QUANTITATIVE FT–IR ANALYSIS FOR CHONDRITIC METEORITES: SEARCH FOR C_{60} IN METEORITES

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ABSTRACT

Infrared absorption spectra of 9 bulk samples and 3 acid residues of meteorites were obtained in the mid-infrared region ($4000{\sim}400 cm^{-1}$). From the known composition of meteorites studied, the possible absorption modes were investigated. Most bands of bulk samples occur in the region below $1200 cm^{-1}$ and they are due to metallic oxides and silicates. The spectra of each group can be distinguished by its own characteristic bands. Acid residues show very distinct features from their bulk samples, and absorption bands due to organic compounds are not evident in their spectra. Quantitative analyses for two carbonaceous (Allende CV3 and Murchison CM2) and one ordinary (Carraweena L3.9) chondrites were performed for the presence of fullerene (C_{60}) in the meteorites. We calculated the concentration of C_{60} in the acid residues by curve-fitting the spectra with Gaussian functions. The upper limit of C_{60} concentration in these meteorites appears to be less than an order of a few hundred ppm.

1. INTRODUCTION

Spectral analyses of interstellar medium and interstellar grain particles have provided deep understanding of interstellar materials and the formation of the solar system. Some primitive components in meteorites are thought to be derived from the interstellar medium, and the discovery of various isotopic anomalies confirmed the extraterrestrial origin of meteorites (Clayton *et al.* 1976, Yang & Epstein 1984).

A comparison between the infrared spectra of meteorites and those of the interstellar dust can provide important clues for the relationship between the two extraterrestrial materials (Allamandola *et al.* 1987). Knacke & Kratschmer (1980) suggested bands around 1430 (7.0μm) and $3330 cm^{-1}$ (3.0μm) in carbonaceous chondrites as counterparts of the interstellar absorption bands near 1450 (6.9μm) and $3260 cm^{-1}$ (3.07μm). Bradley *et al.* (1988) reviewed the studies on the connection

151

between carbonaceous chondrites and interplanetary dust particles (IDPs). IDPs were classified into three groups; olivines, layer-lattice silicates, and pyroxenes (Sandford & Walker 1985). In addition to the studies about IDPs, spectroscopic analyses on the infrared spectrum of the interstellar medium were performed and many unidentified infrared (UIR) emission bands still remain (Herbig 1975, Sellgren 1984, Leger *et al.* 1988, Roche *et al.* 1994). The polycyclic hydrocarbons (PAHs) and silicate grains have been suggested for the candidates of UIR bands (Leger & Puget 1984, Allamandola *et al.* 1985, Roche *et al.* 1994).

In 1983, a new isomer of carbon, fullerene (C_{60}) was discovered and it was suggested to ubiquitously exist in the interstellar medium for its highly symmetrical structure and stability (Kroto *et al.* 1985, Kratschmer *et al.* 1990, Hare & Kroto 1992, Buss *et al.* 1993, Petrie *et al.* 1993). Besides neutral C_{60}, various types of fullerene, fullerane ($C_{60}H_n$), and ionized C_{60} were suggested for interstellar material (Paquette *et al.* 1983, Sellgren 1984, Allamandola *et al.* 1985, Snow & Seab 1989, Webster 1992). However, the previous studies of the existence of C_{60} in interstellar medium by spectroscopic analyses were not positive (Kratschmer *et al.* 1990, Webster 1992, Roche *et al.* 1994). If C_{60} has survived in the harsh conditions in the interstellar medium, the meteorites may also contain an appreciable amount of C_{60}. However, it is clear that C_{60} should have been altered during the formation of solar nebula and/or during the accretion process of meteorites. It is important to determine the presence and the limits of C_{60} concentration by various available analysing techniques. Attempts to estimate the upper limit for C_{60} concentration in meteorites were made in laboratories. A Fourier transform ion cyclotron resonance (FTICR) mass spectrometer using two frequencies of laser pulses for vaporization and ionization and a laser desorption (reflection) time-of-flight (TOF) mass spectrometer (LDMS) were used. The results were 2~5ppb for Murchison and 5~10ppb for Allende (de Vries *et al.* 1993, Beker & Bunch 1997). Only a certain carbon rich inclusion of Allende showed that the concentration of C_{60} is about 100ppb (Beker *et al.* 1994).

