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IN-SITU MICRO RAMAN STUDIES ON GRAPHITIC CARBON IN SOME ANTARCTIC UREILITES

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Abstract: The fine structures of graphitic materials contained in four Antarctic ureilites (ALH-77257, ALH-78019, MET-78008 and Y-791538) were investigated using a laser light (514.5 nm), which could be focused onto a spot of 1 μm in diameter. Raman spectra obtained differ not only among individual ureilite samples, but also among positions within a single carbonaceous vein of the same specimen. Moreover, one can classify the carbon into several groups on the basis of the spectra concerned. For all samples, both well-ordered graphitic carbon and semi-ordered graphitic carbon were observed. Amorphous carbon was detected in ALH-77257 and MET-78008. The difference in structural ordering among the samples is attributed to the difference in distribution of the components of carbonaceous material, indicating minor difference in genetic conditions or in locality within the parent body. Structural heterogeneity of carbon within a single carbonaceous vein implies the occurrence of two (or three) types of carbonaceous matters which have fairly different physicochemical properties and distinct histories. For the genesis of the carbonaceous matter in ureilites, a two-stage model is proposed assuming the graphite crystallization from metallic phase followed by the inflow of semi-ordered graphitic carbon or amorphous carbon into the well-ordered graphitic carbon produced from the metal.

1. Introduction

The genetic history of ureilites has been a question open to debate, and there are various opinions about their origin (TAKEDA, 1986, 1989; TAKEDA *et al.*, 1988). The quite unique characteristic of this group of meteorites is the appearance of carbonaceous veins in the grain boundaries of silicate minerals. In general, the veins comprise graphite, metallic iron, troilite and grains of diamond or lonsdaleite with size of several micrometers. The formation process of diamond in the vein has been discussed by FUKUNAGA *et al.* (1987), who suggested CVD (chemical vapor deposition) as a genetic process for the ureilitic diamonds. Some spectroscopic investigations on the ureilitic diamond were undertaken recently. MIYAMOTO *et al.* (1988) discussed the origin of diamond in ALH-77257 ureilite on the basis of the broadening of Raman peaks at 1332 cm^{-1} in Raman shift and supported CVD origin. KAGI *et al.* (1990a) found a strange diamond particulate in Y-791538, whose Raman band showed a con-

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siderable shift towards low wavenumber by about 10 cm^{-1} , in the course of their studies of laser-induced photoluminescence spectroscopy (KAGI *et al.*, 1990b). From the viewpoint of isotope cosmochemistry, isotopically anomalous noble gases extracted from the carbonaceous matter in ureilites have aroused much interest (WACKER, 1986; GOEBEL *et al.*, 1978). Petrologic studies on graphitic carbon in the vein were carried out by BERKLEY and JONES (1982), who suggested that “most” graphite in ureilites originated from crystallization out of a C-rich metallic phase.

Besides these experimental researches, investigation of the graphitic matters can be an important clue to elucidation of the history of ureilite formation, because graphitic matters are sensitive to high temperature, high pressure and shock event. Furthermore, the possible bearings of the ordering of carbonaceous matter on the scavenging ability for noble gases are expected to provide us with interesting information on the process of scavenging of noble gases in ureilites. Study on the structural ordering and the distribution of the graphitic matter in ureilite will strongly help us to understand the origin of carbon in ureilites.

In general, chemical characterization of the insoluble organic polymer in meteorites has been performed with pyrolytic GC-MS, ^{13}C NMR or some other spectroscopic methods after mild decomposition of minerals with HCl and HF (MURAE *et al.*, 1987; CRONIN *et al.*, 1987). Although this method is convenient, there has been a fear of structural changes of the carbonaceous materials under acid treatment. Moreover, it is impossible to study the relationship between the chemical structure and the microtextural information in the meteorites by these methods. Beyond question, Raman microprobe spectroscopy is one of the most potent means in order to obtain the *in-situ* structural information without damaging the precious meteoritic samples. In some cosmochemical studies, Raman spectroscopy was used to determine the structure of poorly ordered carbonaceous materials which were included in primitive undifferentiated chondrites or interplanetary dust particles (MAKJANIC *et al.*, 1989; WOPENKA, 1988). HEYMANN (1987) and HEYMANN and READ (1987) obtained Raman spectra for carbonaceous matters in the Canyon Diablo iron meteorite and the Allende meteorites, and discussed the structural ordering of carbon in them.

