

Significance of melt inclusions in Zrn in estimating the duration of high-T metamorphism -An example of the Ryoke belt

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It is important to understand when and how Zrn was formed in order to interpret the U-Pb Zrn ages. Melt inclusion in Zrn is an important evidence of Zrn growth in the presence of melt. Therefore, they contribute to constrain the timing of Zrn growth in high-T metamorphic rocks. In this contribution, we report the occurrence of melt inclusions in Zrn from the migmatite of the Ryoke metamorphic belt at Aoyama area, SW Japan.

In the Aoyama area, the pelitic-psammitic schists dominate in the north, and migmatites (metatexites and diatexites) dominate in the south [1]. Zircon (Zrn) in pelitic-psammitic schists from the low-T part of the Grt-Crd zone is coarse-grained and shows almost no metamorphic overgrowth. On the other hand, Zrn in migmatites from the mid- and high-temperature part of the Grt-Crd zone has a thin, bright layer under BSE image along which tiny inclusions of several microns are aligned [cf. 2]. TEM observation of some of these tiny inclusions gave halo patterns revealing that they are the glass (formerly melt) rich in Si, Al and K. This melt inclusion alignment divides the core with various detrital ages from the rim that gives U-Pb concordia age of 93.1 +/- 2.9 Ma. The rim of the Zrn from the high-T part of the Grt-Crd zone is over 20 um in thickness, and its Th/U ratio is less than 0.02. Presence of melt inclusion alignment at the core/rim boundary shows that the melt was present when the Zrn rim grew. Therefore, the Zrn rim probably grew under the presence of melt and monazite during the Ryoke metamorphism. The melting reaction that consumes Bt + Sil + Qtz and produces Grt + Crd + Kfs +/- Ilm + melt plays an important role in the formation of melt in this area [1]. However, Bt is not an important sink of zirconium [3], and Bt breakdown cannot supply zirconium enough for new Zrn rim growth. In this case, dissolution of pre-existing Zrn is required. It would be difficult to saturate melt in terms of Zrn component by dissolving Zrn when the amount of melt is increasing. Therefore, it is likely that 93.1 +/- 2.9 Ma Zrn rim crystallized during the solidification of the melt in migmatites, possibly near the wet-solidus. Mixed analysis of U-Pb dating of Zrn core and rim reveals that similar young rim is developed, although thin, in Zrn from the mid-T part of the Grt-Crd zone. These results imply that presence of partial melts plays an important role in the dissolution and recrystallization of Zrn [e.g., 4].

Although the whole-rock zirconium content is not especially high in the pelitic-psammitic schists from the low-T part of the Grt-Crd zone, modal amount of Zrn more than 20 um in diameter is higher in them. Zrn less than 20 um in diameter is confirmed to become common in mid-T and high-T part of the Grt-Crd zone, and ca. 30 um Zrn without detrital core are rarely found in the high-T part of the Grt-Crd zone. From these observations, these tiny Zrn grains are considered to have nucleated during the Ryoke metamorphism.

On the other hand, monazite grows at amphibolite facies grade and the presence of the melt does not largely affect its recrystallization [4]. In the case of the Aoyama area, Mnz from the migmatites records the prograde growth age of 96.5 +/- 1.9 Ma during regional metamorphism [5]. Using the difference of growth timing of Mnz and Zrn, that is, Mnz being prograde and Zrn being post peak, the duration of metamorphism higher than the amphibolite facies could be constrained, and it is at least ca. 3.5 Ma in the case of the Aoyama area.

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Keywords: zircon, glass inclusion, migmatite, LA-ICP-MS, partial melting

The chlorine-rich fluid activity during granulite facies metamorphism in the continental collision zone

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Metamorphic fluids play important roles in thermal transport, mass transfer (e.g., Helgeson, 1964), metasomatism (e.g., Meyer & Hemley, 1967) and changing stability field of mineral assemblages (e.g., Powell et al., 1991). In the granulite facies rocks, CO₂-rich fluid has been considered important and studies on Cl-rich fluid are not sufficiently available, because fluid inclusions of the Cl-rich one are less observed than CO₂-rich ones. Some of the reasons Cl-rich fluid inclusion is less found are low viscosity and low wetting angle of brines (Watson & Brenan, 1987). However, Cl-bearing brines are increasingly recognized as playing an important role in high-*T* metamorphic rocks (Newton & Manning, 2010). Using Cl concentration of minerals, it is possible to decipher the Cl-rich fluid activity and its role of them in the lower crust.

We have investigated the field distribution of Cl-rich biotite in the pelitic gneisses of the Sor Rondane Mountains, East Antarctica where Late Proterozoic to Cambrian granulites are widely exposed (Shiraishi et al., 2008). Among more than 20 samples studied, a Grt-Bt-Sil gneiss from Balchenfjella was selected as best suited sample to constrain the *P-T-t* condition of Cl-rich fluid activity. This gneiss contains garnet porphyroblasts (5-10 mm) that have P-rich core with oscillatory zoning in P. The core with oscillatory zoning is discontinuously overgrown by the P-poor rim. The discontinuous zoning in P suggests that garnet porphyroblasts have experienced resorption and overgrowth. The garnet core includes Cl-poor biotite and apatite, and those included at the rim are Cl-rich. Coarse-grained (ca. 100 μm), round zircon grains are exclusively included in the rim of the garnet porphyroblast and also present in the matrix. This mode of occurrence suggests that Cl-rich biotite and apatite and round coarse-grained zircon were formed almost simultaneously.

The *P-T* conditions of the Cl-rich biotite entrapment in the garnet rim were estimated to be ca. 800 °C and 8 kbar, and those of the peak metamorphic condition were ca. 850 °C and 11 kbar, using Grt-Bt geothermometer and GASP geobarometer (Hodges & Spear, 1982). The f_{HCl}/f_{H_2O} ratio of the fluid in equilibrium with Cl-rich biotite (Selby & Nesbitt, 2000) and apatite (Piccoli & Candela, 1994) in the garnet rim are ten times larger than that in equilibrium with Cl-poor biotite and apatite in the matrix and the garnet core. The LA-ICP-MS U-Pb dating of the coarse-grained zircon included in the garnet rim gave a concordia age of 600 ± 13 Ma. Therefore, the Cl-rich fluid infiltration took place at near the metamorphic peak condition of ca. 800 °C and 8 kbar at 600 ± 13 Ma and formed Cl-rich biotite and apatite (e.g., Sisson, 1987).

