Structure and Chemistry of Carbon in Meteorites

Tatsushi Murae, Hiroyuki Kagi, and Akimasa Masuda

Department of Chemistry, The University of Tokyo, Tokyo 118, Japan

1. Introduction

Carbon is considered as one of the first elements produced when the density of the elements, formed after the Big Bang (H, He, Li, and Be: Boesgaard and Steigman, 1985), was orders of magnitude greater than the critical density. Carbon is also one of the most important major elements for the current terrestrial living matter and it is a very unique element because of its capability to have a numerous number of stable forms. The structure of carbonaceous matter changes according to the environmental conditions, and in some cases both of the processes, the initial formation processes of the carbonaceous matter and the following environmental changes, can be presumed by the structure. Therefore, examination of the carbonaceous matter in meteorites, especially in carbonaceous chondrites, is very important to know more about the primitive solar nebula and origin of the planets.

Recent studies of carbonaceous matters in carbonaceous chondrites indicated that some parts of the carbonaceous matter were formed outside the solar system (e.g. Kerridge, 1983; Amari et al., 1990). On the other hand, astronomical observations suggested the presence of interstellar carbon. The candidates for the interstellar carbon are graphite, amorphous carbon, polycyclic aromatic hydrocarbons (PAHs), diamond, fullerenes, and bacteria. Recent far-infrared observations suggested that thermal dust emission from supernova 1987A is probably due to graphite, which was being formed in the supernova ejecta (Moseley et al., 1989). It was suggested that both interplanetary dust particles (IDPs) and meteorites contained a
material similar to PAHs in some astronomical objects (Allamandola et al., 1987).

The major component of the organic compounds in carbonaceous chondrites is contained in the form of an insoluble high molecular organic material, and depending on the carbonaceous chondrite type, this insoluble material may account for about 70 percent to essentially all of the meteoritic carbon (Hayatsu and Anders, 1981). The major carbonaceous matter has been characterized as graphitic (Smith and Buseck, 1981; Reitmeijer and Mackinnon, 1985), amorphous, and kerogen-like (Hayatsu et al., 1983; Ming et al., 1989). Although it has been shown that diamond was also present in carbonaceous chondrites (e.g. Lewis et al., 1987), most of the carbon (in the case of Murray, ca. 88% of carbon) presented as a structurally unclear high molecular organic compound (Ming et al., 1989).

A number of models have been proposed to account for the formation of interstellar organic molecules and of organic components in carbonaceous chondrites, no model, however, succeeded to interpret the growth of macromolecules in carbonaceous chondrites. The difficulty in the proposal of growth models of organic macromolecules (major carbonaceous matter) in carbonaceous chondrites lies in the uncertainty of the structure, while elucidation of the structure of the major carbonaceous components is essential in the understanding of primordial carbon chemistry as well as the origin and chemical history of the p carbonaceous chondrites.

Some differentiated meteorites, such as iron meteorite or ureilite, also contain a considerable amount of carbon as so-called graphite or less ordered graphitic matter. The genetic history of ureilite is enigmatic, and the origin of carbonaceous matter in ureilite has been a crux of controversy (Takeda et al., 1988; Takeda, 1989). Ureilite, grouped as an achondrite, has lower contents of metallic nickel-iron and coarser textures than most chondrites. One of the most important features of this meteorite is the presence of graphitic matter in the grain boundaries mainly composed of graphite, metallic iron, troilite, diamond, and lonsdaleite. Enclosed silicate minerals reacted with the carbonaceous vein, and edges of olivine crystals were reduced to pyroxene. To understand the nature of the ureilitic graphitic matter, not only informations on the bulk structure but precise investigations by other methods are also necessary. Although the transmission electron microscope method (TEM) has been widely used in mineralogy.
it is difficult to prepare the carbonaceous sample for measurement because of its weakness and fluffiness. Furthermore, observation of the structural heterogeneity in a sub-millimeter order by TEM is almost hopeless. On the other hand, micro-Raman spectroscopy is one of the suitable methods for the investigation of carbon enriched in the grain boundary, such as in ureilite.

