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## Mid-infrared transmission spectra of individual Antarctic micrometeorites and carbonaceous chondrites

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**Abstract:** Mid-infrared absorption spectra were obtained for 6 carbonaceous chondrites and 6 Antarctic micrometeorites (AMMs) with transmission light using an IR microscope. Obvious absorption bands caused by O-H stretching vibration at  $3400\text{ cm}^{-1}$  and H-O-H bending vibration at  $1640\text{ cm}^{-1}$  were detected for CI, CM2, CR2, and CO3 chondrites. All the chondrite samples had Si-O stretching band at around  $1000\text{ cm}^{-1}$ . Allende (CV3) exhibited only Si-O stretching band at near  $900\text{ cm}^{-1}$  and no O-H bands. Infrared absorption spectra for AMMs showed no O-H stretching vibration reflecting their dry condition, except for F97AC019 and F97AC017 with weak O-H stretching band.

Heating experiments on the grains of Murchison and Orgueil with sizes as small as AMMs ( $\sim 100\mu\text{m}$ ) were carried out in order to clarify the dehydration effect of micrometeorite during the atmospheric entry. Heating times were 30 and 60 s at temperatures every  $100^\circ\text{C}$  from  $500^\circ\text{C}$  to  $1000^\circ\text{C}$ . At relatively lower temperature condition ( $\leq 700^\circ\text{C}$ ), water in carbonaceous chondrites was not depleted. O-H stretching vibration at  $3400\text{ cm}^{-1}$  was, however, vanished at higher temperature ( $\geq 800^\circ\text{C}$ ). This might show that AMMs were heated to  $800^\circ\text{C}$  or more during atmospheric entry if our heating duration is reasonable.

Noble gas measurement using laser heating was performed for individual AMMs after the infrared microscopic analyses. Solar-He was detected for 4 samples. F97AC019 with very high concentration of helium ( $8.1 \times 10^{-3}\text{ cm}^3\text{ STP/g}$ ) preserve solar-Ne and primordial trapped argon component.

We have discovered an extraordinary AMM, F97AC021, with highly concentrated organic matters. Intense C-H stretching vibration at  $2900\text{ cm}^{-1}$  and complex absorption pattern appeared in the range from  $1400\text{ cm}^{-1}$  to  $1800\text{ cm}^{-1}$  were detected. The AMM might have a potential to have plenty of extraterrestrial organic compounds.

### 1. Introduction

Among the spectroscopic analyses, fourier-transform infrared spectroscopy is utilized as a powerful means to analyze the molecular structures in various research fields. Organic function groups can be identified from the group frequency whose concept rests on the assumption that the vibrations of a particular group are relatively independent of those of the rest, and hydrous component can be sensitively detected due to the large dipole moment of O-H bond. IR spectroscopic analysis can be applied to research of various meteorites. For example, reflective infrared spectroscopic measurements of meteorites were used to compare the optical properties of meteorites with those

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of celestial objects in order to identify candidate parent bodies for different meteorite types. The comprehensive mid-infrared analyses with transmission mode of 53 meteorites were presented in Sandford (1984) and reflectance spectra of 50 meteorites are reported by Salisbury *et al.* (1991). Sandford (1993) reported the transmission spectra of 7 Antarctic ureilites and 10 Antarctic H5 ordinary chondrites. Infrared diffusive reflectance spectra of carbonaceous chondrites were measured in order to identify the hydrous minerals (*e.g.*, Miyamoto, 1992; Miyamoto and Zolensky, 1994).

In contrast to the numerous reports on meteorites samples, laboratory measurements for cosmic dusts are very rare because of their small sizes. IR microspectroscopic analysis is a valuable method in order to observe microstructure of various materials. For example, it can be applied to minerals to analyze hydrous microphases (*e.g.*, Nakashima *et al.*, 1989), and to very small particles such as Interplanetary dust particles (IDPs) or micrometeorites. Because micrometeorites are considered to be primitive materials in the solar system, we can expect preservation of organic matters and water as primordial extraterrestrial materials. A search for these primordial materials will throw light not only on the genetic history of AMMs, but also on the secondary effects such as the atmospheric entry and weathering effects on Antarctica. Sandford and Walker (1985) reported the infrared transmission spectra of 26 individual IDPs from 2.5 to 25  $\mu\text{m}$  and almost all the samples have an intense absorption at 10  $\mu\text{m}$  ( $1000\text{ cm}^{-1}$ ) which is a characteristic silicate absorption.

We present here the infrared absorption spectra for individual AMMs and some typical carbonaceous chondrites using a combination of diamond-press method and microspectroscopy. The spectra of AMMs were compared with those of meteorites. Moreover, noble gas measurement for the individual AMMs was carried out after the infrared microscopic analyses. Since our FTIR analysis with diamond-press method without KBr pellet is not a completely destructive operation, noble gases can be maintained in the minerals which compose micrometeorites. The objectives of this study are to search for organic compounds in individual AMMs and to clarify their thermal history.

## 2. Samples

All AMMs measured in this study were picked up from precipitated fine particles taken from a water tank at Dome Fuji Station in 1997. These micrometeorites were collected by filtration of new fallen snow around the station located at the top of moraine 3810 m above sea level in Queen Maud Land at  $77^{\circ}19'$  south latitude,  $39^{\circ}42'$  east longitude (Nakamura *et al.*, 1999). All samples used in this study had been identified as extraterrestrial materials from their texture and major element composition determined with a scanning electron microscope with energy dispersive spectrometer (SEM/EDS). Details of the criterion of this identification were described in Nakamura *et al.* (1999). All 6 samples are unmelted chondritic particles 0.7–1.6  $\mu\text{g}$  in weight and about 100  $\mu\text{m}$  in diameter.

### 3. Experimental procedures

#### 3.1. IR microspectroscopy

For the spectroscopic observations, both of AMMs and crushed meteorites ( $\sim 100 \mu\text{m}$ ) were pressed between a pair of diamonds and thinned in order that infrared light can go through the samples. A diamond cell consisting of a pair of synthetic type IIa diamonds (Diamond express, Sumitomo Electric Co. Ltd.) (Fig. 1a) was utilized in this study. Matrix material was selected from the fragments of carbonaceous chondrites and placed between the diamonds. Type IIa diamond is nitrogen-free and has a high transmittance in a wide range of infrared light region. Infrared spectra were recorded on an FTIR spectrometer (Spectra 2000, Perkin Elmer) equipped with an IR microscope. Global light as an IR incident light source, a liquid-nitrogen-cooled HgCdTe (MCT) detector and a KBr beam splitter were used. Infrared spectra in a transmission mode were obtained through a square optical aperture ( $60 \times 60 \mu\text{m}^2$ ) with a spectral resolution of  $4 \text{cm}^{-1}$ , and all spectra were averaged from at least 100 single scans. Dry nitrogen gas was constantly pumped into the microscope to eliminate water vapor. The light source and the interferometer in our FTIR were equipped in closed box. The light path was purged for 5 min in the microscope and MCT detector with nitrogen before each measurement. Reference spectra were obtained on the sample-free region prior to the measurements of samples (see Fig. 1b). We confirmed that the spectra obtained by the diamond press method were identical with those obtained from the conventional KBr pellet method for several standard samples, thus the present method can be

