

Possible polymetamorphism and brine infiltration recorded in the garnet-sillimanite gneiss, Skallevikshalsen, Lützow-Holm Complex, East Antarctica

\*Tetsuo Kawakami<sup>1</sup>, Tomokazu Hokada<sup>2</sup>, Shuhei Sakata<sup>1</sup>, Takafumi Hirata<sup>1</sup>

1. Graduate School of Science, Kyoto University, 2. National Institute of Polar Research

The core of garnet porphyroblasts in the garnet-sillimanite gneiss from Skallevikshalsen, Lützow-Holm Complex, East Antarctica, includes Cl-rich (>0.3wt%Cl) biotite and nanogranite/felsite inclusions (former granitic melt). These are estimated to be stable at >1.2 GPa and 820-850 °C. Rare occurrence of matrix biotite suggests almost complete consumption of pre-existed matrix biotite during prograde to peak metamorphism. Brine infiltration during prograde to peak metamorphism is supported by Cl-rich scapolite described in previous studies [e.g., 1]. Brine infiltration and progress of continuous biotite-consuming melting reactions were probably responsible for elevating the Cl content of biotite.

*In situ* electron microprobe U-Th-Pb dating of monazite and the *in situ* LA-ICPMS U-Pb dating of zircon in the garnet-sillimanite gneiss revealed that both monazite and zircon has the 'older age population' with ca. 650-580 Ma and the 'younger age population' with ca. 560-500 Ma. The REE and trace element pattern of one of the P-rich patches in the garnet core is different from the P-rich garnet rim. The isotope mapping of the same patch by LA-ICPMS revealed that the patch is also observed as a domain depleted in <sup>51</sup>V, <sup>89</sup>Y, <sup>165</sup>Ho, <sup>166</sup>Er, <sup>169</sup>Tm, <sup>172</sup>Yb, and <sup>175</sup>Lu. Clear difference in <sup>51</sup>V concentration between the patch and the rim of the garnet suggests that this patch is not a continuous part from the garnet rim, but is likely a relic of preexisted garnet. Kyanite included in the patch suggests that medium- to high-pressure type metamorphic rock was the precursor. Presence of the older age population (ca. 650-580 Ma) monazites in Skallevikshalsen and Skallen [2] also suggest that rocks in these areas experienced polymetamorphism, and resetting by the ca. 560-500 Ma metamorphic event was incomplete. Taking into account the presence of Cl-rich biotite inclusions in garnet, infiltration of brine accompanied by partial melting is one probable event that took place at ca. 560-500 Ma in the Skallevikshalsen area, and part of the monazite possibly recrystallized by this brine infiltration.

References: [1] Satish-Kumar et al., 2006, JMG. [2] Hokada and Motoyoshi, 2006, Polar Geosci.

Keywords: brine, partial melting, continental collision, monazite, zircon, polymetamorphism

## Possible process of microstructure formation around Cl-rich mineral-bearing vein under upper amphibolite facies conditions

\*Fumiko Higashino<sup>1</sup>, Tetsuo Kawakami<sup>1</sup>, Noriyoshi Tsuchiya<sup>2</sup>, Madhusoodhan Satish-Kumar<sup>3</sup>, Masahiro Ishikawa<sup>4</sup>, Geoffrey Grantham<sup>5</sup>, Shuhei Sakata<sup>1</sup>, Kentaro Hattori<sup>1</sup>, Takafumi Hirata<sup>1</sup>

1.Graduate School of Science, Kyoto University, 2.Tohoku University, 3.Niigata University, 4.Tokohama National University, 5.University of Johannesburg

Fluids in the crust play important roles in heat and mass transfer. Evidence for the presence of fluids in the deep crust is recorded as fluid inclusions or as hydrous minerals. Existence of brines in the deep crust is recently recognized in addition to CO<sub>2</sub>-rich fluids (e.g., Newton et al., 1998; Shmulovich & Graham, 2004). Brines have higher solubility of minerals and lower viscosity and wetting angle than CO<sub>2</sub>-rich fluids. This makes it possible to induce mass transfer along grain boundaries over vast distances on the km scale (e.g., Harlov, 2012), while it is difficult to be preserved in rocks as fluid inclusions. Therefore, it is important to establish microstructural indicators of the presence of brine in order to understand the distribution and role of brine in the crust.

This study deals with about 1 cm-thick garnet-hornblende (Grt-Hbl) vein that discordantly cuts the gneissose structure of garnet-orthopyroxene-hornblende (Grt-Opx-Hbl) gneiss from Brattnipene, Sor Rondane Mountains (SRM), East Antarctica. The Grt-Hbl vein is likely to have been formed from the wall rock, because the continuous gneissose structure is preserved as arrangements of biotite inclusions in the vein-forming Grt. With distance from the vein center, Cl concentration of Hbl and biotite (Bt), K content of Hbl, and thickness of Na-rich rim of plagioclase (Pl) decrease and become constant at a few cm away from the vein center. These compositional changes imply that the Grt-Hbl vein was possibly formed by NaCl-KCl-bearing fluid or melt infiltration. The *P-T* conditions for the vein formation is estimated to be ca. 700°C and 0.7 GPa, using geothermobarometers.

In this study, Zr is confirmed as immobile during the Grt-Hbl vein formation by almost constant bulk rock Zr content with distance from the vein (Higashino et al., 2015). Using Zr as an immobile element, the mass balance analysis was performed based on the fractionation mass change value (Ague, 2003). The bulk rock chemical variation with distance from the vein was evaluated. As a result, elements which are compatible to alkali-chloride-rich fluid (Keppler, 1996) were added to the wall rock rather than melt compatible and chloride-free-fluid compatible elements (Keppler, 1996). This supports that the Grt-Hbl vein was formed by brine infiltration.

In addition to Na, K and Cl concentrations, some trace element concentrations of constituent minerals gradually decrease or increase with distance from the vein center and become constant. It is important to note that distances where the trace element concentrations become constant are dependent on elements, and not on mineral species. These decreasing/increasing trends show diffusion-like profiles with distance from the vein. Trace element zoning within each grain is small, and almost negligible compared to chemical variation with distance from the vein. However, Pl preserves discontinuous zoning in terms of anorthite content. Discontinuous boundary between Pl rim and mantle implies that the brine infiltration caused dissolution-reprecipitation process. The preserved sharp mantle-rim boundary compared to flat zoning profile of trace elements would be explained by the sluggish NaSi-CaAl interdiffusion compared to the lattice diffusion of trace elements (e.g., Grove et al., 1984; Cherniak, 1995). It is likely that the brine infiltrated through the grain boundaries and altered the rim composition of minerals. Therefore, microstructure indicating dissolution-reprecipitation process, such as stepwise zoning of anorthite content of

plagioclase, coexisting with Cl-bearing minerals may become an indicator of passage of brines. Field mapping of these microstructures would have a potential to unravel the large-scale distributions and movement of brines in the lower crust.

Keywords: brine, metasomatism, dissolution-reprecipitation, continental crust

U-Pb zircon ages younger than regional metamorphism obtained from gneissose granitoids in the Mikawa area, Ryoke belt

\*Kota Takatsuka<sup>1</sup>, Tetsuo Kawakami<sup>1</sup>, Etienne Skrzypek<sup>1</sup>, Shuhei Sakata<sup>2</sup>, Hideyuki Obayashi<sup>1</sup>, Takafumi Hirata<sup>1</sup>

1.Kyoto University, 2.University of Tokyo

The Ryoke belt consists of Late Cretaceous high-T/low-P type metamorphic and plutonic rocks, and records magmatic activity at the continental margin of East Asia. In the Mikawa area, the temporal and spatial distribution of protracted magmatism associated with subduction and its effects on the development of high-T/low-P type metamorphism can be observed, because plutonic rocks intrude continuously during and after Ryoke regional metamorphism [1].