In this study, we used the infrared spectrometry for nine bulk samples and three acid residues. From the laboratory measurements, we compared the spectra of bulk samples of meteorites to those of interstellar features such as IDPs and UIRs. Also we calculated the concentrations of C_{60} in three acid residues of Allende (CV3), Murchison (CM2), and Carraweena (L3.9). These residues were previously studied for their isotopic anomalies (Yang & Epstein 1983). Acid residues were chosen because they should contain most of C_{60} in meteorites and thus they can provide more accurate data of C_{60} concentration if it exist.

2. PROCEDURE

We used the standard KBr pellet method with the mixture of 0.5mg of sample and 75mg of KBr powder. Mixed powder was pressed at 8 ton for 5 minutes to avoid overpressing. All meteoritic samples were made to pellets in previous work where the samples were pressed at 9.5 ton for 30 seconds (Ha 1987). We confirmed that the pressure did not make any significant differences in a
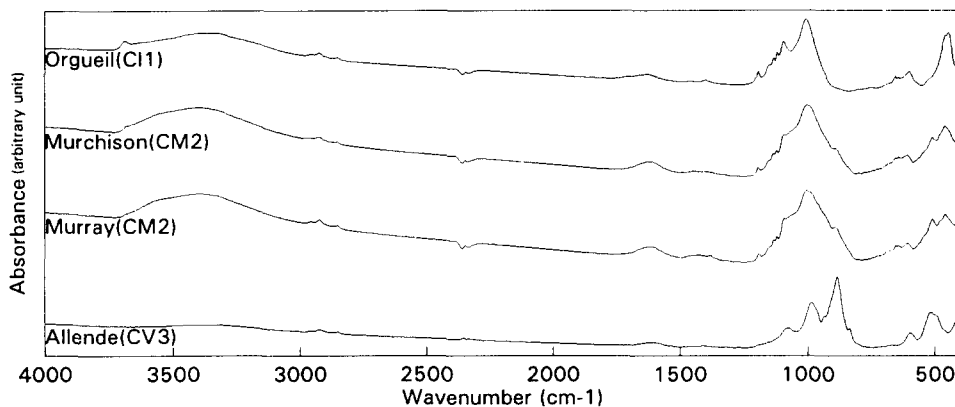
Figure 1. The absorption spectra of carbonaceous chondrites. The strongest band near $1000cm^{-1}$ is characteristic of hydrated silicates. Allende shows quite distinct features from C1 and C2 chondrites. It shows the carbonate absorption at $885cm^{-1}$.

spectrum. When the mixed powder was prepared to make a transparent disk of 13mm diameter, we tried to minimize the grinding time to avoid the deformation of crystal structure, the ion exchange, and the water absorption from the atmosphere. Sample preparation tools were cleaned with methylenechloride (CH_2Cl_2). Room temperatures were varied from -5 to 30°C during this experiment.

The absorption spectra were obtained by the BIO-RAD FTS 165 Fourier Transform Infrared (FT-IR) spectrometer in mid-infrared region ($4000\sim400cm^{-1}$). Each spectrum was obtained after 32 times of scanning with a resolution of $8cm^{-1}$, which is the best for solid state samples.

The HPL (100% line) test was performed before sample measurements using the background (KBr blank) to check any systematic error and contamination from methylenechloride. It used the background and sample spectrum which was scanned immediately after scanning background. Ideally, the ratio between them should make a straight line at 100% transmission. We obtained almost flat line around 100% of transmission with some fluctuation due to an electronic noise. Therefore the contamination from solvent can be neglected in this experiment.