2. Sample preparations and experimental apparatus

The samples of carbonaceous chondrites used in the present work were taken from small chips delivered from the meteorite curator of the National Institute of Polar Research (NIPR). After washing with hexane, the chips were powdered (grain size: 10–20 μm), and the powder was used for pyrolytic studies. Pyrolysis was carried out using a Curie point pyrolyser (Japan Analytical Industry Co., LTD: Model JHP-2) connected to a Shimadzu 7A-PF instrument for detection by a flame ionization detector (FID), or to a JEOL JMS D-300 mass spectrometer equipped with a JMA-2000 mass data analyzer for detection by a mass spectrometer. Open tubular fused silica capillary columns (25 m × 0.25 mm i.d.), coated with silicon OV-101 or chemically bonded with silicon OV-1 as stationary phase, were used for GC-FID analyses and GC-MS analyses.

The acid-resistant residues from ALH(Allan Hills)-77307 were prepared by repeated digestion with HCl and HF, centrifugal separation, and extraction with benzene-methanol (Murae et al., 1990). By this procedure 1.0 g sample of ALH-77307 (C: 0.74%) gave 10 mg of the residues (C: 45.5%), yield: 60% of total meteorite carbon. By a similar treatment Allende (11.5 g, C: 0.23%) yielded residues of 302 mg, C: 7.57%, yield: 86% of total meteorite carbon; and 51.3 g of Y(Yamato)-791717 (C: 0.16%) gave 2.1 g of the residue (C: 3.08%, yield: 78% of total meteorite carbon) (Murae et al., 1990).

Laser ionization mass spectra was determined with a Shimadzu LAMS-50K time of flight mass spectrometer (TOF-MS) equipped with a N₂ laser pulse (337 nm) ionization system. The powdered samples were held on the surface of a copper-sampling block using a glycerol matrix as a binder. The data obtained on 200 times laser irradiation were accumulated. IR spectra was recorded with a Horiba FT-300 FT-IR spectrometer equipped
with an attachment for diffuse reflection. $^{13}$C NMR spectra was obtained at 125.76 MHz with a Bruker AM-500 spectrometer with a CP-MAS probe. Samples were loaded in a bullet rotor and spun at 4.0 KHz. The spectra were acquired with spectral width of 41555 Hz; acquisition time, 26 ms with decoupler at the Hartman-Hahn match level; pulse repetition time, 4 s.

Polished thin sections of Antarctic ureilites; ALH-77257, 64-4, ALH-78019, 56, MET(Meteorite Hills)-78008, 61-3, and Y-791538, 71-4 supplied from NIPR were used for the examinations of graphitic matter by Raman spectroscopy. For the study on micro-diamonds, a small chip of Y-791538 (ca. 0.2 g) was decomposed with HCl/HF at room temperature, and the diamond particulates associated with graphitic carbon were collected from the residue.

Raman spectra was measured by a Jobin Yvon RAMANOR U-1000 laser Raman microprobe. Green line (514.5 nm) of argon ion laser (Spectra Physics model 168 B) was used for exciting radiation, whose power was suppressed to 10 mW at the sample surface to avoid damaging the graphitic structure by heating. The Hamamatsu Photonics photon counting system consisting of a PMT-R464S (photomultiplier) and PHC-C1230S (photon counter) was used for the detection. All spectra were obtained with a spectral slit width of 4.5 cm$^{-1}$, step size of 1 cm$^{-1}$ and a counting time of 1 second per step. The exciting beam size was about 1 micrometer in diameter.

3. Results and Discussion

*Pyrolytic studies and structure of the major carbonaceous matter in carbonaceous chondrites*

The carbonaceous chondrites used in the pyrolytic investigations are enumerated in Table I. Although minor changes of relative intensity among the peaks were observed, the patterns of chromatogram were essentially the same at different pyrolysis temperatures. The pyrolyses were carried out most effectively at ca. 700°C. This probably means that the carbon-hydrogen bond in aromatic compounds is the major one cleaved at the pyrolysis.