The field distribution of Cl-rich fluid activity shows somewhat linear distribution. Some of them are located near the ductile shear zones (Ishikawa et al., 2011), and suggesting its relation to high-strain zones (e.g., Kullerud et al., 2001). Regional distribution of near-peak metamorphic Cl-rich fluid activity in the Sor Rondane Mountains implies that it is one of the major phenomena in the continental collision processes.

Keywords: chlorine, fluid, biotite, apatite, Sor Rondane Mountains

High-T metamorphic rocks and exhumation process of the Tseel terrane, SW Mongolia

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Tseel area, Tseel metamorphic terrane, SW Mongolia is mainly composed of metapelitic gneisses, amphibolites (sillimanite zone) and intruded by ring structure of the granitoids (sillimanite zone) and covered by sediments. Three mineral zones in the pelitic gneisses determined based on the petrographic study and mineral assemblages of each zones as follows: (1) Biotite zone (Bt + Pl + Qtz + Ms + Chl + Cal) (2) Garnet zone (Grt + Bt + Pl + Qtz +/- Chl +/- Ru + Il + Cal) (3) Sillimanite zone (Grt + Bt + Pl + Qtz + Sil + Ms + Chl +/- Crd +/- St + Ru + Il + Cal +/- Fe-Mg Amp). Biotite zone observed in most area of southern and northern parts of Tseel area. Garnet zone is determined between biotite and sillimanite zones. The sillimanite zone is observed in the central parts of Tseel area. All mineral zones observed along the foliation from E to W trends at Tseel area.

We showed the characteristic features of chemical compositions of garnet, biotite and plagioclase in the pelitic gneisses and determine the P-T paths deduced from the garnet chemical zoning using thermodynamic equilibria in Tseel area as follows: Garnet in the pelitic gneisses shows almandine-rich compositions and some samples show clear compositional zoning. Based on the Ca (grossular) composition of garnet, the sillimanite zone is subdivided into sillimanite A and B zones. Garnet in the garnet zone shows relatively homogeneous compositions in the range of (530-600 °C and 6.0-10.0 kbar). The garnet chemical compositions in the sillimanite B zone show a homogeneous composition in a range of (620-750 °C and 1.8-6.0 kbar), and sometimes contain the retrograde rim produced by post-growth diffusion. The garnet chemical zoning in the sillimanite A zone typically is divided into three zones from core to rim: zone 1 (high Ca with homogeneous), zone 2 (decrease in Ca), and zone 3 (low Ca). The compositions of zones 1 and 2 correspond to those of garnet in the garnet and sillimanite B zones, respectively, and zone 3 indicate the effect of the post-growth diffusion. The P-T conditions during garnet growth were calculated by garnet-biotite geothermometry and garnet-biotite-plagioclase-quartz geobarometry. In application of geothermobarometry to garnet zonings, we calculated P-T conditions for four cases with highest and lowest XMg, Bt and XAn, Pl, that provide the possible P-T ranges for a given garnet composition and constrain roughly the shape of P-T path. The shapes of the P-T paths obtained for individual garnets are similar among the four cases, and the differences in pressure and temperature among the four cases are within 15 °C and 2.5 kbar, respectively. The P-T conditions estimated from the garnet zone are in a range of 530-600 °C and 6.0-10 kbar, that are located at the kyanite stability field. The P-T conditions estimated from the sillimanite B zone are in a range of (570-690 °C and 1.8-8.0 kbar). The longest P-T path is obtained from the samples in the sillimanite A zone, such as sample 3001, which shows a decompression from zone 1 (530-570 °C and 6.0-9.6 kbar) to zone 3 (570-620 °C and 2.0-4.0 kbar), corresponding with a change from the kyanite stability field to the sillimanite stability field. Zone 2 shows an increase in temperature by ~40 °C and a decrease in pressure by 4-6 kbar.

The intrusions of the granitoids occurred during the exhumation of the Tseel terrane, and produced the regional anticline structures and mineral zones. The high temperatures and homogeneous garnet zoning of the sillimanite B zone were resulted from the thermal effects from the granitoids. The sillimanite A and B zones experienced the P-T conditions of the kyanite stability field, that was similar to the garnet zone. The high temperature of the garnet zone cannot be explained solely by the contact metamorphism by granitoids, but the regional high geothermal gradient is expected in the subduction zones.

Keywords: Tseel terrane, garnet, P-T paths, exhumation process

Timing of HP and HT-UHT metamorphism in the Red River shear zone, northern Vietnam: Paleogene vs. Permo-Triassic

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The Red River shear zone is left-lateral shear zone caused by collision of the India to the Eurasian continent at the Paleogene. Although most metamorphic rocks were reset by the deformation, recent U-Pb and Th-Pb in-situ chronological investigations have suggested complex ages from 262 to 25 Ma. In this presentation, we make clear the timing of the high-grade metamorphism using HP and HT-UHT granulites.

To realize the metamorphic conditions and timing of the high-grade event, we use the fluid inclusion technique in association with in-situ U-Pb zircon age. Abundant fluid inclusions are observed in garnet, corundum, staurolite, while are rare in quartz and zircon. Raman analysis shows that all fluid inclusions are composed of CO₂. Their average densities calculated from two Raman peaks are 1.00 +/- 0.06, 1.07 +/- 0.04, 1.09 +/- 0.03, 0.29 +/- 0.07, and 1.15 +/- 0.05 g/cm³ for garnet, corundum, staurolite, quartz, and zircon, respectively. The low-density CO₂ fluids in quartz imply that garnet and corundum have grown up at the different stage than quartz. The estimating pressure-temperature condition based on the mineral paragenesis (exclude quartz) and isochemical phase diagrams using whole rock chemistries of 3 rock types (garnet-corundum-sillimanite, garnet-spinel-sillimanite, and garnet-corundum-spinel granulites), former eclogite-facies (>2.0 GPa at 800 C) metamorphism and subsequent decompression under granulite-facies condition (>1000 C at 1.5 GPa) are identified.

