

RAMAN FREQUENCIES OF GRAPHITIC CARBON IN ANTARCTIC UREILITES

Hiroyuki KAGI^{1,2*}, Kazuya TAKAHASHI²
and Akimasa MASUDA³

¹*Institute of Materials Science, University of Tsukuba, Tsukuba 305*

²*Earth Science Laboratory, Institute of Physical and
Chemical Research (RIKEN), Wako 351-01*

³*Department of Chemistry, University of Electro-Communications,
Chofu-shi, Tokyo 182*

Abstract: Raman frequencies for the in-plane lattice vibration of graphite were surveyed for four Antarctic ureilites in order to construct a paradigm for structural properties of graphitic carbon in ureilites. Raman spectra were obtained by point-by-point measurements using a laser microbeam 1 μm in diameter. The measured results formed an array in a two-dimensional plot between the E_{2g} frequency and intensity ratio of two graphite-derived Raman bands. The graphitic matter in ALH-78019 gave the averaged E_{2g} frequency at 1582.0 cm^{-1} , which agrees with the well-established wavenumber of the E_{2g} in-plane lattice vibration of graphite. On the contrary, some graphitic matter in the ureilites (ALH-77257, Y-791538 and MET-78008) exhibited considerably up-shifted E_{2g} frequency. Distribution in the array was proved to be closely linked to the extent of shock which the ureilites suffered.

1. Introduction

Carbonaceous chondrites, some achondrites and iron meteorites contain considerable amounts of carbon. In ureilites, 0.2–6 wt% graphitic matter occurs along the grain boundaries of olivine and pigeonite (GOODRICH, 1992). Since ureilites have survived intensive shock processes on a parent body, it is of particular interest to investigate whether the shock induced any changes in Raman spectra of the graphitic veins in ureilites. Micro-Raman spectroscopy has several technical advantages for investigation of the structural form of carbonaceous materials in those meteorites, it is non-destructive, the observation is *in situ* and the spatial resolution is excellent. Raman spectra of graphitic materials exhibit one intrinsic band (the so called G-band) originating from lattice vibration of graphite, and in addition a defect-induced band (the so called D-band). The intensity ratios of these two bands have been used previously for evaluation of the crystallite size and structural ordering of graphitic matters in meteorites (CHRISTOPHE MICHEL-LEVY and LAUTE, 1982; HEYMANN, 1987; HEYMANN and READ, 1987; MAKJANIC *et al.*, 1989; KAGI *et al.*, 1991; MAKJANIC *et al.*, 1993). Information on first-order band

* To whom all correspondence should be addressed.

widths and second-order Raman bands is also used to evaluate the structural ordering of carbonaceous matter (WOPENKA and PASTERIS, 1993). Thus, Raman spectroscopy has the potential to establish the ordering of carbon of meteoritical interest. Although little attention to the band position of the E_{2g} vibration has been paid as it exhibited a constant wavenumber (1582 cm^{-1}), recently anomalous Raman spectra have been found in some natural graphite samples; terrestrial graphite contained in metamorphic rocks (WOPENKA *et al.*, 1988; WOPENKA and PASTERIS, 1988; WOPENKA and PASTERIS, 1993), and interstellar graphite grains extracted from the Murchison meteorite (ZINNER *et al.*, 1990). These graphites show considerable down-shifts of about $7\text{--}15\text{ cm}^{-1}$ in the E_{2g} Raman frequency compared to typical graphite samples. The cause of the down-shift had not been explained by theory or spectrochemical experiment. However, EVERALL and LUMSON (1991) and EVERALL *et al.* (1991) showed that the exciting laser beam induced an increase of sample temperature resulting in the down-shift in Raman spectra of graphite. Therefore it seems likely that the anomalous Raman spectra of natural graphite previously reported were not intrinsic but caused by laser-induced heating of samples. Further study attempted in-situ estimation of sample temperature from the intensity ratio of the anti-Stokes to the Stokes line (KAGI *et al.*, 1994). Consequently, caution is required to discuss the Raman frequency of the G-band in micro-Raman spectroscopy.