Some carbonaceous chondrites contain several weight percent carbonaceous matters in the matrix, but it is quite difficult to detect them by laser Raman microprobe without concentrating them with acid treatment. But in the case of ureilite, the carbonaceous materials are enriched in grain boundaries, and it is easy to take Raman spectra for the carbonaceous matter in ureilite. In this study, *in-situ* Raman spectra of the carbonaceous materials were obtained using polished thin sections of several ureilites. The purpose of this study is to examine the spatial heterogeneity in chemical structure of the carbonaceous matter within a ureilite. For this purpose, *in-situ* micro Raman spectroscopy has a great advantage because of freedom from physical destruction and possible modification of the grain.

2. Experimental Method

2.1. Samples

The ureilites studied were Allan Hills (ALH)-77257,64-4, ALH-78019,56, Me-

teorite Hills (MET)-78008,61-3 and Yamato (Y)-791538,71-4. Polished thin sections (PTS) were examined with a micro Raman spectrometer (RAMANOR U-1000 Laser Raman microprobe manufactured by Jobin Yvon) at the Institute of Physical and Chemical Research (RIKEN). In order to avoid contamination from the diamond abrasive, all thin sections except ALH-78019 (unshocked ureilite with no diamond) were polished only with alumina abrasive at the National Institute of Polar Research (NIPR).

2.2. Analytical conditions

The exciting radiation was the 514.5 nm green line of an argon gas ion laser, model 168B, manufactured by Spectra Physics. The power of the laser was suppressed to 10 mW at the sample surface to avoid damaging the graphitic structure by heating. The exciting laser beam is focused on a spot of approximately 1 μm diameter. The photon counting detection system consists of a PMT-R464S (photomultiplier) and a PHC-C1230S (photon counter) manufactured by Hamamatsu Photonics. The sample stage can be moved with a precision of 0.05 μm using stepping motors controlled by a minicomputer.

All spectra were obtained covering 1200 through 1700 wavenumbers, relative to the exciting laser light, with a spectral slit width of 4.5 cm^{-1} . The wavenumber step size was 1 cm^{-1} and the counting time was 1 second per step. The analyzed thin section was imaged through a 90-power objective lens manufactured by Atago Bussan combined with an Olympus microscope. An NEC PC-9801 VX is used to control the monochromator and the data reduction.

2.3. Raman spectra of graphite

In Raman spectrum of graphite, one or two first order Raman bands are observed depending on its crystallinity. In a highly ordered single crystal, one intense band at 1582 cm^{-1} is observed corresponding to Raman active E_{2g} mode, *i. e.*, deformation vibration within graphite layers (TUINSTRA and KOENIG, 1970). With a decrease of the crystallite size of graphite plane, an additional band at 1350 cm^{-1} appears.

This phenomenon has been rationalized by considering the phonon dispersion curve of graphite (LESPADE *et al.*, 1982). The intensity ratio ($R=I_{1585}/I_{1350}$) of these two Raman bands is highly correlated with the mean size of crystallite parallel to the crystallographic a -axis, L_a , which can be determined with powder X-ray diffraction analysis. It is empirically known that R is directly proportional to L_a , namely,

$$L_a(\text{nm})=4.5R. \quad (1)$$

In this study, L_a of the graphitic carbon is estimated from eq. (1). In order to calculate the intensity ratio, R , between the two bands of 1582 cm^{-1} and 1352 cm^{-1} , spectral smoothing with average conversion, baseline subtraction and Lorentzian fitting were carried out.

In this paper, the carbonaceous matters are classified as follows according to the degree of graphitization, namely the value of R .

- $R \sim 1.3$ amorphous carbon,
- $R \sim 2$ semi-ordered graphitic carbon,

$R \sim 4$ well-ordered graphitic carbon,
 $R \sim \infty$ holo-ordered graphitic carbon.

This classification and naming might not follow the general description in material sciences on carbon, but will be adopted here based on the Raman study on the carbonaceous matters in meteorites. The amorphous carbon with $R \sim 1.3$ is detected in carbonaceous chondrites (HEYMANN and READ, 1987), and the well-ordered graphitic carbon with $R \sim 4$ is detected in iron meteorites (HEYMANN, 1987).

3. Results

3.1. General features of the spectral shapes

Raman spectra of the graphitic material found in the four ureilites are shown in Fig. 1. As mentioned below, each ureilite contains graphitic matters with various degrees of structural ordering. Raman spectra of the most representative and abundant graphitic matter in each ureilite are displayed in Fig. 1. Intense bands at 1582 cm^{-1} , additional bands at 1352 cm^{-1} and very weak shoulder bands at 1620 cm^{-1} were observed in all spectra.