For quantitative analysis of C_{60} in meteorites, we obtained four absorption spectra of synthetic C_{60} 99.5% (Southern Chemical Group) powder samples with 0.49, 0.89, 1.48, 1.95mg of C_{60} in a total weight of 75.5mg pellet. The total weights of the pellets were kept same for comparison. We obtained linear relationships among three parameters, intensity, area, and the weight of C_{60}. The linear dependence of intensity on weight of C_{60} was used to estimate the amount of C_{60} in meteorites. Baseline correction was performed before curvefitting of spectra. The curvefit application allows us to assume the probable function of certain shape with arbitrary width and height. Then, the para-
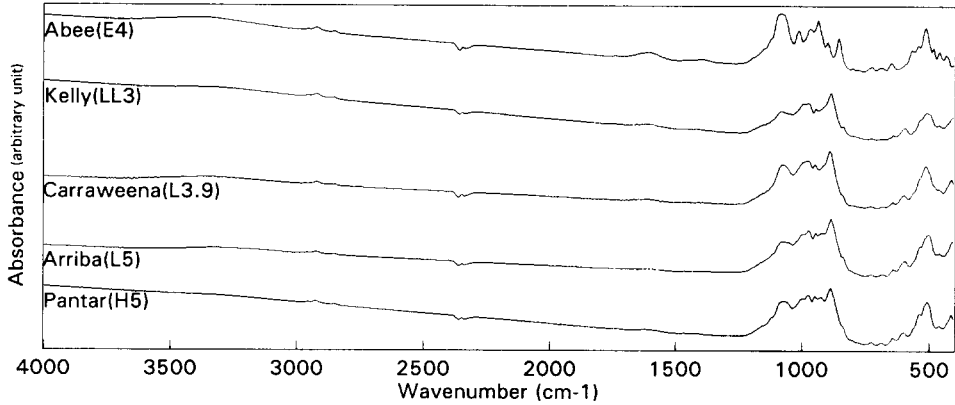
Figure 2. The absorption spectra of enstatite and ordinary chondrites. The silicate band at 1084cm^{-1} is apparent in Abee (E4). Ordinary chondrites show multi-component features of olivine and pyroxene in the region of 1100-800cm^{-1}.

meters were iterated to obtain the best fitting curve to the original spectrum. We used Gaussian functions and assigned constraints to center, width or height if needed. After the curvefitting, possible absorption bands due to chemical species other than C_{60} were subtracted and the amounts of C_{60} in meteorite samples were calculated using the Beer-Lambert's law.

3. IR SPECTRA OF METEORITES

3.1. Carbonaceous Chondrites

Four carbonaceous chondrites were studied. C1 (Orgueil) and C2 (Murchison and Murray) chondrites show very similar spectra (Figure 1). Absorption bands due to the hydrated silicates near 1000cm^{-1} (10.0μm) and carbonate near 1430cm^{-1} (7.0μm) are observed, which is consistent with previous study (Knacke & Kratschmer 1980). 1000cm^{-1} band was also suggested to be responsible for the silicate grain particles in the interstellar medium (Roche *et al.* 1994). Allende (CV3) shows somewhat different spectrum from the other two more primitive chondrites (C1 and C2). The strongest peak occurs at 885cm^{-1} (11.3μm). This band coincides with the carbonate emission feature in the H$_{II}$ region (Knacke & Kratschmer 1980, Roche *et al.* 1994). Allende has been known to contain more calcium and other refractory components than other meteorites in the form of CAIs (Sears & Dodd 1988). It is possible that crystalline carbonates, such as $FeCO_3$ and $CaCO_3$ or mixed state with other metal compounds could contribute to this band. The peaks around 500cm^{-1} (20.0μm) are from various metallic oxides.

Besides the absorption bands due to inorganic compounds, the most interesting feature in carbonaceous chondrites are their strong water absorption features. All carbonaceous chondrites show

bands near 3330 (3.0μm) and 1610cm^{-1} (6.2μm) due to H$_2$O stretching and bending modes, which is consistent with literatures (Bellamy 1975, Knacke & Kratschmer 1980). Some UIR from interstellar medium also showed 3330 (3.0μm) and 1610cm^{-1} (6.2μm) bands and these were suggested as the evidence of PAHs (Allamandola *et al.* 1987, Buss *et al.* 1993). The carbon-rich transition objects also show the extinction features at 3030 (3.3μm), 1610 (6.2μm), 1300 (7.7μm) and 885cm^{-1} (11.3μm) with a broad continuum due to dust extinction (Buss *et al.* 1993). Most peaks appear in the spectra of carbonaceous chondrites except a peak at 1300cm^{-1} (7.7μm). Carbonaceous chondrites are known to contain significant amount of PAHs, and therefore these two water bands indicate the extraterrestrial origin of meteorites with their deuterium excess (Kerridge 1983, Yang & Epstein 1983, de Vries *et al.* 1993). Orgueil (CI1) has the strongest water absorption among the samples examined and shows a sharp band near 3688cm^{-1} (2.7μm) due to free O-H stretching. Allende shows much weaker water absorption than C1 and C2 chondrites.