The chromatograms of components yielded by pyrolysis at 740°C of several carbonaceous chondrites are shown in Fig. 1. The major products
Table I. Subdivisions, carbon contents, and ratio of naphthalene produced on pyrolysis to total carbon contained in the sample before pyrolysis.

<table>
<thead>
<tr>
<th>Meteorites</th>
<th>Class&lt;sup&gt;a)&lt;/sup&gt;</th>
<th>Carbon content (%)</th>
<th>Total carbon (µg)</th>
<th>Produced naphthalene (ng)</th>
<th>Naphthalene /carbon (w/w %)</th>
<th>TL Type&lt;sup&gt;b)&lt;/sup&gt;</th>
<th>EFP class&lt;sup&gt;c)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-791198</td>
<td>CM2</td>
<td>2.17</td>
<td>106</td>
<td>380</td>
<td>0.36</td>
<td>I</td>
<td></td>
</tr>
<tr>
<td>ALH-77003</td>
<td>C3(0)</td>
<td>0.28</td>
<td>35</td>
<td>105</td>
<td>0.30</td>
<td>3.3</td>
<td>I</td>
</tr>
<tr>
<td>Y-74662</td>
<td>CM2</td>
<td>1.89</td>
<td>95</td>
<td>100</td>
<td>0.11</td>
<td>II</td>
<td></td>
</tr>
<tr>
<td>Murchison</td>
<td>CM2</td>
<td>1.98</td>
<td>40</td>
<td>52</td>
<td>0.13</td>
<td>II</td>
<td></td>
</tr>
<tr>
<td>Allende</td>
<td>C3(V)</td>
<td>0.23</td>
<td>35</td>
<td>50</td>
<td>0.14</td>
<td>II</td>
<td></td>
</tr>
<tr>
<td>Y-790992</td>
<td>C3(0)</td>
<td>0.25</td>
<td>31</td>
<td>20</td>
<td>0.065</td>
<td>III</td>
<td></td>
</tr>
<tr>
<td>B-7904</td>
<td>CM2</td>
<td>0.96</td>
<td>144</td>
<td>20</td>
<td>0.014</td>
<td>IV</td>
<td></td>
</tr>
<tr>
<td>ALH-77307</td>
<td>C3(0)</td>
<td>0.74</td>
<td>148</td>
<td>20</td>
<td>0.014</td>
<td>3.0</td>
<td>IV</td>
</tr>
<tr>
<td>Y-791717</td>
<td>C3(0)</td>
<td>0.12</td>
<td>17</td>
<td>3</td>
<td>0.018</td>
<td>3.4</td>
<td>IV</td>
</tr>
<tr>
<td>Y-793321</td>
<td>CM2</td>
<td>1.77</td>
<td>266</td>
<td>9</td>
<td>0.003</td>
<td>V</td>
<td></td>
</tr>
<tr>
<td>Y-81020</td>
<td>C3(0)</td>
<td>0.96</td>
<td>120</td>
<td>3</td>
<td>0.003</td>
<td>3.4</td>
<td>V</td>
</tr>
</tbody>
</table>

<sup>a)</sup> Classification according to the criterion by Van Schumus and Wood (1967).

<sup>b)</sup> Subdivision based on thermoluminescence (TL) sensitivities (the type number increases with increasing metamorphism: Sears et al., 1990).

<sup>c)</sup> Subdivision based on efficiency of formation of Pyrolysis products (EFP: the type number increases with decreasing degree of EFP).
Fig. 1. Examples of gas chromatograms of the products yielded in pyrolysis at 740°C for 3 s using Curie point pyrolyser for A: Y-791198 (5 mg), B: Y-74662 (3 mg), C: ALH-77307 (15 mg), D: B-7904 (15 mg), E: Y-791717 (16 mg), and F: Y-793321 (15 mg). Column: OV-101, 25 m x 0.25 mm i.d. Detector: FID, Attenuation: 1 for all chromatograms. Range: 16 for A, B, D, and F, and 8 for C and E.

