

The fundamental tool for locating new examples of ultra-high pressure metamorphism:
your eyes!

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In the space of just over 30 years ultra-high pressure (UHP) metamorphic rocks of continental origin, with characteristic indicators coesite and/or microdiamond, have gone from being an enigmatic, difficult to explain local feature of eclogite-bearing terranes to become an integral feature of numerous subduction-collision orogens the world over. The recognition of the over 100 km depths reached by crustal rocks as well as the extraordinary rates at which these rocks exhumed are now accepted features of modern studies in geodynamics. Surprisingly, however, in the present-day scientific world of phenomenal computer power and seemingly unlimited automated analysis and data production, the investigation of UHP rocks, including the search for possible new coesite, microdiamond or minerals recording even deeper subduction (e.g. K-Hollandite or Stishovite) still requires skills in fieldwork and optical microscopy: aspects that are fast disappearing from modern earth science curricula. The search for coesite in the Himalaya was initiated by geothermobarometric calculations using published analyses for phengite-bearing eclogite to indicate rocks that had potentially experienced coesite-depth pressures. The prediction of UHP conditions was confirmed after fieldwork in Pakistan unearthed fine-grained eclogites with multiple coesite inclusions (found optically and confirmed by micro-Raman) in omphacite. Soon after, the predicted UHP was also confirmed in the Indian Himalaya (Tso Moriri). In the Variscan Orogenic belt, typified by high temperature metamorphism and granulites, UHP metamorphism was not to be expected. However, an important UHP indicator is the widespread presence of garnet peridotite with granulites of granitic composition. With a knowledge of the optical microstructures from well documented microdiamond samples it was possible to work systematically through existing thin section collections of the granulites and identify inclusions in garnet, kyanite and zircon of microdiamond, and its breakdown product graphite, by reflected light microscopy. Again, micro-Raman was used to confirm these finds. In a third example, from the Norwegian Western Gneiss Region, left-over eclogite zircons from a geochronology study were mounted and polished and tiny rounded inclusions investigated by micro-Raman. In this study it was much harder to find coesite inclusions as they appear very similar optically to quartz, apatite and other phases and in addition the connection to the primary rock texture is lost. In summary, preserved UHP minerals make up only a tiny fraction of material collected even from well documented UHP terranes. Skills in the field (you must collect the right rock!) and skill on the microscope (you must learn the features of UHP minerals from good standard samples in order to find the phases in new rocks) are still the most reliable and efficient way to expand our database of UHP samples and advance our knowledge of these exciting rocks.

キーワード: UHP metamorphism, coesite, microdiamond, Himalaya, Variscan

Keywords: UHP metamorphism, coesite, microdiamond, Himalaya, Variscan

The origin of oriented mineral inclusions in garnet/clinopyroxene of UHP rocks: Insight from the TEM study
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The phase formed by a solid-state exsolution process generally occurs as oriented lamellae, plates, needles, or short prisms with definite crystal forms and follows specific crystallographic orientation relations (CORs) with the host mineral to reduce the kinetic barriers for nucleation and growth and also to minimize the interfacial and the strain energy. Accordingly, oriented inclusions to be categorized as exsolution products must be ascertained by rigorous crystallographic, energetics and mass balance examinations. Oriented mineral inclusions are known to occur in garnet and clinopyroxene of various ultra-high pressure (UHP) rock types, e.g. garnet peridotite, eclogites, metapelites, and gneisses, and are usually considered to be the exsolution products upon P-T decreasing and have been taken as important UHP indicators. Our TEM study in the past few years, however, showed that the geneses of such tiny oriented inclusions within UHP garnet/clinopyroxene are rather complicated. They could occur either as single-phase inclusions or multiple-phase inclusion pockets with specific phase-assemblage, following either single or multiple CORs, or even without any specific COR with the mineral host. These observations, along with the energetic and mass balance considerations, do suggest that these tiny oriented inclusions in UHP garnet/clinopyroxene might have various petrogenetic origins, including solid-state exsolution, co-precipitation, cleaving-infiltration-healing, and metasomatic alteration. Only through very detailed petrographic, chemical and crystallographic studies as demonstrated in our previous studies of the kokchetavite-bearing multiple-phase needles/prisms in clinopyroxene (Hwang et al., 2004; 2013a), the rutile needles in garnet (Hwang et al., 2007, 2014; Proyer et al., 2013), the ilmenite/spinel plates in clinopyroxene of garnet pyroxenite (Hwang et al., 2011), the orthopyroxene blades in peridotite garnet (Zhang et al., 2011; Hwang et al., 2013b), can the true origins of such oriented inclusions in UHP minerals be deciphered.

