

## Placing time constraints on a P-T-D evolution: insights from Lu-Hf garnet and U-Th-Pb monazite dating

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The best approach for understanding the tectono-thermal evolution of a crustal level is through reconstructing its pressure-temperature-deformation-time (*P-T-D-t*) evolution. Whereas *P-T-D* paths can be inferred from crystallization-deformation relationships, placing absolute time constraints on such paths remains challenging, especially because a link between major element-bearing index minerals and trace element-bearing geochronometers needs to be established.

We present the example of medium-grade metasedimentary rocks (Orlica-Snieznik Dome, European Variscan Belt) for which results of Lu-Hf garnet and U-Th-Pb monazite dating are linked with prograde and retrograde stages of the *P-T-D* evolution, respectively. On the macroscopic scale, a succession of three metamorphic foliations is recognized: initial subhorizontal S1, intermediate subvertical S2, and late subhorizontal S3. A garnet±staurolite assemblage is ascribed to the S1 foliation, whereas the S2 fabric is associated with staurolite demise producing a garnet-biotite-sillimanite/andalusite assemblage. Post-S2 garnet and cordierite blastesis is followed by chlorite growth during and after the formation of the S3 foliation. Garnet porphyroblasts show a peculiar zoning pattern with a linear Mn-Ca decrease in the allanite-bearing core, an inner rim of alternating Ca-Y- and P-rich annuli, and a Ca-poor outer rim. Monazite is found as subhedral aggregates at garnet rim, and lone matrix grains close to partially resorbed garnet, staurolite or apatite. Textural observations and modelling of the garnet composition suggest that the inner rim with Ca-Y-rich annuli reflects the allanite-to-monazite transition which occurred close to the staurolite isograd. In this inner rim, a Lu oscillatory zoning pattern coincides with the zone of Ca-Y-rich annuli. Since the inner rim dominates the Lu budget of garnet, the associated Lu-Hf garnet-whole-rock isochron age of  $344 \pm 3$  Ma is ascribed to *P-T* conditions of the staurolite isograd, i.e.  $\sim 5$  kbar/ $575$  °C in the S1 fabric. A subsequent temperature increase to peak conditions of  $\sim 5$  kbar/ $580-625$  °C in the S2 fabric is indicated by the Ca-poor garnet outer rim that reflects staurolite breakdown. LA-ICP-MS monazite dating yields  $^{208}\text{Pb}/^{232}\text{Th}$  ages defining a dominant group at  $313 \pm 2$  Ma and a secondary peak at  $328 \pm 2$  Ma. Based on monazite textures, these relatively young ages are ascribed to fluid influx during retrograde chloritization.

The short time span between prograde garnet growth ( $\sim 344$  Ma) and existing Ar-Ar cooling ages on micas ( $\sim 335$  Ma) points to a tectono-thermal event of about 10 Ma. Assumed high heating and cooling rates during this event are explained by the synchronous intrusion of granitoid sheets. Nevertheless, monazite ages indicate that a low-grade overprint occurred more than 20 Ma after peak conditions.

Keywords: P-T-D-t path, prograde garnet zoning, retrograde monazite

## Microdiamond - bearing UHP chromitite from the Higo Metamorphic Rocks, Central Kyushu, Japan

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Microdiamond-bearing ultrahigh-pressure (UHP) chromitite was newly found from a spinifex-textured metaperidotite in the Higo Metamorphic Rocks (HMR), Central Kyushu, Japan. This is the first finding of microdiamond from Japanese metamorphic rocks and the second finding in Japan following the first one from a mantle xenolith in a Cenozoic lamprophyre dyke in Shikoku<sup>1</sup>. The HMR represents a low P/T metamorphism of Cretaceous in age, however, the precursor HP or UHP metamorphism of ca. 250Ma has been inferred<sup>2</sup>. A great deal of debate has been done on whether or how the Dabie-Sulu UHP terrane extends eastward to the Korean Peninsula and also to Japan. The HMR is one of the candidates<sup>3</sup> for the eastern extension in Japan, but no definitive evidence has been given yet.