shown in Fig. 1 were identified by the comparison of mass spectrum and retention time in gas chromatography with those of the authentic samples. Although the pyrolyzates in this investigation may not reflect the structure of the polymer in meteorites directly, because of the coexistence of a large amount of minerals, the similarity in the chromatographic patterns (com-
ponents and their relative intensities) of the pyrolysis products suggested the presence of similar structures in the carbonaceous matter of these chondrites. All pyrolyzates except for benzothiophen were composed by aromatic hydrocarbon, therefore the existence of functional groups containing heteroatoms such as oxygen and nitrogen in the polymer is negligible. The carbon contents of these chondrites (Table I: determined by combustion method using a CHN analyzer) did not agree with the formation efficiency of pyrolysis products. Those differences were attributed to the differences in number of the partial structures which were cleaved off on pyrolysis from the main part of the macromolecule.

In order to interpret the results of the pyrolytic studies, we proposed a molecular model characterized by a sheet of polycyclic aromatic network bearing substituents as edge defects (Fig. 2: Murae et al., 1987). The structures of the edge defects, which give the pyrolyzates, are common to all of the carbonaceous chondrites, but the number of edge defects in one molecule and the network size of the macromolecule are different among the chondrites. The graphitic nature appears more clearly in the molecule with a larger network size and fewer edge defects. When the molecule has a small network size and many edge defects, the compound is characterized as a complex mixture of aromatic organic compounds, and the compound shows a similarity to terrestrial coal and kerogen up on examination by some methods. Synthesis and isolation of a single compound bearing a condensed aromatic structure with a network size larger than hexa-peri-benzocoronene are very difficult because of their poor solubility (Hendel, 1986).

This molecular model differs from the kerogen model proposed by Hayatsu et al., (1983) for the organic polymer in Murchison (CM2), and from the tangled graphitic model proposed by Smith and Buseck (1981) for Allende (CV3) residue carbon. Our molecular model can interpret the similarity of pyrolyzates from different chondrites. The inconsistency between the efficiency of pyrolyzate formation and carbon contents was also interpreted by the model. This molecular model indicated that the major carbonaceous matters in carbonaceous chondrites are intermediates in the growth of inorganic carbon from small condensed polycyclic aromatic organic compounds. For network sizes of less than 5 nm it is claimed that the spacing increases more or less smoothly. In practice, a layer disorder often accompanies break-up of the hexagonal networks and results primarily from edge
type defects (Holliday et al., 1973). The interlayer spacing indicates the degree of graphitization. Rietmeijer and Mackinnon (1985) used the degree as a cosmothermometer for Orgueil (CI), Cold Bokkeveld (CM), and Allende (CV). By the tangled graphitic model (Smith and Buseck, 1981) it is hard to explain the variety of interlayer spacing. The kerogen model (Hayatsu et al., 1983) is limited to the carbonaceous matter in Murchison, the model has difficulty for the interpretation of NMR data (Cronin et al., 1987) and
the absence of compounds having heteroatoms, except for benzothiophen in pyrolysis products.

*Spectroscopic studies of acid-resistant residues from carbonaceous chondrites*

Recent developments in spectroscopic instrumentation made it possible to obtain mass spectra of nonvolatile high molecular organic compounds without decomposition, IR spectra of black fine powder with considerable intensity, and natural abundance $^{13}$C NMR spectra of solid samples with sufficient resolution. But it was unsuccessful to obtain the spectra of the organic polymer in carbonaceous chondrites without the concentration of carbon by acid treatments.

The laser ionization TOF-MS of the acid resistant residues from ALH-77307 showed two weak peaks, at m/z ca. 34,100 and ca. 45,200 (Murae et al., 1990). If these peaks were due to the molecular ions of organic residues, then the residue might contain two types of polymers. These molecular weight roughly corresponds to two and three units of the Murchison polymer, respectively, whose composition $\text{C}_{100}\text{H}_{70}\text{N}_{2.5}\text{S}_{2}\text{O}_{12}$ was estimated by Hayatsu et al. (1983). According to the structure proposed by the authors (Fig. 2: Murae et al., 1987), the molecular ions indicate that the residues contain two types of polymers having different molecular sizes. The length from a corner to the opposite corner of the smaller molecule, including edge defects, is ca. 10.4 nm and that of the larger one is ca. 11.9 nm, provided that the molecules had regular hexagonal structures (Fig. 2, B). These molecular sizes are compatible with those proposed based on pyrolytic nature (6, 8, 8, and 12 nm for the carbon in Murchison, Y-74662, Y-793321, and B(Belgica)-7904, respectively (Murae et al., 1989)).