Hwang et al., 2004. *Contrib. Mineral. Petrol.*, **148**, 380-389. Hwang et al., 2007. *J. Metamorph. Geol.*, **25**, 349-362. Hwang et al., 2011. *Contrib. Mineral. Petrol.*, **161**, 901-920. Hwang et al., 2013a. *J. Asian Earth Sci.*, **63**, 56-69. Hwang et al., 2013b. *J. Metamorph. Geol.*, **31**, 113-130. Hwang et al., 2014. *J. Metamorph. Geol.*, DOI: 10.1111/jmg.12119. Proyer et al., 2013. *Contrib. Mineral. Petrol.*, **166**, 211-234. Zhang et al., 2011. *J. Metamorph. Geol.*, **29**, 741-751.

キーワード: oriented inclusion, ultra-high pressure rock, garnet, clinopyroxene, TEM
Keywords: oriented inclusion, ultra-high pressure rock, garnet, clinopyroxene, TEM

Unusual mineral inclusions in the Luobusa chromitite: Evidence of ultra-deep origin and recycled crustal materials

Unusual mineral inclusions in the Luobusa chromitite: Evidence of ultra-deep origin and recycled crustal materials

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Podiform chromitites in Luobusa ophiolite, southern Tibet, yield a wide variety of unusual minerals, including UHP minerals (micro-diamond, coesite, moissanite), highly reduced minerals (native elements, carbide, nitride, alloys), and crustal minerals (quartz, corundum, sillimanite, kyanite, zircon etc.). We reported unusual silicate lamellae (coesite, clinopyroxene and MgSiO₃ phase) exsolved from chromite using TEM analysis (Yamamoto et al., 2009), and unusual ancient crustal zircon separates from chromitites using LA-ICPMS and Laser-Raman analysis (Yamamoto et al., 2013). To deduce long history of mantle convection, micro-inclusions preserved in refractory minerals can provide potential mineralogical and geochemical evidence.

Coesite as an exsolution in chromite is diagnostic UHP evidence and clinopyroxene exsolution in chromite is possible evidence of former CF-type high-pressure polymorph of chromite (>380 km deep). Silicate exsolutions in chromites are restricted in the nodular- and massive-type chromites, and disseminated-type chromites have no exsolutions. Petrographically, nodular-type chromites with abundant silicate-exsolutions are gradually modified into disseminated-type chromites in their morphology. The characteristic of the disseminated-type chromite, such as their interstitial distribution, euhedral to subhedral morphology and absence of silicate-exsolutions, suggest their formation under the low-pressure magmatic conditions.

We have measured the U-Pb age of zircon grains separated from podiform chromitites. Spot analyses with LA-ICPMS, assisted by CL images gave a wide age range, from the Cretaceous to the Late Archean (ca 100 – 2700 Ma). Most of the ages are much older than those of the chromitite and ophiolite formation. Laser Raman analyses revealed that the zircons contain crustal mineral inclusions, such as quartz and K-feldspar, but lack mantle minerals (e.g., olivine, pyroxene, and chromite), suggesting that they had a crustal origin. From these results, we conclude that ancient crustal zircons in chromitites are xenocrysts that originated from continental materials that were brought into the upper mantle by ancient subduction processes, such as sediment subduction and subduction erosion.

We conclude that the podiform chromitites at the Luobusa retain evidence of their multi-stage development from ultrahigh-pressure environment to low-pressure magmatic processes, and tiny inclusions shielded by refractory minerals, such as chromite, diamond and zircon, record their prolonged history from the shallow crustal levels to the deep-mantle environments.