Metaperidotites occur in two localities in the HMR: one at Yamato Town in the biotite zone and the other in Matsubase Town in the garnet-cordierite I zone<sup>4</sup>. The metaperidotites from Matsubase Town show distinct spinifex-texture with decimeter-sized elongated olivine (mostly serpentinized) and enstatite. Those from Yamato Town shows either spinifex-texture or granular texture of finer grains (several mm to 1 cm across), and is strongly serpentinized. The metaperidotite bodies occur in mostly pelitic gneisses as small lenticular bodies about several ten meters in size, which are concordant to the gneissosity. The mineral assemblage of the metaperidotite is olivine (mostly serpentinized) + enstatite with secondary tremolite and antigorite. Talc occurs locally along the cleavage of enstatite. A podiform chromitite occurs in such a strongly serpentinized metaperidotite at Yamato Town as a nodular form of about 10 cm in diameter, in which we found many inclusions of microdiamond 1 to 10  $\mu\text{m}$  in size. We have made four thin sections, polished with colloidal silica, from one chromitite sample, and found many microdiamond inclusions in all thin sections. Microdiamonds occur both in chromite and in nickeline, and they are all monocrystalline. Many euhedral to subhedral grains (mostly 1  $\mu\text{m}$  in size) of microdiamond occurs in chromite, making several lines of aligned grains. Identification of diamond was carried out with an energy dispersive X-ray spectroscopy (EDS) analysis (carbon peak) and Raman spectroscopy with a He-Ne laser. We observed a Raman peak at  $1333.5\text{ cm}^{-1}$ , which is comparable to the peak ( $1332\text{ cm}^{-1}$ ) characteristic of diamond. They show no evidence of partial or total graphitization. The occurrence suggests that the striations represent healed cracks and that microdiamonds precipitated from a reduced C-O-H fluid<sup>5,6</sup>. Our finding presents a convincing evidence for the hypothesis that the Higo Metamorphic Rocks is an eastern extension of the Dabie-Sulu UHP terrane in Japan. The second implication of our finding is on the nature of UHP chromitite. Microdiamonds are found from several UHP metamorphic terranes<sup>5,6,7</sup>, however, microdiamond-bearing UHP chromitite has been found from ophiolites in non-UHP metamorphic terrane<sup>8</sup>, making the occurrence of UHP chromitite as an enigma<sup>9</sup>. The Higo UHP chromitite represents a deep subduction product as indicated by spinifex-texture in the host metaperidotite due to high pressure breakdown of antigorite (serpentine), instead of a product of mantle migration<sup>10</sup>. Therefore the origin of the UHP chromitite requires a specific interpretation in each case.

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Keywords: microdiamond, UHP chromitite, Higo Metamorphic Rocks, Ultrahigh-pressure metamorphic rocks, Spinifex-texture, Dabie-Sulu UHP terrane

## Grain Size Grading of Garnet in the Liesegang Metamorphism

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The very puzzling phenomena is that the grain size of metamorphic garnet shows apparently gradational in both basic and pelitic schists, for bulk chemistries of large grain and small - grain layers are not different with each other and for chemical zonings of large and small grains of garnet display very similar pattern. These facts suggest that the domain structure by diffusion and growth of garnet should be formed in the layer and the spacing of the domain changes gradually across the grain - size layering in the metamorphism.

The layering shows parallel to subparallel against the schistosity plane, suggesting the parameter changes uniaxially along the normal direction against the schistosity. The length scales of the grain size layering ranges from several to several ten cm, being likely to those of the compositional banding derived from metasomatism. Judging from these facts, it seems that the size grading process in the plate boundary metamorphism is governed by the diffusion, reaction and grain growth mechanism, that is the precipitation mechanism in the Liesegang bands. The precipitation in the Liesegang band is considered as the Cahn - Hillert - Cook process (1), which is characterized by the relation of average grain size, size distribution, width of the layer, and spacing distribution among grains.

In this paper, we would like to investigate these relations of the size grading of garnet in the subduction zone metamorphism.

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Keywords: grain size, grading, Liesegang, metamorphism

## Metamorphism of sodic pyroxene-bearing quartz schists from the Bizan area, Sambagawa belt, eastern Shikoku, Japan

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The Bizan area of the Sambagawa metamorphic belt is occurs in easternmost Shikoku, southwest Japan. The Bizan and Kotsu areas are located in the same tectonostratigraphic horizon, i.e. the Kotsu Formation in eastern Shikoku. The Kotsu Formation in the Kotsu-Bizan area is structurally overlying and underlying by the Kawata Formation and the Kawatayama Formation, respectively. The main rock types in the Bizan area include pelitic, basic and siliceous schists, with minor amounts of psammitic and calcareous schists (Iwasaki, 1963). Faure (1983) suggested a melange zone containing tectonic blocks of serpentinite, metagabbro and garnet-amphibolite (garnet-glaucophane schist) occurs along a ductile shear zone between spotted and non-spotted schist zones. Sodic pyroxene-bearing quartz schists consist mainly of quartz and phengite, with minor amounts of amphibole (Fgl, Mrbk, Rbk, Mkt, Wnc, Brs, Fbrs), garnet, Na-Ca pyroxene (hereafter sodic pyroxene) (aegirine, aegirine-augite and omphacite) and albite. Hematite, chlorite, and epidote occur occasionally. A schistosity is defined by preferred orientation of phengite and quartz.

