

Prograde infiltration of Cl-rich fluid into the granulitic continental crust from a collision zone in Perlebandet, Sør Rondane Mountains, East Antarctica

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Timing of Cl-rich fluid infiltration is correlated with the pressure-temperature-time (P - T - t) path of upper amphibolite- to granulite-facies metamorphic rocks utilizing microstructures of Cl-bearing biotite in pelitic and felsic metamorphic rock from the continental collision zone (Perlebandet, Sør Rondane Mountains (SRM), East Antarctica). Microstructural observation indicates that the stable Al_2SiO_5 polymorph changed from sillimanite to kyanite + andalusite + sillimanite, and P - T estimates from geothermobarometry point to a counterclockwise P - T path characteristic of the SW terrane of the SRM (e.g., Osanai et al., 2013) *In situ* LA-ICPMS U-Pb dating of zircon inclusions in garnet yielded ca. 580 Ma, likely representing the age of garnet-forming metamorphism at Perlebandet.

Inclusion-host relationships among garnet, sillimanite, and Cl-rich biotite (Cl > 0.4 wt%) reveal that formation of Cl-rich biotite took place during prograde metamorphism in the sillimanite stability field. This process probably predated partial melting consuming biotite (Cl = 0.1-0.3 wt%). This was followed by retrograde, moderately Cl-bearing biotite (Cl = 0.1-0.3 wt%) replacing garnet. Similar timings of Cl-rich biotite formation in different samples, and similar $f(\text{H}_2\text{O})/f(\text{HCl})$ values of coexisting fluid estimated for each stage can be best explained by Cl-rich fluid infiltration during prograde metamorphism.

Fluid-present partial melting at the onset of prograde metamorphism probably contributed to elevate Cl concentration (and possibly salinity) of the fluid, and consumption of the fluid resulted in the progress of dehydration melting. The retrograde fluid was released from crystallizing Cl-bearing partial melts or derived externally.

The prograde Cl-rich fluid infiltration in Perlebandet presumably took place at the uppermost part of the footwall of the collision boundary. Localized distribution of Cl-rich biotite and hornblende along large-scale shear zones and detachments in the SRM (Higashino et al., 2013; 2015) supports external input of Cl-rich fluids through tectonic boundaries during continental collision.

Keywords: Fluid, Metamorphism, Partial melting, Chlorine, Continental collision

Formation of Corona around Corundum from Akarui Point in the Lützow-Holm Complex, East Antarctica: Controlling factor and P-T slope of reaction

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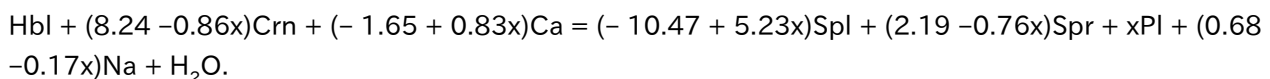
Corona, a disequilibrium texture, is often found in metamorphic rocks. Its textural feature that preserves both reactant and product minerals gives us various information for metamorphic reactions including mass transfer, diffusion and pressure (P) –temperature (T) path. In this study, we dealt with a corona developing between corundum and hornblende in ultrabasic gneiss, and revealed controlling factor of zonal arrangement, reaction, volume change and P-T slope of corona formation.

The studied gneiss composed mainly amphibole and plagioclase was collected from Akarui Point in the Lützow-Holm Complex, East Antarctica. Corundum grains in the rock are surrounded by corona composed of green spinel, sapphirine and plagioclase that are regularly arranged from corundum to the matrix. In the matrix, hornblende, plagioclase and gedrite occur together with minor brownish-green spinel, biotite and opaque minerals. The brownish-green spinel also occurs as inclusion in corona plagioclase or at the outer border of corona sapphirine.

Chemical composition of corundum is almost pure Al_2O_3 . Cr content in green spinel is as low as 0.00 –0.01 apfu (O = 4), while brownish-green spinel contains significant amount of Cr as 0.08 –0.26 apfu. Si content of corona sapphirine increases and Al content decreases outward. Anorthite content $[=100 \cdot \text{Ca}/(\text{Ca}+\text{Na})]$ of corona plagioclase decreases from inner to outer part (from 89 to 78). Hornblende and gedrite are classified with pargasite and sodicgedrite according to Leake et al. (1997), respectively. $\text{Ca}/(\text{Ca}+\text{Na})$ of hornblende ranges from 0.67 to 0.74.

