

Characterization of carbonaceous matter

By

Tatsushi MURAE* and Eiji IKEDA*

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Abstract: The test samples, 1B and 2B, delivered from ISAS were examined by microscopic laser Raman, microscopic FT-IR, and microscopic fluorescence spectrometry. The spectral data indicate that the sample 1B contains small amount of PAHs and that the sample 2B contains significant amount of carbonaceous matter that is closely related to that in Allende.

1. INTRODUCTION

Many of meteorites are considered to originate from the asteroid belt. C type asteroids may be closely related to carbonaceous chondrites. Carbonaceous chondrites are the most primitive in all of meteorites. Most characteristic components of carbonaceous chondrites are organic compounds, which give us significant informations about origin of life on the Earth. There are several analytical methods for characterisation of organic compounds. The most popular analytical method for known organic compounds is gaschromatography/mass spectrometry (GC/MS). However, GC/MS analysis needs extraction procedure, which may destruct the original characteristics of samples. Therefore, we used spectroscopical methods other than GC/MS. All of the spectra (Raman spectrum infra red spectrum and fluorescence spectrum) which we used in this work can be determined without destruction of the sample. Combination of microscopic technic and the spectroscopy is very useful for identification of minor amount of organic compounds in the sample, So we analysed the test samples using microscopic laser Raman, microscopic FT-IR, and microscopic fluorescence spectroscopy.

2. ANALYTICAL INSTRUMENTS

Microscopic Laser Raman (JEOL JRS-SYS2000 + Olympus BHSM) This instrument is very useful for characterization of small particles ($\sim 1 \mu\text{m}$) of carbonaceous matter by Raman spectra and for determination of distribution pattern of specified carbonaceous matter in small area using CCD imaging by specific Raman band.

Microscopic FT-IR (Perkin-Elmer 1600 + Spectra Tech IR-Plan): This instrument is very useful for characterization of organic compounds. It is possible by reflection mode to obtain

* Department of Earth and Planetary Sciences, Faculty of Science, Kyushu University, Hakozaki, Fukuoka, Japan.

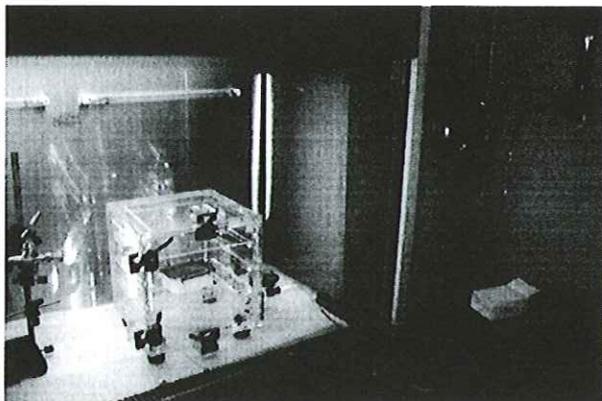


Fig. 1: The clean bench in a semi-clean room.

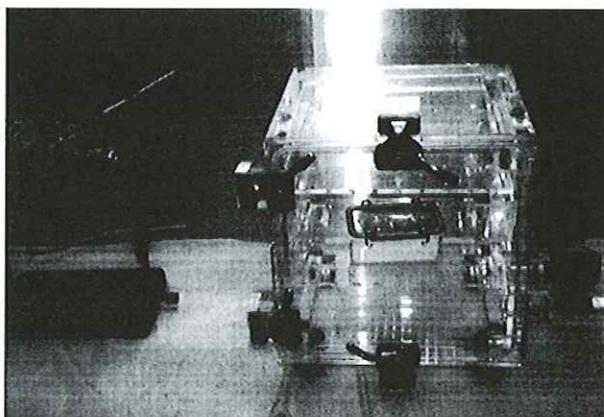


Fig. 2: Samples in the desiccator.

absorption spectra of powder samples under the microscope when the powder pressed on aluminum foil in thin film form. When the amount of the components in the sample is very low, partial high concentration of the compound is necessary.

Microscope Fluorescence Spectrometer (Carl Zeiss MPM 400): This instrument is very useful for detection of small amount of fluorescent matter. Although the fluorescence spectrum is usable for characterization of compounds, additional data are necessary for exact identification of the compound.

Measuring Mode: All spectra were determined by reflectance mode in order to get meaningful spectrum from powdered samples without destruction.