Garnets are spessartine-rich in composition, show a growth zoning with decreasing spessartine ( $X_{Spss}$  0.82-0.35) and increasing almandine ( $X_{Alm}$  0.01-0.41) and pyrope ( $X_{Prp}$  0.03-0.09) from core to the rim and contain inclusions of phengite (6.84 pfu), epidote, hematite and quartz. The garnets are occasionally replaced by chlorite and biotite along cracks and at the rims. Amphiboles occurring as inclusions in porphyroblastic albite are compositionally zoned, with Fbrs and Brs cores and Rbk rims. Matrix amphiboles are Brs and Mkt core, Fgl mantle and Rbk and Mrbk rims, and contain inclusions of phengite (6.50-6.51 pfu), hematite and quartz. Sodic pyroxenes occurring as inclusions in porphyroblastic albite are aegirine, aegirine-augite and omphacite with  $X_{Jd}$  0.08-0.37 contents. Some of them are compositionally zoned, with aegirine-augite and omphacite cores ( $X_{Jd}$  0.34-0.37) to aegirine-augite and aegirine rims ( $X_{Jd}$  0.34-0.21). Matrix sodic pyroxenes are aegirine-augite ( $X_{Jd}$  0.09-0.27), decreasing  $X_{Jd}$  from cores (0.22-0.25) to the rims (0.22-0.17). Some other sodic pyroxenes in the matrix display increasing  $X_{Jd}$  from core to the mantle (0.13-0.19) and decreasing towards the rim (0.19-0.12). They contain inclusions of amphibole (Brs, Fbrs, Rbk), phengite (6.66-6.82 pfu), hematite and quartz, and are partially replaced by chlorite along their cleavages. Porphyroblastic albite crystals up to 2 mm across contain inclusions of garnet, amphibole (Brs, Fbrs, Rbk), sodic pyroxene ( $X_{Jd}$  0.10-0.37), phengite (6.57-6.76 pfu) and quartz. Matrix phengites show relatively higher in Si (6.33-6.98 pfu) contents than inclusions.

According to the occurrence of mineral assemblage the Kwata, Kotsu and Kawatayama Formation probably correlate with the albite-biotite zone of the Besshi area (Enami *et al.*, 1994). Jadeite content in the sodic pyroxenes are significantly higher in sodic pyroxene-bearing quartz schists ( $X_{Jd}$  0.08-0.37) than those of garnet-aegirine augite-alkali amphibole-quartz schist ( $X_{Jd}$  0.30) in the Bizan area (Iwasaki, 1963) and Asemigawa ( $X_{Jd}$  0.15-0.19), Besshi ( $X_{Jd}$  0.14-0.23) and the Sarutagawa area ( $X_{Jd}$  0.17-0.30) in the central Shikoku (Enami *et al.*, 1994). This higher jadeite content in sodic pyroxenes suggests metamorphic conditions in the Bizan sodic pyroxene-bearing quartz schists might be higher in pressure than those of the metamorphic zonation in the albite-biotite zone of the Sambagawa belt central Shikoku by Enami *et al.* (1994).

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Keywords: Sambagawa (Sanbagawa) metamorphic belt, Bizan area, quartz schist, omphacite, aegirine-augite

## Application of the Raman carbonaceous material thermometer to the Chichibu-Sanbagawa belt in the Kanto Mountains, Japan

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The structure and tectonic history of the Chichibu-Sanbagawa belt have been investigated by the lithological structure, radiolarian age, radiometric age, deformation microstructural analysis, and X-ray diffraction analysis of carbonaceous material (CM). The structural discontinuities (nappe boundaries) within the Chichibu-Sanbagawa belt are proposed in several studies (e.g., Shimizu 1988, *J.Geol. Soc. Japan*; Isozaki & Maruyama 1991, *J. Geogr.*; Hirajima *et al.* 1992, *J.Geol. Soc. Japan*). However, the boundary between the Chichibu and Sanbagawa belts and their structural relationship are still under debate. In addition, the thermal structure was not well investigated because the geothermometer that can be applied over the temperature range of the Chichibu and Sanbagawa belts was not available. Recently, several studies proposed the geothermometers applying the Raman spectroscopy. Kouketsu *et al.* (2014, *Island Arc*) analyzed the CMs with a wide range of crystallinity, from amorphous carbon to well-crystallized graphite, in sedimentary and metamorphic rocks and proposed a new Raman CM geothermometer. By using this technique, we evaluate the peak temperatures of the rocks in the Chichibu and Sanbagawa belts in the Kanto Mountains, which is the type locality of these belts.

We investigated the mudstone, sandstone, and pelitic schist taken from the Kannagawa, Sanbagawa, and Ayukawa River districts in the Kanto Mountains, Gunma Prefecture. In the studied area, the accretionary complexes of the Northern Chichibu belt are distributed in the south, crystalline schists of the Sanbagawa belt are distributed in the north, and the Mikabu greenstones are exposed between them. The Chichibu belt is divided into three units: Kamiyoshida, Manba, and Kashiwagi units, in descending structural order (Shimizu & Yoshida 2004, *Island Arc*). The Sanbagawa belt is divided into three metamorphic zones: chlorite, garnet, and biotite zones, in order of ascending metamorphic grade (Yano & Tagiri 1998, *J.Geol. Soc. Japan*). The strata gently dip to the north and the metamorphic grade monotonously increases towards the lower structural level.

