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MICRO RAMAN SPECTROSCOPY OF DIAMONDS IN THE CANYON DIABLO IRON METEORITE: IMPLICATION FOR THE SHOCK ORIGIN

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Abstract: Raman spectra were measured for diamonds in an inclusion of the Canyon Diablo iron meteorite. The wavenumber position of a Raman peak was found in the range between 1333 and 1318 cm^{-1}, and the full width at half maximum (FWHM) of the Raman peak ranges from 25 to 117 cm^{-1}. These results are similar to those of Raman spectra of diamonds synthesized by shock-induced high pressure and are consistent with the consensus that diamond in Canyon Diablo formed by impact shock. No diamond grains showing a relatively narrow FWHM (7 cm^{-1}) were found in the inclusion.

1. Introduction

Diamond shows a strong Raman peak (F_{2g}) near 1332 cm^{-1} (*e.g.*, SOLIN and RAMDAS, 1970) which is usually used for the identification of the micro-structure of diamond. MIYAMOTO *et al.* (1988) measured the Raman spectrum of a diamond in the ALHA77257 ureilite and suggested that ureilite diamond has formed from vapor in the primitive solar nebula because the FWHM (full width at half maximum) of the 1332 cm^{-1} Raman peak of a ureilite diamond is as much broad as about 10 cm^{-1}. SATO (1984) had pointed out that the FWHM varies with the mode of the diamond synthesis. In fact, the FWHM of the 1332 cm^{-1} Raman peak of shock-produced diamonds (*e.g.*, DECARLI and JAMIESON, 1961) is enhanced from 10 to 120 cm^{-1}, that of diamonds synthesized by chemical vapor deposition (CVD) (*e.g.*, DERJAGUIN *et al.*, 1968) is from 3 to 25 cm^{-1}, and that by static high pressure (*e.g.*, BUNDY, 1963) is from 2 to 3 cm^{-1} (MIYAMOTO *et al.*, 1993; SATO, 1984).

On the other hand, HEYMANN (1989) measured the Raman spectrum of a diamond in the Canyon Diablo iron meteorite and showed that the FWHM was 7±2 cm^{-1}, which is within the range for CVD diamonds. Since the majority of meteorite researchers have concluded that diamonds in Canyon Diablo formed by impact shock when the meteorite struck the Earth (*e.g.*, HEYMANN *et al.*, 1966), then HEYMANN (1989) cautioned that the Raman evidence for the CVD origin of ureilite diamond may be much less firm than stated by MIYAMOTO *et al.* (1988). Therefore, in the present study Raman spectra of diamonds in Canyon Diablo were remeasured to confirm the result reported by HEYMANN (1989). In addition, Raman measurements on meteoritic diamonds may distinguish between CVD and shock-produced diamonds and further the Raman signature can be used as an additional quantitative indicator of shock pressure in iron meteorite fragments.

2. Sample and Experiments

Raman spectra were measured for diamonds in an inclusion of the Canyon Diablo sample, which was kindly supplied by Robert A. HAAG - Meteorites. The inclusion of about 0.5 cm in diameter, which consists mainly of graphite and diamond, lies within a rough slice (3.5 cm×2.5 cm×0.3 cm in size) of the Canyon Diablo iron meteorite. Diamonds, which are from about 1 μm to a few tens of μm in size, are found among graphite grains in the inclusion.

Raman spectra were measured with a JASCO micro Raman spectrometer with a triple monochromator (3×60 cm). The 488 nm line of an argon laser was focused to an area of about 1 μm across on the sample surface through a microscope (backscattering (180°) geometry). The laser power was about 3 mW on the surface of the sample. The spectra were accumulated for 10 min to enhance the signal-to-noise ratio by using a multichannel detector composed of photodiode array. The wavenumber position and the full width at half maximum (FWHM) of the Raman peak were determined by carrying out a Lorentzian fitting of the spectrum. The wavenumber position of the Raman peak was calibrated by using both the 1293.952 cm^{-1} and 1343.517 cm^{-1} emission lines in Raman shift of a Ne lamp. Spectral slit width was about 2 cm^{-1} and the variation in room temperature was within ±5 °C.

Besides the Raman spectroscopic investigation, the inclusion and some diamonds were observed also by using a scanning electron microscope (SEM, JEOL 840A) equipped with an energy dispersive spectrometer (EDS) combined with a wavelength dispersive spectrometer (WDS) using the utilities of the Kevex Super 8000 system. Carbon was detected by using the WDS system.