U-Pb zircon ages show wide range from 265 to 36 Ma, however dark luminescent core of zircon containing high-density CO₂ inclusions yields a concordia age of 257 +/- 8 Ma, clearly indicating time of high-grade metamorphic event. This simple technique of combining Raman microscopy and U-Pb age could be easily and widely applicable to evaluate the zircon age and mineral associations in considering pressure-temperature-time evolution of multi-metamorphic events.

Keywords: in-situ U-Pb dating, fluid inclusion, high-grade metamorphism, Red River shear zone, Vietnam

Monazite age of pelitic gneiss in the Lhenice shear zone (southern Bohemian Massif) and its significance

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Recently, multiple equilibrium stages were identified from Grt-rich gneiss at Kti? in the Lhenice shear zone, located along the western margin of the Blansky les massif (Kobayashi et al., 2011). The characteristic matrix mineral assemblage of the Grt-rich gneiss is Crd+Sil+Bt+Grt+/-Spl with Qtz+Kfs+Pl. The coarse-grained Grts are commonly composed of dusty core and clear rim. The dusty core is defined by the alignment of fluid (CO₂-N₂) and micro-sized solid inclusions (Qtz, Kfs, Pl, Rt, Ap, Mnz and Zrn) of which outline are hexagonal in shape. Some coarse-grained (> 3 mm) Grts show chemical heterogeneity both in major and minor elements; Grs-content is homogeneous and high (Xgrs = 0.27) in an apparent core of the grain and continuously decreases towards the rim (Xgrs = 0.02). However, Prp-content shows an inverse pattern against Grs-content, i.e., Prp content is low and constant (Xprp = 0.03) in the core and gradually increases towards the rim (up to Xprp = 0.28). The outline of Grs and Prp content contours show symmetrical hexagonal shapes. Phosphorous (P)-content is almost below the detection limit of EPMA in the apparent core but it is high at the margin of the grain with local development of P-poor outermost rim. The outline of P-poor core shows a hexagonal shape, similar to that of Grs and Prp content contours. The geothermobarometry, based on the mode of occurrence of constituent minerals and the zoning pattern of Grt, depicts following developing history of the host rock, such as, a prograde stage defined by the assemblage of P-poor Grt core (Grs=27) + Pl (An₁₁₋₁₅) under 1.5-2.3 GPa at 700-900 °C (Stage 1), a subsequent Grt-rim forming stage represented by P-rich Grt (Grs5) + Pl (An₁₂₋₁₉) + Ky/Sil at 730-830 °C and 1.0-1.3 GPa (Stage 2), and a following decompression stage by the outermost rim of Grt (Grs₂) + Sil + Crd +/- Spl at 740-850 °C and 0.6-0.8 GPa (Stage 3) (Kobayashi et al., 2011).

To evaluate age of multiple equilibrium stages, chemical Th-U-Pb isochron method (CHIME) Mnz age dating was carried out for Grt-rich gneiss. Mnzs which included in core of Grt show bimodal grain size; coarse-grained (1 mm in diameter) and fine-grained (10 micrometer in diameter). Mnzs which included in rim of Grt have fine-middle grained size (10 micrometer to 0.5 mm in diameter). Mnzs in matrix have middle-coarse grained size (0.5 mm to 3 mm in diameter). Most of middle-coarse grained Mnzs show a chemical zoning; relatively low Th constant in the core and high Th constant in the rim. The Mnz grains which included in the core of Grt give an age of 336+/-11 Ma. The Mnz grains which included in the rim of Grt give an age of 335.4+/-7.2 Ma. The Mnz grains in matrix give 334.9+/-3.9 Ma. These results suggest that the studied rock experienced very fast exhumation from stage 1 to stage 3. Furthermore, felsic volcanic rock-like inclusions (FVRLI) are found from the core and rim of coarse-grained Grt. The FVRLI mainly consists of micro to cryptocrystalline aggregate of Qtz, Pl and Kfs. The FVRLI show spherulitic, granophyric, and porphyritic textures in addition to quartz dendrites. These features of the inclusions are similar to those of "nanogranites" which are FVRLIs enclosed within Grt in high- to ultrahigh-temperature pelitic migmatites and/or granulites as reported by Cesare et al. (2009) and Hiroi et al. (2011). Cesare et al. (2009) concluded that nanogranites are the crystallized anatectic melts which were trapped by peritectic minerals growing during partial melting. The FVRLI in this study may suggest that partial melts formed during early high-pressure metamorphism stage (stage 1) and trapped by garnet have undergone nonequilibrium crystallization under specific conditions of continuous rapid cooling. The possible corresponding geotectonic process may be "vertical extrusion and horizontal channel flow" (e.g. Schulmann et al., 2008) proposed for the Himalayan-Tibetan and Variscan (Bohemian Massif) orogeny.

Keywords: Bohemian Massif, Monazite age, Grt-rich gneiss, Partial melting, Felsic volcanic rock-like inclusions (FVRLI), Rapid cooling

Thermobaric structure in low P/T type metamorphic belt -Case study of the Ryoke metamorphic belt in the eastern Yamaguc

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Recent seismic studies and EM monitoring imply that there is thermal heterogeneity in present subduction zone (Nakajima et al., 2009., Ogawa et al., 2001), furthermore numerical simulation predicts time variation of these heterogeneities (Iwamori, 2000). On the other hand, by petrological method, the same phenomenon is observed in ancient crust and mantle (Baker, 1987) and the Gibbs method is enabled to estimate P-T path (Okamoto and Toriumi, 2001). In this way, seismic and petrological studies are complementary, extensive data which is corresponded to seismic research should be provided by petrological studies. In this study, we provide specific data on thermally heterogeneity by using petrological method, for the Ryoke metamorphic belt in the eastern Yamaguchi Prefecture.

Using pelitic and psammitic mineral assemblages, the study area can be divided into seven zones, i.e. chlorite, chlorite-biotite, biotite, muscovite-cordierite, K-feldspar-cordierite, garnet-cordierite, sillimanite-K-feldspar zones. The K-feldspar-cordierite, garnet-cordierite and sillimanite- K-feldspar zones continue to east part where Ikeda (1998) performed metamorphic zonation. The garnet-cordierite zone decreases its width toward west and disappears in around Hikari city. On the other hand, the sillimanite-K-feldspar zone is widely distributed in Murotsu-Kudamatsu-Oshima area.