3.2. Enstatite and Ordinary Chondrites

One enstatite chondrite (Abee) and four ordinary chondrites (Kelly, Carraweena, Arriba, and Pantar) were studied (Figure 2). The multi-component bands in the region of 1100~800cm^{-1} (9.09~12.5μm) indicate the mineralogical complexity of these meteorites. Abee (E4) has strong peaks at 1084 (9.2μm) and 513cm^{-1} (19.5μm) which can be interpreted as Si-O and Mg-O vibration modes in enstatite (MgSiO$_3$) with slight shifts in the matrix (Nakamoto 1978).

Ordinary chondrites also have absorption bands at lower energy regions and they are probably due to metallic oxides and silicates. Sandford & Walker (1985) studied 22 interplanetary dust particles and classified them into three groups, such as olivine ((Fe, Mg)$_2$SiO$_4$), pyroxene ((Fe, Mg)SiO$_3$), and layer-lattice silicates. The ordinary chondrites show patterns which match with the olivine- and pyroxene-like interplanetary dust particles. For example, Carraweena shows multi-component bands at 1077 (9.3μm), 1000 (10.0μm), 889 (11.2μm), and 511cm^{-1} (19.6μm), and weaker bands at 729 (13.7μm), 681 (14.7μm), and 642cm^{-1} (15.6μm) which can be interpreted as the olivine feature which were found in some IDPs (Sandford & Walker 1985). There is an interesting relation between metallicity and spectral intensity for ordinary chondrites. The absorption intensity increases with higher metallicity. Pantar (H5) and Arriba (L5), the petrologic type 5 chondrites, have two strong peaks at 973 (10.3μm) and 535cm^{-1} (18.7μm) which may be related to Fe-O and Mg-O stretching modes (Liese 1967, Nyquist & Kagel 1971) which are less for the other chondrites. When we compare the peak intensities due to Fe and Ni in four ordinary chondrites, the data confirm the classification scheme that metallic concentration is LL(very low iron group)< L< H(high iron group). due to bounded water near 3330cm^{-1}.

3.3. HF-HCl Residues of Meteorites

HF-HCl residues of Allende (CV3), Murchison (CM2), and Carraweena (L3.9) were prepared previously (Yang & Epstein 1983, Ha 1987). Since the acid residues were prepared to remove major silicate and metallic components in meteorites by demineralization processes, they contain organic
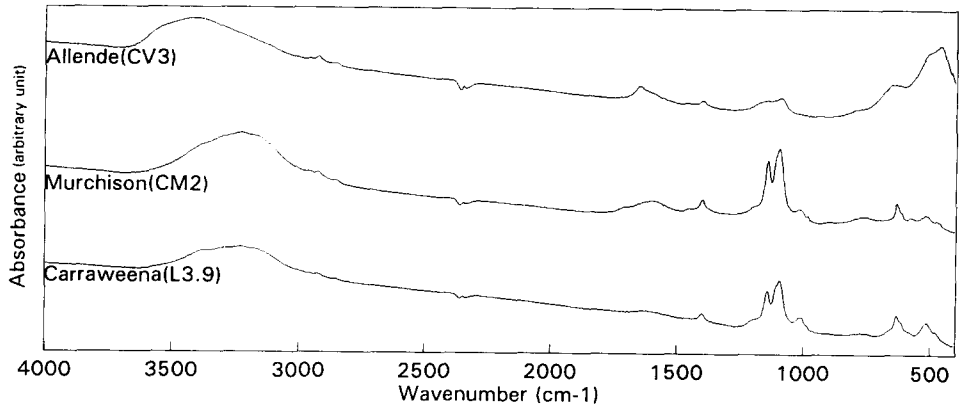
Figure 3. The absorption spectra of HF-HCl residues of Allende (CV3), Murchison (CM2), and Carraweena (L3.9). Although Carraweena is ordinary chondrite, it shows very similar feature with Murchison, carbonaceous chondrite. The two strong peaks near 1144 and 1098cm^{-1} can be interpreted to sulfides and oxides (chromite). Allende shows no sharp absorption bands and the major peak at 465cm^{-1} may be due to carbon compounds. All residues show strong absorption.
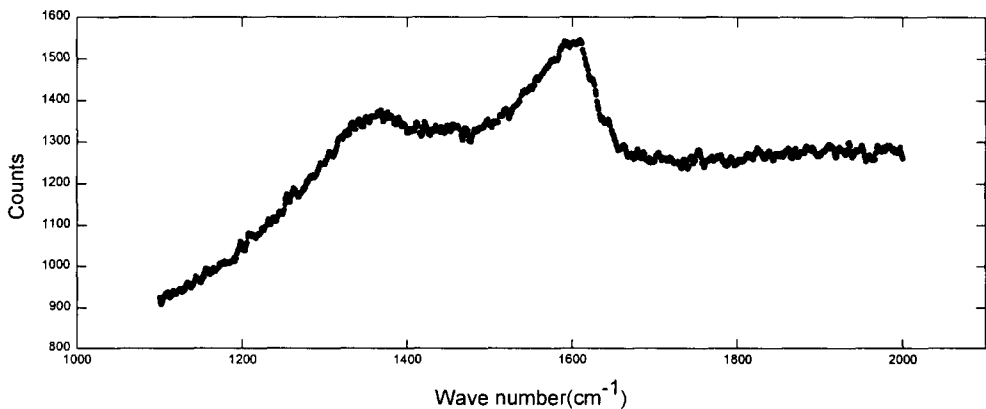