Some characteristic absorptions for aromatic hydrocarbons (Bellamy, 1958) were observed at 3070, 1580, 1490, 810, and 720 cm$^{-1}$ in the diffuse reflection IR spectrum of the above-mentioned acid resistant residues from ALH-77307 (Murae et al., 1990). No remarkable absorption due to other functional groups was observed in the IR spectrum. This is compatible with the structure proposed by the authors (Fig. 2) and suggests that the remaining edge defects after the acid treatments are mainly composed of aromatic hydrocarbons. The intensities of absorptions in the spectrum are weak as a whole, compared to the amount of the sample. This is interpretable as the presence of the large condensed aromatic network which shows no specific
IR absorption band. This result is compatible with that obtained by the mass spectrometry.

High-power decoupled CP-MAS $^{13}$C NMR spectra of the acid-resistant residues from the Allende and Y-791717 meteorites (Fig. 3) showed two major peaks centered at 60 and 150 ppm. These spectra are similar to that of coronene, a compound bearing the smallest basic unit of the structure proposed by the authors for the organic polymer in carbonaceous chondrites. The peaks are very broad, and the width of the line may indicate a structural complexity of the samples. The width of the peaks may also

Fig. 3. $^{13}$C CP-MAS NMR spectra of the acid resistant residues from Allende and Y-791717, and commercial coronene. **A**: Allende (C: 7.57%) 17,200 scans; **B**: Y-791717 (C: 3.08%) 38,500 scans; **C**: coronene (Tokyo kasei kogyo: no further purification) 100 mg in 200 mg of NaCl, 2,800 scans. The hatched peaks in the spectrum of coronene are spinning side bands.
be partially caused by paramagnetic broadening due to the presence of free electrons in the meteoritic insoluble carbon (Cronin et al. 1987) and also by the appearance of many spinning side bands under the standard conditions for CP-MAS $^{13}$C NMR of our instrument. The CP-MAS $^{13}$C NMR spectral intensities were not representative of the total carbon in the sample and tended to underestimate the sp$^2$-hybridized carbon because of its common occurrence in “invisible”, proton-poor domains. The structure proposed by the authors (Fig. 2) contains a condensed aromatic ring structure in which most of carbon atoms are located at a considerable distance from protons, and their slow cross-polarization rates tend to diminish the contribution of these carbon atoms to the spectrum. The similarity of the spectra among coronene and the acid-resistant residues from Orgueil (CI) (Cronin et al., 1987), Murchison (CM2) (Cronin et al., 1987), Allende (CV3) (Cronin et al., 1987; Murae et al., 1990), and Y-791717 (CO3) (Murae et al., 1990) indicated that the structure proposed by the authors (Fig. 2) is general for acid-resistant residues from the carbonaceous chondrites.

Efficiency of formation of pyrolysis products and metamorphism of carbonaceous chondrites

Kallemeyn and Wasson (1981) classified the carbonaceous chondrites into 4 clans CI, CM, CO, and CV based on their elemental composition. In Van Schmus and Wood’s (1967) scheme of petrologic types, CI are all type 1, CM are all type 2 and CV and CO are primarily type 3 (Keck and Sears, 1987). It is now clear that CI and CM were heavily altered by aqueous processes (e.g. DuFresne and Anders, 1962; Kojima et al., 1984; Tomeoka, 1990). Although carbon-carbon bonds in organic compounds in meteorites could be modified under metamorphic conditions, those in carbonaceous chondrites were probably not affected under the aqueous alteration conditions, because the temperature was low (< 20°C: Clayton and Mayeda, 1984).