超高压变成岩研究と造山帯、マントルダイナミクス、地球の熱的物質的進化からの推測

Research of UHP metamorphism and implication to Orogeny, Mantle dynamics, and thermal material evolution of Earth

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The most important research results of UHP metamorphism and belts are as follows; 1) Continental crust can subduct down to 100-200km depth at least, suggesting the concept that only density controls the survival of TTG crust on the surface through time forever is wrong, which is thought to be common sense geologically. Theory of continental crust subduction leads the three layers model of continents on the Earth (Kawai et al., 2008). 2) UHP-HP belts is a thin unit less than 2km which is sandwiched by a paired faults at the top and bottom, indicating the tectonic intrusion of regional metamorphic belt caused by wedge extrusion due to slab breakoff or ridge subduction. This led the orogenic model by continent-continent collision. 3) Barrovian metamorphism is not a progressive metamorphism but retrogressed hydration product during the exhumation to the surface at mid-crustal level. Role of water is to control the material circulation within the Earth from the surface to the bottom of upper mantle. 4) UHP-HP belts appear on the surface of the Earth only after 630Ma. It indicates rapid change of subduction geotherm at the onset of Phanerozoic, which initiated the return-flow of seawater into mantle. This was a trigger of emergence of huge landmass to deliver huge amount of nutrients to the continental margin and created the paradise on continental shelf for metazoans and sea plants because the sunlight was shining down to the bottom of continental shelf. 5) Specifically, the spatial limit of equilibrium domain contributed to understand the species and amounts of light elements in the core, and material circulation of the Earth's interior.

沈み込み物質内超高压交代変成作用による大陸物質深部沈み込みの流体制御—コク
チェタフ超高压変成岩によるモデリング
Fluid control of deeply subducted continental materials and diamond formation by In-
traslab UHP metasomatism

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Deep continental subductions are an input for material cycling from surface to deep mantle. UHPM rocks mean the part of the direct evidence of this process. The Kokchetav UHPM rocks are the best samples and evidence to understand chemical processes in the subducting materials in global material cycling. During subductions, volatiles are carried into deep mantle together with major components and control the chemical reactions in subducting materials. Transportation of H₂O and CO₂, is the most important role of the deep continental subduction. Silicate rocks are H₂O reservoirs as hydrate minerals and carbonate and calc-silicate rocks are CO₂ reservoirs during subduction. The timings of dehydration in silicate rocks and decarbonation in carbonate and calc-silicate rocks are different. Dehydrations precede decarbonations by different P-T-V relations of CO₂ and H₂O, and H₂O play as a trigger to occur decarbonations in carbonate and calc-silicate rocks. Decarbonations are a CO₂ extraction from carbonate and calc-silicate rocks and are difficult to occur under dry conditions in P-T range of UHP metamorphism. The amount of H₂O infiltrating in carbonate and calc-silicate rocks controls the amount of CO₂ carried into the mantle. Poor H₂O supply means abundant CO₂ transportation into the mantle.

H₂O-bearing fluid plays an important role for diamond formation during subduction of continental materials. Diamonds form and dissolve in subducting materials through H₂O fluid. In UHP dolomite marble, diamonds formed at two different stages and 2nd stage growth was from H₂O fluid. The diamond at 2nd stage growth has light carbon isotope compositions, -17 to -27 ‰, whereas 1st stage diamond has -8 to -15 ‰. The light carbon of 2nd stage could be organic carbon in gneisses carried by fluid; dissolution of diamond in gneisses had occurred. H₂O fluid infiltration into dolomite marble caused the change of carbon solubility in fluid itself to precipitate abundant fine-grained (10-20 μm) diamonds quickly. Recently discovered sp² graphitic carbon inclusions in 2nd stage diamond suggest the fluid participation in diamond growth from H₂O fluid. Very large cubic diamond (max. 200 μm) in garnet-clinopyroxene rocks could be different fluid conditions; low oversaturation degree of carbon in fluid and slow crystallization, and led to low abundance of diamond.

In deeply subducting carbonate rocks, the abundant carbonate remains after decarbonations and are carried to the mantle. H₂O is stored in NAMs, which become new water carriers to the mantle. The amount of H₂O in carbonate rocks carried to the mantle is smaller than calc-silicate rocks because of small modal compositions of silicate minerals. In the case of calc-silicate rocks, for example garnet-clinopyroxene rocks of the Kokchetav, the modal compositions of carbonate is small; therefore, even a small amount of H₂O can decompose all amount of carbonate to form garnet and clinopyroxene. These NAMs contain several hundreds to 1,000 ppm order of water (OH and H₂O) as new water reservoirs and carriers. The modal compositions of H₂O-bearing NAMs control the potential of water transportation. UHP metasomatism with skarn mineral formation brings the swapping of H₂O carrier from hydrate minerals in silicate rocks to NAMs in calc-silicate rocks to expand the life of H₂O transportation into mantle much longer.

