Graphite–3R in a fault fracture zone associated with black jadeitite from Kanayamadani, Itoigawa, central Japan

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Graphite–3R was found at an outcrop in Kanayamadani, central Japan that had green-black jadeitite, altered jadeitite, and fracture zones in serpentine mélangé. The graphite from the three zones was characterized using polarizing microscopy, XRD, Raman spectroscopy, SEM, HRTEM, and stable carbon-isotope mass spectrometry. Graphite in the black jadeitite zone is possibly crystallized simultaneously with prehnite in the stability field of prehnite (P < 0.6 GPa and at T = 150–420 °C). The δ13C of graphite in the black jadeitite zone ranged from −8.570‰ to −7.870‰, suggesting that it does not have an organic origin. The graphite of the black jadeitite zone was possibly formed in CO2–CH4 rich fluid.

XRD, Raman spectroscopy, and HRTEM observations suggested that the altered jadeitite zone had both low and high crystalline graphite. The altered jadeitite zone was located at the outer region of the green-black jadeitite zone and penetrated by many prehnite veins during a later stage. Amorphous carbon and graphite–3R found from the fracture zone may have formed as a result of graphite–2H crushing during fault movement between green-black and altered jadeitite zones. Changes in the crystal structure and detailed mineralogy of graphite can effectively be used to study tectonics and are key to understanding tectonic movement in geological processes.

Keywords: Raman spectroscopy, HRTEM, Graphite–3R, Black jadeitite, Crystallinity

INTRODUCTION

Carbon is the fourth most abundant element in the universe and many varieties of solid carbon exist: The polymorphs of carbon in nature include diamond, graphite, lonsdaleite (Frondel and Marvin, 1967), and graphene (Novoselov et al., 2004). In addition, graphite has two polytypes, 2H (hexagonal graphite) and 3R (rhombohedral graphite). Most graphite in nature is 2H, and only four occurrences of graphite–3R have been reported: Sri Lanka; Spain; Borrowdale, England; and Burugubanda-Tapasikonda, India. All of these 3R graphites were deposited from fluids (Luque et al., 1998; Parthasarathy et al., 2006). Moreover, a relationship between carbon behavior and fault movement has been suggested by vitrinite reflectance analyses (Sakaguchi, 2009), carbon mineral quantity (Oohashi and Shimamoto, 2010), amorphization in grinding (Ozawa and Takizawa, 2007), and shear heating effects studied with Raman spectroscopy (Mori et al., 2011).

We discovered a new outcrop of jadeitite that belongs to the Renge Metamorphic belt (Shibata and Noszawa, 1968; Nishimura, 1998; Tsujimori and Itaya, 1999; Kunugiza et al., 2004; Tsukada et al., 2004), a region well-known for deposits of jadeitite in serpentine mélangé matrices (Kawano, 1939; Ohmori, 1939; Chihara, 1989; Harlow and Sorensen, 2004). The main jadeite localities in the Renge Metamorphic belt include Ohmi, Hashidate, and Kanayamadani (Kawano, 1939; Chihara, 1958). The formation of jadeite in this region has been attributed to various causes, but recent studies have begun to explore the potential hydrothermal effects on jadeite formation (Miyajima et al., 1999, 2001, 2002, 2003; Morishita, 2005). Varieties of jadeitite found in this region are white, blue, lavender, green, and black (Iwao, 1953; Chihara, 1971, 1987, 1989; Oba et al., 1992; Miyajima et al., 1997, 2001, 2004, 2005; Smith and Gendron, 1997).
Black jadeitite in this region is predominantly black in color and contains spheres of carbonaceous materials (CM) with a diameter of ~1 um (Chihara, 1987; Miyajima et al., 2005, Miyajima and Mitsuishi, 2009). This study characterized the CM using high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy, stable carbon-isotope mass spectrometry, and polarizing microscopy. The black jadeitite contains 10–20 wt% graphite-3R that originated in the fracture zone. We propose that the graphite-3R formed during fault activities.