However, the intensity ratios, R , differ from each other (see Table 1), which means variation of crystallite size along the "a"-axis, L_a . The values of L_a are evaluated using eq. (1). The structural ordering of the graphite crystal along the "a"-axis is

$$\text{ALH-78019} > \text{ALH-77257} \sim \text{Y-791538} > \text{MET-78008} .$$

KITAJIMA *et al.* (1990) performed a pyrolysis-GC-FID and pyrolysis-GC-MS study on the three Antarctic ureilites, Y-791538, ALH-77257 and MET-78008, and arrived at the conclusion that the quantity of the pyrolysis product, which reflects the number of edge defects in the graphitic material, was

$$\text{MET-78008} > \text{ALH-77257} \sim \text{Y-791538} .$$

In other words, the degree of crystalline perfection is

$$\text{ALH-77257} \sim \text{Y-791538} > \text{MET-78008} ,$$

which is consistent with our findings. However, their pyrolytic conclusion is not thoroughly reliable, because interaction between the graphitic matter and various minerals during the pyrolysis cannot be neglected.

3.2. Fine structure of graphitic matter in carbonaceous veins

While the graphitic matter in the four ureilites displays considerable structural variation, probably reflecting the extent of shock effect or the surrounding temperature and pressure, significant structural heterogeneity was observed within a single sample, even within a polished thin section and a carbonaceous vein.

3.2.1. ALH-78019

A graphitic vein in ALH-78019 contains carbonaceous material whose structure ranges from well-ordered graphitic carbon to semi-ordered graphitic carbon. In Fig. 2, three types of graphites observed in the single carbonaceous vein in ALH-78019 are shown. The spectrum shown in Fig. 2a is the most typical graphitic matter

observed in ALH-78019, while the adjacent graphite gives a fairly distinct spectrum as shown in Fig. 2b, which corresponds to semi-ordered graphitic carbon. The latter is the main component of the graphitic matter found in ALH-77257 and Y-

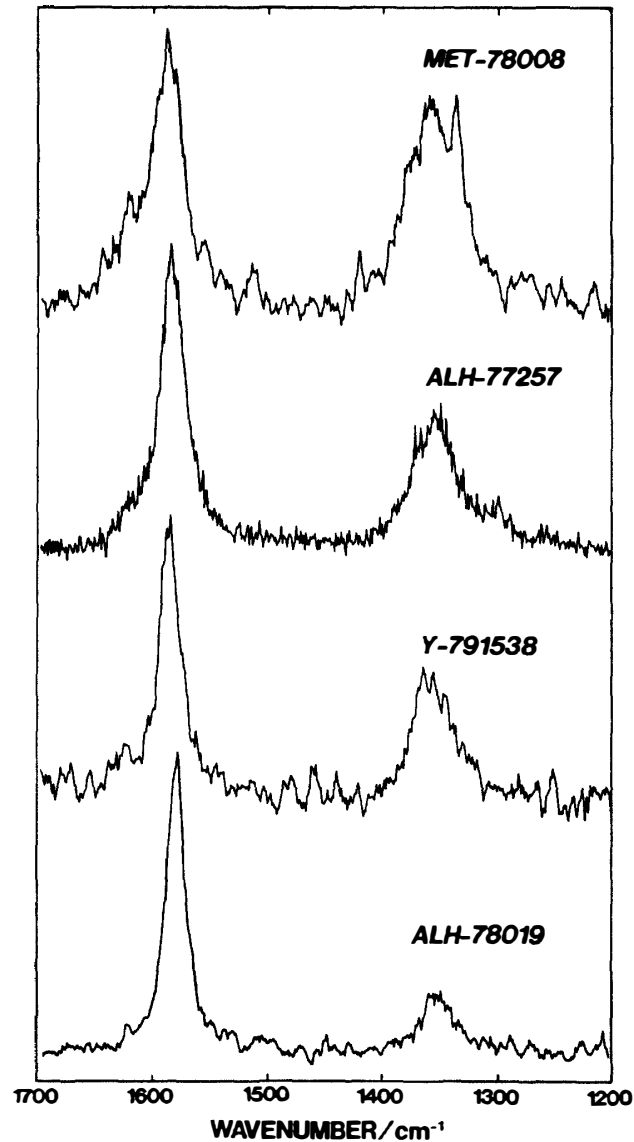


Fig. 1. Raman spectra of the most abundant graphitic matter included in each PTS of the Antarctic ureilites, MET-78008, ALH-77257, Y-791538 and ALH-78019.

