SOME CONSIDERATIONS ON THE CENTER NUCLEI OF SNOW CRYSTALS

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Abstract: By adopting ultra-marine blue particles as standard material, a simple method for converting the X-ray intensity ratio in the energy spectra into the weight concentration ratio was developed. This method was applied to the center nuclei of snow crystals and airborne aerosol particles to find information on the origin of nuclei and particles. At Moshiri and Mt. Teine, the center nuclei of snow crystals mainly consisted of soil particles and sea salt particles, while at Yukomambetsu, they mainly consisted of soil particles and particles rich in S. From the comparison between the Si : Na : S ratios of the center nuclei of snow crystals and those of airborne aerosol particles collected at Mt. Teine, it was concluded that soil particles and sea salt particles of some size functioned as the center nuclei of snow crystals. In order to determine the materials of center nuclei of snow crystals in more detail, however, the relative weight fractions of the elemental compositions other than Si, Na, and S must be considered.

1. Introduction

The identification of material of the center nuclei of snow crystals was done with the aid of electron micrographs and electron diffraction patterns thirty years ago (KUMAI, 1951, 1961; ISONO, 1955; KUMAI and FRANCIS, 1962). On the other hand, an energy dispersive X-ray microanalyzer can detect all elements with an atomic number greater than eleven (Na) in one spectrum. Combined with a scanning electron microscope, therefore, information about the morphology of particles can be obtained simultaneously with the elemental composition. As the analytical time of the energy dispersive X-ray microanalyzer is of a very short duration and the analytical procedure is very easy as compared with the wave-length dispersive X-ray microanalyzer, the energy dispersive X-ray microanalyzer interfaced with a scanning electron microscope has the great advantage of giving the elemental composition of center nuclei of snow crystals in the growth mechanism of snow crystals in cloud physics and the scavenging effects in aerosol science in which too many

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particles must be treated.

The authors (KIKUCHI *et al.*, 1982) analyzed the elemental composition of center nuclei of general and peculiar shapes of snow crystals with a scanning electron microscope (SEM) and energy dispersive X-ray microanalyzer (EMAX) in the previous paper. On the basis of the frequency distribution of elements contained in the center nuclei of snow crystals, they suggested that the elemental composition of center nuclei of general shapes of snow crystals differs with the sampling locations and that the elemental composition of center nuclei of peculiar shapes of snow crystals has only slight differences compared with those of general shapes of snow crystals. However, they indicated the percentage in number of particles containing a certain element, but not the mass percentage of the element. So the frequency distributions of elements present in the center nuclei alone are not sufficient to identify the materials of the center nuclei or to determine the origin of materials. In order to investigate the origin of materials of center nuclei of snow crystals, the relative weight fraction of three elements present in center nuclei was considered. Especially in this work, the elements of Si, Na, and S were selected as standards for soil particles, sea salt particles, and sulfate particles, as combustion products originating in human activity, respectively. Similar considerations were also given to atmospheric aerosols which were closely related to center nuclei of snow crystals.

2. Conversion of X-ray Intensity Ratio into Weight Concentration Ratio

The information which is directly obtained from an energy dispersive X-ray microanalyzer (EMAX) is an intensity of characteristic lines of individual elements in the form of an X-ray energy spectrum. In general, the X-ray intensity ratio is not equal to the weight concentration ratio. Accordingly, in order to convert the X-ray intensity ratio into a weight concentration ratio, a relationship between both ratios must be obtained in advance. When ISHIZAKA and ISONO (1980) analyzed the aerosol particles with an electron microprobe, they used pure oxides with flat surfaces as a standard in order to determine the weight concentration ratio of elements. In this work, a simple method was adopted for this purpose. This will be described as follows:

A weight concentration ratio (C_d^A/C_d^B) of the elements A to B present in a particle of diameter (d) can be approximately given by

$$\frac{C_d^A}{C_d^B} = \frac{K_d^A}{K_d^B} \cdot \frac{S_d^A}{S_d^B} \cdot \frac{A_d^A}{A_d^B} \cdot \frac{Z_d^A}{Z_d^B} \cdot \frac{F_d^A}{F_d^B} , \qquad (1)$$

where

K_d^A (K_d^B) : the ratio of the background-corrected X-ray intensity of element A (B) present in the particle of diameter (d) relative to that of pure A (B) with a flat surface,

S_d^A (S_d^B) : the correction factor of particle size effect,

A_d^A (A_d^B) : the correction factor of absorption path effect,

Z_d^A (Z_d^B) : the correction factor of atomic number effect,

F_d^A (F_d^B) : the correction factor of secondary fluorescence effect.

