PRELIMINARY MEASUREMENTS OF THE CENTER NUCLEUS OF SNOW CRYSTALS USING AN ENERGY DISPERSIVE X-RAY MICROANALYZER

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***Abstract*:** Using a scanning electron microscope and energy dispersive X-ray microanalyzer, the elemental composition of center nuclei of general and peculiar shapes of snow crystals was analyzed. As a result, it seems that the elemental composition of center nuclei of general shapes of snow crystals differs with the sampling locations. Further, in comparison with the elemental composition between the center nuclei of general and peculiar shapes of snow crystals, it seems that there is a slight differences between the both shapes of snow crystals.

1. Introduction

It is very important to know the elemental composition of the center nucleus of snow crystals in the growth mechanism of snow crystals in cloud physics and in the snow scavenging effect in aerosol science. However, there have been a few measurements up to the present. In the past thirty years, the identification of nuclei of snow crystals was mainly carried out by means of electron micrographs and electron diffraction patterns of the specimens of snow crystals collected in the Northern Hemisphere (KUMAI, 1951, 1961; ISONO, 1955; KUMAI and FRANCIS, 1962). The results of these works showed that the center nuclei of snow crystals were mainly clay minerals. Recently, KUMAI (1976) identified the center nuclei of snow crystals collected at the South Pole Station, Antarctica by means of the same techniques described above, and he concluded that the nuclei were mainly composed of clay minerals and sodium chloride particles. Further, he reported that clay mineral nuclei were illite 20%, kaoline 8%, halloysite 4%, vermiculite 3%, and related minerals 24%, and for the other nuclei sodium chloride 20% and unidentified nuclei 5%. However, 15% of snow crystals did not appear to have nuclei. The shapes of snow crystals collected at South Pole Station, Antarctica were mainly columnar forms, that is, single bullets, combination of bullets, and hexagonal hollow columns under the temperature conditions between -30° and -35°C. On the other hand, the analysis techniques of the composition of nuclei and aerosol particles are progressing; for instance, an energy dispersive X-ray microanalyzer seems to be the most useful. PARUNGO *et al.* (1979) examined the composition of aerosol particles in the free atmosphere at South Pole Station, Antarctica by means of a scanning electron microscope (SEM) interfaced with an X-ray energy spectrometer (XES). They indicated that more than 50% (in number) of the giant particles contain Al and Si, and more than 20% contain S, Cl, K, and Fe. For Aitken particles, more than 50% contain Al and S, 35% contain Si; other elements are in minute percentages. Thus, an energy dispersive X-ray microanalyzer interfaced with a scanning electron microscope can identify the elements heavier than Na constituting the specimens and the surface of specimens can be examined simultaneously. It is thought that the above-described instruments would be reliable techniques for the identification of center nuclei of snow crystals.

Concerning the shapes of snow crystals, one of the authors (K.K.) discovered a number of peculiar shapes of snow crystals at Syowa Station and South Pole Station, Antarctica and Arctic Canada (KIKUCHI, 1969, 1970; KIKUCHI and YANAI, 1971; KIKUCHI and HOGAN, 1976, 1979; KIKUCHI and KAJIKAWA, 1979; KAJIKAWA *et al.*, 1980; MAGONO and KIKUCHI, 1980; KIKUCHI *et al.*, 1982). In general, the crystal habits of snow crystals have been well known to be decided by the air temperature and supersaturation with respect to ice surface (NAKAYA, 1954) or the air temperature and excess vapor density (KOBAYASHI, 1961). Crystal habits of peculiar shapes of snow crystals, however, have not been well known until the present. KOBAYASHI *et al.* (1976) attempted to explain the growth mechanisms to one of the peculiar shapes, for instance, "Gohei" shaped snow crystals by the "Generalized Coincidence Lattice Site" model. Certainly, although the crystal habits of snow crystals are decided by the air temperature and water vapor in the atmosphere, it may be considered that the center nucleus has an effect on determining the crystal habits of snow crystals. Therefore, we attempted to examine the composition of center nuclei of snow crystals by means of the energy dispersive X-ray microanalyzer interfaced with the scanning electron microanalyzer.

2. Instruments and Preparation of Specimens

Instruments used to identify the center nuclei of snow crystals are the HITACHI SEM-S430 scanning electron microscope and the HORIBA EMAX-1800E energy dispersive X-ray microanalyzer. The resolving power guaranteed by the manufacturer is 60 Å (0.006 μm) of the SEM. Concerning the collection of snow crystals for the analysis of the SEM, the following three methods were used: an ordinary replica solution method made one volume percent of polyvinylformvar to dichroethane coated on glass slides, a vapor method using 30% chroloform coated on glass slides, and methyl 2-cyanoacrylate (MCA) replica (ODENCRANTZ and HILDEBRAND, 1971) on carbon stages. The thickness of the polyvinylformvar, chroloform, and MCA was adjusted for use in the SEM in such a way that it was not too thick to give good resolution and not so thin that it would be damaged by irradiation by the electron beam. In our measurements, the MCA replica on carbon stages was good for these measurements.

3. Sampling Locations for Snow Crystals

Moshiri, Yukomambetsu, and Mt. Teine, Hokkaido Island, Japan were selected as the sampling locations for snow crystals. These are the Moshiri Branch, Uryu Experimental Forest, Faculty of Agriculture, Hokkaido University, Mt. Taisetsu Natural Science Research Laboratory at Yukomambetsu, Hokkaido University of Education, and Mt. Teine Cloud Physics Observatory, Faculty of Science, Hokkaido University, respectively. The locations are shown in Fig. 1. Moshiri is 290 m (a.s.l.) and is in a small basin surrounded by heights of several hundred meters. It is famous because it has recorded a minimum temperature about −40°C, the lowest in Japan. It is hoped that Moshiri will provide a favorable environment for growing peculiar shapes of snow crystals. The altitude of Yukomambetsu is 1100 m (a.s.l.) and the depth of snow cover here is approximately 3 m. Since Yukomambetsu is at the foot of Mt. Asahi (2290 m a.s.l.), the mean minimum air temperature in mid-winter is lower than −15°C and aesthetic and non-rimed snow crystals may be expected to be grown under the conditions of sublimation and condensation. The Mt. Teine Cloud Physics Observatory is situated close to the summit of Mt. Teine (1024 m a.s.l.). Mt. Teine is located approximately 10 km from the shoreline of Ishikari Bay. It snows frequently under the winter monsoon condition under the pressure pattern of west-high and east-low.

