

**Infiltration process of brine in the deep crust
constrained from multi-scale major and trace element
zonings in high-grade metamorphic rocks**

Fumiko HIGASHINO

Abstract

Infiltration process of brine in the deep crust constrained from multi-scale major and trace element zonings in high-grade metamorphic rocks

In the lower continental crust, CO₂-rich fluid has been considered to be dominant. Recently, high salinity fluid inclusions, halite and sylvite inclusions, and hydrous minerals with high Cl concentration are interpreted as important evidence of brine in natural rocks (e.g., Van Reenen and Hollister, 1988; Kullerud, 1995; Markl and Bucher, 1998). In the deep crust, NaCl- and KCl-bearing brine can coexist with CO₂-rich fluid, dissolves various major and accessory minerals, and enables large-scale mass transfer in kilometer scale without partial melting (Ayers and Watson, 1991; Newton et al., 1998; Heinrich, 2007; Newton and Manning, 2010; Tropper et al., 2011; Harlov, 2012).

There is an argument that fluid inclusions should be regarded as the only evidence of brine, because major cations in the fluid cannot be determined directly from Cl-bearing minerals (e.g., Van den Kerkhof et al., 2014). Since brine has low wetting angle and low viscosity, it is difficult to be trapped in rocks as fluid inclusions. In addition, especially in deformed rocks, early-stage

fluid inclusions alone tend to be hardly preserved, and instead, late-stage fluid inclusions are often preserved together. Therefore, it is difficult to correlate metamorphism with fluid inclusions. Mineral inclusions can be protected from strong deformation and later chemical modification if included in hard, container minerals. Microstructural and chemical features of such inclusion minerals would be useful in constraining the timing of fluid-related mineral formation and coexisted fluid compositions. Therefore, establishing new indicators of brine using mineral compositions and microstructures could contribute to further understand the natural occurrence of brine in the lower crust and brine-induced mass transfer. This study aims to establish such a new indicator and to constrain the trace element compositions of brine in the deep crust, especially focusing on addition and loss of fluid compatible elements and chemical zonings of minerals.

This thesis consists of two parts. Both parts deal with the same sample, a garnet-hornblende (Grt-Hbl) vein that discordantly cut the gneissose structure of a garnet-orthopyroxene-hornblende gneiss from the Sør Rondane Mountains, East Antarctica. The biotite grains defining the gneissose structure are included in the vein-forming garnet and hornblende, suggesting that most part of the Grt-Hbl vein was originated from the wall rock. In the wall rock, Cl contents of hornblende and biotite and K content of hornblende, as well as the thickness of Na-rich rim of plagioclase decrease with distance from the Grt-Hbl vein. This implies that the Grt-Hbl vein was potentially formed through the infiltration of NaCl-KCl-bearing brine in the middle to the lower crust.

In Part 1, the appropriateness of Zr as an ‘immobile element’ is discussed in order to estimate a relative mass addition/loss during the Grt-Hbl vein formation. Modal analysis of minerals in the wall rock and the vein combined with the quantitative determination of their Zr contents revealed that most of the bulk rock Zr resides in zircon. Garnet and hornblende host ~5 % of Zr in the wall rock and ~20 % of Zr in the vein, respectively. The Zr concentration of garnet and hornblende is constant irrespective of the distance from the vein. This implies that geochemical behavior of Zr in the wall rock is mostly controlled by the behavior of zircon. U-Pb age and rare earth element pattern of zircon rims are constant and unchanged irrespective of distance from the vein. Zircon shows any microstructure suggesting dissolution or overgrowth during the Grt-Hbl vein formation. Therefore, Zr can be considered as an appropriate ‘immobile element’ during the Grt-Hbl vein formation in the wall rock, and also in the vein itself if ~10% error is taken into account.

In Part 2, mass transfer during the Grt-Hbl vein formation was examined using Zr as an immobile element. It is revealed that Li, Cu, Rb, Ba, Pb, and U were added to the wall rock at the vicinity of the vein. Previous studies indicate that these trace elements tend to be mobile in fluids rather than in melts. Therefore, the Grt-Hbl vein would be formed by the infiltration of NaCl-KCl-bearing brine.

Trace element concentrations in each mineral in the wall rock decrease with distance from the vein and in most cases show concave up/down profiles (termed ‘diffusion-like’ profiles in this

study). The compositional variations within each mineral grain of plagioclase and apatite are almost negligible compared to the variation with distance from the vein. Distances where these element concentrations become constant depend on elements, and not on mineral species. On the other hand, while anorthite content of plagioclase discontinuously decreases at the rim, plagioclase has flat trace element zoning within each single grain. This would be explained by the sluggish (7-9 orders slower) NaSi-CaAl interdiffusion compared to the lattice diffusion of trace elements in plagioclase. Different zoning patterns in plagioclase observed between trace and major elements helps to reveal possible brine-induced processes. Brine advection through grain boundaries into the wall rock and chemical evolution of brine successfully explain chemical characteristics and microstructures described above. In this study, changing brine compositions were likely incorporated into the rim of minerals by dissolution-reprecipitation process and/or grain boundary diffusion simultaneously with the advection of brine. Lattice diffusion of trace elements within the wall-rock-minerals followed, resulting in flat trace element zonings. Time duration required to form the plagioclase zoning is estimated to be less than 1 Ma, using diffusion coefficients of Sr, Ba, and Pb in plagioclase at 700 °C. NaSi-CaAl interdiffusion hardly proceeded during this time span. This is consistent with preservation of discontinuous major element zoning at the rim of plagioclase.

Next, trace element concentration of brine in the studied sample was estimated using

published partition coefficients, and compared with the published trace element compositions of deep subduction-zone fluids. As a result, estimated Ba, Pb, and U concentrations in brine of this study were higher than the aqueous fluid liberated at the blueschist to eclogite facies transition, bearing in mind the error resulting from using partition coefficients at different *P-T* conditions. Consequently, the brine in the deep crust can potentially contribute to enrich the middle to upper crust with Ba, Pb, and U.

In the studied sample, coexistence of Cl-rich hornblende or biotite and plagioclase with discontinuous Na-richer rim would represent the characteristic microstructure found in the region of brine advection. Therefore, this coexisting microstructure is proposed as a new indicator of brine advection. Utilization of this indicator would help detecting the former presence of brine even from samples without visible fluid passages and fluid inclusions, and facilitate understanding of brine-induced mass transfer in the deep crust.

“I’ll see their trail first. Bring in the evidence”

King Lear, William Shakespeare

Contents

Abstract.....	i
Contents.....	vi
Preface.....	1
 Part 1. Geochemical behavior of zirconium during Cl-rich fluid or melt infiltration	
 under upper amphibolite facies metamorphism – A case study from	
Brattnipene, Sør Rondane Mountains, East Antarctica	
1.1. Introduction.....	18
1.2. Geological setting.....	20
1.3. Analytical methods.....	24
1.4. Sample locality.....	25
1.5. Sample description of the Grt-Opx-Hbl gneiss with a Grt-Hbl vein.....	30
1.5.1. <i>In situ</i> Zr analysis of minerals and whole-rock Zr concentration.....	31
1.5.2. <i>In situ</i> LA-ICPMS U-Pb zircon dating and REE analysis.....	35
1.6. Discussion.....	46
1.6.1. Host minerals of Zr.....	46
1.6.2. Zircon included in the minerals affected by the Grt-Hbl vein formation.....	48
1.6.3. Evaluation of Zr as an immobile element.....	48

References.....	52
-----------------	----

Supplementary materials.....	60
------------------------------	----

Part 2. A possible process of brine infiltration constrained from mass transfer and chemical zonings within a grain to a hand specimen scale

2.1. Introduction.....	64
------------------------	----

2.2. Geological setting.....	67
------------------------------	----

2.3. Analytical methods.....	71
------------------------------	----

2.4. Sample description.....	72
------------------------------	----

2.5. Mineral description.....	83
-------------------------------	----

2.5.1. Garnet.....	83
--------------------	----

2.5.2. Hornblende.....	91
------------------------	----

2.5.3. Biotite.....	98
---------------------	----

2.5.4. Plagioclase.....	101
-------------------------	-----

2.5.5. Orthopyroxene.....	104
---------------------------	-----

2.5.6. Apatite.....	104
---------------------	-----

2.6. Bulk rock compositional variation as distance from the vein.....	105
---	-----

2.7. Discussion.....	108
----------------------	-----

2.7.1. The Grt-Hbl vein formation through brine infiltration	108
--	-----

2.7.1.1. Evidence for the Grt-Hbl vein formation through an open system process.....	108
2.7.1.2. Brine infiltration implied by the elements added to the Grt-Hbl vein and its wall rock.....	112
2.7.1.3. Interpretation of chemical zonings and microstructures in minerals.....	116
2.7.1.4. Possible reaction on the brine infiltration.....	118
2.7.1.5. <i>P-T</i> condition for the brine infiltration.....	119
2.7.2. Formation process of mineral microstructures related to brine infiltration.....	123
2.7.2.1. Possible process of plagioclase rim formation.....	123
2.7.2.2. Possible mechanism for ‘diffusion-like’ profile formation.....	124
2.7.3. Brine composition and implications for a microstructural evidence of brine.....	129
References.....	134
Conclusions.....	147
Acknowledgements.....	149

Preface

Fluids in the crust play important roles in mass and heat transfer (e.g., Ague, 2003; Thompson, 2010; Yardley and Bodnar, 2014), and are responsible for the formation of ore deposits and deformation of rocks (e.g., Helgeson, 1964; Sibson, 1994; Thompson, 2010). Presence of fluids, especially in the deep crust, promotes partial melting (e.g., Holtz and Johannes, 1994).