In our pyrolytic studies of meteorites, the efficiency of formation of pyrolysis products (EFP) could be expressed by the ratio of the amount of naphthalene produced on the pyrolysis to that of the carbon contained before the pyrolysis (Table I). The EFP reflects the molecular size and the number of edge defects, and correlates with the degree of graphitization. Therefore, if the organic polymers had been incorporated in the
parent body after completion of the structure with similar molecular size and with similar number of edge defects, then the EFP would reflect the thermal history of the meteorites. The lower EFP indicated the experience of higher temperature. The carbonaceous chondrites were subdivided into several groups according to the EFP (Table I). This subdivision does not accord with the conventional classifications. However, a recent mineralogical investigation suggested the presence of carbonaceous chondrites which experienced heating events at the latest stage in its process before atmospheric entry to the Earth (Akai, 1989). The EFPs of Y-793321 and B-7904 (CM2) were low and this fact is compatible with the possible heating experienced over 500°C by the meteorites, as shown by mineralogical methods (Akai, 1989). Minor metamorphism of CO chondrites have been examined by thermoluminescence (TL) (Keck and Sears, 1987; Sears et al., 1990). The EFP of ALH-77307 was much lower than that of ALH-77003 indicating that the temperature which the carbonaceous matter in ALH-77307 experienced, was much higher than that experienced by the carbonaceous matter in ALH-77003. This fact does not correspond to the subdivision of CO chondrites by TL sensitivity (Table I) and we need some other explanation.

A model of growth of organic macromolecule in carbonaceous chondrites

All high molecular organic compounds are synthesized by biological or nonbiological polymerization of low molecular carbon compounds. Most of the terrestrial organic high molecular compounds, except artificial ones, are considered to be initially produced by living organisms and then modified by geochemical reactions to give a structurally undeterminable very complex polymer (kerogen). Many works indicated that the organic compounds in carbonaceous chondrites were not synthesized by the living matter, which had metabolic pathways similar to those of terrestrial one. There are two ways for the nonbiological growth of high molecular organic compounds. One is through the supply of energies of polymerization reactions into the place where low molecular carbon compounds are present in high concentration, and the other is through the continuous supply of low molecular carbon compounds with suitable energy for polymerization reactions into a reaction field.

Although the Fisher-Tropsch-type (FTT) model can interpret the formation of the solvent-extractable organic components of Murchison (Hay-
atsu and Anders, 1981), it is hard to interpret, by this model, the growth of the solvent extractable organic components into the polymer similar to terrestrial kerogen, without life activities followed by geological activities.

In the model proposed by Frenklach et al. (1989) the carbonaceous materials were deposited as amorphous carbon on silicon carbide (SiC). The silicon carbide was assumed to be an early and abundant condensate in the cooling of carbon-rich stellar envelopes. As the temperature falls further, aromatic molecules begin to form in the gas phase and then condense onto the growing particles. These aromatic species are held to the grain by van der Waals forces and form “graphitic” microstructures. Although this model can give an interpretation to the origin of interstellar carbon grains, there are some difficulties in its application to the formation processes of the major carbonaceous matter in carbonaceous chondrites. SiC in meteorites is extremely rare, and the proposed destruction processes of SiC (Ming et al., 1989) have difficulty in the interpretation of the selective removal of SiC without the loss of carbonaceous matters deposited around SiC.