Since the atomic numbers of elements present in the center nuclei of snow crystals and aerosol particles in the free atmosphere, as seen in Figs. 12 and 13 of the previous paper (KIKUCHI et al., 1982), are relatively small and further in a narrow range, four correction factors in eq.(1) are considered to be almost negligible in the case of the same particles. Therefore, eq.(1) is rewritten as:

$$\frac{C_d^A}{C_d^B} \doteq \frac{K_d^A}{K_d^B} = \frac{k_d^A}{k_d^B} \cdot \frac{k_p^B}{k_p^A} , \qquad (2)$$

where

k_d^A (k_d^B) : the background-corrected X-ray intensity of element A (B) present in the particle of diameter (d),

k_p^A (k_p^B) : the background-corrected X-ray intensity of element A (B) present in the pure A (B) with a flat surface.

The ratio of the background-corrected X-ray intensity of pure A with a flat surface to that of pure B with a flat surface is considered to be constant, so that using the proportional constant γ_B^A, eq.(2) can also be rewritten as:

$$\frac{C_d^A}{C_d^B} \doteq \gamma_B^A \frac{k_d^A}{k_d^B} . \qquad (3)$$

The proportional constant γ is determined by examining the X-ray intensities of the elements present in the standard particles of which the weight concentration ratio is known. The weight concentration ratios of center nuclei of snow crystals and aerosol particles in the free atmosphere are obtained using eq.(3).

In this work, an ultra-marine blue ($Na_x \cdot Al_x \cdot Si_{(12-x)} \cdot O_{24} \cdot Na_y \cdot S_z$) was adopted as the standard material which contained the individual elements of Si, Na, and S. Although the chemical composition of the ultra-marine blue has some uncertainty as seen from its chemical formula, the average weight percentages of individual elements of Si, Na, and S are $18 \pm 1\%$, $16 \pm 1\%$, and $12.5 \pm 1\%$, respectively. Therefore, the weight concentration ratio of these three elements in ultra-marine blue is considered to be nearly constant.

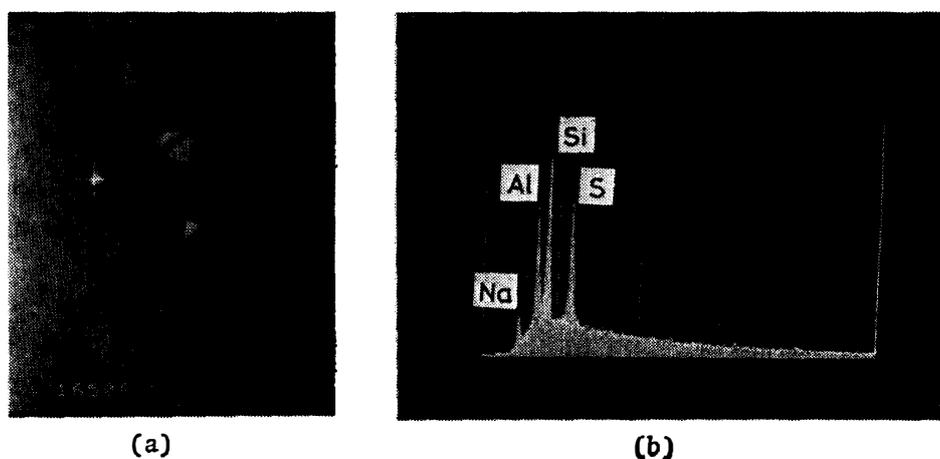Figure 1 shows an electron micrograph of an ultra-marine blue particle (left)

(a)   (b)

