Chemical Composition of Snow in Relation to Their Crystal Shapes

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(Manuscript received 12 November 1963)

Abstract

Chemical composition of snow crystals has been investigated by the analysis of snow samples collected separately according to snow crystal shapes. The chemical elements analysed were Cl, Na, NH_4 , SO_4 , Mg, Ca, NO_2 , Fe and Si. Snow crystals collected were classified into several groups; columns, rimed or not rimed dendrites, rimed radiating dendrites and graupels, etc. It has been found that the chemical composition shows marked dependence on the shape of snow crystals as follows;

- (1) The concentrations of Na, Cl and NH_4 in columnar crystals were lowest among those in all shapes of crystals.
- (2) The concentration of NH_4 was highest in dendritic crystals.
- (3) The concentrations of Cl and Na were highest in graupel. The relative concentration of the chemical elements of graupel was close to that of sea water.

1. Introduction

Chemical composition of rain water and snow has been investigated by many workers (Miyake 1939, Sugawara 1956, Junge and Werby 1958, Gorham 1958, Eriksson 1959), but our knowledge of chemical composition of snow in relation to shapes of snow crystal has not yet been obtained.

Investigation of chemical composition of snow crystals is considered to have an advantage over that of rain water for the elucidation of both the mechanism by which the chemical elements are captured in raindrops and snow crystals, and the mechanism of precipitation in cloud, because the form and the size of a snow crystal provide much information on the history of its growth including temperature, humidity, abundance of supercooled droplets in a cloud, in which it has grown. (Nakaya and Terada 1935, Nakaya 1951)

The present paper shows the chemical composition of snow which was collected separately according to the shape of snow crystals. The snow samples were collected at Kitamoshiri, which is in the northern part of Hokkaido, 600 m high above the sea level and far from industrial areas (Fig. 1).

Fig. 1. Observation site, Kitamoshiri, Hokkaido.

2. Methods of observation and measurement

Observation and sampling of snow crystals during snowfall were carried out at Kitamoshiri, 10th through 20th, January, 1963.

Procedures:

- (1) Sampling of snow crystals.
- (2) Preparation of plastic replicas of snow crystals.

To collect snow, a vinyl-sheet (2m×2m) was spread on the surface of ground snow (Photo. 1). When an appropriate amount of snow had been collected or when a shape of crystals falling was observed to change, snow on the sheet was inserted into a vinyl-sack and kept in an Igloo. After a time, the snow in the sack was put into a large glass beaker which was warmed with hot water. After the snow had been melted in the beaker, thus obtained water was poured into a polyethylene bottle and was frozen again. About one hundred of such snow samples were carried to the laboratory and chemical analyses were made with them.

While the sampling of snow crystals was made, replicas of snow crystals were prepared by the use of formar solution every 10 or 15 minutes to fix the shape and size of snow crystals. The methods of chemical analyses employed were as follows ;

Cl	Colorimetric	Mercuric-Thiocyanate
Na	Flame photometric	
NH ₄	Colorimetric	Alkaline phenol, and hypochlorite solution
SO ₄	Colorimetric	Barium chromate
	Nephelometric	Barium chloride
Mg	Titration	Mg-EDTA, EBT
Ca	Titration	KOH, 2-Hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic Acid
NO ₂	Colorimetric	1-Amino-2-naphthol-4-sulfonic Acid
Fe	Colorimetric	Thiocyanate
Si	Colorimetric	Ammonium Molybdate

3. Results

3.1 Columns

The result obtained on 13th, January, 1963 is shown in Fig. 2. Cloud form and temperatures of cloud top and cloud base obtained from radiosonde observation of Wakkanai Weather Station are shown in the upper part of this figure. The shapes and the sizes of snow crystals and the concentrations of Cl, Na, SO₄, NH₄, Mg, NO₂ and Fe in the snow crystals which were collected at each time, are also shown in the figure. In the bottom of the figure, the intensity of precipitation is shown.

Fig. 2. Time variation of concentration in columnar crystal and dendrites.

Graphic symbols and their photographs of snow shapes are given in Table 1 and in Photos. 2, 3, 4 and 5 respectively. As is seen

Table 1. Graphic symbol of snow crystal.

•	Irregular-rimed particles
⌣	Irregular snow crystals with rimed particles
□	Columns
⬡	Plates
✧	Dendrites
✳	Radiating dendrites
△	Graupel
✧•	Dendrites and Rimed-Dendrites
✳	Rimed Radiating dendrites

in the figure, the concentrations of Cl, Na and NH₄ in columnar crystals were low. With decreasing proportion of columnar crystals to dendritic crystals in snowfall, concentrations of Cl, Na and NH₄ increased.