Since 1980s, variation in fluid composition depending on depth of the crust has been gradually recognized and low H₂O-activity fluid is considered to be dominant in the lower crust (e.g., Etheridge et al., 1983) (Fig. 1). Such a low H₂O-activity was simply supposed to be due to dilution of H₂O by CO₂ and CH₄ from fluid inclusion studies (e.g., Condie et al., 1982; Etheridge et al., 1983; Touret, 1985; Aranovich et al., 1987). Following the findings of CO₂-rich fluid, however, halite and sylvite inclusions (or metamorphic salts) and Cl-rich minerals which are regarded as evidence of brines have been also found in high-temperature metamorphic rocks of deep crustal origin (e.g., Van Reenen and Hollister, 1988; Kullerud, 1995; Markl and Bucher, 1998; Touret and Huizenga, 2011). In cases where the major coexisting cation in the aqueous fluid is other than H, the terminology ‘brine’ could be used in a strict sense. Many experimental studies dealing with Cl-bearing fluids have been performed since brine was found in natural samples (e.g., Shmulovich and Graham, 2004; Newton and Manning, 2010; Tropper et al.,

2011). They showed that under the lower crustal P - T conditions, NaCl- and KCl-bearing brine can coexist with CO₂-rich fluid (Fig. 2), dissolves various major and accessory minerals, and has potential to transport trace and rare earth elements (REE) (Fig. 3). The solubility of minerals in brine is higher than CO₂-rich fluid. Additionally, it is proposed that low wetting angle and low viscosity of brine (Watson and Brenan, 1987; Holness, 1997) could allow its transport along grain boundaries over vast distances without partial melting (e.g., Newton et al., 1998; Harlov, 2012). Therefore, understanding the role of brine in mass transfer processes in the deep crust is increasingly getting important.

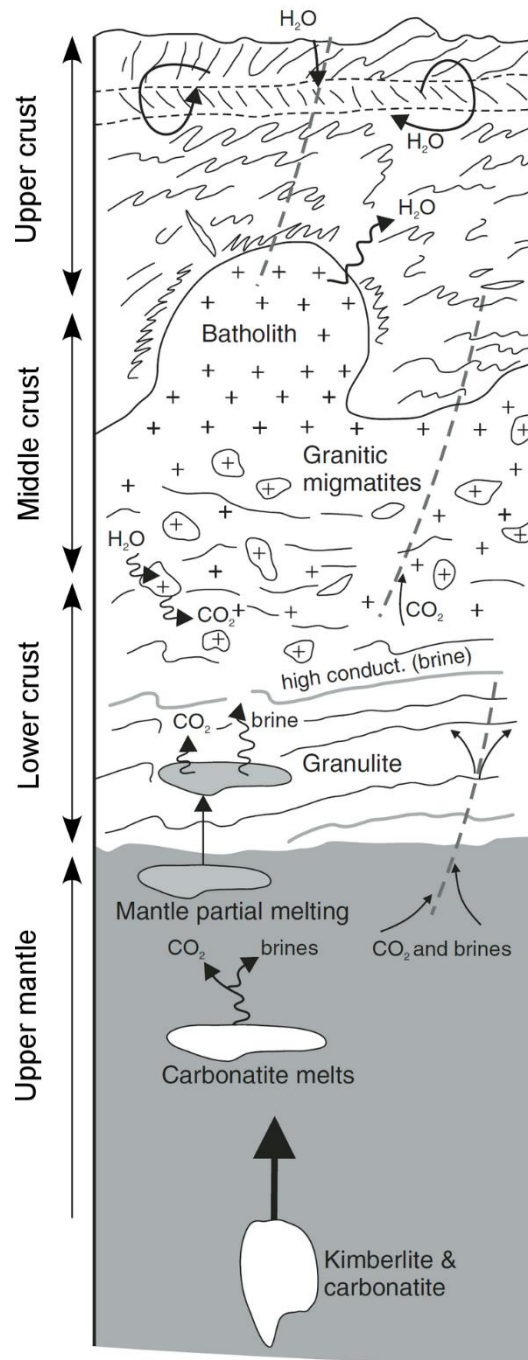


Figure 1. Conceptual diagram of fluid compositions related to the depth of the continental crust

(after Touret and Huizenga, 2011). Brine is considered to be exclusively present in the lower crust and the upper mantle.

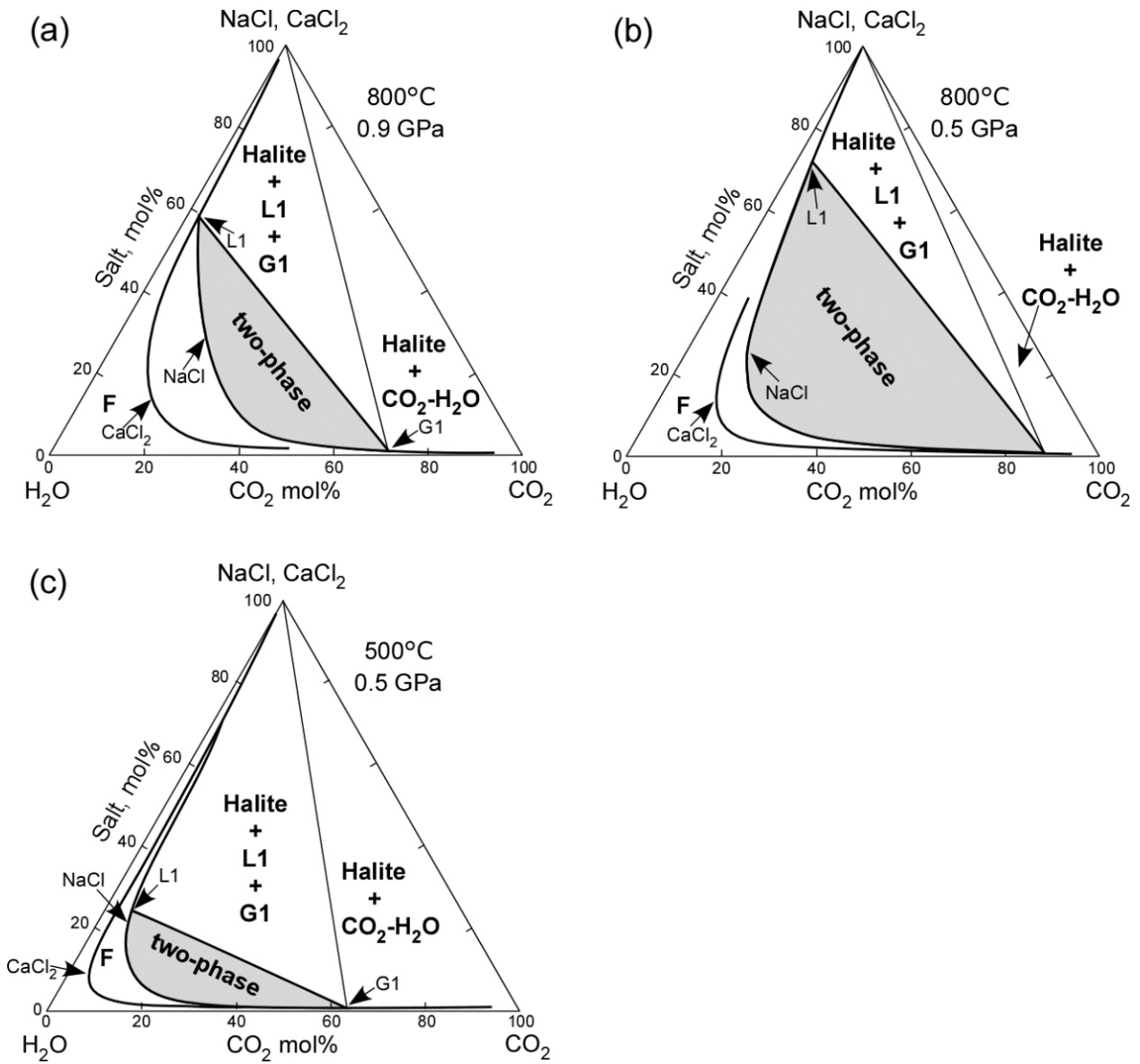


Figure 2. Phase diagram for the system H₂O-CO₂-NaCl and H₂O-CO₂-CaCl₂ (Shmulovich and

Graham, 2004). In these diagrams, F indicates one-phase fluid phase; point L1 indicates

halite saturation in the ternary system; point G1 indicates CO₂-rich phase coexisting with

L1. Two fluid phases (NaCl brine and CO₂-rich fluid) coexist in shaded areas. (a) 800 °C,

0.9 GPa. (b) 800 °C, 0.5 GPa. (c) 500 °C, 0.5 GPa. The edge of the shaded field moves

towards H₂O apex under with decreasing P - T conditions. Therefore, decreasing P - T conditions possibly produce two fluid phases, one is dense brine and the other is CO₂-rich fluid.