We can regard deep continental subduction as the transportation mechanism of H₂O and CO₂. CO₂ transportation is controlled by H₂O behavior in deeply subducted materials and poor amount of H₂O expands the volume of CO₂ transportation into the deep mantle as carbonate. Summarizing these, *Intraslab UHP metasomatism* was proposed and will be available for volatile transportation into the mantle. All these ideas were occurred from the research on the Kokchetav UHPM rocks. The author thanks Prof. Shige Maruyama, who gave me a great opportunity to study exciting materials, Kokchetav UHPM rocks and diamonds.

Keywords: UHP metamorphism, Intraslab UHP metasomatism, metamorphic diamond, fluid, Kokchetav Massif, deep continental subduction

ダイヤモンドと共存する新鉱物丸山電気石の発見と超高压変成岩中の電気石の多様性

Maruyamaite, a new K-dominant tourmaline coexisting with diamond: Significance of tourmaline in UHP rocks

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Maruyamaite is a new end-member species of the tourmaline supergroup (IMA 2013-123, Lussier et al., 2014). The ideal chemical formula of maruyamaite is $K(MgAl_2)(Al_5Mg)(BO_3)_3(Si_6O_{18})(OH)_3O$, which is the K-analog of oxy-dravite. This new mineral was first reported as a K-dominant tourmaline coexisting with microdiamond inclusions from the Kokchetav Massif, Kazakhstan (Shimizu & Ogasawara, 2005) and named in honor of Professor Shigenori Maruyama (Earth-Life Science Institute, Tokyo Institute of Technology, Japan), who led the Japan-U.S.-Kazakhstan cooperative project on Kokchetav ultrahigh-pressure (UHP) metamorphism. The K content in maruyamaite is up to 0.576 apfu (2.76 wt% K_2O). Currently, the occurrence of maruyamaite has been reported exclusively from the type locality (the Kokchetav Massif) and maruyamaite is a unique K-dominant tourmaline species. Moreover, no K-rich dravitic tourmaline has been found from other UHP terranes (Marschall et al., 2009). The rarity of K-dominant tourmaline is probably due to the large ionic radius of K with respect to the X-site of magnesian tourmalines.

The systematic chemical analysis of various tourmalines including maruyamaite in diamond-bearing Kokchetav UHP rocks combined with detailed inclusion mineralogy demonstrated that K in tourmaline decrease with pressure (and temperature) decrease (Shimizu & Ogasawara, 2013). For instance, the figure shows that microdiamond occurs only in K-dominant core (maruyamaite) and the surrounding low-K parts (K-bearing dravite or oxy-dravite) contain low-pressure minerals such as graphite and quartz. Maruyamaite or "K-dravite" component can form continuous solid solutions with other magnesian tourmalines up to ~58% of K in the X-site, with a close relationship to pressure. In particular, the limited occurrence of microdiamond in maruyamaite strongly indicates that K-dominant tourmaline is a UHP phase. Ota et al. (2008) concluded that partial melting of gneisses under UHP condition had formed the maruyamaite-bearing tourmaline-rich quartzofeldspathic rock from the high $\delta^{11}B$ values of maruyamaite, which is quite unusual for high-grade metamorphic tourmaline.

There had been no experimental constraint on K-incorporation in tourmaline until fairly recently, however, K-dominant tourmaline (up to 0.71 K apfu) has been synthesized for the first time by Berryman et al. (2014). They showed that K-dominant tourmaline is stable at UHP conditions (2-4 GPa). It means that K-dominant tourmaline including maruyamaite can be a new UHP indicator. K in tourmaline also is a potential geobarometer once partition coefficient of K and Na between tourmaline and mica or feldspar is experimentally determined. Another important constraint is that K-incorporation in tourmaline structure requires not only high-pressure but also very high K/Na conditions (Berryman et al., 2014). A number of studies (e.g., Hwang et al., 2005) have shown that K-rich fluid had been present at the Kokchetav UHP stages and played an important role for the formation of metamorphic diamond and other UHP minerals such as K-rich clinopyroxene. The experimental results were consistent with the interpretation of the occurrence and chemical analyses of the natural maruyamaite-bearing rock.