Photo. 1. Vinyl sheet spread on the ground snow.

Photo. 2. Dendrite.

Photo. 3. Rimed Dendrite.

Photo. 4. Column-partly rimed.

Photo. 5. Graupel.

1 MM

3.2 Dendrites

Variation of the concentration of chemical elements in rimed dendritic snow crystals and not-rimed dendritic snow crystals in a snowfall is shown in Fig. 3. The concentrations of Cl, Na and NH₄ in dendritic snow crystals were high. When rimed dendritic snow crystals

Fig. 3. Time variation of concentration in dendritic crystal.

appeared, the concentration of Cl, Na and NH₄ became low.

3.3 Graupel

Fig. 4 shows time variation of the chemical but concentration of NH₄ did not change. When rimed radiating dendritic crystals fell, concentrations of Cl, Na and NH₄ became low.

	Cl ⁻	Na ⁺	NH ₄ ⁺	SO ₄ ⁻	Mg ⁺⁺	Ca ⁺⁺	NO ₂ ⁻	Fe ⁺⁺ ,***	Si
□ □ □	1.1	0.42	0.05 (1.6)	0.15	0.037	0.0008	0.026	(0.018)	
✕	4.1	1.5	0.27 (4.4)	(0.34)	(0.27)	(0.001)	0.042	(0.043)	
✕ ✕	2.3	0.68	0.25	—	(0.08)	(0.07)	(0.006)	0.045	—
✕	2.1	1.0	0.03	0.61	0.11	0.015	0.001	0.04	0.014
✕ △	4.3	1.9	0.03	1.3	0.28	0.045	0.001	0.03	0.011
Total Average	2.1	0.82	0.06	1.1	0.16	0.035	0.002	0.035	0.014

Fig. 4. Time variation of concentration in graupel and others.

elements in graupel. The concentrations of Cl, Na and NH₄ decreased with time. When dendritic snow crystals appeared, concentrations of Cl, Na and NH₄ became high. When dendritic snow crystals disappeared, the concentration of the elements decreased. When graupel began to fall, the concentrations of Na, Cl, Mg, NO₂ and Si increased abruptly, but concentration of NH₄ did not change.

When rimed radiating dendritic crystals fell, concentrations of Cl, Na and NH₄ became low.

4. Discussion

Average concentrations of chemical elements in each typical shape of snow crystals are shown in Table 2 (The samples of snow crystals obtained when snow crystals of more than two kinds of crystal shapes fell simultaneously, were omitted.). These values are an average concentration of total precipitation of each crystal shape.

The concentrations of Cl, Na and

NH_4 in snow of columnar shape were 1.1 mg l^{-1} , 0.42 mg l^{-1} and 0.05 mg l^{-1} respectively. The concentrations of Cl, Na and NH_4 in snow of dendritic shape were 4.1 mg l^{-1} , 1.5 mg l^{-1} and 0.27 mg l^{-1} respectively. The concentrations of Cl, Na, and NH_4 in graupel shape were 4.3 mg l^{-1} , 1.9 mg l^{-1} , 0.03 mg l^{-1} respectively. The values in parentheses can not be considered as representative, because the number of samples for each of time was small.

In order to consider the origins of chemical substances in snow crystals, chemical composition of snow was compared with that of the sea water and with that of aerosols of continental or industrial origin.

The ratios of the concentration of Na to Cl, Na to Mg, Na to SO_4 are shown in Fig. 5, 6, 7, respectively (The symbol $\blacktriangle$ means

Fig. 5. The ratio of the concentration of Na and Cl.

the graupel which was collected in Hokuriku district, Honshu.). The ratios between these chemical elements in graupel were close to the ratios in sea water, but the ratios in dendritic crystals were far from that in sea water. The ratio between NH_4 and SO_4 in snow crystals is shown in Fig. 8. Dendritic snow crystals contained larger amount of NH_4 than the graupel. The ratio NH_4/SO_4 in snow and graupel was very different from that of $(\text{NH}_4)_2\text{SO}_4$, as can be seen from the figure.

From a consideration of geochemical aspects of these substances, Na may be taken for

Fig. 6. The ratio of the concentration of Na and Mg.

Fig. 7. The ratio of the concentration of Na and SO_4 .

Fig. 8. The ratio of the concentration of NH_4 and SO_4 .

Fig. 9. The ratio of the concentration of Na and NH_4 for each shape of crystals.

- I. columnar crystal
- II. dendritic crystal
- III. graupel and radiating dendritic crystal

the representative chemical elements of sea origin, and NH_4 may be taken for that of industrial at least in Hokkaido. The relation between them is shown in Fig. 9.