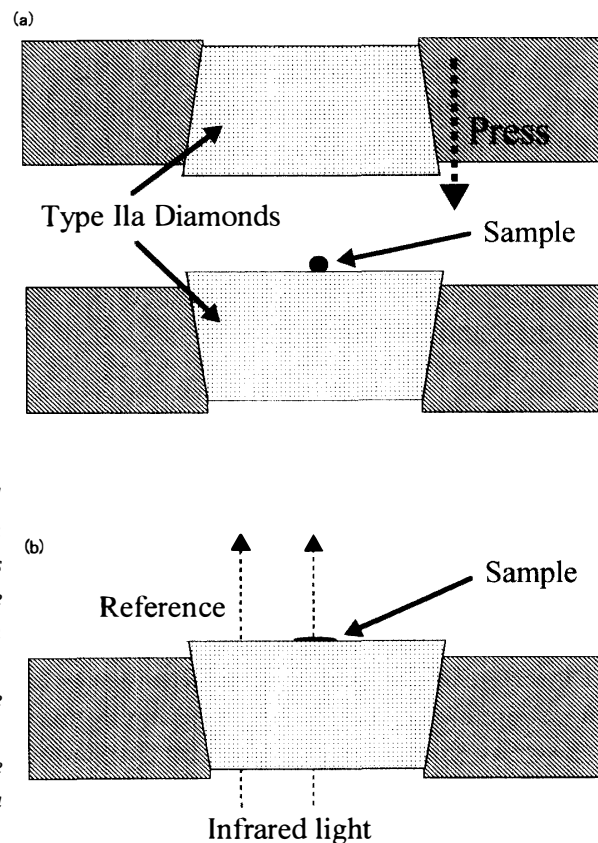


Fig. 1. A schematic illustration of the diamond press method. Samples were compressed between two diamonds (a) and upper diamond was removed when reference and sample spectra were measured (b). Diameter of the diamond is 2 mm and diameter of the sample is about  $100 \mu\text{m}$ . Infrared spectra in a transmission mode were obtained through a square aperture of  $60 \times 60 \mu\text{m}^2$ . Obtained spectra did not have large heterogeneity among the site of analyses in a sample.

justified. Advantages of this method are easy operation and to be able to obtain infrared spectra even with an extremely small sample, such as micrometeorite. Another merit is that destructive experiments such as noble gas measurement can be carried out after IR analysis. Before the spectral acquisition, the upper diamond was removed to avoid the generation of interference fringes (Fig. 1b).

### 3.2. Noble gas measurement

Noble gas measurements were done after infrared microscopic analyses. Main points of the experimental procedure are the same as our previous report (Osawa *et al.*, 2000). Individual micrometeorites which have already been pressed and crushed by the diamonds were carefully recollected and dropped into each platinum crucible and settled in a crucible holder made of stainless steel. The platinum crucibles with 2.0 and 1.8 mm outside and inside diameters, respectively, were made from platinum tube. After all samples were set, the sample holder was put in the ultra-high vacuum chamber connected to a noble gas purification line. For noble gas extraction, individual samples were heated using a slightly defocused Nd-YAG continuous wave laser beam by increasing the output power. The range of output power of YAG laser is 2.5–3.5 W. The heating time is about 5 min. The sample can be observed through the optical microscope equipped with the laser-system, and also displayed on a CRT monitor through a CCD camera. Extracted gases were purified by two Ti-Zr getters and noble gases except for He were trapped on a cryogenically cooled trap at 15 K. Ne, Ar, Kr and Xe were released successively at 45, 100, 135 and 250 K and the isotopic composition of each gas was analyzed on a modified VG-5400 mass spectrometer (MS-III) at the Laboratory for Earthquake Chemistry, The University of Tokyo. All noble gas elements were measured by an ion counting collector. Sensitivities for all noble gases and mass discrimination effects were calibrated by measurement of atmospheric noble gases, and a helium standard gas with  $^3\text{He}/^4\text{He} = 1.71 \times 10^{-4}$  prepared by mixing pure  $^3\text{He}$  and  $^4\text{He}$  gases in our laboratory. In neon analysis, mass interferences of  $^{40}\text{Ar}^{++}$  and  $\text{CO}_2^{++}$  were corrected. Blank corrections were carried out for all data, but blank correction cannot be done for some data due to small amounts of released noble gases comparable to blank level. The average value of six blank measurements was taken as blank value for the blank correction.

### 3.3. Heating simulation

Experimental heating simulation of atmospheric entry heating of AMMs was done by using carbonaceous chondrites in order to determine the temperature of dehydration. A fragment of crushed matrix material of Murchison or Orgueil was dropped into Pt crucible and heated in an electric furnace. The size of particle selected for the experiment was approximately  $100\mu\text{m}$  in diameter which is the same range of AMMs. The crucible was fixed to a spiral tungsten wire which connected with stainless wire. It inserted in the heated furnace and was taken out after 30 or 60 s. The temperature in crucible was recorded by a hand made alumel-chromel thermocouple. Heating temperature was set in every  $100^\circ\text{C}$  from  $500^\circ\text{C}$  to  $1000^\circ\text{C}$ .

## 4. Results and discussion

### 4.1. IR spectra

Infrared activity of crystal is produced when a change in the dipole moment of the unit cell occurs during the vibration. In the four normal modes of vibration of an  $\text{SiO}_4$ -tetrahedra, symmetric stretching and symmetric bending vibrations are infrared-inactive, though these modes are Raman-active. Strong infrared-activity occurs in a mode of asymmetric stretching vibration in the range of  $850\text{--}1000\text{ cm}^{-1}$ . There is a general decrease in wavenumber with decreases in bond strength for different isoelectronic and isostructural groupings (Williams, 1995).

In minerals, hydrogen is usually bonded to oxygen, the strongly polarized O-H groups absorb infrared photons efficiently. In general, the frequency of O-H stretch occurs at lower energies in system in which the O-H ion is more strongly hydrogen bonded.

#### 4.1.1. Carbonaceous chondrites

Infrared transmission spectra of several carbonaceous chondrites measured in this study are presented in Fig. 2. Orgueil (CI) which is the most primordial meteorite with plenty of water and organic matters has an intense absorption of O-H stretching band in the range of  $3000\text{--}3700\text{ cm}^{-1}$  and H-O-H bending vibration at  $1640\text{ cm}^{-1}$ . A couple of peaks around  $2400\text{ cm}^{-1}$  arise from atmospheric carbon dioxide. However, no C-H ( $\sim 2900\text{ cm}^{-1}$ ) or C=C ( $\sim 1650\text{ cm}^{-1}$ ) band was detected in this analyses. A sharp O-H stretching absorption band was detected at  $3685\text{ cm}^{-1}$ , which is caused by hydroxyl ion. It is consistent with the previous work which reported infrared diffuse reflectance spectrum of Orgueil with a sharp absorption band at the same wavenumber (Miyamoto and Zolensky, 1994). Si-O stretching band clearly appeared at about  $1000\text{ cm}^{-1}$ , which is saturated in absorbance due to the thickness of the sample. Spectrum of Murchison (CM2) is similar to that of Orgueil but has no sharp peak at  $3685\text{ cm}^{-1}$ . Two Antarctic CR2 chondrites Y-790112 and Y-793495 have the spectra which look like Murchison. Kainsaz meteorite that is classified to CO3 has obvious O-H stretching band. Our results confirm that these five carbonaceous chondrites contain considerable amount of water. On the other hand, Allende CV3 chondrite has only Si-O stretching band that appeared at about  $900\text{ cm}^{-1}$  and no O-H band, which indicates the lack of water in it.