Four generations of tourmaline from K-dominant maruyamaite to K-free low-grade tourmalines were recognized in the Kokchetav UHP gneisses based on their chemical compositions and inclusion contents. The tourmalines record the retrograde history from a diamond-grade partial melting to the latest greenschist facies overprint. This interpretation further emphasizes the feature of tourmaline for an excellent geochemical recorder of metamorphic events and a sink of light element such as boron in deeply subducted crustal materials.

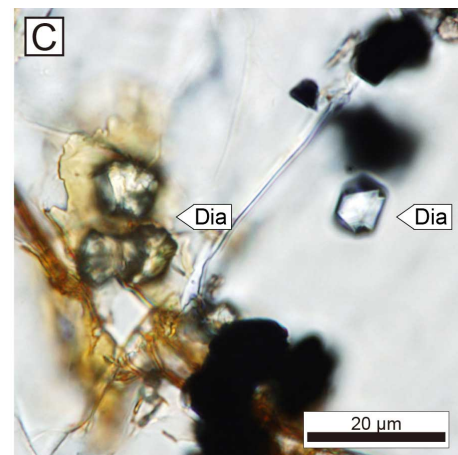
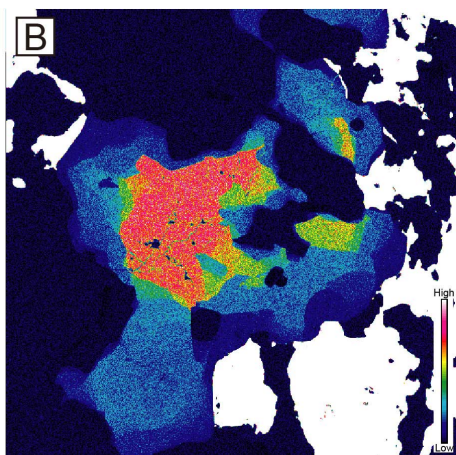
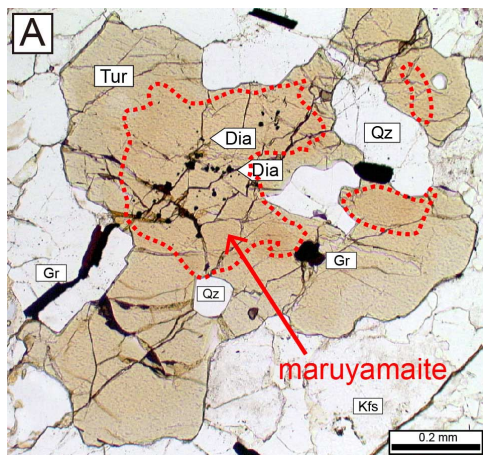
Figure captions: (A) Photomicrograph of K-bearing tourmaline showing maruyamaite as domains rounded by red broken lines; (B) K zoning of tourmaline; and (C) Microdiamond inclusions in maruyamaite.

Keywords: maruyamaite, tourmaline, diamond, ultrahigh-pressure metamorphism, Kokchetav Massif, inclusion

SMP10-06

会場:A05

時間:5月26日 16:45-17:15



沈み込みスラブ内超高压交代変成作用中の流体の挙動-ザクロ石単斜輝石岩中の水- Water behavior in diamond-bearing and diamond-free garnet-clinopyroxene rocks from the Kokchetav Massif

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Garnet and clinopyroxene are important nominally anhydrous minerals (NAMs) in the ultrahigh-pressure (UHP) rocks because they contain significant amounts of water as OH in their structures. Diamond-free and diamond-bearing garnet-clinopyroxene rocks from the Kokchetav Massif are mainly composed of garnet and clinopyroxene. In the rocks, UHP evidences are recognized; supersilicic titanite in diamond-free rock and diamond with three morphologies: cubic form (up to 200 μm), ball-shaped form (covered with graphite) (up to 150 μm), and fine-grain (ca. 10 μm) which was discovered recently (Takabe et al., 2014). The mineral assemblages are similar to skarn and suggest a metasomatic product in the subducted slab at UHP conditions.