In regards to the concentration of Na and NH_4 , snow crystals were divided into three groups. The first of them is the group of the columnar snow crystals (I). The concentrations of Na and NH_4 in this group of snow were both less than those in the other shapes of snow crystal.

The second group (II) is that of dendritic snow crystals; the concentration of NH_4 was highest and also the concentration of Na was relatively high. The ratio of chemical elements, NH_4/Na , was highest.

The third group (III) is that of graupel and rimed radiating dendritic crystals. In this case the ratio Na/NH_4 was highest of three groups. The concentration of Na was highest in graupel. Although chemical elements found in snow is considered to have been included in snow by complicated processes, it may be

reasonable to consider the following processes:

- (1) chemical elements included in ice nuclei on which snow crystal was formed.
- (2) chemical elements included in condensation nuclei of water droplets which were adhered to snow crystal especially in the case of rimed crystals.
- (3) chemical elements in aerosols captured by snow crystal during its growth in clouds.
- (4) chemical elements in aerosols captured by a snow crystal after its leaving from cloud base (a) by Brownian motion of aerosol particles to snow crystal or (b) by the gravitational accretion process.

In order to know which process was important, some considerations are made. The facts that chemical concentration in columnar crystal was less than in the other shapes of snow crystals and that the cloud base from which columnar crystals fell was very near to the ground, show that the process (1) may be discarded so far as the chemical elements

discussed in the present paper are concerned, because the ice nuclei in the atmosphere over Japan have been found to be mainly particles of minerals, and loess (Kumai 1961, Isono 1955) in the concentration to be considered. Loess include Na element only about 1% to total chemical elements (Miyake and others 1956). Columnar crystal whose length is 1 mm, is 0.005 mg according to Nakaya. If this columnar crystal is formed on loess particle of diameter 2μ , the concentration of Na in columnar crystal is below 0.1 mg l^{-1} . The concentration of Si in snow crystals which is considered to be due to clay minerals or loess was 0.02 mg l^{-1} . This fact also shows that Na which is due to clay minerals or loess must be below 0.002 mg l^{-1} . As the concentration of chemical element in irregular rimed particles and rimed columnar crystal was low, cloud droplets on such crystals must have been formed on small condensation nuclei which do not include large amount of soluble Na and NH_4 . The amount of chemical elements obtained in cloud must have been small, because the concentration of aerosol

particles in cloud must be low. Therefore, the fact that the concentration in dendritic crystal is higher than columnar crystal may result from the longer distance from cloud base to ground in dendritic crystal. If most amount of chemical elements of dendritic snow crystals is captured below cloud base, the chemical concentration in dendritic snow crystals must have some relation with the height of cloud base above the ground. Fig. 10 is a plot of the concentration of NH_4 and Na in dendritic and columnar crystal obtained at first stage of snow fall against the height of the cloud base above the ground. According to Nakaya's diagram, dendritic crystals grow at temperatures between -14°C and -17°C and columnar crystals grow between -9°C and -14°C or between -17°C and -21°C under the condition whose relative humidity over ice is 110%. As it is difficult to determine the height of the cloud base from 12-hour radiosonde's data, the height of cloud base is assumed to be the height at which snow crystal ceased to grow. It is tentatively assumed that grown up dendritic crystals fall out of the cloud base at -14°C and grown up columnar crystals fall out of the cloud base at -9°C . During the fall no growth and no evaporation are assumed to occur. The height of these temperature levels are determined from radiosonde's data and the surface data at the site. The fall speed of dendrite is assumed to be 30 cm sec^{-1} by Nakaya and Terada.

The relation between concentration and the height of cloud base is shown at the upper part of Fig. 10. When the height of cloud base increases from 500 m to 1000 m, the concentration of NH_4 increases with the height of cloud base. Sample (A) was collected at the beginning of a snowfall after absence of snowfall longer than a day, so that the concentration of aerosol particles in air in this case was likely to be higher as compared with that in other samples.

As for Na, the relation between its concentration in snow and the height of cloud base is shown in the lower part of Fig. 10. The concentration of Na increases with the height of cloud base except the sample (A). This fact shows that the aerosol particles containing Na reach at least the level 1500 m above the ground. In order to explain above

Fig. 10. Upper: Concentration of NH_4 against the height of cloud base.

Lower: Concentration of Na against the height of cloud base.

results, two mechanisms are considered. One of these is that due to the Brownian motion of aerosol particles to snow crystals and the other is that due to washing out of aerosol particles by the gravitational accretion process.

