

## Coarse-grained cubic diamond overgrowth on fine-grained diamond in the Kokchetav UHP garnet-clinopyroxene rock

TAKABE, Shota<sup>1\*</sup> ; OGASAWARA, Yoshihide<sup>1</sup> ; SCHERTL, Hans-peter<sup>2</sup>

<sup>1</sup>Department of Earth Sciences, Waseda University, <sup>2</sup>Institute of Geology, Mineralogy and Geophysics, Ruhr-University Bochum

Using multilayered 2D laser Raman mappings, an overgrowth of coarse-grained (max. 200  $\mu\text{m}$  across) cubic diamond on a fine-grained diamond (ca. 10  $\mu\text{m}$ ) was confirmed in diamond-bearing garnet-clinopyroxene rock from the Kokchetav Massif. Garnet-clinopyroxene rock is one of the diamond-bearing rock types which were first reported as metamorphic diamonds by Sobolev and Shatsky (1990), whereas diamond-free garnet-clinopyroxene rock with coesite exsolution in titanite was reported later by Sakamaki and Ogasawara (2014). The occurrence of extraordinary coarse grains (cubic and “ball-shaped”) as “microdiamond” in this rock has been well known to UHP metamorphic petrologists (e.g., Dobrzhinetskaya, 2012; Schertl and Sobolev, 2013). Recently, we found 4 grains of fine-grained diamond having different morphology (rounded-shaped with smooth surface) in the same rock sample, and these two types suggest that diamonds in garnet-clinopyroxene rock formed at two different stages and environments.

Diamonds in garnet-clinopyroxene rock were analyzed by laser Raman spectroscopy using Ar<sup>+</sup> laser (514.5 nm) and solid-state laser (487.9 nm). All diamonds showed a Raman peak at ca. 1332  $\text{cm}^{-1}$ . The peak positions and the values of the FWHM (full widths at half maximum) of the Raman bands are followings: (1) cubic: 1330.8-1332.0  $\text{cm}^{-1}$ , 4.29-5.34  $\text{cm}^{-1}$ , and (2) fine-grained: 1332.1-1335.2  $\text{cm}^{-1}$ , 4.75-5.43  $\text{cm}^{-1}$ . 2D Raman mappings at different focal depths were conducted to examine the internal structure of cubic diamond. Very clear internal zonation (core domain and rim domain) of peak positions and FWHMs of diamond Raman band were recognized in the three grains; the peak positions slightly decrease from the center (1331.8-1331.9  $\text{cm}^{-1}$ ) to the outside (1331.1-1331.6  $\text{cm}^{-1}$ ) and the values of FWHM decrease from the center (4.73-5.13  $\text{cm}^{-1}$ ) to the outside (4.21-4.81  $\text{cm}^{-1}$ ). Fine-grained diamond recently found showed similar peak positions and FWHMs with the core domain of the cubic grains. Diamonds in dolomite marble and in garnet-biotite gneiss did not show such internal structure. Such heterogeneity of peak positions and FWHMs cannot be explained by the residual pressure of homogeneous diamond grain itself according to the results of Raman spectroscopy of Kimberlite diamonds. The zonation pattern like the core domain and the rim domain shows heterogeneous characters in coarse-grained cubic diamond and strongly suggests the overgrowth of cubic diamond on fine-grained one as a seed crystal. We concluded that in diamond-bearing garnet-clinopyroxene rock the diamonds crystallized at two different stages and the cubic diamond at the 2<sup>nd</sup> stage was probably crystallized from aqueous fluid.

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Keywords: microdiamond, the Kokchetav Massif, garnet-clinopyroxene rock, ultrahigh-pressure metamorphism, Raman spectroscopy, internal zonation

## Diamond formation through intermediate $sp^2$ carbon from fluid in dolomite marble during the Kokchetav UHP metamorphism

MIURA, Sho<sup>1\*</sup>; OGASAWARA, Yoshihide<sup>1</sup>

<sup>1</sup>Department of Earth Sciences, Waseda University

Graphitic carbon inclusions were discovered inside microdiamond grains in dolomite marble from the Kokchetav Massif. The discovered inclusions are  $sp^2$  carbon species and are probably relics of an intermediate metastable phase for diamond formation from  $H_2O$ -rich fluid during UHP metamorphism; on our previous studies on diamond and graphite, these carbon species are not metamorphic graphite relics, not graphite changed from diamond, and not graphite crystallized from  $H_2O$ -rich fluid at later stage.