Absorption band of O-H stretching vibration detected around  $3400\text{ cm}^{-1}$  may be due to mixing of several conditions of water; structurally bound water in some minerals, fluid inclusion, adsorbed water, etc. Liquid water has a broad band at  $3400\text{ cm}^{-1}$  consisting of a symmetric stretching absorption at  $3220\text{ cm}^{-1}$  and antisymmetric stretching absorption at  $3445\text{ cm}^{-1}$  (Aines and Rossman, 1984). In fact, there is a difference in a spectral shape of broad O-H stretching band among these hydrous carbonaceous chondrites. We think that the band is composed of three main absorption bands, *i.e.*, a very broad band at around  $3400\text{ cm}^{-1}$ , a sharper band at  $3600\text{ cm}^{-1}$  and a very sharp absorption band at  $3685\text{ cm}^{-1}$ . When water is not fixed in crystal lattice but is hydrogen-bonded to other water molecules or mineral surface, it results in a broad spectral feature with a peak position near  $3400\text{ cm}^{-1}$  (Kagi and Takahashi, 1998; Salisbury *et al.*, 1992). Sharper O-H stretching band at  $3600\text{ cm}^{-1}$  is produced by

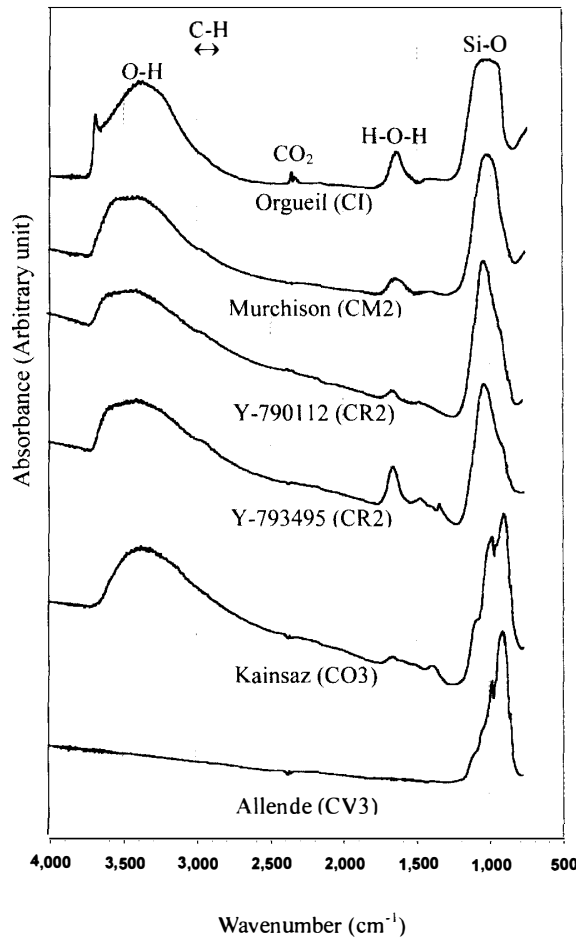


Fig. 2. Mid-infrared transmission spectra of 6 typical carbonaceous chondrites. Matrix materials were selected in these analyses.

hydrous component fixed in crystal. O-H bands of three carbonaceous chondrites, Murchison (CM2), Y-790112 (CR2) and Y-793495 (CR2) are composed of two absorption bands mentioned above. On the other hand, Kainsaz (CO3) has only broad O-H band at approximately  $3400\text{ cm}^{-1}$ .

When hydroxyl ions are contained in minerals as isolated condition without hydrogen bonding interaction, O-H stretching vibration band is very sharp and occurs at high wavenumber (Nakamoto *et al.*, 1955). For example, serpentine-group minerals exhibit a sharp O-H stretching band at  $3685\text{ cm}^{-1}$  as shown in Fig. 3. In the spectra of carbonaceous chondrites, it is noteworthy that only Orgueil has this sharp absorption band which is not seen in the spectra of the CM, CR, or CO chondrites. The position of the sharp absorption band observed for Orgueil is similar to that of serpentine. Zaikowski (1979) calculated the abundance of serpentine in Orgueil which must be low judging from the absorption at  $3685\text{ cm}^{-1}$ . If this sharp absorption band is derived from serpentine, it is curious that CM chondrites do not have this band, though CM chondrites contain serpentine. However, it might be because serpentine in CM chondrite is well crystallized than that in Orgueil (Bass, 1971). Tomeoka and Buseck (1988) demonstrated that the Orgueil matrix contains major amounts of saponite and ferrihydrite in addition to serpentine, in contrast with CM chondrite matrix consisting mainly of serpentine. Absorption features of Orgueil from  $1300$  to  $800\text{ cm}^{-1}$  resemble

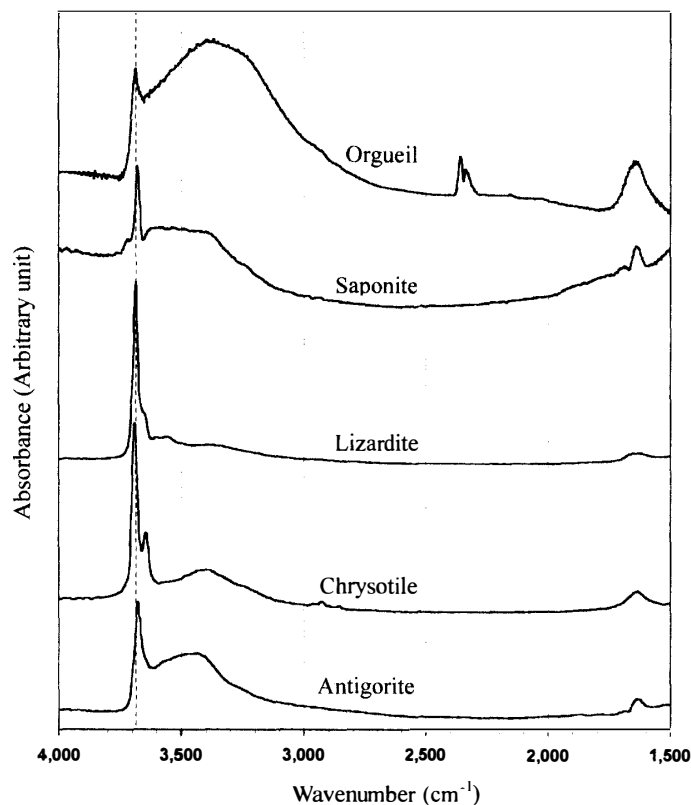


Fig. 3. Comparison between the spectrum of Orgueil and those of some phyllosilicates, saponite and serpentine (lizardite, chrysotile and antigorite), at  $1500\text{--}4000\text{cm}^{-1}$ . Data for 4 hydrous minerals from Salisbury *et al.* (1992). Dashed line shows the wavenumber at  $3685\text{cm}^{-1}$ .

that of the mixture of serpentine and saponite (Miyamoto and Zolensky, 1994). Infrared transmission spectra of Orgueil measured in the present work, saponite, and serpentine-group minerals (lizardite, chrysotile, and antigorite) after Salisbury *et al.* (1992) are shown in Fig. 3. Sharp absorption bands at  $3680\text{--}3690\text{cm}^{-1}$  observed for saponite and serpentine correspond to the sharp absorption of Orgueil. Only chrysotile has a pair of sharp bands at  $3690$  and  $3644\text{cm}^{-1}$ , though Orgueil has no intense absorption at  $3644\text{cm}^{-1}$ , which presumably show that Orgueil contains no chrysotile.