Pressure-temperature conditions of seven samples from the sillimanite-K-feldspar zone and three samples from the garnet-cordierite were estimated by using the garnet-biotite thermometer of Hodges and Spear (1982) and the relative geothermometry of Ikeda (2004). Addition of result of Ikeda (2004) enables us to reveal the thermobaric structure of this area. Temperature increases toward southeast, exceeding 800 degree in relatively-limited area around Hizumi area, and decrease further toward south below 800 degree. In contrast, pressure increases toward southeast monotonously and it reaches 5-6kbar in the south of Hizumi district-Cape Kandori. The isotherms are oblique to isobaric lines, suggesting that the crust have thermally heterogeneity at the same depth.

Applying the concept proposed by Miyazaki (2007) to the present results suggests that rate of melt migration increases and duration of melt migration decreases in the following order: Yanai-Hizumi area which is east part, Oshima-Murotsu area which is south part, and Kudamatsu area which is west part in study area. Additionally, estimated thermobaric structure enables us to impress west and south parts were formed in same depth.

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Keywords: metamorphic rock, Low P/T metamorphic belt, Ryoke belt, subduction zone, Thermobaric structure, biotite

Dehydration breakdown of antigorite and the formation of b-type olivine CPO

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Observations of the seismic waves in the mantle wedge (MW) above many subduction zones display a fast seismic direction perpendicular to plate motion. This cause of this anisotropy is considered by many workers to be due to the existence of b-type olivine (Ol) CPO in the MW with [100] axes concentrated perpendicular to the flow direction parallel to plate motion.

Deformation experiments show that b-type CPO patterns can be formed as a result of dislocation creep under water-present high-stress conditions⁽¹⁾ and thermomechanical models have been used to suggest that conditions necessary to form b-type Ol CPO may be achieved close to subduction boundaries⁽²⁾.

However, work on hydrated antigorite (Atg) bearing forearc mantle shows that the presence of Atg destroys any preexisting CPO and prevents strong Ol CPO from being developed⁽³⁾. The reduction in CPO strength is thought to be due to slip concentrating in the weaker Atg layers with associated grain-boundary sliding occurring between Ol and Atg. This result suggests that b-type Ol CPO fabrics are unlikely to be developed close to subduction boundaries where Atg is expected to be stable.

Nevertheless, several examples of naturally occurring b-type Ol CPO have been reported. A review of published reports shows some of these were formed at relatively high temperatures and low stress, which is incompatible with the predictions from experimental work. Natural samples also lack evidence for c-slip, which is expected for the formation of b-type Ol CPO by dislocation creep.

These considerations show that the formation of naturally occurring b-type Ol CPO is not well understood.

Here we document b-type Ol CPO formed by the topotaxial growth of Ol on Atg from the Happo-One region of the Hida Marginal belt, Japan. Before dehydration and conversion to Ol, the Atg had a strong preexisting CPO due to deformation at relatively shallow levels under low temperatures and hydrated conditions. In the Happo-One region, non-deformed secondary Ol formed in veins as a result of the dehydration of foliated Atg, due to contact metamorphism⁽⁴⁾.

The CPO of the vein Ol shows a strong b-Type fabric that is characterized by a c-axis concentration parallel to the stretching lineation and a b-axis concentration normal to the foliation. The CPO of the Atg bordering the vein shows a strong concentration of c-axes at a high angle to the foliation and a strong alignment of b-axes parallel to the lineation. Many recent studies have shown this type of Atg CPO is the most widespread in the forearc MW.

Two types of topotaxial growth relationships are known between Ol and Atg: in both cases [010]atg is parallel [001]ol but [010]ol may be parallel to either [100]atg (type 1) or [001]atg (type 2)⁽⁵⁾. The observed relationships between the Ol and Atg CPO patterns in this study imply type 2 topotaxial relationships between the two minerals.

Atg-bearing mantle is predicted to be a widespread component of forearc mantle. As this material is dragged down by the traction of the downgoing slab, it will become deformed and foliated. When this foliated antigorite schist reaches sufficiently high T and P conditions, it will undergo dehydration. Our results show that when this dehydration occurs, the newly formed Ol is likely to have a b-type Ol CPO. This topotactic Ol CPO can form in the MW away from the coldest part immediately adjacent to the subduction boundary.

The CPO formation mechanism reported here can reconcile the differences between the laboratory and natural examples of b-type Ol CPO patterns and also explain why such b-type CPO is found associated with subduction zones.

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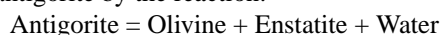
Keywords: topotaxy, olivine, CPO, antigorite, seismic anisotropy

Spinifex-textured olivine-enstatite rock and clinoenstatite formed by high pressure breakdown of antigorite

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Occurrence of spinifex-textured meta-peridotite is well known from the Higo Metamorphic Rocks (Mizuta, 1978), Central Kyushu. The rock occurs as massive sheet like bodies in pelitic and basic gneisses, and is composed mainly of elongated crystals of olivine and coarse-grained enstatite. Olivine crystals do not show preferred orientation, and is mostly altered to antigorite. Enstatite is fresh in most cases, but replaced partly by talc in some cases. Small amounts of spinel, tremolite, and anthophyllite occur as secondary minerals, therefore the rock is a metamorphosed olivine-enstatite rock or hartzburgite. Trommsdorff et al.(1998) studied a spinifex-textured olivine-enstatite rock from Spain, and discussed its origin as a breakdown product of antigorite at high pressures (2 GPa) based on its mineral assemblage and texture. They argued that the spinifex texture, either of igneous or metamorphic origin, formed under fluid (melt or metamorphic fluid)-rich environment, resulting in formation of olivine crystals elongated to [001]. Recently, Kendrick et al. (2011) analyzed fluid inclusions from this rock and clarified that they retain the composition rich in chlorine and noble gas elements originated from seawater. These features suggest that a subducting mantle was hydrated and serpentinized by seawater along fractures, which was caused by slab-bending at fore-arc. The rock from Higo has features common to those from Spain, therefore it is natural to consider that the rock formed by dehydration of antigorite by the reaction:



This reaction takes place at about 600-700 C and 2 GPa. Although most of the Higo metamorphic rocks are the product of high T/low P metamorphism of Cretaceous in age (e.g.Obata et al., 1994, Miyazaki 2004), several studies revealed that they contain some mineral assemblages showing high pressure conditions incompatible with the high T/low P metamorphism (Kano and Uruno, 1995; Karakida et al., 1989; Osanai et al., 1998; Maki et al., 2004 and 2009). Our finding shows that the spinifex-textured olivine-enstatite rock shows a pressure condition much higher than that ever known for the Higo metamorphic rocks.