3. Results and Discussion

Raman spectra were measured on the cores of diamond grains in the inclusion of the Canyon Diablo sample. Figure 1 shows the Raman spectrum of a diamond in Can-

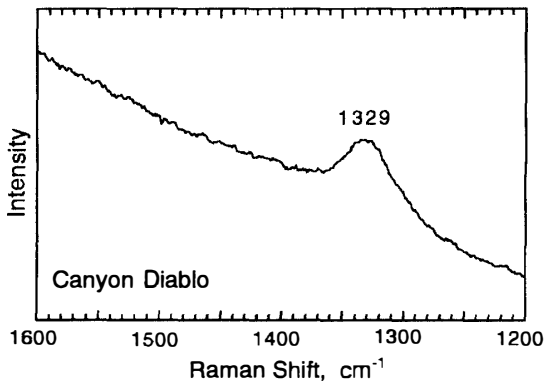

Fig. 1. The Raman spectrum of a diamond in the Canyon Diablo iron meteorite. The peak position is 1329 cm^{-1} and the FWHM (full width at half maximum) is 50 cm^{-1}.

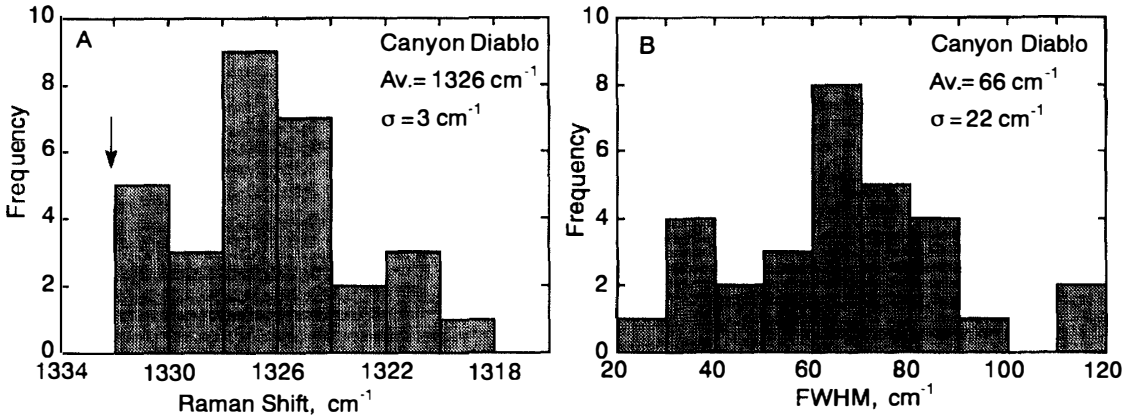

Fig. 2. Distributions of the wavenumber position (a) and FWHM (b) of a Raman peak near 1332 cm^{-1} of diamonds in the Canyon Diablo iron meteorite. An arrow indicates the wavenumber position of a diamond from South Africa (1332.13 cm^{-1}, MIYAMOTO and OHSUMI, 1995).

yon Diablo. Figure 2a shows the distribution of the wavenumber position of a Raman peak near 1332 cm^{-1} of diamond (SOLIN and RAMDAS, 1970). The peak positions are widely distributed from 1333 to 1318 cm^{-1} (The average is 1326±3 cm^{-1}). The FWHM of the Raman peak of the Canyon Diablo diamonds (Fig. 2b) is also very large, ranging from 25 to 117 cm^{-1} with an average of 66±2 cm^{-1}.

The FWHM of the Raman peak against the wavenumber position shows no correlation between the FWHM and wavenumber position (Fig. 3a). Each solid circle in Fig.

