concn. ( $\mu\text{g}/\text{kg}$ )	(Na/Cl) Wt. mean
Greenland interior 1815	52 $\pm$ 2	21 $\pm$ 1	0.40 $\pm$ 0.02
	52 $\pm$ 2	21 $\pm$ 1	0.40 $\pm$ 0.02
1946	66 $\pm$ 2	26 $\pm$ 1	0.39 $\pm$ 0.01
	68 $\pm$ 2	29 $\pm$ 1	0.43 $\pm$ 0.01
1892	71 $\pm$ 2	30 $\pm$ 1	0.42 $\pm$ 0.01
	73 $\pm$ 2	32 $\pm$ 1	0.44 $\pm$ 0.01
1938	41 $\pm$ 1	14 $\pm$ 1	0.34 $\pm$ 0.02
	39 $\pm$ 1	13 $\pm$ 1	0.33 $\pm$ 0.02
1881	40 $\pm$ 1	18 $\pm$ 1	0.45 $\pm$ 0.03
	38 $\pm$ 1	19 $\pm$ 1	0.50 $\pm$ 0.03
1859	43 $\pm$ 1	17 $\pm$ 1	0.40 $\pm$ 0.03
	45 $\pm$ 1	17 $\pm$ 1	0.38 $\pm$ 0.02
1835	60 $\pm$ 1	29 $\pm$ 1	0.48 $\pm$ 0.02
	58 $\pm$ 1	28 $\pm$ 1	0.48 $\pm$ 0.02
1965 Summer	30 $\pm$ 1	8 $\pm$ 1	0.27 $\pm$ 0.03
	30 $\pm$ 1	9 $\pm$ 1	0.30 $\pm$ 0.03
1965 Winter	72 $\pm$ 2	29 $\pm$ 1	0.40 $\pm$ 0.01
	69 $\pm$ 2	28 $\pm$ 1	0.41 $\pm$ 0.01
1964 Winter	43 $\pm$ 1	21 $\pm$ 1	0.49 $\pm$ 0.01
	49 $\pm$ 1	22 $\pm$ 1	0.45 $\pm$ 0.01
1964 Fall	69 $\pm$ 2	31 $\pm$ 1	0.45 $\pm$ 0.01
	72 $\pm$ 2	33 $\pm$ 1	0.46 $\pm$ 0.01
1965 Spring	26 $\pm$ 1	6 $\pm$ 1	0.23 $\pm$ 0.03
	26 $\pm$ 1	5 $\pm$ 1	0.19 $\pm$ 0.04
1965 Spring	50 $\pm$ 2	21 $\pm$ 1	0.42 $\pm$ 0.01
	53 $\pm$ 2	24 $\pm$ 1	0.42 $\pm$ 0.01
1753	58 $\pm$ 2	20 $\pm$ 1	0.35 $\pm$ 0.01
	58 $\pm$ 2+	21 $\pm$ 1	0.36 $\pm$ 0.01
Coastal 800 B.C.	570 $\pm$ 23	350 $\pm$ 15	0.61 $\pm$ 0.02
	580 $\pm$ 23	350 $\pm$ 15	0.60 $\pm$ 0.02
Antarctic interior 1942	68 $\pm$ 2	31 $\pm$ 1	0.46 $\pm$ 0.01
	72 $\pm$ 2	30 $\pm$ 1	0.42 $\pm$ 0.01
1857	58 $\pm$ 2	22 $\pm$ 1	0.38 $\pm$ 0.01
	59 $\pm$ 2	22 $\pm$ 1	0.37 $\pm$ 0.01
1775	71 $\pm$ 2	37 $\pm$ 1	0.52 $\pm$ 0.02
	75 $\pm$ 2	34 $\pm$ 1	0.45 $\pm$ 0.01
1694	80 $\pm$ 2	35 $\pm$ 1	0.44 $\pm$ 0.01
	75 $\pm$ 2	38 $\pm$ 1	0.51 $\pm$ 0.02
1965	34 $\pm$ 1	15 $\pm$ 1	0.44 $\pm$ 0.03
	37 $\pm$ 1	14 $\pm$ 1	0.38 $\pm$ 0.03

This leads to a suspicion that those components have their origin in sea water.

The extraordinarily higher values of Ca/Na were found in snow than that of sea water. This high concentration of Ca in snow and ice may be a problem for the future study.

### 3.3. Observed differentiation between Na and Cl

Na/Cl values observed at Byrd Station and Camp Century are listed in Table 7. As Na/Cl value of sea water is 0.55 in weight ratio, those of the both Polar interior sites are without exception smaller than the sea water value. This indicates that there may be a mutual differentiation between Na and Cl through the transportation process from the sea. Further, addition of either element from other sources may take place before precipitation.

Table 8. Annual amounts of fallout in  $\mu\text{g}/\text{cm}^2$ .

