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Nondestructive characterization of Antarctic micrometeorites collected at the Dome Fuji Station by synchrotron radiation X-ray fluorescence analysis

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Abstract: The bulk trace element composition (Ca, Ti, Cr, Mn, Ni, Cu, Zn, Ge, Se, Rb, Sr, Y, Zr, Mo) of eighty-three Antarctic micrometeorites was nondestructively analyzed using synchrotron radiation X-ray fluorescence analysis (SR-XRF), and these elements were characterized in terms of their abundance ratio relative to Murchison matrix composition. The relationship between heating history and chemical composition is also examined. We found a complementary relationship among I-type, S-type and unmelted AMMs in the micrometeorites' elemental abundance, which is consistent with the hypothesis that I-type and S-type spherules were separated from chondritic meteoroids.

1. Introduction

This study is part of a consortium study of Antarctic micrometeorites (AMMs) (Noguchi *et al.*, 2000). This research has two purposes. One is to carry out an initial characterization of the AMMs, which were collected at the Dome Fuji Station. The AMM working group is conducting a joint examination of the AMMs using various analytical methods such as the X-ray microprobe analysis (XMA), secondary ion mass spectrometry (SIMS), instrumental neutron activation analysis (INAA), and the like, and our X-ray fluorescence (XRF) analysis was undertaken first because of the nondestructive nature of this method. The second purpose of this research is to find a way to classify the micrometeorites by their trace element composition as determined by nondestructive analysis. Because of the extremely small size of the samples available for analysis, it is difficult to effect mineral identification through microscopic observation and the XMA technique (Noguchi *et al.*, 2000). Therefore, nondestructive chemical analysis is useful. This classification

also helps to distinguish the origin and history of the micrometeorites, and hence helps us to study the origin and evolution of the solar system.

We have analyzed 83 unmelted AMMs with irregularly shaped fragments, indicating minimal physical evidence of heating through atmospheric entry. In order to clarify the chemical compositional characteristics of unmelted AMMs, S-type spherules from the South Pole and I-type spherules from deep-sea sediments were also examined. Spherules have undergone a complete melt during atmospheric entry.

We utilized synchrotron radiation (SR) as an excitation source in the XRF analysis because (1) this technique employs a nondestructive procedure for sample preparation and data acquisition suitable for preliminary analysis; (2) it is a multielemental analysis that allows us to find key elements suitable for characterization and classification of the micrometeorites; (3) it is a high-sensitivity analysis suitable for detection of trace elements characteristic to the samples; and (4) it is a rapid analysis suitable for working with a large number of samples. These advantages of the SR-XRF technique over other conventional analytical techniques have been clearly demonstrated by several pioneer researchers (Sutton and Flynn, 1988; Flynn and Sutton, 1990; Sutton *et al.*, 1994; Bajt *et al.*, 1994; Nozaki *et al.*, 1999).

2. Samples and techniques

The samples were 83 unmelted AMMs of irregular shape collected at the Dome Fuji Station in 1996 (Nakamura *et al.*, 1999). The I-type spherules (7 samples) were collected from sediment dredged from the sea floor at 5800 m off the coast of the Hawaiian Islands (Nozaki *et al.*, 1999). The S-type spherules are also from the Dome Fuji Station (9 samples). As a reference, 4 samples (diameter *ca.* 100 μm) taken from the matrix of Murchison CM chondrite were also analyzed.

SR-XRF measurements were made at beam-line BL-4A of the Photon Factory, Tsukuba, using monochromatized radiation (X-ray energy: 20.55 keV) with Si(111) double crystals. The experimental system is illustrated in Fig. 1. The samples were mounted on a mylar film on a plastic holder with acetone soluble bond. XRF spectra were measured nondestructively with Si(Li)-SSD for 600 to 1000 s in a vacuum. The beam size was $0.2 \times 0.2 \text{ mm}^2$, which was larger than all of the samples.

The net intensities of the XRF spectrum of each element were calculated by background subtraction. Since the XRF intensity depends not only on the nature of a sample but also on the sample size, some normalization is essential to compare the analytical result. Iron is a major component and is always the most abundant element among the analyzed elements. The XRF intensities of the rest of the elements are almost always less than one-tenth of the intensity of the iron. Therefore, XRF intensities of the analyzed elements were divided by the intensity of the iron to obtain the normalized intensity (I_i).