3. SAMPLES

General View of the Samples The sample 1B was finely powdered and showed gray color and the sample 2B was black fine powder.

Storage and Handling of Samples The samples were handled in a clean bench (class 100: Fig. 1) in a semi-clean room (Fig. 1). The vials containing the samples were stored in an acrylic desiccator (Fig. 2) filled with supremely pure nitrogen in the clean bench.

4. SAMPLE 1B

4.1 Analysis by laser raman microscopy

Instrument: The Raman spectra were observed by a JEOL JRS-SYS2000 spectrometer equipped with a Olympus BHSM microscope (Fig. 3). Laser light of Ar⁺ (514.5 nm) and of He-Ne (632.8 nm) were used as the source for exciting.



Fig. 3: Laser Raman spectrometer.

Sampling method: The sample was pressed over an aluminum-foil disk ($\phi = 6$ mm) using squeezing wrench (Fig. 4). About 0.2mg of the sample was enough for the analysis.

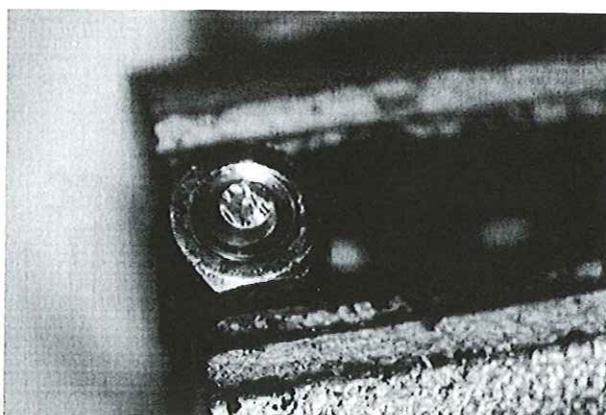


Fig. 4: Sample on aluminum foil.

Component identified by Raman spectrum: Component A: Some of the particles in the powder was identified as olivine by the Raman bands at 952, 914, 850, 820, 585, 537, 417, 300 cm^{-1} . (Fig. 5). Component B: Some of the particles in the powder was identified as clinopyroxene by the Raman bands at 1006, 677, 659, 394, 334, 231 cm^{-1} . (Fig. 6). Most of the particles in the powder were very fine and observed as the mixture of A + B (olivine and clinopyroxene) as shown in Fig. 7.

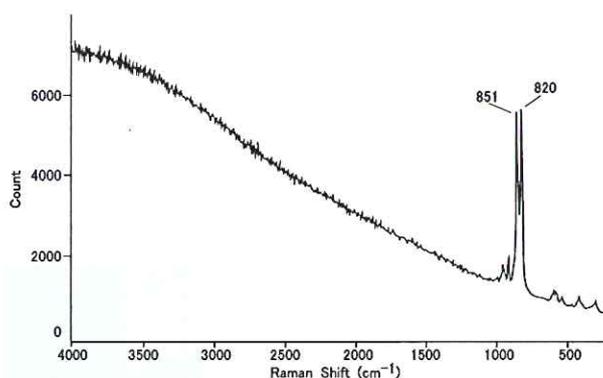


Fig. 5: Raman spectrum of component A in 1B at objective $\times 100$.

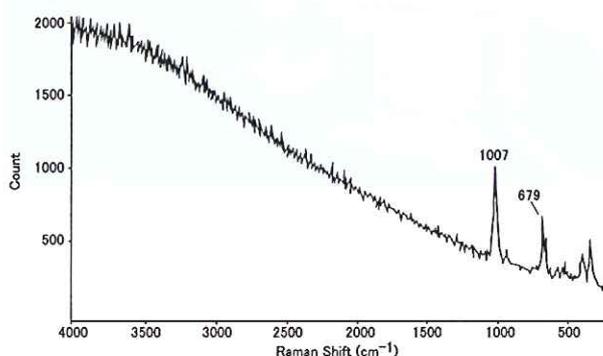


Fig. 6: Raman spectrum of component B in 1B. at objective $\times 100$.