We examined over 5,000 diamond grains in 40 thin sections of dolomite marbles under a transmission optical microscope. Five  $sp^2$  carbon inclusions have been discovered in five diamond grains. These host diamond grains are 4-15  $\mu m$  in diameter. These graphitic carbon inclusions are black under a microscope and their sizes are 1-5  $\mu m$  across.

The microdiamond in dolomite marble has been classified into S-type, T-type, and R-type grains on the basis of the morphologies [1], Raman spectra [1], cathodoluminescence spectra [2], and carbon isotopic compositions [3]. R-type and the core of S-type formed at 1<sup>st</sup> stage, and T-type and the rim of S-type crystallized at 2<sup>nd</sup> stage from  $H_2O$ -rich fluid. All  $sp^2$  carbon inclusions were found only in the rim of S-type (one grain) and T-type (four grains).

Using multilayered 2D Raman mappings at different focal depths with solid-state laser (487.9 nm),  $Ar^+$  laser (514.5 nm), and He-Ne laser (632.8 nm), the Raman spectra of the examined graphitic carbon inclusions show a peak at ca.  $1580\text{ cm}^{-1}$  (assigned to G-band caused by  $sp^2$  bond of carbon), and these  $sp^2$  carbon inclusions are completely included inside the host diamond grains. The G-bands of peak position with FWHM for the  $sp^2$  carbon inclusions are as follows: (the rim of S-type)  $1572.0\text{ cm}^{-1}$  with  $17.8\text{ cm}^{-1}$ ,  $1581.3\text{ cm}^{-1}$  with  $17.7\text{ cm}^{-1}$ , and  $1576.5\text{ cm}^{-1}$  with  $16.5\text{ cm}^{-1}$ ; (T-type)  $1574.9\text{--}1584.0\text{ cm}^{-1}$  with  $18.0\text{--}28.3\text{ cm}^{-1}$ ,  $1580.3\text{--}1587.1\text{ cm}^{-1}$  with  $17.3\text{--}41.9\text{ cm}^{-1}$ , and  $1581.5\text{--}1584.2\text{ cm}^{-1}$  with  $17.7\text{--}31.0\text{ cm}^{-1}$ . The relative peak intensities of G-band to the host diamond band (ca.  $1332\text{ cm}^{-1}$ ) are less than 10 %, and the strongest G-band peaks were detected at the center of the host diamond grains. The spectra of the inclusions often show disordered graphite bands; D1-band (ca.  $1360\text{ cm}^{-1}$ ) and D2-band (ca.  $1620\text{ cm}^{-1}$ ), but these bands are usually weak rather than G-band.

The discovered  $sp^2$  carbon inclusions were formed at the 2<sup>nd</sup> stage of the diamond formation, and could be relics of an intermediate metastable phase precipitated from  $H_2O$ -rich fluid and followed by the transformation to diamond. This interpretation is consistent with the previous studies of diamond synthesis using C-O-H fluid at diamond stability fields (e.g. [4]).

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Keywords: microdiamond,  $sp^2$  carbon inclusion, diamond formation, intermediate metastable phase,  $H_2O$ -rich fluid, Kokchetav UHP metamorphism

## Mg-enrichment at retrograde stage of the Kokchetav UHPM -Pyrope-rich rim of garnet porphyroblasts from the Kulet area -

TAKEBAYASHI, Tomohiro<sup>1\*</sup>; SAKAMAKI, Kunihiko<sup>1</sup>; OGASAWARA, Yoshihide<sup>1</sup>

<sup>1</sup>Department of Earth Sciences, Waseda University

Garnet porphyroblasts (group A) with pyrope-rich rims (as high as Prp = 68 mol%) were found in discrete subhedral to euhedral crystals (5-35 mm across) without matrices (sample no. ZW61), probably from porphyroblasts in whiteschist, from the Kulet area of the Kokchetav Massif. We also examined garnet porphyroblasts (group B) in a whiteschist (sample no. ZW42) collected from the same outcrop. In the group B, garnet porphyroblasts lack pyrope-rich rim; pyrope components in the outer parts and the margin are up to ca. 30 mol%. Pyrope components of groups A and B garnets are much higher even in the cores than those of coesite-bearing garnets from the same area by Parkinson (2000) (Prp: up to 12.37 mol% at the inner rim).