At first, the rate of capture of aerosol by Brownian motion is calculated, assuming the form of the dendritic crystal as a disk of radius r in order to simplify the following calculation. The electrostatic capacity of this disk is denoted by c , a mass of this disk by m , the radius of aerosol particles by r' and the number of the aerosol particles per unit volume in the air by n . The total number of aerosol particles which is captured to the snow crystal by the process of Brownian motion (n') is

$$\frac{dn'}{dt} = 4\pi c D n \quad (1)$$

, where D is the diffusion constant of the aerosols in the air due to Brownian motion. In the case of a disk, this equation becomes

$$\frac{dn'}{dt} = 4\pi \frac{2r}{\pi} \frac{RT(1+AL/r')}{6\pi\eta r' N} n \quad (2)$$

, where η is viscosity of the air, R is the gas constant, L is the mean free path of air molecules, N is the Loschmidt's number, and A is a constant. If we put $r=0.1$ cm, the mass m of that snow crystal is 0.02 mg according to Nakaya and Terada (1935). The mass of an aerosol particle is denoted by M , and the concentration of NH_4 or Na in it by k . The concentration (K) of aerosol particles in the snow crystal at 1000 seconds after the beginning of attachment is given by

$$K_{1000 \text{ sec}} = \frac{kM}{m} \int_0^{1000} \frac{dn'}{dt} dt \\ = 5 \cdot 10^{-4} \frac{1+8 \cdot 10^{-6}/r'}{r'} nkM \quad (3)$$

The concentration of aerosol calculated by this equation is given in Table 3.

Table 3. The concentration of aerosol particles in a snow crystal calculated.

	$r'=1 \mu$	0.1μ	0.01μ
$K(1000 \text{ sec})$	$5 \cdot 10^{-4} \text{ mg } l^{-1}$	$10^{-3} \text{ mg } l^{-1}$	$0.05 \text{ mg } l^{-1}$

As for washing out of the aerosol particles

by the gravitational accretion process, the concentration aerosol in a snow crystal (K) is given by

$$K = k' \frac{knML'\pi r^2}{m} \quad (4)$$

, where L' is the height of cloud base and K' is the collection efficiency. The collection efficiency is calculated by Langmuir's diagram. It is assumed that the collection efficiency concerning snow crystal can apply to the calculation concerning ribbon. As for the case when diameter of snow crystal is replaced by the width of ribbon, the collection efficiency (K') of aerosol particle whose radius is 5μ becomes 0.05. When the aerosol particle is assumed to be captured to the branch of snow crystal, the collection efficiency of aerosol particle whose radius is 1.2μ , becomes 0.05, assuming the width of branch of snow crystal is one tenth of the diameter of this crystal. The concentration of sea salt nuclei is referred to the observation of Woodcock (1953). As observation site, Kitamoshiri is only 20 km far from sea coast, the observation of Woodcock of the height 1000 m over sea is assumed to be able to use in Hokkaido. The concentration of sea salt nuclei whose radius is greater than 5μ , is $0.3 \mu\text{g m}^{-3}$ and that is greater than 1.2μ , is $1.6 \mu\text{g m}^{-3}$. When the concentration of Na in giant sea salt nuclei is assumed to be 0.5, the concentration of aerosol particles captured in a snow crystal while it fell from the cloud base 1000 m above the ground, is given in Table 4, where it is assumed that the size of sea salt nuclei is uniformly 5μ or 1.2μ , and their concentration is $0.3 \mu\text{g m}^{-3}$ or $1.6 \mu\text{g m}^{-3}$ respectively. Surface area is assumed to be the same in both considerations.

Table 4. The concentration of aerosol particles in a snow crystal captured by gravitational accretion process.

	As the ribbon whose width is 2mm	As the ribbon whose width is 0.2mm
$K_{1000 \text{ m}}$	$1.1 \text{ mg } l^{-1}$	$5.8 \text{ mg } l^{-1}$

Though the chemical composition of containing NH_4 does not seem to be $(\text{NH}_4)_2\text{SO}_4$ as suggested by Junge (1953), the size of aerosol

particles containing NH_4 must be below radius 1μ . As the size of radius smaller than 1μ can not be captured in snow crystal by the gravitational accretion process, NH_4 is captured in crystal by Brownian motion. The calculated values in which the radius of aerosol particle is assumed to 0.01μ , are plotted in the upper part in Fig. 10. The order of observed value can be explained. Therefore, NH_4 might be captured by the snow crystal by Brownian motion from the cloud base to the ground. A line which is denoted at the lower part of Fig. 10, shows the calculated value in which aerosol particle is captured by the gravitational accretion process. The calculated value may also explain the order of observed value. This concentration becomes higher if the aerosol particle is captured to the branch of snow crystal. If aerosol particle was captured by the Brownian motion, $r'=0.01\mu$, $n=1000\mu\text{gm}^{-3}$ must be assumed in order to explain the observed value. Therefore, it might be said that Na in dendritic crystal is captured by the gravitational accretion process from the cloud base to the ground.