We calculated the relative abundance of major and minor elements against the chemical composition of the matrix of Murchison CM chondrite, which is very

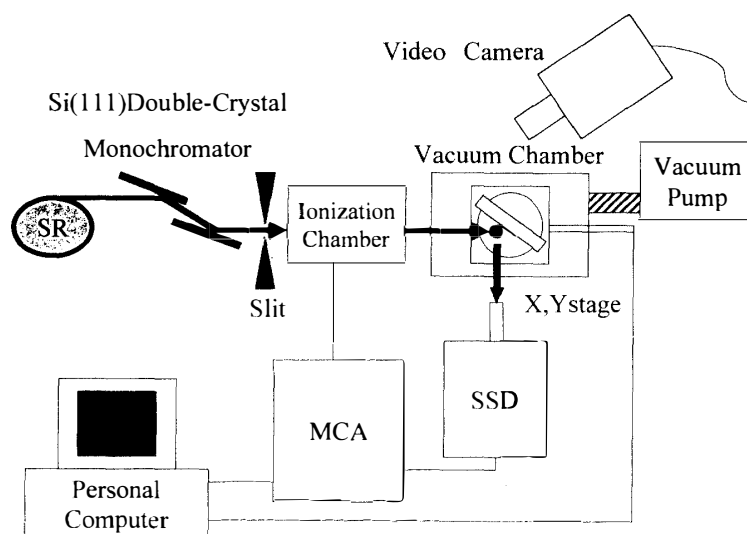


Fig. 1. The experimental system for SR-XRF analysis at the Photon Factory.

similar to the cosmic abundance of elements in the solar nebula by dividing the normalized value (I_i) of each element by that of the Murchison matrix (I_m) (an average of the analyses of 4 grains). To evaluate the number of samples belonging to a certain value of I_i/I_m , the samples were classified into 8 groups based on their $\log(I_i/I_m)$ values. Next, a histogram was prepared for a particular element by plotting the frequency ratio as the ordinate against $\log(I_i/I_m)$ as the abscissa. The frequency ratio is then defined as the number of samples belonging to a particular $\log(I_i/I_m)$ group divided by the total number of analyzed samples for the particular element.

For trace elements, the histogram was expressed differently. The ordinate was the frequency ratio, and the abscissa was expressed by one of three groups: group I: the element is absent; group II: the element exists, but the concentration level is near the detection limit (< 1 ppm) of the SR-XRF method; group III: the element exists in trace level. The concentration range of the matrix of Murchison is expressed by the arrow in the figures.

3. Results

Figure 2 shows typical examples of the XRF spectra measured for the (a) I-type and (b) S-type spherules and the (c) unmelted AMM. As can be seen from Fig. 2, iron is the most abundant element in all samples, and the peak of titanium overlapped with that of the escape peak of iron. Therefore, titanium was excluded from the discussion. The I-type spherules are characterized by the absence of Ca, Mn, Cu, Rb, Sr, Y, and Zr and the existence of Mo. The S-type spherules are characterized by an abundance of Ca, Cr, and Mn and the presence of a small amount of Sr and Zr. Cu is absent in most cases, and Se and Rb are depleted in the S-type spherules. The unmelted AMMs are enriched in Cu and Pb and contain appreciable amounts of Cr, Mn, and Zn.