In this study, structural ordering of graphite in ureilites was investigated in view of the frequency of the E_{2g} mode taking into account the technical problem of Raman spectroscopy. We will disclose the assemblies of Raman frequencies of the graphite in ureilites in order to consider the conditions of formation of the graphitic matter.

2. Samples and Analytical Methods

2.1. Raman spectra of graphite

Highly ordered graphite gives rise to a single first-order Raman band (the so-called G-band) derived from the in-plane vibrational mode. Two Raman-active E_{2g} modes and infrared-active modes of A_{2u} and E_{1u} symmetry are expected for perfectly crystallized graphite. The E_{1u} and one of the E_{2g} vibrations correspond to C-C stretching vibrations within the honeycomb lattice of the graphite layer and occur at 1588 and 1582 cm^{-1} , respectively (DRESSELHAUS and DRESSELHAUS, 1981). The second Raman-active mode is associated with relative displacement of the layers, and is so low in frequency (at 42 cm^{-1}) and in intensity that it is fairly difficult to observe. With decreasing in-plane crystallite size L_a , the additional disorder-induced Raman band (the so-called D-band) appears at 1355 cm^{-1} in Raman shift. TUINSTRA and KOENIG (1970) plotted the intensity ratio of G- and D-bands for various types of carbonaceous matter as a function of the crystallite size L_a , and found a linear relationship between L_a and Raman intensity ratio. Their L_a values were determined by X-ray diffraction analysis. For disordered graphite samples with a small L_a value, a further Raman band is detected around 1620 cm^{-1}

as a shoulder of the G-band. The vibrational energy of the G-band is detected at the constant value ($1582 \text{ } \Delta\text{cm}^{-1}$) for highly-ordered graphitic matter of either natural or artificial origin, and shows a slight up-shift when the crystallite size (L_a) decreases. Most of the structural characterization by means of Raman spectroscopy of carbonaceous matters has been carried out in terms of the intensity ratio of the G-band to the D-band. In the present study, our attention was focused on the frequency of the E_{2g} mode in addition to the intensity ratio of the two Raman bands.

2.2. Samples

Polished thin sections (PTS) of Antarctic ureilite, Allan Hills (ALH)-77257,64-4, ALH-78019,56, Meteorite Hills (MET)-78008,61-3, and Yamato (Y)-791538,71-4 allocated from NIPR were examined with micro-Raman spectroscopy. All of the PTS exhibited the presence of carbon veins in the grain boundaries of silicate minerals. We carried out point-by-point analysis in the carbon veins using a laser microbeam $1 \mu\text{m}$ in diameter as described below, and the numbers of measured points are listed in Table 1. The locations for the measurement were selected arbitrarily.

Table 1. Number of measured spot in graphitic veins, E_{2g} frequency and I_G/I_D value. Standard deviations are designated in parentheses.

Sample	Number of the points	E_{2g} frequency (cm^{-1})	I_G/I_D
ALH-77257	23	1582.2 (0.83)	3.00 (1.25)
MET-78008	25	1584.8 (2.44)	1.75 (0.64)
Y-791538	33	1582.4 (1.82)	2.65 (1.02)
ALH-78019	20	1582.0 (0.75)	4.22 (2.65)

According to PASTERIS (1989), Raman-active vibrational modes from the organic mounting medium overlap with Raman bands of the geological phase of interest. In this case, no additional Raman peaks other than the graphite-derived Raman bands could be detected throughout our measurements, so that the artifacts concerning the overlap of mounting medium could be excluded in our sample preparation.

2.3. Micro-Raman spectrometry

Detailed analytical conditions for the Raman measurement were described in our previous published paper (KAGI *et al.*, 1991). Raman spectra were taken with a RAMANOR U-1000 micro-Raman spectrometer manufactured by Jobin Yvon using 514.5 nm green light with a power of 10 mW at the sample surface, a typical energy value applied for the analysis of natural carbonaceous matter of geochemical interest, as the exciting laser radiation. The exciting laser beam was focused on a spot $1 \mu\text{m}$ in diameter. In this condition, laser-induced high temperature at the sample surface induces considerable down-shifts in the Raman spectra for graphite powder samples. However, no down-shift of the first-order peak positions can be observed for PTS samples due to its efficient heat conduction (see results). Raman

spectra were collected in the region from 1200 cm^{-1} to 1700 cm^{-1} , which is of interest for the evaluation of structural ordering of graphitic materials. The sampling step was 1 cm^{-1} , and the sampling time was 2 s per point.