The Raman spectra of CM in mudstone and sandstone taken from the Chichibu belt include broad peaks that are characteristic of the amorphous carbon structure. The temperatures of most samples estimated by full width and half maximum (FWHM) of the D1-band are around 260-300 °C. Several CMs in the rocks near the Mt. Nishi-Mikabo show the temperature higher than 300 °C.

The intensities of Raman spectra of CM in the Sanbagawa schists are one order weaker than those in the rocks taken from the Chichibu belt. The D4-band, which is the characteristic peak in amorphous carbon, is not observed. Instead, G-band, which is the characteristic peak in well-crystallized graphite, becomes the most prominent peak at higher-grade zone. The metamorphic temperatures are estimated by using the FWHM of D1- and D2-bands and area ratio (R2) of CM Raman spectra. The metamorphic temperatures of the samples are estimated around 360-400 °C, 420-450 °C, and 460-510 °C in the chlorite, garnet, and biotite zones, respectively.

The temperatures estimated from CM show the gap of several tens of degrees or more between the Chichibu and the Sanbagawa belts. Further sampling and analysis will be proceeded.

Keywords: Raman spectroscopy, Carbonaceous material, Geothermometer, Chichibu belt, Sanbagawa belt, Kanto Mountains

## Fission track and U-Pb zircon ages of psammitic rocks from the Harushinai unit of the Kamuikotan belt, Hokkaido

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In order to discuss exhumation processes and mechanisms for high-*P/T* type metamorphic rocks, it is necessary to obtain correct informations on pressure-temperature-time paths of these rocks from sedimentation to exhumation through maximum burial. We conducted coupled fission-track (FT) and U-Pb dating on detrital zircon grains in two psammitic rock samples collected from the Harushinai unit of the Kamuikotan metamorphic rocks using a Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). The results indicate that the concordant zircon U-Pb ages greatly vary between 1980-90 Ma. Among them, the youngest U-Pb age cluster (*c.* 110-90 Ma) is dominant, yielding the weighted mean ages of Albian ( $100.8 \pm 1.1$  and  $99.3 \pm 1.0$  Ma with  $2\sigma$  errors) for both samples. According to an oscillatory zoning of igneous origin without any overgrown rims in the analyzed zircon, the zircon U-Pb ages were not reset by the high-*P/T* type metamorphism, and hence the youngest U-Pb ages indicate the upper bound of sedimentary ages. On the other hand, the zircon FT data show the spectra with a single peak age at 100-90 Ma, which are comparable with the youngest U-Pb age cluster. The fact indicates that these zircon FT ages were once reset at *c.* 100 Ma due to an intense igneous activity at the provenance, but have not been essentially reset since the sedimentation. The scenario is supported by the temperature conditions slightly less than those of brittle-ductile transition of quartz (*c.* 300 °C, also closure temperature of zircon FT) estimated from the microstructures in deformed quartz detrital grains constituting the psammitic rocks. Combining these results with the previously reported K-Ar ages of white mica, it is inferred that Harushinai unit was deposited after *c.* 100 Ma, dragged down to the maximum depth, and further affected by a localized thermal overprint during exhumation (*c.* 58 Ma).

Keywords: Kamuikotan metamorphic rocks, zircon, U-Pb ages, Fission track ages, deformation microstructure

## Shape evolution of spinel grains in the Horoman Peridotite Complex, Hokkaido

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We present the evolution of spinel grains in the Horoman Peridotite Complex, Hokkaido. For deformation under differential stresses at high temperature conditions, both diffusion processes including diffusion creep and annealing process and dislocation creep will affect shape change of a crystal inclusion (Okamoto and Michibayashi, 2005 JGR). Grain size and grain shape are related to the shape change of the crystal with respect to given temperature and differential stress conditions. We applied this theory to spinel grains in the Horoman Peridotite Complex, Hokkaido. As a result, grain shapes of coarser spinel grains more than 100 micron are dominantly controlled by dislocation creep, whereas those of smaller spinel grains less than 100 micron are influenced by both diffusion processes and dislocation creep. Moreover, we found that grain shapes of the smaller spinel grains can be only explained by post-tectonic annealing process after their intense deformation. Our result will provide a new insight to understand the deformation processes in mantle.

Keywords: spinel, grain shape, diffusion process, dislocation creep, Horoman

## Verification of ultra-low strain rate effect from microstructural observation on naturally deformed olivine

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Kitamura et al. (1986) and Ando et al. (2001) reported Fe concentration on dislocation core in naturally deformed olivine. They suggested that compositional heterogeneity is formed by Cottrell atmosphere of solute atoms. This phenomenon is well known in the realm of metallurgical science, and only occurs during dislocation creep at very low strain rate condition. The presence of Cottrell atmosphere has a pinning effect on dislocations and prohibits their movements. As a consequence, plastic behavior of materials is drastically changed in the presence of Cottrell atmosphere. On the basis of this compositional heterogeneity, they demonstrate that the study of ultra-low strain rate effect on olivine plasticity is very important to understand the dynamics of the upper mantle.