Table 1. Raman data of the most abundant graphitic matters in each of the four ureilites.

| | R | L_a/nm |
|-----------|-----|-----------------|
| MET-78008 | 1.3 | 7 |
| ALH-77257 | 2 | 9 |
| Y-791538 | 2 | 9 |
| ALH-78019 | 4 | 18 |

R is defined as I_{1585}/I_{1352} , and crystallite size L_a is evaluated using eq. (1).

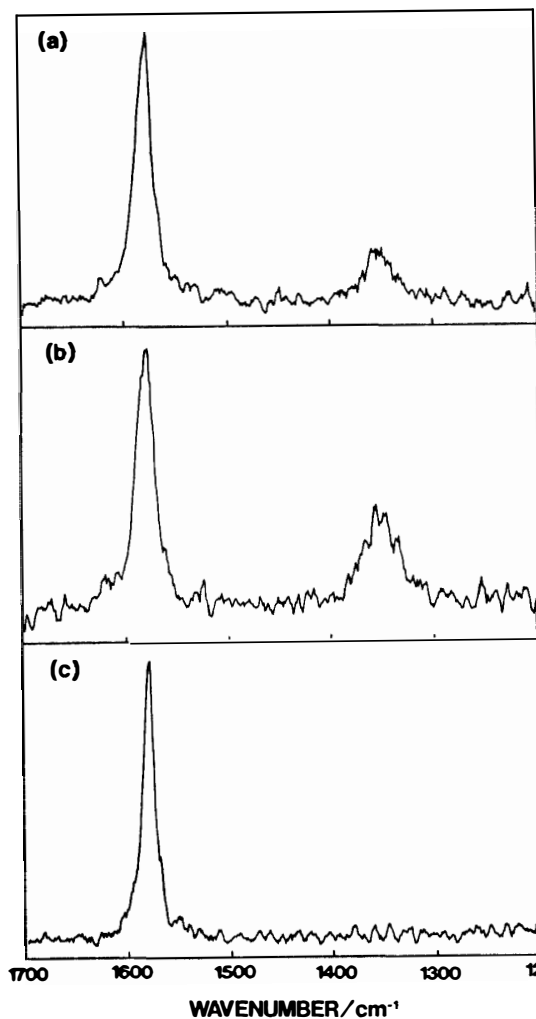


Fig. 2. Raman spectra of the graphitic matters in ALH-78019, unshocked ureilite. (a) Well-ordered graphitic carbon, the most abundant graphitic matter in ALH-78019. (b) Semi-ordered graphitic carbon. (c) Holo-ordered graphitic carbon.

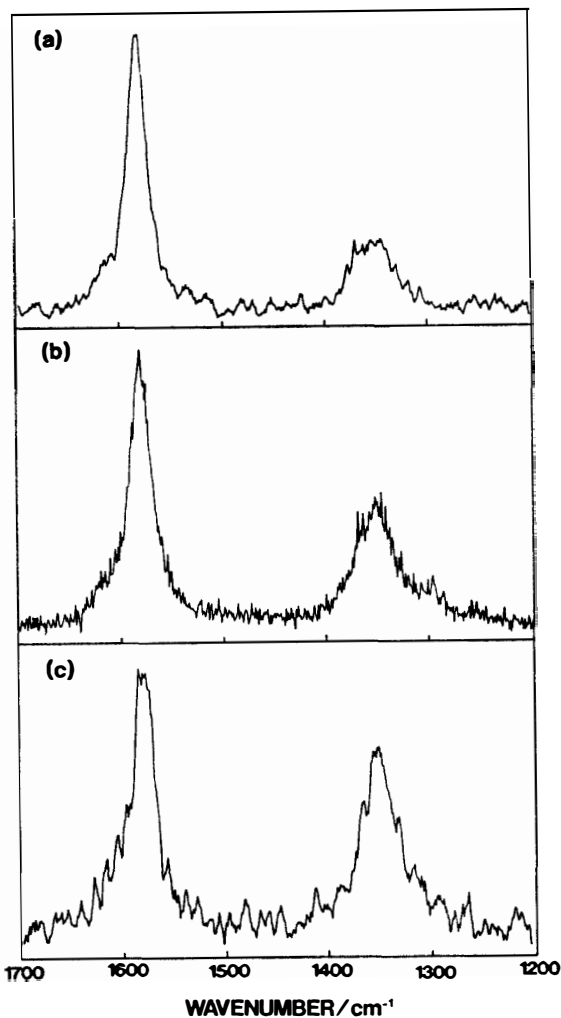


Fig. 3. Raman spectra of the graphitic matters in ALH-77257. Three types of the graphitic matter were observed. (a) Well-ordered graphitic carbon. (b) Semi-ordered graphitic carbon, the most abundant graphitic matter in ALH-77257. (c) Amorphous carbon.