The raw spectral data were smoothed, and were fitted into the Lorentzian curves after eliminating background curves. The Raman intensities and band positions were determined from the three curves fitted into a Lorentzian function. These Lorentzian curves were centered at approximately 1352 cm^{-1} , 1582 cm^{-1} and 1620 cm^{-1} , respectively, which derived from Raman bands of graphite (see next section). The fitted wavenumbers varied sample by sample depending on their structural ordering, and the 1620 cm^{-1} band could be detected only for measured spots corresponding to disordered graphite.

3. Results and Discussion

3.1. Raman spectra of graphitic matter in Antarctic ureilites

Typical Raman spectra for the Antarctic ureilites are shown in Fig. 1. All

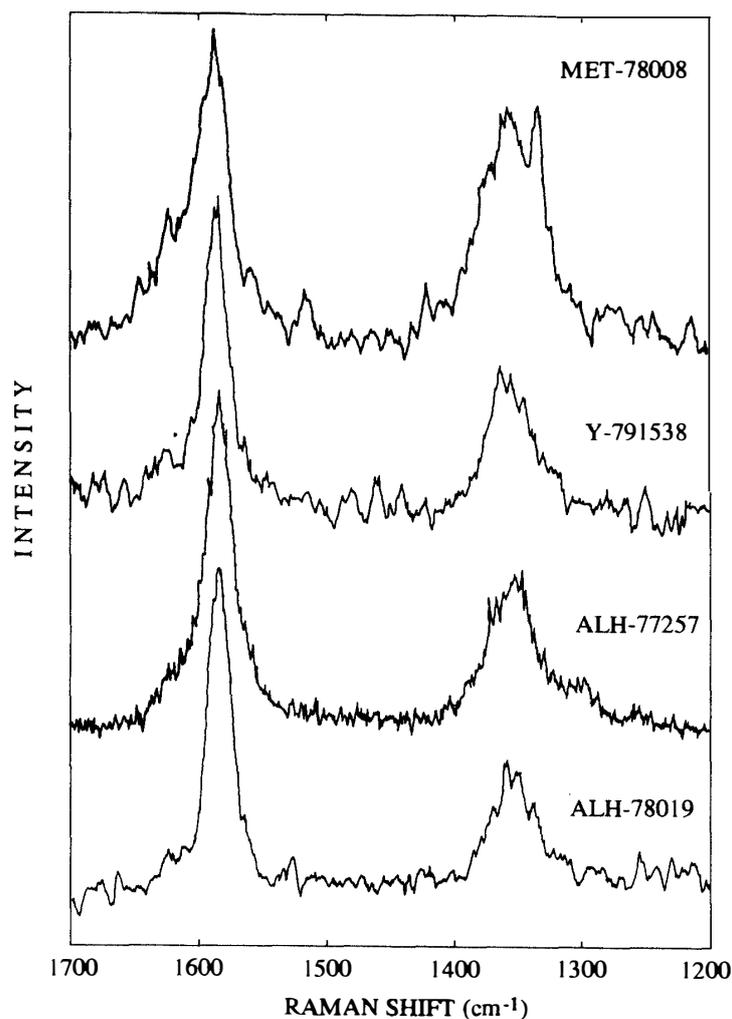


Fig. 1. Typical Raman spectra of graphitic matter from ALH-77257, Y-791538, MET-78008, ALH-78019.