Figure 4. The Raman spectra of acid residue of Murchison meteorite. The C-C and C-H vibration modes at 1350 and 1600cm^{-1} are apparent and these are due to amorphous hydrocarbon compounds in the acid residue.

polymer type of matter with some very refractory components. IR spectra show such features (Figure 3). Carraweena bulk sample shows very complex multi-component bands, but its acid residue shows two strong bands at 1144 (8.7μm) and 1098cm^{-1} (9.1μm) and weak bands in the region below 1000cm^{-1} (10.0μm). All acid residues show bands near 1098cm^{-1}, although Allende has much weaker intensities. Sulfides and sulfates combined with metal may be responsible for these strong bands (Bellamy 1975, Nakamoto 1978). Especially, significant amount of sulfides were remained in acid residues of Carraweena and Murchison, possibly combined with metallic compounds probably as a form of daubreelite, $FeCr_2S_4$ (Yang & Epstein 1983). Other metallic or organic compounds do not match with this band. Buss *et al.* (1993) observed 1140cm^{-1} (8.8μm) peak in the transition objects. The peak at 631cm^{-1} (15.8μm) may be due to metallic oxides such as chromite and spinel (Nyquist & Kagel 1971).

The lack of organic absorption bands should be discussed. In our data, there are no strong absorption peaks due to organic materials. Only a very weak absorption near 1701cm^{-1} (5.9μm) in Murchiso can be interpreted as ketone (C=O absorption), but other strong absorptions due to expected functional groups are not observed. This can be understood by the polymeric structure of meteoritic organic matter. Kerridge *et al.* (1987) suggested that the organic matter in meteorites formed "kerogen-like" structure, and the skeletal vibration of C-C or C-H modes have extremely weak intensities in infrared region (Bellamy 1975). Also the strong water absorption near 3330cm^{-1}(3.0μm) could make the C-H band ambiguous. However, we observed amorphous C-H stretching mode in Murchison sample by using in Raman spectra at 1350 and 1600cm^{-1} (Figure 4) which confirms the work of Sandford & Walker (1985).

It is well-known that type 1, 2 and some type 3 meteorites have large amount of carbon up to 58% of the residues. However, most type 3 meteorites, such as Allende, Chainpur, and Arriba, have a small amount of organic polymer (Yang & Epstein 1983). Allende is known to contain a lot of carbon compounds such as silicon carbide (SiC) and diamond (Anders & Zinner 1993, Huss & Lewis 1995). A band near 465cm^{-1} (21.5μm) in Allende meteorite may be interpreted to carbon compounds. A band around 700cm^{-1} (14.3μm) may be interpreted to chromite and spinel which are abundant in acid residue samples.

All acid residue samples show stronger bounded water absorption feature at 3330cm^{-1} (3.0μm) than their bulk samples. Water could be absorbed during the acid treatment procedure. However it is important to note that a large portion of the water is proved to be indigenous, which is obtained by the hydrogen isotope analyses (Yang & Epstein 1983).