With this background, the purposes of the present research are: (1) to confirm whether the Fe concentration on dislocation core is a common phenomenon in deformed olivine grains of mantle-derived peridotite, (2) to verify the deformation condition at which Fe concentration was occurred, from the microstructural observation of each studied peridotite samples, (3) to clarify the exact mechanism of Fe concentration, namely Cottrell atmosphere or pipe diffusion. The studied peridotite samples are xenoliths from basalt (Takashima, Megata, Kurose and Salt Lake), and alpine rocks (Uenzaru and Horoman). The techniques employed for the present study include optical microscopy, EPMA, SEM-EBSD, TEM and ATEM.

The main results are as follows:

- 1) Fe concentration on dislocation core in all olivine samples is detected, which suggests that it is common phenomenon in mantle peridotite.
- 2) The mechanism of Fe concentration on dislocation core in olivine grains is preferably Cottrell atmosphere than other phenomena such as pipe diffusion. However we need to carry out more careful and detailed observations to confirm it.
- 3) The microstructural observations indicate that the all peridotites preserve the deformation characteristics developed at the upper mantle. This fact suggests strongly that the Fe concentration on dislocation core in olivine grains occurred in the upper mantle condition.

Ando et al. (2001) *Nature*, 414, 893; Kitamura et al. (1986) *Proc. Japan Acad.*, 62, 149.

Keywords: Olivine, Cottrell atmosphere, Dislocation creep



## The relationship between microstructures and metasomatism preserved within coarse granular peridotites derived from Kaap

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Kimberlite was generated in deep upper mantle (70-250km) beneath craton and subsequently ascended to surface rapidly. Peridotite xenoliths, which were entrained by kimberlite, record composition and texture formed in upper mantle beneath the craton. We studied coarse granular peridotites obtained from Kimberley pipe, South Africa, as they have a few studies in terms of microstructural development, presumably because of very coarser grains. We performed mineral crystal-fabric analyses of the coarse granular peridotites in order to understand the structure of the cratonic lithosphere. The peridotites consist mostly of olivine and orthopyroxene with clinopyroxene, garnet and a minor amount of spinel and phlogopite. The crystallization of clinopyroxene appears to be associated with melt metasomatism, whereas that of phlogopite could be associated with hydration metasomatism. Garnet grains occur commonly with kelyphite consisting of fine-grained orthopyroxene, clinopyroxene and spinel, indicating that these peridotites could have been uplifted above the phase boundary between garnet peridotite and spinel peridotite stability fields. Although both foliation and lineation are not commonly identified because of coarse granular texture, olivine crystal fabrics are characterized by a single maximum of [010] with single maxima or weak girdles of [100] and [001]. We found that the intensities of olivine and orthopyroxene crystal-fabrics are correlated to the modal composition of clinopyroxene and phlogopite. It suggests that the melt metasomatism weakened crystal-fabrics, whereas the hydration metasomatism intensified crystal-fabrics. As a consequence, the metasomatism could result in the development of different types of microstructures in the peridotites and may weaken the craton lithosphere.

Keywords: kimberlite, peridotite, garnet, olivine, craton, crystal-fabrics

## Corona-forming reaction in the Lutzow-Holm Complex, East Antarctica at Ongul Island

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### [Introduction]

Corona is a microstructure that aggregate of one or several species of mineral surrounds another mineral. This suggests that corona was formed by the reaction between the interior mineral and the matrix minerals (Passchier and Trouw 1996). Estimating this reaction enables us to know which component transferred and how temperature and pressure changed. In this study, we estimated corona-forming reaction by describing the microstructure and chemical composition of a corona in the Lutzow-Holm Complex at Ongul Island.

### [Geological Outline]

In the Lutzow-Holm Complex, metamorphic grade increases from amphibolites facies in the northeast to granulite facies in southwest (Hiroi et al., 2006). The granulite facies metamorphic rocks are widely distributed throughout East Ongul Island. The rock types are mainly garnet gneiss and hornblende gneiss (Shiraishi et al., 1994). Ultramafic rocks occur as thin layers in the garnet gneiss. The ultramafic rocks analyzed in this study are composed mainly of hornblende and porphyroblasts of garnet. Corona structure forms around the garnet.

### [Microstructure]

In the ultramafic rocks, hornblende-rich domain and plagioclase-rich domain occur. Both domains consist of hornblende, plagioclase, brown biotite and orthopyroxene. The corona consists mainly of green biotite and plagioclase, and occurs around the garnet. Plagioclase in the matrix and the corona has twin and chemical zoning. Garnet porphyroblast (about 15mm diameter) shows concavo-convex shape. In the embayed part of garnet, biotite tends to occur with long axis is at right angles to garnet surface.

### [Chemical Composition]

Garnet; Rim shows higher Fe and lower Mg than the interior.

Plagioclase; Ca/(Ca+Na) increases in the order of Pl-rich domain, Hbl-rich domain and corona. Ca/(Ca+Na) in every domain increases from core to rim.

Biotite; Mg/(Fe+Mg) decreases in the order of Hbl-rich domain, Pl-rich domain and corona. Rim in every domain shows lower Al than the core.