Water contents of garnet and clinopyroxene by micro-FTIR proved water-rich environment of the formation of garnet-clinopyroxene rocks and support the metasomatic origin at UHP condition (Sakamaki et al. 2014). Garnet contains significant amounts of structural OH and nonstructural molecular H_2O ; 1727 ppm (wt. H_2O) of OH and 1592 ppm of H_2O at maximum in garnet of diamond-bearing, and 1655 ppm of OH and 1203 ppm of H_2O at maximum in garnet of diamond-free rock. In clinopyroxene, structural OH in exsolved phases and clinopyroxene host and nonstructural molecular H_2O were identified. Total water (OH+ H_2O) contents in clinopyroxene are up to 8215 ppm in diamond-free rock and 4384 ppm in diamond-bearing rock, respectively.

Bulk water contents in garnet-clinopyroxene rocks reach into 3000 ppm which is much higher than that of diamond-facies eclogite from the Kokchetav Massif (e.g., 460 ppm by Katayama et al., 2006). Our analytical results suggest that formation of garnet-clinopyroxene rocks by metasomatism during deep continental subductions can be a trapping process of H_2O -rich metasomatic fluids and carrying into deep mantle. Such NAMs in UHP skarn means the birth of new water reservoirs and carriers into the mantle, as swapped for hydrous minerals in gneisses. This idea was based on "Intraslab UHP metasomatism" model and its improvement.

In gneisses, which play as a main water reservoir at relatively early stage during the slab subduction, water is transported as OH in phengite to the mantle up to the stability limit of phengite. Phengite is gradually dehydrated and releases H_2O fluids during subduction. The dehydrated H_2O fluids from gneisses infiltrate into subducted materials themselves, such as carbonate and calc-silicate rocks, to occur decarbonations. As a result, the calc-silicate protoliths (silicate and carbonate mixtures) are transformed to skarn-like rocks, e.g., garnet-clinopyroxene rocks. Since garnet and clinopyroxene were formed by H_2O -mediated metasomatic processes at UHP condition, significant amounts of water were dissolved into NAMs, garnet and clinopyroxene. Such water-rich environments and UHP condition during "Intraslab UHP metasomatism" are indispensable for water dissolution to NAMs.

Deep continental subduction has an aspect of the input of silicate rocks (e.g., gneisses) as "wet" materials, and carbonate and calc-silicate rocks as "dry" materials into the mantle. Dehydrations in gneisses are the extracting process of H_2O from "wet" materials while decarbonations, which are the extracting process of CO_2 from "dry" materials, were triggered off by water supply from dehydrations of gneisses. Water infiltration into carbonate and calc-silicate rocks has three aspects: 1) water transportation from wet materials to dry materials ("dry" materials are getting a little "wet", and "wet" materials are getting "dry"), 2) formation of UHP skarn by metasomatism, and 3) hydration of NAMs by metasomatic fluid (the birth of new water carrier). These processes in "Intraslab UHP metasomatism" model are regarded as water transportation from "wet" materials to "dry" materials and expand the water input process into the mantle much deeper such as the mantle transition zone.

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

Zircon U-Pb, Hf isotope and trace element geochemistry: source of the Himalayan UHP eclogites

Zircon U-Pb, Hf isotope and trace element geochemistry: source of the Himalayan UHP eclogites

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To understand the magmatic source and the metamorphic evolution of Himalayan ultrahigh-pressure rocks in the Kaghan Valley of Pakistan, we conducted an integrated study of U?Pb age-dating, Hf isotope and trace element geochemistry on zircons. Zircon Laser Ablation-Inductively Coupled Plasma-Mass Spectrometer (LA-ICP-MS) U?Pb age between 143 and 277Ma was obtained from zircons in High-pressure (Group I eclogites) with a concordant age of 255 ± 9 Ma (MSWD = 0.87, 95% conf., and probability = 0.56). Identical age values were obtained from the core portions of zircons in felsic gneisses. The rims of the oscillatory zoned zircons in felsic gneisses yielded 47 Ma. In contrast, zircons in ultrahigh-pressure (Group II) eclogites yielded U?Pb concordant age of 48 ± 4 Ma (MSWD = 1.4, 95% conf., and probability = 0.18).