**LOCALITY AND SPECIMENS**

The study area is located within the Renge Metamorphic Belt (330-280 Ma) (Shibata and Nozawa, 1968; Nishimura, 1998; Tsujimori and Iyata, 1999; Kunugiza et al., 2004; Tsukada et al., 2004) and is situated at the border of Toyama and Niigata Prefectures (Fig. 1). Jadeitites and eclogites in this area are a component of the serpentine-matrix mélangé (Banno, 1958; Chihara, 1987; Chihara et al., 1979; Nakamizu et al., 1989; Komatsu, 1990; Nishimura, 1998; Tsujimori et al., 2000; Tsujimori, 2002). The groundmass of ultramafic rock is composed of serpentinized dunite–harzburgite, serpentine–carbonate rock (Harlow et al., 2004; Iwao, 1953; Yokoyama, 1985), and trace amounts of chromitite (Yamane et al., 1988; Tsujimori, 2004). The jadeitite may have formed by alkali metasomatism of igneous rocks in the serpentinite mélangé (Shido, 1958; Chihara, 1989; Shigeno et al., 2005) or precipitation from fluid (Coleman, 1961; Harlow, 1994; Okay, 1997; Harlow and Sorensen, 2001; Miyajima et al., 1999, 2001, 2002; Shi et al., 2003; Shigeno et al., 2005; Morishita, 2005). More specifically, Morishita (2005) suggests that jadeitites in the Itoigawa-Ohmi district formed from high field strength element fluids.

We recently discovered an outcrop of serpentinite mélangé containing jadeite in Kanayamadani, Itoigawa in central Japan (Fig. 2). The outcrop is ~5 m high and ~10 m wide and composed of serpentinite, jadeite, and albite blocks with prehnite and analcime veins. The boundary between the jadeite and serpentinite matrix (Zone D) contains a fracture zone (Zone C) that resulted from fault activities most likely associated with the mélangé. Zone A is a green–black jadeite block with little alteration, whereas Zone B contains a large amount of prehnite veins. The samples described in this study are as follows: KT00jd from the green–black jadeite zone (Zone A); KT06cly and KT07cly from the fracture zone (Zone C); KT09jd, KT10jd, and KT11jd from the altered jadeite zone (Zone B).

**EXPERIMENTAL**

Graphite was extracted by using hydrofluoric and hydrochloric acid treatment, following Itaya (1981).

X-ray diffraction analyses were conducted with a Rigaku Ultima IV diffractometer with CuKα radiation.
The samples were placed on a Si with an internal silicon standard (10 fi standard. PDXL2 was used to perform peak values of the peaks obtained were calibrated using the JASCO Raman microscope (NRS  Scherrer equation (K constant at 1.0).

The graphite samples chosen for stable carbon isotope analysis were also examined by XRD analysis. The samples were prepared in sealed quartz tubes and combusted at 1000 °C for 2 h to oxidize the graphite to CO2. The resulting CO2 gas was analyzed for carbon isotopes.

HRTEM was performed with a JEM-2010 (JEOL) microscope operated at 200 kV. The graphite samples analyzed were also used for XRD analysis. The samples were placed in holey carbon TEM grids.

SEM was carried out on a JSM-6510LA (JEOL) microscope operated at either 5 or 20 kV. The samples were slightly Os– or Au-coated. Back-scattered electron (BSE) and secondary electron (SE) images were obtained.

RESULTS

Polarizing microscopic observations

The green–black jadeiteite zone is composed of green jadeite, black jadeite with graphite aggregates, and prehnite veins (Fig. 3a). Prehnite veins are white in color and have a thickness of 10–500 μm. The veins disconnect the jadeite crystals. Graphite grains occur as black spherical aggregates in black jadeiteite. The graphite aggregates are also found filling veins. Graphite occurs at the boundaries of jadeite crystals. The size of the graphite aggregate filling the cracks in jadeite crystals is 10–50 μm in width. The vein-like graphite aggregates are 50–100 μm in width and 1–5 cm in length. These graphite aggregates are cutting jadeite grains. This texture indicates that graphite was precipitated after jadeite mineralization.