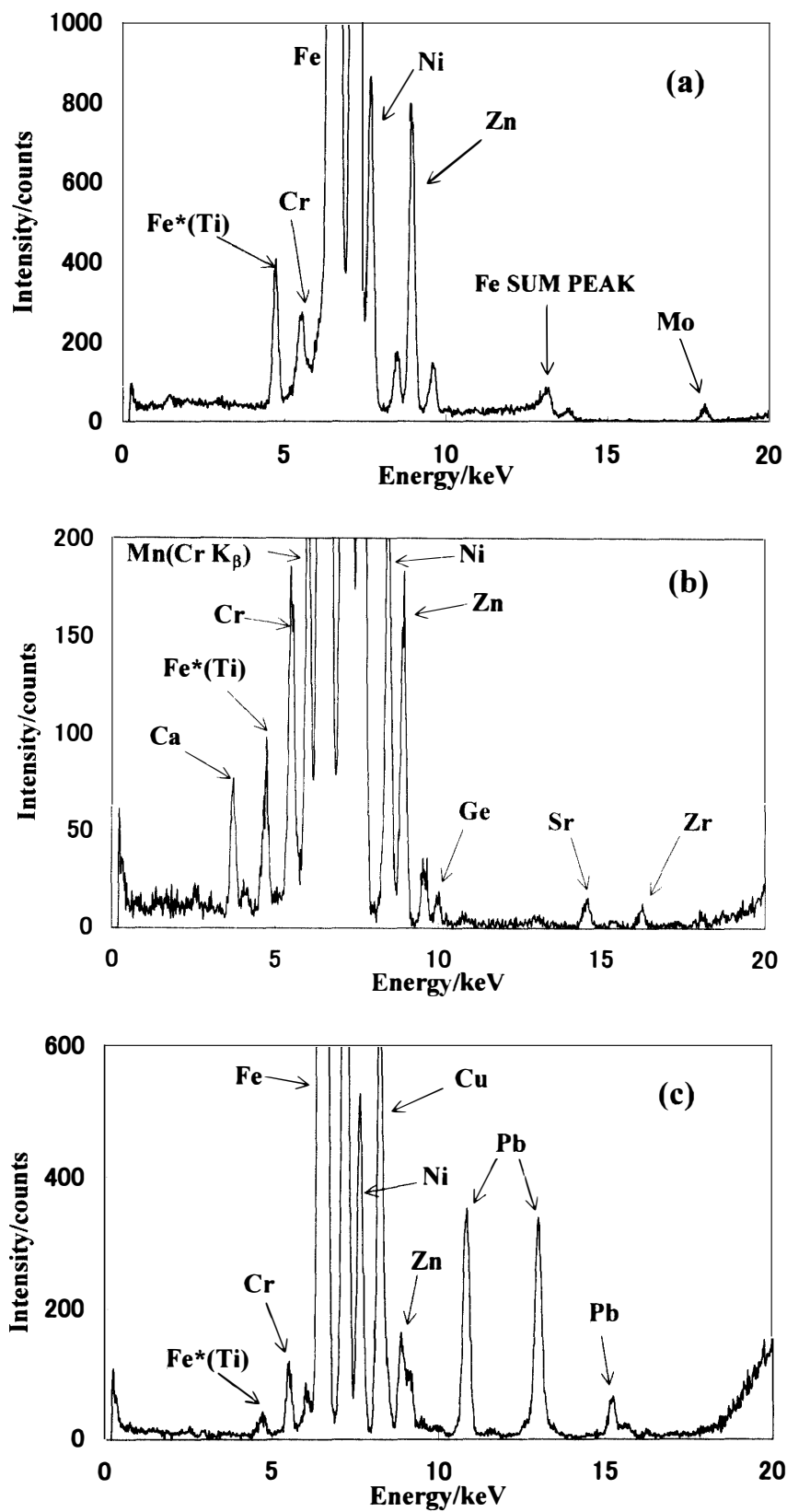


Fig. 2. XRF spectra typical for (a) an I-type spherule, (b) an S-type spherule, and (c) an unmelted AMM. The Ti peak overlapped with the escape peak of Fe.