3.4. Quantitative Analysis for Fullerene (C_{60}) in Meteorites

Since C_{60} has a highly symmetrical structure, only four vibrational modes are active in the mid-infrared region. Figure 5 shows the four strong bands at 1428 (7.0μm), 1181 (8.5μm), 575 (17.4μm), and 525cm^{-1} (19.0μm) of C_{60}, which are consistent with the previous studies (Kroto *et al.* 1985, Kratschmer *et al.* 1990). We measured the intensities from their spectra and integrated the peak area. There are good linear relations between intensities and the weight of C_{60} in a pellet (Figure
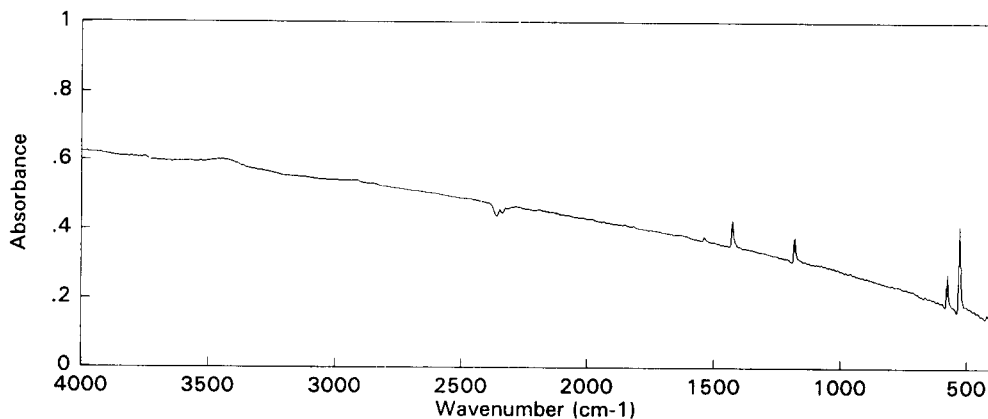
Figure 5. The absorption spectrum of a fullerene. Four absorption bands at 1428, 1181, 575, and 525cm^{-1} are consistent with previous studies. The relative intensities increase with the weight of C$_{60}$ in a pellet.

6a). Similar relations were found for area and the weight of C$_{60}$ (Figure 6b), and also for intensity and area (Figure 6c). Among the four straight lines with different slopes, we considered the two lines of stronger peaks at 575 (17.4μm) and 525cm^{-1} (19.0μm) for quantitative analysis.

It is very difficult to find a direct evidence for the existence of fullerene in the acid residues because of its small concentration (de Vries et al. 1993, Beker & Bunch 1997). Among the four major peaks of C$_{60}$, we focused on the two stronger peaks because other two weaker bands contribute less than 30% of total intensity and area. To calculate the amount of C$_{60}$ in acid residues, we used the relation between intensity and weight. Because no apparent C$_{60}$ peaks are found in all meteorite residue spectra, we subtracted the fitted functions from original spectra, and obtained the difference for the analysis. Since the residual spectra do not show any evidence of C$_{60}$, we concentrated our effort to set an upper limit of the amount of C$_{60}$ in meteorites. The relative intensity can be changed by the structure and adjacent elements which surround C$_{60}$, and therefore these results must be considered as a rough estimate.

The fitting results for three chondrites are given in Figure 7a, b, c. We subtract fitted Gaussian functions which have their centers near 578 (17.3μm) and 515cm^{-1} (19.4μm) from the original spectra of Murchison and Carraweena. These two bands can be interpreted by chromite or spinel (Nyquist & Kagel 1971). Similarly, bands at 632 (15.8μm), 527 (19.0μm), and 455cm^{-1} (22.0μm) are subtracted in the case of Allende.