Fig. 1.   An electron micrograph of an ultra-marine blue particle (a) and its X-ray energy spectrum (b).
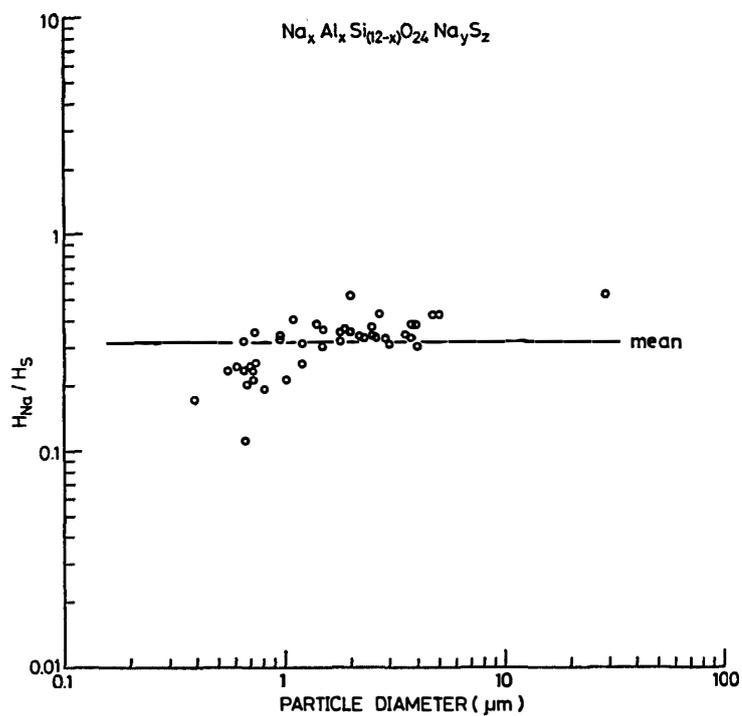
Fig. 2. *Peak height ratios in the X-ray energy spectrum of Na to S present in the ultra-marine blue particles related to their diameters.*
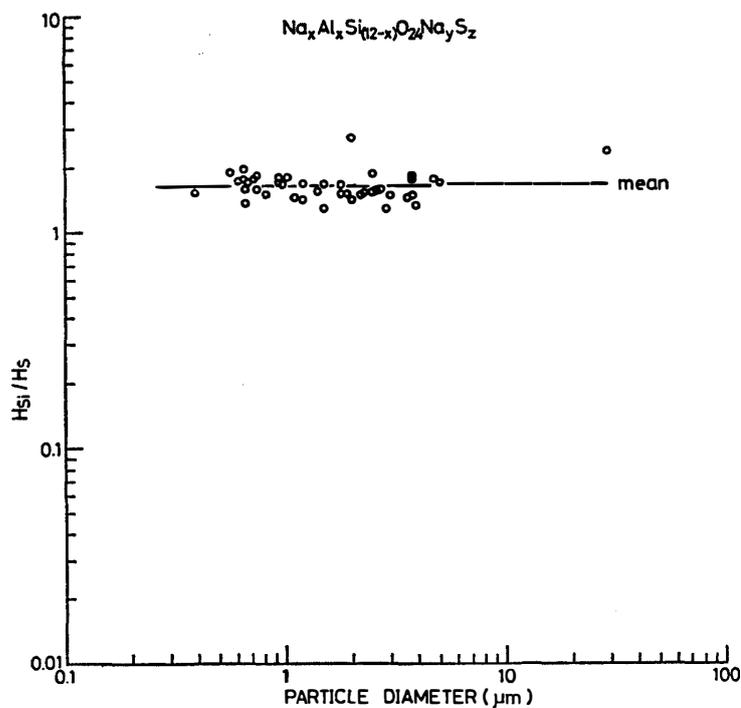