Group A garnets show strong chemical zonations of Mg and Fe from the core (Prp: 15-35 mol%, Alm: 70-67 mol%) to the rim (Prp: 35-68 mol%, Alm: 67-39 mol%). The pyrope-rich rim characterizes this group. These garnets include chloritoid (Mg/(Mg+Fe): 0.3), rutile, and corundum at the core, and Mg-chloritoid (Mg/(Mg+Fe): 0.7), rutile, chlorite, zircon, talc, and monazite at the rim.

Group B garnets in the whiteschist (ZW42) are subhedral to euhedral crystals (4-15 mm across) and show chemical zonations of Mg and Fe from the inner part (Prp: 16 mol%, Alm: 73 mol%) to the outer part (Prp: 30 mol%, Alm: 72 mol%). The lack of pyrope-rich rim in group B is strong contrast with group A. Garnet in the group B includes chloritoid, quartz, rutile, chlorite, apatite, and monazite throughout a grain. The matrix of the whiteschist (ZW42) shows lepidoblastic texture and consists of phengite, biotite, quartz, and kyanite; the mineral assemblage of the matrix is similar to that of whiteschist described by Parkinson (2000)

Pyrope-rich rim is recognized only in discrete grains (group A). In spite of no direct information about matrices for group A, the inclusion mineralogy of the garnet indicates that the protolith of group A was not rich in Mg. To explain the overgrowth of extremely pyrope-rich rim requires other factors excepting the bulk chemical composition of the protolith. In addition, the lack of pyrope-rich rim in group B garnet from the same outcrop suggests that the overgrowth process of pyrope-rich rim was strongly heterogeneous on the order of a meter. One possible cause is Mg-enrichment by aqueous fluid and its heterogeneous effect to the whiteschist from Kulet area during the retrograde stage. During Mg-enrichment in the retrograde stage, the portions strongly affected by Mg-rich fluid were altered completely except for garnet porphyroblasts and changed protolith bulk chemistry mainly in matrices to Mg-dominant chemistry. The portions not affected by Mg-enrichment kept the protolith bulk chemistry and the overgrowth of pyrope-rich rim did not occur. Later, another fluid infiltration occurred to change matrices completely; the micaceous matrices of whiteschist are the product of the later stage alteration. The matrices of already Mg-enriched portions could be easily altered during later fluid effect and weathering; so, only garnet porphyroblasts remain as discrete grains with pyrope-rich rim. The lack of pyrope-rich rim in group B means no or very weak participation of Mg-enrichment in whiteschist.

Conclusively, at least two stage fluid effects during the exhumation process could be possible for the Kulet whiteschist; the first stage means the Mg-enrichment by fluid and the second stage implies alteration of matrices to the phengitic assemblage after Mg-enrichment. As described above, the petrology based on the matrix mineralogy and the bulk chemistry only gives the retrograde stage information strongly affected by fluid infiltrations. Only garnet porphyroblasts have the information of the protolith chemistry and the metamorphic history as their chemical compositions and inclusions. There are some possibilities of misunderstanding UHPM rocks based on the matrix information.

Keywords: garnet, Kokchetav, Kulet, pyrope-rich, whiteschist, Mg-enrichment

## Petrology of garnet-clinopyroxene rocks from the Kokchetav Massif, northern Kazakhstan

SAKAMAKI, Kunihiro<sup>1\*</sup> ; SCHERTL, Hans-peter<sup>2</sup> ; OGASAWARA, Yoshihide<sup>1</sup>

<sup>1</sup>Department of Earth Sciences, Waseda University, <sup>2</sup>Institute of Geology, Mineralogy and Geophysics, Ruhr-University Bochum