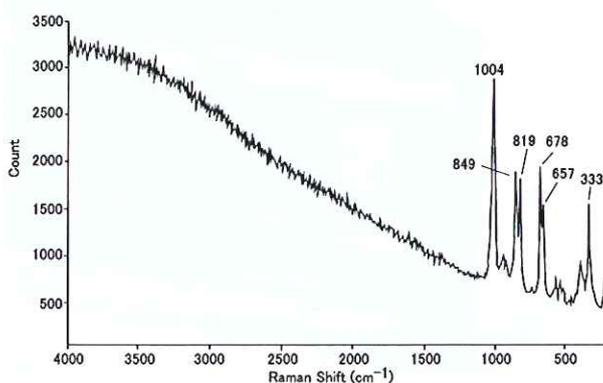


Fig. 7: Raman spectrum of components A + B in 1B. at objective $\times 20$.

Typical distribution pattern of the components determined using imaging system: Figs. 8b and f show the image obtained with the Raman band of 850 cm^{-1} showing the distribution pattern of olivine. Figs. 8c and g show the image given by the Raman band of 1010 cm^{-1} indicating distribution of clinopyroxene.

Overall distribution pattern of the components: Both components showed almost the same distribution pattern at the same area indicating that each component is very fine grain and

mixed very well each other. Therefore, the spectral feature as shown in figure 7 afforded by mixing of components [(A and B) is usually observed when low power objective was used. The patterns corresponding to different Raman band in the same area are shown in figures 8a~c and d~g). The difference between the images obtained using different Raman band at the same area indicates that olivine and clinopyroxene differently are distributed at the area.

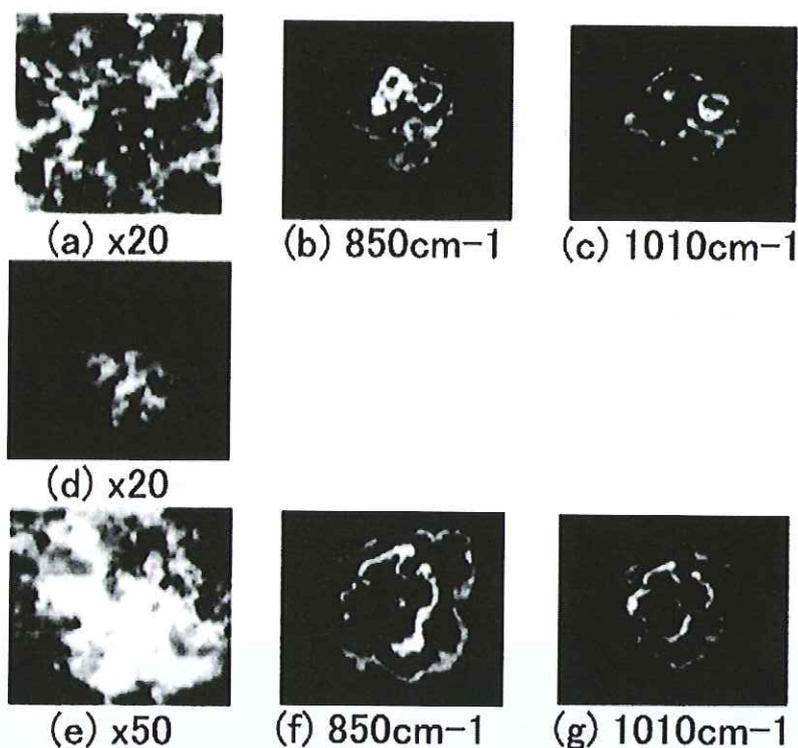


Fig. 8: Raman image of 1B; Images a, b and c were obtained at the same area. Image e is enlarged one of d. Images e, f and g were obtained at the same area. Images a, d and e are obtained by white light. Images b and f are images by 850 cm^{-1} band, images c and g: are by 1010 cm^{-1} band

4.2 Analysis by FT-IR microscope

Instrument: IR analyses were carried out using a Perkin-Elmer 1600 spectrometer equipped with a Spectra Tech IR-Plan microscope at Objective x15.

Results: Space resolving power using the infrared ray is low; therefore it was impossible to characterize each component. The spectrum in Fig. 9 includes absorptions due to almost all components in the sample 1B. The absorption band at 2960 cm^{-1} may suggest the existence of aliphatic organic compound, and the bands at 1613 and 1648 cm^{-1} may suggest the existence of aromatic organic compound. However, the signals at fingerprint region are overlapped with other strong signals due to inorganic compounds, so further characterization by gas chromatography/mass spectrometry (GC/MS) is necessary for the confirmation of existence of the organic compounds.