The altered jadeiteite zone has white prehnite and transparent analcime veins penetrating into the black jadeiteite (Fig. 3b). The vein of euhedral analcime crystals has a width of 1–3 mm. Graphite grains occur closely associated with prehnite. The altered jadeiteite zone samples (KT09jd) have more veins of prehnite and analcime, suggesting that the penetration of these veins causes the alteration of jadeiteite.

The fracture zone is composed of a green–gray chlorite fault gouge containing jadeite, prehnite, graphite, and serpentine fragments (Fig. 3c). The green–black jadeiteite zone sample (KT00jd) has randomly oriented prismatic jadeiteite crystals (typically <0.3 mm × <0.1 mm in size). The distribution of black graphite grains suggests plastic deformation of flow–texture in 50–100 μm width. The fragment size is 0.5–1 mm. Fragments might have formed by mechanical fracturing such as fault activity.

SEM analysis

Jadeite crystals are long, prismatic, and have a euhedral shape of 500 μm in length. Prehnite veins are cutting jade-
ite grains (Figs. 4a and 4b). Graphite grains are embedded in prehnite crystals and do not directly contact jadeite grains. Therefore, the graphite could have precipitated from a fluid and formed simultaneously with prehnite. The graphite crystals occur as hexagonal plates with a diameter of 1 μm or as stacked aggregates (Fig. 4c).

**XRD analysis**

Figure 5a shows an experimental XRD pattern (KT06cly) from the fracture zone. In the XRD pattern, graphite–3R peaks were clearly confirmed by using PDXL2 software (Fig. 5b). Both graphite–3R and graphite–2H were iden-
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Sharp peaks of Graphite–3R were observed in the XRD pattern at 43.45° (2θ), suggesting that considerable amounts of the graphite–3R exist. The Graphite–3R fraction of the fracture zone sample was estimated to be 10–20 wt% in the total graphite using the semi-quantitative method proposed by Shi et al. (1997) and Dittrich and Wohlfahrt-Mehrens (2001).

The dispersion of d002 values from the graphite of all three zones has a relatively narrow range of 3.353–3.357 Å (Table 1). However, the full width at half maximum intensity (FWHM) values of (002) graphite from the fracture zone have a wide range of 0.250°–0.279°, whereas those of altered jadeitite zone samples have a narrower range of 0.198°–0.258°. The FWHM value of graphite from the green-black jadeitite zone is 0.204° and is within the range of the altered jadeitite zone graphite. The crystallite sizes of the c-axis direction estimated by the Scherrer equation are as follows: \( L_c = 418 \) Å (the green-black jadeitite zone), \( L_c = 331–431 \) Å (the altered jadeitite zone), and \( L_c = 305–341 \) Å (the fracture zone).

**Raman spectroscopy analysis**

The most characteristic feature in the Raman spectra of graphite is the G band appearing at ~ 1580 cm\(^{-1}\), D1 band at ~ 1350 cm\(^{-1}\), D2 band at ~ 1620 cm\(^{-1}\), and D3 at ~ 1510 cm\(^{-1}\). The G band occurs in carbon containing sp\(^2\) carbon networks. The D1, D2, and D3 bands are defect-induced Raman features, thus these bands cannot appear for a highly crystalline graphite (Fig. 6). R1 (the peak height ratio of D1/G) and R2 [the peak area ratio of D1/(G + D1 + D2)] are commonly used to describe the defect quantity in graphitic materials (Table 1).

Raman spectroscopy indicates that graphite crystals from the green-black jadeitite zone are highly crystalline, whereas graphite crystals from the altered jadeitite zone have various crystallinities. In the Raman spectra of the green-black jadeitite zone sample (KT00jd), the peaks of G and D1 bands are sharp. The ranges of the FWHM of G and D1 bands are 18.94–21.92 cm\(^{-1}\) and 43.17–43.19 cm\(^{-1}\), respectively. The FWHMs of G and D1 bands in

Figure 4. BSE images in green-black jadeitite zone sample. (a) and (b) Thin section. (c) and (d) SEI image in green-black jadeitite zone sample. Jd, Jadeite.