Al contents of constituent minerals normalized by 40 oxygen decrease in the following order: corundum, spinel, sapphirine, plagioclase and hornblende. Corona sapphirine and plagioclase show a similar feature that Al decreases outward. Si content shows inverse trend to Al in sapphirine and plagioclase, so these features suggest that diffusion of Al and Si controlled corona formation.

Stoichiometric equation of the reaction is estimated by considering mass-balance in the $\text{Na}_2\text{O} - \text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ system. The value of $\text{Ca}/(\text{Ca}+\text{Na})$ differs between hornblende and plagioclase, which requires to treat Na, Ca or both as mobile component. The resultant equations are inconsistent with the microstructure in the case of only one mobile component (Na or Ca). Calculation with treating both Na and Ca as mobile component provides following equations in which stoichiometric coefficient of plagioclase, x, is introduced as a variable.



The microstructure constrained the range of x as 2.00 –2.87. This result suggests that inflow of Ca and outflow of Na occurred during corona formation.

We also estimated volume change and slope in P-T space of the reaction by using standard molar volume and entropy of Holland and Powell (1998). Total volume and entropy of products are always larger than those of reactant in the range of $2.00 < x < 2.87$. This result means that volume increased by the corona formation and the slope of the reaction is positive. Previous studies (e.g., Iwamura et al. 2013) have revealed that the complex experienced nearly isothermal decompression in a clockwise P-T path. It may be suggested that the corona-forming reaction took place during the decompression.

We conclude the history of the corona formation as bellow. Corundum contacts with hornblende before corona formation at high pressure. The corona-forming reaction that has positive P-T slope was triggered by decompression. The diffusion of Al and Si controlled the rate of mass transfer, during which Ca was supplied and Na was released.

Keywords: corona, reaction texture, the Lützow-Holm Complex

Multiply hydration events of pyroxenite and amphibolite in the middle crustal conditions, Sør Rondane Mountains, East Antarctica

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Fluids in the crust are important for ore deposition, crust evolution and geothermal activity in subduction zones. Fluids supplied from the subducting slab cause hydration reactions, which induce mass and heat transport, redistribution of elements, formation of new minerals, and changes rheology of rocks. The extent, chemistry, time of infiltration, distribution and flow mechanisms mode of such hydration reactions are determined by fluid flow rate, fluid sources and properties of rocks where reaction has happened. Therefore, it is important to understand flow rate and source of fluid for estimating evolution of the Earth's crust in terms of fluid-rock interaction. The main target of this study is estimating of time and conditions of fluid infiltration.

Pyroxenite and amphibolite that is partly hydrated along veins and fractures were collected from Mefiell, Sør Rondane Mountains, East Antarctica during JARE-51 (2009-2010 years). The basement rocks of Sør Rondane Mountains can be divided into amphibolite-facies to granulite-facies Southwestern terrane and granulite-facies to greenschist-facies Northeastern terrane. NE-terrane exhibits a clockwise pressure-temperature-time (P-T-t) path and the SW-terrane exhibits a counter-clockwise P-T-t path (Osanaï et al., 2013). Samples analyzed in this study were collected from SW-terrane.

For pyroxenite, the host rock is dominated by clinopyroxene, orthopyroxene, plagioclase, potassium feldspar with minor amount of ilmenite, apatite and biotite, which are replaced partially by hornblende, biotite, apatite in the veins. Calculated weight percentage of water ranges from 0.1% for host rock to 1.3% as the maximum for the veins.

In the vein, altered clinopyroxene grains are surrounded by hornblende and orthopyroxene grains are surrounded by cummingtonite and actinolite. The X_{Mg} is different between two pyroxenes (X_{Mg} around 0.61 for clinopyroxene in the vein, 0.59 in the host rock and X_{Mg} around 0.48 for orthopyroxene in the vein, 0.46 in the host rock).