If it is general that only CI chondrites has the sharp absorption at  $3685\text{cm}^{-1}$  and other CM or CR chondrites do not have it, infrared microscopic analysis using diamond press method will be able to be utilized as a handy new classification method of carbonaceous chondrites.

#### 4.1.2. AMMs

No infrared spectra for AMMs have been reported so far, this study will be a start of systematical spectroscopic survey of micrometeorites. Infrared transmission spectra of 5 AMMs measured in this study are shown in Fig. 4. All spectra resemble among them and strong absorption bands at  $1000\text{cm}^{-1}$  attributable to Si-O stretching vibrations were detected for all samples. F97AC017 and F97AC019 have weak O-H stretching band at around  $3400\text{cm}^{-1}$  and H-O-H stretching vibration at near  $1640\text{cm}^{-1}$ . On the other hand, other three AMMs do not have O-H stretching bands. It is unambiguous that micrometeorites are extremely dry in contrast to the hydrous carbonaceous

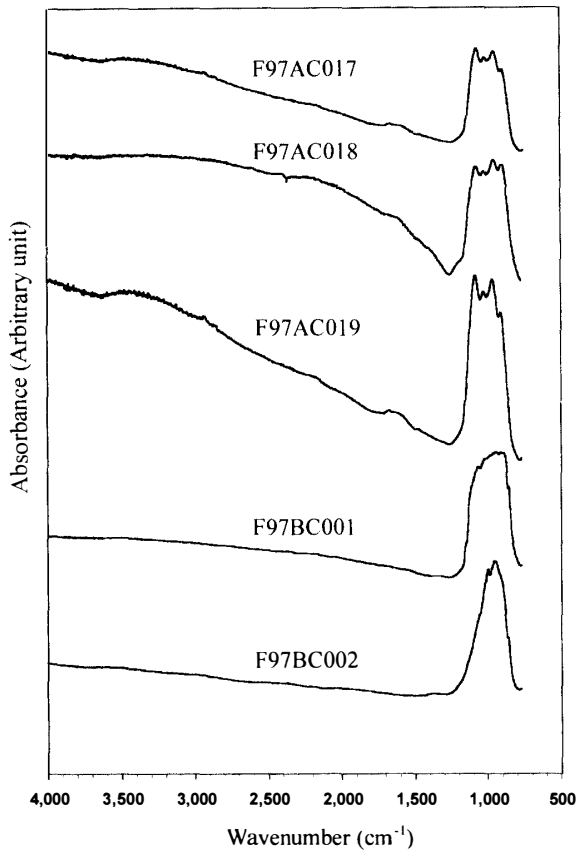


Fig. 4. Mid-infrared transmission spectra of 5 AMMs. Intense absorption bands at about  $1000\text{ cm}^{-1}$  are attributable to Si-O stretching vibrations. Absorption bands which originate from water is very weak.

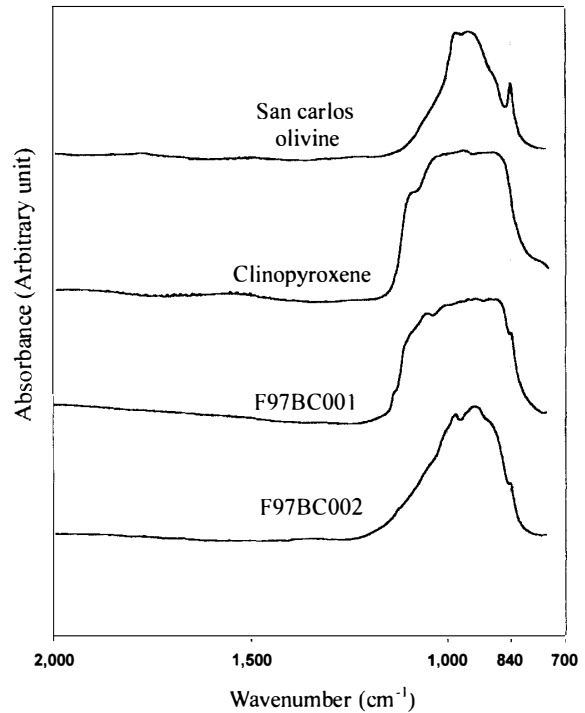


Fig. 5. Comparison among two standard minerals; olivine and pyroxene, and 2 AMMs. Olivine has characteristic and sharp peak at  $840\text{ cm}^{-1}$ . Absorption band at  $1000\text{ cm}^{-1}$  for AMMs can be explained by a mixing of these two minerals.

chondrites. F97BC001 and F97BC002 have very flat spectra in the wide region of  $1300\text{--}4000\text{ cm}^{-1}$ , which are similar to that of Allende.

Water and hydrous carbonate can be indicators of terrestrial weathering. An absorption bands near  $1350\text{ cm}^{-1}$  probably caused by hydrous carbonate may show the degree of terrestrial weathering of extraterrestrial material (Miyamoto, 1991). Spectra of AMMs measured in this study have no intense absorption bands at  $1350\text{ cm}^{-1}$ , which shows the low degree of terrestrial weathering of these samples. Trace of organic compounds cannot be detected in three samples, F97AC018, F97BC001 and F97BC002, while very weak C-H stretching bands at around  $2900\text{ cm}^{-1}$  can be detected in F97AC017 and F97AC019.

AMMs are usually composed of only four main minerals, *i.e.*, olivine, pyroxene, magnetite and some kind of sulfide, such as troilite and pyrrhotite. However, magnetite and sulfide have no intense absorption in mid-infrared region including the region of Si-O bond vibrations. Hence, Si-O stretching vibration at  $1000\text{ cm}^{-1}$  reflects only two minerals, such as olivine and pyroxene. Figure 5 shows the infrared transmission spectra of two AMMs; F97BC001 and F97BC002, and two standard minerals; San Carlos olivine and clinopyroxene separated from alkaline basalt sampled in Takashima



northwestern Kyushu Japan. Difference between these two standard minerals is that clinopyroxene has broad absorption tailing toward higher wavenumber from 1000–1150  $\text{cm}^{-1}$ , while olivine does not have intense absorption in this region. Characteristic sharp absorption band of olivine at 840  $\text{cm}^{-1}$  can be detected both in F97BC001 and F97BC002, which implies that these micrometeorites contain olivine. On the other hand, clinopyroxene has a broad Si-O stretching band in the range of 800–1150  $\text{cm}^{-1}$  and no sharp absorption at 840  $\text{cm}^{-1}$ . Spectra of two AMMs can be explained by mixing of these two minerals, and F97BC001 is enriched in pyroxene while F97BC002 in olivine. IR spectra can be a convenient tool estimating a mineral composition of AMMs.

#### 4.2. Noble gas compositions for AMMs

Since noble gas is one of the most powerful indicator to identify the extraterrestrial materials, some reports concerning the noble gas composition for individual IDPs and micrometeorites have been published (*e.g.*, Pepin *et al.*, 2000; Maurette *et al.*, 1991). Dome Fuji samples collected in 1996 (F96 series) are the first Japanese micrometeorite collections and the consortium study was carried out for F96 samples. As a part of this consortium study, two studies on noble gas were reported for F96 samples. Osawa *et al.* (2000) reported the all noble gas compositions for 12 individual F96 AMMs, and stepped pyrolysis at 400–1700°C for 16.1 mg of the fraction of <70  $\mu\text{m}$  particles was done by Nakamura and Takaoka (2000).