Figure 5. (a) XRD pattern (KT06cly) from the fracture zone. (b) Graphite–3R and 2H peaks fitting by using PDXL2 software. Thick line is measured. Thin line is fitting. Si, Silicon standard; Gr, Graphite; 2H, Graphite–2H; 3R, Graphite–3R.
the altered jadeitite zone have larger ranges than those from green–black jadeitite zone samples, and are 19.19–23.19 cm\(^{-1}\) and 46.66–52.10 cm\(^{-1}\), respectively. The ranges of the FWHM of G and D1 bands from the fracture zone are the largest of the three zones and are 24.48 and 83.49–84.89, respectively. The graphite from the fracture zone shows the lowest crystallinity. The D3 band in Raman spectra was only found in the graphite from the fracture zone, suggesting that these samples contain amorphous graphite (Cuesta et al., 1994; Tan et al., 2004; Makarova et al., 2008).

Raman spectra of graphite from the fracture zone show three prominent features that can differentiate it from those of graphite from the green–black jadeitite and altered jadeitite zones. First, the D1 position dispersion as a function of G position has a strong positive linear correlation in all the samples, which has also been reported by previous researchers (Katagiri, 1996, 1998; Yoshida et al., 2006) (Fig. 7a). Second, R1 plots and R2 plots for the green–black jadeitite zone and altered jadeitite zone samples are correlated (Fig. 7b), while

### Table 1. Results of Raman spectra, Stable carbon isotope (\(\delta^{13}C\)), XRD analysis

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<th>KT06cly</th>
<th>KT07cly</th>
<th>KT09jd</th>
<th>KT10jd</th>
<th>KT11jd</th>
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**Raman**

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<td>15.1</td>
<td>5.32</td>
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Av., Average; s.d., standard deviation; NA, not applicable.

Mean values of La (Å) and Lc (Å) are calculated by following Tuinstra and Koenig (1970), and Scherrer equation (K = 1.0), respectively.

Figure 6. Raman spectra of the studied samples. D3 band (1480 cm\(^{-1}\)) is a broad peak and appears between G and D1 bands.

Figure 7a. Raman spectra of graphite from the fracture zone.
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the graphite from the fracture zone has a slightly different trend (Fig. 7b, region 2). Third, the D1 FWHM and G FWHM dispersions for green-black jadeitite zone samples and altered jadeitite zone samples are correlated (Fig. 7c), and the graphite from the fracture zone encompasses a broad region (Fig. 7c, region 2).

δ¹³C analysis

The δ¹³C values are summarized in Table 1. The KT11jd sample was too small to measure δ¹³C data. All the data from the samples range from −7.870‰ (KT10jd) to −8.570‰ (KT06cly). The difference of δ¹³C values was within 0.810‰ for all the samples. This indicates that the origin of graphite from the fracture zones is fundamentally identical to those of the green-black jadeitite and the altered jadeitite zones.

HRTEM analysis

TEM observations indicate that the crystallinity of graphite increases in the order: fracture zone < altered jadeitite zone < green-black jadeitite zone.

Graphite (KT00jd) from the green-black jadeitite zone has a hexagonal plate-like shape (Fig. 8a). The HRTEM image and the selected-area electron diffraction pattern (SAED) confirmed that the hexagonal plate was viewed along c-axis (Fig. 8b). This shape was observed in both green-black jadeitite zone and altered jadeitite zone samples in many cases.

The graphite crystals from the altered jadeitite zone (KT09jd) and fracture zone (KT06cly) samples are filamentous or flake-like aggregates (Fig. 9a). This type of graphite crystal is common in the fracture zone and the altered jadeitite zone samples. However, small flake-like aggregates were found more frequently in the fracture zone than in the altered jadeitite zone. Nearly amorphous graphite occurs in the fracture zone samples (Fig. 9b).