Hornblende; Hbl-rich domain shows higher Al and Mg/(Fe+Mg) than Pl-rich domain. The rim of both domains shows higher Al than the core.

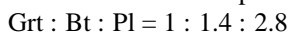
Orthopyroxene; Composition is almost homogeneous within the domain.

### [Discussion]

The compositional difference between core and rim of each mineral in the matrix can be regarded as growth zoning. We used the rim-composition in each domain to estimate the corona-forming reaction. The average of analyses was used for plagioclase and biotite in the corona and for garnet. The corona-forming reaction employing the compositions of Hbl-rich domain was given as follows.



On the other hand, the reaction using the compositions of Pl-rich domain expects garnet as products, which is inconsistent with the observation that garnet was consumed. This suggests that K is supplied from the outside through fluid during corona formation. We also compared volume of left side minerals, that is,



Garnet is minimum in amount. Nevertheless, corona formed around garnet. This suggests that diffusion of component from garnet controlled the rate of the reaction.

Keywords: corona, East Antarctica, Lutzow-Holm Complex

## Possible tectonic models before, during and after mylonitization in the Sor Rondane Mountains, East Antarctica

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The deformational history in the Sor Rondane Mountains (SRMs), eastern Dronning Maud Land (DML), East Antarctica, is divided into 13 stages (D1?D13). The tectonic regime varied frequently from extension (D3?D4) to layer-normal compression and layer-parallel extension (D5), to compression (D6), top-to-the S shearing (D7), top-to-the SE shearing and sinistral strike-slip (D8), compression (D9?D11), and ?nally extension related to dextral shearing (D12?D13). In this paper we discuss change in deformation and P-T conditions before, during and after the D7-D8 mylonitization, using mineral textures, assemblage, compositions and microstructures of D7 and D8 mylonites.

Garnet porphyroclasts of the D7-D8 mylonites include high-Ca mantles and crenulation microfolds defined by sillimanite fibrolites. The high-Ca mantles of garnets and their plagioclase inclusions in the mylonites imply an increase in pressure before the D7-D8 mylonitization. S-tectonites having a dominant planar fabric were formed before the D7-D8 mylonites and after the high-Ca mantles of the garnets. The planar fabric (foliation) of the S-tectonites is produced by fan-shaped arrangement of sillimanite and biotite grains. The sillimanite and biotite grains were formed by breakdown of garnet. Most of the sillimanite and biotite grains have been rotated and folded by the D7-D8 mylonitization. The D7-D8 mylonite foliations are parallel to the planar fabric of the S-tectonites. The S-tectonites indicate a flattening type of strain and resulted from the layer-normal shortening after the increase in pressure and before the D7-D8 mylonitization. kyanite-quartz porphyroblasts and randomly oriented crystals of sillimanite/kyanite and biotite were formed after the D7-D8 mylonitization. The randomly oriented crystals of sillimanite/kyanite and biotite resulted from the breakdown of garnet porphyroclasts of the D7-D8 mylonites. The kyanite-quartz porphyroblasts accompany leucogranite veins cutting the D7-D8 mylonite foliations. The randomly oriented crystals and porphyroblasts imply non-deformational conditions after the D7-D8 mylonitization and D9 folding.

Three possible tectonic models for D7 and D8 mylonite-forming events before the D9 deformation can be considered as follows: extensional tectonic model, positive flower structure model and rotated mylonite model. In the former model, D7 and D8 indicate major extensional tectonic activity in the southern part of the East African and Antarctic Orogen (EAAO) before the Pan-African compressional event, and after the 650-600 Ma peak of metamorphism. In the latter two models, D7 and D8 mylonites may have resulted from the compressional events. In the positive flower structure model, the SRMs are the southern half of the E-trending positive flower structure. The flower structure model needs top-to-the N shear zones to the north of the SRMs. In the rotated mylonite model, the present S-dip of the D7 and D8 mylonites results from the rotation and folding of originally N-dipping reverse (top-to-the S-SE, normal-sinistral shear, present day coordinates) mylonites. The Pan-African compressional event resulted in the formation of upright folds with horizontal axes that curve along the coastline in central to eastern DML during the D9 deformation that took place between 600 and 560 Ma. The coastline-parallel fold axes and subvertical axial-planes correspond to the X-axes and the XY-planes, respectively, of strain ellipsoids that were progressively rotated counterclockwise toward the central parts of a sinistral shear zone. Therefore, the curved fold axes and axial-planes suggest the EAAO acted as a zone of sinistral transpression during the collision of parts of East and West Gondwana.

Keywords: S-tectonite, flattening, mylonitization, Sor Rondane Mountains, Gondwana, East Antarctica

## Significance of multi-stage chloride brine activity- An example from Sor Rondane Mountains, East Antarctica

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It has been gradually recognized chloride brine potentially plays an important role in large-scale mass transfer during high-grade metamorphism without partial melting. This is because brine is a powerful solvent, can coexist with CO<sub>2</sub>-rich fluid under the granulite facies conditions and has low-H<sub>2</sub>O activity (Newton & Manning, 2010; Heinrich et al., 2004). In natural observation, evidence for the presence of brine is often found as fluid inclusions. In metamorphic rocks under granulite facies conditions, however, brine inclusions are only rarely found (Markl & Bucher, 1998). This is partly because brines have a high mobility due to their low viscosity and low wetting angle (Watson & Brenan, 1987; Holness, 1997).