Hereby we propose a new growth model of organic macromolecules in carbonaceous chondrites based on its structure. Every circumstellar space of a carbon-creating star with suitable mass can be a candidate of the organic-polymer-formation field. Although the temperature may be too high for the formation of the high molecular carbon compounds at the place near the center of the nuclear synthesis (Stein and Fahr, 1985), the carbon released outside from the center forms CH by the collision with surrounding cold H. The concentration of CH increases by the continuous supply of carbon having suitable energy to react with other molecules. Thus a field for vapor-phase organic reactions is formed. And then the reactions between C and CH and between CH and CH occur to give rise to C≡CH and HC≡CH in the field. The reaction products, C≡CH and HC≡CH, do not have enough energy to drift away the reaction field and come into collision with newly supplied C and CH to form condensed aromatic networks as illustrated in Fig. 4 (in actual case the reaction species and reaction mechanisms are probably much more complicated). Toward the end of the growth of the molecule, various small organic compounds react at the edge of the condensed polycyclic aromatic ring to terminate the polymerization and form edge defects. Aromatic compounds having a condensed network are stabilized by the enlargement of their molecular size (Dias, 1984). Thus, once
Fig. 4. Chemical processes of the growth of condensed polycyclic aromatic macromolecules by radical reactions of CH. Only growing processes to a coronene-like molecule are illustrated. Further growth is achieved by repetition of similar reactions. When C is involved in the reaction, the removal of hydrogen on the carbon adjacent to aromatic ring is unnecessary.
the products grow up to a high molecular compound, they would survive under various cosmic conditions. Various reactions, however, can occur at the edges of the aromatic high molecular compound, and the number and structure of edge defects are probably altered by cosmic conditions.

Strange Raman band of diamond particulates in ureilite

Some micro-diamond particulates contained in acid treated residues from Y-791538 provided peculiar Raman spectra, different from typical diamond spectra. The Raman spectra of the diamond particulates are shown in Fig. 5. In a part of the residue, a sharp Raman band at 1332 cm$^{-1}$ and a broad two-fold fluorescence band were observed (Fig. 5a). The majority of the diamonds in ureilites show similar features as displayed in Fig. 5a. However, the fluorescence-free diamonds, as shown in Fig. 5b, were also found in the same residue. The vibrational energy of the fluorescence-free diamonds (Raman band centered at 1323 cm$^{-1}$) was significantly lower than that of ordinary diamonds.

The observed energy shift of about 10 cm$^{-1}$ may be open to two possibilities at present (Kagi et al., 1990). (1) The unusual band at 1323 cm$^{-1}$ might be assigned to the lattice vibration of lonsdaleite, which is a hexagonal polymorphism of diamond. However there is no published Raman spectral data for lonsdaleite because of the absence of pure lonsdaleite crystal in terrestrial environment. (2) The energy shift toward the lower energy might be attributed to an enrichment of $^{13}$C in the ureilitic diamonds. While the natural abundance ratio of $^{12}$C/$^{13}$C is usually 89 in the solar system, the $^{12}$C/$^{13}$C ratio estimated from the frequency of the anomalous Raman band at 1323 cm$^{-1}$ was evaluated to be about 10, based on the assumption that the lattice vibration including $^{13}$C atoms is delocalized and the vibrational frequency is inversely proportional to the square root of the average mass of carbon atoms. The isotope ratio determined here coincides with the lower limit of $^{12}$C/$^{13}$C ratio observed on interstellar graphite in the Murchison C2 chondrite by Amari et al. (1990). If diamonds in ureilites were directly converted by a shock event from primordial carbonaceous material, retaining high heterogeneity with considerable carbon isotope anomaly, such a low $^{12}$C/$^{13}$C ratio of the anomalous diamonds might be comprehensible. Survival of the carbonaceous matter from carbonaceous chondrite conserving its skeleton during the formation of the ureilitic parent body is consistent
with observed structural heterogeneity of graphitic matter in ureilites, as described in the next section. At present, although we can not tell which is the true origin of the energy shift, the presence of the anomalous diamond would throw a new light on meteoritics and cosmochemistry.

Wide structural variety of graphitic matter in ureilites

In the Raman spectrum of graphite, one or two first order Raman bands are observed, depending on its crystallinity. Relative intensities of the 1582 cm\(^{-1}\) and 1350 cm\(^{-1}\) Raman bands are strongly correlated to the crystallite size parallel to the crystallographic a-axis; L\(_a\) (crystallite size in the surface layer), can be determined by powder X-ray diffraction analysis (Tuinstra
and Koenig, 1970). It is known empirically that $R = I_{1585}/I_{1350}$ is directly proportional to $L_a$, as follows,

$$L_a \text{ (nm)} = 4.5 \times R.$$  \hspace{1cm} (1)

In this study, the $L_a$ of graphitic carbon were estimated from Eq.(1).