791538. These two components of graphite are adjacent to each other in the area examined and it is not so difficult to distinguish them under a microscope in reflection mode, which means distinction between their particle sizes.

Furthermore, the most well-ordered graphite has also been observed in the vein (the spectrum shown in Fig. 2c). Such a complete graphite was rare, and difficult to detect under a microscope. Calculated crystallite sizes are 30, 12 and ∞ nm corresponding to Figs. 2a, b and c, respectively.

3.2.2. ALH-77257

The main component of graphitic matter found in ALH-77257 is semi-ordered graphitic carbon with the mean crystallite size (L_a) of about 9 nm (Table 1), but well-ordered graphitic carbon and amorphous carbon have been observed to coexist. Raman spectra for the three types of carbon contained in the carbonaceous vein of

ALH-77257 are displayed in Fig. 3. Mean crystallite sizes are about 21 nm and 6 nm for well-ordered graphitic carbon and amorphous carbon, whose spectra are shown in Figs. 3a and c, respectively. It is not so easy to distinguish these various types of carbonaceous matters under a microscope unlike ALH-78019.

3.2.3. MET-78008

Like ALH-77257, the graphitic matter found in MET-78008 ranges from well-ordered graphitic carbon to amorphous carbon. Figures 4a, b and c correspond to well-ordered graphitic carbon, semi-ordered graphitic carbon and amorphous carbon, respectively.

3.2.4. Y-791538

Similar structural variety is to be expected for Y-791538. However, amorphous

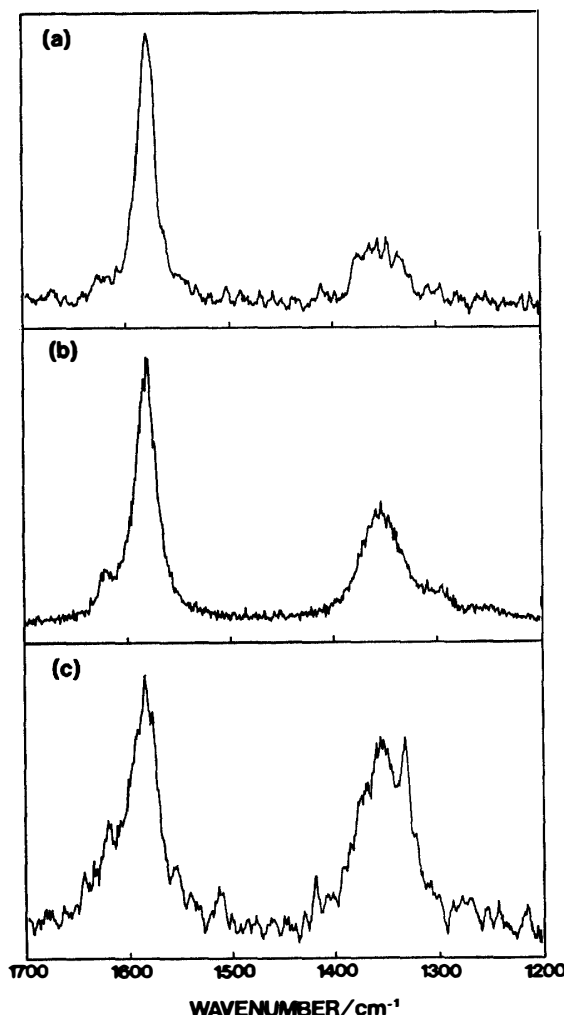


Fig. 4. Raman spectra of the graphitic matters in MET-78008. Same as the case of ALH-77257, three types of the graphitic matters were observed. (a) Well-ordered graphitic carbon. (b) Semi-ordered graphitic carbon. (c) Amorphous carbon, the most abundant form in MET-78008.