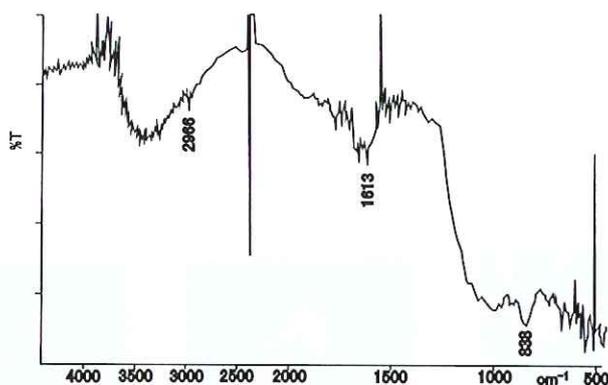


Fig. 9: FT-IR spectra of 1B obtained microscopic reflectance mode.

4.3 Analysis by microscope fluorescence spectrometer

Dispersed small fluorescent particles were observed. Fig. 10 shows photos taken by fluorescence (a) and white light (b) of the area where the fluorescent particles condensed. Usual fluorescent particles give the spectrum such as Fig. 11, which shows two extinction-maxima at 500 nm and 780 nm. Some particles show an extinction maximum only at 780 nm (Fig. 12). These fluorescent particles supposed to be PAHs, because fine structure accompanied with blue shift in the fluorescence spectrum by changing the light source from blue (460 nm) to UV (390 nm) as shown in Fig. 13.

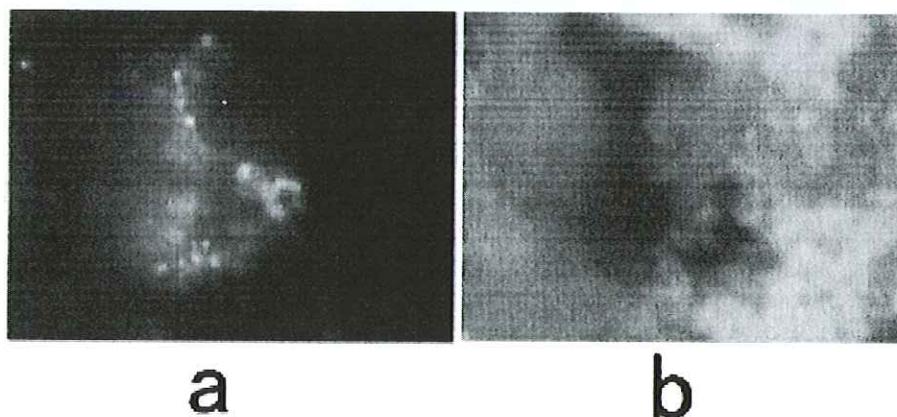


Fig. 10: Microscopic photos of 1B by. a:fluorescence and b:white light.

5. SAMPLE 2B

5.1 Analysis by laser raman microscopy

Instrument: The Raman spectra were observed by a JEOL JRS-SYS2000 spectrometer equipped with a Olympus BHSM microscope (Fig. 3). Ar⁺ (514.5 nm) and He-Ne (632.8 nm) were used for excitation.

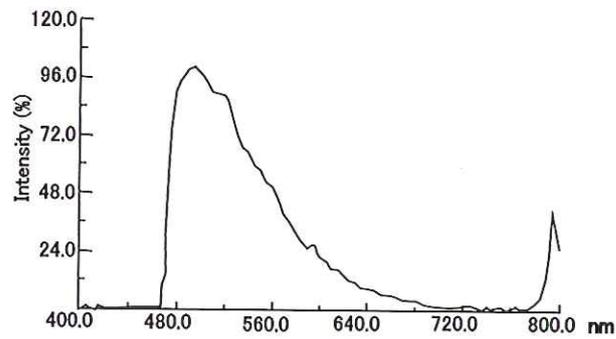


Fig. 11: Fluorescence spectrum of 1B: most popular feature.

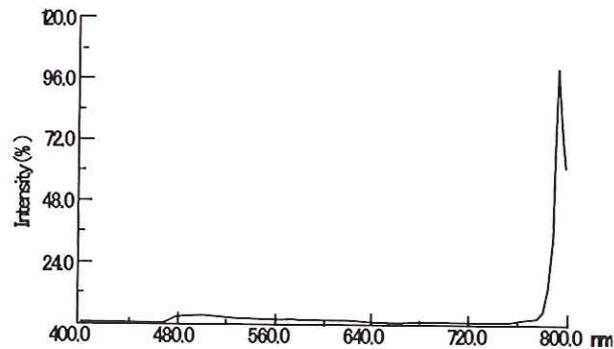


Fig. 12: Fluorescence spectrum of 1B: redish particle.

