In situ observation, X-ray diffraction and Raman analyses of carbon minerals in ureilites: Origin and formation mechanisms of diamond in ureilites

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Carbon minerals in sixteen monomict ureilites which are variable in shock features in olivine were observed in situ by optical microscopy, scanning electron microscopy, X-ray powder diffraction, and Raman analyses. Euhedral blade-like shaped or amoeboid shaped graphite crystals occur in the very low-shock ureilites, not associated with diamond. In the low, medium, and high-shock ureilites, diamond occurs together with graphite. X-ray diffraction and Raman analyses reveal that crystallinity of diamond is relatively well in the low-shock ureilites, although it varies in a wide range in the high-shock ureilites. Diamond formation in the low-shock ureilites occurred as a result of solid-state catalytic transformation of graphite at a pressure lower than 10 GPa, with metallic iron as the catalyst, while diamond in the high-shock ureilites formed by spontaneous transformation of graphite together with the catalytic transformation at a pressure higher than 12 GPa. The relative crystal-axes orientations between graphite (Gr) and diamond (Di) determined by EBSD analyses in the low-shock Y-8448 ureilite is the same as that observed for graphite and diamond in a carbon grain from the high-shock Goalpara ureilite. The metallic iron catalyst promoted the sliding and puckering of the hexagonal carbon planes of graphite in the solid-state transformation processes of graphite to diamond after intercalating into its interplanar spaces. It is shown that noble gas systematics in ureilites can be matched with the shock formation origin of diamond in ureilites.

Keywords: Ureilite, Graphite, Diamond, Origin, Formation mechanism, Tetrahedral amorphous carbon

INTRODUCTION

The ureilites are a group of achondrites, mainly composed of coarse-grained olivine and pyroxene. Ureilites are unique, because they contain relatively large amounts of carbon occurring as diamond, lonsdaleite, or graphite (Kunz, 1888; Urey et al., 1957; Vdovik, 1970). Lippschutz (1964) observed that diamond in the Goalpara and Novo Urei ureilites shows a pronounced crystallographic orientation. This observation suggests that diamond in ureilites formed under conditions of anisotropic pressure, leading to the development of a model that diamond formed by shock conversion of graphite during the breakup of a ureilite parent body (UPB).

Another hypothesis proposes that ureilite diamond might be a disequilibrium condensate formed directly from a low-pressure vapor phase in the solar nebula by chemical vapor deposition (CVD) (Arrhenius and Alfvén, 1971). Fukunaga et al. (1987) showed that diamond in ureilites is one of the noble gas carriers, while graphite is gas-free. As gas-rich diamond never forms from gas-free graphite, their results support the CVD origin of diamond. Matsuda et al. (1991) showed that vapor-growth diamond synthesized by using microwaves traps large amounts of noble gases although shock-produced diamond traps much less noble gases. Matsuda et al. (1995) also showed that considerable amounts of noble gases are trapped in the shock-produced diamond when starting material is sealed inside the container (closed system experiment), but are not trapped when employing vented containers (open system experiment). Matsuda et al. (1995) referred to the results of open system experiment and suggested that the vapor-growth model is better.
than the shock model as the origin of ureilite diamond.

Miyamoto et al. (1988) measured Raman spectra of ureilite diamond and showed that the FWHM (full width at half maximum) of the Raman line at 1330 cm$^{-1}$ from diamond in ALH-77257 ureilite is about 10 cm$^{-1}$ which is narrower than those of artificially shock-produced diamonds (>20 cm$^{-1}$) but within the range of CVD diamond. The result suggests the CVD origin of ureilite diamond. Heymann (1989), however, showed that Raman line at 1332 cm$^{-1}$ of shock-produced diamond in Canyon Diablo iron meteorite has an FWHM value of 7 cm$^{-1}$, which is in the range of CVD diamond.

Nakamuta and Toh (2013) directly observed a carbon grain from the high-shock Goalpara ureilite by high-resolution transmission electron microscopy (HR-TEM) and showed that diamond and lonsdaleite have properties similar to those synthesized by explosive shock experiments (DeCarli and Jamieson, 1961; Miyamoto et al., 1993) and formed by spontaneous transformation of graphite. Graphite, diamond, and lonsdaleite in the carbon grain observed by TEM are a few tens of nm in size and exist with a complex mosaic texture. Diamond in NWA 4742 polymict ureilite is also a few tens nm in size similar to that in the high-shock ureilite (Le Guillou et al., 2010).

In contrast to diamond in the high-shock ureilites, diamond in the low-shock ureilites shows a sharp Raman line of diamond at 1332 cm$^{-1}$ (Miyamoto et al., 1988; Hezel et al., 2008) and has a relatively large crystal size (Nakamuta and Aoki, 2000; Valter et al., 2003; Hezel et al., 2008; Miao et al., 2008). Hezel et al. (2008) suggested that the relatively sharp Raman line of diamond in ureilites may be explained by prolonged shock duration during an impact compared to shock experiments, i.e., the degree of ordering in the diamond lattice might increase over time towards the well-ordered lattice of diamond.

Bischoff et al. (1999) found euhedral graphite crystals in eleven ureilites. They determined the shock degrees of ureilites by shock features in olivine and show that presence or absence of diamond in ureilites is related to the shock pressure recorded by olivine. They showed that low-shock ureilites do not contain diamond. These results suggest that it is important to investigate the properties of carbon minerals in relation to the shock pressure recorded by olivine. However, such investigations have not been done until now.