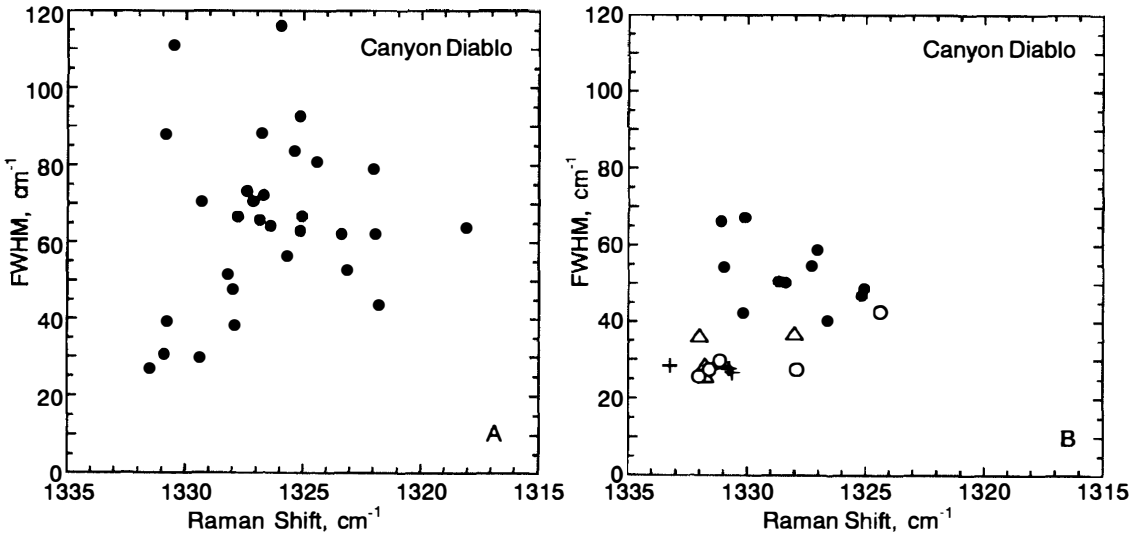

Fig. 3. Plot of the wavenumber position versus FWHM of the Raman peak near 1332 cm^{-1} in the Canyon Diablo iron meteorite. (a) Diamonds shown in Fig. 2. Each solid circle stands for the value of the core of an individual diamond grain (b) Some relatively large diamond grains. Each symbol stands for the values within the same grain.

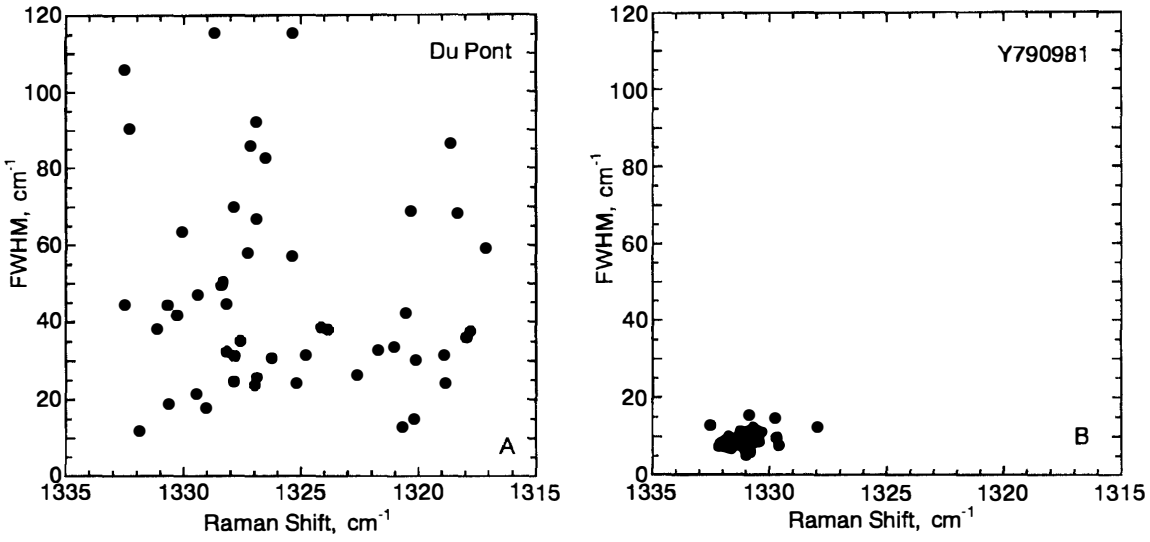

Fig. 4. Plot of the wavenumber position versus FWHM of a Raman peak near 1332 cm^{-1}. Data are from MIYAMOTO et al. (1993). (a) Diamonds synthesized by shock-induced high pressure (made by Du Pont de Nemours, E. I. & Co.). (b) Diamonds in the Yamato-790981 ureilite.

3a corresponds to one spot in one individual grain of diamond. Figure 3b shows the variation in the wavenumber position and FWHM of the Raman peak within each grain. Several measurements were performed for some large grains at various locations, because the laser beam for the Raman measurement is about 1 μm across which is smaller compared with the sizes of the measured grains. The wavenumber position and FWHM are varied in different locations within each grain. This result implies that the diamond grains may be polycrystalline. The ranges of both the wavenumber position and FWHM of the Raman peak (Fig. 3a) are similar to those of diamonds synthesized by shock-induced high pressure (Fig. 4a) (MIYAMOTO *et al.*, 1993). Consequently the present Raman measurements suggest that the Canyon Diablo diamonds formed by impact shock.

HEYMANN (1989) reported that a Canyon Diablo diamond shows a Raman peak at 1332 cm^{-1} having a narrow FWHM (7±2 cm^{-1}). However, no diamond grains in the inclusion studied showed as narrow FWHM as reported by HEYMANN (1989) (Fig. 2b). This is probably caused by sample heterogeneity. Crystallinity of diamond may be different in individual inclusions in Canyon Diablo, because the degree and duration of shock pressure depend on the location of Canyon Diablo. Further Raman measurements will be needed for different inclusions.

The SEM/EDS/WDS study of typical diamond grains in Canyon Diablo confirmed that the major element is carbon, although further study is needed for the detection of minor elements. Some diamond grains showed weak fluorescence under electron beam irradiation.