Noble gas compositions and concentrations for individual AMMs measured in this study are listed in Table 1. Concentrations and isotopic ratios of helium for 4 AMMs except for F97AC017 and F97BC001 were determined. Among them, F97AC019 has extremely high concentration of solar energetic particles (SEP)-like helium ( $8 \times 10^{-3} \text{cm}^3 \text{STP/g}$ ). As described above a weak O-H stretching band observed in this sample would be evidence that this AMM was not severely heated during atmospheric entry.  $^3\text{He}/^4\text{He}$  ratios for 4 AMMs are higher than SEP-He ( $2.17 \times 10^{-4} \pm 0.05$ ; Benkert *et al.*, 1993) and ratios of F97AC021 and F97BC002 are similar to solar wind (SW)-He ( $4.57 \times 10^{-4} \pm 0.08$ ; Benkert *et al.*, 1993). F97AC019 has  $^3\text{He}/^4\text{He}$  ratio similar to that of F96DK026 with abundant solar helium ( $^3\text{He}/^4\text{He} = 2.58 \times 10^{-4} \pm 0.21$ ) reported by Osawa *et al.* (2000). It seems a general trend that AMMs with high He concentration of solar origin have characteristic  $^3\text{He}/^4\text{He}$  ratio of  $2.5\text{--}3.0 \times 10^{-4}$  which is comparatively close to SEP-He.

Neon compositions of three AMMs and argon compositions of two AMMs were determined. Previous studies showed that most micrometeorites have abundant solar light noble gases, and have negligible amount of cosmogenic  $^{21}\text{Ne}$ , which indicates very short cosmic-ray exposure ages (*e.g.*, Osawa *et al.*, 2000; Olinger *et al.*, 1990).  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio of F97AC019 is higher than the SEP-Ne, which can be explained by a mixing of SEP and SW. Spallogenic  $^{21}\text{Ne}$  for 3 AMMs was not detected within experimental error limits, which suggests short cosmic-ray exposure ages. Generally, most AMMs show very short exposure ages (Osawa *et al.*, 2000). Although AMMs resemble to CM chondrites with short exposure ages in mineralogy and chemical composition, F97BC001 and F97BC002 showed infrared spectra similar to that of Allende (CV3) (see Figs. 2 and 4), and CV chondrites usually have relatively long cosmic-ray exposure ages (*e.g.*, Scherer and Schultz, 2000). Presumably, the AMMs except for F97AC019 were

Table 1. Noble gas compositions for individual AMMs.

Sample	Weight ( $\mu$ g)	$^4\text{He}$ ( $10^{-12}\text{cm}^3\text{STP}$ )	$^4\text{He}$ ( $10^{-6}\text{cm}^3\text{STP/g}$ )	$^3\text{He}/^4\text{He}$ ( $10^{-4}$ )	$^{20}\text{Ne}$ ( $10^{-12}\text{cm}^3\text{STP}$ )	$^{20}\text{Ne}$ ( $10^{-6}\text{cm}^3\text{STP/g}$ )	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$
F97AC017 <sup>1)</sup>	0.7	---	---	---	---	---	---	---
F97AC018	1.6	11.4	7.1	3.72 $\pm 1.14$	0.13	0.08	nd <sup>2)</sup>	nd <sup>2)</sup>
F97AC019	0.9	7280	8100	2.88 $\pm 0.25$	20.9	23.19	12.16 $\pm 0.87$	0.042 $\pm 0.019$
F97AC021	1.2	14.7	12.3	4.57 $\pm 1.58$	0.08	0.06	nd <sup>2)</sup>	nd <sup>2)</sup>
F97BC001	1.1	1.2	1.1	nd <sup>2)</sup>	26.9	24.42	10.59 $\pm 1.78$	0.018 $\pm 0.018$
F97BC002	1.2	15.4	12.8	4.72 $\pm 1.35$	32.9	27.40	11.06 $\pm 1.29$	0.023 $\pm 0.015$

Sample	$^{36}\text{Ar}$ ( $10^{-12}\text{cm}^3\text{STP}$ )	$^{36}\text{Ar}$ ( $10^{-6}\text{cm}^3\text{STP/g}$ )	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{38}\text{Ar}/^{36}\text{Ar}$	$^4\text{He}/^{36}\text{Ar}$	$^{20}\text{Ne}/^{36}\text{Ar}$
F97AC017 <sup>1)</sup>	---	---	---	---	---	---
F97AC018	0.37	0.23	121.2 $\pm 18.1$	0.199 $\pm 0.037$	30.4	0.35
F97AC019	0.73	0.81	0.11 $\pm 15.77$	0.202 $\pm 0.013$	10039	28.8
F97AC021	nd <sup>3)</sup>	---	nd <sup>2)</sup>	nd <sup>2)</sup>	---	---
F97BC001	0.086	0.08	nd <sup>2)</sup>	nd <sup>2)</sup>	13.8	314
F97BC002	0.042	0.03	nd <sup>2)</sup>	nd <sup>2)</sup>	367	784

All data are corrected for blank

1) Noble gas composition could not be determined due to losing the sample.

2) Isotopic ratio cannot be determined due to low concentration of noble gas in a sample.

3) cannot corrected for blank.

severely heated during atmospheric entry and became to have the spectra which look like Allende. In fact, helium gases in these AMMs are well depleted (Table 1), especially, F97BC001 preserve only  $1.1 \times 10^{-6}\text{cm}^3\text{STP/g}$  of  $^4\text{He}$ , though Ne concentrations are comparable to that of F97AC019.

F97AC019 has very low  $^{40}\text{Ar}/^{36}\text{Ar}$  isotopic ratio and high concentration of  $^{36}\text{Ar}$ .

Conceivably, Ar composition of this AMM mainly reflects solar-Ar since noble gas elemental composition of this AMM similar to that of SW. F97AC018 has the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio that is lower than atmospheric value (296) and considerably higher than that of F97AC019.

#### 4.3. Dehydration by the atmospheric entry heating

Micrometeorites are severely heated upon the atmospheric entry and the maximum temperature reached on the atmospheric entry increases as the particle size, density, and entry velocity increase. Computer simulations show that among IDPs with  $>75\mu\text{m}$  in diameter only those with entry velocities near earth escape velocity survive atmospheric entry without completely melting (Flynn *et al.*, 1993). The X-ray diffraction analysis for individual AMMs shows that only 2 samples among 61 samples contain phyllosilicate (Nakamura *et al.*, 2000), hence it is reasonable that water was not detected in the five samples as shown in Fig. 4. Presumably, water was lost by the atmospheric entry heating.

Mineralogy and chemical composition of AMMs are similar to those of CM chondrites (Kurat *et al.*, 1994). However, the present study showed that IR spectra of micrometeorites are different from CM chondrite with respect to the lack of O-H stretching band. Then, we had experimental simulations of atmospheric entry heating in order to clarify the effect of dehydration. Details of the experimental procedure were described in Section 3.3. Figure 6 shows temperature rise pattern in a crucible. Sample was rapidly heated within about 30 s and temperatures became constant after 30 s. According to numerical simulations, micrometeorites are heated during only one or two second at maximum temperature (Love and Brownlee, 1991). Then, in this experiment, we heated samples for 30 and 60 s to simulate the effect of dehydration by the heating for a short time. Matza and Lipschutz (1977) and Hiroi *et al.* (1994) performed the heating experiment for Murchison at 400–1000°C. However, they heated the sample in a low-pressure hydrogen atmosphere for 1 week, which is remarkably different from our experimental condition.