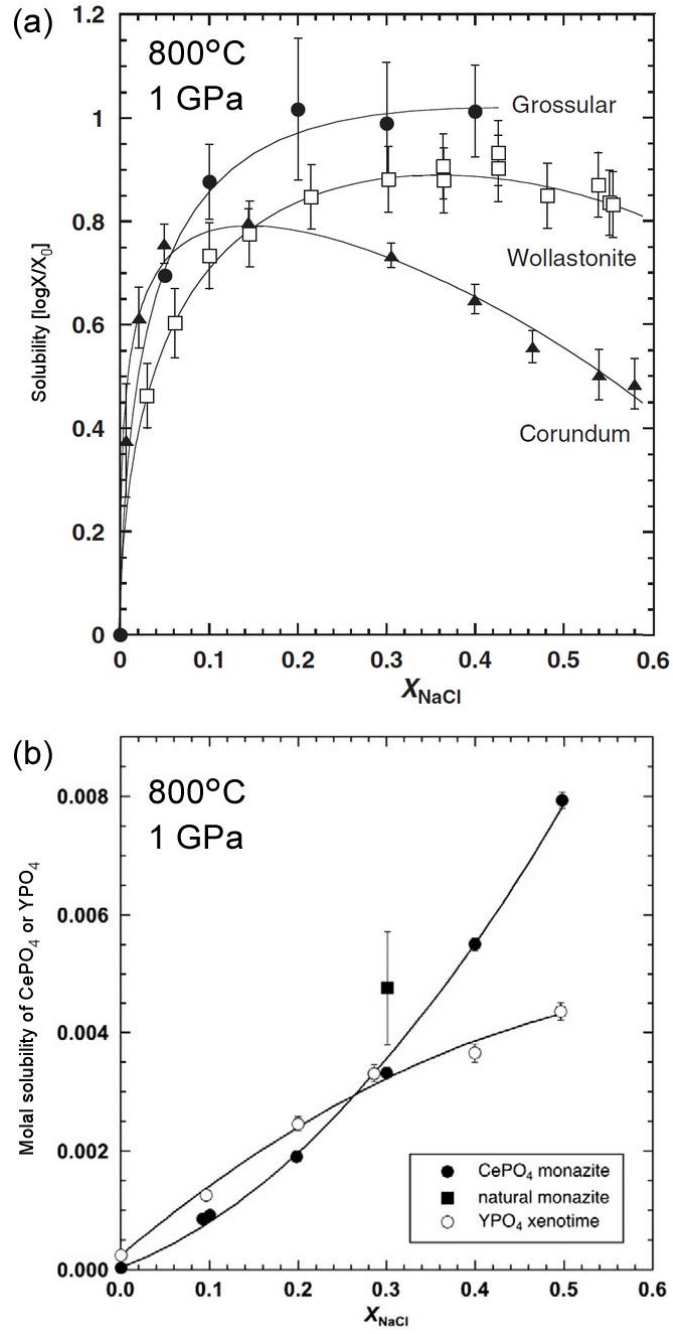


Figure 3. (a) Solubility of corundum, wollastonite and grossular in NaCl-H₂O solutions (Newton and Manning, 2010). Halite saturation is almost at molar ratio X_{NaCl} [= NaCl/(NaCl + H₂O)] = 0.6. The reason why corundum dissolution in NaCl solutions shows a different behavior is the dissolution reaction induced by H⁺ or OH⁻, as well. The reaction $2\text{Al}_2\text{O}_3 +$

$\text{NaCl} + 6\text{H}_2\text{O} = \text{NaAl}(\text{OH})_4 + \text{Al}(\text{OH})_2\text{Cl} + 2\text{Al}(\text{OH})_3$ is satisfied at $X_{\text{NaCl}} = 0.143$, where

the maximum corundum solubility is recognized. (b) Molal solubility of synthetic monazite,

natural monazite, and synthetic xenotime versus X_{NaCl} in solutions (Tropper et al., 2011).

The error bars are 2σ calculated based on the weighing uncertainties. Addition of NaCl

causes an increase of solubility, comparing pure H_2O fluid.

Fluid inclusion is used as a direct evidence of brine, and its salinity can be estimated (e.g., Bodnar, 1993). However, brine is less frequently included in rocks as fluid inclusions possibly due to its low wetting angle and low viscosity (Watson and Brenan, 1987; Holness, 1997). Post-entrapment modification of fluid inclusions due to diffusion or deformation is more likely for brine than for CO₂-rich fluid inclusions because of higher mineral solubility and reactivity (e.g., Sterner and Bodnar, 1989; Baker, 1995; Newton and Manning, 2010). In deformed rocks, primary fluid inclusions are difficult to be preserved, and instead, multi-stage fluid inclusions are often preserved (e.g., Yoshida et al., 2015). On the other hand, mineral inclusions in hard container minerals, such as garnet, can be protected from deformation and later chemical modification. Therefore, it is valuable to have microstructural and chemical indicators of the former presence of brine in natural samples with or without fluid inclusions. It should be noted, however, that Cl concentration in the hydrous minerals is not a direct evidence of brine. This is because formulated equation to determine fugacity ratio $f_{\text{HCl}}/f_{\text{H}_2\text{O}}$ from hydrous mineral composition is based on HCl in the fluid, and not on NaCl or KCl (e.g., Munoz, 1992).

One of the microstructural indicators of the former presence of brine is K-feldspar veins along plagioclase and quartz grain boundaries in high-grade metamorphic terranes (e.g., Griffin, 1969; Todd and Evans, 1994; Harlov et al., 1998). It is considered that K-feldspar veins result from the exchange of alkali elements between plagioclase and a migrating alkali-rich fluid (e.g.,

Griffin, 1969; Todd and Evans, 1994). Furthermore, Harlov et al. (1998) pointed out that K-feldspar veins formed by low H_2O -activity fluids such as brine, because those in direct contact with orthopyroxene and amphibole show no evidence of retrograde hydration. Another microstructure to indicate the presence of brine is the less intense cathodoluminescence of quartz overgrowths on the detrital core observed in sandstone (Demars et al., 1996). The quartz rim was shown to have precipitated from a fluid originated from a Li-enriched primary brine derived from evaporates. They used fluid inclusions in order to detect the brine (Demars et al., 1996). These microstructures possibly represent the passages of brines. As another evidence for fluid passages, “zoned feldspar” in which the mesoperthitic zone, the anti-perthitic zone, and the lamella-free plagioclase zone coexist within a single crystal, and the serrate boundary between alkali-feldspar and biotite are suggested as microstructural evidences of local input of low- a_{H_2O} fluid in the lower crust (Nakamura et al., 2014).

On the other hand, multiphase solid inclusions (MSIs) are often regarded as possible remnants of entrapped supercritical fluids. Studies on them might unravel their chemical characteristics and P - T conditions of their entrapment (e.g., Ferrando et al., 2005, 2009; Malaspina et al., 2006; Naemura et al., 2009). Ferrando et al. (2005) described a method to estimate a semi-quantitative composition of the fluid preserved as MSIs, using volume, density, and composition of daughter minerals.

Even in the rock without fluid inclusions or MSIs, fluid compositions can be estimated utilizing mineral compositions and partition coefficients between fluid and appropriate minerals (e.g., Hermann et al., 2006; Scambelluri et al., 2010). Scambelluri et al. (2010) studied a majoritic garnet veins cutting orthopyroxene present in the matrix of garnet peridotite formed at 1000 °C, 6 GPa, and pointed that the calculated fluid composition in equilibrium with majorite has many features indicating that subduction fluid from associated crustal rocks infiltrated into peridotite. Hermann et al. (2006) estimated composition of fluids that formed an omphacite domain of an eclogite-facies vein at 650 °C, 3 GPa, and discussed the capacity of the fluid to transport significant amounts of trace elements.

As mentioned above, there are various microstructures and chemical characteristics to indicate the former presence of fluids. However, studies that revealed trace element composition of brine in the deep continental crust is scarce, despite the powerful transport capacity of brine. Therefore, the aim of this study is to reveal passages of brine, to estimate the brine composition in the middle to lower continental crust, and to propose a new microstructural and chemical indicator of former presence of brine. This was done using a garnet-hornblende (Grt-Hbl) vein that discordantly cut the gneissose structure of garnet-orthopyroxene-hornblende gneiss from the Sør Rondane Mountains, East Antarctica. Possible process of brine infiltration and brine composition are discussed, focusing on mass transfer of fluid compatible elements and

microstructures of minerals.

This thesis composed of two parts. In Part 1, appropriate ‘immobile element’ as a framework element to evaluate mass transfer during the Grt-Hbl vein formation is discussed. In numerous previous studies, Zr is described as an immobile element (e.g., Gao et al., 2007; Mori et al., 2007). However, zircon which is a major host mineral of Zr in the crustal rocks could be altered by Ca-Cl-bearing fluids during high-temperature metamorphism (Dunkley, 2010). Therefore, appropriateness of Zr as an immobile element in the studied sample is discussed.