The FWHM and wavenumber position of a Raman peak are dependent on some factors such as the crystallite size, lattice stress, crystal-structural disorder, the presence of impurities, and sample temperature (*e.g.*, MIYAMOTO *et al.*, 1993). It has been re-

ported that both the FWHM and wavenumber position of a Raman peak vary with the crystallite size (*e.g.*, IQBAL *et al.*, 1981; YOSHIKAWA *et al.*, 1993). For example, the Raman peak of diamond powders was found to become broader, weaker, and more asymmetric with decreasing particle size (YOSHIKAWA *et al.*, 1993). The calculations based on the phonon confinement model (*e.g.*, RICHTER *et al.*, 1981) also predict that the wavenumber position shifts toward a smaller wavenumber (downshift) and the FWHM becomes wider with decreasing particle size. The calculated Raman spectrum of diamond of about 5 nm in size shows a broad peak with the downshift of 13 cm^{-1} and FWHM of about 38 cm^{-1} (YOSHIKAWA *et al.*, 1993). Similar downshift and broadening due to small crystallite are observed for Si (IQBAL *et al.*, 1981). The threshold of the particle size for this effect is apparently in the range of 10–100 nm, although it varies with different materials (W. B. WHITE, personal communication, 1997).

There is, however, no clear correlation between the FWHM and wavenumber position of the Raman peak of Canyon Diablo diamonds (Fig. 3a). A similar result was obtained for shock-produced diamonds (Fig. 4a) (MIYAMOTO *et al.*, 1993). If the downshift and broadening are caused by the small crystallite size, the downshift should show a positive correlation with the broadening. In addition, no clear asymmetry of the Raman peak of Canyon Diablo diamond was observed (Fig. 1). These results imply that the changes in the FWHM and wavenumber position found in Canyon Diablo diamond cannot solely depend on the crystallite size.

The shift of a Raman peak caused by lattice stress can go to both higher and lower wavenumbers depending of whether the sample is under tension or under compression. This is well documented in KNIGHT and WHITE (1989).

Crystal-structure disorder usually produces a line broadening rather than the peak shift, although "disorder" is one of the glib terms which is rarely defined precisely in terms of the defect structure of the "disordered" crystal (W. B. WHITE, personal communication, 1997).

The downshift of the Raman peak of Canyon Diablo diamond may be due to the presence of lonsdaleite (hexagonal diamond) (*e.g.*, KNIGHT and WHITE, 1989; MIYAMOTO *et al.*, 1993), because it has been reported that Canyon Diablo diamond and shock-produced diamond contain lonsdaleite by X-ray powder diffraction study (*e.g.*, FRONDEL and MARVIN, 1967; HANNEMAN *et al.*, 1967; BUNDY and KASPER, 1967). In fact, KNIGHT *et al.* (1991) reported that the original lonsdaleite was mixed with a lot of graphitic material, while one grain gave a sharp Raman band at 1318 cm^{-1}.

Nitrogen- or boron-doped diamonds show the peak shift of no more than 1–2 cm^{-1} (ANDREYEV *et al.*, 1992).

The downshift and broadening of a Raman peak are also caused by elevating sample temperature under a laser beam. Although diamond in Canyon Diablo is embedded in graphitic materials and is not an isolated grain, a rise in sample temperature is unavoidable. ANDREYEV *et al.* (1992) and ZHAO *et al.* (1997) reported that the observed downshifts of 2–10 cm^{-1} for diamond powders were caused by heating from 200 to 500°C by a laser beam. Although the Raman spectra of several diamonds in Canyon Diablo were measured by reducing the laser power to 1.5 mW, no significant peak shift was detected. Asymmetry of a Raman peak due to heating as was reported by ANDREYEV *et al.* (1992)

could not be found (Fig. 1).

The FWHM of the Raman peak of diamonds in the ALHA77257, Yamato (Y-)-790981, and Y-791538 ureilites is significantly narrower than that of diamonds in this inclusion of Canyon Diablo (Fig. 3a) (MIYAMOTO *et al.*, 1988, 1993). For example, Fig. 4b shows the ranges of both the wavenumber position and FWHM of the Raman peak of the Y-790981 ureilite (MIYAMOTO *et al.*, 1993). Although the range of the FWHM of ureilite diamonds is closer to that of CVD diamonds than to that of shock-produced diamonds (MIYAMOTO *et al.*, 1993), the CVD origin of ureilite diamond cannot be made solely by the Raman data. Coincidence of the FWHM of the Raman peak does not necessarily mean coincidence of their occurrence (HEYMANN, 1989) because the FWHM of the Raman peak depends on many complex factors as was discussed. The CVD origin of ureilite diamond should be further explored.

Acknowledgments

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