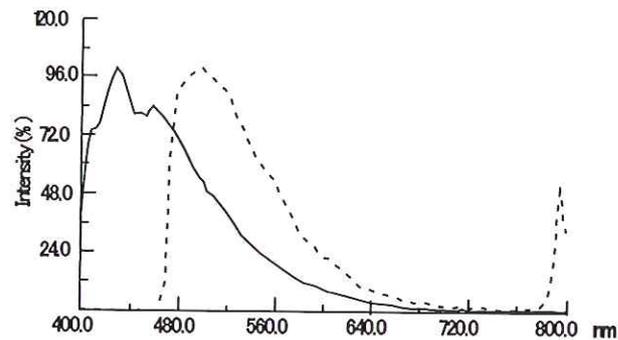


Fig. 13: Fluorescence spectrum of 1B: spectrum shifted by changing light source from 460nm (dotted line) to 390 nm (solid line).

Sampling method: The sample was pressed over an aluminum-foil disk $\phi = 6$ mm using squeezing wrench (Fig. 4). About 0.2mg of the sample was used for the analysis.

Component identified by Raman spectrum: Three different components were identified by the Raman spectra. The spectrum (Raman bands: 952, 914, 850, 820, 585, 537, 417, 300 cm^{-1}) of the first component is almost the same as that of component A in the sample 1B

and identified as Olivine. The second component showed Raman bands at 1006, 677, 659, 394, 334, 231 cm^{-1} , which are the same as those of component B in the sample 1B and identified as clinopyroxene. The third component C showed Raman bands at 3228, 2931, 2688, 1590, 1345 cm^{-1} (Fig. 14) that are typical for graphitic carbon. The spectrum obtained using a low power objective shows the mixing of components A, B, and C.

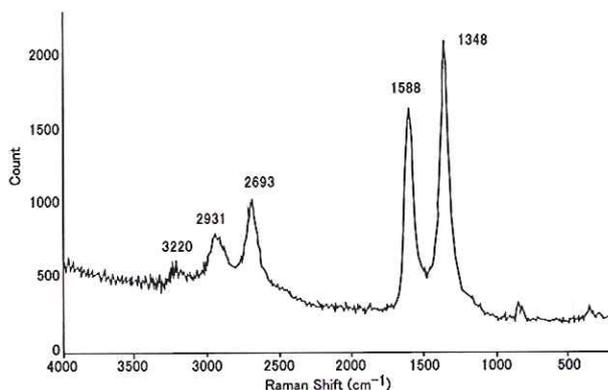


Fig. 14: Raman spectrum of component C in 2B at objective $\times 100$.

The Raman spectral feature of the carbonaceous matter in 2B is very close to that in Allende (C3V) (Fig. 15). The broadness and relative intensity of the peaks at 1590 and 1350 cm^{-1} indicate that the carbonaceous matter in the sample 2B is much more graphitic than that in Murchison (CM2 Fig. 16) and less graphitic than commercial pyrolytic graphite (Fig. 17).

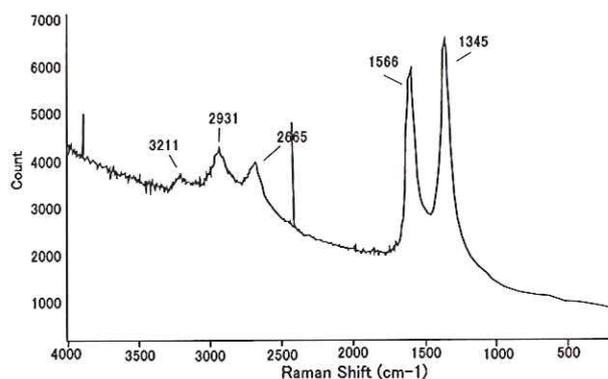


Fig. 15: Raman spectrum of carbon in Allende at objective $\times 50$.