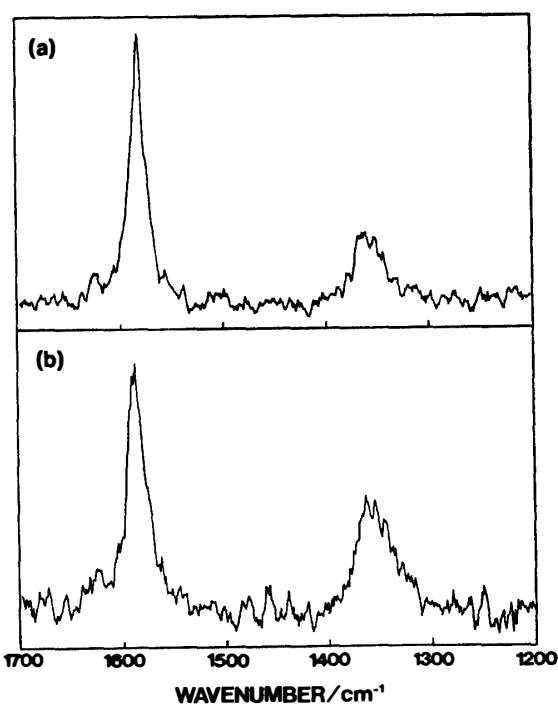


Fig. 5. Raman spectra of the graphitic matters in Y-791538. (a) Well-ordered graphitic carbon. (b) Semi-ordered graphitic carbon, the most abundant structure of the graphitic matter in Y-791538.

carbon was not observed in Y-791538. In Figs. 5a and b, Raman spectra from well-ordered graphitic carbon and semi-ordered graphitic carbon are given. Further examination would be necessary to disclose the wide structural heterogeneity in Y-791538.

4. Discussion

It is shown that carbonaceous material in ureilites has a wide structural variety within a single PTS. On the other hand, the average structural feature observed with GC-FID is considered to reflect the most abundant structural group of the carbonaceous material. The abundant carbonaceous matter is amorphous carbon in MET-78008, semi-ordered graphitic carbon in ALH-77257 and Y-791538, and well-ordered graphitic carbon in ALH-78019, respectively. Such a structural difference among the samples might result from the difference in their genetic conditions such as temperature, pressure, passage of time under high temperature and molecular characteristics of the precursor carbonaceous material. Generally, as the surrounding temperature rises, graphitic material polymerizes to cause the increase of crystallite size. Considering the average degree of structural order (Table 1), the order of the temperature which the ureilites suffered is evaluated simply as follows,

$$\text{ALH-78019} > \text{ALH-77257} \sim \text{Y-791538} > \text{MET-78008} . \quad (2)$$

Similar discussion about meteoritical temperature is reported by CHRISTOPHE MICHEL-LEVY and LAUTIE (1981) from the standpoint of crystallite size of carbon in the Tieschitz chondrite. However, as described above, there are many physical and chemical variables influencing the graphitization other than temperature. Therefore, it is fairly difficult to conclude the order of the temperature as described in eq. (2). Apart from the difficulty of discussion about the absolute temperature, it is noteworthy that unshocked ureilite ALH-78019 has well-ordered graphitic carbon as the main component of the carbonaceous matter. It means that the meteorite ALH-78019 was exposed to metamorphism with high temperature and high pressure.

4.1. Survival of primitive carbon

ALH-77257 and MET-78008 contain amorphous carbon whose crystallite size parallel to the *a*-axis, L_a , is estimated to be about 6 nm using eq. (1). The size of ureilitic amorphous carbon is reported to be of the same order as carbonaceous matter found in carbonaceous chondrite (MURAE *et al.*, 1987). However, it should be noted that their conclusion has been derived from pyrolytic study. The remarkable difference in the structure of the carbonaceous matter between carbonaceous chondrite and ureilite lies in the content of the chemical substituent. KITAJIMA *et al.* (1990) reported that the graphitic matter in ureilites has little substituent groups such as $-\text{C}=\text{O}$, $=\text{N}-\text{H}$ and so on, unlike rich substituent groups in the carbonaceous matter in carbonaceous chondrites.

Carbonaceous material in interplanetary dust particles investigated with Raman spectroscopy by WOPENKA (1988) looks similar to the ureilitic amorphous carbon judging from their band shapes. Carbonaceous matter in carbonaceous chondrite

shows similar Raman spectra to that of the ureilitic amorphous carbon (HEYMANN, 1987), and the oxygen isotopic study suggests close genetic relationship between carbonaceous chondrite and ureilite. Furthermore, carbonaceous matter contained in the Tieschitz H3 chondrite (CHRISTOPHE MICHEL-LEVY and LAUTIE, 1981) has crystallite sizes close to that of the ureilitic amorphous carbon.