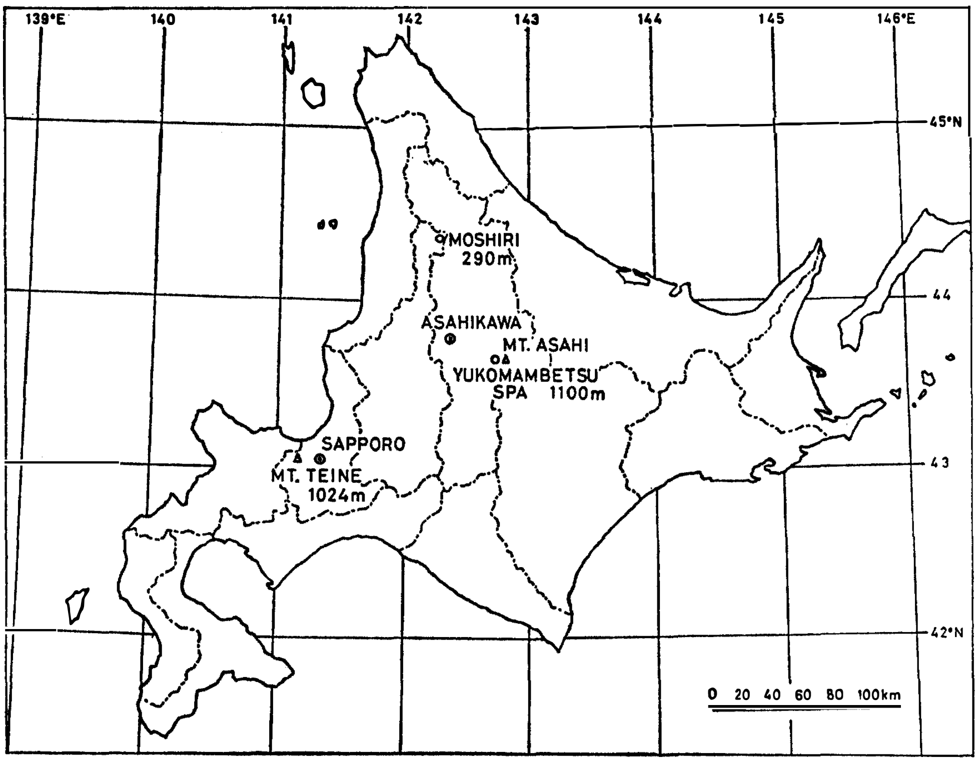


Fig. 1. Sampling locations of snow crystals.

4. Results and Discussion

4.1. Analysis of individual particles of general shapes of snow crystals

Figures 2 and 3 show analyzed examples of snow crystals collected at Mt. Teine. Figure 2 is one of the cases of stellar crystals as shown in (a). An inserted scale shows 500 μm in length, hence the crystal diameter is approximately 1.2 mm.

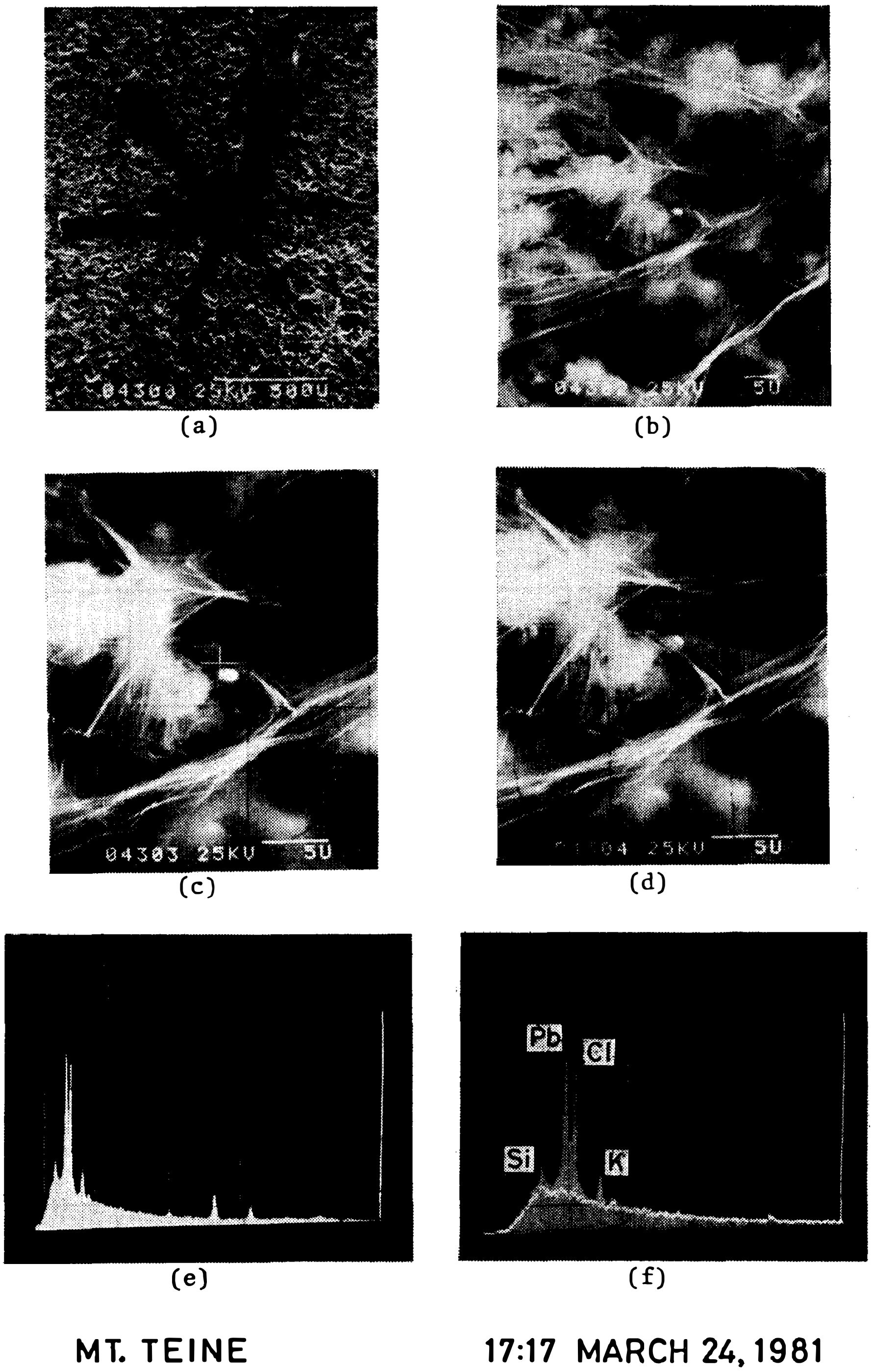
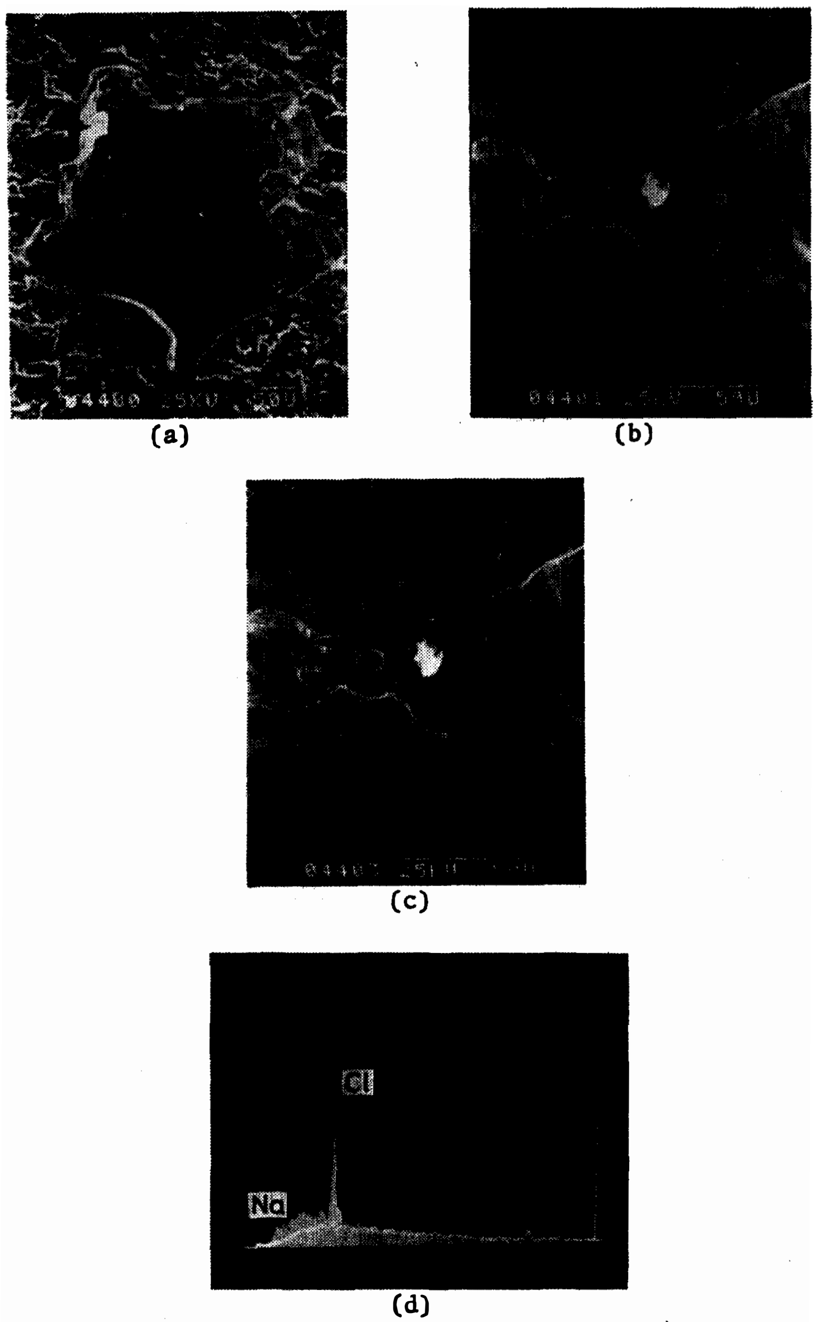