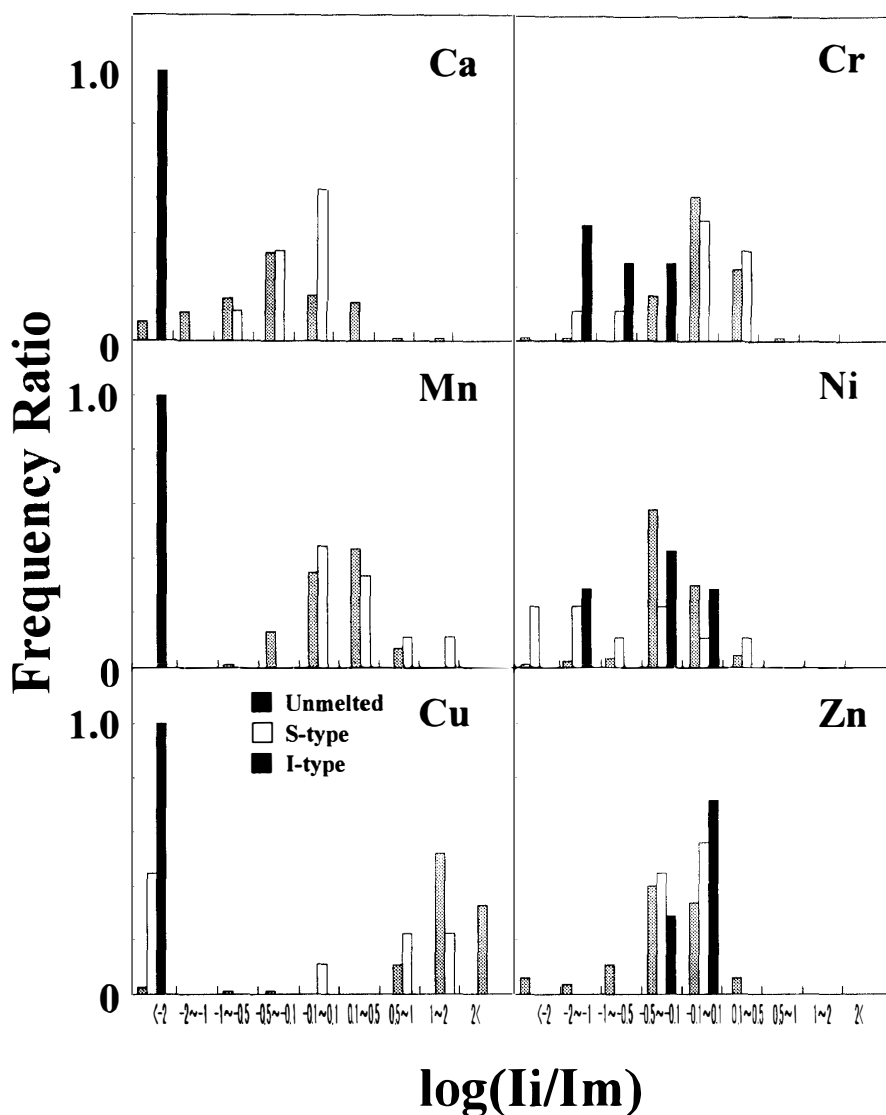


Fig. 3. Histograms showing the relative abundance of Ca, Cr, Mn, Ni, Cu, and Zn against that of the matrix of Murchison CM chondrite.

The relative abundance of Ca, Cr, Mn, Ni, Cu, and Zn compared with that of the matrix of Murchison CM chondrite is shown in histogram form in Fig. 3. The analytical data of four grains (a, b, c, and d) obtained from Murchison are given in Table 1, which shows the variation of the relative X-ray fluorescence intensity normalized to that of Fe to be 1000000; for trace elements the concentration level are given by group number from I to III, as defined in Fig. 4. The relative abundance of trace Se, Ge, Pb, Rb, Sr, Zr, Y, and Mo is shown in Fig. 4. As is defined in the previous section, the abscissa of Fig. 3 is a range of $\log(I_i/I_m)$ values, which is the logarithm of the intensity ratio of the sample to the Murchison matrix for a particular element. For example, if the normalized Ni intensity in the XRF spectrum of a sample agrees with that of the Murchison matrix, $\log(I_i/I_m)$ becomes 0, which is classified into the abscissa range of $-0.1 \sim 0.1$. The ordinate is the frequency ratio belonging to each $\log(I_i/I_m)$ group.

Table 1. Analytical results of the matrix of Murchison CM chondrite expressed by the relative X-ray fluorescence intensity of iron.

| Sample | Ca | Cr | Mn | Fe | Ni | Cu | Zn | Se | Ge | Pb | Rb | Sr | Zr | Y |
|--------|------|-------|------|---------|-------|-----|-------|----|-----|----|----|----|----|---|
| a | 1496 | 5223 | 3195 | 1000000 | 33036 | 33 | 8885 | II | III | II | II | II | I | I |
| b | 1806 | 15173 | 3921 | 1000000 | 40517 | 179 | 9155 | I | III | II | II | II | II | I |
| c | 4890 | 7306 | 4233 | 1000000 | 58954 | 121 | 11037 | II | II | II | II | II | II | I |
| d | 3281 | 3812 | 3258 | 1000000 | 85313 | 118 | 9500 | II | III | II | II | II | II | I |
| Ave. | 2868 | 7878 | 3652 | | 54455 | 113 | 9645 | II | III | II | II | II | II | I |