Pyroxene from the olivine-enstatite rock has the composition of En90Fs10-En95Fs5 and is very poor in CaO and Al₂O₃. The pyroxene consists of ortho-enstatite (Pbca) with lamellae of clinoenstatite (P2₁/c) according to the study with a single X-ray diffractometer (Rigaku RAPID) and a transmission electron microscopy (TOPCON, EM-002B at 200 kV). Clinoenstatite has usually the same composition as orthoenstatite, but in some samples it shows slightly iron-rich composition than orthoenstatite. Clinoenstatite lamella occurs along (100) plane with a width of nanometer to several tens of micrometer vertical to the a* direction. Based on the rule of absent reflection and a model analysis of clino- and ortho- structures, the space groups, lattice parameters and structures of the two pyroxenes are confirmed.

The occurrence of clinoenstatite from the terrestrial rocks is very limited. Recently, high pressure phase of clinoenstatite (C2/c) has been found by several experiments (e.g. Kanzaki, 1991), and some authors discuss it as the possible candidate for the origin of natural clinoenstatite from peridotites and clinopyroxenites especially of the ultra-high pressure metamorphic terrane. Zhang et al.(2002) reported wide occurrence of clinoenstatite in garnet-pyroxenites from the Dabie-Sulu ultra-high pressure metamorphic terrane, and estimated the formation condition to be about 750 C and 6.7 GPa. In the case of Higo, the condition of spinifex-textured olivine-enstatite rock is about 600-700 C and 2 GPa,so it is natural to consider at present that clinoenstatite lamellae and domains formed by shear stress from orthoenstatite, however, the possibility of transition from high pressure phase still remains.

Keywords: serpentinite, spinifex texture, clinoenstatite, ultra-high pressure metamorphic rock, Higo Metamorphic Rocks

Petrogenesis and implications of jadeite-kyanite eclogite from the Iratsu body of the Sanbagawa belt, SW Japan

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Discovery of a new occurrence of jadeite- and kyanite-bearing eclogite from an outcrop within the Iratsu body of the subduction-type Sanbagawa belt, SW Japan, allows us to assess existing solid-solution models for clinopyroxene, and obtain insights into spatial variation in P-T conditions and/or H₂O activity during the eclogite-facies metamorphism of this region. The jadeite + kyanite assemblage is stable at higher P-T conditions or lower H₂O activity compared to paragonite. There is no significant difference in bulk rock composition between the newly found jadeite-kyanite eclogite and paragonite eclogite, which is the predominant eclogite type in the Iratsu body. The jadeite-kyanite eclogite is a medium-grained massive metagabbro consisting mainly of garnet, omphacite, kyanite, quartz, epidote, phengite, subcalcic amphibole and rutile. Pre-eclogitic relics of sodic augite (Jd₇₋₂₄Acm₆₋₁₆), actinolitic hornblende, Fe-rich garnet (Alm₆₂₋₇₁Grs₁₉₋₂₅Prp₅₋₁₃Sps₃₋₄) and magnetite are sporadically preserved. Eclogitic garnet (Alm₅₄₋₆₁Grs₁₆₋₂₀Prp₂₀₋₂₅Sps₁₋₂) optically shows a dusty appearance due to abundant microscopic inclusions of kyanite, quartz, epidote, phengite, omphacite (Jd₄₀₋₅₅Acm₇₋₁₃) and impure jadeite (Jd₆₂₋₈₆Acm₀₋₇). Jadeite is exclusively present as inclusions in garnet. The miscibility gap between the ordered omphacite (P2/n) and disordered impure jadeite (C2/c) progressively narrows during garnet growth, implying the temperature of the solvus apex coincides with the thermal peak of metamorphism. The observed compositional gap and the result of garnet-clinopyroxene Fe²⁺-Mg exchange thermometry are consistent with the phase diagram calculated in the pseudo-binary augite (Di₆₆Hd₁₄Acm₂₀)-jadeite system by using the newest solid-solution model of Deiner and Powell (2012), and the calculated apex of the omphacite-jadeite solvus is at 625 deg.C. However, calculated pseudosections with XRF-derived bulk rock composition and the solid-solution model have no jadeite stability field for any reasonable values of P, T, X_{Fe3+} and M_{H2O}, although the matrix assemblage is satisfactorily reproduced. This may suggest effective bulk composition around growing garnet was significantly different from the XRF-derived bulk rock composition. The localized feature of eclogite-facies equilibration is also inferred from the observed microstructures such as Omp + Qz + Amp pseudomorphs (prograde symplectites) after igneous augite. We obtain the jadeite stability field in the calculated pseudosections by subtracting augite from the XRF-derived bulk composition. High chlorine contents of amphibole (<1.5 wt% Cl) and apatite (<7.0 wt% Cl) indicate that the eclogite-facies equilibration was triggered by an influx of saline fluids. Multi-equilibrium thermobarometry for the assemblage Grt + Omp + Ky + Ph + Ep + Qz gives metamorphic P-T conditions of around 2.3 GPa and 600 deg.C. The estimated high-P conditions are also supported by high residual pressure (max. delta omega-1 = 13.3 cm⁻¹, equivalent to 0.85 GPa) of quartz inclusions in garnet. These results imply the presence of a significant metamorphic pressure gradient within the Iratsu body, and detailed baric structure of this region will be revealed by further application of the quartz-in-garnet barometry (Enami et al. 2007).

Reference: Deiner and Powell (2012) *J Metam Geol* 30, 113-130; Enami et al. (2007) *Am Mineral* 93, 1303-1315.