Fig. 2. Electron micrographs of a stellar shape of snow crystals collected at Mt. Teine (a), target particle (b, c), background (d), and X-ray energy spectra (e, f).

After careful scrutinization of the center of the crystal under the SEM, a particle 1 μm in diameter was discovered, as shown in (b) and (c). White crosses in photographs (c) and (d) show particle analyzed (c) by X-ray microanalyzer, and background (d) was selected to compare the particle, respectively. Photographs (e) and (f) show the analyzed results, and (f) is two times that of the scale of



MT. TEINE 18:00 MARCH 24,1981

Fig. 3. Electron micrographs of a plate shape of snow crystals collected at Mt. Teine (a), target particle (b), background (c), and an X-ray energy spectrum (d).

(e). The major components of the particle are Pb and Cl, and the minor components are Si and K. The result of the background is shown in (f) in the form of continuous white dots. Figure 3 is one of the cases of plate crystal as shown in (a). Close to the center of the crystal, a relatively large particle 10 μm in diameter in photographs (a) to (c) is found. The major component of the particle is Cl, and the minor component is Na; therefore, the particle probably comes

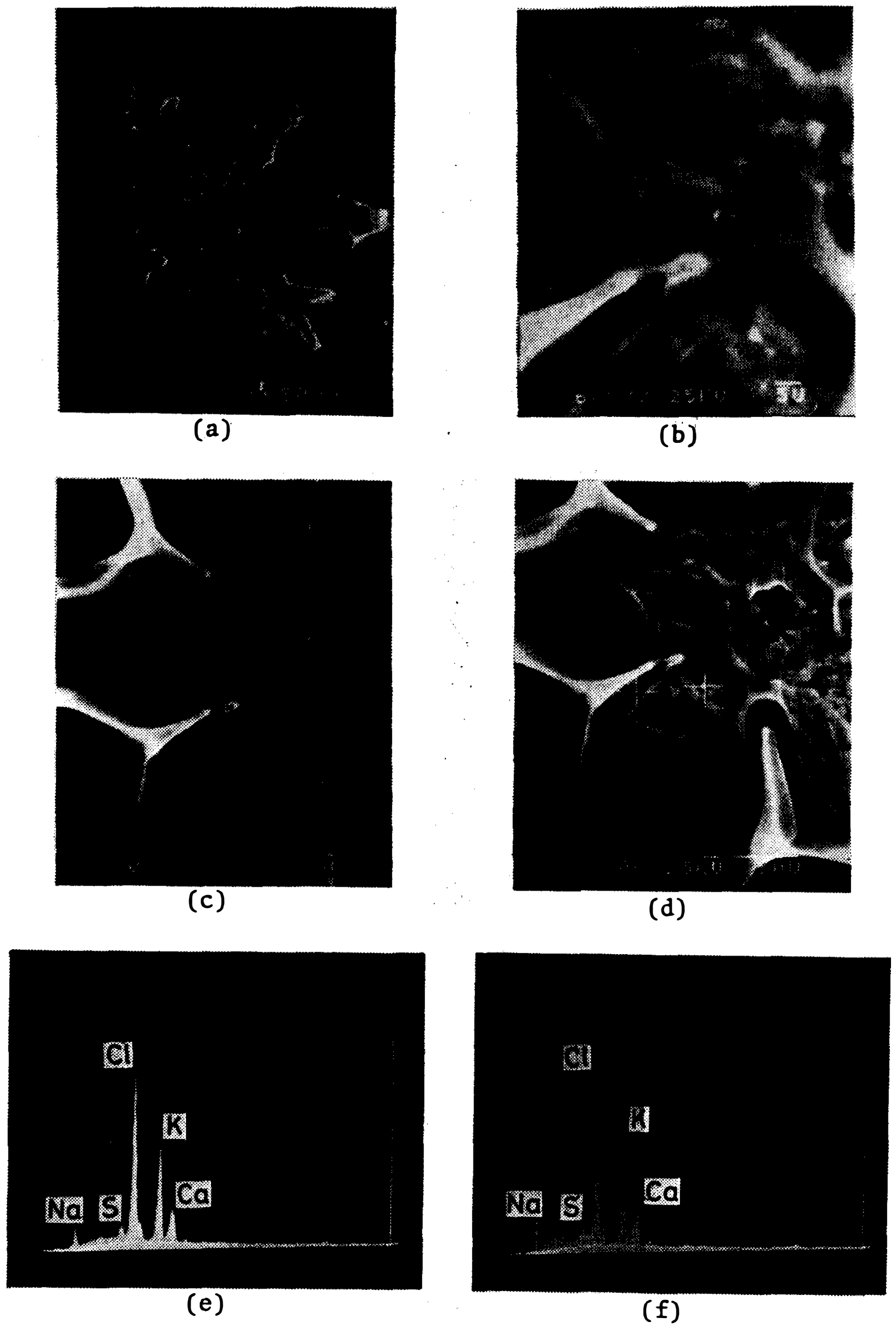


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Fig. 4. Electron micrographs of a dendritic shape of snow crystals collected at Moshiri (a), target particles and background (b, c, d), and X-ray energy spectra (e, f).

from marine air.

Figures 4 and 5 show analyzed examples of snow crystals collected at Moshiri. Figure 4 is one of the cases of dendritic shape of snow crystals as shown in (a). As two particles of micron size are found near the center of the crystal as seen in (b) and (d), both particles are analyzed and are shown in (e) and (f), respectively. As clearly seen from the results, the major components of both