Granitoids in the Mikawa area have been classified based on their lithology and intrusive relationships [2]. The Kamihara tonalite and the Tenryukyo granite have gneissose structures and are classified into the Older Ryoke granitoids. They are considered to be the heat source of regional metamorphism [3]. This interpretation is supported by CHIME monazite (Mnz) ages from the Ryoke metamorphic rocks (102-98 Ma), the Kamihara tonalite, (ca. 95 Ma) and the Tenryukyo granite (ca. 91 Ma) [1] and by the fact that most of the Older Ryoke granitoids occur structurally below the Ryoke metamorphic rocks.

However, it has been reported that granitoids in the Yanai area show discrepancies between U-Pb zircon (Zrn) ages and CHIME Mnz ages; some massive granitoids yielded U-Pb Zrn ages older than those of gneissose granitoids [4]. In this study, we carried out LA-ICP-MS U-Pb Zrn dating of gneissose granitoids in the Mikawa area in order to discuss whether the classification of granitoids based on their gneissose structure is consistent with U-Pb Zrn ages or not.

Granitoid samples were collected from Toyokawa, Gamagori and Shimoyama localities (2 samples each); they are mapped as parts of the Kamihara tonalite or the Tenryukyo granite. All samples show a gneissose structure which is defined by the arrangement of biotite and/or hornblende, and is concordant with the foliation of the surrounding metamorphic rocks. Granitoids collected from Toyokawa intrude into the highest grade metamorphic rocks of the garnet-cordierite zone [5], and those from Gamagori intrude structurally below the sillimanite-K-feldspar zone [6]. The contact between these granitoids and metamorphic rocks was not observed. Granitoids from Shimoyama are located structurally above the biotite zone, but the actual intrusive relationship with metamorphic rocks is not known.

The results of LA-ICP-MS U-Pb Zrn dating are given below as weighted means of <sup>238</sup>U-<sup>206</sup>Pb ages ( $\pm 2\sigma$  error) calculated with concordant data. Two granitoid samples from Toyokawa gave 77.5 $\pm$ 0.6 Ma and 77.1 $\pm$ 0.6 Ma, and two granitoid samples from Gamagori gave a similar age of 81.1 $\pm$ 1.0 Ma. Two granitoid samples from Shimoyama gave 98.9 $\pm$ 0.9 Ma and 99.4 $\pm$ 0.9 Ma. These ages are interpreted to represent the timing of solidification of the granitoids.

In the Gamagori locality, a CHIME Mnz age of 92.2 $\pm$ 6.0 Ma [1] is reported from the same body as the one dated in this study, and is about 10 Ma older than the U-Pb Zrn age. The U-Pb Zrn age obtained for gneissose granitoid samples from Shimoyama (ca. 99 Ma) is similar to CHIME Mnz ages (102-98 Ma) [1] reported from the neighbouring metamorphic rocks. On the other hand, U-Pb Zrn ages of gneissose granitoid samples from Toyokawa and Gamagori (81-77 Ma) are younger than SHRIMP U-Pb Zrn ages from migmatites (87.4 $\pm$ 0.2 Ma, 87.1 $\pm$ 0.5 Ma) [7] that are thought to represent the age of peak regional metamorphism.

These results show that the development of a gneissosity in granitoids is not a suitable criterion for estimating the relative timing of intrusions. Furthermore, since the ages of gneissose

granitoids in Toyokawa and Gamagori are younger than that of peak regional metamorphism, these granitoids could not represent a heat source of the Ryoke regional metamorphism.

#### References

[1]Suzuki & Adachi, 1998. [2]Ryoke Research Group, 1972. [3]Harayama et al, 1985. [4]Skrzypek et al., in review. [5]Miyazaki et al, 2008. [6]Asami, 1977. [7]Nakajima et al, 2013.

Keywords: Ryoke belt, LA-ICP-MS, U-Pb zircon dating, Gneissose granitoid

## Did the Ryoke belt form beneath the Cretaceous volcanic arc?

\*Tadao Nishiyama<sup>1</sup>

1. Department of Earth and Environmental Sciences, School of Science, Graduate School of Science and Technology, Kumamoto University

The tectonic relation between the Sambagawa and Ryoke belts has been an enigma since the Miyashiro's (1961) proposal of the paired metamorphic belts. In his theory, the high  $P/T$  metamorphic belt like the Sambagawa belt forms at the subduction zone, whereas the low  $P/T$  metamorphic belt like the Ryoke belt forms beneath the volcanic arc. There is an arc-trench gap typically about 100 km wide between them, however, the Sambagawa and Ryoke belts are at present in contact with each other by the Median Tectonic Line. How did the two belts come together? That is the problem. Ito et al. (2009) made a substantial progress on this issue. They studied the crustal structure of the Southwest Japan by the integrated seismic experiment and showed a magnificent result with respect to the subsurface structure of the Ryoke belt. They found a prism structure named the SSP (Seto Subsurface Prism) that is a 60 km wide and 20 km thick prism with cross section of an isosceles triangle. The SSP is bordered to the south with the Sambagawa belt by the MTL and grades into the Jurassic nappe units of the inner zone of the Southwest Japan to the north. The SSP consists of the Ryoke metamorphic rocks and Ryoke and Sanyo granites at the surface, and probably so does the subsurface constituent. In the Ryoke belt at the Chugoku and Shikoku districts, basic intrusives of Cretaceous in age occur sporadically in granites in the south (Nakajima et al., 2004), and the metamorphic rocks occur in the north of the belt, of which metamorphic grade generally increases southward except local thermal disturbance (Nakajima, 1994; Ikeda 2004). Granites of the Ryoke belt belong to the ilmenite series and grades to the magnetite series from the Sanyo to San-in belt to the north (Ishihara, 1977).

The morphology and tectonic location of the SSP is very similar to that of the Great Valley forearc basin in the West Coast of north America. The essence of my new hypothesis is that the SSP formed as accumulated accretionary complex at the tectonic location equivalent to the forearc basin. That is, the Ryoke belt formed in situ at the present position (the past forearc basin). The protolith of the Ryoke metamorphic rocks are known as Jurassic accretionary complexes. During the formation of Jurassic accretionary prism, the thickening of accretionary complex was enhanced by out-of-sequence thrust (Kimura, 1998). The thickened complex developed laterally towards the arc from the subduction zone to make nappes on the arc. At the forearc, the thickened complex caused subsidence of the forearc region with a flexure of middle crust, finally making the SSP. The sediments within the SSP were then heated by radiogenic heat and also by basic magmas intruded into the lower part of the SSP, leading to the partial melting of the SSP sediments to form granitic magmas. Thus the sediments in the SSP were converted into granites and low  $P$  metamorphic rocks, which are now recognized as the Ryoke belt. The fact that the Ryoke granites belong to I-type granites may contradict the above hypothesis, however, the ilmenite series nature of the Ryoke granites represents reduced condition for the genesis of Ryoke granites, which strongly suggests the partial melting or assimilation of sediments.

The Ryoke metamorphic rocks represent the burial depth of about 15 km (e.g. Ikeda, 2004), therefore, the original depth of the SSP may have reached 35 km. Such thick sediments in the SSP may pressurized the structurally lower Sambagawa belt to make it squeezed out to the surface. Thus the formation of the SSP may be a cause of the exhumation of the Sambagawa belt. The thick SSP may have uplifted due to buoyancy to keep isostasy, then the upper portion of the SSP may have been eroded out to crop the lower portion, consisting of metamorphic rocks and plutonic rocks, out to

the surface.