Fig. 3. *Peak height ratios in the X-ray energy spectrum of Si to S present in the ultra-marine blue particles related to their diameters.*

and its X-ray energy spectrum (right). The horizontal bar at the lower right corner of the electron micrograph is on the scale of 5 μm. The four peaks which are shown in the X-ray energy spectrum, are the K$_\alpha$ line of Na, the K$_\alpha$ line of Al, the K$_\alpha$ line of Si, and the K$_\alpha$ line of S from left to right, respectively. A white continuous dotted line in the X-ray energy spectrum shows the background of the spectrum. In this work, the ratio of the background-corrected peak heights of the X-ray energy spectrum was substituted for the X-ray intensity ratio. Figure 2 shows the peak height ratios in the X-ray energy spectrum of Na to S present in the ultra-marine blue particles related to their diameters. The mean value of these ratios is 0.32 as shown by a horizontal line in the figure although their values were scattered to some extent. Figure 3 shows the peak height ratios of Si to S present in the particles described above related to their diameters. The mean value of these ratios is 1.64.

In order to check whether the scattering of the peak height ratios in Figs. 2 and 3 may be attributed to the uncertainty of the chemical composition of the ultra-marine blue, the peak height ratios of Na to Cl in sodium chloride particles that have uniform chemical compositions were examined by the same X-ray microanalyzer, and the results are shown in Fig. 4. As seen in Fig. 4, these ratios were scattered to some extent in spite of the uniformity of their chemical composition. Accordingly it is considered that the scattering of peak height ratios may be attributed to the marginal errors in measuring the peak height and the statistical fluctuation of the X-ray intensity. Therefore, the values of γ_S^{Na} γ_S^{Si} which are determined using the peak height ratios of the three elements of Na, Si, and S, and
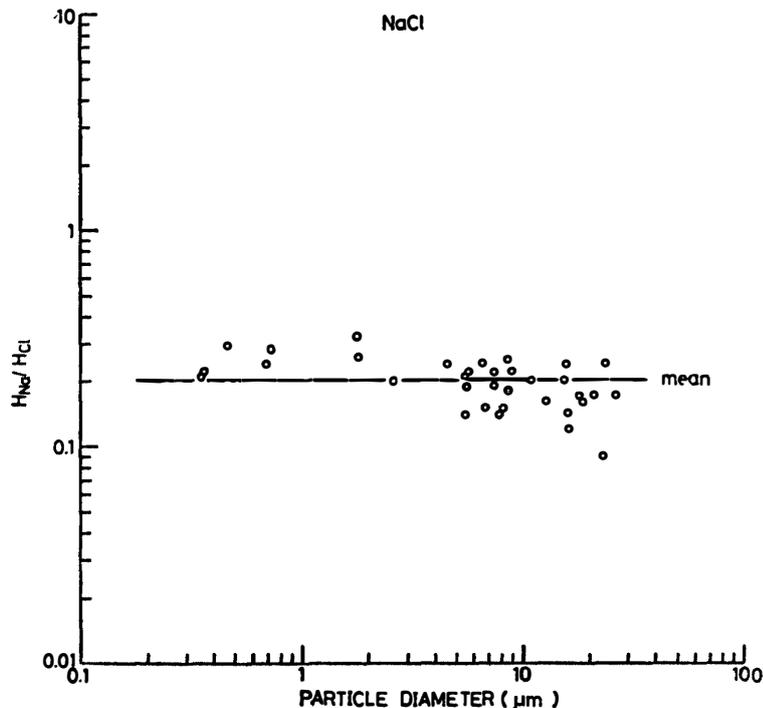