In some plagioclase grains cores are represented by albite and rims by anorthite. Anorthite rims boundaries are in contact with tschermakite rims boundaries which surrounding hornblende cores. Conditions estimated by hornblende-plagioclase (Holland and Blundy, 1994), Ti in biotite (Henry et al., 2005) thermometers and Al in hornblende geobarometer (Anderson and Smith, 1995) reveal that P-T conditions of vein formation was estimated to be around 6 kbar and $635\pm 50^\circ\text{C}$ for hornblende and $575\pm 75^\circ\text{C}$ for tschermakite respectively. Contrary, application of two pyroxene thermometer (Wells, 1977) to the host rock shows $850\pm 50^\circ\text{C}$.

These results suggest that hydration of the pyroxenite had occurred through brittle fracture during cooling from granulite-facies to amphibolite-facies under middle crustal condition.

For amphibolite, major minerals are orthopyroxene and amphiboles, with minor amount of ilmenite, anorthite, spinels, muscovite and apatite. In the vein actinolite, serpentine, epidote and magnetite were observed.

Symplectite consists from muscovite and anorthite surrounded by spinels was found along veins.

Temperature around $400\pm 50^\circ\text{C}$ was estimated using ilmenite magnetite thermometer (Andersen and Lindsley, 1985) for the veins.

Cl and F were enriched in apatite and micas in the veins.

Foliation parallel veins were formed by hydration events under greenschist-facies to amphibolite-facies, and then foliation vertical veins were occurred in later stage which suggests several infiltration events.

Keywords: hydration, metamorphic rocks

Petrological study of the serpentinite melange from the Nagasaki Metamorphic Rocks in the Nomo Peninsula

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The Nagasaki Metamorphic Rocks are low temperature and high pressure metamorphic rocks mainly composed of crystalline schists distributed in Nishisonogi, Nomo and Amakusa. The metamorphic rocks in the Nomo Peninsula consist of three rock units: crystalline schists, serpentinites and metagabbros. The serpentinite melange occurs associated with the serpentinite, and the matrix of the serpentinite melange consists mainly of actinolite schist and chlorite - actinolite schist. This rock is strongly schistose and contains lens-like rock masses as tectonic blocks. The representative mineral assemblage of the matrix is actinolite + hornblende + albite + chlorite + epidote + muscovite + calcite + magnetite. Actinolite are oriented parallel to the schistosity. The matrix also contains porphyroclasts of epidote and brown hornblende. The tectonic blocks in this serpentinite melange include the metavolcanic rocks (pillow lava, pillow breccia, hyaloclastite and volcanic breccia), amphibolite, mylonite, cataclasite, albitite, metagabbro and serpentinite. Metavolcanic rocks generally occur as large blocks, which are 1 to 10m in size. The pillow lava is hardly deformed and round pillow laves are seen with epidote -rich layers inbetween. The mineral assemblages is omphacite + chlorite + muscovite + epidote + albite + titanomagnetite. The pillow breccia, shows a transition from pillow lava, and calcite filling the original vesicles is observed. The mineral assemblages is winchite + chlorite + epidote + albite + calcite + titanomagnetite. In the angular rock fragments show jig-sow puzzled structures indicating brecciaation owing to rapid quench in the water. The mineral assemblage is winchite + barrosite + chlorite + epidote + muscovite + albite + titanomagnetite. In contrast to the hyaloclastite, the volcanic breccia consists of various round blocks in the matrix. The mineral assemblages is winchite - barrosite + actinolite + chlorite + epidote + albite + titanomagnetite. The amphibolite occurs as blocks of 1 to 2 m in size. The mineral assemblages is winchite - barrosite + actinolite - tremolite + chlorite + epidote + muscovite + albite + titanomagnetite. The mylonite occurs as blocks of less than 1 m in size. It shows strong foliation, and banded structures. Fine grained aggregates of albite and epidote occurs in the mylonite, including porphyroclasts of amphibole. The mineral assemblages is actinolite + tschermakite + chlorite + epidote + albite + titanomagnetite. The tschermakite contains 10.40wt% of Al_2O_3 , suggesting high temperature origin. The cataclasite occurs as blocks of less than 1 m in size, consisting of rock fragments with various orientations. The mineral assemblages is actinolite + winchite - barrosite + chlorite + epidote + albite + titanomagnetite. The metagabbro is accompanied by a reaction zone of chlorite. The mineral assemblages is barrosite + magnesioriebeckite + chlorite + epidote + muscovite + albite + titanomagnetite. Amphiboles are mostly barrosite, but rarely magnesioriebeckite. The albitite occurs as blocks of 10cm in size. The mineral assemblages is actinolite + epidote + chlorite + albite + titanomagnetite. The serpentinite mélangé has undergone epidote blueschist facies metamorphism, as suggested by the occurrence of omphacite, winchite - barrosite and magnesio-riebeckite. Some peculiar rocks rich in calcite and hematite occur as blocks in the serpentinite melange. The mineral assemblages is cpx + epidote + mica + amphibole + chromite + albite + chlorite + calcite + hematite. Cpx, epidote, mica and amphibole occur in cracks or peripheries of chromite grains. All minerals contain Cr except albite and calcite. Cpx contains up to 6.82wt% of Cr_2O_3 and no compositional zoning is observed from the core to the rim. Chemical zoning owing to diffusion of Cr is not observed in these Cr-by minerals, therefore the reaction halos surrounding chromite grains do not represent diffusion-controlled process.