Keywords: eclogite, Iratsu body, jadeite, metagabbro, omphacite

Metamorphism of garnet glaucophane schists from the Bizan area, Sambagawa metamorphic belt, eastern Shikoku, Japan

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The Bizan area is located in the Tokushima Prefecture of eastern Shikoku, Japan and it is mainly composed of pelitic schists, basic schists and siliceous schists with minor garnet glaucophane schists. Faure (1983) suggested that there occur a melange with tectonic blocks of serpentinite, metagabbro and garnet-amphibolite (garnet glaucophane schists in this study) along the ductile shear zone between spotted and non-spotted zones in the Bizan area. Garnet glaucophane schists consist mainly of garnet, amphibole, epidote, phengite (Si 6.41-6.80 pfu), paragonite, chloritoid, chlorite, albite, rutile, titanite, ilmenite and quartz. A schistosity is defined by preferred orientation of glaucophane, phengite and chlorite.

Garnets are almandine-rich composition and display prograde growth zoning with decreasing X_{Sps} (0.18-0.01) and increasing X_{Alm} (0.54-0.70) from the core to the rim. The cores of garnet contain inclusions of chloritoid (X_{Mg} 0.08-0.23), chlorite, epidote, phengite (Si 6.41-6.55 pfu), paragonite, titanite and quartz and polyphase inclusions of phengite + paragonite + epidote + chloritoid + chlorite + quartz assemblage. The rims of garnet contain inclusions of amphiboles (glaucophane; zoned amphibole with barroisite core and glaucophane rim), epidote and quartz and polyphase inclusions of glaucophane + epidote. Garnets are partly replaced by chlorite. Glaucophanes in the matrix contain inclusions of phengite, epidote, chlorite, titanite and quartz. Some of them are partly replaced by Wnc, Brs, Mg-Ktp and Act at their rims and cracks. Phengites (Si 6.50-6.80 pfu) in the matrix are contain inclusions of glaucophane, epidote and chlorite. Some large grains of epidotes and chlorites contain inclusions of glaucophane, phengite, epidote, titanite and quartz.

Textural relationship, mineral assemblage and thermobarometric results suggest a polyphase tectonometamorphic evolution of the garnet glaucophane schists. The mineral assemblages of polyphase inclusions within the cores of the garnet such as barroisitic amphiboles, chloritoid, chlorite, epidote, phengite, paragonite and quartz constrain the P - T conditions of a prograde stage at 450-500°C and 9-11 kbar (by THERMOCALC) at epidote-blueschist facies metamorphic conditions. The rims of the porphyroblastic garnets include inclusions of glaucophane, epidote, quartz and schistosity-forming matrix phengite suggesting the peak metamorphic mineral assemblages. THERMOCALC average P - T calculation suggests a metamorphic condition of the eclogite facies metamorphism of 550-600°C and 17-19 kbar. Porphyroblastic garnets are partly replaced by chlorite at their rims, and matrix glaucophanes are replaced by Wnc, Brs, Mg-Ktp and Act along rims and cracks suggests a retrograde metamorphism took place at the epidote-amphibolite facies to follow a clockwise decompression path.

Large grains of epidotes and chlorites in the matrix which contain peak metamorphic mineral assemblages of glaucophane, phengite, epidote and quartz suggesting another high-pressure prograde metamorphism took place. This high-pressure metamorphism can be correlated with the Sambagawa metamorphism in the Besshi area, central Shikoku (Aoya, 2001; Kabir and Takasu, 2010a, b).

The eclogite facies metamorphism followed by another high-pressure metamorphism as the Sambagawa metamorphism is first described from the garnet glaucophane schists in the Bizan area, Sambagawa metamorphic belt. The metamorphic evolution is similar to that of the eclogites in the Besshi area, central Shikoku (Kabir and Takasu, 2010a, b). Eclogite in the Sambagawa belt occurs mainly in the Besshi area, central Shikoku and slightly in the Kotsu area, eastern Shikoku. This study revealed that the occurrence of eclogites now extend to the Bizan area in eastern Shikoku.

Reference:

Aoya (2001) *J Petrology*, 42, 1225-1248; Faure (1983) *J Geol Soc of Japan*, 89, 319-329. Kabir and Takasu (2010a) *J Meta Geol*, 28, 873-893; Kabir and Takasu (2010b) *Earth Sci*, 64, 183-192.

Keywords: Sambagawa metamorphic belt, garnet-glaucophane schist, eclogite, chloritoid, Bizan area, eastern Shikoku

Metamorphic conditions of kyanite-garnet-chloritoid schists associated with eclogites in the Lake Zone, SW Mongolia

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The kyanite-garnet-chloritoid schists associated with eclogites from the Alag Khadny metamorphic complex, Chandman district, Lake Zone, SW Mongolia, consist of garnet, chloritoid, muscovite, phengite, chlorite, paragonite, kyanite, rutile, ilmenite, zircon, quartz and carbonaceous matter. Garnets occur as subhedral to anhedral porphyroblast up to 5 mm across and they are almandine-rich variety in composition. The garnets are zoned with inclusion-rich cores and inclusion-poor rims. The garnets display a prograde pattern of compositional zoning, X_{Sps} decreasing and X_{Prp} increasing from core to rim. The cores contain inclusions of muscovite ($Si=6.06-6.29$ cations per formula unit, *pfu*), paragonite, chlorite, chloritoid and quartz. The rims contain inclusions of kyanite ($Fe_2O_3 < 1.24$ wt%; $Cr_2O_3 < 0.03$ wt%), phengite ($Si=6.40-6.63$ *pfu*), chloritoid ($X_{Mg} [Mg/(Fe+Mg)]=0.08-0.18$), chlorite ($X_{Mg} < 0.42$), and quartz. A well-developed schistosity is defined by preferred orientation of chloritoid ($X_{Mg} = 0.11-0.21$), chlorite ($X_{Mg}=0.36-0.53$) and white micas [phengite ($Si=6.57-6.63$ *pfu*) and muscovite ($Si=6.23-6.34$ *pfu*)] in the matrix.

Based on the textural relationship and chemical composition of minerals, following metamorphic stages are distinguished in the kyanite-garnet-chloritoid schists, i.e. (i) pre-peak stage, (ii) peak metamorphic stage, and (iii) retrograde stage.