One of the major questions is why carbonaceous matter with such seemingly primordial structure was retained in ureilite, whose parent body is considered to have been subjected to high temperature and high pressure in the igneous event or some shock events. Although some shock events in the parent body might have made conversion of the well-ordered graphitic carbon into the amorphous carbon, the presence of the semi-ordered graphitic carbon (carbon with low degree of structural order as observed in unshocked ALH-78019) conflicts with the above possible interpretation. Furthermore, in the case of Canyon Diablo, moderately shocked graphite shows a very similar spectrum to that of unshocked graphite (HEYMANN, 1987).

WACKER (1986) has suggested that two types of carbon exist in ALH-78019 and the major part of the noble gases in ALH-78019 is contained in finer-grained, amorphous carbon. He compared his data of $^{132}\text{Xe}/\text{C}$ ratios for the gas-rich carbon in ALH-78019 with those for bulk chondrites (ANDERS and ZADNIK, 1985), pointing out that the gas-rich carbon in ALH-78019 had survived the solar nebula. Although it has not been confirmed that the fine-grained carbon observed by WACKER and the semi-ordered graphitic carbon observed by us are identical, it seems to be certain that they are closely related. Therefore, the amorphous or semi-ordered graphitic carbon should be regarded as residual skeleton of the primitive carbonaceous material which had been inherited from carbonaceous chondrite, during the metamorphic event in the ureilitic parent body. In our Raman study, coexistence of the various types of carbon was observed within a single carbonaceous vein in ALH-78019. In Fig. 6, a portion showing coexistence of two types of carbon in ALH-78019 is illustrated. Such a heterogeneous distribution of the two types of carbon in ALH-78019 would imply the miraculous and colossal forming process of ureilites.

4.2. *Origin of the structural heterogeneity of carbon*

BERKLEY and JONES (1982) suggested that most graphite in ureilites originated from crystallization from a C-rich metallic phase. Figure 7 displays the Raman spectrum of graphite found in the Odessa iron meteorite. This spectrum shows that the mean crystallite size of graphite in the Odessa iron meteorite is about 20 nm nearly equal to the well-ordered graphitic carbon in ureilites. Similar spectra were reported for the carbon in Canyon Diablo by HEYMANN (1987). It is thought that the graphite in the iron meteorite had been formed by crystallization of carbon contained in iron melt in the same way as the model suggested by BERKLEY and JONES for the ureilites. Accepting their theory, holo-ordered graphitic or well-ordered graphitic carbon in ureilite might have come from the metallic phase.

However, our result implies that not all graphite in ureilites originated from the metallic phase. Survival of primitive carbon coming from the carbonaceous chondrite is possible only in case where no interaction occurs between the carbon and the melt and/or the metallic phase. In this connection, however, such a considerable tem-

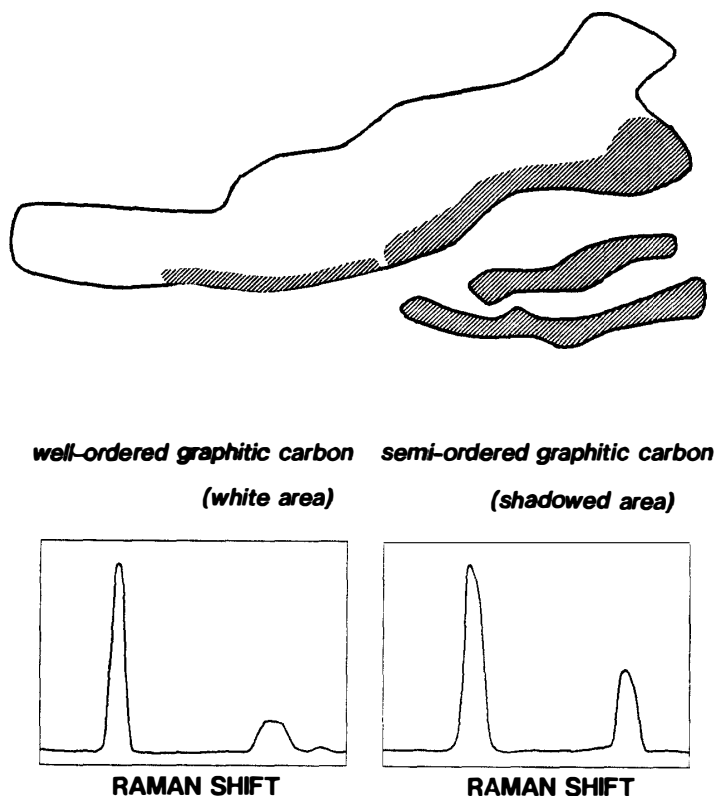


Fig. 6. Illustration showing a portion of carbonaceous vein in ALH-78019 unshocked ureilite. Shadowed area indicates the semi-ordered graphitic carbon, white area indicates the well-ordered graphitic carbon.