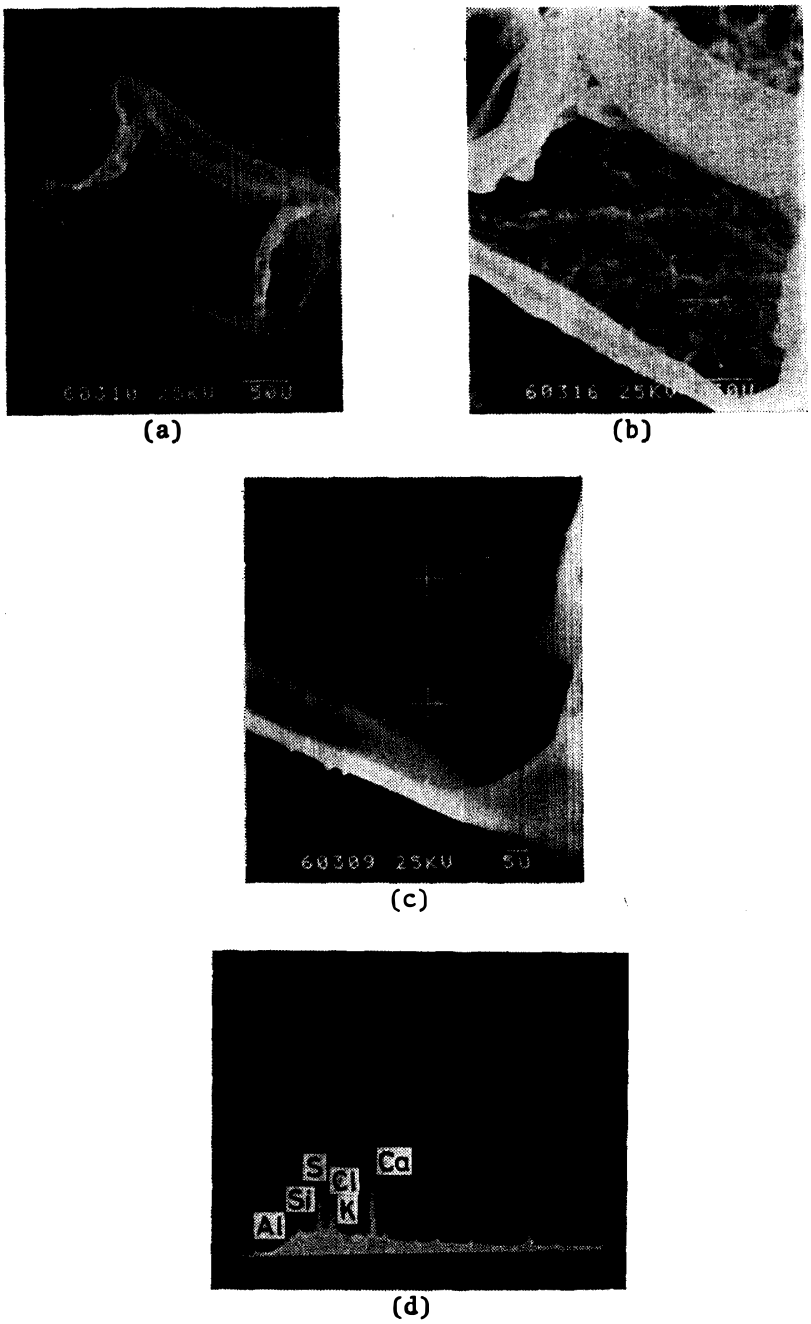

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Fig. 5. Electron micrographs of a column shape of snow crystals collected at Moshiri (a, b), target particle and background (c), and an X-ray energy spectrum (d).

particles are the same as Cl and K, and the minor components are the same as Na, S, and Ca. Further, the peak heights of energy spectra of both particles are nearly the same. Figure 5 is an example of column type crystal as shown in (a). In this crystal, a particle is found near the lower right corner of the crystal as seen in

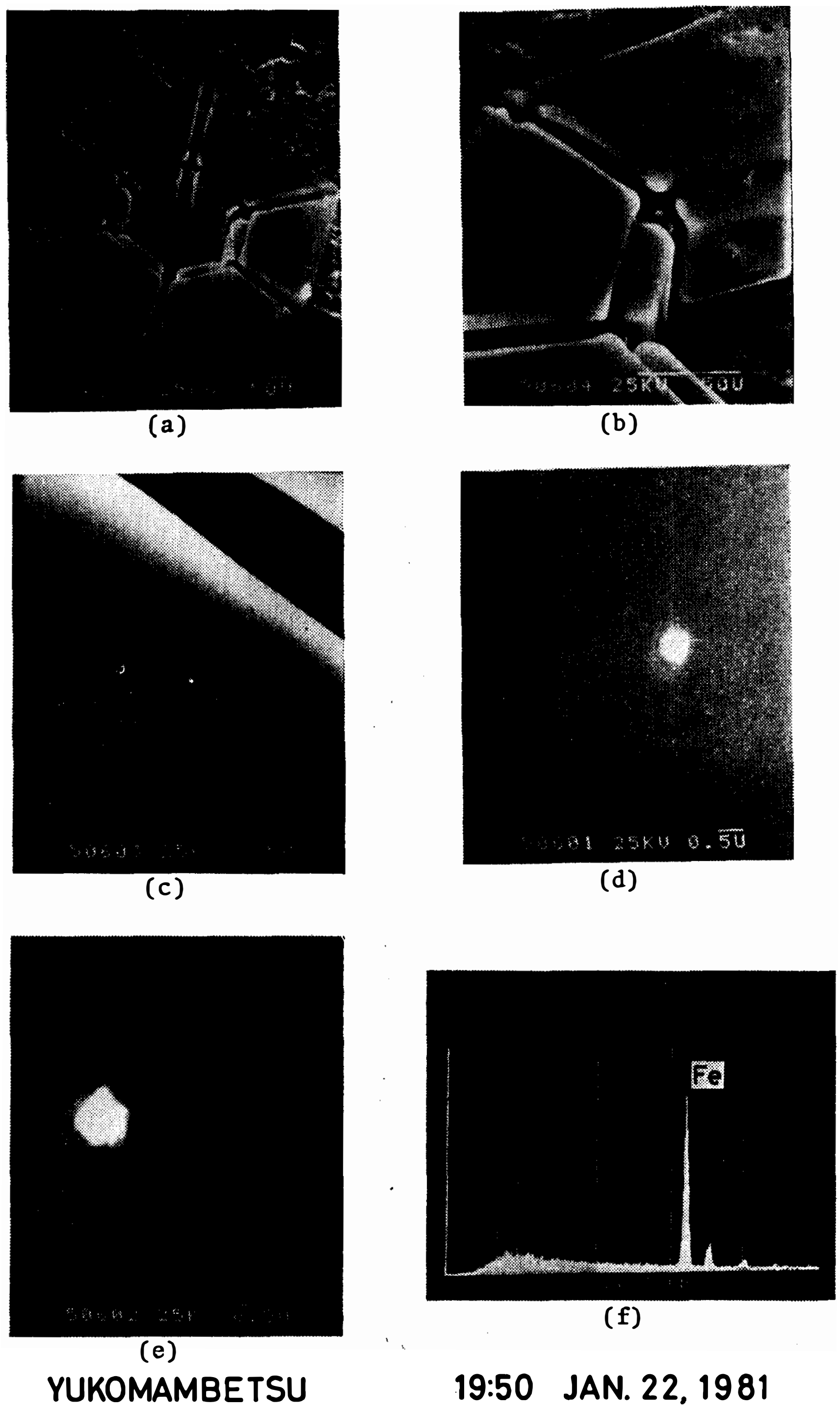

Fig. 6. Electron micrographs of a plate shape of snow crystals collected at Yukomambetsu (a, b), target particle (c, d), background (e), and an X-ray energy spectrum (f).

(b) and (c). The composition of particle consists of many elements of Al, Si, S, Cl, K, and Ca.