The porphyroblastic garnets represent a typical prograde zoning, X_{Sps} decreasing and X_{Prp} increasing from core to rim. The pre-peak stage (i) is defined by the mineral inclusions in the cores of the garnets. They are muscovite ($Si=6.06-6.29$ *pfu*), paragonite, chlorite, chloritoid ($X_{Mg}=0.08-0.13$) and quartz, and they indicate relatively low-pressure and low-temperature conditions such as the greenschist facies. The peak metamorphic stage (ii) is defined by the mineral assemblage of the inclusions in the rims ($X_{Prp} < 0.13$) of the garnets, i.e. kyanite, phengite ($Si=6.40-6.63$ *pfu*), chloritoid ($X_{Mg}=0.08-0.18$), chlorite ($X_{Mg}=0.42$), rutile and quartz, and schistosity forming minerals, i.e. chloritoid ($X_{Mg} = 0.11-0.21$), phengite ($Si=6.57-6.63$ *pfu*), and chlorite ($X_{Mg}=0.36-0.53$) coexisting with the rims of porphyroblastic garnet. THERMOCALC (V. 3.33) (Powell and Holland, 1994) calculations for the rim of the garnet coexisting minerals of kyanite, phengite, chloritoid, and chlorite yielded P-T conditions of $T=575-585^\circ C$ and $P=10-11$ kbar of high-pressure epidote-amphibolite to low-pressure eclogite facies conditions of the high-pressure intermediate type metamorphism which are distinctly lower in metamorphic pressure than accompanied eclogites ($T=590-610^\circ C$, $P=20-22.5$ kbar; Stipska et al., 2010) even though the similar temperature conditions. However, $^{40}Ar/^{39}Ar$ muscovite plateau ages of the eclogite (543 +/- 3.9 Ma) and kyanite-garnet-chloritoid schist (537 +/- 2.7 Ma) are similar (Stipska et al., 2010), indicating simultaneous exhumation of both metamorphic rocks to the crustal level. There is no evidence of high-pressure type metamorphic event similar to the eclogites in the kyanite-garnet-chloritoid schists. These fact suggest that subduction within low-geothermal gradient conditions to produce the eclogites occurred first, subsequently relatively high-geothermal gradient metamorphism for the kyanite-garnet-chloritoid schists took place, and then whole sequence of metamorphic rocks were exhume to the shallower levels at ~ 540 Ma.

Reference:

Powell, R. and Holland, T.J.B. (1994). *Amer. Miner.*, 79, 120-133

Stipska, P., Schulmann, K., Lehmann, J., Corsini, J., Lexa, O. and Tomurhuu, D. (2010) *J. of Meta. Geol.*, 28, 915-933

Keywords: Kyanite-garnet-chloritoid schist, Eclogite, Alag Khadny metamorphic complex, Lake Zone, Mongolia

Raman spectra and reflectances of carbonaceous matters showing graphitization temperatures at around 300 - 400 C

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The degree of graphitization of carbonaceous matter (CM) has long been investigated using X-ray diffraction analyses, optical (reflectance) studies and Raman spectroscopies to analyze thermal histories of sedimentary rocks. Hirota and Hoshino (2007) noted that the degree of graphitization may reveal much detailed thermal histories than those recorded in the mineral assemblages. Komorek and Morga (2003) also demonstrated that the reflectances of CMs increased by only several hours heating in an oven. Therefore, we may expect the CM geothermometers for analyses of short-range thermal events such as dike intrusion, vein formation and faulting.

However, the thermometer using Raman spectrum of CM proposed by Beyssac et al. (2002) can be applied to the temperature range from 640 to 330 C with poor correlations at low temperatures. On the other hand, the thermometers by reflectance of CM ('vitrinite reflectance') are probably limited below 300 C (e.g., Hashimoto et al, 2004). Therefore, we have studied detailed characteristics of Raman spectra and reflectances of CMs showing their graphitization temperatures at around 300 - 400 C to investigate a future possibility of the CM geothermometer as a tool for analyses of the short-range thermal events.

We collected pelitic rock samples of the Kuga formation of the Jurassic accretion complex from the Yasaka contact aureole, Yamaguchi Prefecture, where the Hiroshima-type granite of the Cretaceous age intruded. Takami et al. (1993) classified the contact aureole into the cordierite zone (ca. < 1 km from the contact) and the biotite zone (1 - 2 km wide). Takami and Nishimura (2000) mentioned that the apparent d002 of CM decreases sharply in the biotite zone at around 1 km from the contact.

Two types of CM can be identified under microscopic observations of the collected rock samples. Hereafter, we may call them temporarily as M-type and P-type CMs. The former shows visible reflection pleochroism as well as anisotropism, while the latter does non- or weak ones. Therefore, the P-type CM is probably collinite for so-called 'vitrinite reflectance' measurements. They can be identified clearly also by their Raman spectra. The G bands of the P-type CMs are broad, while those of the M-type are characteristically narrow and sharp. It is interesting that the P-type CM could not be observed in the samples collected from the vicinities of the contact with granite.

The R2 ratio of the Raman spectrum of the M-type CM shows a systematic change with a distance from the contact. It increases from 0.47 (= 430 C, estimated from the equation of Beyssac et al., 2002) at Loc. 03 (0.1 km away from the contact) to 0.60 (370 C) at Loc. 10 (2.4 km). On the other hand, although the ratio of the P-type CM is the highest as 0.77 (300 C) at Loc. 10, the ratio in the other samples closer to the contact does not vary with the distance and is stable as 0.75 (310 C), implying the lower limit of the ratio of the P-type CM.

The P-type CM from Loc. 10 shows the lowest reflectance as 3.2 % (= 270 C, from the equation of Barker, 1988), while those from the other localities are around 5.0 % (310 C) and show no significant variation with the distance, implying also the upper limit of the reflectance of the P-type CM. Although the reflectance of the M-type CM is slightly higher than that of the P-type CM in the sample from Loc. 10, no obvious difference between the two could be seen in the other samples.

It should be emphasized that there may be a size dependency of the M-type CM on its R2 ratio in the samples close to the boundary, that is, a smaller CM tends to show a higher temperature. Hence, it can be expected to apply the R2 ratio of the M-type CM not only as a thermometer but also as a 'chronometer' for short-range thermal events.

An estimation of a P-T condition of the vein-formation in the footwall of the Nobeoka thrust will be presented as an example of the analyses of the thermal events.