Fig. 4. Peak height ratios in the X-ray energy spectrum of Na to Cl present in the sodium chloride particles related to their diameters.
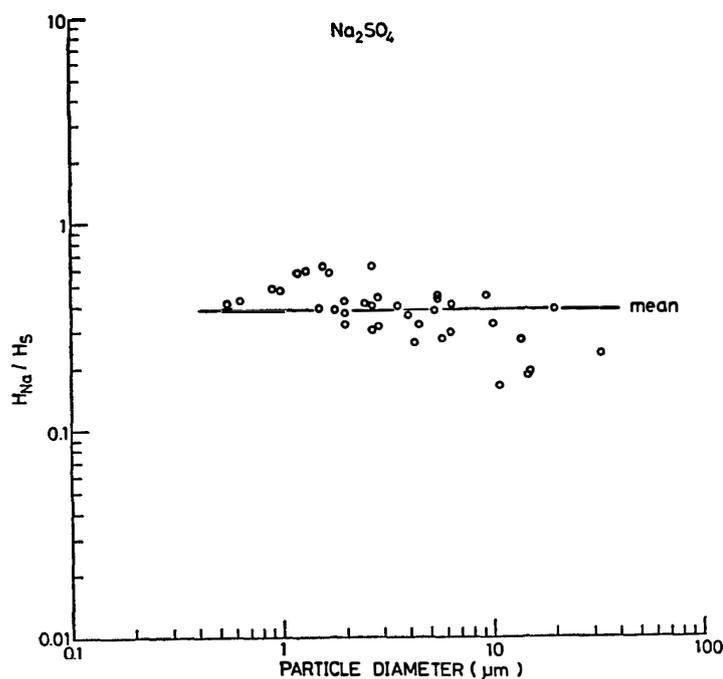
*Fig. 5.   Peak height ratios in the X-ray energy spectrum of Na to S present
in the sodium sulfate particles related to their diameters.*

their weight concentration ratios in the ultra-marine blue particles, are 4.0 and
0.91, respectively. In order to ascertain whether eq.(3) is applicable to other mate-
rials, sodium sulfate particles whose weight concentration ratios of Na to S are
different from those of the ultra-marine blue particles were examined. Figure 5
shows the peak height ratios of the X-ray energy spectrum of Na to S present in
sodium sulfate particles related to their diameters. The mean value of these ratios
is 0.38, as shown by a horizontal line. Using this value and the weight concentra-
tion ratios of Na to S present in sodium sulfate particles, the r_S^{Na} is determined to
be 3.8. This value is nearly equal to 4.0 for the ultra-marine blue particles. The
applicability of eq.(3) to other materials is also supported by WHITE (1964).

The results described above indicate that eq.(3) is applicable to obtain in-
formation about the center nuclei of snow crystals and aerosol particles with suffi-
cient accuracy.

3.   The Si : Na : S Ratio of Center Nuclei of Snow Crystals

Figure 6 shows triangle diagrams of the Si : Na : S ratios of center nuclei of
snow crystals collected at Moshiri, Yukomambetsu, and Mt. Teine from January
to March 1981. These locations will be referred to in Fig. 1 by KIKUCHI *et al.*
(1982). In the figure, each solid circle and each open rectangle in the diagrams
indicates the relative weight fractions of Si, Na, and S present in the center nuclei
of general- and peculiar-shaped snow crystals, respectively. The relative weight
fraction to the composition of sea water is also marked with a cross in the diagrams.

In the case of snow crystals collected at Moshiri, the center nuclei rich in Si

Fig. 6. Relative weight fractions of Si, Na, and S in the center nuclei of snow crystals collected at Moshiri, Yukomambetsu, and Mt. Teine in the winter season of 1981. ● : general-shaped snow crystals, □ : peculiar-shaped snow crystals, X : relative weight fraction values for the elemental composition of sea water.

and Na are predominant. As Moshiri is located 30 km leeward inland from the seashore of the Sea of Japan, the air containing many sea salt particles may arrive over Moshiri when the northwest monsoon is prevailing. Therefore, it may be expected that center nuclei rich in Na are sea salt particles originating from the Sea of Japan. On the other hand, it may expected that center nuclei rich in Si are soil particles originating from the Asia continent because in the winter season, almost all of Hokkaido Island is covered by a deep snow cover. Thus the soil particles cannot be blown from the ground surface.

In the case of snow crystals collected at Yukomambetsu, the center nuclei rich in Si and S are predominant. Center nuclei consisting of sea salt particles were very scarce. The reason for this may be that Yukomambetsu is located 100 km leeward inland from the seashore of the Sea of Japan, so that sea salt particles are scarce in Yukomambetsu because of precipitation scavenging and dry deposition on their way. The center nuclei rich in S may be not sulfate particles originating from human activities but particles originating from volcanic fumaroles, considering that there are many volcanic fumaroles near the Yukomambetsu area. Although four center nuclei of peculiar shapes of snow crystals were analyzed, no clear tendency was seen. Namely, there were two nuclei rich in Si, one nucleus rich in Na, and one nucleus rich in S.