In Part 2, using the result of Part 1, mass transfer during the Grt-Hbl vein formation is examined. This made it possible to distinguish whether the Grt-Hbl vein was formed by fluid or melt infiltration, based on the elements added to the wall rock of the vein. Furthermore, possible process to form the multiscale major and trace element zonings in the wall rock, especially the zoning in mineral grains and that developed in the wall rock with distance from the vein are discussed. As a conclusion, dissolution-reprecipitation microstructure of plagioclase coexisting with Cl-bearing minerals is proposed to be a new indicator of the former presence of brine.

References

- Ague, J. 2003. Fluid infiltration and transport of major, minor, and trace elements during regional metamorphism of carbonate rocks, Wepawaug Schist, Connecticut, USA. *American Journal of Science* 303, 753-816.
- Aranovich, L.Y., Shmupovich, K.I., Fed'kin, V.V. 1987. The H₂O and CO₂ regime in regional metamorphism. *International Geology Review*, 29, 1379-1401.
- Barker, A.J. 1995. Post-entrapment modification of fluid inclusions due to overpressure: evidence from natural samples. *Journal of Metamorphic Geology*, 13, 737–750.
- Bodnar, R. J. 1983. Revised equation and table for determining the freezing point depression of H₂O-NaCl solutions. *Geochimica et Cosmochimica Acta* 57, 683-684.
- Condie, K.C., Allen, P., Narayana, B.L. 1982. Geochemistry of the Archean low-to high-grade transition zone, southern India. *Contributions to Mineralogy and Petrology*, 81, 157-167.
- Demars, C., Pagel, M., Deloule, E., Blanc, P. 1996. Cathodoluminescence of quartz from sandstones: Interpretation of the UV range by determination of trace element distributions and fluid-inclusion PTX properties in authigenic quartz. *American Mineralogist* 81, 891-901.
- Dunkley, D.J. 2010. Textural diagnosis of zircon re-equilibration by fluids and melts during

- high- T metamorphism. *Geochimica et Cosmochimica Acta* 74, A252.
- Etheridge, M. A., Wall, V. J., Vernon, R. H. 1983. The role of the fluid phase during regional metamorphism and deformation. *Journal of Metamorphic Geology* 1, 205-226.
- Ferrando, S., Frezzotti, M. L., Dallai, L., Compagnoni, R. 2005. Multiphase solid inclusions in UHP rocks (Su-Lu, China): remnants of supercritical silicate-rich aqueous fluids released during continental subduction. *Chemical Geology* 223, 68-81.
- Ferrando, S., Frezzotti, M. L., Petrelli, M., Compagnoni, R. 2009. Metasomatism of continental crust during subduction: the UHP whiteschists from the Southern Dora - Maira Massif (Italian Western Alps). *Journal of Metamorphic Geology* 27, 739-756.
- Gao, J., John, T., Klemd, R., Xiong, X. 2007. Mobilization of Ti-Nb-Ta during subduction: Evidence from rutile-bearing dehydration segregations and veins hosted in eclogite, Tianshan, NW China. *Geochimica et Cosmochimica Acta* 71, 4974-4996.
- Griffin, W. L. 1969. Replacement antiperthites in gneisses of the Babbitt-Embarrass area, Minnesota, USA. *Lithos* 2, 171-186.
- Harlov, D.E. 2012. The potential role of fluids during regional granulite-facies dehydration in the lower crust. *Geoscience Frontiers* 3, 813-827.
- Harlov, D. E., Hansen, E. C., Bigler, C. 1998. Petrologic evidence for K-feldspar metasomatism in granulite facies rocks. *Chemical Geology* 151, 373-386.

- Helgeson, H. C. 1964. Complexing and hydrothermal ore deposits. Macmillan, New York, pp. 56-64.
- Hermann, J., Spandler, C., Hack, A., Korsakov, A. V. 2006. Aqueous fluids and hydrous melts in high-pressure and ultra-high pressure rocks: implications for element transfer in subduction zones. *Lithos* 92, 399-417.
- Holness, M.B. 1997. Surface chemical controls on pore-fluid connectivity in texturally equilibrated materials. In *Fluid flow and transport in rocks* (pp. 149-169). Springer Netherlands.
- Holtz, F., Johannes, W. 1994. Maximum and minimum water contents of granitic melts: implications for chemical and physical properties of ascending magmas. *Lithos* 32, 149-159.
- Kullerød, K. 1995. Chlorine, titanium and barium-rich biotites: factors controlling biotite composition and the implications for garnet-biotite geothermometry. *Contributions to Mineralogy and Petrology*, 120, 42-59.
- Malaspina, N., Hermann, J., Scambelluri, M., Compagnoni, R. 2006. Polyphase inclusions in garnet–orthopyroxenite (Dabie Shan, China) as monitors for metasomatism and fluid-related trace element transfer in subduction zone peridotite. *Earth and Planetary Science Letters* 249, 173-187.

- Markl, G., Bucher, K. 1998. Composition of fluids in the lower crust inferred from metamorphic salt in lower crustal rocks. *Nature* 391, 781-783.
- Mori, Y., Nishiyama, T., Yanagi, T. 2007. Chemical mass balance in a reaction zone between serpentinite and metapelites in the Nishisonogi metamorphic rocks, Kyushu, Japan: Implications for devolatilization. *Island Arc* 16, 28-39.
- Munoz, J. L. 1992. Calculation of HF and HCl fugacities from biotite compositions: revised equations. *Geological Society of America, Abstracts with Programs* 24, A221.
- Naemura, K., Hirajima, T., Svojtka, M. 2009. The pressure–temperature path and the origin of phlogopite in spinel–garnet peridotites from the Blanský les Massif of the Moldanubian Zone, Czech Republic. *Journal of Petrology* 50, 1795-1827.
- Nakamura, A., Kitamura, M., Kawakami, T. 2014. Microstructural records of multiple retrograde local H₂O supplement in the pelitic gneiss, Lützow-Holm Complex at Akarui Point, East Antarctica. *Mineralogy and Petrology* 108, 177-186.
- Newton, R.C., Manning, C.E. 2010. Role of saline fluids in deep - crustal and upper - mantle metasomatism: insights from experimental studies. *Geofluids*, 10, 58-72.
- Newton, R.C., Aranovich, L.Ya., Hansen, E.C., Vandenheuvel, B.A. 1998. Hypersaline fluids in Precambrian deep-crustal metamorphism. *Precambrian Research* 91, 41-63.
- Scambelluri, M., Van Roermund, H. L., Pettke, T. 2010. Mantle wedge peridotites: fossil

- reservoirs of deep subduction zone processes: inferences from high and ultrahigh-pressure rocks from Bardane (Western Norway) and Ulten (Italian Alps). *Lithos* 120, 186-201.
- Shmulovich, K.I., Graham, C.M. 2004. An experimental study of phase equilibria in the systems $\text{H}_2\text{O}-\text{CO}_2-\text{CaCl}_2$ and $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ at high pressures and temperatures (500-800 °C, 0.5-0.9 GPa): geological and geophysical applications. *Contributions to Mineralogy and Petrology* 146, 450-462.
- Sibson, R. H. 1994. Crustal stress, faulting and fluid flow. Geological Society, London, Special Publications, 78, 69-84.
- Sterner, S. M., Bodnar, R. J. 1989. Synthetic fluid inclusions - VII. Re - equilibration of fluid inclusions in quartz during laboratory - simulated metamorphic burial and uplift. *Journal of Metamorphic Geology* 7, 243-260.
- Thompson, A.B. 2010. Perspectives on metamorphic processes and fluids. *Elements* 6, 142-143.
- Todd, C.S., Evans, B.W. 1994. Properties of CO_2 -induced dehydration of amphibolite. *Journal of Petrology* 35, 1213-1239.
- Touret, J.L. 1985. Fluid regime in southern Norway: the record of fluid inclusions. In *The deep proterozoic crust in the north Atlantic provinces* (pp. 517-549). Springer Netherlands.
- Touret, J.L., Huizenga, J.M. 2011. Fluids in granulites. *Geological Society of America Memoirs*,

207, 25-37.

Tropper, P., Manning, C.E., Harlov, D.E. 2011. Solubility of CePO_4 monazite and YPO_4 xenotime in H_2O and $\text{H}_2\text{O}-\text{NaCl}$ at 800 °C and 1GPa: implications for REE and Y transport during high-grade metamorphism. *Chemical Geology*, 282, 58-66.

Van Reenen, D.D., Hollister, L.S. 1988. Fluid inclusions in hydrated granulite facies rocks, southern marginal zone of the Limpopo Belt, South Africa. *Geochimica et Cosmochimica Acta*, 52, 1057-1064.

Watson, E.B., Brenan, J.M. 1987. Fluids in the lithosphere, 1. Experimentally-determined wetting characteristics of CO_2 - H_2O fluids and their implications for fluid transport, host-rock physical properties, and fluid inclusion formation. *Earth and Planetary Science Letters*, 85, 497-515.

Yardley, B.E.D., Bodnar, R.J. 2014. Fluids in the continental crust. *Geochemical Perspectives* 3, 1-127.