Keywords: Nagasaki Metamorphic Rocks, serpentinite melange, metavolcanic rocks

Zircon U–Pb geochronology and P–T estimation of gneisses and amphibolites from the southwestern Gyeonggi Massif, South Korea: Implication for regional middle Paleozoic metamorphism

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The Hongseong area, characterized by the Permo–Triassic eclogite and high-grade rocks, in the southwestern Gyeonggi Massif, South Korea, is considered as a part of eastern extension of the Dabie–Sulu collision belt in China (e.g., Oh and Kusky, 2007). Recently, middle Paleozoic igneous and metamorphic events are also known in this area (Oh et al., 2009, 2014; Kim et al., 2008, 2014; Kwon et al., 2014). However, it is still questionable 1) whether middle Paleozoic events regionally occurred or not and 2) what kind of metamorphism occur in the southwestern Gyeonggi massif. We carried out zircon U–Pb SHRIMP ages and P–T estimation of gneisses and amphibolites in this area to constrain multiple protolith ages and metamorphic events. Migmatitic biotite gneisses in eastern Wolhyeonri complex formed during Neoproterozoic and underwent the granulite facies metamorphism (750–880 °C, 12–15 kbar) at 442–413 Ma and subsequent amphibolite facies retrograde metamorphism at 585–660 °C and 7.5–10.3 kbar. Mylonitic biotite gneiss, hornblende gneiss, and folded amphibolite also yield the metamorphic ages ranging between 429 and 420 Ma. The protoliths of several garnet amphibolites formed at 470–456 Ma due to arc magmatism, and they were also metamorphosed before 418 Ma by high pressure amphibolite facies metamorphism at ca. 625–700 °C and 13–15.5 kbar, followed by retrograde amphibolite facies metamorphism at ca. 625–700 °C and 8–9 kbar at 418–405 Ma. The SHRIMP ages obtained from a various rock type indicate that the middle Paleozoic metamorphism regionally occurred in this area. In contrast, the Paleoproterozoic augen gneisses block in the Deokjeongri gneiss complex preserve high pressure metamorphism (840–960 °C, 17–21.8 kbar) at 234–230 Ma as eclogite previously reported in this area. Regional middle Paleozoic metamorphism before high pressure Permo-Triassic metamorphism could be comparable with the middle Paleozoic Qinling orogeny in China, which were caused by the microcontinental collision before the Permo-Triassic collision between the North and South China Cratons.

Keywords: southwestern Gyeonggi Massif, zircon U–Pb ages, middle Paleozoic metamorphism

The numerical simulation of rigid ellipsoids rotation within Newtonian viscous matrix for the comparison with the arrangement of columnar tourmaline grains within quartz matrix in metacherts

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We performed the numerical simulation for the rigid ellipsoids rotation within the Newtonian viscous matrix. The simulation provided the variation of the shape preferred orientation of the ellipsoids with respect to variables between the degree of non-coaxiality ($\Theta = 0^\circ\text{--}90^\circ$) and Flinn parameter ($K = 0\text{--}\infty$). We used the width and length data collected from 3621 of tourmaline grains as the shape factor of the ellipsoids, and the initial distribution pattern of the ellipsoids is assumed to be random in their orientation. Calculation results are obtained on the plane parallel to the foliation (XY-plane) and the plane vertical to the foliation in parallel with the mineral lineation (XZ-plane), because this facilitates the comparison with nature. Using the calculation result, we compared these results with the natural shape preferred orientation of tourmaline grains embedded within quartz matrix of metacherts. The comparison suggests that natural shape preferred orientation of the tourmaline grains from three metacherts correspond to a pure shear ($\Theta = 90^\circ$) and plane to constrictional strain ($K = 1\text{--}10$) with about 1–2 of finite strain.