In the Kumdy-Kol area of the Kokchetav Massif, two types of garnet-clinopyroxene rocks occur: one is diamond-bearing and one diamond-free. Sobolev and Shatsky (1990) described diamond-bearing garnet-clinopyroxene rock as one of the diamond-bearing rocky types in their first report on the metamorphic diamond. Recent study reports the other type, diamond-free garnet-clinopyroxene rock, from the same area (Sakamaki and Ogasawara, 2014). Both diamond-bearing and diamond-free garnet-clinopyroxene rocks are mainly composed of garnet, Na-free clinopyroxene with minor amount of calcite, quartz, similar to the mineral assemblage like "skarn", and have evidence of UHP conditions; the latter has coesite exsolution in titanite. Diamond-bearing garnet-clinopyroxene rock is composed of garnet layers and clinopyroxene layers, and contains rutile and coarse-grained microdiamond. Microdiamond occurs as inclusion of garnet and clinopyroxene, and as an intergranular phase. The morphologies are cubic form (up to 200  $\mu\text{m}$ ), ball-shaped form (covered with graphite) (up to 150  $\mu\text{m}$ ), and fine-grained (ca. 10  $\mu\text{m}$ ) which was discovered recently (Takabe et al., 2014). Diamond-free garnet-clinopyroxene shows granoblastic texture and consists of garnet, clinopyroxene, calcite, quartz, titanite with minor amount of K-feldspar. Titanite contains exsolved coesite needles and plates in the core, which indicate excess Si incorporated in six coordinated site; pressure-drop stage was still in coesite stability field ( $>2.5$  GPa). Clinopyroxene in both garnet-clinopyroxene rocks contain K-bearing exsolved phases, K-feldspar and phengite, which indicates K-rich compositions of original clinopyroxene prior to exsolution. Reintegrated  $\text{K}_2\text{O}$  contents in precursor clinopyroxene were estimated at 0.60-1.04 wt.% in diamond-bearing rock, and up to 1.14 wt.% in diamond-free rock.

The bulk composition of each garnet-clinopyroxene rock was estimated on the basis of volume fractions and chemical compositions of rock-forming minerals. Diamond-bearing garnet-clinopyroxene rock is characterized by relatively high  $\text{SiO}_2$  of ca. 50 wt.% while diamond-free rock contains significant amounts of CaO (33 wt.%) and  $\text{CO}_2$  (12 wt.%) indicating calcite-rich modal composition.

Garnet and clinopyroxene can contain significant amounts of OH at UHP conditions and record fluid environments during the UHP metamorphism (Sakamaki and Ogasawara, 2014). We conducted micro-FTIR spectroscopy of garnet and clinopyroxene and identified significant amounts of structural OH and non-structural molecular  $\text{H}_2\text{O}$  suggesting submicron fluid inclusions in garnet;

(Dia-free, no. XX16), OH: 360+  $\text{H}_2\text{O}$ : 20 to OH: 1655+  $\text{H}_2\text{O}$ : 1203 ppm (wt.  $\text{H}_2\text{O}$ )

(Dia-bearing, no. 25018) OH: 391+  $\text{H}_2\text{O}$ : 294 to OH: 1165+  $\text{H}_2\text{O}$ : 1218 ppm

(Dia-bearing, no. 24997) 0 to OH: 1727+  $\text{H}_2\text{O}$ : 1592 ppm.

IR spectra of clinopyroxene show complex absorption bands of structural OH in clinopyroxene host and exsolved minerals, and nonstructural molecular  $\text{H}_2\text{O}$ . Bulk water (OH and  $\text{H}_2\text{O}$ ) contents in clinopyroxene were conveniently estimated at (Dia-free) 1657 to 8215 ppm and (Dia-bearing) 700 to 4384 ppm, respectively. Such high concentrations of water in garnet and clinopyroxene suggest that diamond-bearing and diamond-free garnet-clinopyroxene rocks were formed in  $\text{H}_2\text{O}$ -rich environment at UHP conditions.

These two types of garnet-clinopyroxene rocks have similar appearances like skarn but have different carbonate modal compositions, diamond occurrences, and Ti-phase stability. The difference in carbonate modal compositions reflects the difference of bulk chemical composition of protoliths and the difference of diamond occurrences and Ti-phase stability in garnet-clinopyroxene rocks were perhaps controlled by bulk compositions of protoliths and fluid environments during the metasomatism stage.