Yoshida, K., Hirajima, T., Ohsawa, S., Kobayashi, T., Mishima, T., Sengen, Y. 2015. Geochemical features and relative B–Li–Cl compositions of deep-origin fluids trapped in high-pressure metamorphic rocks. *Lithos* 226, 50-64.

Part 1: Geochemical behavior of zirconium during Cl-rich fluid or melt infiltration under upper amphibolite facies metamorphism – A case study from Brattnipene, Sør Rondane Mountains, East Antarctica

1.1. Introduction

In order to estimate a relative mass addition/loss during metasomatism and weathering, methods such as isocon analysis (e.g., Grant, 1986) and calculation of the fractional mass change (Ague, 2003) are proposed. In these methods, at least one ‘immobile element’ must be determined as a reference element (e.g., Olsen and Grant, 1991; Whitbread and Moore, 2004; Mori et al., 2007). The ‘immobile element’ should be carefully selected based on supporting evidence and not simply assumed, because whether and how much of other elements are added or lost greatly depends on this selection. In many previous studies, elemental immobility was established by using a bootstrap estimation (Ague and Van Haren, 1996) or by using petrological and mineralogical microstructures as evidence (e.g., Gao et al., 2007; Mori et al., 2007). As a result, Zr, Nb, Y, Hf, and Th are often described as immobile elements (Gao et al., 2007). These elements could be stored in minerals difficult to be dissolved by hydrothermal fluids in the case of high-grade metamorphic rocks.

Most of the whole-rock Zr in crustal rocks is hosted in zircon (Hermann, 2002; Dill, 2010). Zircon is less susceptible to secondary alteration in the presence of fluids compared to other rock-forming minerals (Rubin et al., 1993; Ayers and Watson, 1991; Taylor et al. 2014). This would be the reason Zr is often selected as being an ‘immobile element’. However, an experimental study by Harlov and Dunkley (2011) concluded that zircon can be dissolved in fluids depending on fluid compositions and pressure-temperature (*P-T*) conditions. Zircon can also be altered by Cl-rich brines during high-*T* metamorphism (Dunkley, 2010). Therefore, in mass transfer analysis, it is important to select appropriate ‘immobile elements’ for each sample, taking into account the microstructures of rock-forming minerals and petrographic observations (Olsen and Grant, 1991).

In Brattnipene, central Sør Rondane Mountains, East Antarctica, about 1 cm-thick garnet-hornblende (Grt-Hbl) veins discordantly cut the gneissose structure of the wall rock (Higashino et al., 2013a). Infiltration of Cl-rich fluid or melt is inferred in this sample, because major and trace element compositions of minerals in the vein and the wall rock, including Cl content in biotite and hornblende, systematically change with distance from the vein center (Higashino et al., 2013a). Using this sample, this study firstly shows that zircon hosts most of the whole-rock Zr. Secondly, we discuss the appropriateness of Zr as an ‘immobile element’ in the wall rock, based on the detailed microstructural observations, chemistry of Zr-hosting minerals, and the U-Pb ages of zircon. Mineral abbreviations are after Kretz (1983).

1.2. Geological setting

The Sør Rondane Mountains (SRM; 22°-28°E, 71.5°-72.5°S), eastern Dronning Maud Land, East Antarctica are dominated by granulite facies metamorphic rocks and granitoids (Shiraishi et al., 1991; Asami et al., 1992). The SRM is thought to be a part of the collision zone between East and West Gondwana during the East African-Antarctic Orogen (Jacobs and Thomas, 2004) and is also interpreted to be in the hanging wall of a mega-nappe complex involving continental collision between northern and southern Gondwana (Grantham et al., 2013) during the Kuunga Orogeny of Meert (2003). The SRM have been divided into the NE terrane and the SW terrane by a mylonite zone named the Main Tectonic Boundary that dips gently to the north and northeast (Osanai et al., 2013) (Fig. 1.1). The NE terrane rocks record clockwise *P-T* paths, whereas the SW terrane rocks record counter-clockwise *P-T* paths (Osanai et al., 2013) (Fig. 1.2). For further detailed geological and tectonic explanation, see Osanai et al. (2013) and Toyoshima et al. (2013). In northern Brattnipene, which belongs to the SW terrane, peak metamorphic *P-T* conditions are estimated to be about 800 °C and 0.70-0.85 GPa (Shiraishi and Kojima, 1987; Adachi et al., 2013a), and a counter-clockwise *P-T* path is proposed (Adachi et al., 2013a). Previous SHRIMP U-Pb zircon dating of an enderbitic orthogneiss from northwestern Brattnipene gave an igneous protolith age of 951 ± 17 Ma, and a granulite-grade metamorphic age of 602 ± 15 Ma (Shiraishi

et al., 2008). From northwestern Brattnipene, SHRIMP U-Pb zircon ages of an orthopyroxene-clinopyroxene (Opx-Cpx) felsic gneiss and an undeformed pegmatite vein which intrudes the Opx-Cpx felsic gneiss are also reported (Adachi et al., 2013b). The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of unzoned, bright-cathodoluminescence (bright-CL) zircon domains from the Opx-Cpx felsic gneiss gave 627 ± 15 Ma, and was interpreted as the timing of metamorphism (Adachi et al., 2013b). Timing of the pegmatite intrusion, on the other hand, was dated to be 546 ± 4 Ma (weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age; Adachi et al., 2013b).

The Cl-rich mineral distribution can be traced for about 200 km from the east to the west of the SRM (Higashino et al., 2013b) (Fig. 1.1). Higashino et al. (2013b) reported that the Cl-rich fluid or melt activity affected biotite and apatite in pelitic gneisses, during early retrograde metamorphism near the peak metamorphic *P-T* condition of about 800 °C and 0.8 GPa at Balchenfjella, eastern SRM. Magmatic hornblende has also been reported to show relatively high halogen contents in some granitoids in the SRM. Li et al. (2007) reported hornblende with 1.15-1.23 wt% F and 0.28-0.32 wt% Cl from the Dufek granite, and hornblende with 0.25-0.43 wt% F and 0.31-0.41 wt% Cl from the Pingvinane granite.

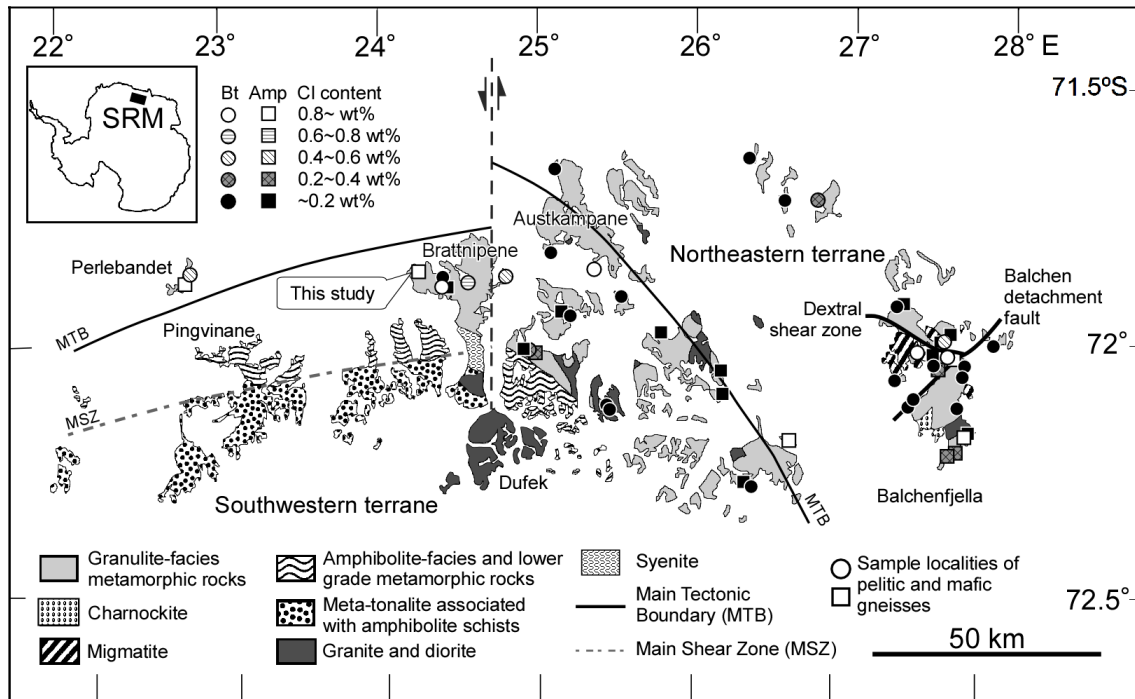


Figure 1.1. Simplified geological map of the Sør Rondane Mountains (after Shiraishi et al., 2008;

Osanai et al., 2013; Toyoshima et al., 2013; Ishikawa et al., 2013; Higashino et al., 2013b).

Detailed geological and tectonic explanation can be found in Osanai et al. (2013) and

Toyoshima et al. (2013).