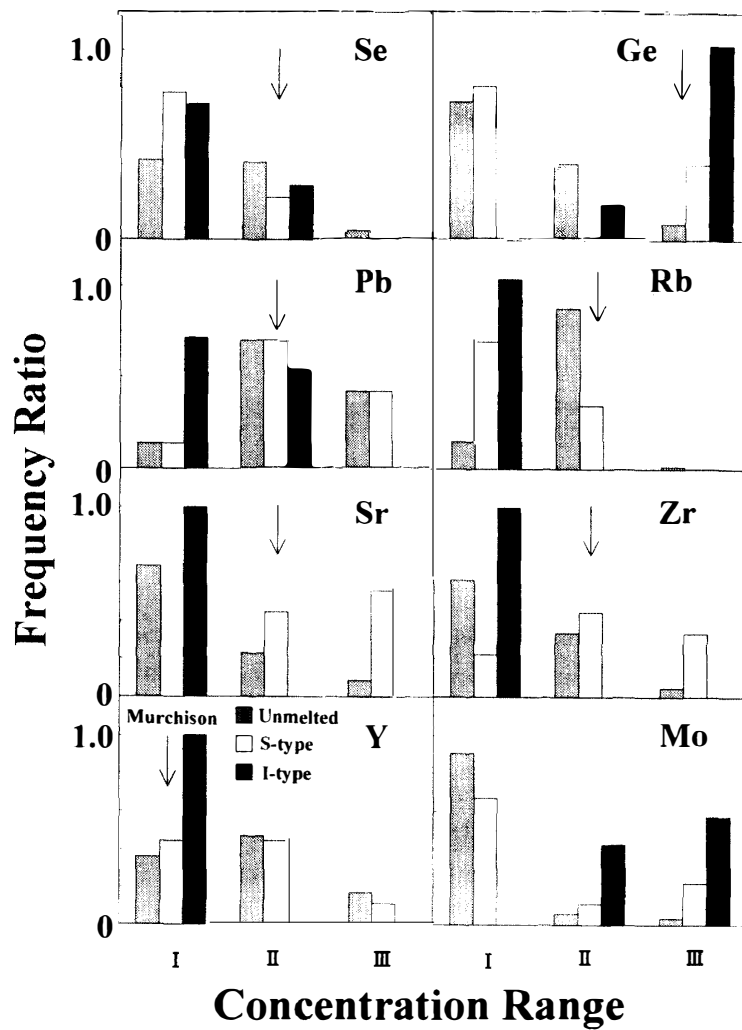


Fig. 4. Histograms showing the relative abundance of trace Se, Ge, Pb, Rb, Sr, Zr, Y, and Mo. The abscissa is expressed one of three groups: group I: the element is absent, group II: the element exists but the concentration level is near the detection limit of the SR-XRF method, group III: the element exists at a trace level. The abundance in the matrix of Murchison CM chondrite is indicated by arrows.

As can be seen from Figs. 3 and 4, the chemical compositions of the I-type spherules are characterized by the abundance of Mo and the absence of Ca, Cu, Mn, Sr, Y, Rb, and Zr relative to Murchison abundance. The S-type spherules are characterized by the abundance of Cr and Mn and by Ni and Pb depletion compared to the Murchison matrix. The unmelted AMMs contain significant amounts of Cu, Pb, Cr, and Mn compared with the Murchison matrix. Ge is always depleted compared to the Murchison matrix in all micrometeorites. Moreover, most samples

show Ni depletions compared to Murchison abundance, but the concentration range is broad.

4. Discussion

We observed a noteworthy complementary relationship among the elemental distributions in the I-type and S-type spherules: that is, Ca, Cr, Mn, Sr, Y, and Zr are relatively abundant in the S-type spherules while they are depleted in the I-type spherules (Figs. 3 and 4). Moreover, the abundance of these elements in unmelted AMMs tends to be between the abundance in the I-type and S-type spherules. Brownlee *et al.* (1983) proposed that I-type spherules are droplets of a metallic melt that has been separated from a chondritic melt consisting of silicate and metallic parts and that the remaining silicate melt becomes S-type cosmic spherules. The observed complementary relationship in the abundance of Ca, Cr, Mn, Sr, Y, and Zr among the S-type, I-type, and unmelted AMMs is consistent with their hypothesis. Ca, Cr, Mn, Rb, Sr, Y, and Zr are all lithophile elements, and their depletion from I-type spherules and their relative enrichment in the S-type spherules are chemically reasonable. On the other hand, Ni, Ge, and Mo are siderophile elements, and their relative enrichment in the I-type spherules and their relative depletion in the S-type spherules are also reasonable.