To date, the properties of diamond, i.e., crystallinities and/or crystallite sizes, in relation to conditions and mechanisms of diamond formation are not well known and controversial. In this study, carbon minerals in sixteen monomict ureilites which are variable in shock features in olivine were observed in situ by optical microscopy, scanning electron microscopy (SEM), X-ray powder diffraction (XRPD) and Raman analyses. The relative crystal-axes orientations between graphite and diamond in a carbon grain from the low-shock Y-8448 were also determined from electron backscattered diffraction (EBSD) patterns of diamond and graphite crystals. Based on these results, the origin and formation mechanisms of diamond in ureilites are discussed.

### MATERIALS AND EXPERIMENTAL METHODS

Table 1 shows the list of ureilites investigated in this study. Carbon grains for X-ray diffraction analysis, each a few hundred microns in size, were selected from disaggregated samples of ureilites listed in Table 1 at the National Institute of Polar Research (NIPR), Tokyo, Japan. Each grain was mounted on a glass fiber (diameter: 10 µm). An XRPD pattern was obtained using a 114-mm-diameter Gandolfi camera (Gandolfi, 1967). The X-ray source was a rotating anode X-ray generator, equipped with a Cr-anode, a 0.2 × 2.0 mm fine-filament, and a V-filter. The XRPD pattern was recorded in two-dimensions (2-D) on an imaging plate (IP) (width: 35 mm; length: 350 mm), and the intensity data on the IP were read using a Fuji-film BAS-2500 IP-scanner (pixel size: 50 × 50 µm). The intensity of the diffracted X-rays for each Bragg angle was obtained at intervals of 0.025° (2θ) by averaging along the Laue cone, over 300 pixels of the central part of the IP that had a width of 560 pixels.

Polished thin sections (PTSs) of monomict ureilites from Antarctica were loaned to our research group by

| Meteorite | X-ray Analysis | Raman analysis | Diamond | Shock level |
|-----------|----------------|----------------|----------|-------------|
| ALH 78019 | 10              | -              | -        | Very low    |
| Y-82100   | 6               | -              | -        | Very low    |
| Y-8448    | 18              | 24             | 38       | Low         |
| ALH 77257 | 9               | 28             | 31       | Low         |
| Y-74123   | 16              | 36             | 58       | Low         |
| ALH 78262 | 6               | -              | -        | Low         |
| Asuka-87031 | -             | 30             | 52       | Low         |
| Y-791839  | -               | 11             | 46       | Low         |
| Kenna     | -               | 39             | 41       | Low         |
| Asuka-881931 | 12             | 27             | 38       | Medium      |
| MET 78008 | 14              | 56             | 21       | Medium      |
| Y-74659   | 6               | 113            | 40       | Medium      |
| Y-74130   | 18              | 105            | 37       | High        |
| Goalpara  | 19              | 44             | 55       | High        |
| Y-74154   | -               | 60             | 47       | High        |
| Y-792663  | -               | 68             | 25       | High        |

* The number of analyzed grains in the X-ray diffraction analysis.
* The number of analyzed points of graphite in the Raman analysis.
* The number of analyzed points of diamond in the Raman analysis.
NIPR. PTSs of Kenna and Goalpara ureilites were prepared in our laboratory. The shock level of each ureilite was determined by the observation of shock textures of olivine in transmitted light based on the criteria proposed for ordinary chondrites (Stöfler et al., 1991). The modes of occurrence of carbon minerals in the PTSs were observed with reflected light through an optical microscope, and with a SEM.

SEM observations of carbon minerals in PTSs were performed at the Faculty of Science, Kyushu University, using a JEOL JSM-7001F (accelerating voltage: 15 kV; sample current: 5 nA; beam spot size: 100 nm) after C-coating for discharge. For EBSD analysis, a carbon grain selected from a disaggregated sample of Y–8448 was put on a C-coated glass slide, 5 × 5 mm in size, and analyzed by SEM without coating which is commonly done for discharge. EBSD patterns of graphite and diamond were obtained in smooth areas of crystals in the carbon grain with tilt angle of 70° and working distance of 15 mm and analyzed using the Oxford Instruments Channel 5 software.

Micro Raman spectra of the carbon grains in the PTSs were recorded with a Jobin Yvon T64000 triple-grating spectrometer, equipped with confocal optics and a nitrogen-cooled charged-coupled device (CCD) detector. The resolution of the spectrometer is less than one cm\(^{-1}\). A microscope was used to focus the 514.5 nm Ar excitation laser beam to a 1 µm spot for accumulation over a 120 s time period. The laser power on the sample surface was 2 mW. Micro Raman spectra of the grain from a disaggregated sample of Y–8448 were recorded with a JEOL JRS SYSTEM 2000 Raman Spectrometer (1800 lines/mm grating). A microscope was used to focus the 514.5 nm Ar excitation laser beam to a 2 µm spot for accumulation over a 5 s time period with the 1 mW laser power on the sample surface to avoid sample damage.

Integral breadth and position of an X-ray line and FWHM and position of a Raman line were precisely determined by applying a profile-fitting technique. The integral breadth (β) is a measure of X-ray line broadening of an X-ray line as given by SI/\(\text{SI}+\text{SI}'\), where S and I are the area and the height of an X-ray line, respectively. The profile-fitting was carried out with a pseudo-Voigt type profile-shape function (Hindeleh and Johnson, 1978; Young and Wiles, 1982; Nakamuta and Aoki, 2000).