On the other hand, hydrous minerals such as biotite (Bt), hornblende (Hb) and apatite can record the  $f_{H_2O}/f_{HCl}$  of the last equilibrated Cl-rich fluid as their mineral compositions. In order to understand the metamorphic fluid activity using these minerals, *P-T* condition under which these minerals equilibrated with a fluid as well as the crystallographic requirements for these minerals to record the fluid composition should be known (e.g., Makino, 2000). However, there still are a lot of unsolved issues about brines, for example, cations transported in the fluid, *P-T* condition and areal scale of brine activity, and its origin (Newton et al., 1998).

In order to understand the multiple brine activities and the cation composition in brines, two meta-mafic gneisses are studied in detail in Brattnipene, Sor Rondane Mountains (SRM), East Antarctica.

In a Grt-Bt-Hb gneiss, Cl-rich Bt is exclusively included in garnet (Grt). Bt, Hb, and cummingtonite (Cum) in the matrix are Cl-poor. These compositional differences imply that Bt included in the Grt formed under the presence of chloride brine and Cl-poor fluid infiltrated after Grt formation. Grt is enveloped by the gneissosity defined by the arrangement of Cum overgrown by Hb, and Bt. Therefore, chloride brine activity predated or was simultaneous with the penetrative gneissosity formation in this area. After considering the effect of Mg-Cl avoidance rule and compositional change during retrogression, the geothermobarometry (Holdaway, 2000; Wu et al., 2004) gave 650 < *T* < 800 °C and 0.96 GPa for the peak *P-T* condition of this sample. The Cl-rich Bt entrapment was probably predated or simultaneous with the attainment of this *P-T* condition.

In a Grt-Opx-Hb gneiss, ca. 1cm-thick Grt-Hb vein cut the penetrative gneissosity in this area. Cl-content of Hb and Bt, and K-content of Hb decrease with the distance from the vein center and become constant at ca. 1.6 cm from the vein center. Plagioclase present next to the vein has a core (An<sub>55</sub>) and mantle (An<sub>68</sub>) which is sharply overgrown by Na-richer rim (An<sub>51</sub>). Plagioclase in the vein is An<sub>51</sub> without zoning, and development of Na-richer rim gets thinner with a distance from the vein. Therefore, the Grt-Hb vein was probably formed by NaCl-KCl brine infiltration. This is also supported by the isocon analysis of whole-rock chemistry determined for wall rock of the vein. *P-T* condition of the vein formation is estimated as 720 °C and 0.70 GPa (Holdaway, 2000; Wu et al., 2004).

*P-T* conditions of multi-stage chloride brine activity, cation composition of the brine, and outcrop-scale pathways of the brine are constrained in SRM from these two gneisses. From the pelitic gneisses in SRM, Cl-rich fluid or melt activity with a linear distribution over 200 km has been reported (Higashino et al., 2013). Additionally, this study revealed that the brine activity in SRM is not controlled by the lithology or specific deformational stages. It is clear that chloride brine in SRM was not a result of *in situ* fractionation through the selective consumption of H<sub>2</sub>O in the fluid (Kullerud, 1995), but substantial amount of brine was actually moving, and was playing an important role in mass transfer.

Keywords: NaCl-KCl brine, fluid infiltration, continental collision zone, Sor Rondane Mountains

## Rate-limiting process and degree of disequilibrium of garnet-forming reaction

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Water released by dehydration reaction in metamorphic rocks will take a major role in rheology, mass transport, and reactivity of metamorphic rocks. Rate-limiting process of the dehydration reaction can be divided into the following three steps, such as reaction at interface, diffusion, and heat-flow. Garnet is one of the common minerals produced by dehydration reaction in metamorphic rocks. The rate-limiting process of garnet-forming reaction is usually assumed to be diffusion-controlled reaction. However, there are few cases where clear evidences for diffusion-controlled reaction were proposed. In addition, degree of disequilibrium of the diffusion-controlled reaction is not well known. Here, I report evidence of diffusion-controlled reaction and estimation of degree of disequilibrium of garnet-forming reaction in the Tsukuba Metamorphic Rocks.

Garnets in the Tsukuba Metamorphic Rocks are formed by the dehydration reaction of biotite + sillimanite + quartz = garnet + cordierite + K-feldspar + water. Biotite-depleted region surround the irregular shaped garnet. The depleted region of reactant is typically expected for diffusion-controlled reaction, but is rare for natural garnet-forming reaction. Irregular shape of garnet is also expected for diffusional instability of growing interface (Mullins & Sekerka, 1963). These sets of observations strongly suggest that the garnets were formed by diffusion-controlled reaction.