samples exhibited the E_{2g} band (G-band) at about 1582 cm^{-1} and the defect-induced band (D-band) at about 1355 cm^{-1} . As described in our previous paper (KAGI *et al.*, 1991), the intensity ratios between these two bands differed not only among the sample specimens but also within the same sample specimen depending on the measured location. A histogram of the wavenumber of the E_{2g} mode for the ureilites investigated in this study is shown in Fig. 2, and for each meteorite the averaged frequency of the E_{2g} mode and the averaged I_G/I_D values with their standard deviations are listed in Table 1. Since the spectral resolution determined by an optical slit width was 4.5 cm^{-1} in the series of measurements, the normal E_{2g} mode at 1582 cm^{-1} is detected in the region of $1582 \pm 2\text{ cm}^{-1}$. One might think that the optical resolution, 4.5 cm^{-1} , is too large for discussion of Raman spectra, but this is fine enough for Raman spectra of graphite because graphite is known to exhibit much broader Raman bands than the spectral resolution. Figure 2 shows that the graphitic matter in the Antarctic ureilites did not exhibit considerable down-shifts (lower than 1578 cm^{-1} in Raman shift) which are frequently caused by laser heating for powder samples. This means that our present measurements on PTS were carried out in an appropriate condition and the problem of the artificial down-shift seems to be eliminated.

Another point to be noted in Fig. 2 is that some graphitic matter in ureilites shows considerable up-shifts in the G-band higher than 1585 cm^{-1} . In Fig. 3, the E_{2g} frequencies of graphitic matter in the ureilites examined are plotted against the ratios of intensity of the E_{2g} mode (I_G) to that of the defect-induced band (I_D). The distribution profile of these spots on Fig. 3 looks like the letter "L". All graphitic matter showing up-shifts has poor crystallinity indicated by I_G/I_D values lower than 2. The crystallite size along the a -axis (L_a) of graphite is known to be proportional to the intensity ratio, I_G/I_D . Moreover, with increasing disorder the 1582 cm^{-1} band broadens, and moves to higher frequency (TUINSTRAN and KOENIG, 1970; LESPADE

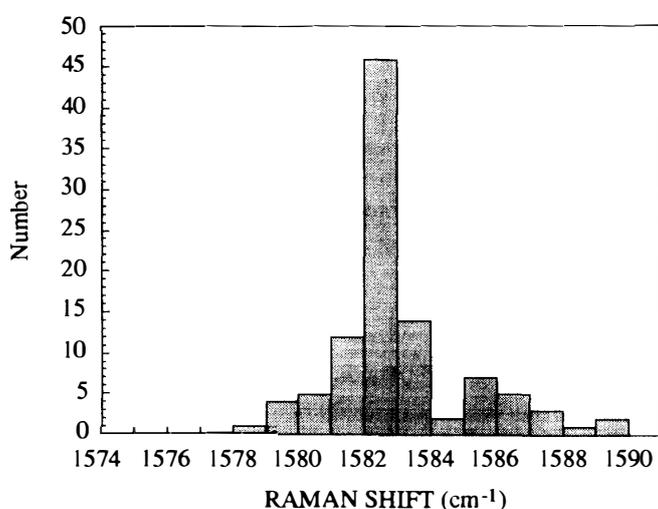


Fig. 2. Histogram of the vibrational energy of the G-band of graphitic matter in the Antarctic ureilites.