**RESULTS**

**Determination of the shock level of each ureilite**

Stöfler et al. (1991) proposed six stages of shock (S1 to S6), based on shock effects in olivine and plagioclase as recognized by thin section microscopy. The characteristic shock effects of each shock stage are: S1—sharp optical extinction; S2—undulatory extinction of olivine; S3—planar fractures in olivine; S4—mosaicism in olivine; S5—iso-tropization of plagioclase and planar deformation features in olivine; and S6—recrystallization of olivine.

In this study, shock stages of ureilites are determined based on shock effects in olivine, as very weak, weak, moderate, and high levels, according to the criteria proposed by Stöfler et al. (1991). Olivine in very weak, weak, moderate, and high levels shows sharp extinction, undulatory extinction, planar fractures, and mosaicism, respectively. The very low, low, medium, and high levels of shock, then, correspond to S1–S2, S2, S3, and S4 shock stages of ordinary chondrites of Stöfler et al. (1991), respectively. The representative optical microscope images are shown in Figure 1 and shock level of each ureilite is shown in Table 1.

**X-ray diffraction analyses of carbon grains selected from disaggregated samples of ureilites**

Platy carbon grains, a few hundred microns in width and a few tens of microns in thickness, were selected from disaggregated samples of ureilites. Representative XRPD patterns of carbon grains are shown in Figure 2. All grains from ALH 78019 and Y–82100 and some grains from Y–8448 are composed only of graphite, of which a representative XRPD pattern is shown in Figure 2a. The 100 and 102 reflections in the pattern reveal that graphite has 2H-stacking. Carbon grains from low, medium, and high-shock ureilites are a mixture of graphite and diamond, with varying amounts of each (Figs. 2b–2d). Kamacite is observed along with diamond, although kamacite is not observed in carbon grains from the very low-shock ureilites. Basal spacing of compressed graphite is in the range between 3.2 and 3.4 Å and tends to be smaller in the high-shock ureilites than in the low and medium-shock ureilites. Lonsdaleite is observed only in the high-shock ureilites.

Figure 3a shows the plot of integral breadths of 004 and 110 reflections of graphite from the very low–shock ALH 78019 and Y–82100 ureilites and the low–shock Y–8448 ureilite. Carbon atoms in graphite form hexagonal rings, which extend two-dimensionally in sheets, using the sp\(^2\) C–C bond. The 004 and 110 reflections occur from lattice planes parallel and perpendicular to the hexagonal rings, respectively. The reflections from graphite associated with diamond are much broader equally in both [004] and [110] directions than graphite which is not associated with diamond (Fig. 3a). X-ray line broadening usually occurs because of small particle size of a crystal or the strain in a crystal (Wilson, 1962). Nakamuta and Aoki

\[ \text{Area} = \frac{\text{Height} \times \text{Width}}{2} \]
(2000) shows that the broadening of X-ray lines of graphite in the very low and low-shock ureilites is mainly due to the strain in the crystal based on the Williamson-Hall plot, by which X-ray line broadening can be resolved into those due to small particle size of a crystal and the strain in a crystal as an intercept and a slope of a regression line, respectively (Williamson and Hall, 1953).

Figure 3b shows the plot of integral breadths of diamond 220 and graphite 110 reflections. The integral breadths of X-ray lines of graphite and diamond vary in a wide range. The integral breadths of graphite in low, medium, and high-shock ureilites are in the ranges between 0.6–2.0°, 1.2–2.4°, and 1.2–2.4°, respectively. Those in the medium and high-shock ureilites are in a similar range and a little larger than the integral breadths of graphite in the low-shock ureilites.

The integral breadths of diamond in low, medium, and high-shock ureilites are in the ranges between 0.4–1.2°, 0.8–2.2°, and 1.6–3.4°, respectively. It is noticeable that diamond in the low-shock ureilites shows much sharper reflections than in the high-shock ureilites. Diamond in medium-shock ureilites is in the range intermediate between low and high-shock ureilites. The Williamson-Hall plot reveals that particle size of diamond in the low-shock ureilites, i.e., Y-791538, Kenna, and ALH 77257, is larger than a few micrometers and that the line broadening is mainly due to the strain in a crystal (Nakamuta and Aoki, 2000). In the high-shock Goalpara ureilite, a few nm sized diamond was directly observed to exist as a complex mixture of diamond, graphite and lonsdaleite in a carbon grain by TEM (Nakamuta and Toh, 2013). The observation suggests that the X-ray line broad-
ening of diamond in the high–shock ureilites is due to both small particle size of crystal and the strain in a crystal.

Modes of occurrence of graphite and diamond in PTSs

Figure 4 shows reflected light views of PTSs containing carbon minerals and Figure 5 shows enlarged images of carbon grains observed by SEM.

In the very low–shock ureilites, graphite crystals with tan–gray color and metallic luster occur (Figs. 4a and 4b). XRPD analyses reveal that these graphite crystals are well–crystallized as those from terrestrial igneous or high–grade metamorphic rocks. The blade–like shaped graphite in ALH 78019 occurs at grain boundaries or inside of olivine crystals. Like this occurrence suggests that the growth of the blade–like shaped graphite was concurrent with the growth of olivine crystals. In contrast to the blade–like shaped graphite, amoeboid shaped graphite in Y–82100 encloses rounded olivine crystals, suggesting that graphite crystallized after olivine. Averaged mg#, i.e., Mg/(Mg + Fe) × 100, of olivine cores of ALH 78019 and Y–82100 are 77.8 and 85.5, respectively. The mg# of olivine core is an important parameter to know the petrogenesis of ureilites (Goodrich et al., 2004). Then, the morphology of graphite could be related to petrogenetic conditions of each ureilite, although further investigations are necessary to verify the relations.