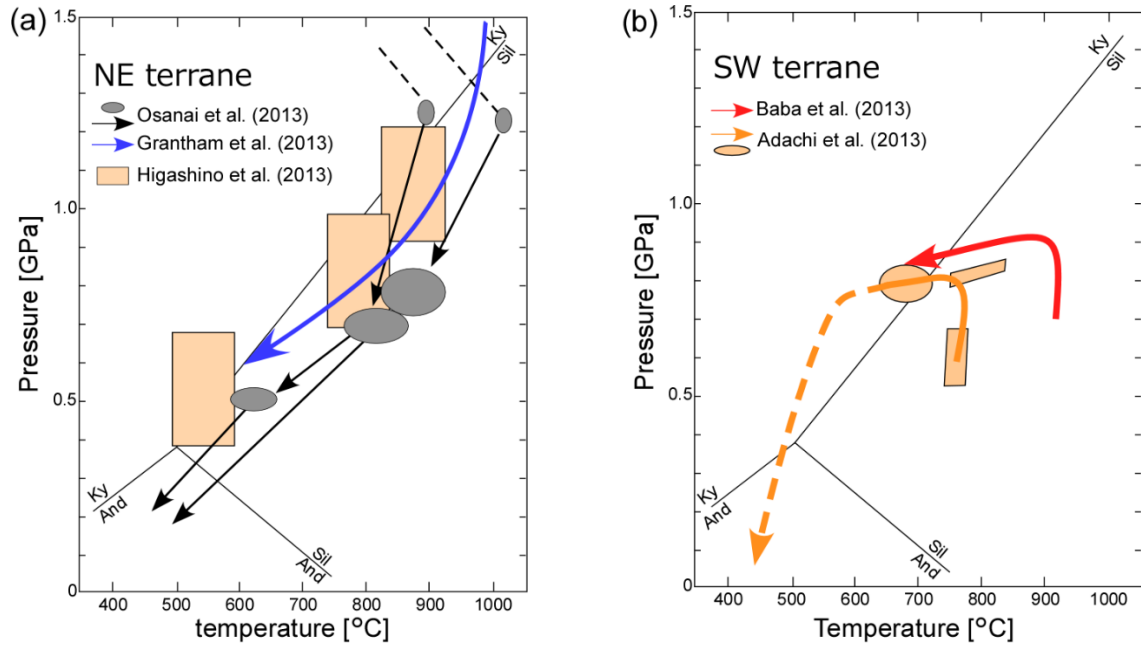


Figure 1.2. Metamorphic P - T paths in the Sør Rondane Mountains, East Antarctica. (a) Clockwise P - T paths estimated from the NE terrane. (b) Counter-clockwise P - T paths estimated from the SW terrane. Brattnipene area studied in this thesis belongs to the SW terrane.

1.3. Analytical methods

Quantitative analysis, and X-ray elemental mapping of minerals, and CL imaging of zircon were performed using a JEOL JXA-8105 superprobe equipped with Hamamatsu Photonics high voltage power supply C9525 and photon counting unit C9744 at Kyoto University. Analytical conditions for quantitative analyses were an accelerating voltage of 15.0 kV and a beam current of 10 nA with a probe diameter of 3 μm . Counting time for the peak and backgrounds were 30 s and 15 s for Cl, 60 s and 30 s for F, and 10 s and 5 s for other elements, respectively. Natural and synthetic minerals were used as standards and a ZAF correction method was applied. Analytical conditions for X-ray elemental mapping were an accelerating voltage of 15.0 kV and a probe current of 60 nA with a focused beam to defocused beam having a diameter of 10 μm .

In situ U-Pb zircon dating on thin section samples by a laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) was carried out using a Nu Plasma II HR-MC-ICPMS coupled to a NWR Femto femtosecond laser-ablation system (Hirata and Nesbitt, 1995; Iizuka and Hirata, 2004). Backscattered electron (BSE) and CL images were obtained prior to the analyses to identify spot positions, overlapping multiple growth zones, grain edges, cracks or damaged zircon grains. Data were processed and plotted using *Isoplot 4.13* (Ludwig, 2008). *In situ* LA-ICPMS analyses of rare earth elements (REE) and trace element concentrations of zircon, garnet, hornblende, orthopyroxene, biotite, plagioclase and apatite were performed by an iCAP-

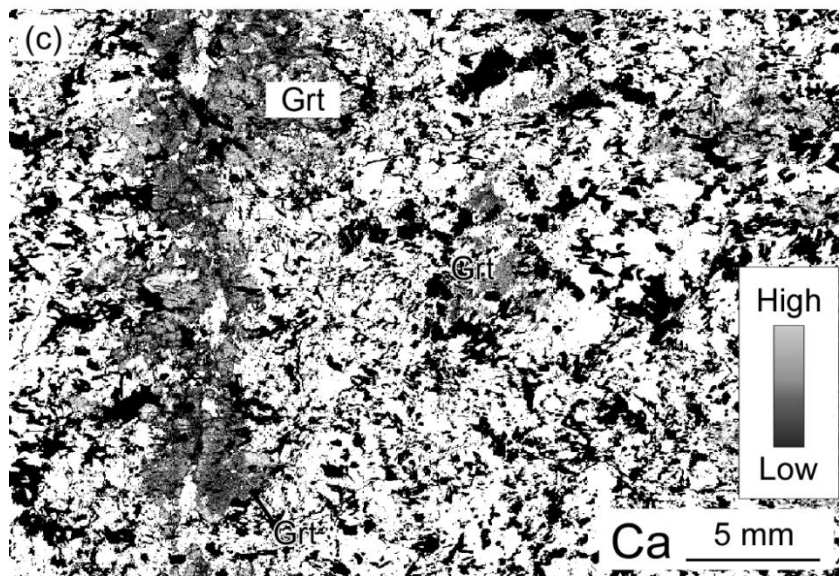
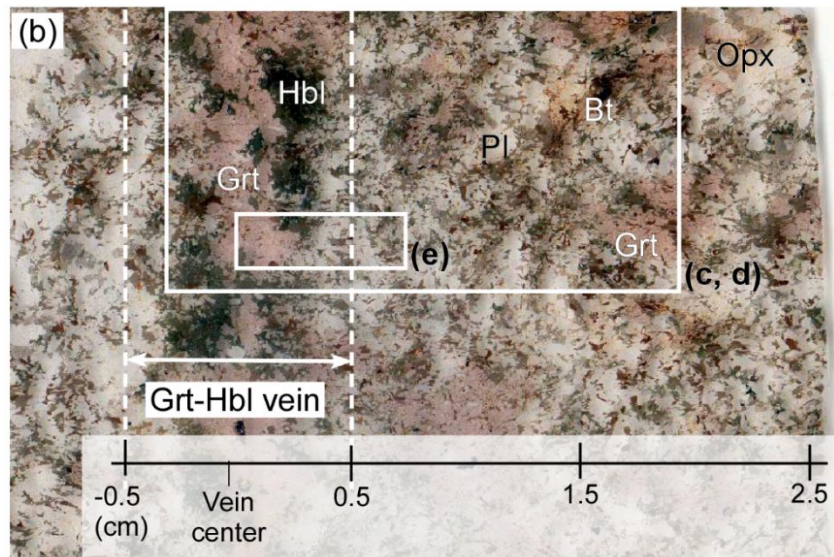
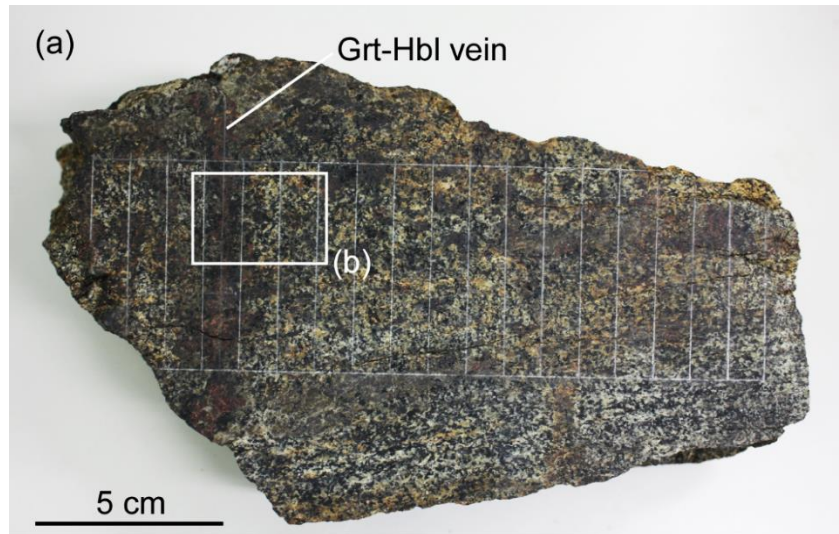
Qc quadrupole-based ICPMS coupled with a NWR Femto femtosecond laser-ablation system or a NWR-193 ArF Excimer laser-ablation system (Hirata and Kon, 2008; Sakata et al., 2014). Analytical conditions for the LA-ICPMS analyses are summarized in supplementary Tables S1 and S2. All of the above analyses were done at Department of Geology and Mineralogy, Kyoto University.

Concentration of whole-rock Zr was determined using solution ICPMS at Tohoku University. Rock powders were prepared in a tungsten-carbide mill at Kyoto University and samples were prepared by acid digestion after alkali fusion. Indium was used for an internal standard (Yamasaki, 1996; Yamasaki et al., 2013).