Keywords: Ryoke belt, volcanic arc, paired metamorphic belt

Crustal-scale pattern of rising buoyancy of viscous fluids and mid Cretaceous geology related to high-temperature metamorphic belt in northern Kyushu, Japan

\*Kazuhiro Miyazaki<sup>1</sup>, Hirohisa Matsuura<sup>1</sup>, Takeshi Ikeda<sup>2</sup>

1.Orogenic Processes Research Group, Institute of Geology and Geoinformation, Geological Survey of Japan/National Institute of Advanced Industrial Science and Technology, 2.Petrology and Volcanology, Department of Earth and Planetary Sciences, Kyushu University

We compare crustal-scale pattern of rising buoyancy of viscous fluids with mid Cretaceous geology related to high-temperature metamorphic belt in northern Kyushu. The results of numerical simulation of crustal-scale rising of viscous fluids show that the pattern of rising viscous fluids transform from diapir-like to branching dike-like patterns with increasing viscosity and density contrasts. Blob-like and dike-like patterns appear at the transient conditions between the diapir-like and dike-like patterns. The patterns are similar to stock or batholith of plutonic rocks. Because a slow horizontal velocity is adopted at the bottom of the system, horizontal-elongated patterns, which are resembled to metamorphic belt, are formed in the diapir regime when viscosity and density contrasts are small. Consequently, the patterns of rising viscous fluids change as follows with increasing viscosity and density contrasts; metamorphic belt-like pattern, diapir-like pattern, blob-like and dike-like pattern, and dike-like pattern.

We also reviewed the mid Cretaceous geology of the northern Kyushu, Japan as follows; 1) the Suo metamorphic rocks (including Chizu metamorphic rocks) have occupied shallow (near surface) to middle crust (up to 25 km depth), 2) large amounts of felsic plutonic rocks (batholith) intruded into the Suo metamorphic rocks at around 10 km depths, 3) high-temperature metamorphic rocks, which have been formed at 20-25 km depths, are exposed in the southern area of the northern Kyushu, 4) felsic volcanic tuffs are intercalated in the Kanmon Groups in the northern area of the northern Kyushu. Zircon U-Pb ages for 2) and 3) are 107-97 Ma (felsic plutonic rocks) and 105.1±5.1 Ma (high-T metamorphic rocks) (Miyazaki et al., 2014). We obtained zircon U-Pb ages from the felsic tuffs in the Kanmon Group as follows; 111.6±0.8 Ma (Wakino Subgroup) and 106.3±0.7 Ma (Shimonoseki Subgroup). These ages imply that high-T metamorphic belt, batholith of felsic-plutonic rocks and volcanic rocks in sedimentary rocks were formed simultaneously in mid Cretaceous.

The high-T metamorphic belt, batholith of felsic plutonic rocks and volcanic rocks were formed by rising viscous fluids, such as mixtures of melt and solids, magma, or melt. The results of the simulation suggest that when a degree of separation of melt from solids is small, such as slowly rising partial melted metamorphic rocks, the rising pattern should be large metamorphic belt-like pattern elongated toward trench side from arc side due to drag of horizontal mantle flow. On the other hand, intrusion of plutonic rocks as batholith or eruption of volcanic rock through dike will be formed when a degree of separation of melt from solids is large. Although the simulations of viscous crust predict to form dike-like patterns, deformation rate of the viscous crust becomes so large. The realistic crust cannot deform as viscous fluids at such high deformation rate. It is suggested that ascent of magma through dike is progressed by brittle failure. It is also expected that surface of marginal area of the intrusion of large amounts of magma as batholith or rising of large metamorphic belt should be relatively descending. The sedimentary basin of the Kanmon Group is possibly formed in such a relative descending area.

Keywords: Crust, Metamorphic belt, Viscous fluids, Northern Kyushu, High-temperature metamorphic rocks





## Material transfer in kelyphitization of garnet (part 2): metamorphic differentiation caused by the internal stress?

\*Masaaki Obata<sup>1</sup>

1. Graduate School of Science, Kyoto University

It has been known that when a garnet is broken down to form a fine-grained mineral assemblage called kelyphite, its bulk composition is usually modified from the original garnet. From the observations the kelyphitization of garnet has been generally considered to be a geochemically open-system phenomenon. I have shown a case of a zoned kelyphite, where chemical and mineralogical differentiation took place in a zoned kelyphite from a garnet pyroxenite, Ronda peridotite, Spain (Obata, 2014). In this presentation I present a new model for the mechanism of such a metamorphic differentiation. The kelyphite is composed of an inner zone consisting of spinel (Sp)-plagioclase (Pl)-orthopyroxene (Opx) symplectite and the outer marginal zone consisting of Sp-Cpx-Opx symplectite that lack plagioclase. Bulk microprobe analysis of the symplectites using a broad electron beam (3-10 microns) shows that the inner zone contains more Si and Ca and less Mg and Fe and the outer zone contains more Mg, Fe, and less Si and Ca than the garnet. It is shown that the integration of the two zones, assuming an ultrafine-grained Sp-Cpx-Opx symplectite in the outer marginal zone represents a primary material of this zone, can match that of garnet. I deduced from the garnet and the local kelyphite bulk compositions a two separate metasomatic reactions, which are coupled via element transfer between the two reaction sites. It is suggested that the metamorphic reactions and the intra-kelyphite differentiation was driven by the internal stress and stress gradient generated by the progress of the volume-increase reactions in the solid media confined in a solid kelyphite shell.

Reference: Obata, M. (2014) Material transfer in the kelyphitization of garnet: a centrifugal segregation in a chemically closed system. Abstract of 2014 Annual Meeting of Japan Association of Mineralogical Sciences (Kumamoto)

Keywords: kelyphite, garnet, material transfer, metamorphic differentiation, internal stress, Ronda peridotite

## Determination of channel CO<sub>2</sub> contents in random cordierite crystals using Raman spectroscopy

\*Miyako Abe<sup>1</sup>, Madhusoodhan Satish-Kumar<sup>2</sup>, Hiroyuki Kagi<sup>3</sup>, Simon Harley<sup>4</sup>

1. Graduate School of Science and Technology, Niigata University, 2. Department of Geology, Faculty of Science, Niigata University, 3. Geochemical Research Center, Graduate School of Science, University of Tokyo, 4. School of Geosciences, The University of Edinburgh

Cordierite is a common metamorphic mineral, which entraps volatiles such as CO<sub>2</sub>, H<sub>2</sub>O in its channel, consisting of six-membered rings of (Al, Si) O<sub>4</sub>. Carbon dioxide is orientated linearly along the *a*-axis in cordierite channel, and therefore the peak intensity of CO<sub>2</sub> at 1383cm<sup>-1</sup> obtained from Raman spectroscopy varies considerably depending on the crystal orientation of cordierite. Kaindl et al. (2006) has shown that the Raman spectral intensity of CO<sub>2</sub> band in crystallographically oriented cordierite grains can be used to estimate the CO<sub>2</sub> contents. These previous studies suggested the importance of applying a correction on the effect of crystal orientation for the determination of intrinsic contents of CO<sub>2</sub> in randomly oriented cordierite crystals. The purpose of this study is to reveal the relationship between Raman spectral patterns and crystal orientation of cordierite, and to construct a new method for the determination of CO<sub>2</sub> content in cordierite using Raman spectroscopy.