In the low–shock ureilites (Figs. 4c–4f), carbon grains with similar shapes to graphite in the very low–shock ureilites occur. Carbon grains in Y–8448 show blade–like shapes (Fig. 4c) and those in ALH 77257 (mg# 85.5) show amoeboid shapes (Fig. 4f). In low–magnification images, carbon grains are black in color and do not show metallic luster in contrast to graphite in the very low–shock ureilites. SEM images (Figs. 5a–5d) show that the black–colored parts of carbon grains by an optical microscope contain many fine–grained particles of a few micrometer in size, which are in high relief maybe due to difficulty in polishing. Each
Figure 4. Reflected light views of carbon minerals in PTSs. (a) Very low-shock ALH 78019. (b) Very low-shock Y–82100. (c) and (d) Low-shock Y–8448. (e) and (f) Low-shock ALH 77257. (g) and (h) High-shock Goalpara ureilite. Gr, Di and Ol show graphite, diamond, and olivine, respectively. S1, S2, and S3 rectangles in (d), (f), and (h) images show the areas observed by SEM as shown in Figure 5. Color version of Figure 4 is available online from http://doi.org/10.2465/jmps.150906.
Figure 5. SEM images of carbon minerals. (a) and (b) Y–8448. (c) and (d) ALH 77257. (e) and (f) Goalpara ureilite. (g) and (h) X-ray mappings of Fe and Ni of the same area as (f), respectively. Rectangles in (a) and (c) show the areas of enlarged images shown in (b) and (d), respectively. Gr and Di show graphite and diamond, respectively. (R1)-(R7) Positions at which Raman spectra shown in Figure 6 were obtained.
particle in high relief appears to be a stack of platy crystals (Figs. 5b and 5d). These fine-grained particles were identified as diamond by Raman analyses as described in the next section. Diamond in the diamond polishing agent used in the final polishing shows an angular shape different from that observed here. The shapes and the mode of occurrence of diamond in the PTSs exclude that we accidentally observed polishing diamond.

Carbon grains in the high-shock Goalpara ureilite occur at grain boundaries of olivine (Fig. 4g). In the carbon grain, two types of particles in high relief are observed, i.e., a relatively large particle, a few tens μm in size, made up of sheaves of thin crystals (Fig. 5e) and a small particle, a few μm in size, made up of platy crystals (Fig. 5f). The particles in high relief were identified as diamond by Raman analyses, as described in the next section. The small diamond particles shown in Figure 5f are similar in shape to those observed in the low-shock ureilites (Figs. 5b and 5d). The occurrence of relatively large particles as shown in Figure 5e is unique to high-shock ureilites. These two types of diamond are observed in the same grain (Fig. 4h) and it is noticeable that X-ray mappings of Fe and Ni (Figs. 5g and 5h) reveal that kamacite vein exists near the small particles but such a kamacite vein is not evident near the relatively large particles.

**Raman analyses**

Raman spectra were obtained at positions indicated by R1–R7 in Figure 5. The spectra are shown in Figure 6. Raman spectra of particles in high relief in carbon grains (positions R1, R3, R5, and R6 in Figs. 5a, 5d, 5e, and 5f, respectively) show a Raman line at 1332–1333 cm$^{-1}$, which corresponds to a phonon band of diamond. It is noticeable that the Raman lines of diamond obtained from the small-grained particles (R1, R3, and R6) are much sharper than that obtained from the relatively large sheaves (R5).

Raman spectra obtained from surrounding areas of diamond (positions R2, R4, and R7 in Figs. 5a, 5d, and 5f, respectively) show a relatively sharp line at 1581–1583 cm$^{-1}$, which corresponds to the Raman active E$_{2g}$ mode of graphite (the G-band). The lines at 1354–1357 and 1622 cm$^{-1}$ are also observed.

Raman spectra of diamond and graphite were obtained randomly in PTSs of ureilites. The positions and FWHMs of Raman lines of diamond and graphite were precisely determined by applying a profile-fitting technique. The results are summarized in Tables 2 and 3 for diamond and graphite, respectively. All analyzed lines are plotted on the diagrams showing the position and FWHM of a line in Figure 7.
Peak positions of diamond do not differ among the ureilites studied and locate at 1332 (±2) cm\(^{-1}\), being a position of normal diamond, except that maximum values of the high-shock Y-74130, Y-74154, and Y-792663 ureilites are a little larger than the others (Table 2 and Fig. 7e). The minimum FWHM values of diamond also do not differ among the ureilites studied and are near to 3–4 cm\(^{-1}\) of jewelry diamond which is measured together with diamonds in ureilites as reference. However, maximum FWHM values of diamond differ among the ureilites studied and those for low, medium, and high-shock ureilites are in the ranges between 10–17, 15–33, and 39–48 cm\(^{-1}\), respectively. As the minimum FWHM values do not differ between the low and high-shock ureilites but maximum FWHM values of the high-shock ureilites are larger than those of the low-shock ureilites, the FWHMs of diamond from the high-shock ureilites are then in a wider range than those of the low-shock ureilites (Table 2 and Fig. 7). The medium-shock ureilites are intermediate between the low and high-shock ureilites.