Keywords: shape preferred orientation, numerical simulation, rigid ellipsoid, tourmaline, degree of non-coaxiality

Re-examination of pressure difference based on geobarometry and its geological significance

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Conventional geobarometers contain, in general, uncertainty that exceeds 100 MPa. The uncertainty of 100 MPa corresponds to the uncertainty in depth of 3.6-3.7 km. These features have caused difficulty in deciphering precise thermobaric structures (isobaric lines) in a metamorphic region, as well as in employing them as constraints to evaluate the validity of any numerical models of crustal evolution. This study re-examined the formulation of conventional geobarometers and revealed that the difference in the estimated pressures based on the same geobarometer contains uncertainty that is smaller, in one order of magnitude, than that of the absolute pressure.

The uncertainty in pressure estimation of conventional geobarometers is derived from the uncertainties of enthalpy and entropy changes of the reaction, provided that volume change of the reaction, equilibrium constant and temperature were well-established. The uncertainties derived from the enthalpy change and entropy change represent similar magnitude at temperatures of most crustal conditions. For example, the geobarometers based on the reaction among garnet, clinopyroxene, plagioclase and quartz show uncertainty derived from enthalpy change of 120 MPa, that from entropy change of 120 MPa at 727 °C, and in total of 160 MPa.

In contrast, comparison of two samples based on the same pair of geothermobarometers provides uncertainty of pressure difference in which the uncertainty derived from enthalpy change disappears. Further the uncertainty of entropy change is multiplied by temperature difference but not by absolute temperature, the former is much smaller than the latter. As a result the geobarometers shown above represent uncertainty in pressure difference of 32 MPa at temperature difference of 200 °C. This indicates that we can determine the difference in depth precisely with uncertainty of c. 1.2 km.

As an example of geological application, we chose a high-temperature metamorphic complex in the Omuta area, northern Kyushu, SW Japan. The metamorphic complex is in contact with a Cretaceous granitic complex, which has raised a question whether the metamorphism was regional or thermal. Two examined samples are spatially 6.8 km distant (2.3 km perpendicular to the isograds) from each other, and show the pressure difference of 320 MPa with uncertainty of 10 MPa. This pressure difference corresponds to 11-12 km difference in depth with uncertainty of 0.3 km, and is significantly larger than the geographic distance. No fault with large separation is present between the localities. The result leads us to the conclusion that the significant crustal thinning took place during retrograde metamorphism, implying regional origin of the metamorphism.

Keywords: pressure difference, geothermobarometer, uncertainty

Improving spatial resolution for quantitative microanalysis by SEM-EDS using lower accelerating voltage

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Abstract

It is challenging to measure the chemical compositions of very fine-grained minerals. A method with broad utility to measure with high spatial resolution for quantitative microanalysis has not yet been established for geological materials. We are developing such a method using energy-dispersive spectrometry (EDS) in a scanning electron microscope (SEM), evaluating the effects of two corrections to improve the spatial resolution and quantitative accuracy: (1) reducing the accelerating voltage and (2) reducing the probe diameter.

We impose these corrections to counteract the fact that the interaction volume of incident electrons within a mineral expands due to electron scattering, resulting in X-rays being generated from a wider region than the incident probe diameter. It has been demonstrated that the X-ray generation volume is smaller at lower accelerating voltage, so reduction of the accelerating voltage results in an improvement of spatial resolution (e.g., Barkshire et al., 2000; Burgress et al., 2013). Reducing probe current also reduces the size of the X-ray generation volume and improves spatial resolution. Both of our corrections also result in a significant decrease in the signal intensity of the X-ray spectra.