Third group (III) is that of graupel and rimed radiating dendritic crystals. The characteristic nature of this group is highest concentration of Na and low concentration of NH_4 . The high concentration of Na in graupel may be explained as follows. Graupel has been found to consist of many large frozen droplets from microscopic study of thin section of graupel (Magono and the author 1961). From the fact that the chemical composition of graupel was close to that of sea water, it is considered that large frozen droplets included in graupel were formed initially on giant sea salt nuclei. Low concentration of NH_4 in graupel may be explained as follows; falling speed of graupel is 2m sec^{-1} by Nakaya and Terada, which is seven times of the falling speed of dendritic crystal, so that elapsed time from cloud base to the ground becomes one-seventh of that of dendritic crystal, assuming height of cloud base is the same in both crystal shapes. If NH_4 is captured by Brownian motion, graupel may capture only one-seventh of NH_4 as compared with the value of dendritic crystal. The reason why rimed radiating dendritic crystal has less concentration of

NH_4 than the other groups, may be explained as the same as the case of graupel. The value of the concentration of Na in rimed radiating dendritic crystal varied with samples. These variations may be explained as follows; even if the amount of Na captured below cloud base in graupel and rimed radiating dendritic crystal, is the same of dendritic crystal, the concentration in the former must be lower than the latter, because the mass of graupel, rimed radiating dendritic crystal and dendritic crystal of each same diameter 2mm , is 0.4mg , 0.1mg and 0.02mg respectively. The concentration becomes one 20th and one 5th compared with dendritic crystal. Therefore, the concentration of Na in graupel and radiating dendritic crystal may not be settled below cloud but in the cloud. The high concentration of Na in some rimed radiating dendritic crystal must be due to the capturing of cloud droplets formed on giant nuclei in cloud.

5. Conclusion

Chemical elements have been analysed for each shape of snow crystals. Results obtained are as follows:

- (a) The concentrations of chemical elements differed in each shape of snow crystals systematically, that is, columnar crystal, dendritic crystal and graupel had different chemical compositions respectively.
- (b) The concentration of Na, Cl and NH_4 in columnar crystals was lowest among other shapes. The low concentration may be due to the shorter path from cloud base to the ground.
- (c) The concentration of NH_4 was greatest in the dendritic crystals. The ratio of chemical elements, NH_4 to Na in dendritic snow crystal was largest among that ratio in all shapes. Na and NH_4 in dendritic crystal are considered to have been captured mainly during the fall from cloud base to the ground.
- (d) The concentrations of Cl and Na were greatest in graupel. The ratio of Na to NH_4 is largest in graupel and rimed radiating dendritic crystal. The relative composition of the chemical elements of graupel was close to that of the sea water. This may be due to

the large frozen droplets formed on giant sea salt nuclei which were present in graupel body.

To clarify the present problem more definitely, simultaneous measurements of chemical elements of snow crystal and aerosol particles in the air is considered to be urgently needed.

Acknowledgement

The author wishes to express his best thanks to Prof. K. Isono and Dr. M. Komabayasi for their useful suggestions. The author is deeply indebted to Prof. Y. Kitano, Prof. Y. Saijo, Dr. N. Kanamori and Dr. N. Handa for their kind instructions for the procedure of chemical analyses. His great thanks is to Prof. S. Sasao, Hokkaido University who offered many facilities for the observation in Kitamoshiri area.

This work is a part of "Studies of cloud physics and mechanisms of rainfall over the Pacific and isolated island."

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雪の形と化学成分

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雪の形別に採集した試料について、その含有化学成分、Cl, Na, NH_4 , SO_4 , Ca, Mg, NO_2 , Fe, Si を測定した。雪は柱状結晶・雲粒つき六花・六花・放射状六花・霰などに分類された。含有化学成分は、雪の形別に特徴的なあらわれ方をすることがわかった。

- (1) 柱状結晶中では、Na, Cl, NH_4 の濃度は他の結晶形のものに比べ最も少ない。
- (2) NH_4 の量は六花に最も多く含まれている。
- (3) Cl と Na の濃度は、霰で最大で、Cl と Na の比は、海水中の Cl と Na の比と非常に近い。