The minimum peak positions of graphite do not differ among the ureilites studied and locate at 1581 (±2) cm\(^{-1}\), being a position of well-crystallized graphite at an ambient pressure (Hanfland et al., 1989). The minimum FWHM values of graphite also do not differ among the ureilites studied and are near to that of well-crystallized graphite. The maximum peak positions of graphite are in the ranges between 1585–1592, 1591–1597, and 1598–1607 cm\(^{-1}\) for the low, medium, and high-shock ureilites, respectively. The maximum FWHM values of graphite also differ among ureilites and those for the low, medium and high–shock ureilites are in the ranges between 35–63, 56–63, and 63–104 cm\(^{-1}\), respectively. The peak positions and FWHMs of graphite vary with a positive correlation (Figs. 7b, 7d, and 7f). It is then clear that maximum peak positions and FWHMs of graphite in the high-shock ureilites are larger than those of graphite in the low–shock ureilites. The medium-shock ureilites are intermediate between low and high-shock ureilites.
Observation of a carbon grain selected from a disaggregated Y–8448 sample

The precise crystallographic relationship between diamond and graphite in a carbon grain is difficult to determine with a PTS because of polishing effects. Crystallographic relationship between diamond and graphite in the high-shock Goalpara ureilite was already determined by
TEM (Nakamuta and Toh, 2013). A carbon grain was then selected from a disaggregated sample of the low-shock Y-8448 and observed by SEM together with Raman analyses. The crystallographic orientations of diamond and graphite in the grain were determined by electron-backscattered diffraction (EBSD) analyses.

Figure 8 shows SEM images of the surface of a platy carbon grain. The grain shows an XRPD pattern similar to that shown in Figure 2b and is composed of graphite and diamond with a small amount of kamacite. The areas of diamond and graphite on the surface of the grain were determined by Raman analyses. The Raman spectra obtained at positions R8, R9, and R10 in Figure 8a are shown in Figure 9. Raman spectrum of graphite (R8 in Fig. 9) shows a line at 1582 cm\(^{-1}\) which is assigned to the G-band of graphite but the lines at 1354 and 1622 cm\(^{-1}\), being observed in the spectrum of graphite in the PTS of Y-8448 (R2 in Fig. 6), are not observed in this spectrum. Mostefaoui et al. (2000) observed that unpolished graphite from the Canyon Diablo iron meteorite showed the line only at 1580 cm\(^{-1}\), although the Raman spectrum obtained on polished graphite revealed the presence of a much more intense peak at 1355 cm\(^{-1}\) and an additional one at 1620 cm\(^{-1}\). The lines near 1355 and 1622 cm\(^{-1}\) have been observed only for disordered graphite having a small crystallite size (Tuinstra and Koenig, 1970). As the surface of graphite is roughed by polishing and covered by small and disordered crystals, the lines at 1354 and 1622 cm\(^{-1}\) observed in the PTS of Y-8448 were then caused by polishing. Raman spectrum of diamond (R9 in Fig. 9) shows a line of diamond at 1332 cm\(^{-1}\) similar to that observed in the PTS of Y-8448 (R1 in Fig. 6).

In Figure 8a, aggregates of diamond crystals occur in high relief in graphite. In some regions of the grain (Region A of the image in Fig. 8a), individual diamond crys-
tals show triangular faces parallel to the surface of the grain. Figure 8b shows an enlarged image of the diamond crystals in Region A; the form of each diamond crystal appears to be a triangular prism, rather than an octahedron (a characteristic diamond form). Additionally, it is noticeable that the triangular faces of the diamond crystals are arranged in the same direction on the surface of the grain.

Raman spectrum obtained from the triangular pit area (position R10 in Fig. 8b) shows a very broad Raman line at 1580 cm\(^{-1}\), in addition to a line at 1332 cm\(^{-1}\) assigned to diamond (R10 in Fig. 9). The line at 1580 cm\(^{-1}\) may be assigned to the G-band of graphite; however, this line is anomalously broad, suggesting that the crystallites are very disordered and small in size (Robertson, 2002). Disordered and small crystallites of graphite usually exhibit a strong D-band around 1350 cm\(^{-1}\), similar to that for glassy carbon (McCulloch et al., 1994). However, R10 spectrum shown in Figure 9 does not show a D-band. Like this pattern has been reported as tetrahedral amorphous carbon (ta-C) in the process of C-deposition on a substrate (Ferrari and Robertson, 2000; Robertson, 2002), whereas it has not been observed in nature.

EBSD patterns of crystals were obtained from three regions of the carbon grain of Y–8448, as shown in Figure 8a (denoted by A, B, and C); the analyzed crystals are marked with ‘+’. Figure 10 shows representative EBSD patterns and their corresponding indices. The crystals from Regions A and B exhibited a pattern similar to that shown in Figure 10a which is assigned to diamond. The crystals in Region C exhibited a pattern similar to that shown in Figure 10c which is assigned to graphite. Clear EBSD patterns were obtained from all analyzed crystals by using an electron beam of which spot size is 100 nm on a sample. The coherent crystallite sizes of diamond and graphite are, then, thought to be larger than 100 nm.

Stereographic projections of the crystal faces, determined by EBSD, are shown in Figure 11a and crystal forms showing relative crystallographic orientations of crystals from each region are also shown in Figures 11b–11d. The equator of the stereogram is parallel with respect to the surface of the carbon grain; the directions on the equator coincide with those shown in Figure 8a. The stereogram shows that the [111] direction of the diamond crystals in Regions A and B and the [001] direction of the graphite crystals in Region C are parallel to each other and perpendicular to the surface of the carbon grain. As shown in Figures 11c and 11d, the diamond crystals in Regions A and B are related by the spinel twin law. The (100) and (001) planes of the graphite crystal and (111) and (111) planes of the diamond crystal are plotted on the same great circles of the stereogram. These results reveal the following relative crystal–axes orientation between graphite (Gr) and diamond (Di):

\[(001)_{Gr} // [111]_{Di} \text{ and } [210]_{Gr} // [\bar{2}11]_{Di} // [2\bar{1}1]_{Di}.\]

This relative orientation between the graphite and diamond structures in the carbon grain is the same as that
observed in the carbon grain of the high-shock Goalpara ureilite (Nakamuta and Toh, 2013).