Figures 6, 7, and 8 show the analyzed examples of snow crystals collected at Yukomambetsu. Figure 6 is one of the cases of thick plate crystal as shown in (a). Since the replica film near the center of the crystal is broken as seen in photograph

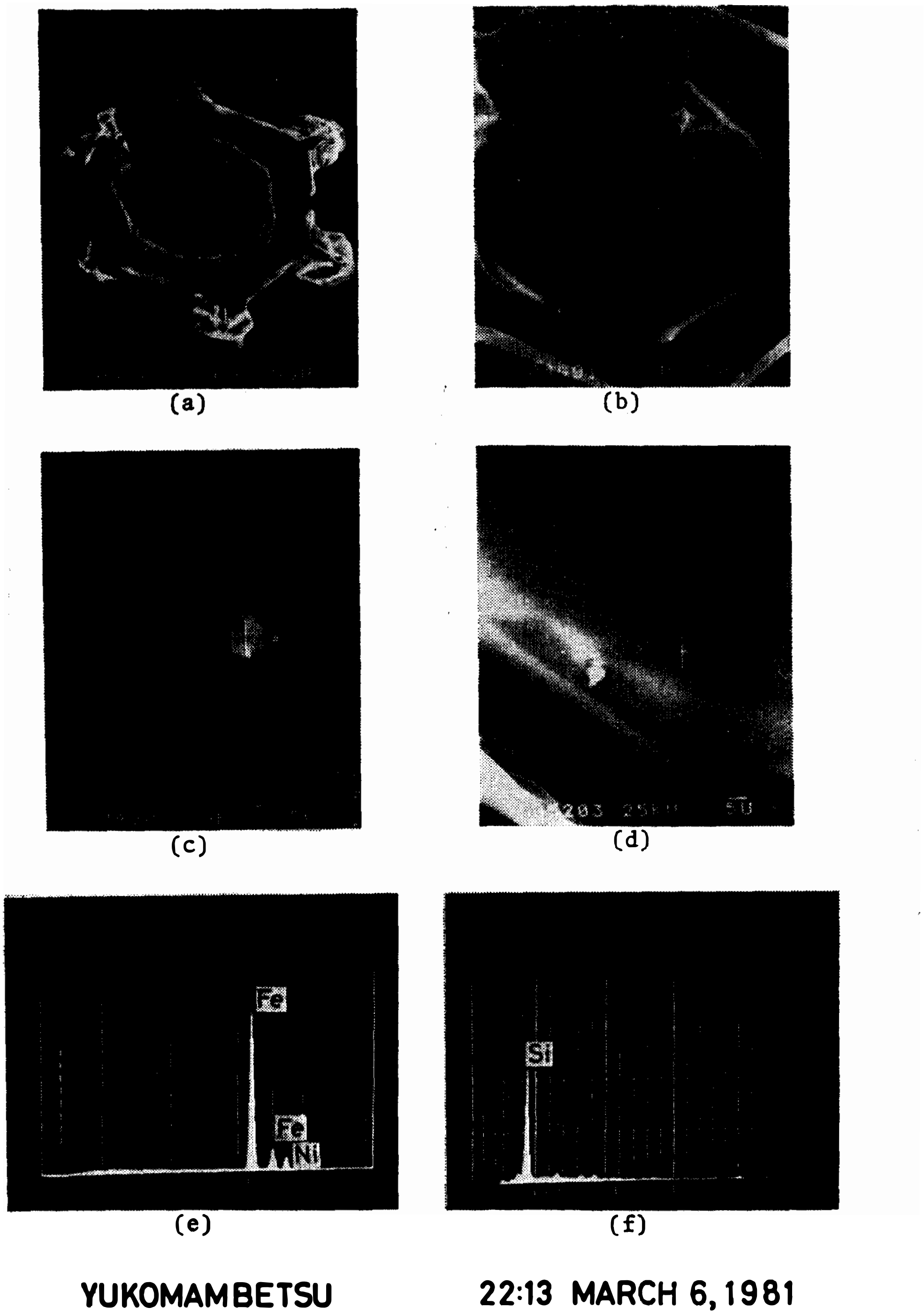

Fig. 7. Electron micrographs of a plate with broad branches of snow crystals collected at Yukomambetsu (a, b), target particles and background (c, d), and X-ray energy spectra (e, f).

(a), a submicron particle on a flat surface of the crystal as seen in (b) to (d) and the background near the particle as seen in (e) are analyzed. The predominant peak of Fe is indicated as seen in (f). It is not clear, however, whether the element Fe is an airborne particle or not. At times, the element Fe was recognized during the operation of analysis. Figure 7 is one of the cases of the snow crystal

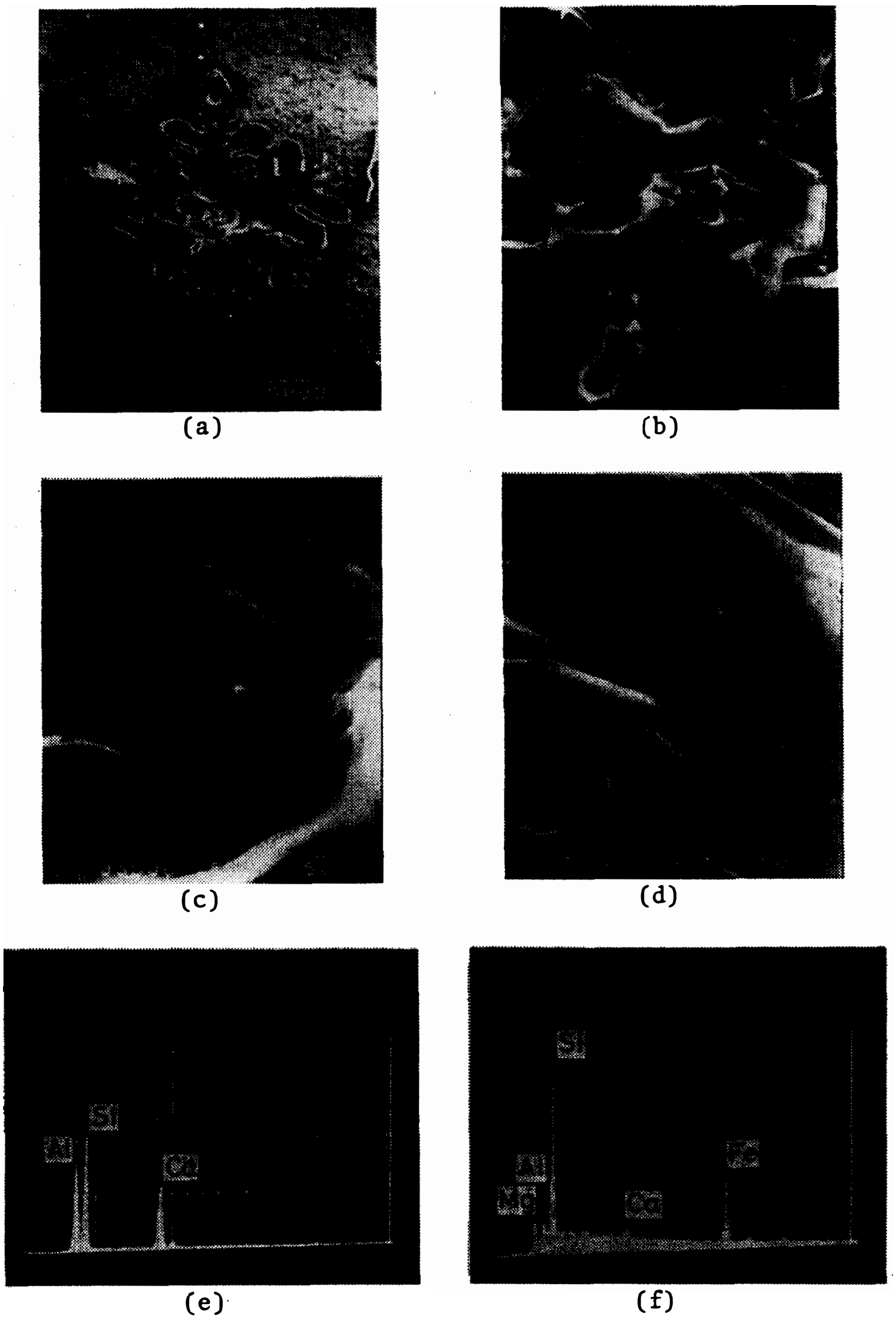

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Fig. 8. Electron micrographs of a dendritic shape of snow crystals collected at Yukomambetsu (a, b), target particles and background (c, d), and X-ray energy spectra (e, f).