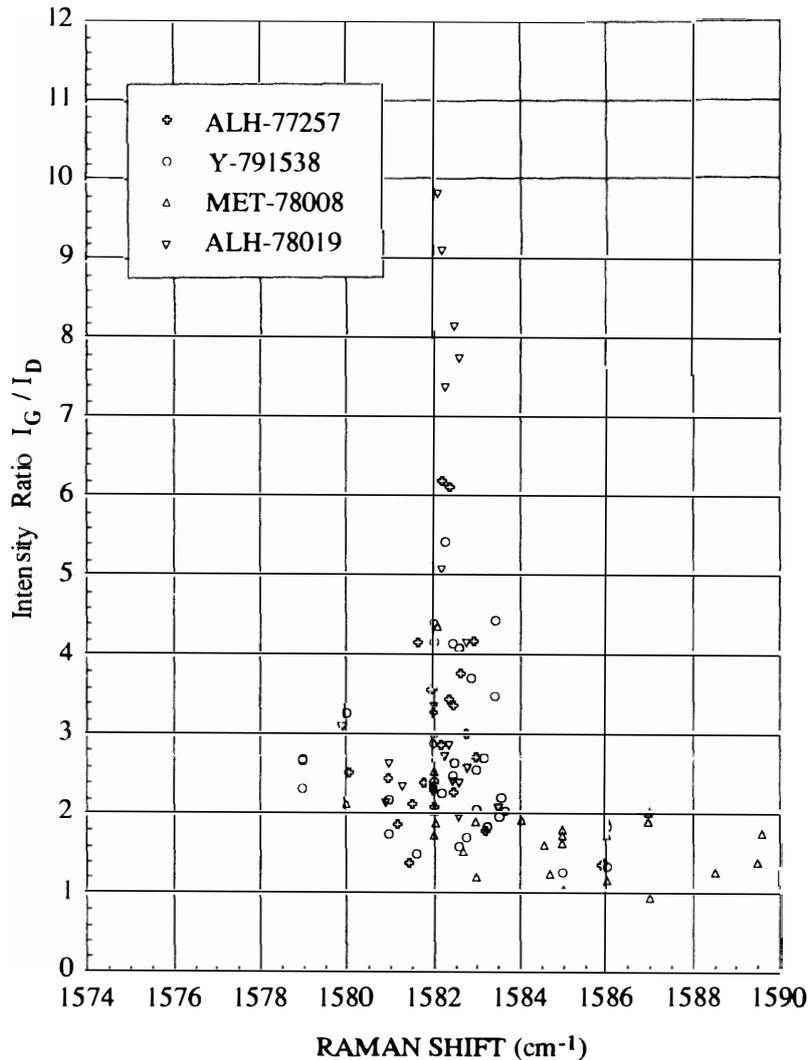


Fig. 3. Intensity ratio between the G-band and the D-band (I_G/I_D) vs. the frequency of the G-band for the Antarctic ureilites. The distribution array for the measured spot looks like a letter "L".

et al., 1982; LESPAGE *et al.*, 1984). Therefore, the profile shown in Fig. 3 is consistent with the dependence of the E_{2g} frequency upon the crystallite size, L_a . The same kind of up-shift in G-band position has been reported for interplanetary dust particles (WOPENKA, 1988).

From Figs. 2 and 3, it is demonstrated that the E_{2g} frequencies of graphitic matter in the Antarctic ureilites is determined by crystallite size. One might deduce that the distribution profiles in the $I_G/I_D - E_{2g}$ plot (Fig. 3) differ from each other among the ureilites and can provide us with novel information on the genetic history of ureilite. This speculation is partly right because it was confirmed that the structural ordering of graphite estimated from I_G/I_D ratios is as follows:

$$ALH-78019 > ALH-77257 \approx Y-791538 > MET-78008 ,$$

in the course of this study (Table 1), which correlates with the extent of shock

suffered (GOODRICH, 1992).

A further point to be noted is the distribution of E_{2g} frequency and I_G/I_D ratio in a single sample. Table 1 reveals substantial dispersions of these values for each sample specimen. These distributions can be affected by the following three factors. The first is sample-derived intrinsic structural heterogeneity in the crystallite size of the graphitic matter. The second is the sample-orientation, which affects the I_G/I_D ratio critically (PASTERIS, 1989). The third is an artificial polish-induced disorder in graphitic matter. This third factor, however, can be eliminated in this case except in ALH-78019, which is known to be a ureilite containing no diamond. To eliminate the effects of polishing, one should focus the laser beam into the graphite not intersected by the surface (PASTERIS, 1989). Carbonaceous matter in the PTS of ureilites used in this study never lies on the sample surface, because micro-diamonds appear on the top surface and the polish-sensitive carbonaceous matter is not intersected by the surface. This situation can be easily observed under a microscope. Although we cannot elucidate at present whether the first or second factor is the most important cause of the heterogeneity of the E_{2g} frequency, it is likely that the distribution results not from a sampling problem but a purely ureilite-derived factor. This is also supported by the good correlation between the distribution and the extent of shock which ureilites suffered as mentioned below.