For the identification of crystal orientation of cordierite, euhedral cordierite crystals, from the volcanic ash deposit in the Takiga swamp, Gunma Prefecture, Japan were used to prepare crystallographically oriented thin sections, and examined in detail using micro-Raman spectroscopy. In addition, to examine the effect of crystal orientation to the intensity of CO<sub>2</sub> for its determination, two cordierite samples were analyzed. One is cordierite crystal from a pelitic cordierite-bearing from gneisses in the Kerala Khondalite Belt (KKB), southern India, and the other is a standard cordierite with known CO<sub>2</sub> contents (SH). Since Raman spectral intensity also depends on polarization of the incident laser, Raman spectra were obtained by rotating the sample at an interval of 10°. The crystal orientation of cordierite was cross-checked by using 5-axis universal stage and conoscopic figures.

Raman spectral patterns obtained for (001), (100) and (010) crystallographic planes change cyclically with the polarization of incident laser. We selected six peaks of cordierite (1: 554 cm<sup>-1</sup>, 2: 575 cm<sup>-1</sup>, 3: 670 cm<sup>-1</sup>, 4: 970 cm<sup>-1</sup>, 5: 1010 cm<sup>-1</sup>, 6: 1180 cm<sup>-1</sup>) for a detailed analysis. The intensity of peak-5 and peak-6 changed systematically when compared with other peaks, and so these peaks were used for the identification of crystal orientation. The intensity of peak-3 did not change and we used it as a normalizing peak for instrumental intensity variations. The intensity ratio of peak-5/ peak-3 versus intensity ratio of peak-6/ peak-3 ( $I_5/I_3$  vs.  $I_6/I_3$ ) in (001), (100) and (010) plane showed a linear relation. The value of other oriented cordierite crystals and random ones fell within this range. Therefore, it is possible to identify the crystal orientation of cordierite using the relation of  $I_5/I_3$  vs.  $I_6/I_3$ . The cyclic patterns can be expressed mathematically using a combination of sine curves, where it is possible to determine the crystal orientation. Furthermore, the peak intensity of CO<sub>2</sub> for SH cordierite with known CO<sub>2</sub> contents also showed cyclic variations, similar to the periodicity of the peak-6 in the crystallographically oriented crystals. Accordingly, using the mathematical expression we could retrieve the maximum peak intensity of CO<sub>2</sub> at 1383cm<sup>-1</sup> from a random crystal, which was then used for determining the CO<sub>2</sub> contents of unknown cordierite crystals.

### References

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Keywords: Cordierite, Raman spectroscopy, Crystal orientation, CO<sub>2</sub> determination

## Correlations between the apparent interlayer spacings $d_{002}$ and the Raman $R_2$ parameters of carbonaceous matters in metamorphic rocks

\*Ayaka Shiraishi<sup>2</sup>, Kenichi Hoshino<sup>1</sup>

1.Department of Earth and Planetary Systems Science, Hiroshima University, 2.Department of Earth and Planetary Systems Science, Hiroshima Univ.

Interlayer spacings  $d_{002}$  of carbonaceous matters (CMs) in sedimentary rocks have long been used to investigate degrees of metamorphism. Itaya (1981) showed that the apparent  $d_{002}$  values decrease with increasing metamorphic grades along the Asemi river in the Sanbagawa metamorphic belt in Ehime Prefecture. Takami and Nishimura (2000) presented that the apparent values of CMs in the Jurassic Kuga Group tend to decrease toward the contact boundary with the Late Cretaceous Hiroshima granite in the Yasaka area, Hiroshima Prefecture. Chijiwa et al. (1993) also noted that the apparent values of CMs in the Miocene Susa Group decrease toward the contact boundary with the Pleistocene Koyama gabbro in the Susa area, Yamaguchi Prefecture. On the other hand, Beyssac et al. (2002) proposed a geothermometer based on the Raman  $R_2$  parameters of CMs,  $T$  ( $^{\circ}\text{C}$ ) =  $-445 R_2 + 641$ , and applied it for the temperature analyses in the Asemi area.

We have analyzed the Raman  $R_2$  parameters of CMs in rocks from the above three areas and compared them with the apparent  $d_{002}$  values reported in the above studies. Although standard deviations of the  $R_2$  parameters in individual rock specimens are large, the modal  $R_2$  parameters show good positive correlations with the apparent  $d_{002}$  values in the ranges  $R_2 \leq 0.75$  and  $d_{002} < 3.60$ , while no clear correlation is shown out of the ranges (Fig. 1).

The correlation can be approximated by a simple hyperbolic equation,  $(R_2 - a)(d_{002} - b) = k$ . Hence, we may estimate a metamorphic temperature in the above area from the previously reported apparent  $d_{002}$  value by combining the above two equations as  $T$  ( $^{\circ}\text{C}$ ) =  $-445 (k / (d_{002} - b) + a) + 641$ . Asymptotic values for  $R_2$  (a) and  $d_{002}$  (b) and  $k$  for the all data in the above ranges are 0.95, 3.26 and  $-0.064$ , respectively, with  $R^2$  as 0.94. On the other hand, those only for the Asemi area are 0.96, 3.28 and  $-0.058$ , respectively, with  $R^2$  as 0.94, and for the Yasaka area are 0.89, 3.27 and  $-0.046$ , respectively, with  $R^2$  as 0.97, while those only for the Susa area can not be obtained, since the most data are out of the ranges.

Since the geothermometer of Beyssac et al. (2002) is applicable for the range,  $R_2 < 0.7$ , the parameter set of the Asemi area obtained from the data mostly within the range is better to take for practical temperature estimations.