Fig. 18c shows the image obtained using Raman band of 850 cm^{-1} , which indicates typical distribution pattern of olivine. Distribution pattern of clinopyroxene obtained using the band of 1010 cm^{-1} is shown in Fig. 18d. Distribution patterns of graphite are shown in Fig. 18e and 18h as the images obtained using the band of 1595 cm^{-1} .

Overall distribution pattern of the components: Olivine (component A: Fig. 18c) and clinopyroxene (component B: Fig. 18d) are resembled very much each other in images at the

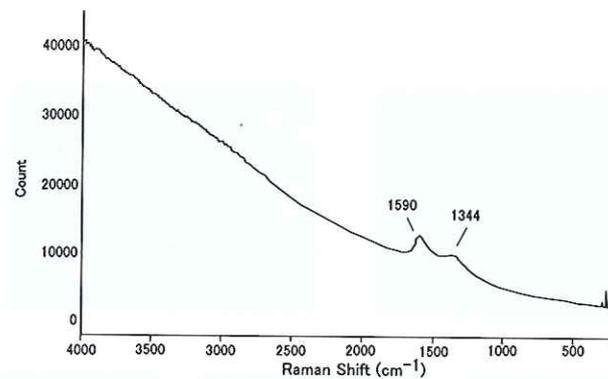


Fig. 16: Raman spectrum of carbon in Murchison at objective $\times 50$.

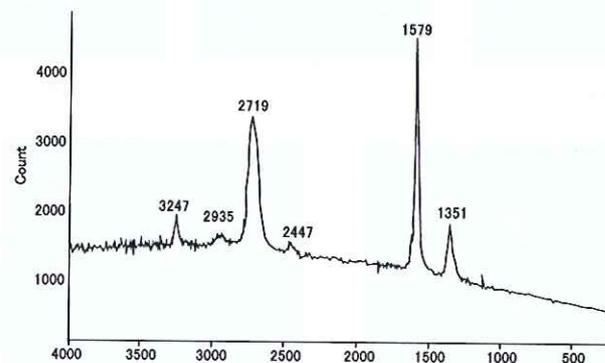


Fig. 17: Raman spectrum of pyrolytic graphite at objective $\times 50$.

same area. This fact indicates that each component is very fine grains and mixed well each other although the concentration of each component is slightly different. Although the carbonaceous matter (component C) was observed at the whole area of the sample, the imaging pattern of the carbonaceous matter (Fig. 18h) was different from those of olivine (Fig. 18i) observed at the same area. Because the grain size of the carbonaceous matter is larger than other components, the carbonaceous grain is not mixed well with other components. Therefore, the carbonaceous grain is observed separately from other components by Raman band imaging.

5.2 Analysis by FT-IR microscope:

Instrument: Examination by microscopic FT-IR spectroscopy was carried out using a Perkin-Elmer 1600 spectrometer equipped with Spectra Tech IR-Plan microscope (objective $\times 15$)

Results: The absorption bands at 1606 and 1873 cm^{-1} (Fig. 19 indicate the presence of kelogen-like carbonaceous matter in carbonaceous chondrites. No signals due to other organic compounds were detected in the spectrum.

5.3 Analysis by microscope fluorescence spectrometer:

Results: Some fluorescent particles were observed. The concentration of the fluorescent matter is much lower than that in the sample 1B. A few particles show weak orange color