	Camp Century	Byrd Station	Enderby Land
Annual accumulation	$20 \times 10^6$	$10 \times 10^6$	$30 \times 10^6$
Si	0.14	0.004	n.d.
Ti	0.002	0.0001	0.001
Silicate dusts	0.6	0.03	0.1
Cl	0.80	1.2	n.d.
Na	0.40	0.62	0.40
K	0.054	0.032	0.03
Mg	0.11	0.074	0.1
Ca	0.13	0.026	0.06

Table 9. Vertical distribution of Na and Mg concentration in Enderby Land, Antarctica.

Depth (cm)	Na ( $\mu\text{g}/\text{kg}$ )	Mg ( $\mu\text{g}/\text{kg}$ )
1884-1889	314	21
1923-1933	48	3
2645-2660	54	10
2742-2755	57	7
2882-2893	358	44
3309-3313	107	67
3460-3470	156	76
3992-4006	858	125
4500-4512	33	37
4987-4997	170	58
5985-5996	11	2
6086-6095	5	3

Collected by T. YAMADA, The Institute of Low Temperature Science, Hokkaido University.

### 3.4. Annual fallout of chemical components

The annual fallout of chemical components in  $\mu\text{g}/\text{cm}^2$  calculated from the concentration of each component and annual accumulation of  $\text{H}_2\text{O}$  is listed in Table 8. The fallout of silicate condensation-nuclei is  $0.1 \mu\text{g}/\text{cm}^2$  and Na, K, Mg and Ca from sea water are 0.4, 0.03, 0.1 and  $0.06 \mu\text{g}/\text{cm}^2$  in Mizuho Plateau.

### 3.5. Vertical distribution of chemical components in Mizuho Plateau

The vertical distribution profile of Na and Mg was determined by atomic absorption spectrophotometry. Data based on a deep core analyses is shown in Table 9. The fluctuation of vertical distribution is extraordinarily large, despite of the homogeneous surface distribution over a wide area as shown in Table 3.

Table 10. Mercury profile in an ice core sample from Mizuho Camp, Antarctica (Mercury by atomic absorption method).

Core sample Depth (m)	Sample taken (g)	Mercury found ( $10^{-9}$ g)	Mercury concn. (ppt)	Annual accumulation ( $10^{-9}$ g/cm <sup>2</sup> )
4.0 — 4.1	93	0.80	8.60	0.09
6.0 — 6.1	107	2.35	21.9	0.22
8.0 — 8.1	195	2.25	13.0	0.13
10.0 — 10.1	121	1.80	14.8	0.14
12.0 — 12.1	207	0.55	2.65	0.03
15.37— 15.55	230	10.95	47.6	0.48
19.0 — 19.1	225	1.24	5.51	0.06
23.48— 23.66	230	11.25	48.9	0.49 (Pb 0.72 ppb)
28.38— 28.52	137	1.35	9.85	0.10
32.44— 32.62	128	0.75	5.85	0.06
36.26— 36.41	126	2.17	17.2	0.17
44.37— 44.52	227	0.65	2.86	0.02
64.52— 64.68	213	0.65	3.05	0.03
68.82— 68.97	275	0.35	1.27	0.01
72.49— 72.65	280	0.25	0.89	0.01
80.37— 80.53	253	0.25	0.98	0.01 (Pb 0.03 ppb)
92.40— 92.56	243	0.00	0.00	0.00
96.42— 96.57	125	0.00	0.00	0.00
100.70—100.85	135	0.35	2.59	0.03
106.43—106.70	261	0.54	2.06	0.02
116.54—116.70	190	0.33	1.74	0.02
128.49—128.64	246	0.35	1.42	0.01 (Pb 0.03 ppb)
132.50—132.66	172	0.00	0.00	0.00
136.70—136.87	332	0.65	1.95	0.02
140.55—140.70	246	0.43	1.74	0.02
144.54—144.70	221	0.35	1.58	0.02 (Pb 0.02 ppb)

This may call for a study of long term changes in meteorological conditions and their bearing on the chemical fallout.

As for the vertical distribution of Hg, it is clear that recent snow has much higher concentration than ancient ice. This fact, together with the concentration of Pb (Table 10), reflects the increase of the worldwide consumption of these elements and the progressive atmospheric pollution due to heavy metals since the Industrial Revolution Age.

#### 4. Concluding Remarks

The newly developed analytical techniques, atomic absorption spectrophotometry, neutron activation analysis and isotope dilution mass spectrometry, have revealed the chemical features and profiles of ice sheets in polar regions. Snow is a message from heaven as a pioneer in this scientific field said and the ice sheet of the polar regions may be a collection of messages from the sky. The characters of this collection of messages are too subtle, and the legible characters are too few to be read by the most sensitive analytical methods. It may be possible, however, to read and interpret roughly 2–3 orders of these messages by the best use of these techniques and through the cooperation of a large number of geochemists.

The geochemist needs pure samples (not contaminated during sampling and subsequent storage), proper analytical equipment and clean laboratory.

This is the present situation although it has been slow in coming.

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