Keywords: carbonaceous matter,  $d_{002}$ , Raman  $R_2$

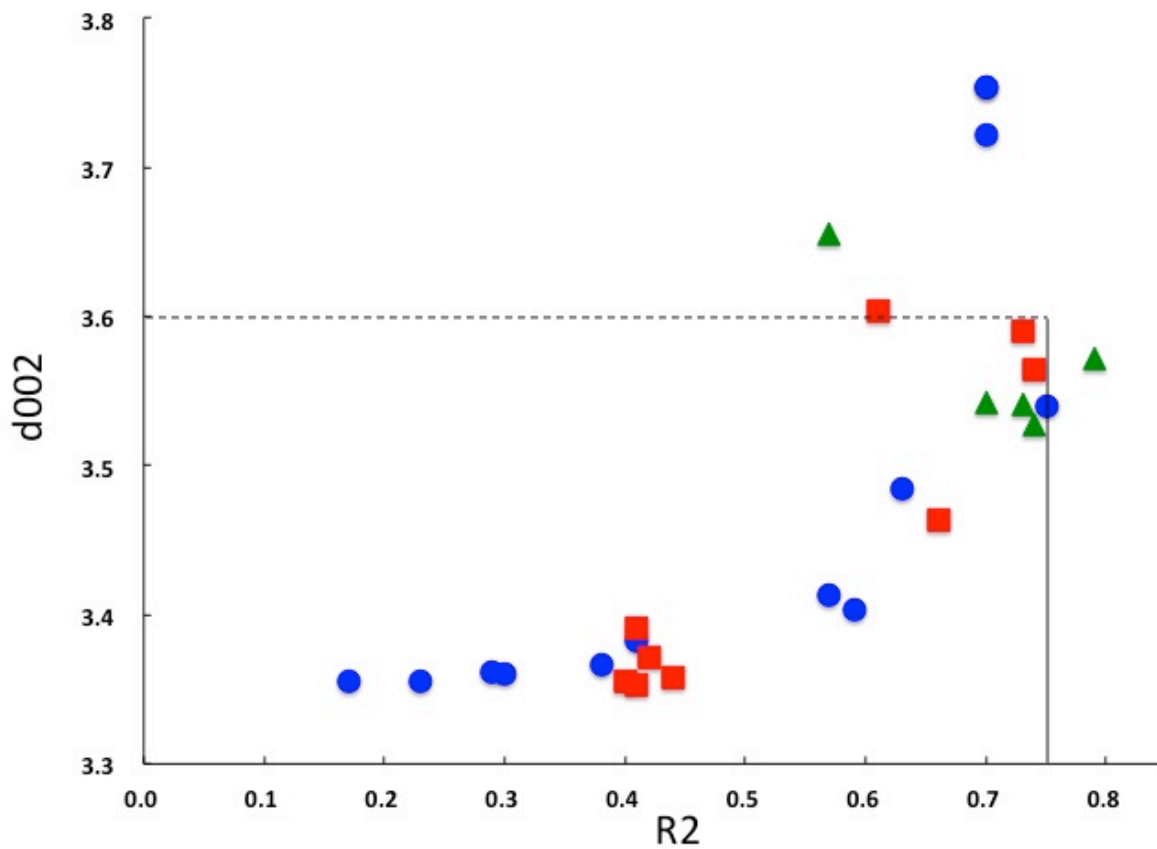


Fig. 1 Correlations between d002 and R2 of CMs in the Asemi (circle), Yasaka (square) and Susa (triangle) areas.

## Preliminary results of the CM Raman geothermometry of the Kebara Formation and the proximal areas in the Kii Peninsula

\*Kenta Yoshida<sup>1</sup>, Naoki Aoyagi<sup>2</sup>, Ryoji Kato<sup>2</sup>, Takao Hirajima<sup>2</sup>

1. Graduate School of Science, Osaka City University, 2. Graduate School of Science, Kyoto University

The Outer Zone of Southwest Japan in the Kii Peninsula is composed of the Sanbagawa metamorphic belt, the Mikabu belt, the Chichibu belt, the Kurosegawa belt, and the Shimanto belt from the north to the south (Kurimoto, 1986). In the Shimizu-Misato area of the Wakayama prefecture, components of above-mentioned five belts are exposed and the Mikabu belt disappears in the eastern part, where the Kebara Formation is exposed between the Sanbagawa metamorphic belt and the Chichibu belt. One of petrologic characteristics of the Kebara Formation is a common occurrence of lawsonite in both meta-mafic rocks and metapelites (Hada, 1967; Kurimoto, 1986; Tomiyoshi & Takasu, 2009), although surrounding geological units are free from lawsonite. Therefore, the attribution of the Kebara Formation is a lasting question for the researchers of the Kii Peninsula. Since thermodynamic approach for the low-grade metamorphic rocks has some difficulties, we applied carbonaceous material (CM-) Raman geothermometer for the metapelitic rocks of the Shimizu-Misato area including the Kebara Formation, Mikabu belt, Sanbagawa belt, Chichibu belt, and Shimanto belt, following the procedure of Kouketsu et al. (2014), which is developed for the low-grade metamorphic rocks covering 165-400 deg. C. We obtained a mean temperature of 318 deg. C for the Kebara Formation, which is comparable with that of the neighboring unit of the Mikabu belt (320 deg. C). On the other hand, the Sanbagawa belt of the Shimizu-Misato area shows the average temperature of 291 deg. C, which is slightly but evidently lower value within an apparent distance of a few kilometers. Temperatures obtained from the Chichibu belt of the relevant area yields about 283 deg. C, and the Shimanto area does the lowest of 212 deg. C. The estimated temperature of the Kebara Formation is equivalent to that of the Sanbagawa belt of the Ise area, eastern Kii Peninsula (316 +/- 5 deg. C: Ueno, 2001), which shows a gap with that of the Sanbagawa metamorphic belt of the Shimizu-Misato area. This temperature gap suggests that the Kebara Formation and the Sanbagawa metamorphic belt of the Shimizu-Misato area are not a coherent unit but in tectonic contact with each other. This fact is also suggested by the geochronological data: K-Ar/Ar-Ar age data of the Kebara Formation have a range of 103-89 Ma (Isozaki et al., 1992; Kurimoto, 1993; de Jong et al., 2000) while those in the Sanbagawa metamorphic belt of the Shimizu-Misato area mostly range 85-72 Ma with a few exceptions (Kurimoto, 1993; Kurimoto, 1995; Kurimoto, 2013). Compared to the Sanbagawa metamorphic belt in the study area, the metamorphic temperature and geochronological data of the Kebara Formation is similar to the Mikabu belt. The similarity in the CM-Raman geothermometry in addition to the previously investigated geochronological data possibly suggest that the Kebara Formation is correlated with the Mikabu belt.

Keywords: carbonaceous material Raman geothermometer, the Kebara Formation, the Sanbagawa belt, the Mikabu belt

Pressure-temperature-time dependence of structural evolution of CM to graphite:  
Implication for fast graphitization in metamorphic terrain

\*Yoshihiro Nakamura<sup>1</sup>, Takashi Yoshino<sup>2</sup>, Madhusoodhan Satish-Kumar<sup>3</sup>

1.Graduate School of Science and Technology, Niigata University, 2.Institute for Study of the Earth's Interior, Okayama University, 3.Department of Geology, Faculty of Science, Niigata University

The structural evolution of carbonaceous material (CM) to graphite is one of the most important thermal indicators for geological regimes of very low to medium metamorphic temperature. The process *sensu stricto* depended not only on peak metamorphism but also lithostatic pressure, tectonic deformation and catalytic effects. Some studies argued that the pressure dependence during graphitization was one of the most important factor to recrystallize from CM to graphite (e.g. Beyssac et al. 2003). However, the natural and experimental studies regarding the pressure dependence on graphitization are very limited.

We report here new experimental data on the structural evolution of CM to graphite at various pressures of 0.5 to 8 GPa at 1200 degree C for 1 hour. Natural CMs extracted from sedimentary rocks in the Shimanto accretionary complex and the Hidaka metamorphic belt transformed its morphology and crystallinity with increasing pressure. Both the starting materials were converted to a graphitic structure above 2 GPa, suggesting either the termination of crystal growth or only sluggish growth. Based on the results of pressure dependence, we compared the relation between the effective activation energies and experimental pressures by combining our results with previous studies. It was found that the effective activation energy empirically decreases with increasing pressure. The pressure dependence was given by:

$$Ea = -71.66\ln(P) + 789 \quad (R^2 = 0.98)$$

Thus we are able to express the effective activation energy  $Ea$  at any pressure conditions using the above regression curve. Combining the previous experimental data on thermal dependence of graphitization (Nakamura et al. 2015), the structural evolution of CM can be expressed by three different factors of pressure  $P$ , metamorphic temperature  $T$  and duration  $t$ :