Keywords: carbonaceous matter, Raman, reflectance, geothermometer

Study of negative residual pressure of quartz in garnet: Quartz Raman spectra of high-temperature metamorphic rocks

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The volume of quartz inclusions in garnet porphyroblasts changes with temperature and pressure until the rock reaches the surface of the earth. Positive residual pressure is preserved by the compressional stress when the volume of the included quartz becomes larger than that of the surrounding garnet, whereas negative residual pressure is preserved by the elongational stress when the volume of quartz becomes smaller than that of the garnet. The peak position of quartz Raman spectrum shifts toward high wavenumbers with increasing compressional stress and toward low wavenumbers with increasing elongational stress. Enami et al. (2007) measured the peak shift of quartz Raman spectra of several samples and estimated the residual pressure. They showed that there is a positive correlation between the residual pressure and metamorphic pressure. They also showed that there is almost no dependence of the residual pressure on temperature or on the chemical composition of garnet, and proposed that this technique can be applied to a quartz Raman barometer. Since quartz Raman barometry is independent of the thermodynamic model, this barometer is applied as one of the indices of pressure estimation of high-pressure metamorphic rocks in several studies (e.g., Kouketsu et al., 2010).

Recently, the quartz inclusions that preserve the negative residual pressure in the Higo metamorphic rocks were reported (Nishiyama and Aikawa, 2011). The simple elastic model used by Enami et al. (2007) shows almost no P - T range where the quartz inclusion acquires negative residual pressure (Van der Molen, 1981). Hence, Nishiyama and Aikawa (2011) interpreted that the negative residual pressure was acquired by the transition of the included quartz from beta- to alpha-phase.

In this study, we analyzed the rocks formed under high-temperature conditions to investigate in detail about the negative residual pressure that is not evaluated by the conventional quartz Raman barometer. We analyzed samples from Yanai Ryoke, collected from 5 different metamorphic zones and from East Antarctica. The metamorphic P - T conditions of Yanai Ryoke were estimated in detail by Ikeda (2004); Chl-Bt, Ms-Crd, and Kfs-Crd zones are stable in alpha-quartz, and Grt-Crd zone is stable in beta-quartz. The Sill-Kfs zone is near the alpha-beta transition line. The samples from East Antarctica are estimated to have formed at ultra-high temperatures.

The results of the analysis showed that the quartz included in the garnets of every sample from Yanai Ryoke have comparable values of negative residual pressure. In the sample from East Antarctica, quartz with very low residual pressure was commonly observed. This result implies that negative residual pressure is acquired when the metamorphic condition of the quartz included in the garnet is stable whether in alpha or beta phases. This result implies that the explanation provided by Nishiyama and Aikawa (2011) is insufficient. Hence, we reexamined the conventional elastic model; it became clear that the model of Van der Molen (1981) is not suitable for estimating the relation between the residual pressure and metamorphic pressure, and that the model of Zhang (1998) is more appropriate for the quartz Raman barometer. We improved the model to estimate the residual pressure by taking into consideration the pressure dependency of the bulk modulus and the temperature dependency of the thermal expansion.

The new model can explain the negative range of the quartz Raman barometer qualitatively. It was shown that the quartz acquires negative residual pressure even if it had been included in the garnet under the metamorphic conditions in a stable alpha-phase. In addition, it was also shown that the quartz included under the ultra-high temperature conditions, as in the case of the sample from Eastern Antarctica, acquires much lower values of residual pressure than that observed in the case of samples from Yanai Ryoke.

Keywords: negative residual pressure, quartz Raman barometer, high temperature metamorphism, inclusion-host system, elastic model

Correlation stress history with statistical analysis on mineral composition at small brittle fault in the borehole core

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The Median Tectonic Line (MTL), the largest on-land fault in Japan, has a long history of displacement, and the fault rocks deformed under variable conditions are distributed. The analysis of internal structure of the MTL, therefore, helps to improve our understandings of variable fault behavior depend on the physical conditions and development of fault zone.

AIST drilled a borehole penetrating the MTL for predicting Tonaikai-Nankai Earthquake at Iitaka, Matsusaka, Mie prefecture. The drilling length is 600m. It crosses MTL at the depth of 473.9m. Hangingwall of the MTL consists of Ryoke-derived tonalitic mylonite and footwall of the MTL consists of fractured rocks derived from Sanbagawa metamorphic rocks.

The rocks in the hangingwall experienced the four kinds of stress pattern after the mylonitization. These are stresses which caused normal faultings (vertical compressive stress (Stress-A) and North-South tensional stress (Stress-B), order of the two is unknown), North-South compressive stress and East-West compressive stress (present stress pattern) in turn with time (Shigematsu et al., oral presentation in the 117th Annual Meeting of the Geological Society of Japan, 2010). Among the 327 small brittle faults contributed to stress inversion on Shigematsu et al. (2010), 153 faults could be uniquely attributed to one of the four stress patterns, 127 faults could be attributed to two or three of them, and 47 faults belong to none of them (Tanaka et al., oral presentation in the 118th Annual Meeting of the Geological Society of Japan, 2011).

We tried to infer a suitable stress pattern each of those 127 faults from statistical analysis on the fault material on the slip surfaces of the small brittle faults.

We sampled the fault material on the 129 of those 153 faults, analyzed mineral composition of those samples by X-ray diffraction (XRD) and applied principle component analysis (PCA) to the 129 mineral composition data sets. As a result, an inverse relationship between quartz and carbonate was proved to be most significant characteristic. The fragmented wall rock is dominant in the quartz rich samples; in contrast, alteration minerals are dominant in the carbonate rich ones. Correlating among the four with removal of the carbonate rich ones, the newer (shallower) stress pattern is, the more carbonate content in fault material is. In the fault material, Stress-A contains less carbonate than Stress-B. Thus, the former may be older than the latter.

We sampled the fault material on the 113 of those 127 faults, analyzed mineral composition of those samples by XRD and applied discriminant analysis to the 113 mineral composition data sets. Assuming the stress pattern having minimum Mahalanobis' distance is valid, the 78 faults could be attributed to a suitable stress pattern. Combining the 153 faults and the 78 faults, the faults attributed to Stress-A and Stress-B are densely distributed from 140m to 250m depth, about 300m far from the MTL. In contrast, the faults attributed to the other two stresses are concentrated within 200m from the MTL. Thus, the width of the brittle deformation zone along the MTL might be narrower as regional uplifting and faulting.

Keywords: Median Tectonic Line, fault, borehole core, mineral composition, statistical analysis, stress history