In the case of snow crystals collected at the top of Mt. Teine, the center nuclei rich in Si and Na are predominant, although the number of center nuclei analyzed is limited. The reason why the sea salt particles are predominant is that Mt. Teine is located only 10 km inland from the seashore.

4. The Si : Na : S Ratio of Airborne Aerosol Particles

Aerosol particles in the free atmosphere were collected onto Nucleopore filters of 47 mm diameter with pore size of 0.2 μm during the collection of snow crystals simultaneously at the top of Mt. Teine (KIKUCHI et al., 1982). Figure 7 shows a diagram of the Si : Na : S ratios of aerosol particles. In this figure, the Si : Na : S ratios of giant particles ($d \geq 2 \mu$m), large particles (0.2 μm$<d<2 \mu$m), and Aitken particles ($d \leq 0.2 \mu$m) are marked with open triangles, open circles, and solid circles,
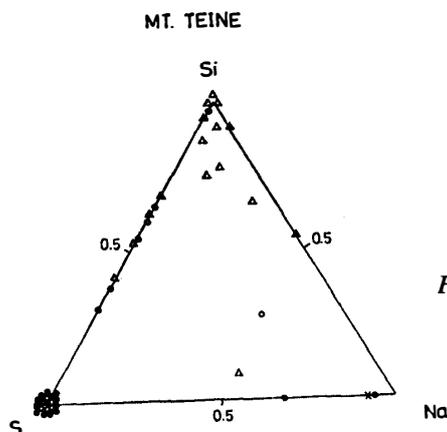
MT. TEINE

Fig. 7. Relative weight fractions of Si, Na, and S in the aerosol particles collected at Mt. Teine in the winter season of 1981. △ : giant particles (d ≥ 2 μm), ○ : large particles (0.2 μm < d < 2 μm), ● : Aitken particles (d ≤ 0.2 μm).

respectively. As clearly seen from the figure, most of the giant particles consist of soil particles rich in Si, while most of the Aitken particles consist of sulfate particles rich in S. Large particles show characteristics falling between giant and Aitken particles. The reason why airborne giant and large particles rarely consist of sea salt particles rich in Na may be that sea salt particles in these size ranges are efficiently consumed as cloud condensation nuclei in the free atmosphere. Accordingly, it should be considered that sea salt particles existing in the layer where the precipitation particles were formed although they scarcely existed in the subcloud layer. Taking the elemental compositions of center nuclei of snow crystals and aerosol particles into consideration, as far as the snow crystals collected at Mt. Teine are concerned, it is thought that soil particles and sea salt particles whose sizes were relatively large functioned as the nuclei of snow crystals exclusively, while sulfate particles whose sizes were relatively small did not.

5. Conclusions

By adopting the ultra-marine blue particles as a standard material, a simple method for converting X-ray intensity ratio in energy spectra into the weight concentration ratio was developed. And then, this method was applied to the center nuclei of snow crystals and airborne aerosol particles to obtain information about the origin of nuclei and particles. From considerations of the Si : Na : S ratios, the following results were obtained: at Moshiri and Mt. Teine, the center nuclei of snow crystals mainly consisted of soil particles and sea salt particles, while at Yukomambetsu, they mainly consisted of soil particles and particles rich in S. Particles rich in S at Yukomambetsu may be not sulfate particles originating from human activity but particles originating from volcanic fumaroles existing around the sampling locations. The center nuclei of snow crystals rich in Si, which were predominant at each sampling location, were considered to be soil particles originating from the Asiatic continent, because in the midwinter season, Hokkaido Island was almost all covered with deep snow.

From the comparison between the Si : Na : S ratios of the center nuclei of snow crystals and those of airborne aerosol particles collected at the top of Mt. Teine, it was concluded that soil particles and sea salt particles of certain sizes

functioned as center nuclei of snow crystals. In order to determine the materials of center nuclei of snow crystals in more detail, however, the relative weight fractions of the elemental compositions other than Si, Na, and S must be considered.

Acknowledgments

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