1.4. Sample locality

At Brattnipene, mafic lithologies are commonly intercalated with pelitic lithologies, intermediate hornblende gneisses, marble, and locally contain peridotite and pyroxenite lenses. The gneissose structure of the host gneiss is discordantly cut by a network of cm-thick Grt-Hbl veins. The vein consists of garnet and hornblende that are coarser-grained than the host mafic gneiss (Fig. 1.3a). Sample TK2009121002C, used in this study contains a Grt-Hbl vein which cuts mafic gneisses (Grt-Opx-Hbl gneiss) and was collected from a layered sequence of mafic gneisses in northwestern Brattnipene during 51st Japan Antarctic Research Expedition (JARE51)

(Tsuchiya et al., 2012) (Fig. 1.1). The sample locality of TK2009121002C is about 700 m SE from that of the enderbitic orthogneiss whose metamorphic age was estimated to be 602 ± 15 Ma (Shiraishi et al., 2008), and about 190 m SE from that of the Opx-Cpx felsic gneiss whose metamorphic age was estimated to be 627 ± 15 Ma (Adachi et al., 2013b).



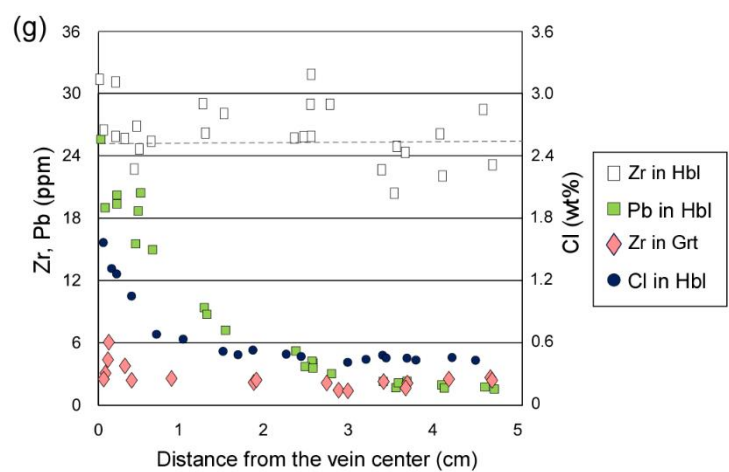
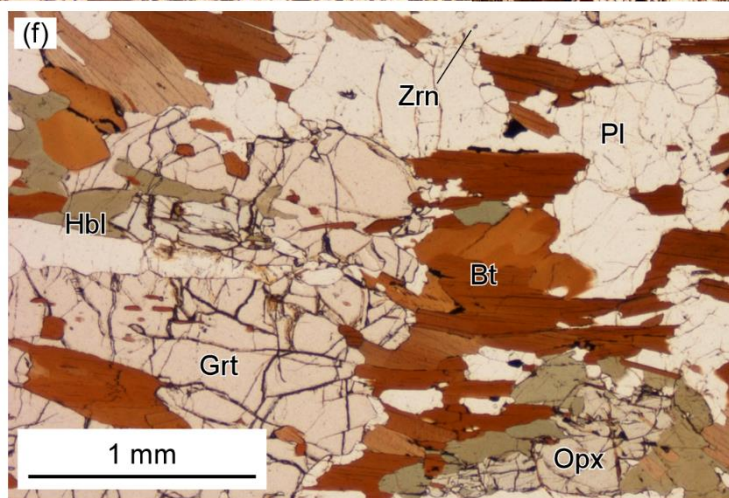
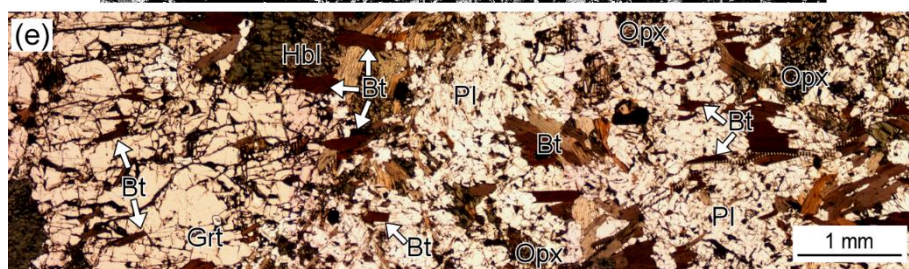
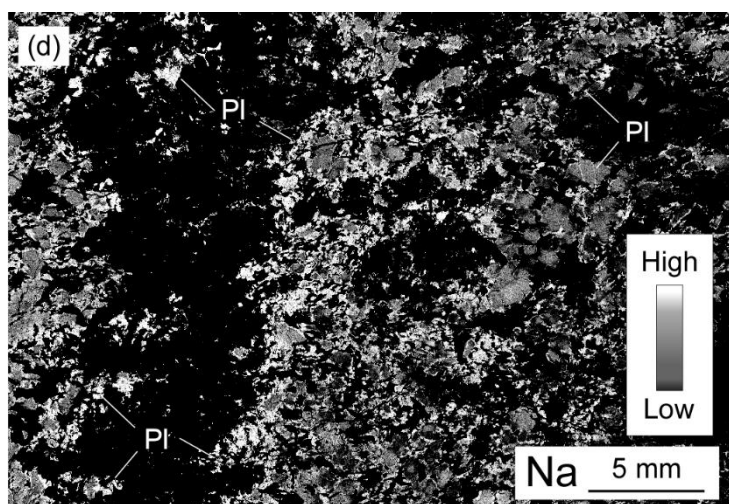


Figure 1.3. (a) Slab photo of the Grt-Opx-Hbl gneiss (sample TK2009121002C) used in this study.

About 1 cm-thick Grt-Hbl vein discordantly cuts the gneissose structure. (b) Photo of a thin section of boxed area in (a). A Grt-Hbl vein consists of coarse-grained garnet and hornblende.

Plane polarized light (PPL). (c) X-ray elemental map of Ca of boxed area in (b). The Ca-poor domain of garnet is abundant near the vein. (d) X-ray elemental map of Na of boxed area in (b). The Na-rich rim of plagioclase gets thinner with distance from the vein center.

(e) Photomicrograph of boxed area in (b), which corresponds to the area from the vein center to the wall rock. Orthopyroxene is absent in the vein. Note the continuous gneissose structure preserved as biotite arrangements included in the vein-forming garnet. PPL. (f)

Photomicrograph of the area about 3 cm away from the vein center. Garnet and orthopyroxene is present. Quartz is rarely present. PPL. (g) Variation in hornblende and garnet composition as a function of distance from the Grt-Hbl vein center. Chlorine and Pb

concentration of hornblende decreases with distance from the vein center. Dotted line shows an approximate line defined for Zr concentration of hornblende.

1.5. Sample description of the Grt-Opx-Hbl gneiss with a Grt-Hbl vein

The studied Grt-Hbl vein (about 1 cm-thick) mainly consists of garnet, hornblende, biotite, plagioclase and quartz. It discordantly cuts the gneissose structure of the host (or the wall rock) Grt-Opx-Hbl gneiss (Figs. 1.3a and 1.3b). The Grt-Hbl vein is orthopyroxene-free (Fig. 1.3e). In the host gneiss, orthopyroxene is present in addition to garnet, hornblende, biotite, and plagioclase with rare quartz (Fig. 1.3f). This sample also contains accessory minerals of zircon, sulfide, ilmenite, iron oxide, and secondary Fe-hydroxide. Garnet is slightly zoned and has almandine-rich compositions both in the vein ($\text{Alm}_{57-62}\text{Prp}_{19-25}\text{Grs}_{15-19}\text{Sps}_{2-3}$; $X_{\text{Mg}} = 0.24-0.30$) and away from the vein ($\text{Alm}_{58-63}\text{Prp}_{20-24}\text{Grs}_{14-18}\text{Sps}_{2-3}$; $X_{\text{Mg}} = 0.24-0.28$). Calcium-rich domains in garnet become dominant with distance from the vein (Fig. 1.3c). Hornblende and biotite compositions at the vein center are 2.0 wt% Cl and $X_{\text{Mg}} = 0.49$, and 1.1 wt% Cl and $X_{\text{Mg}} = 0.61$, respectively. Plagioclase is andesine to labradorite and is chemically zoned (An_{45-69}). Sodium-rich rim of plagioclase gets thinner with distance from the vein (Fig. 1.3d). The mineral assemblage in the vein is typical of upper amphibolite facies *P-T* conditions.

With distance from the Grt-Hbl vein center, the Cl concentration of hornblende and biotite decreases and becomes constant at about 1.6 cm away (Fig. 1.3g). The Pb concentrations of hornblende, biotite and plagioclase decrease as well and become constant at about 3.6 cm. Figure 1.3g shows decreasing Cl and Pb concentrations in hornblende. These observations imply that the

Grt-Hbl vein formation altered wall rock mineral compositions up to about 3.6 cm from the vein center.