**DISCUSSION**

**Origin of diamond**

Two hypotheses, i.e., the shock model (Lipschutz, 1964) and the CVD model (Fukunaga et al., 1987), have been proposed and the origins of diamond in ureilites are still unclear. The modes of occurrence and X-ray diffraction and Raman properties of diamond and graphite revealed in this study are intimately related to shock levels recorded on olivine (Figs. 2, 3, and 7) and suggest that diamond in ureilites formed from graphite by shock.

It is known that noble gas contents in diamond, graphite, and silicates in ureilites are difficult to be interpreted by the shock model (Matsuda et al., 1995; Nagashima et al., 2012). Diamond in ureilites traps abundant planetary type noble gases while graphite and silicates are gas-free (Fukunaga et al., 1987; Göbel et al., 1978). It has been argued that gas-rich diamond has never been formed from gas-free graphite in the shock processes (Fukunaga et al., 1987; Le Guillou et al., 2010). However, noble gas contents of diamond and graphite in ureilites can also be interpreted by the shock model as discussed below.

Matsuda et al. (1995) showed in their shock experiments that considerable amounts of noble gases are trapped in the shock-produced diamond when starting material is sealed inside the container (closed system experiment) while the amounts of noble gases in the shocked graphite are very small compared to those in shock-produced diamond. The difference of the amounts of noble gases between diamond and graphite is thought to be due to the difference of retentivity of noble gases between them (Matsuda et al., 1995). Matsuda et al. (1995) also reveals that the elemental abundance patterns of noble gases are similar to that of air in the closed system experiments, suggesting that noble gases in the pore spaces within the starting material are driven into and/or dissolved in the diamond without significant fractionation.

Mineralogical studies of ureilites (Takeda, 1989; Weber et al., 2003; Goodrich et al., 2004; Herrin et al., 2010; Mikouchi et al., 2010) show that ureilites undergo a two-stage cooling history: slow cooling at temperatures above 1200–1250 °C, followed by very rapid cooling at rates possibly as high as 20 °C h⁻¹. The second stage is thought to be caused by impact excavation, possibly involving extensive parent body disruption (Goodrich et al., 2004). Goodrich et al. (2004) reviewed the petrologic studies of ureilites and showed a picture of a UPB as follows: 1) The monomict ureilites are ultramafic rocks, which represent the mantle of a partially melted (~ 25–30%), carbon-rich asteroid ≥125 km in radius. 2) Melt extraction on the UPB was a rapid, fractional process in which trace element and oxygen isotopic equilibrium was not achieved. 3) Our sample is limited to depths equivalent to 15–100 bars pressure because of the coexistence of graphite and olivine with mg# between 92 and 76.

Pre-magmatic silicates recrystallized at temperatures above 1200–1250 °C in the UPB (Goodrich et al., 2004). The XRPD pattern of graphite in the very low–shock ureilites (Fig. 2a) shows sharp 100 and 102 reflections which reveal that graphite has 2H–stacking. The XRPD pattern resembles the pattern of well-crystallized graphite from terrestrial igneous or high-grade metamorphic rocks and suggests igneous or high-grade metamorphic origin of graphite in ureilites. It is then reasonable to think that carbon associated with silicates crystallized as graphite during the first stage of UPB differentiation as observed in the very low–shock ureilites (Figs. 4a and 4b). Noble gases contained and trapped in pre-magmatic minerals may have moved to grain boundaries and/or graphite interlayers under 15–100 bars pressure. Silicates have be-
come gas-free due to recrystallization. At the second stage, graphite has been shocked and a part of it was transformed into diamond and/or lonsdaleite. As our samples of ureilites existed in the depths equivalent to 15–100 bars pressure when they were shocked (Goodrich et al., 2004), it is reasonable to think that the shock conversion of graphite to diamond occurred in a closed system like the sealed experiments by Matsuda et al. (1995). Referred to the results of the sealed experiments by Matsuda et al. (1995), it is natural that diamond in ureilites traps abundant noble gases without fractionation while graphite is gas-poor. Therefore, noble gas contents in diamond, graphite, and silicates are not a serious problem for the shock model but agree well with a picture of the UPB differentiation and a two-stage cooling history of ureilites summarized by Goodrich et al. (2004).

**Tetrahedral amorphous carbon in ureilites**

Raman spectrum obtained at the triangular pit of the Y-8448 ureilite (position R10 in Fig. 8b) shows a very broad Raman line at 1580 cm⁻¹ which is not associated with a D-band at 1350 cm⁻¹ (R10 in Fig. 9). C-material exhibiting such a pattern was reported as tetrahedral amorphous carbon (ta-C) (Ferrari and Robertson, 2001; Robertson, 2002).