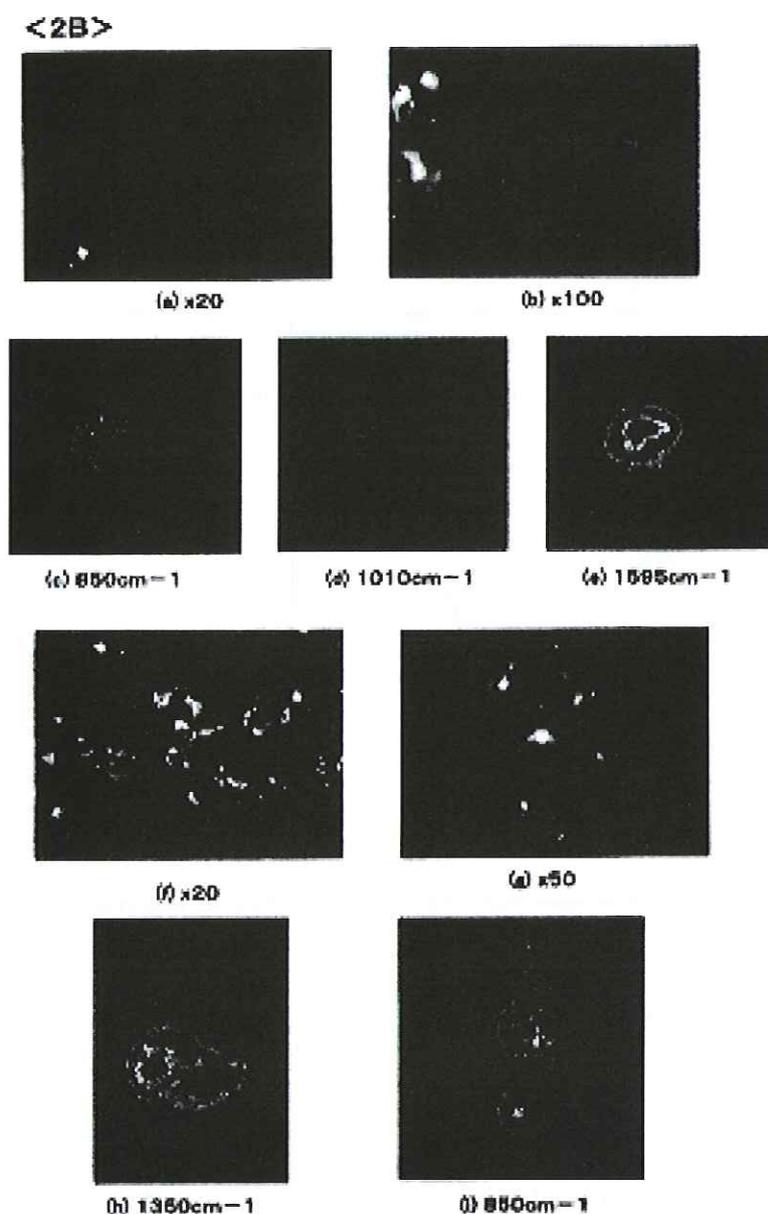


Fig. 18: Microscopic images of the sample 2B by white light and Raman bnd: Images a, b, f and g were taken under white light; Images c, d, e were given by the characteristic Raman bands for olvine, clinopyroxene and graphite at the same area as b; Images h and i were obtained at the same area as g using characteristic Raman band for graphite and olvine.

specifically whose fluorescence spectrum is shown in Fig. 20. It is uncertain whether these particles are organic compound or not; yet these may well be kerogen-like compounds bearing edge defects.

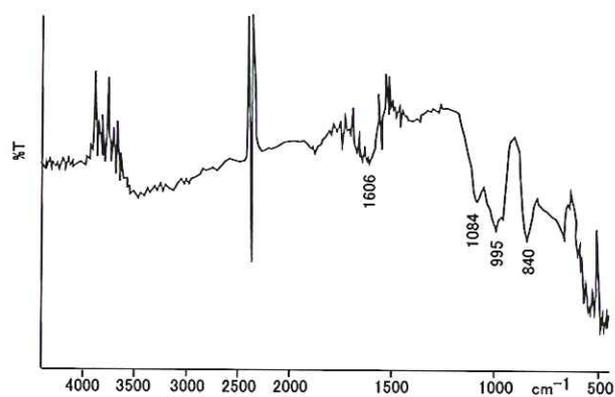


Fig. 19: FT-IR spectra of 2B; obtained microscopic reflectance mode.

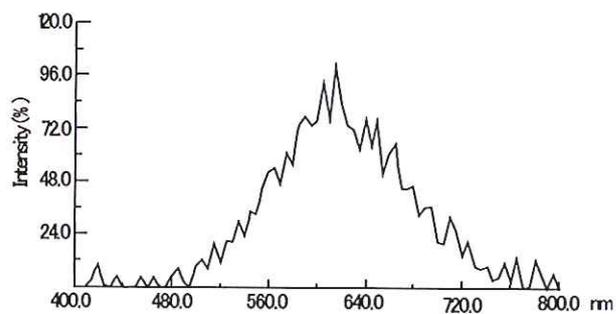


Fig. 20: Fluorescence spectrum of a fuluorescent particle in 2B.

6. CONCLUSION

Analyses using microscopic laser Raman, microscopic FT-IR, and microscopic fluorescence spectroscopy suggested that the sample 1B contains organic compounds as very minor components and the sample 2B contains carbonaceous matter closely related to that in Allende meteorite.