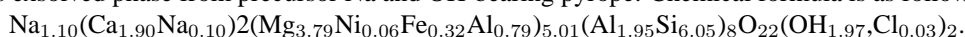
Keywords: the Kokchetav Massif, UHP metamorphism, diamond, supersilicic titanite, nominally anhydrous minerals, micro-FTIR spectroscopy

## Na and OH-bearing pyrope garnet - Evidence of mantle metasomatism by ancient oceanic crusts underneath Colorado Plateau

OGASAWARA, Yoshihide<sup>1\*</sup> ; SAKAMAKI, Kunihiko<sup>1</sup> ; SATO, Yuto<sup>1</sup>

<sup>1</sup>Department of Earth Sciences, Waseda University

Na-amphibole lamellae together with clinopyroxene, ilmenite, and rutile, were discovered in pyrope-rich garnet from the Garnet Ridge, northern Arizona, Colorado Plateau. Oriented amphibole lamella has a pargasitic composition and was identified as exsolved phase from precursor Na and OH-bearing pyrope. Chemical formula is as follows:



Pargasite lamella in pyrope and its precursor hydro-sodic composition are the first report from the Navajo Volcanic Field. The garnets in the Garnet Ridge are xenocrysts delivered from wide range of the depths from the mantle to crustal level by kimberlite diatremes (ca. 30 Ma). We classified the diverse garnets of the Garnet Ridge into 10 groups (Sato et al. 2014, 2015). There are two types of pyrope-rich garnets in this area: group A: Cr and pyrope-rich ( $\text{Cr}_2\text{O}_3$ : 1-6 wt.%, Prp: 67-71 mol%), purple color (called *Navajo Ruby*), and group B: pyrope-rich reddish brown garnet (Prp:xx-71 mol%). The garnet in this paper belongs to group B (pyrope-rich reddish brown garnet). Group B garnet has a continuous compositional range (from pyrope to almandine-rich) in Ca-Mg-Fe compositional triangle from the compositions of group A, and this continuous compositional variation suggests that group B garnet is a metasomatic product of group A.

On the basis of exsolved phases, group B is subdivided into 4 subgroups, B<sub>1</sub>: amphibole type, B<sub>2</sub>: ilmenite type, B<sub>3</sub>: black type, and B<sub>4</sub>: clinopyroxene-amphibole type. B<sub>1</sub>, B<sub>3</sub>, and B<sub>4</sub> contain Na-amphibole lamella. B<sub>1</sub>: amphibole type (Prp: 49-66; Alm: 18-28; Grs: 16-26 mol%) contains exsolved phases of amphibole, rutile, ilmenite, and clinopyroxene. A few chlorite inclusions which are trapped during crystallization also occurs. B<sub>2</sub>: ilmenite type (Prp:49-68; Alm: 20-38; Grs: 12-19 mol%) contain fluid inclusions and exsolved ilmenite; the other exsolved phases are never identified. B<sub>3</sub>: black type (Prp:54-72; Alm: 18-33; Grs: 12-15 mol%) looks like a opaque mineral because it has exsolved lamellae of rutile, amphibole, ilmenite, pyroxene, apatite, and srilankite densely. Sometimes, carbonate inclusions are recognized. B<sub>4</sub>: clinopyroxene-amphibole type (Prp:61-76; Alm: 13-27; Grs: 8-11 mol%) have exsolved rutile, pyroxene, amphibole, and ilmenite.

Although Na is a trace component of garnet even at UHP condition, Na-bearing garnet is reported garnet peridotite in the North Qaidam UHPM terrane (Song et al., 2005). The rare occurrence of Na-bearing garnet reflects very low Na solubility in garnet and very low Na content in the mantle (<0.6 oxide wt.%).