Allende has much broader bands than Murchison and Carraweena, and this makes it difficult to obtain the appropriate functions for fitting. We gave constraints in the center and height of the strong peak in the region of analysis if needed.
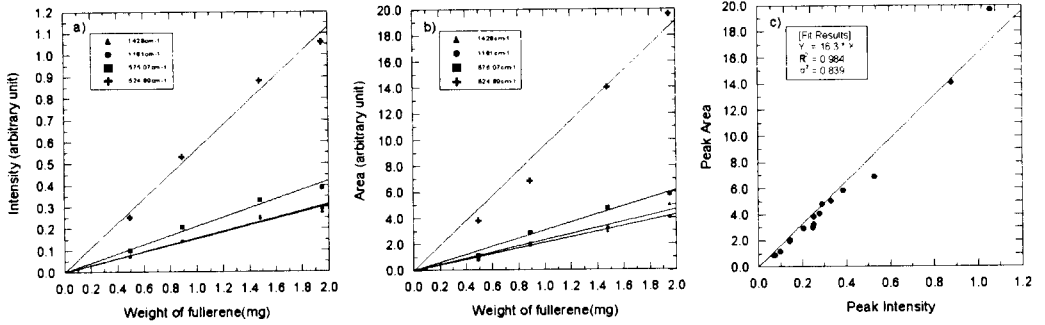
Figure 6. The relation between (a) intensity and the weight of C_{60} (The slopes for 575 and 525cm^{-1} are 0.210 and 0.564.), (b) area and the weight of C_{60} in a pellet, and (c) area and intensity in a pellet.
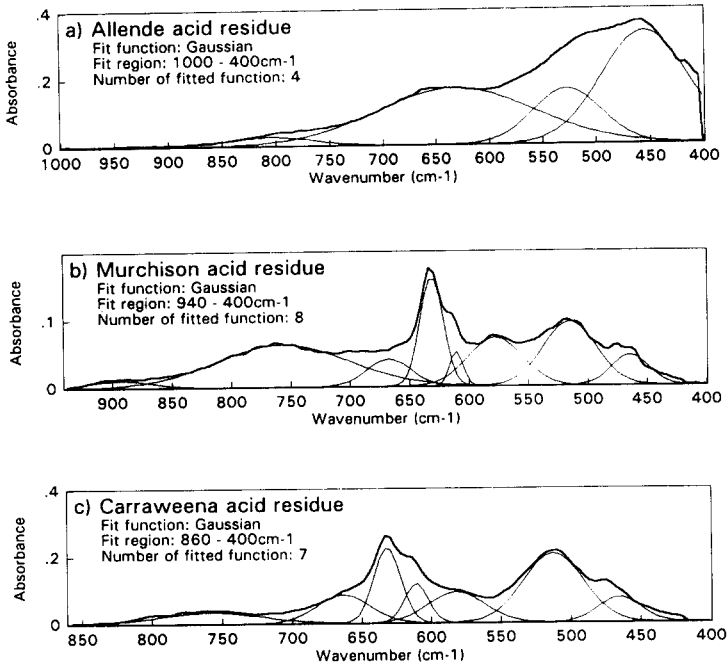

Figure 7. The curvefit of (a) Allende(CV3), (b) Murchison (CM2), and (c) Carraweena (L3.9). We subtracted the bands at 632, 527, and 455cm^{-1} for Allende, 578 (582) and 515 (512)cm^{-1} for Murchison (Carraweena). Most metallic compounds, such as chromite and spinel, have vibrational modes in 500cm^{-1} region. Fitted residual contour is not added in the figures.

Table 1. The Amount of Fullerene C_{60} in Three Meteorites.

Meteorites	Upper Limit of the Concentration of C_{60} in Bulk Samples (ppm)
Murchison (CM2)	700
Allende (CV3)	200
Carraweena (L3.9)	300

Considering the formation of C_{60} in interstellar medium, the amount of C_{60} may be related to the amount of organic matters in the meteorite. Therefore carbonaceous chondrites are expected to have the best possibility of detecting C_{60}. We also examined one ordinary chondrite to see if it shows different spectroscopic features than those of two carbonaceous chondrites. Table 1 shows the results of C_{60} concentration in three chondritic meteorites. From the previous studies, the upper limit of C_{60} in Allende and Murchison were given by 2~10ppb (de Vries *et al.* 1993, Beker & Bunch 1997). Although only the very rough limits can be obtained from the spectroscopic analyses, our results are also against the ubiquitous existence of C_{60} in interstellar medium.

4. SUMMARY

In mid-infrared region, nine meteorite bulk samples show the dominant silicate features, and their spectra are very similar to the interstellar dust grain particles. Carbonaceous chondrites show the PAHs bands similar to those of the carbon-rich transition nebulae. Most absorption bands are interpreted to olivine, pyroxene, and hydrated silicates. The spectra reveal the characteristic features of the mineralogical groups and the petrologic types of samples. Absorption bands due to organic compounds are not dominant in acid residues. Instead, sulfides and metallic compounds such as chromite are more evident. Three acid residues of Allende, Carraweena, and Murchison are examined for the presence of C_{60} and the calculated amount of C_{60} appeared to be less than an order of a few hundred ppm.

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