LA-ICP-MS trace element compositions from the same spots on zircons analyzed for U?Pb age show two contrasting compositional groups. Zircons in felsic gneisses are trace-element enriched at the core domains and have higher Th/U ratios (>0.5) indicating their magmatic origin. Zircons in Group I eclogites are also trace element enriched and have higher Th/U ratios (>0.5) indicating typical magmatic protolith signatures. In contrast, zircons in Group II eclogites have significantly lower contents of trace elements, lower Th/U ratios (<0.5) and are typical of metamorphic origin. The identical age values and trace element compositions of zircons in felsic gneisses and eclogites suggest their crystallization from a same magma source which potentially produced both mafic and felsic rocks intermittently. The rim portions in zircons from felsic gneisses grew during the Himalayan UHP metamorphism. Zircons found in UHP eclogites, with no age data representing the protolith event, were recrystallized from the formerly formed zircons during the Himalayan UHP eclogite facies metamorphism. The Hf isotope data of zircons, obtained from the same age spots, support our interpretation. The relatively narrow range in the $\delta^{177}\text{Hf}$, mostly positive, values (9.5 to -3.1 in zircons of Group I eclogites; +10.8 to -0.9 in zircons of Group II eclogites; and +15.6 to -2.6 in zircons of felsic gneisses), suggest their formation from a juvenile enriched mantle source.

キーワード: Himalaya, Zircon U-Pb age, Hf isotope, trace element, eclogites, Kaghan

Keywords: Himalaya, Zircon U-Pb age, Hf isotope, trace element, eclogites, Kaghan

コクチェタフ産超高压ザクロ石単斜輝石岩中のダイヤモンド—細粒ダイヤモンドへの立方体ダイヤモンドの二段階成長
Coarse-grained cubic diamond overgrowth on fine-grained diamond in the Kokchetav UHP garnet-clinopyroxene rock

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Using multilayered 2D laser Raman mappings, an overgrowth of coarse-grained (max. 200 μm across) cubic diamond on a fine-grained diamond (ca. 10 μm) 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⁺ laser (514.5 nm) and solid-state laser (487.9 nm). All diamonds showed a Raman peak at ca. 1332 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 cm^{-1} , 4.29-5.34 cm^{-1} , and (2) fine-grained: 1332.1-1335.2 cm^{-1} , 4.75-5.43 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 cm^{-1}) to the outside (1331.1-1331.6 cm^{-1}) and the values of FWHM decrease from the center (4.73-5.13 cm^{-1}) to the outside (4.21-4.81 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 2nd stage was probably crystallized from aqueous fluid.

References

Dobrzhinetskaya, L.F., 2012. Microdiamonds - frontier of ultrahigh-pressure metamorphism: a review. *Gondwana Research*, 21, 207-223.

Sakamaki, K. and Ogasawara, Y., 2014. Hydroxyl in clinopyroxene and titanite in a UHP diamond-free garnet-clinopyroxene rock from the Kokchetav Massif, northern Kazakhstan. *International Geology Review*, 56, 133-149.

Schertl, H.P., and Sobolev, N.V., 2013. The Kokchetav Massif, Kazakhstan: “Type locality” of diamond-bearing UHP metamorphic rocks. *Journal of Asian Earth Sciences*, 63, 5-38.

Sobolev, N.V., and Shatsky, V.S., 1990. Diamond inclusions in garnets from metamorphic rocks. *Nature*, 343, 742-746.

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

コクचेタフ産マイクロダイヤモンド中の炭素包有物の発見—超高压変成作用起源のダイヤモンド形成に伴う sp^2 結合炭素の介在
Diamond formation through intermediate sp^2 carbon from fluid in dolomite marble during the Kokchetav UHP metamorphism

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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 μm in diameter. These graphitic carbon inclusions are black under a microscope and their sizes are 1-5 μm 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 1st stage, and T-type and the rim of S-type crystallized at 2nd 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 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 cm^{-1} with 17.8 cm^{-1} , 1581.3 cm^{-1} with 17.7 cm^{-1} , and 1576.5 cm^{-1} with 16.5 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 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 cm^{-1}) and D2-band (ca. 1620 cm^{-1}), but these bands are usually weak rather than G-band.

The discovered sp^2 carbon inclusions were formed at the 2nd 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]).