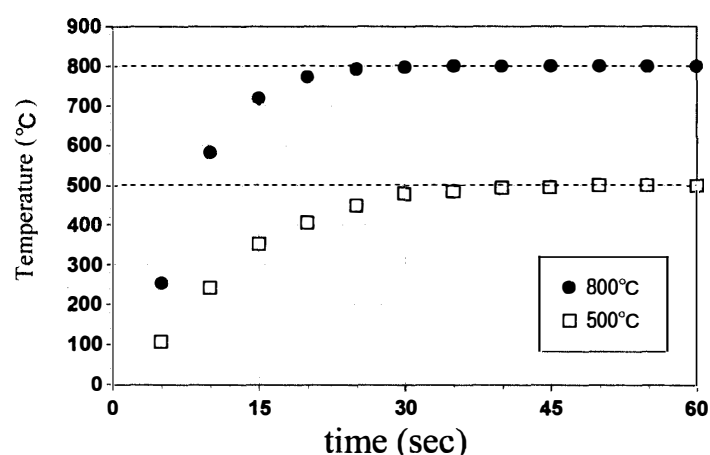


Fig. 6. Time dependence of temperature rise in a platinum crucible. The temperatures in the inset denote the temperature of furnace. Matrix fragments ( $\sim 100\mu\text{m}$  in diameter) are heated rapidly in 30 s.

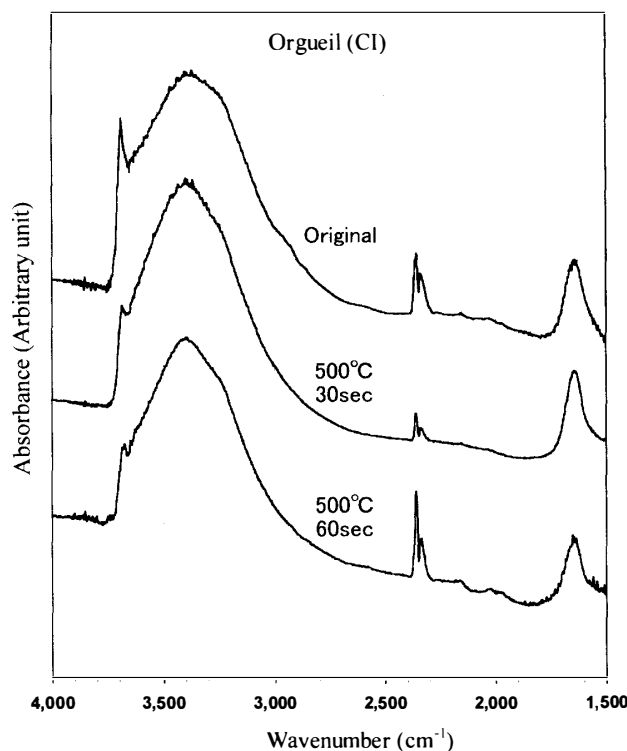


Fig. 7. Mid-infrared transmission spectra of Orgueil (CI) heated at 500°C for 30 and 60 s. Although peak at 3685  $\text{cm}^{-1}$  has weakened by heating, absorption bands at 3400  $\text{cm}^{-1}$  and 1640  $\text{cm}^{-1}$  do not weaken. No difference in spectra can be detected between the heated durations of 30 s and 60 s.

IR spectrum of Orgueil heated at 500°C for 30 and 60 s are illustrated in Fig. 7. The intensities of O-H stretching bands at 3400  $\text{cm}^{-1}$  and H-O-H bending vibration at 1640  $\text{cm}^{-1}$  do not decrease significantly compared with the original spectrum. There is no difference between heating time of 30 s and 60 s. This result clearly indicates that the particle from Orgueil cannot be dehydrated at 500°C within a short period ( $\leq 60$  s). Detailed results of heating experiment of Murchison are presented in Fig. 8a and b. In the case of low temperature ( $\leq 700^\circ\text{C}$ ), the dehydration hardly happens, though apparent dehydration are observed in the case of high temperature ( $\geq 800^\circ\text{C}$ ), bands at 3400  $\text{cm}^{-1}$  and 1640  $\text{cm}^{-1}$  vanished after only 30 s heating. The difference in temperature between 700°C and 800°C is critical in the effect of dehydration. It is noteworthy that absorption band at about 1000  $\text{cm}^{-1}$  obviously moved to higher wavenumber by heating. This may be caused by the structural change in silicate mineral due to the dehydration reaction. The experiment indicates that most AMMs were exposed to a considerably high temperature condition ( $\geq 800^\circ\text{C}$ ) during the atmospheric entry.

#### 4.4. Organic compounds in an extraordinary micrometeorite

IR spectroscopy can be applied to the field of the planetary science to detect extraterrestrial organic compounds, for example, IR analysis can be used to detect organic compounds in meteorite (e.g., Breger *et al.*, 1972). Detection of organic matters in micrometeorites is an important topic to reveal the implication between

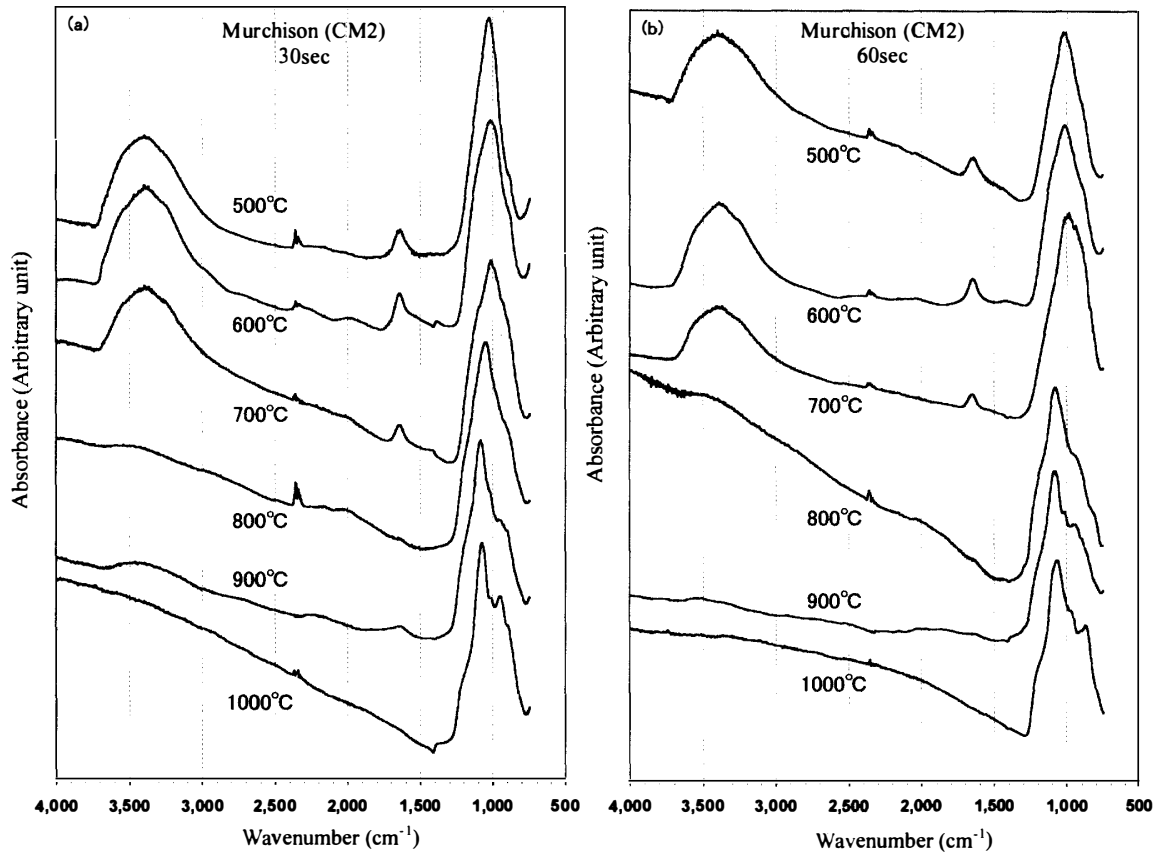


Fig. 8. Dehydration of Murchison (CM2) by heating from 500°C to 1000°C for 30 s (a) and 60 s (b). Clear dehydration has happened at the temperature > 700°C and the difference between 700°C and 800°C is definite. Presumably, AMMs might have been heated to 800°C or more during atmospheric entry.