Figure 7. Scatter plots between Raman parameters. (a) G position versus D1 position. (b) G FWHM versus D1 FWHM. (c) R1 ratio versus R2 ratio. 1. Distribution of the values of green-black jadeitite zone sample and altered jadeitite zone sample. 2. Distribution of the values of fracture zone sample.
and $La$ values were obtained by measuring lattice fringes in the HRTEM images. The $La$ value is 500–1000 nm, whereas the $Lc$ value is 10–50 nm. The crystallite size in the fracture zone is smaller than that in the green-black jadeitite zone. The fracture zone sample (KT 06cly) has more defects (Fig. 9c).

The [010] SAED pattern indicates that graphite–3R occurs in this sample (Fig. 10a). The SAED pattern and HRTEM image indicate that the interfacial angle between (011) and (003) in the 3R–graphite structure is 78° (Fig. 10b). This value reasonably matches that calculated from the structural refinement data (Aoki and Akai, 2008; Lin et al., 2012) of graphite–3R, but not graphite–2H (72°). The observed widths of the graphite–3R structure along the $c$-axis are 20–30 nm in many cases (Fig. 10c). In
Figure 11, the layer structure of graphite-3R does not always extend laterally, but the region of graphite-3R is present as a domain-like structure.

**DISCUSSIONS**

**Genesis of graphite in jadeitite**

The presence of graphite was confirmed in all the black jadeitite samples from the Kanayamadani outcrop, and thus the graphite could be responsible for the black color of the black jadeitite as suggested by Miyajima et al. (2005). Lattice vibrations of graphite bands were found in all the samples in Raman analysis. These bands are D (1350 cm\(^{-1}\)) and G band (1580 cm\(^{-1}\)) peaks (Kawahima and Katagiri, 1995, 1999). Furthermore, in the XRD analysis patterns, both graphite-2H and graphite-3R peaks were identified.

The paragenesis of graphite and prehnite restricts the formation conditions of graphite. Our SEM observations of green-black jadeitite zone samples show that graphite occurs as inclusions in prehnite veins in black jadeitite. The graphite grains coexist with prehnite, whereas they do not coexist with jadeite. Thus, graphite in the black jadeitite might have crystallized simultaneously with the prehnite. Prehnite likely formed after jadeite crystallization because prehnite veins cut jadeite grains. Prehnite is commonly found as a low-grade (<350 °C) metamorphic mineral (Frey et al., 1991; Spear, 1993; Banno, 1998; Miyazaki and Okamura, 2002; Harlow et al., 2011). The stability field of prehnite is \( P < 0.6 \text{ GPa} \) and \( T = 150-420 \text{ °C} \) in the CaO-Al\(_2\)O\(_3\)-SiO\(_2\)-H\(_2\)O system (Frey et al. 1991). The graphite could have crystallized in the stability field of prehnite (\( P < 0.6 \text{ GPa} \) and \( T = 150-420 \text{ °C} \)). Morishita (2005) and Morishita et al. (2007) suggested that the Lavender-Jade in Itoigawa-Omhi district formed at a pressure of roughly 0.6 GPa and a temperature of less than 350 °C. These conditions are consistent with our estimates.

High stable carbon isotopes (\( \delta^{13}C \)) values (−8.57 to −7.87‰) of the graphite in black jadeitite suggest that graphite crystals may not have had an organic origin. The \( \delta^{13}C \) value difference is about 0.81‰ for all the samples. The \( \delta^{13}C \) value depends largely on the source materials (e.g., Wickman and Ubisch, 1951; Craig, 1957; Wickman, 1956; Ley et al., 1980; Weis, 1980; Hans-Weinheimer and Hirner 1981). Low \( \delta^{13}C \) values (<−20.0‰) suggest that graphite crystals have at least a partially preserved primary biogenic signature (e.g., Santosh and Wada, 1993).