Raman spectra of the carbonaceous vein in ALH-78019, unshocked ureilite with no presence of diamonds, are shown in Fig. 6. Figure 6a shows the spectrum for “graphitic carbon” with an $L_a$ of 20 nm, Fig. 6b shows that of “semi-graphitic carbon” with an $L_a$ of 10 nm, and Fig. 6c shows that of “well-graphitic carbon” with an infinite crystallite size $L_a$, evaluated from Raman spectroscopic data. It is noteworthy that these three types of graphitic matter coexist in a single carbonaceous vein. (Kagi et al., 1991)

Similar structural heterogeneity of graphitic matter was observed for MET-78008. The spectra of “amorphous carbon” with an $L_a$ of 5 nm (Fig. 7c), “semi-graphitic carbon” with $L_a$ of 10 nm (Fig. 7b), and “graphitic carbon” with $L_a$ of 20 nm (Fig. 7a) were observed in a single carbonaceous vein of the meteorite. In a similar manner, structural heterogeneity was observed in the graphitic matter of Y-791538 and ALH-77257. The crystallite sizes of “amorphous carbon” in ALH-77257, ALH-78019, and MET-78008 are in the same order as those of the carbonaceous matter contained in carbonaceous chondrites (Murae et al., 1989).

The above Raman data bring up two problems having a significant correlation with the origin and history of ureilite.

1) Why could the ureilitic “amorphous carbon” be retained in the ureilitic parent body during the metamorphic events. Wacker (1986) suggested that much of the primitive noble gases in ALH-78019 are contained in fine-grained carbon and that two types of carbon exist in ALH-78019. Moreover, he pointed out that the amorphous carbon has survived from the solar nebula judging from $^{132}$Xe/$^6$C ratios. It has not yet been confirmed if the fine-grained carbon observed by Wacker and the “semi-graphitic” or “amorphous carbon” observed in this study are identical, however it seems sure that they are closely related.

2) What caused the considerable heterogeneity of the carbon structure in a single carbonaceous vein in the ureilite. Berkley and Jones (1982) suggested that “most” graphite in ureilites originated by the crystallization from a C-rich metallic phase, however, our results implied that not all of the
Fig. 6. Raman spectra of a single carbonaceous vein in ALH-78019 unshocked ureilite. 
(a) Graphitic carbon. (b) Semi-graphitic carbon.
Fig. 7. Raman spectra of a single carbonaceous vein in MET-78008 ureilite. (a) Graphitic carbon. (b) Semi-graphitic carbon. (c) Amorphous carbon.
graphite in ureilites originated from the metallic phase. As one speculation, it is considered that the “semi-graphitic” or “amorphous” carbon observed here was retained in the static part of the parent body without a large scale of metamorphic events and they migrated to the present portion in the carbonaceous vein after crystallization of the graphitic carbon from the metallic phase. This speculation is consistent with the durability of the less ordered “semi-graphitic” or “amorphous” carbon without removing the primitive noble gases and the presence of the oxygen isotope anomaly (Clayton and Mayeda, 1984) which means the raw materials of ureilite were not equilibrated.

We can summarize the character and origin of the graphitic matter in ureilite inferred from the Raman data as follows. The heterogeneity in the structure implies a two stage crystal growth in the vein, crystallization of graphite from the metallic phase in the first stage was followed by flowing injection of less ordered carbon into the vein from the static part of the parent body in the second stage. The second stage might have resulted from the collision of other planetesimal.

Acknowledgements

This work was supported by the Grant-in-Aid for Scientific Research on Priority Areas (Origin of the Solar System) of the Japanese Ministry of Education, Science, and Culture (Nos. 62611003, 63611003, and 01611003).

References


Boesgaard, A. M. and G. Steigman, 1985. Big bang nucleosynthesis: theo-


Keck, B. D. and W. G. Sears, 1987, Chemical and physical studies of type 3 chondrites-VIII: Thermoluminescence and metamorphism in the CO