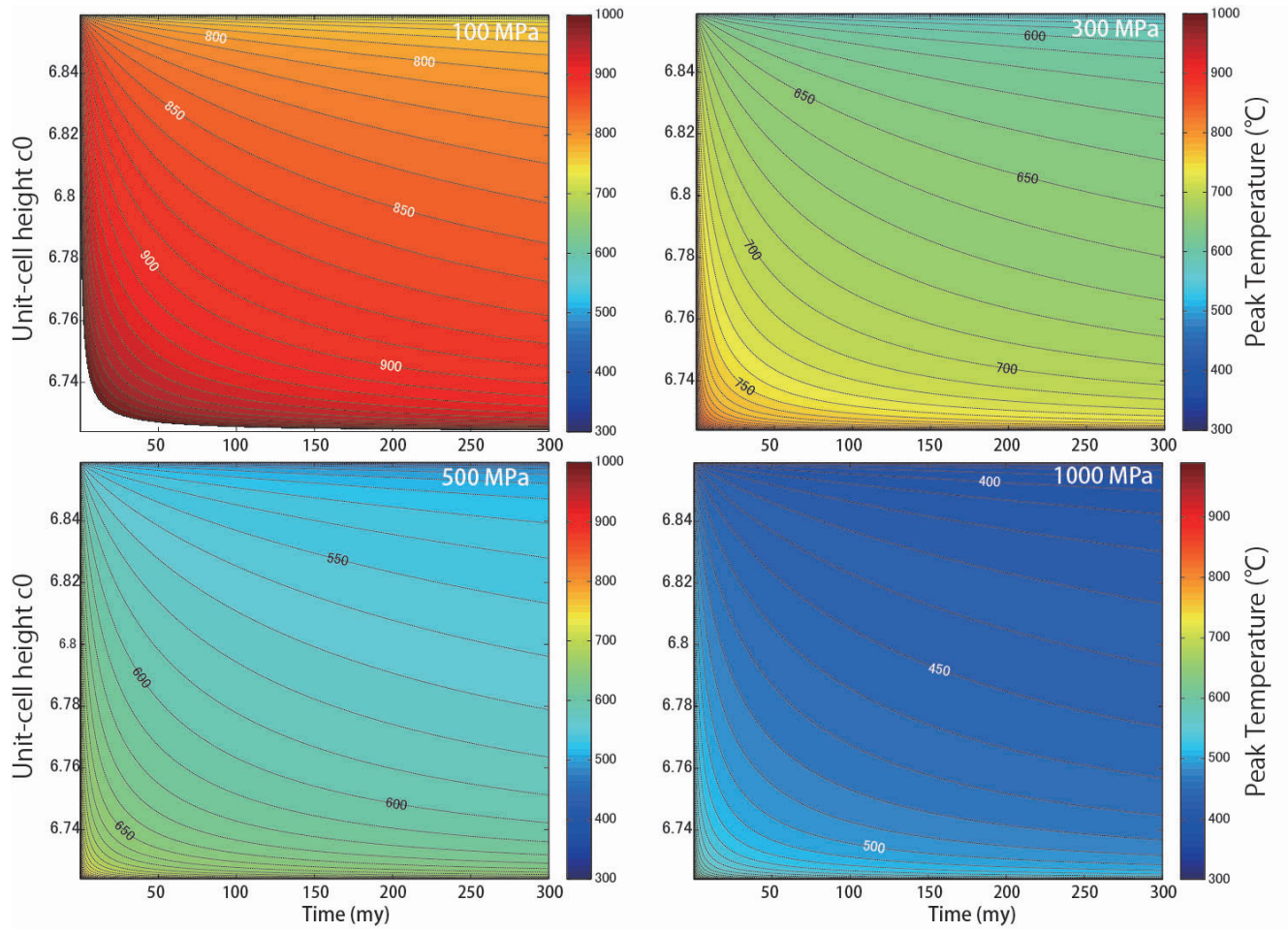
$$f(P, T, t) = C_{\min} + (C_{\max} - C_{\min}) / \{1 + [((A \exp(-71.66\ln(P) + 789) / RT) / t)^h]\},$$

where  $C_{\min}$  and  $C_{\max}$  are respectively the maximum and minimum values of each parameter,  $A$  the intercept of the Arrhenius plot,  $R$  the gas constant, and  $h$  is the reaction rate of the sigmoid function (named as the "Hill coefficient"). Based on the equation combining the thermal and pressure dependences, we attempted to extrapolate to the low-temperature condition (300-1000 degree C) at the pressures of 0.1 to 1 GPa (Fig.1). Detailed results between natural and experimental data will be discussed in the presentation.

Reference: Beyssac et al. (2003) EJM. Nakamura et al. (2015) AGU fall meeting abstract.

Keywords: Graphite, Carbonaceous material, Kinetic model, HTHP experiment





## Petrological study of barroisite-bearing metabasite from the Kebara formation in NW Kii Peninsula and its significance

\*Ryoji Kato<sup>1</sup>, Takao Hirajima<sup>1</sup>

1. Department of Geology and Mineralogy, Graduate School of Science, Kyoto University

The chemical composition of minerals is generally controlled by several factors such as  $P$ - $T$  conditions and bulk composition. Barroisite (Brs) is an intermediate amphibole between glaucophane and tschermakite and its ideal chemical formula is  $(\text{NaCa})\text{Mg}_3\text{Al}_2(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$ . In the Sambagawa belt of central Shikoku, Brs is reported from the higher grade zones, such as the Grt and Ab-Bt zones, and eclogite units. On the other hand, sodic-amphibole, winchite (Wnc), and actinolite (Act) are common in the lower grade zones such as the Chl to Grt zones and the Mikabu belt. In this study, we report the first finding of Brs in metabasite from the Kebara Formation in the NW Kii Peninsula, and discuss its significance. The Kebara Formation is an E-W trending geological unit, 5x1 km, exposed between the Sambagawa and Chichibu belts (Kurimoto, 1986). The Kebara Formation is mainly composed of metapelite with minor amount of lenses or layers of metabasite and siliceous schist (Kurimoto, 1986). Mineral assemblages reported from the Kebara Formation are quartz + albite + chlorite + phengite + lawsonite + calcite in metapelite and lawsonite + pumpellyite + actinolite or sodic-amphibole + pumpellyite + sodic pyroxene + epidote in metabasite (Kurimoto, 1986; Tomiyoshi & Takasu, 2005, 2009). These mineral assemblages are stable from a high- $P$  part of the pumpellyite-actinolite (PA) facies to a low- $P$  part of the epidote-blueschist facies. Although the Kebara Formation is regarded as the Mikabu belt (Kurimoto et al., 1998; Makimoto et al., 2004), its main lithology differs from that of other areas in the Mikabu belt. Brs-bearing metabasite was collected from a continuous, 30m-long outcrop along the Takino-gawa in the SW part of the Kebara Formation. The outcrop exhibits a change from metabasite in the north to metapelite in the south. The main foliation shows ENE-WSW strike and steeply dip to the south. Brs-bearing metabasite, more than 70 cm in thickness, occurs at the transition between metabasite- and metapelite-dominated parts, and its main foliation is consistent with that of the surrounding rocks. Brs-bearing metabasite consists of mm-thick blue-green epidote-rich layers alternating with blue amphibole-rich layers. The blue-green layers are mainly composed of epidote, amphibole, chlorite, white mica, albite, and quartz with minor amount of titanite and apatite. The blue layers contain sodic pyroxene in addition to the above mentioned minerals. Many amphibole grains show a distinct zoning pattern characterized by a Brs core, a sodic amphibole mantle, and a Wnc rim with distinct compositional gap. In some amphibole grains, sodic amphibole and Wnc repeatedly appear at the margin of Brs. Various zoning types of amphibole were reported in the Sambagawa belt: Brs-hornblende(-Wnc)-Act from the Grt and Ab-Bt zones in the Asemi-gawa and Dozan-gawa areas, Brs-sodic amphibole-Wnc/Act from the Ab-Bt zone in the Saruta-gawa area (Otsuki & Banno, 1990; Y. Banno, 2000; Okamoto & Toriumi, 2004). Most of these zoning patterns are attributed to  $P$ - $T$  changes during the exhumation stage, *i.e.*, a decompression with a significant cooling path in the Saruta-gawa area (Y. Banno, 2000) and an isothermal decompression path at an early stage of the exhumation in the Asemi-gawa and Dozan-gawa areas (Okamoto & Toriumi, 2004). The amphibole zoning pattern identified in this study is similar to that of the Saruta-gawa area except for the lack of hematite. This fact suggests that the study samples experienced the epidote-amphibolite facies prior to the PA facies. Multiple recrystallization can be explained by so-called Yo-Yo subduction as reported in the Italian Western Alps (*e.g.* Rubatto et al., 2011).