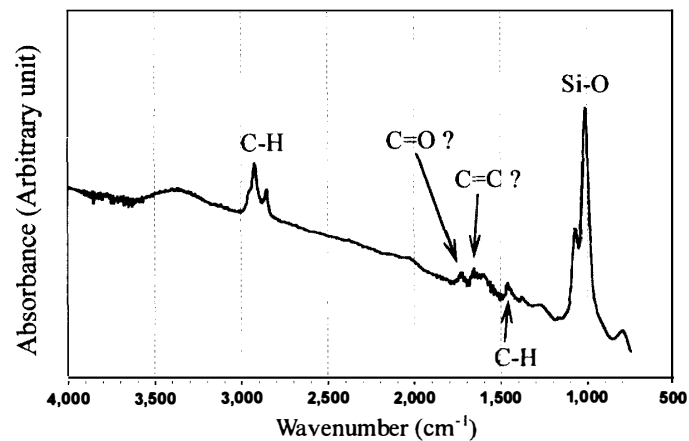


Fig. 9. Mid-infrared transmission spectrum of F97AC021. A pair of absorption bands at about 2900  $\text{cm}^{-1}$  is caused by symmetric and antisymmetric C-H stretching vibration, which shows that this AMM has plenty of organic compounds.

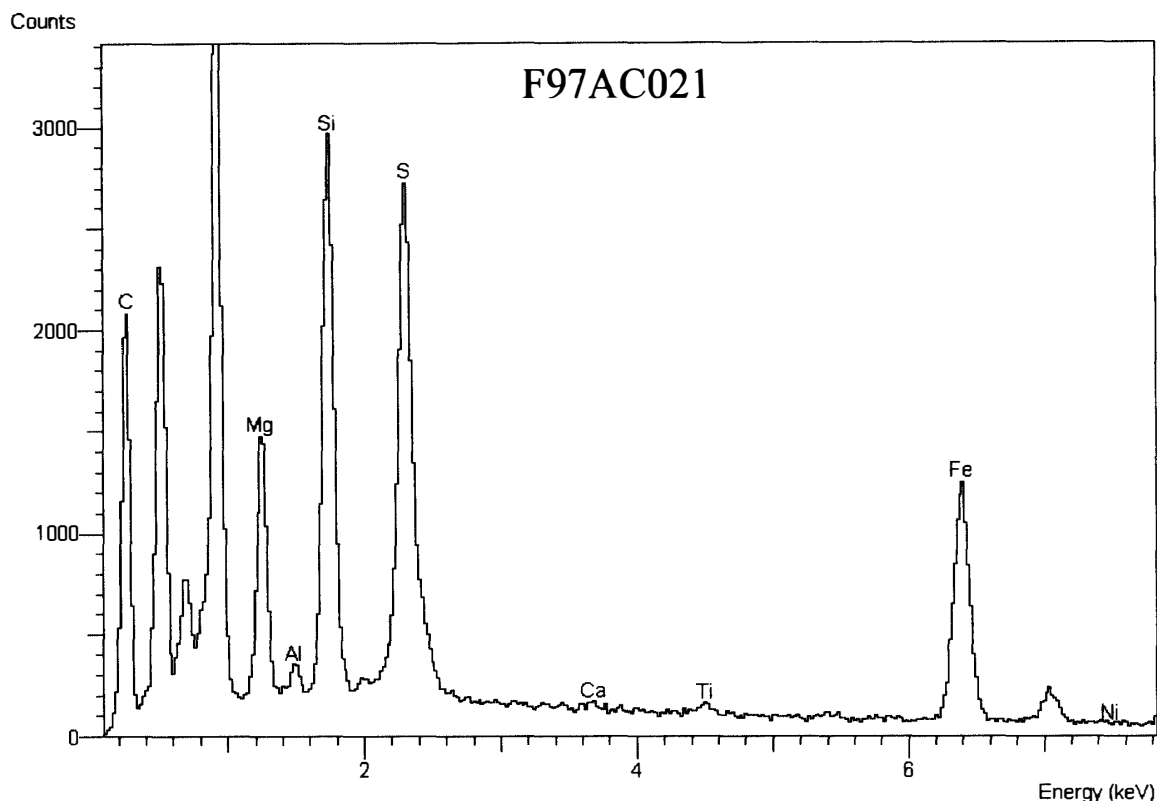


Fig. 10. EDS spectrum of AMM F97AC021. Carbon and sulfur are extremely concentrated in this AMM. Relative abundance of four major elements, i.e. Mg, Al, Si and Fe, is chondritic.

carbonaceous chondrites and micrometeorites. Although, organic compounds were not detected in most of AMMs studied here, we have discovered an extraordinary AMM F97AC021 which is rich in organic matters. This AMM is proved to be an extraterrestrial material by the noble gas measurement showing the solar helium (Table 1). The infrared and EDS spectra of this micrometeorite are shown in Figs. 9 and 10. A pair of intense absorption bands caused by C-H stretching vibration at about  $2900\text{ cm}^{-1}$  and a peak at  $1460\text{ cm}^{-1}$  which may be assigned to C-H bending vibration are detected in this micrometeorite. These absorption bands imply that this AMM contains abundant hydrocarbons. Complex absorption pattern appeared in the range from  $1400\text{ cm}^{-1}$  to  $1800\text{ cm}^{-1}$ , however, it is difficult to assign at present. Anyway, organic compounds are concentrated in this AMM compared with the carbonaceous chondrites. Moreover, high concentrations of sulfur and carbon were detected by the EDS analyses (Fig. 10). Because a terrestrial contamination may not be ignored, a more detailed verification is required to prove the existence of the extraterrestrial organic compounds in the AMM.