Based on the experimental determination of element partitioning between silicate and S-bearing metallic melts at 1260°C, Drake *et al.* (1989) reported that Mn and Cr are lithophile elements that tend to appear in silicate melts under oxygen fugacity higher than 10^{-12} bar, whereas they are siderophilic under oxygen fugacity lower than 10^{-15} bar. At intermediate fugacity from 10^{-12} to 10^{-15} bar, Cr is siderophilic and Mn is lithophilic. In the present samples, Mn is absent in the I-type spherule while Cr is present in the I-type spherules (Fig. 3) though it is much less abundant compared with that in the S-type spherules. Nozaki *et al.* (1999) observed a similar tendency in their study of I-type spherules. The temperature also affects the affinity of these elements, which tend to become siderophilic with increasing temperature from 1260°C under 10^{-6} bar oxygen fugacity (Geßmann and Rubie, 1998). Further quantitative studies will help to estimate such thermodynamic conditions of the evolution of cosmic spherules.

The chemical composition of the unmelted AMMs is characterized by high concentrations of Cu and Pb. Flynn *et al.* (1993) reported the high Pb and Br content in micrometeorites and pointed out the possibility of contamination after atmospheric entry. Zoller *et al.* (1974) analyzed atmospheric particles collected at the south pole and reported that the relatively volatile elements Zn, Cu, Se, Pb, and Br are derived from sources other than crustal weathering or the ocean. They believed these elements came from some vapor-phase condensation or high-temperature-dispersion process. It is reported that the concentration levels of Br and Se in Antarctic micrometeorites are 26 and 12 ppm on average, respectively (Flynn *et al.*, 1993). On the other hand, it is remarkable that the concentration level of Br in the present unmelted AMMs is below the detection limit of SR-XRF

analysis, as shown in Fig. 2c. It is possible that there was a different contamination source for Pb and Cu in our samples.

Micrometeorites have experienced various degrees of heating during atmospheric entry. Nakamura *et al.* (1999) studied 26 samples extracted from our analyzed unmelted AMMS and categorized them into 5 classes of increasing heating effects based on the relative mineral abundance of the samples determined by powder diffraction analysis using a Gandolfi camera. We examined the effect of particle heating on the chemical composition of the micrometeorites but observed no clear correlation between the chemical composition and the diffraction-determined classifications.

Our micrometeorites show slight depletion of Ni compared to the Murchison matrix. Flynn *et al.* (1993) also reported the low Ni content of polar micrometeorites and suggested that the depletion may indicate terrestrial alteration such as the loss of sulfides containing these elements during residence in the polar ice.

Zinc depletion is often observed for stratospheric IDP, and it is explained by the heating of IDPs by atmospheric entry (Flynn *et al.*, 1992). The present analyses showed no zinc depletion compared to the Murchison matrix (Fig. 3) and that the zinc concentration was independent of the heating stage reported by Nakamura *et al.* (1999). A similar tendency was also observed for the polar micrometeorites (Flynn *et al.*, 1993). He explained the difference as follows: Zn increased by interaction with the polar ice or zinc exists in different mineral phases that exhibit different thermal behavior. The present result shows that the concentration range of Zn is rather narrow, which is close to that of the Murchison matrix.

We should mention the limits of the present analysis. The analytical results obtained by the present technique are only semi-quantitative, because the X-ray absorption effect is serious for light elements such as Ca and Cr but not for heavy elements such as Zr and Mo. For example, a theoretical calculation indicates that for an olivine sample of 50- μm thickness with ideal composition of FeMgSiO_4 , 84% of the Cr $K\alpha$ X-ray signal is absorbed by the sample while only 18% of the Mo $K\alpha$ X-ray signal is absorbed. This problem is a result of the difficulty of defining the shape of a sample with an irregular and porous nature. Therefore, in order to complete a quantitative analysis, it is essential to use polished thin samples, which are also advantageous from the viewpoint of removing terrestrial contamination (Flynn *et al.*, 1993). Still, the observations of Figs. 3 and 4 seem to characterize clearly the nature of the samples, and the present technique will be useful for the nondestructive preliminary characterization of cosmic dusts. SR-XRF analysis has ppm sensitivity for heavy elements such as Ge, Sr, Y, Zr, and Mo, which have large ionic radii or high ionic charge and exhibit characteristic behavior during cosmochemical processes. Fortunately, the absorption effect is not serious for $K\alpha$ X-rays of such heavy elements. Therefore, these elements could become fingerprints for the classification of micrometeorites and the estimation of their origin. Though analyzed samples are limited in number and may suffer terrestrial alteration, the present analysis still indicates that most heavy elements tend to exhibit characteristic distribution in each group.

Acknowledgments

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