Keywords: barroisite, the Mikabu belt, the Kebara formation, Kii Peninsula, metabasite, Yo-Yo subduction

## Appraisal of the tectonics of the Kamuikotan metamorphic rocks around the Asahikawa City, central Hokkaido: Zircon U-Pb ages and contact metamorphism by fluid migration

\*Wonji Shin<sup>1</sup>, Toru Takeshita<sup>1</sup>, Ayumi S. Okamoto<sup>1</sup>

1. Graduate School of Science, Hokkaido University

The Cretaceous high-P/T type Kamuikotan metamorphic rocks (KMRs) are distributed in central Hokkaido, northern Japan which extend to the north as far as Sakhalin, Russia. Sakakibara and Ota (1994) divided the KMRs into the six units on the basis of lithology, metamorphic grade, and metamorphic age. The six units also were classified into the following three types based on metamorphic mineral assemblages: high-pressure 1 (HP1; geothermal gradient  $G = \sim 10^{\circ}\text{C}/\text{km}$ ), high-pressure 2 (HP2;  $G = \sim 13^{\circ}\text{C}/\text{km}$ ), and high-pressure intermediate (HI;  $G = \sim 20^{\circ}\text{C}/\text{km}$ ) types. According to Sakakibara and Ota (1994), the K-Ar and  $^{40}\text{Ar}-^{39}\text{Ar}$  ages of phengitic mica from the KMRs are divided into three groups: 108-145 Ma for HP1, 91-107 Ma for HP2 and 50-84 Ma for HI types. Some questions, however, arise concerning these classifications around the Asahikawa City. First, their age distribution seems not unidirectional but random, although each unit appears to occur originally as a thrust sheet. Second, the K-Ar ages of the HI-type Pankehoronai (Pk) unit and younger ones of the HP2-type Harushinai (Hr) unit (after Sakakibara and Ota, 1994) overlap at 70-85 Ma (Okamoto et al., 2015). Third, the age difference between adjacent localities is large and sometimes exceeds a few tens of millions of year. Furthermore, recently reported U-Pb zircon ages (Okamoto et al., 2014) show that the depositional age for the Pk unit (115-120 Ma) along the Ishikari River is slightly older than that for the Hr unit (100 Ma). On the other hand, along the branch of the Ishikari River, 80 Ma of U-Pb age for the Pk unit is also reported (Nagata et al., 2015). Therefore, the Pk unit defined by Sakakibara and Ota (1994) can be divided into two units, older and younger units. This younger unit may be correlated with the Oboke area (i.e. Shimanto belt) in the central Shikoku, which also yielded detrital zircon ages of 80 Ma (Aoki et al., 2007). In this study, we have analyzed lithology and metamorphic minerals from metapelites and metabasites in the Pk unit. The older unit consists of pelitic and mafic schists, calcareous rocks and cherts along the Ishikari River, but in contrast, the younger unit consists of pelitic and mafic schists. For metamorphic minerals, while lawsonite occurs in the older unit, it does not exist in the younger one. These facts support the idea that the previously defined Pk unit can be divided into the older and younger units. In the younger unit, while pumpellyite occurs along the branch of the Ishikari River, epidote occurs along the Pankehoronai and Orowen Rivers from metamorphosed mafic rocks, indicating that the metamorphic temperature is higher in the latter than the former area. This fact together with the spatially heterogeneous distribution of white mica K-Ar ages could be attributed to contact metamorphism caused by fluid migration in the Pk unit.

Keywords: Kamuikotan metamorphic rocks, tectonics, fluid migration, zircon U-Pb ages, white mica K-Ar ages, metamorphic mineral assemblages

## Metamorphic evolution of eclogites in the Alag Khadny metamorphic complex, Lake Zone, SW Mongolia

Otgonkhuu Javkhlan<sup>1</sup>, \*Md Fazle Kabir<sup>2</sup>, Akira Takasu<sup>2</sup>, Dash Bat-Ulzii<sup>1</sup>

1.Mongolian University of Science and Technology, Mongolia, 2.Department of Geoscience, Shimane University, Japan

The eclogite-bearing Alag Khadny metamorphic complex in the Lake Zone, SW Mongolia located in the central part of the Central Asian Orogenic Belt, consist mainly of orthogneisses which interleaving with marbles including lenses of garnet-chloritoid schists of Maykhan Tsakhir Formation. Eclogites occur as lenses or boudins in orthogneisses and marbles, and their peak metamorphic conditions have been estimated as 590-610°C and 20-22.5 kbar (Stipska *et al.*, 2010). Garnet-chloritoid schists occur as lenses or layers within marbles, which lie in contact with eclogite bodies showing distinct lower *P-T* conditions than eclogite (Javkhlan *et al.*, 2013).

Glaucophane-bearing and amphibolitized eclogite consists mainly of garnet, clinopyroxene, sodic, sodic-calcic and calcic amphiboles (Gln, Brs, Fprg, Ts, Fts, Fe/Mg-Hbl, Act) with subordinate amounts of epidote, phengite (Si 6.51-7.11 pfu), plagioclase, K-feldspar, chlorite, rutile, titanite and quartz. Garnets display a prograde zoning (Sps<sub>9-1</sub>, Prp<sub>5-19</sub>, Grs<sub>27-31-20</sub>), and the core of the garnets contains polyphase and discrete inclusions of amphibole (Trm, Prg, Ts) and plagioclase (An<sub><17</sub>), and also contains aegirine-augite/omphacite (Jd<sub>14-21</sub>), epidote, K-feldspar, rutile and titanite. The rim of the garnet contains omphacite (Jd<sub>32-41</sub>), barroisite, phengite, epidote and rutile. Omphacite (Jd<sub>27-46</sub>) in the matrix are zoned, increasing jadeite content from core to rim (Jd<sub>27-41</sub>). Omphacites are partly replaced by symplectite of diopside/aegirine-augite/omphacite (Jd<sub><25</sub>), Mg-hornblende and plagioclase (An<sub><13</sub>). Amphiboles in the matrix are zoned with glaucophane core through barroisite mantle to Mg-hornblende rim, and the others are actinolite/barroisite core and hornblende to tschermakite rim coexisting with large plagioclase (An<sub><18</sub>), which contains fragments of barroisitic amphibole and garnet.

Alag Khadny eclogites experienced multiple metamorphic events, i.e. precursor metamorphic event of relatively high-*T/P* metamorphism of amphibolite facies prior to eclogite metamorphism represented by pargasite/tschermakite and plagioclase (An<sub><17</sub>) inclusions in the core of the garnets. The minerals in the matrix are representative of eclogitic metamorphism and the prograde path pass through the epidote-blueschist facies to the eclogite facies. *P-T* pseudosections were calculated in the NCKFMASHO model system and compositional isopleths of garnet suggest the peak metamorphic conditions of the eclogite as 590-620°C and 21-22 kbar and retrograded into 510-540°C and 9-11 kbar in the epidote-amphibolite facies. Zoned amphiboles in the matrix (Act/Brs core Hbl to Ts rim) and associated large plagioclases suggest another prograde metamorphism of medium-*P* conditions. Peak eclogitic metamorphic conditions are similar to those of Stipska *et al.* (2010), and they correspond to subduction type metamorphic conditions with lower geothermal gradient (8°C/km). Subsequent medium-*P* metamorphism together with garnet-chloritoid schists (560-590°C/10-11 kbar; Javkhlan *et al.*, 2013) took place in the higher geothermal gradient (19-20°C/km), and this metamorphic event is correspond to continental collision type metamorphism.