of a plate with broad branches, as shown in (a). A several-micron sized particle near the center of the crystal as seen in (b) and (c) shows a major peak of Fe (K_α) and minor peaks of Fe (K_β) and Ni in (e). On the other hand, a micron-sized particle near the rim of the crystal as seen in (d) consists mainly of Si as seen in (f), however, minor peaks of Na, Mg, Al, Cl, K, and Ca were recognized

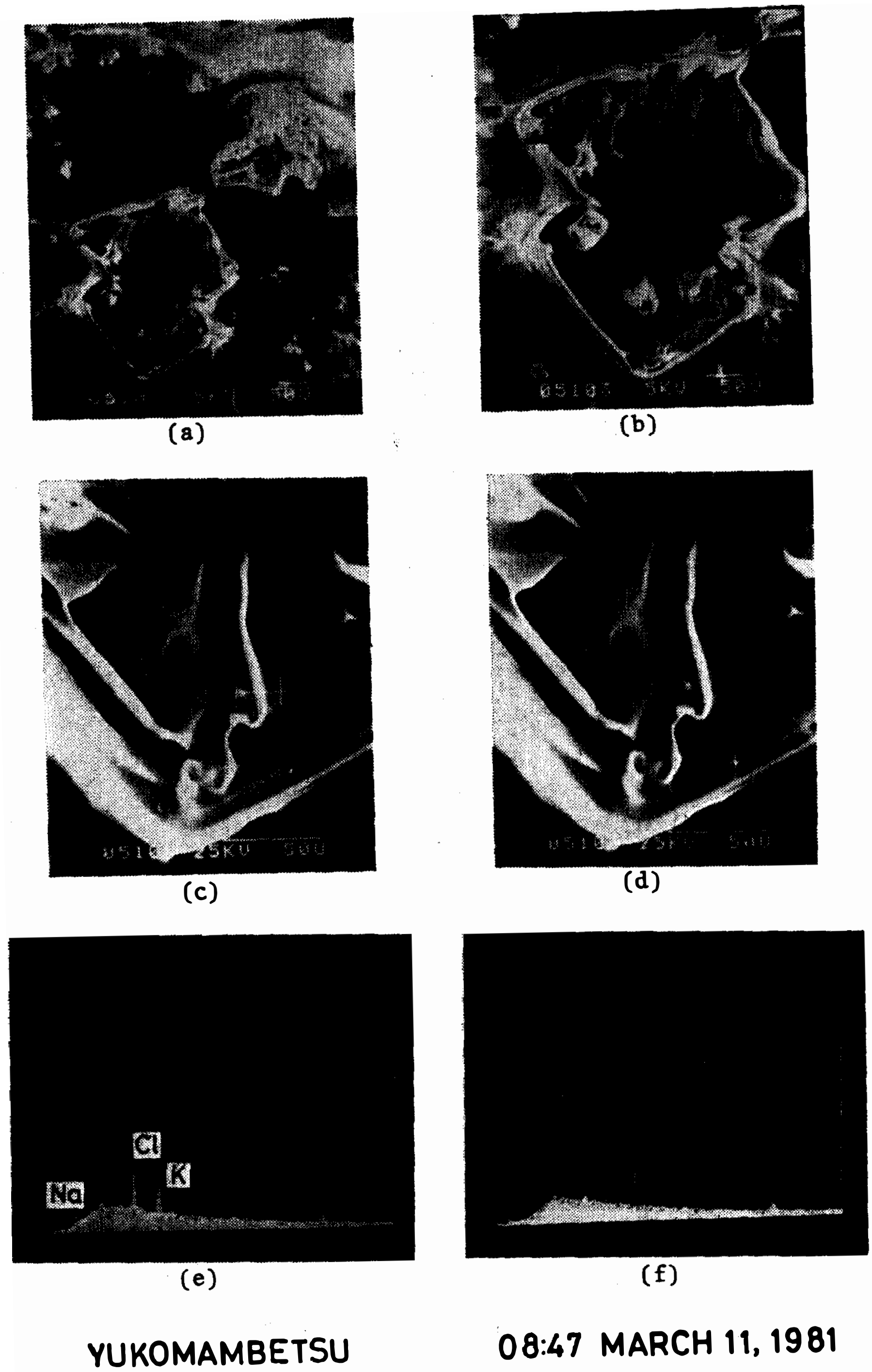

Fig. 9. Electron micrographs of a peculiar shape of snow crystals collected at Yukomambetsu (a, b), target particle and background (c, d), and X-ray energy spectra (e, f).

likewise. Figure 8 is one of the cases of dendritic crystals collected at Yukomambetsu as shown in (a). As seen in (a) and (b), the crystal forms double plates. A particle located around the center of crystal (c) consists of Al, Si, and Ca (K_α and K_β) as seen in (e). On the other hand, a particle located near the rim of the crystal as seen in (d) consists of Mg, Al, Si, Cl, K, Ca, Fe (K_α and K_β), and Cu.