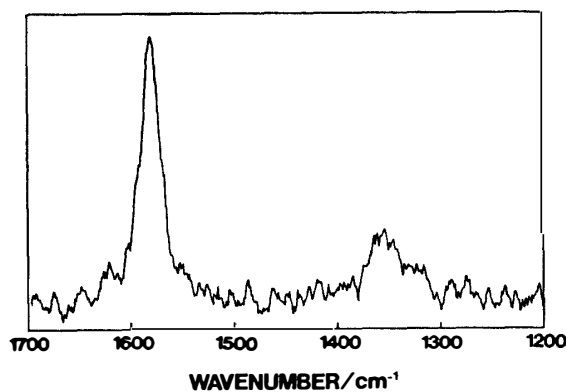


Fig. 7. Raman spectra of the graphitic matter in the Odessa iron meteorite. The measurement conditions were the same as in the case of ureilites. The crystallite size of this graphitic matter is nearly equal to that of the well-ordered graphitic carbon contained in the Antarctic ureilites studied here.

perature gradient yielding structural heterogeneity in the order of $10\ \mu\text{m}$ is unlikely. The immiscibility between the well-ordered graphitic carbon and the semi-ordered graphitic carbon observed in this study for ALH-78019, MET-78008 and ALH-77257 could be the result of the fairly different generation history of the two types of carbon. As one of speculations, it is considered that semi-ordered carbon would have traveled or have been injected to the present portion in the carbonaceous vein after crystallization of well-ordered graphitic carbon from the metallic phases. This speculation explains the durability of semi-ordered graphitic carbon without reacting with the metallic melt. But our conclusive words should be retained until other more con-

vincing evidence is secured.

4.3. Genetic history of the carbonaceous matter in ureilites

After the events of accumulation and sedimentation, planetesimal-scale collisions had induced partial melting at various places in the parent body of ureilites. A part of carbonaceous material, which originated from carbonaceous chondritic precursor material, reacted with melt consisting of silicate and melt, and graphitic carbon crystallized from the melt. This type of carbon had quite similar structural ordering to carbon in iron meteorite. The remainder of the carbonaceous material, retaining a skeleton of the primitive carbon structure, was ejected into the graphitic carbon which had crystallized from the metallic phase, without suffering the interaction with silicate or metal. The ejecting process would have been caused by another event of planetesimal-scale collision. The semi-ordered graphitic and amorphous carbon, which came from a static part of the parent body without partial melting, was not completely equilibrated to the silicate melt; therefore the oxygen isotope anomaly observed in ureilites (CLAYTON and MAYEDA, 1988) might be closely related to the genetic history of the less-ordered carbons in ureilites. We cannot easily presume where "the static parts" were located in the parent body. However, judging from widely observed oxygen isotopic anomaly, such parts are presumed to have existed rather commonly in the parent body. It means the highly heterogeneous structure of the ureilitic parent body.

5. Summary

Physicochemical structure of carbonaceous matters in the Antarctic ureilites was destructively investigated by a laser Raman microprobe. From the first order Raman spectrum, the degree of structural order was evaluated. The mean crystalline size parallel to the a -axis was estimated to be in the order of 10 nm with considerable variation (from 6 nm to 20 nm in L_a among the samples studied here.) The distribution of structural degree and most abundant carbon differs among the investigated Antarctic ureilite samples. The most abundant type of carbon is the amorphous carbon in MET-78008, the semi-ordered graphitic carbon in ALH-77257 and Y-791538, and the well-ordered graphitic carbon in ALH-78019. Our results are consistent with those of pyrolytic studies. The difference in the proportion of each carbon type among the ureilites could result from the degree of shock effect or the difference in sample locality in the parent body.

The characteristic heterogeneity of the crystallite size of carbon within a single carbonaceous vein implies two-stage crystal growth of carbonaceous material in the vein. That is, crystallization of graphite from metallic phase in the first stage had been followed by flowing injection of the less ordered carbon into the vein from the static portion of the parent body in the second stage.

The highly heterogeneous distribution of the graphitic matters in the carbonaceous vein might be a new clue to the origin of the ureilites.

Acknowledgments

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