<sup>40</sup>Ar/<sup>39</sup>Ar muscovite ages in the eclogites (543±3.9 Ma) within marbles and garnet-chloritoid schists (537±2.7 Ma) were determined (Stipska *et al.*, 2010). K-Ar ages for eclogites (c. 600 Ma) within orthogneisses have been obtained by Javkhlan *et al.* (2014). These ages are interpreted as the exhumation ages for the eclogites and the garnet-chloritoid schists.

Keywords: eclogite, pseudosection modelling, garnet-chloritoid schist, Maykhan Tsakhir Formation, Lake Zone, SW Mongolia

## Formation of secondary olivine after orthopyroxene during serpentinization: Evidence from the Hantaishir ophiolite, western Mongolia

\*OTGONBAYAR DANDAR<sup>1</sup>, Masaaki Uno<sup>1</sup>, Atsushi Okamoto<sup>1</sup>, Noriyoshi Tsuchiya<sup>1</sup>

1. Graduate School of Environmental Studies, Tohoku University

Serpentinization plays a crucial role on global water circulation, and causes significant decrease in density and seismic velocity of mantle peridotite. Typically, it advances along slow-spreading ridges, in bending faults during the onset of subduction zone, and wedge mantle in the subduction zone. Serpentine minerals brought into deep part of subducting zone, are broken down to release H<sub>2</sub>O, which is thought to associate with intermediate-depth earthquakes and arc magmatism. Secondary olivine, which is usually interpreted to be formed by dehydration of serpentine, has been reported in several serpentinites from subduction zone. Recently, Plümer et al., (2012) found that a novel texture of the secondary olivine which formed after orthopyroxene via bastite formation. Although the hydration and dehydration processes of ultramafic rock are important on the H<sub>2</sub>O budget within the subduction zone, the detail mechanism of secondary olivine formation is still poorly understood. In this study, we investigate serpentinization processes of ultramafic rocks from the Hantaishir ophiolite in Mongolia, and propose a new mechanism for secondary olivine formation after orthopyroxenes.

The Hantaishir ophiolite is located within the Central Asian Orogenic Belt (CAOB). It is located at the north of the Main Mongolian Lineament in the western Mongolia. The ophiolite composed of ultramafic rocks, pyroxenites and gabbro, sheeted dikes, pillow lavas, and pelagic sediments is strongly sheared and thrust, but well-preserved ophiolitic sequence is partly preserved. It contains two ultramafic complexes, the Taishir and the Naran massifs. Geochemical study of igneous rocks indicates suprasubduction-zone origin (Matsumoto and Tomurtogoo, 2003).

Eighteen ultramafic rock samples were analyzed in detail by using optical microscope, EPMA, and raman spectroscopy. Most of the ultramafic bodies are intensively deformed, and completely serpentinized. Three samples in Naran massif preserve olivine as well as serpentines, spinel, magnetite, and brucite. Serpentine in these samples shows three occurrences; First one is fine-grained lizardite as a mixture with brucite in veins of primary olivine, Second one is chrysotile veins, cutting the all textures, and Third one is antigorite, which dominantly exists in matrix. We found the primary and secondary olivine. Primary and secondary olivine show contrasting Mg#, the former (0.92-0.93) and the latter (0.94-0.98). A plot Mg# of primary olivine vs Cr# (0.70-0.82) of spinel suggests that the ophiolite was formed at fore-arc setting within the subduction zone. It is noted that some secondary olivine exists as fine-grained aggregates. This aggregate looks replace large grain aligned fractures filled with antigorite which shows relatively high Al- and Cr-content. These observations suggest that secondary olivine aggregate was originated from orthopyroxene. Based on the similar textures, Plümer et al., (2012) suggested that bastite is formed after orthopyroxene and then a dehydration reaction occurs to the secondary olivine. In contrast, our sample does not the evidence for formation of bastite, and the secondary olivine and antigorite look formed at the similar stage. Therefore, we propose that the secondary olivine is directly formed by silica-releasing reaction after orthopyroxene, and the releasing silica is reacted with primary olivine to produce antigorite. In this mechanism, the secondary olivine could be formed during the hydration stage within subduction zone.

Keywords: microtextural-chemical evolution, Mg-rich secondary olivine





Backarc-like characteristics and their spatial distributions within serpentinized peridotites in the Mineoka belt, Boso peninsula

\*Katsuyoshi Michibayashi<sup>1</sup>, Toshiyuki Katakai<sup>2</sup>

1.Institute of Geosciences, Shizuoka University, 2.Department of Geosciences, Faculty of Science, Shizuoka University

We studied chemical compositions and crystal-preferred orientations of serpentinized peridotites in Mineoka belt, Boso peninsula, Honshu island, Japan. The chemical compositions of both olivine and spinel are in the range of the olivine-spinel mantle array of Arai (1994, Chemical Geology). Spinel Cr# can be divided into two groups: high Cr# (0.5-0.6) and low Cr# (0.3-0.4). Moreover, we found that olivine crystal-fabrics in these peridotites have two types along with the two chemical compositions: A type with the low Cr# to the west and D type with the high Cr# to the east of the Mineoka belt. The chemical compositions are compatible with those of Parece Vela Rift (Ohara et al., 2003, G3). We suggest that the peridotites in the Mineoka belt could be derived from backarc environment and they have not so dismembered at present, since both structural and petrological characteristics are correlated to their spatial distribution in the Mineoka belt.

Keywords: Mineoka belt, peridotite, chemical composition of mineral, olivine crystallographic orientation

Komperito-like growth of metamorphic minerals and microprobes of metamorphic fluid flow

\*mitsuhiro toriumi<sup>1</sup>

1. Japan agency of marine science and technology

Konpeito-like growth of metamorphic minerals and microprobes of metamorphic fluid flow

Mitsuhiro Toriumi ( OELE, JAMSTEC)

Grain growth of the metamorphic process is basically governed by precipitation from grain boundary thin fluid film and dissolution of preexisting minerals. Morphology of metamorphic minerals appears as a variety between euhedral and anhedral shapes, although it sometimes shows the irregular shape likely to amoeboid but not to dendrite. Amoeboid grains of garnet and albite are very common in the regional metamorphic rocks and are considered as unstable growth by coupling of growth from thin film of boundary solution and fluid flow along the thin film.

The similar grain growth from thin film of flowing solution reveals the Kompeito of sucrose and hails which show the spherical ball having many rounded horns (spikes). Such feature is considered to be derived from growth instability from flowing boundary fluid film (1).

In this paper, I will talk about the occurrence of Kompeito - like grains of garnet, albite, and quartz in the regional metamorphic rocks and discuss the robustness of the spacing of rounded horns on the cross section. He also suggests the possibility of microprobes of metamorphic grain boundary fluid flow inferred from the instability of Kompeito -like growth of these metamorphic minerals.

(1) Sakai I., and Y. Hayakawa, 2006, JPSJ, 75, 10, 104802

Keywords: Kompeito-like growth, metamorphic minerals, grain boundary fluid