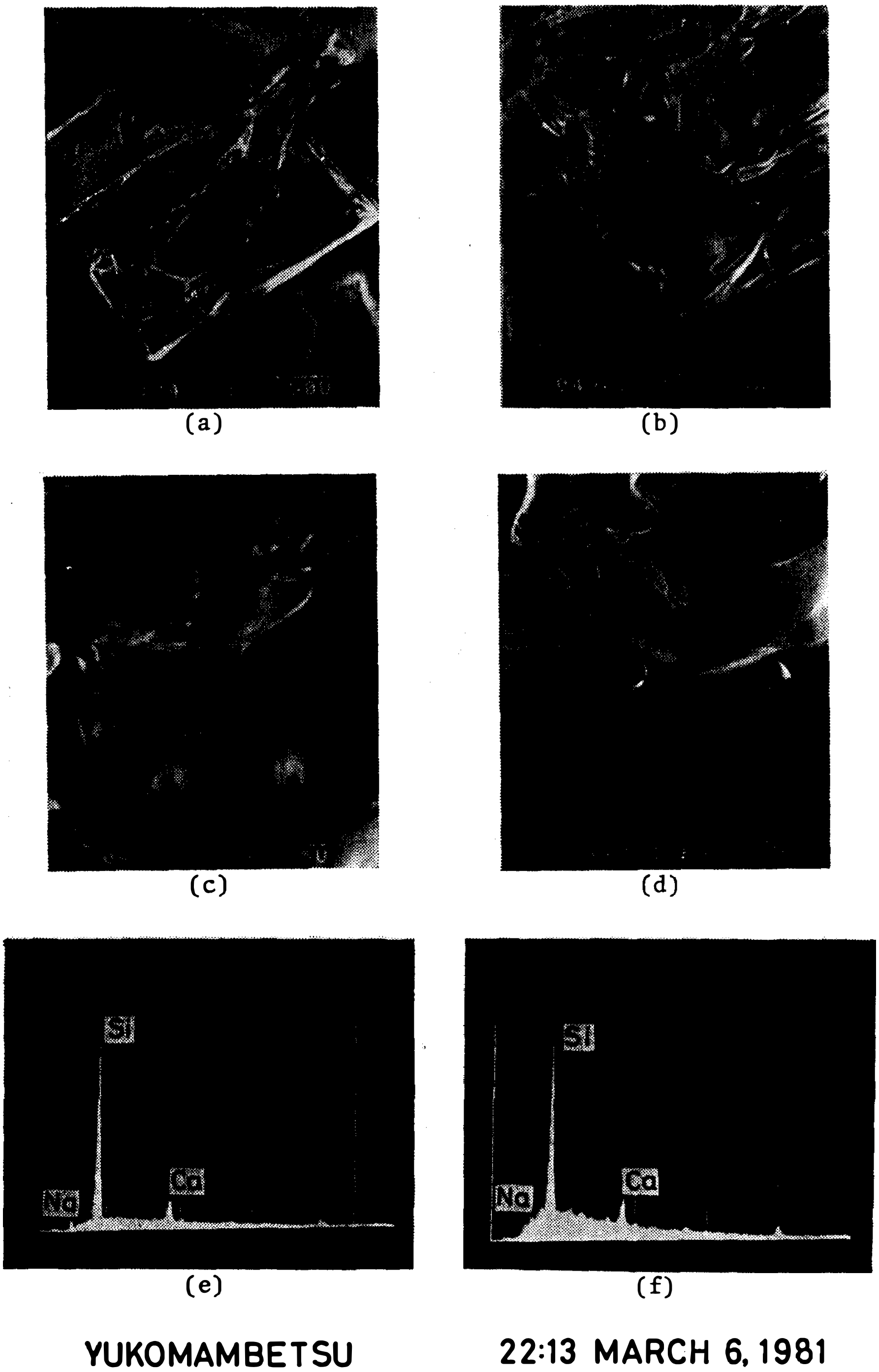

Fig. 10. *Electron micrographs of a peculiar shape of snow crystals collected at Yukomambetsu (a, b), target particles and background (c, d), and X-ray energy spectra (e, f).*

Therefore, both particles are regarded as the same components and they resemble soil or rock suggestive of terrestrial origin.

4.2. Analysis of individual particles of peculiar shapes of snow crystals

The shapes of snow crystals as shown in Fig. 9 (a) is one of the most typical

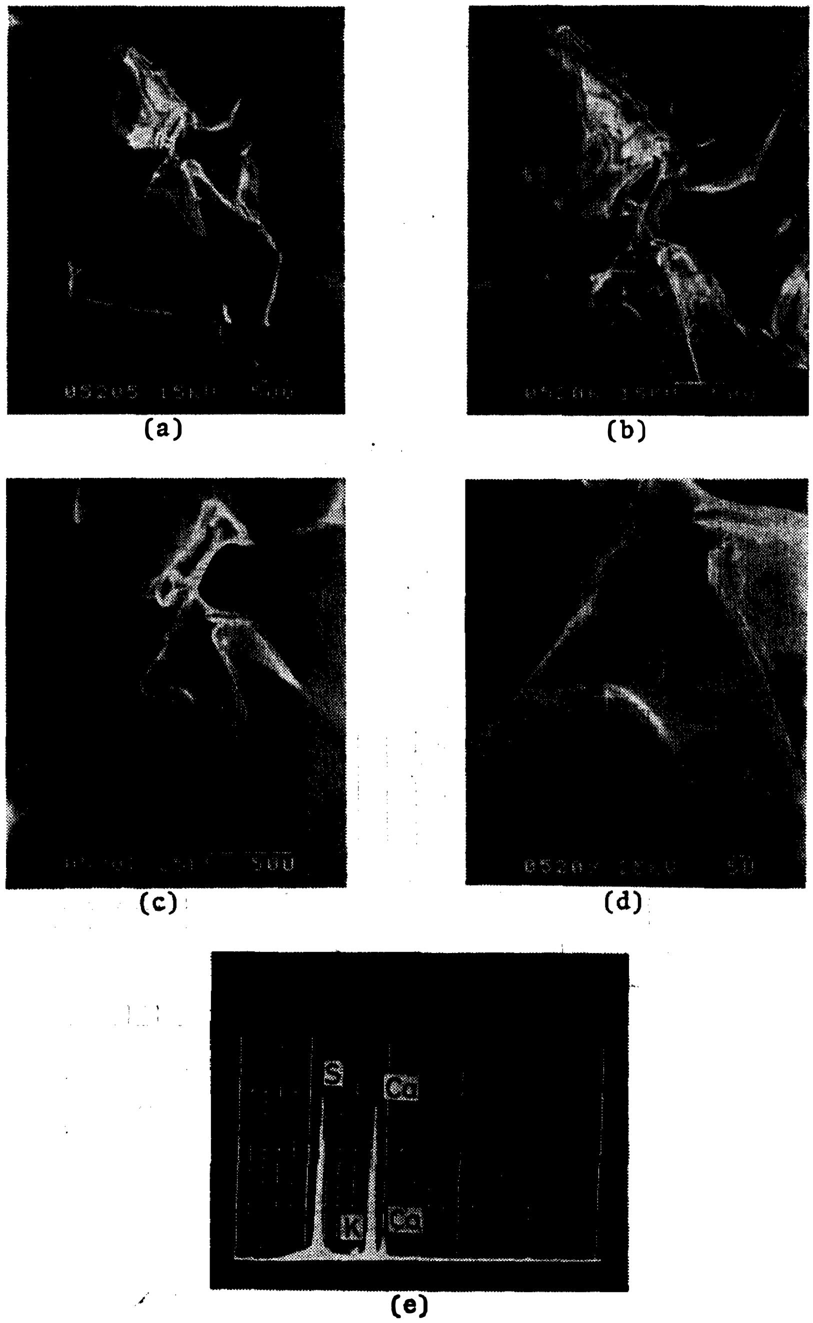

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Fig. 11. Electron micrographs of a peculiar shape of snow crystals collected at Yukomambetsu (a, b, c), target particle and background (d), and an X-ray energy spectrum (e).

peculiar ones, the so-called "Gohei" crystal (KIKUCHI, 1969, 1970; KIKUCHI and HOGAN, 1976; KIKUCHI *et al.*, 1982). Although it is thought that the growth of these crystals is from the upper corner, no particles were found at the corner. Contrary to this, one particle was found near the lower corner as seen in (c). The components of the particle are Na, Cl, and K, suggesting marine origin. A clear white spot as seen in (b) and (d) is not a particle, but a meaningless spot as seen in (f). The snow crystal as shown in Fig. 10 (a) is one of the peculiar shapes of square form (KIKUCHI, 1969, 1970). The two particles on the crystals as shown in (c) and (d) were analyzed. Major peaks of Na, Si, and Ca in both particles are recognized in (e) and (f); however, very minor peaks of Mg, K, Cr, and Cu in (e) and Mg, Al, S, Cl, K, Cr, and Cu in (f) are recognized. From the predominant peak of Si and the second peak of Ca, the component of these particles is suggested to be of terrestrial origin. Figure 11 (a) to (c) likewise show one of the peculiar shapes of snow crystals. A particle of a few microns as shown in (d) is analyzed and the components of these particles are of S, K, and Ca (K_α and K_β).

4.3. Frequency distributions of the element of individual particles of general shapes of snow crystals

Eighty particles in a total of forty one of general shapes of snow crystal were analyzed individually with the SEM-EMAX system. The elemental composition of analyzed particles collected at three sampling locations is summarized in Fig. 12.