In the mantle peridotite, garnet coexists with olivine, orthopyroxene, and clinopyroxene which have a relatively high Na solubility, and Na which is originally little, is preferentially partitioned to clinopyroxene, not to garnet; such features of Na partitioning indicate very rare occurrence of Na-bearing garnet; however, Na and OH-bearing garnet formed in the mantle underneath the Colorado Plateau and this suggests Na metasomatism by Na-bearing H<sub>2</sub>O-fluid at great depths. A possible source of Na-rich metasomatic fluid could be subducted ancient oceanic crusts probably before Farallon Plate subduction. The fragments of ancient oceanic crusts being stagnated in the deep mantle for a long time were dehydrated to released Na-rich H<sub>2</sub>O fluids, which were infiltrated into garnet peridotite and metasomatized to form Na- and OH-bearing garnet. The precursor compositions of Na and OH-bearing garnet from the Garnet Ridge could be a significant key to clarify the complex interactions between the mantle, ancient oceanic materials and fluid underneath the Colorado Plateau.

Keywords: hydrosodic garnet, pargasite exsolution, Garnet Ridge, Colorado Plateau, mantle metasomatism

## Chemistry & inclusion/lamella mineralogy of garnet from the Garnet Ridge; Information of multi-stage mantle metasomatism

SATO, Yuto<sup>1\*</sup>; KOGA, Itaru<sup>1</sup>; SAKAMAKI, Kuniyuki<sup>1</sup>; OGASAWARA, Yoshihide<sup>1</sup>

<sup>1</sup>Department of Earth Sciences, Waseda University

Wide chemical variations and characteristic inclusion mineralogy are recognized in garnet xenocrysts and garnets in xenoliths from the kimberlite diatreme (ca. 30 Ma) at the Garnet Ridge in the Navajo volcanic field, Colorado Plateau. These garnets show the lithologies at a wide range of depths from crustal depths to deep mantle and imply the multi-stage metasomatism underneath the Colorado Plateau.

On the basis of major element chemistry, the garnets from the Garnet Ridge have been classified into the following 10 groups: A) Cr and pyrope-rich garnet, B) pyrope-rich reddish brown garnet, C) garnet aggregate, D) garnet megacryst, E) garnet in eclogite, F) garnet in metasomatized eclogite, G) quartz lamellae-bearing garnet, H) garnet in metasomatic rock I, I) garnet in metasomatic rock II, J) almandine-rich garnet. These garnets belong to the mantle origins (groups A, B, C and D), subducted oceanic crust origins (groups E, F and G) and crustal origins (groups H, I and J).

Groups A and B generally have Mg-rich and Cr-bearing compositions with inclusions of Ol, Cpx and Opx. This indicates mantle peridotite origins. Group A, a typical garnet in the Garnet Ridge, called "Navajo Ruby", has relatively high Cr<sub>2</sub>O<sub>3</sub> (1.0-5.9 wt.%) with a limited range of CaO (4.2-5.8 wt.%), and includes Mgs and Dol. These features suggest carbonated garnet lherzolite origins.

Group B has a wide continuous chemical range in Mg-Fe components (Prp 49-76, Alm 12-43 mol%), suggesting the mantle metasomatism. The inclusion/lamella mineralogy can subdivide this group into four subgroups with unique chemical ranges: B<sub>1</sub>) with lamellae of Amp and Ca-enriched composition (Grs 12-26 mol%), B<sub>2</sub>) with lamellae of Ilm and fluid inclusion, B<sub>3</sub>) with dense lamellae of titanates and inclusions of Mgs and Dol, B<sub>4</sub>) with lamellae of Cpx and Amp, and Ca-poor composition (Grs 8-11 mol%). The variations in the chemical ranges of these subgroups were caused by the metasomatism of group A garnet.

Groups C and D have the compositions with wide variations located in the center area of a Ca-Fe-Mg diagram, and contain Ap lamellae. Group D is an euhedral to subhedral megacryst (max. 8 cm across). Group C is the aggregate of fragmented megacrysts. Both group C and D are products of mantle metasomatism which are different from formation of group B.

Groups E and F (in eclogite xenoliths) are Fe-rich and show chemical zonation (core: Alm 52-56, Prp 6-7 mol%; rim: Alm 59-61, Prp 15-21 mol%). Group E includes aggregate of Zo and Ab, probably from precursor lawsonite inclusion. The host rock of group F is composed of eclogite part (Grt + Cpx) and jadeite-bearing omphacite part (Cpx only), and lacks lawsonite (including relicts) in both parts.