The structure of ta-C is determined to be amorphous and mainly composed of sp³ sites with a small amount of fragmented sp² site (Berger et al., 1988; Gaskell et al., 1991). The sp² site shows a 50–250 times larger Raman cross-section than the sp³ site; thus, it dominates the Raman spectrum. The G-mode of graphite at 1580 cm⁻¹ has E₂g symmetry and is attributed to the in-plane bond-stretching motion of C = C pairs. This mode does not require the presence of sixfold rings, and it occurs at all sp³ sites of aromatic and olefinic molecules, although the D-line of graphite is a breathing mode of A₁g symmetry and arises only from aromatic rings (Robertson, 2002). As aromatic rings are not formed in ta-C structure (McCulloch et al., 2000), ta-C shows a very broad Raman line only around 1580 cm⁻¹ which corresponds to the G-mode of graphite. McKenzie et al. (1993) baked ta-C films in vacuum for 1 hour up to temperatures of 700 °C and showed that ta-C is a stable material at least up to 700 °C.

Films of ta-C were prepared on various substrates by deposition of a filtered beam of C⁺ ions, having medium energy (20–500 eV) (Lifshitz et al., 1989; McKenzie et al., 1991; Fallon et al., 1993; Robertson, 1993; Ferrari and Robertson, 2000; Ferrari et al., 2002; Robertson, 2005). In Y-8448, ta-C exists mainly in the triangular pit and not on the surface of diamond in high relief (Fig. 8b). These observations are not reconciled with the deposition of C⁺ as the formation mechanism of ta-C in ureilites.

Kelires (1994) performed simulations of diamond-like amorphous carbon, formed by quenching C-liquid under high pressure; they showed that ta-C is also formed by quenching of the C-liquid. These simulations imply that ta-C in Y-8448 may have formed by the melting of carbon when diamond formed by shock, followed by quenching caused by disruption of the UPB. The triangular shape of the pit (Fig. 8b) agrees well with a triangular arrangement of atoms at the surface of the grain, i.e., graphite (001) or diamond (111) as observed by EBSD analyses. The triangular faces of diamond are then thought to be the result of melting of the surrounding area.

Observations by an optical microscope reveal that the grain boundaries between carbon grains and olivine crystals in Y-8448 are clear and the margins of olivine crystals have never been melted (Fig. 4). The results suggest that temperature of the ureilite when diamond formed has never been higher than 1500 °C, above which olivine should melt. The XRPD pattern of Y-8448 (Fig. 2b) reveals that kamacite coexists with diamond in the carbon grain. If metallic iron is present, carbon melts at the eutectic melting temperature of metallic iron and carbon (~ 1350 °C), although the melting temperature of pure graphite exceeds 4000 °C (Bundy, 1989). The temperature of ureilites just before diamond formation is above 1200–1250 °C (Goodrich et al., 2004), then, it is easy to raise temperature by 100 °C by shock and cause eutectic melting of carbon. When the UPB was broken up, rapid cooling to 700 °C, under which ta-C is stable, may also have been possible and made ta-C survive in ureilites.

**P-T conditions of diamond formation in ureilites**

Olivine crystals observed in low, medium, and high-shock ureilites show relatively sharp extinction, planar fractures, and a mosaic texture, respectively. These shock textures of olivine crystals correspond to the S2, S3, and S4 shock stages of ordinary chondrites by Stöffler et al. (1991), and suggest that the low, medium, and high-shock ureilites were shocked at 4–10, 5–20, and 15–35 GPa, respectively (Stöffler et al., 1991).

The maximum peak positions of graphite are in the ranges between 1585–1592, 1591–1597, and 1598–1607 cm⁻¹ for low, medium, and high-shock ureilites, respectively (Table 3 and Fig. 7). The peak position of graphite is known to increase with the increase of compressive stress (Hanfland et al., 1989). Then, the maximum peak position of graphite corresponds to the maximum compressive stress retained in the graphite structure. Based on the results of Hanfland et al. (1989), these stresses are...
calculated as 1.3–2.9, 2.7–4.1, and 4.4–6.6 GPa for the low, medium, and high-shock ureilites, respectively. The pressure estimated from a shock texture of olivine corresponds to peak pressure by shock (Stöfler et al., 1991), although the retainability of compressive stress of graphite as residual strain may be largely due to the texture around graphite crystals. Graphite crystals in the high-shock Goalpara ureilite exist surrounded by hard crystals of diamond and lonsdaleite with a complex mosaic texture (Nakamuta and Toh, 2013) and graphite crystals in the low-shock ureilites occur around the relatively coarse-grained diamond particles (Figs. 4 and 5). Like these differences of textures may be the reason for the difference of residual strains retained in graphite crystals.

The pressure–temperature (P–T) diagram for diamond formation by catalytic and spontaneous transformation of graphite is shown in Figure 12. Well-crystalized diamond forms at pressures higher than 5.5 GPa with metallic iron as a catalyst. Without a catalyst, graphite transforms spontaneously into diamond at pressures exceeding 12 GPa and temperatures exceeding ~ 1000 °C. The solid circles in Figure 12 represent the positions where a mixture of diamond, lonsdaleite, and graphite was observed, and the open circles represent the positions where only diamond was obtained by high-pressure experiments without a catalyst (Bundy and Kasper, 1967; Yoshiasa et al., 2003; Irifune et al., 2004).

The shock textures of olivine crystals in the low-shock ureilites correspond to the S2 shock stage of ordinary chondrites, for which the maximum shock pressure is estimated to have been 5–10 GPa (Stöfler et al., 1991). At these levels, the shock pressure is sufficient to initiate a catalytic transformation of graphite into diamond, but too low to cause spontaneous transformation. Shock experiments reveal that diamond forms at a pressure higher than 30 GPa by shock (Decarli and Jamieson, 1961). The shock pressure estimated for the low-shock ureilites is much lower than this while diamond is thought to have formed by shock.