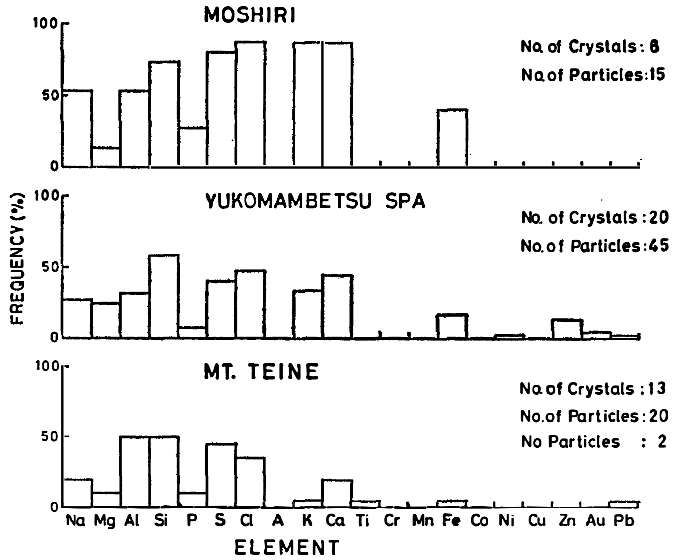

Fig. 12. Frequency distributions of elements present in the center nuclei of snow crystals collected at Moshiri, Yukomambetsu, and Mt. Teine.

The frequency distribution of top, middle, and bottom rows show the results from Moshiri, Yukomambetsu, and Mt. Teine, respectively. They indicate the percentages in number of particles containing a certain element in each location, but not the mass percentage, for instance, 52% of the particles contain Na at Moshiri and so on. The frequency distribution at each location seems to be such that the average peaks are S to Ca at Moshiri, from Si to Ca at Yukomambetsu, and from Al to Cl at Mt. Teine, respectively. It seems that the elemental composition of analyzed particles differs at each location. Therefore, the origin of the center nuclei of snow crystals at Moshiri includes all kinds of nuclei, namely, clay minerals, sea salt particles, and combustion products. On the other hand, at Yukomambetsu, the major composition seems to be clay minerals, and further, S will result from the volcanic smoke of craters. At Mt. Teine, near Ishikari Bay, the Sea of Japan and near Sapporo City, it seems that sea salt particles and combustion products are predominant.

Aerosol particles in the free atmosphere were collected onto Nucleopore filters of 47 mm diameter with a pore size of 0.2 μm during the same observation period at the top of Mt. Teine. The particles collected were classified into three groups; giant particles ($d \geq 2$ μm), large particles (0.2 μm$<d<$2 μm), and Aitken par-

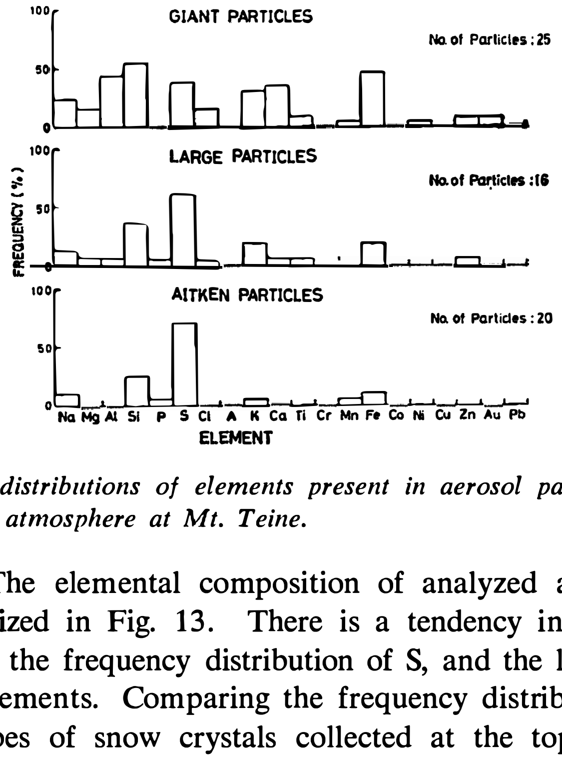

Fig. 13. Frequency distributions of elements present in aerosol particles collected in the free atmosphere at Mt. Teine.

ticles ($d \leq 0.2$ μm). The elemental composition of analyzed aerosol particles in each group is summarized in Fig. 13. There is a tendency in which the smaller the particles the higher the frequency distribution of S, and the lower the frequency distribution of other elements. Comparing the frequency distribution of the center nuclei of general shapes of snow crystals collected at the top of Mt. Teine as shown in Fig. 12 with that of aerosol particles as shown in Fig. 13, the tendency of the elemental composition of giant particles closely resembles that of the center nuclei. It is understood that the size of most center nuclei is in a similar size range of giant particles.

4.4. Frequency distributions of the element of individual particles of peculiar shapes of snow crystals

During the observation period at Yukomambetsu, three peculiar shapes of snow crystals were observed and five particles in their crystals were analyzed. The results are shown in Fig. 14. The frequency distribution of the elemental com-

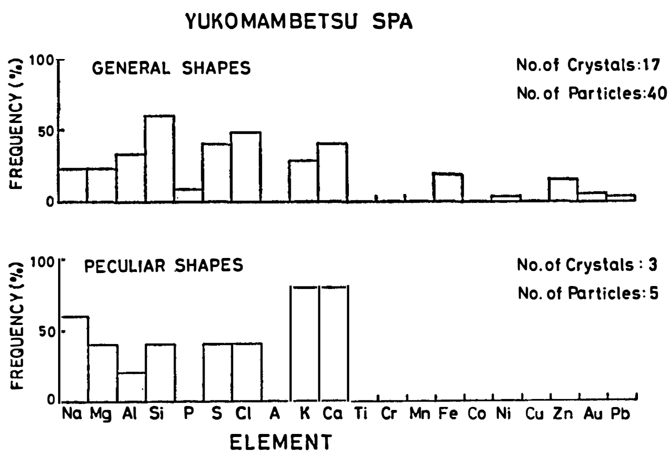

Fig. 14. Frequency distributions of elements present in the center nuclei of general and peculiar shapes of snow crystals collected at Yukomambetsu.

position of the general shapes of snow crystals shown on the upper part in Fig. 14 is the same as shown in the top row in Fig. 12. Regarding the frequency distribution of the elemental composition of peculiar shapes of snow crystals, there is a tendency to more concave, namely, a higher frequency of Na, Mg, K, and Ca, and a lower frequency of Al, Si, S, and Cl. This suggests a marine origin for the center nuclei of peculiar shapes of snow crystals. On the other hand, the frequency distribution of elemental composition of general shapes of snow crystals shows a tendency toward more convex, namely, a higher frequency of Al, Si, S, and Cl, and a lower frequency of Na, Mg, and K. Therefore, the tendency suggests a terrestrial origin for the center nuclei of general shapes of snow crystals. However, the number of crystals analyzed was limited. It is necessary to analyze a large number of peculiar shapes of snow crystals to reach a conclusion.

5. Conclusion

Using a scanning electron microscope and energy dispersive X-ray microanalyzer, the elemental composition of center nuclei of snow crystals was analyzed. As a result, it seems that the elemental composition of center nuclei of general shapes of snow crystals differs with the sampling location, Moshiri, Yukomambetsu, and Mt. Teine. The average peaks are located around S and Ca at Moshiri, Si to Ca at Yukomambetsu, and Al to Cl at Mt. Teine. Further, the center nuclei of general shapes as opposed to peculiar shapes of snow crystals collected at Yukomambetsu were compared. A slight difference is seen between the both shapes of snow crystals. In the frequency distribution of elemental composition of peculiar shapes of snow crystals, there was a tendency showing the concave, namely, a higher frequency of Na, Mg, K, and Ca, and a lower frequency of Al, Si, S, and Cl. On the other hand, regarding the general shapes of snow crystals, there was a tendency to show the convex, namely, a higher frequency of Al, Si, S, and Cl, and a lower frequency of Na, Mg, and K. Therefore, the elemental compositions of center nuclei of peculiar shapes and general shapes of snow crystals were suggestive of marine origin and terrestrial origin, respectively. However, it was concluded that further analysis of more cases of peculiar shapes of snow crystals is necessary.

It may be concluded that this technique is reliable for the analysis of elemental composition of center nuclei of snow crystals and aerosol particles.

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