High \( \delta^{13}C \) values (−8.57‰ to −7.87‰) of the graphite in black jadeitite might have been caused by CO\(_2\)-rich fluids. Barrenechea et al. (1997) and Ray (2009) reported that the isotopic fractionation of graphite was caused by CO\(_2\)-CH\(_4\) metamorphic fluid. Satish-Kumar et al. (2011) also reported that \( \delta^{13}C \) values were enriched by CO\(_2\)-rich fluid reactions at graphite rims. In this case, the \( \delta^{13}C \) values were from −10‰ to −6‰. Our field observations indicate that the boundary between jadeite and the serpentine matrix has a fracture zone, suggesting that fault activities associated with the mélangé influence the black jade formation. The genesis of the jadeite and prehnite in this region could have been the result of fluid effects, suggested by Miyajima et al. (2002). He, H and CO\(_2\) gases can also be supplied along the fault (Sugisaki, 2007).

**Variety of graphite in jadeitite**

It is well known that graphite crystallinity is correlated with the temperature of formation (e.g., Inagaki 1968, 1972; Inagaki et al., 1968; Tanaka et al., 1977). Low temperature conditions result in the formation of low crystalline graphite. The altered jadeitite zone is located on the outer periphery of the green-black jadeitite zone. There is a possibility that the intrusion of prehnite veins occurred at a later stage. Altered jadeitite zone samples have low crystalline graphite because the prehnite vein including graphite formed at a low temperature. Consequently, this may explain why altered jadeitite zone samples contain both the low and high crystalline graphite crystals as detected by XRD, Raman spectroscopy and TEM analysis.

**Natural graphite-3R structure**

Graphite-3R and amorphous carbon only occur in the fracture zone, and the coexistence of graphite-3R and amorphous carbon might indicate that graphite-3R formed by mechanical fracturing of graphite-2H during fault activities. It is well known that graphite-3R forms artificially by ball-milling of graphite-2H in industrial processes (Nakamizo et al., 1978; Aladekomo and Bragg, 1990; Janot and Guerard, 2005; Lin et al., 2012). Only four occurrences of graphite-3R have been reported and the graphite was deposited from fluid in all cases (Luque et al., 1998; Parthasarathy et al., 2006).

The graphite-3R contains many stacking faults and defects, suggesting the transformation from graphite-2H to graphite-3R. The hexagonal-rhombohedral transformation probably occurs through a martensitic-like mechanism. The graphite-3R from Kanayamadani might be formed by shear stress during the faulting process with frictional heating (O’hara, 2004; Matsubara et al., 2006;
Sakaguchi et al., 2007). This process has been previously confirmed by deformation experiments of graphite single crystals (Freise and Kelly, 1963).

The fault activities might have changed the crystallinity of the graphite. Reflectance in vitrinite (CM) is increased by frictional heating during the fault activities in this region. Alternately, the crystallinity of the graphite may be reduced by the fault activity. The change in the crystal structure of graphite can be used effectively to better understand tectonics, and further study of graphite structures may be key to identifying tectonic movement in geological processes.

CONCLUSIONS

1. We recently discovered an outcrop with jadeitite and associated rocks containing graphite-3R in Kanayamadani. The outcrop is composed of green-black jadeite, altered jadeite, and fracture zones. Graphite-3R only occurs in the fracture zone.
2. The graphite was crystallized with the prehnite in the stability field of prehnite (P < 0.6 GPa and at T = 150–420 °C).
3. The δ13C values of graphite range from –8.570‰ to –7.870‰. Higher δ13C values indicate the graphite in the black jadeite does not have an organic origin. The graphite formed in inorganic process from the CO2–CH4 rich fluid.
4. Graphite-3R and the amorphous graphite were confirmed by XRD, HRTEM, and ED analyses in the fracture zone samples. Nearly amorphous graphite and graphite-3R might have formed by crushing graphite-2H.
5. Graphite-3R might be formed by fault activities. The crystallinity of the graphite is reduced during fault activities.
6. The recognition of graphite polytypes could be an effective key to understanding some tectonic movements in a variety of geological processes.

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SUPPLEMENTARY MATERIALS

Color version of Figures 2 and 3 is available online from http://japanlinkcenter.org/DN/JST/JSTAGE/jmps/1131125a.

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