Group G is rich in Fe and Mg (Alm 41-52, Prp 27-40 mol%) and characterized by its occurrence (xenocrysts) and lamellae (Rt, Ap and Qtz), although the chemical composition is similar to groups C, D, E and F. The Fe and Mg-rich chemistry and the inclusion/lamella mineralogy (occurrence of Cpx, Qtz and Zrn) are similar to groups E and F.

Groups H, I (in two types of xenoliths) and J contain minerals at crustal depths such as Qtz, Ab, An and Zo. Rutile lamellae in Qtz inclusions in group I and J, and Opx inclusion in group J suggest high temperature. Group H has Ca-rich composition (Grs 57-63 mol%) and includes Ca-rich silicates (An, Zo and Ttn) and K-rich amphibole. Ca-rich silicate inclusions and matrix assemblages of group H suggest origins of a calc-silicate rock like skarn.

As described above, the garnets from the Garnet Ridge show diverse features in color, morphology, chemistry and inclusion/lamella mineralogy. Such complexities were created by the chemical reactions in mantle peridotites, subducted oceanic crusts and continental crusts at a wide range of the depths. Decoding such information preserved in garnets leads to clarify the multi-stage metasomatism underneath the Colorado Plateau, including the effect of the flat subduction of the Farallon Plate.

Keywords: the Colorado Plateau, pyrope garnet, lawsonite eclogite, kimberlite xenolith and xenocryst, mantle metasomatism

## Radiation-damage-induced variations in Raman spectra of UHPM microdiamond

SHIMIZU, Rentaro<sup>1\*</sup> ; TAKABE, Shota<sup>1</sup> ; OGASAWARA, Yoshihide<sup>1</sup>

<sup>1</sup>Department of Earth Sciences, Waseda University

Raman spectroscopy is a fundamental and very useful technique for characterization of metamorphic microdiamond. It is well known that microdiamonds from several UHP terranes have significant variations in their Raman spectra, which may reflect the difference of genesis (e.g., Perraki et al., 2009). However, Shimizu & Ogasawara (2014) compared Raman, photoluminescence (PL), and cathodoluminescence (CL) spectra of various diamonds in a tourmaline-rich quartzofeldspathic rock and demonstrated that some diamonds had suffered metamictization due to  $\alpha$ -particle emission from host zircon. On the one hand, diamonds in maruyamaite (K-dominant tourmaline) had a sharp Raman band that is similar to that of diamonds with a high crystallinity [full width at half maximum (FWHM):  $2\text{-}3\text{cm}^{-1}$ ]. On the other hand, diamonds in U-rich zircon (up to 0.15 wt.%  $\text{UO}_2$ ) showed broader and more downshifted Raman bands (FWHMs and peak positions varied up to  $9.3\text{ cm}^{-1}$  and  $1328\text{cm}^{-1}$ , respectively), with additional small peaks at  $\sim 1490$  and  $\sim 1630\text{ cm}^{-1}$ . The PL and CL studies also suggested that diamonds in U-rich zircon had been more metamictized. Therefore, it is emphasized that the effect of post-crystallization radiation damage should not be underestimated to discuss the genesis of microdiamond from its Raman spectra. To discuss whether radiation damage is a common phenomenon in metamorphic diamonds, a large number of Raman spectra of microdiamonds in various UHP rocks from the Kokchetav Massif, Kazakhstan were obtained. We report here that some diamonds in garnet also showed spectra with evidence of radiation damage.