Shock experiments are usually conducted at ambient temperature, then, extreme pressure is necessary to raise temperature enough to form diamond. The temperature of ureilites, at which the parent body is thought to have been broken apart, is shown in Figure 12 as T_u (Goodrich et al., 2004). The temperature indicated by T_u is near to the eutectic melting temperature and it is possible to raise the temperature of graphite by ~ 100 °C by shock at pressures less than 10 GPa. Then, it is reasonable to think that the pressure and temperature conditions of the low-shock ureilites were in the catalytic transformation region shown in Figure 12 when they were shocked. XRPD patterns of carbon grains reveal that kamacite is observed along with diamond in the low-shock ureilites (Fig. 2). The coexistence of kamacite with diamond confirms that diamond in the low-shock ureilites formed by the catalytic transformation of graphite.

The high-shock ureilites had been shocked at pressures higher than 15–20 GPa, then, the pressure and temperature conditions are enough to cause spontaneous transformation of graphite to diamond. Nakamuta and Toh (2013) showed that a graphite crystal in the Goalpara ureilite had transformed into a mixture of lonsdaleite and diamond, being a characteristic signature of spontaneous transformation. The well-crystalized diamond coexisting with kamacite is also found in the high shocked ureilites (Fig. 5f), suggesting that catalytic transformation of graphite to diamond also occurred together with the spontaneous transformation. Like this assorted mechanisms observed in carbon grains of the high-shock ureilites are the reason why the crystallinity of diamond in the high-shock ureilites varies in a wide range (Figs. 3 and 7).

**Mechanism of catalytic transformation of graphite to diamond in ureilites**

Many experimental studies have suggested that the molten metal of a catalyst works as a solvent of carbon, and that the transformation from graphite to diamond occurs...
across a very thin film of molten metal; i.e., a catalyst-solvent mechanism (Bovenkerk et al., 1959; Bundy et al., 1996). In contrast to the catalyst-solvent model, it has also been suggested that with the help of catalyst metals, diamond forms as if by a collapse of graphite, with no significant net rotation of the hexagonal sheets of carbon atoms (Vereshchagin et al., 1965; Wentorf Jr, 1965). Wentorf Jr and Bovenkerk (1961) also suggested that graphite might absorb enough catalytic metallic iron and nickel from nearby masses containing these elements to catalyze the formation of diamond in graphite. Laminar compounds of graphite with transition metals are also shown to be easily transformed into diamond in the solid state (Kalashnikov et al., 1982; Clarke and Uher, 1984).

EBSD analyses of this study reveal the orientational relationship between graphite and diamond in a carbon grain as $(001)_C$ // $(111)_D$ and $(210)_C$ // $(211)_D$ (Fig. 11). This relative orientation between graphite and diamond structures is the same as that determined for the spontaneous transformation of graphite into diamond (Nakamuta and Toh, 2013). Nakamuta and Toh (2013) showed that transformation of graphite into diamond occurred by chair-type puckering of the hexagonal carbon planes of graphite after sliding of these planes along the [210] direction of the original graphite. As such, it is reasonable to think that the metallic iron catalyst in ureilitic diamond formed by the spontaneous transformation of graphite, and nickel from nearby masses containing these elements to catalyze the formation of diamond in graphite. Laminar compounds of graphite with transition metals are also shown to be easily transformed into diamond in the solid state (Kalashnikov et al., 1982; Clarke and Uher, 1984).

CONCLUSIONS

Euhedral blade-like shaped or amoeboid shaped graphite crystals not associated with diamond occur in the very low-shock ureilitic samples. In the low, medium, and high-shock ureilitic samples, diamond occurs together with graphite. Diamond in the low-shock ureilitic samples occurs as fine-grained particles of a few micrometers in size associated with kamacite. Diamond in the high-shock ureilitic samples occurs in two types of morphology, i.e., a fine-grained particle of a few micrometers in size, similar to those observed in the low-shock ureilitic samples, and a relatively large particle, a few tens micrometer in size, made up of sheaves of thin crystals and being unique to the high-shock ureilitic samples.

X-ray diffraction and Raman analyses reveal that crystallinity of diamond is relatively well in the low-shock ureilitic samples, although it varies in a wide range in the high-shock ureilitic samples. These results indicate that diamond formation in the low-shock ureilitic samples occurred as a result of the solid-state catalytic transformation of graphite, with metallic iron as the catalyst. In the high-shock ureilitic samples, diamond formed by the spontaneous transformation of graphite together with the catalytic transformation. Like this assorted mechanisms are the reason why the crystallinity of diamond in the high-shock ureilitic samples varies in a wide range. Noble gas contents of ureilitic samples are also interpreted by the shock model of closed system.

SEM observations of a carbon grain selected from a disaggregated sample of the Y–8448 ureilitic sample show that some of the diamond crystals exhibit triangular faces surrounded by triangular pits containing tetrahedral amorphous carbon (ta-C). The ta-C in the triangular pits suggests that the pits formed by the melting of carbon, followed by quenching at high pressure.

The relative crystal-axes orientation between graphite (Gr) and diamond (Di) determined by EBSD analyses in the low-shock Y–8448 ureilitic sample is the same as that observed for graphite and diamond in a carbon grain from the high-shock Goalpara ureilitic. The metallic iron catalyst promoted the sliding and puckering of the hexagonal carbon planes of graphite after intercalating into its interplanar spaces.

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SUPPLEMENTARY MATERIALS

Color version of Figures 1 and 4 are available online from http://doi.org/10.2465/jmps.150906.

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