Analyses were performed by EDS (Oxford X-Max^N 80mm² with AZtec) in a HITACHI SU-3500 SEM at the GSJ-lab in the Geological Survey of Japan, AIST. We have evaluated the spatial resolution and the signal intensity of the X-ray spectra for a range of SEM optics and EDS detector settings. A minimum accelerating voltage of 9 kV is required to quantify Fe-oxides using the signal intensity of Fe K α X-rays. Count rates of X-rays and probe currents measured through a faraday cup can be decreased by reducing accelerating voltage, spot intensity or size of aperture. The count rates of X-rays at dead times of ~45% can be processed to yield acceptable quantitative analyses. A spot intensity (condenser lens) of 63 is required to obtain a dead time of ~45 % when accelerating voltage is 9 kV and aperture is No. 3 (50 μ m) in the system at the GSJ lab, by setting the longest counting time (processing time of 6) possible in AZtec. A probe current of ~0.6 nA is generated by these SEM settings.

We have so far verified the method through measurement of anhydrous and hydrous natural mineral samples. The analyses reveal that the best possible operating conditions are 9 kV accelerating voltage, spot intensity of 63, aperture No. 3, and processing time of 6. Line scans across (potentially dipping) natural mineral boundaries suggest a maximum spatial resolution of the analyses of ~1 μ m, i.e., analysis of 2 μ m diameter grains is possible. The accuracy of weight percentages of oxides is estimated as a relative difference of < 5 % for MgO, Al₂O₃, SiO₂, Na₂O and K₂O and < 10 % for Fe-oxides compared to values obtained by WDS or at an accelerating voltage of 15 kV.

In future we will work to increase the accuracy of quantification of iron by obtaining proper standard

spectra, and to measure spatial resolution by a combination of Monte Carlo simulations, which allow theoretical predictions of spatial resolution, a 'knife edge' technique using a sharp edge which allows measurement of lateral analytical spatial resolution, and further line scan analyses across mineral boundaries of known orientation.

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Keywords: SEM-EDS system, spatial resolution, signal intensity, quantitative microanalysis

Evaluation of the grade of mylonitic rocks using cathodoluminescence

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Cathodoluminescence (CL) microscopy and spectroscopy provide useful information on existence and distribution of impurity elements related to crystal chemistry and lattice defects produced by destruction or distortion of atomic linkages with a high-spatial resolution, which should be more informative to characterize the crystal-chemical features of minerals. In this study, we have conducted to characterize CL features of the minerals in mylonitic rocks distributed in the Ryoke metamorphic belt along the Median Tectonic Line for the evaluation of mylonitization.

Mylonite, protomylonite and their source rocks (Hiji tonalite) were collected from the outcrops around an eastern part of Iida City, Nagano Prefecture. CL imaging was carried out using the Luminoscope with a cooled CCD camera. CL spectra were obtained by an SEM-CL system consisting of SEM with a grating monochromator. CL Spectral data were corrected for total instrumental response.

Color CL imaging of the mylonitic rocks shows yellow for plagioclase, blue for K-feldspar, purple to red for quartz and occasionally cream to yellow for minute zircon and apatite. In CL spectroscopy, the plagioclase with a yellow CL gives a broad band at 730-740 nm in a red region, a broad band at 570-580 nm in a yellow region and weak broad bands from 330 nm up to 430 nm in a blue region, which well correspond to the optical CL. The K-feldspar with a blue CL gives a broad band at 730-740 nm in a red region and a broad emission band at around 420 nm in a blue region. The quartz with purple to red CL gives a broad band at 640-750 nm in a red region and a broad emission band at around 390 nm in a blue region. In the quartz, the emission intensity in the blue region around 390 nm can be assigned to structural defects related to $Al^{3+}-M^+$ (M: Li^+ , Na^+ , K^+ or H^+). Its intensity decreases with the progress of the mylonitization in host rocks, accompanied with its peak shift to the shorter wavelength side (higher energy side). Furthermore, the emission intensity at 640-750 nm in a red region due to structural defects of NBOHC and/or substitutional Fe^{3+} shows a slight increase with the mylonitization. The decrease of blue-emission intensity related to the mylonitization suggests that structural defects originally existed in the quartz for a blue-CL emission were eliminated by shear stress and/or elevated temperature during the formation of mylonite. CL characterization of the quartz could be used as an indicator for the evaluation of the mylonitization process.

Keywords: Cathodoluminescence, Mylonite, Mylonitic rocks