References

- [1] Ishida, H., Ogasawara, Y., Ohsumi, K., Saito, A., 2003, *Journal of Metamorphic Geology*, Vol. 21, p. 515-522.
- [2] Yoshioka, N., Ogasawara, Y., 2005, *International Geology Review*, Vol. 47, p. 703-715.
- [3] Imamura, K., Ogasawara, Y., Yurimoto, H., Kusakabe, M., 2013, *International Geology Review*, Vol. 55, p. 453-467.
- [4] Akaishi, M., Shaji, K., Yamaoka, S., 2001, *Fluid/Slab/Mantle Interactions and Ultrahigh-P Minerals*, UHPM Workshop 2001, Waseda University, p. 26-30 (1A06).

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

後退変成時における Mg 付加作用 - Kokchetav 超高压変成帯 Kulet 地域に産する Mg に富むザクロ石 -
Mg-enrichment at retrograde stage of the Kokchetav UHPM -Pyrope-rich rim of garnet porphyroblasts from the Kulet area -

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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

カザフスタン共和国コクチェタフ変成帯に産する二種類の超高圧ザクロ石単斜輝石岩 Petrology of garnet-clinopyroxene rocks from the Kokchetav Massif, northern Kazakhstan

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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 μm), ball-shaped form (covered with graphite) (up to 150 μm), and fine-grained (ca. 10 μm) 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 K_2O 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 SiO_2 of ca. 50 wt.% while diamond-free rock contains significant amounts of CaO (33 wt.%) and 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 H_2O suggesting submicron fluid inclusions in garnet;

(Dia-free, no. XX16), OH: 360+ H_2O : 20 to OH: 1655+ H_2O : 1203 ppm (wt. H_2O)

(Dia-bearing, no. 25018) OH: 391+ H_2O : 294 to OH: 1165+ H_2O : 1218 ppm

(Dia-bearing, no. 24997) 0 to OH: 1727+ H_2O : 1592 ppm.

IR spectra of clinopyroxene show complex absorption bands of structural OH in clinopyroxene host and exsolved minerals, and nonstructural molecular H_2O . Bulk water (OH and H_2O) 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 H_2O -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

アリゾナ州ガーネットリッジからの含Na, OHパイロープガーネットの新たな発見
—コロラド高原下のマントル交代作用の証拠
Na and OH-bearing pyrope garnet - Evidence of mantle metasomatism by ancient oceanic
crusts underneath Colorado Plateau

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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 (Cr_2O_3 : 1-6 wt.%, Prp: 67-71mol%), 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, B₁: amphibole type, B₂: ilmenite type, B₃: black type, and B₄: clinopyroxene-amphibole type. B₁, B₃, and B₄ contain Na-amphibole lamella. B₁: 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. B₂: 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. B₃: 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. B₄: 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 H₂O-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 H₂O 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

アリゾナ州ガーネットリッジに産するガーネットの多様な化学組成及び包有物/離溶相—コロラド高原下部におけるマントル交代作用
Chemistry & inclusion/lamella mineralogy of garnet from the Garnet Ridge; Information of multi-stage mantle metasomatism

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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 Cr₂O₃ (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: B₁) with lamellae of Amp and Ca-enriched composition (Grs 12-26 mol%), B₂) with lamellae of Ilm and fluid inclusion, B₃) with dense lamellae of titanates and inclusions of Mgs and Dol, B₄) 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 metasomatisms 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 metasomatisms 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

変成ダイヤモンドのラマンスペクトルにおける放射線損傷の影響とその解釈 Radiation-damage-induced variations in Raman spectra of UHPM microdiamond

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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 α -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): 2-3 cm^{-1}]. On the other hand, diamonds in U-rich zircon (up to 0.15 wt.% UO_2) showed broader and more downshifted Raman bands (FWHMs and peak positions varied up to 9.3 cm^{-1} and 1328 cm^{-1} , respectively), with additional small peaks at ~ 1490 and ~ 1630 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 4-8 cm^{-1} and shows various averages for different mineral composition of host rock. Most of peak positions are in the range of 1331-1332 cm^{-1} but some microdiamonds have considerably upshifted peak up to 1334 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 cm^{-1} . In addition, a vacancy-related photoluminescence peak (at 637 nm; attributable to 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-
Eastern extension of the Dabie-Sulu UHP belt -constraints from bulk chemistry of high P/T rocks-

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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.

キーワード: Dabie-Sulu UHP belt, eastern extension, medium P/T metamorphic belt, high P/T metamorphic rocks, bulk chemistry, metabasite

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