Pelitic gneiss is the most abundant diamond-bearing rock in the Kumdy-Kol area of the Kokchetav Massif. Diamond in pelitic gneiss mainly occurs as inclusions in garnet, kyanite, and zircon. The main Raman peak of diamond in garnet and kyanite is broader and downshifted compared with that of non-irradiated diamond such as diamond in kimberlite or in maruyamaite (Shimizu & Ogasawara, 2014). FWHM of the main peak of diamond ranges  $4\text{-}8\text{ cm}^{-1}$  and shows various averages for different mineral composition of host rock. Most of peak positions are in the range of  $1331\text{-}1332\text{ cm}^{-1}$  but some microdiamonds have considerably upshifted peak up to  $1334\text{cm}^{-1}$ . No correlation was found in FWHM vs peak position plots. This contrasts with that of some irradiated diamonds which show a negative linear trend (Orwa et al., 2000; Shimizu & Ogasawara, 2014). However, additional subtle peaks appeared at  $1478$  and  $1637\text{ cm}^{-1}$ . In addition, a vacancy-related photoluminescence peak (at  $637\text{ nm}$ ; attributable to  $\text{N-V}^-$  center) was often observed in the Raman spectra. These facts indicate that some crystal defects derived from radiation also present in diamond in garnet, not only in diamond inclusion in actinide-rich mineral (e.g., zircon). Considering the absence of negative correlation between FWHM and peak position of the Raman peak, the Raman feature of diamond in garnet probably are controlled by combination effect of several factors such as radiation damage, residual pressure, and nitrogen impurities. It means that interpretation of spectroscopic characterization of metamorphic diamond is not quite simple. To adequately discriminate diamond populations by Raman spectroscopy, it is recommended to interpret Raman results in conjunction with other methods (FTIR, PL, CL, and TEM study, etc).

Keywords: microdiamond, radiation damage, Raman spectroscopy, ultrahigh-pressure metamorphism, crystal defect

## Eastern extension of the Dabie-Sulu UHP belt -constraints from bulk chemistry of high P/T rocks-

HAMABATA, Daichi<sup>1</sup> ; ISHIKAWA, Akira<sup>2</sup> ; UEKI, Kenta<sup>3</sup> ; TERABAYASHI, Masaru<sup>4</sup> ; OKAMOTO, Kazuaki<sup>1\*</sup>

<sup>1</sup>Saitama university, <sup>2</sup>The University of Tokyo, <sup>3</sup>JAMSTEC, <sup>4</sup>Kagawa University

It has been controversial for the eastern extent of the Dabie-Sulu UHP belt which is distributed in the boundary between the North China and the South China craton as a collision zone. It was accepted that the Hida belt (Unazuki metamorphic belt) is eastern extension of the Dabie-Sulu belt although the Unazuki belt suffered medium P/T type metamorphism at 250 Ma (e.g. Isozaki, 1997). However, recently two other high P/T metamorphic rocks (Yaeyama and Manotani-Higo metamorphic rocks) have been proposed as possible eastern extension of the UHP belt because metamorphic ages are comparable to the Dabie-Sulu UHP belt (Ishiwatari & Tsujimori, 2003; Osanai et al., 2006). The present study provides protolith information of the new candidates based on bulk major, trace and rare-earth element chemistry. We have systematically collected the metabasite from the pumpellyite-actinolite facies through blueschist facies to epidote-amphibolite facies in the Yaeyama metamorphic belt. Bulk chemistry clearly indicates that protolith of the metabasites in lower grade (PA and blueschist facies) are ascribed as Oceanic Island basalt whereas the highest grade metabasite (epidote amphibolite facies) is considered as N-MORB and E-MORB origin. In the Manotani-Higo belt, the Manotani metamorphic rocks overlie the Higo metamorphic rocks. The former preserves 180 Ma, high P/T metamorphic minerals whereas the latter was overprinted low P/T metamorphism at 90 Ma. The Manotani metamorphic rocks are mainly composed of metabasite with meta-chert, serpentinite and minor meta-pelite. We have collected the metabasites suffered blueschist/greenschist facies condition. Bulk chemistry suggests that the protolith is relatively Mg-rich and ascribed as OIB or oceanic Island Arc. In summary, the Yaeyama high P/T rocks are the product of subduction of oceanic plate. The Manotani-Higo metamorphic rocks were either Oceanic Island or Oceanic Island Arc origin and suffered subduction zone metamorphism.

Ref. Ishiwatari & Tsujimori (2003) *Island Arc*, 12, 190-206. Isozaki (1997) *Island Arc*, 6, 2-24. Osanai et al (2006) *Gondwana Research*, 9, 152-166.

Keywords: Dabie-Sulu UHP belt, eastern extension, medium P/T metamorphic belt, high P/T metamorphic rocks, bulk chemistry, metabasite