Spherical shape of growing particle under diffusion-controlled reaction becomes unstable due to diffusional instability, but interfacial energy will reduce the instability. Using spherical harmonics function, instability of small perturbation from spherical shape can be evaluated. Assuming interfacial energy of garnet, dominant wavelength in unstable regime is predicted with degree of super-saturation under diffusion-limited reaction. Dominant wavelength of the irregular garnet suggests that degree of super-saturation is less than 0.1. This value can be translated to degree of disequilibrium temperature with entropy change of the garnet-forming reaction. The disequilibrium temperature  $\Delta T$  is less than 5 °C, and is very small. This small value of disequilibrium temperature suggests that spherical or euhedral garnets that are more common than irregular garnets, should be produced near equilibrium condition. Otherwise, such common spherical or euhedral garnets should be produced by interface-controlled reaction associated with influent fluid.

Keywords: garnet, dehydration reaction, disequilibrium, metamorphism, metamorphic rock, metamorphic reaction

## FLUID RELATED ORIGIN OF SILLIMANITE VEINS IN POLYMETAMORPHIC ROCKS FROM THE RYOKE BELT, JAPAN

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In the polymetamorphic area, it is important to distinguish the effect of each metamorphism in order to appreciate the evolution of thermal structure of the area. Some authors have successfully distinguished the regional metamorphism from the postdating contact metamorphism (e.g. Miyake et al., 1992), but studies dealing with a fluid activity during polymetamorphism is not sufficiently available. Veins consisting of fibrous sillimanite (Sil) in a contact metamorphic aureole have been previously interpreted as a result of fluid activity (e.g. Johnson et al., 2003).

In Kasagi area (Kyoto, Japan), Ryoke metamorphic rocks are widely exposed and main lithology is pelitic and psammitic schists and gneisses. Younger Ryoke granites discordantly intrude to the metamorphic rocks and, therefore, the regional metamorphic rocks are overprinted by the heat (Ozaki et al., 2000) and fluid flux from the granites. This area belongs to the Sil zone that is defined by the presence of Sil in the pelitic lithology (Ozaki et al., 2000) whose origin has not been discussed in detail.

However in this area, fibrolite bundles are often observed to cross-cut the gneissosity formed by the regional metamorphism and it seems difficult to explain their formation during the regional metamorphism. In this study, we report the mode of occurrence of Sil veins emanating from the granite into psammitic gneiss and discuss the fluid-related origin of them.

The studied psammitic gneiss containing Sil veins is collected from the Sil zone near the granite intrusion contact. Ryoke granite intrudes discordantly to the gneissosity of this sample, and the Sil vein subparallel to the gneissosity emanate from it. The Sil vein consists of fibrolite and retrograde muscovite (Ms) replacing it. Quartz (Qtz) in the matrix near the vein are coarser-grained and they include fibrolite grains. The amount of fibrolite included in the Qtz decreases as a distance from the Sil vein increases. Fibrolite is present in veins and Qtz grains. Fine, retrograde Ms after fibrolite is present along grain boundaries in the matrix. Although plagioclase (Pl) is a common constituent mineral in the matrix, it is almost completely absent near and in the Sil veins. K-feldspar is absent in the studied sample, but instead, retrograde Ms cutting the schistosity is abundant in the matrix.

Cathodoluminescence (CL) observation of the microstructures around the Sil veins revealed that the brightness of CL signal of Qtz grains increases as the distance from the Sil vein increases. That is, Qtz grains near the vein or including Sil are dark under CL observation. In particular, part of a single Qtz grain including more fibrolite grains appears dark under CL image.

From the observation of microstructural relationships described above, we consider that Sil veins were formed by the fluid released from the Ryoke granite. Formation of fibrous Sil by the action of mobile hydrogen ions on pre-existing minerals has been previously discussed (Vernon, 1979). Moreover, experimental work has shown that Al<sub>2</sub>SiO<sub>5</sub> minerals and Ms can be produced by the action of acidic, aqueous solutions on various common silicate minerals (Burnham, 1967). In this study, fibrolite is present in veins and Qtz grains and the amount of fibrolite crystals included in the Qtz crystals decreases as a distance from the vein increases. Pl is absent in and at the vicinity of the veins. From these pieces of observation, a fluid from the granite would have reacted with the matrix to dissolve Pl and to form coarser-grained Qtz and fibrolite bundles simultaneously. Thermodynamic calculation using SUPCRT92 (Johnson et al. 1992) has revealed that infiltration of the aqueous fluid with low Na<sup>+</sup>/H<sup>+</sup> and K<sup>+</sup>/H<sup>+</sup> ratio can destabilize Pl and stabilize Sil under the presence of Qtz at 3 kbar, 600°C. Therefore, Sil in this study is not regional metamorphic in origin, but is probably a result of fluid infiltration during a contact metamorphism by the Ryoke granite.

Keywords: fibrous sillimanite, Ryoke belt, fluid-related origin, polymetamorphism