#### 4.5. Pseudomicrometeorites

We identify a candidate of AMM using EDX analysis when a candidate has a chondritic major elemental composition. Although the validity of this identification method is high, it is not perfect. We encountered some strange particles which look

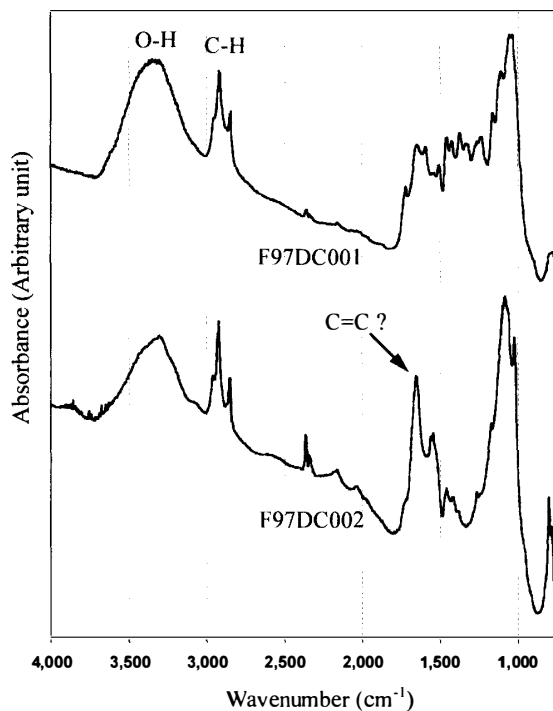


Fig. 11. Mid-infrared transmission spectra of two pseudometeorites, F97DC001 and F97DC002. Intense O-H stretching band at about  $3300\text{ cm}^{-1}$  was detected in these samples. C-H stretching bands at about  $2900\text{ cm}^{-1}$  and complex absorption patterns at  $1000\text{--}1200\text{ cm}^{-1}$  show various organic substances exist in them.

like genuine AMM, which is called us *pseudometeorite*. We present here one example of *pseudometeorite* with chondrite-like elemental composition except for concentration of carbon. F97DC001 and F97DC002, which are pretenders of micrometeorite, have no solar noble gases or cosmogenic nuclei. In the case of F97DC002, only 4 counts of  $^3\text{He}$  were detected during 240s by an ion counting collector and amounts of noble gases are comparable to the background. Infrared transmission spectra and EDS spectra of these two *pseudometeorites* are presented in Figs. 11 and 12. These black particles have very high concentrations of carbon and plenty of organic compounds. Complex pattern in the infrared absorption spectra for these samples shows that these *pseudometeorites* contain various organic compounds.

Although the origin of these dusts is uncertain, it may be smoke exhausted from diesel engines. In this case, it is only a speculation, the volcanic ash etc. might adhere to surface of smoke, and it becomes aggregates with chondritic elemental composition as a result.

## 5. Conclusions

1) Broad band at  $3400\text{ cm}^{-1}$  attributable to the O-H stretching vibration and H-O-H bending vibration at  $1640\text{ cm}^{-1}$  were detected in CI, CM2, CR2 and CO3 chondrites. It shows that the hydrous minerals and molecular water were contained in these meteorites. On the other hand, Allende CV3 chondrite has neither O-H stretching band nor H-O-H bending band.

2) Experimental simulation of atmospheric entry heating for AMMs shows that water in carbonaceous chondrite cannot be depleted at  $\leq 700^\circ\text{C}$  but easily dehydrated at  $\geq 800^\circ\text{C}$  within short period of heating ( $\leq 60\text{ s}$ ).

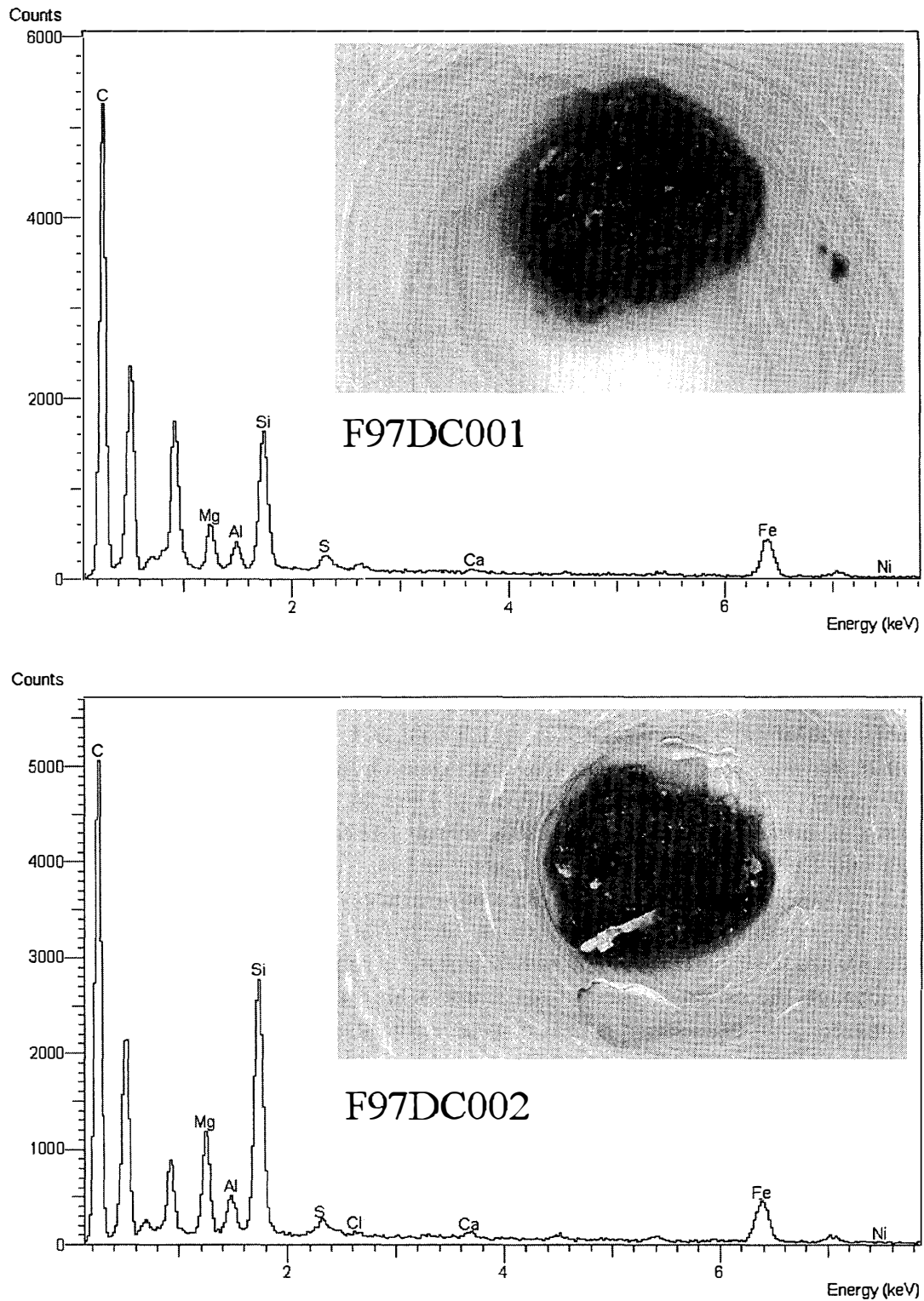


Fig. 12. EDS spectra of two pseudometeorites, F97DC001 and F97DC002. It is very mysterious that their major elemental compositions are chondritic, when extremely high concentrations of carbon are excluded. Conceivably, the most of the carbon exist in the state of the organic compounds in them since graphite has no absorption in mid-infrared region.



3) Most micrometeorites have no intense O-H absorption band, which presumably shows that they were heated to 800°C or more during atmospheric entry, though F97AC017 and F97AC019 has weak O-H stretching bands.

4) Intense C-H stretching vibration was detected in an unusual micrometeorite F97AC021, which shows the existence of various organic compounds in it.

5) Very high concentration of solar-helium ( $8.1 \times 10^{-3} \text{ cm}^3 \text{ STP/g}$ ) has been detected in F97AC019 exhibiting weak O-H stretching band. While, other AMMs F97AC018, F97BC001, and F97BC002 with no O-H stretching band have much smaller amount of solar He than F97AC019. It might suggest that He concentration correlates with the intensity of the infrared absorption attributable to the hydrous matters.

6) Infrared transmission analysis with diamond press is very convenient and useful method for classifying carbonaceous chondrites and clarify the degree of heating of AMMs.

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