3.2. Implication from the energy of the E_{2g} Raman mode

So far the characterization of crystallinity of graphite has been made in terms of the I_G/I_D ratios (CHRISTOPHE MICHEL-LEVY and LAUTE, 1982; HEYMANN, 1987; HEYMANN and READ, 1987; KAGI *et al.*, 1991; MAKJANIC *et al.*, 1993; WOPENKA, 1988; WOPENKA and PASTERIS, 1993), because the I_G/I_D ratio proportionally decreases with decrease of L_a . On the contrary, up-shift of the E_{2g} mode has been reported for poorly crystallized graphite having small I_G/I_D (TUINSTRAN and KOENIG, 1970; LESPADE *et al.*, 1982, 1984; WOPENKA and PASTERIS, 1993). As shown in Fig. 3, the two-dimensional plot of the frequency of the E_{2g} mode against the I_G/I_D value seems to have the potential to provide information about the structural ordering of graphitic carbon. From Fig. 3, the up-shifted Raman spectra were not found to be observed for well-crystallized graphitic matter having an I_G/I_D value higher than 2. In other words, up-shift of the E_{2g} mode was observed for poorly-ordered graphitic matter. The averaged wavenumbers of the E_{2g} mode differ from each other for the meteorites studied here (Table 1). ALH-78019 gave an average value of 1582.0 cm^{-1} , which lies in the range of the well-established E_{2g} mode of graphite. ALH-77257 and Y-791538 gave averaged wavenumbers slightly higher than 1582.0 cm^{-1} . The most interesting point to be noted is an averaged E_{2g} frequency of 1584.8 cm^{-1} for MET-78008, which exhibited a significant up-shift. From the I_G/I_D ratios, one can easily find the difference in the structural ordering of graphite among the meteorites studied here (Table 1). On the other hand, from the wavenumber of the E_{2g} mode, the specificity of the graphitic matter of MET-78008 was proved. Although we cannot conclude this confidently at present, the specificity of MET-78008 seems to be caused by a severe shock process. According to

GOODRICH (1992), ALH-78019 was classified as very low-shock, ALH-77257 and Y-791538 were classified as low-shock, and MET-78008 was classified as medium-shock. The extent of shock events that ureilites suffered seems to be recorded in the structural ordering of graphitic carbon embedded in the grain boundary of silicate minerals. Further study of graphitic matter in ureilites will disclose the relationship between the extent of shock and the Raman profile.

Recently, high-speed rail-gun experiments have demonstrated the shock formation of kerogen-like organic matter from commercial powdered graphite using FT-IR spectra (MURAE, 1993). The shock activity cleaves the graphitic matter, generating organic compounds as fragments, and the graphite structure is disordered. Shock-induced chemical reactions of carbonaceous matter will be of meteoritical interest. Furthermore, the present study clarified that the combination of the wavenumber of the E_{2g} mode and the I_G/I_D ratio gives more information about graphitic carbon than either the wavenumber of E_{2g} mode or the I_G/I_D ratio alone. Raman data of graphitic matter in ureilites lie on the L-like array in the $E_{2g} - I_G/I_D$ plot, and with increasing shock, the Raman-data point descends along the array. Consequently, in evaluation of structural ordering, the I_G/I_D ratio is more informative than the E_{2g} frequency for graphitic carbon with large L_a , while the E_{2g} frequency is more informative for disordered graphite. The difference in Raman profile of the meteoritical graphite investigated in this study was attributable to the difference in the shock processes which meteorites suffered.

4. Conclusions

Raman spectra of graphitic matter in Antarctic ureilites (ALH-77257, ALH-78019, MET-78008, Y-791538) were obtained by point-by-point measurement using a $1\ \mu\text{m}$ laser microbeam. The spectra were investigated in terms of the vibration energy of the E_{2g} in-plane vibration in addition to the crystallite size, and the following conclusions can be drawn.

(1) Graphitic matter from ureilites did not exhibit a heat-induced down-shift in the frequency of the G-band in Raman spectra, which implies that our micro-Raman measurements were carried out under an appropriate condition without considerable heating of the sample under the beam.

(2) Some graphitic matter in the ureilites with low crystallinity ($I_G/I_D < 2$) shows a substantial up-shift in the G-band. The up-shifts are caused by the small L_a (crystallite size along the a -axis) values.

(3) The combination of the I_G/I_D ratio and the E_{2g} frequency was proved to provide information about the genetic history of ureilites, especially on the extent of shock events.

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