1.5.1. *In situ* Zr analysis of minerals and whole-rock Zr concentration

In situ LA-ICPMS analysis of garnet, hornblende, orthopyroxene, biotite, plagioclase and apatite was performed to determine their Zr concentration (Table 1.1). In measuring the Zr concentration of garnet, geometric cores and rims were analyzed over a distance from the vein center, in order to evaluate the chemical zoning in Zr. As a result, garnet showed almost constant Zr concentration (about 3 ppm) irrespective of the location in the grain and of the distance from the vein (Fig. 1.3g). Although the Cl concentration of hornblende decreases away from the vein, major element zoning within each hornblende grain was not observed. The Zr concentration of hornblende is almost constant (about 26 ppm), irrespective of the location in the grain and of the distance from the vein (Fig. 1.3g). The Zr concentration of orthopyroxene, biotite, plagioclase and apatite present in the matrix as well as those included in garnet and orthopyroxene were low, and not correlated with the location in the grain or the distance from the vein (Table 1.1).

Slices of the studied sample (1cm thick) were prepared parallel to the Grt-Hbl vein, and whole-rock Zr concentrations of each slice were determined by ICPMS analysis (Table 1.1). The slices prepared included the Grt-Hbl vein itself (-0.5–0.5 cm; slice 1) and three slices of the wall

rock with distance from the vein center being 0.5–1.5 cm (slice 2), 1.5–2.5 cm (slice 3) and 2.5–3.5 cm (slice 4), respectively. Modal amounts of minerals in each slice were also determined using X-ray elemental mapping and electron microscope observation. The results are summarized in Table 1.2.

Table 1.1. Zirconium concentration in major and accessory minerals* and slices 1–4**

Mineral	Zr (ppm)
Grt	2.8 ± 1.3 (n = 19, 2σ)
Opx	0.8 ± 0.2 (n = 13, 2σ)
Hbl	26.3 ± 2.9 (n = 26, 2σ)
Bt	0.8 ± 0.6 (n = 14, 2σ)
Pl	b.d.
Ap	b.d.
Whole-rock analysis	Zr (ppm)
Slice 1 (Grt-Hbl vein)	45.6
Slice 2	53.2
Slice 3	55.1
Slice 4	57.6

* Determined by LA–ICPMS.

** Determined by ICPMS.

Grt, garnet; Opx, orthopyroxene; Hbl, hornblende; Bt, biotite;

Pl, plagioclase; Ap, apatite.

b.d., below detection limit.

Table 1.2. Modal amount of minerals*

Mineral	Slice 1 (Grt-Hbl vein)	Slice 2	Slice 3	Slice 4
Grt	27.7	6.4	8.2	8.1
Opx	2.9	10.8	9.1	12.1
Hbl	22.3	8.0	4.3	5.0
Bt	9.2	18.1	21.4	17.6
Pl	34.1	56.2	56.4	55.8
Qtz	1.7	0.2	0.2	0.3
Ap	2.2	0.4	0.5	1.1
Zrn	0.01	0.01	0.01	0.01
Total (vol%)	100.0	100.0	100.0	100.0

* Obtained from the X-ray elemental mapping and electron microprobe observation.

Qtz, quartz; Zrn, zircon; Other abbreviations are the same as Table 1.1.

1.5.2. *In situ* LA-ICPMS U-Pb zircon dating and REE analysis

Zircon is included in garnet, orthopyroxene, hornblende, plagioclase and biotite, and is also present in the matrix. Zircon is commonly rounded- to oval-shaped and about 20-50 μm in diameter (Fig. 1.4). Zircon grains share similar microstructural features irrespective of their mode of occurrence and distance from the vein center (Fig. 1.4). Zircon zoning can be described as follows based on U concentrations and Th/U ratios.

Core: U content < 100 ppm and Th/U ratio = 0.19-0.99.

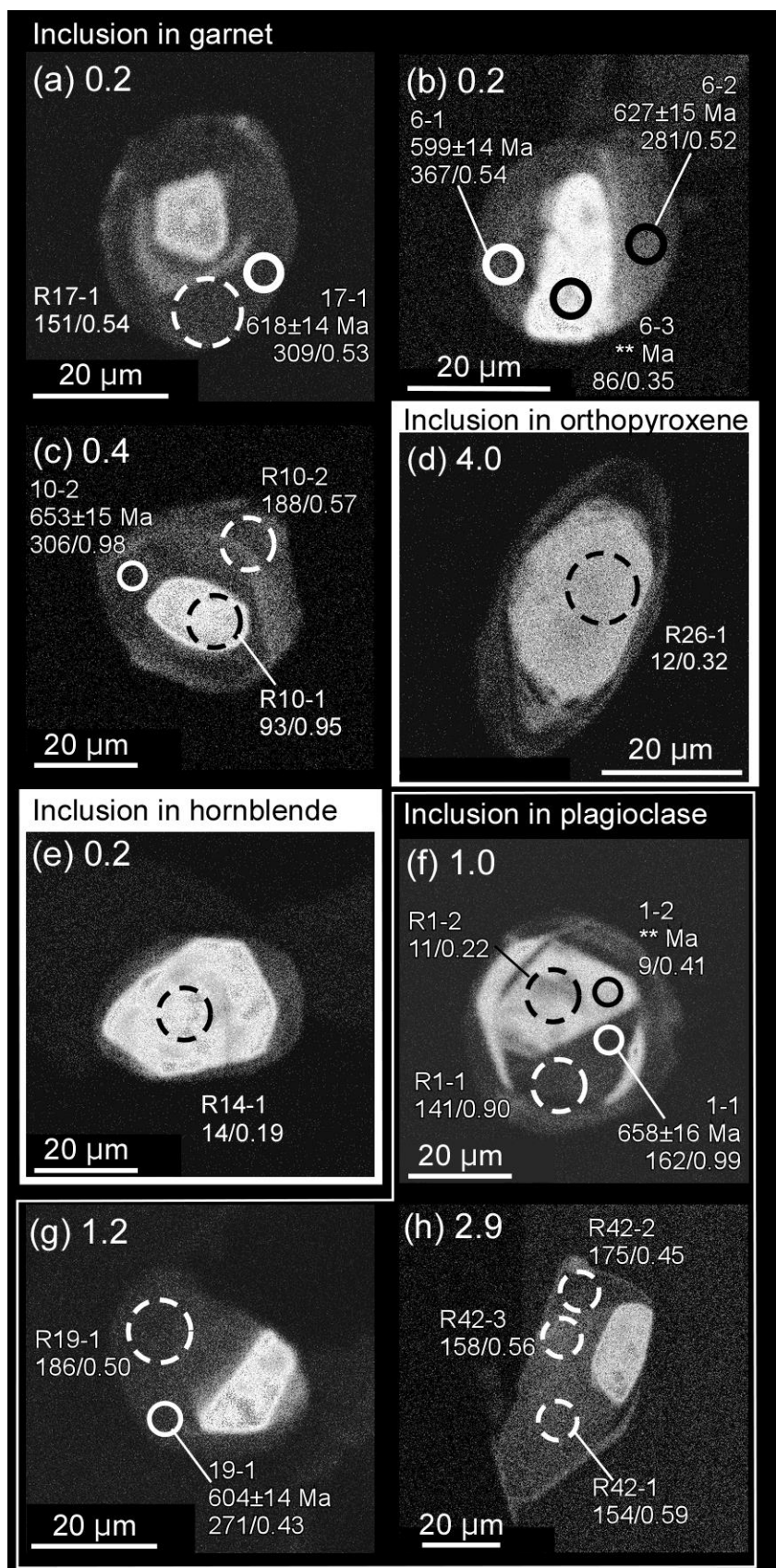
Mantle: U content = 141-306 ppm and Th/U ratio = 0.62-0.99.

Rim: U content = 140-421 ppm and Th/U ratio = 0.43-0.59.

Every zircon grain preserves cores which can be recognized as bright-CL domain (Fig. 1.4). Mantles and rims are characterized by darker-CL domains than the cores (Fig. 1.4). Mantles tend to have higher Th/U ratio than the rims. Mantle-rim boundaries are more ambiguous than core-mantle boundaries in CL images. Some zircon grains show very thin mantles or rims, or lack one of them (Fig. 1.4). No inclusions were seen in the zircon grains studied.

The U-Pb zircon ages and REE concentrations of zircon were determined in order to evaluate the presence or absence of zircon resorption as a function of distance from the vein (Figs. 1.4, 1.5

and Table 1.3). The U-Pb ages with better than 95-105% concordance (where concordance = $(^{206}\text{Pb}/^{238}\text{U age}) * 100 / (^{207}\text{Pb}/^{235}\text{U age})$) are interpreted as being meaningful concordant ages in this study. Two cores gave $^{206}\text{Pb}/^{238}\text{U}$ ages of 1175 ± 58 Ma (U=10 ppm; Th/U = 0.36) and 685 ± 34 Ma (U=19 ppm; Th/U = 0.25). The mantles (n=4) gave $^{206}\text{Pb}/^{238}\text{U}$ ages of 658-630 Ma. The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of the rims (n=8) is 617 ± 9 Ma (Fig. 1.5b). Mantles and rims have similar REE concentrations and share the same positively-sloping MREE-HREE pattern with $\text{Yb/Dy} = 4.7 \pm 0.9$ (2σ) irrespective of a distance from the Grt-Hbl vein (Fig. 1.6a; Table 1.4). Mantles and rims commonly show positive Ce and negative Eu anomalies in chondrite-normalized REE patterns (Fig. 1.6a). Three core analyses showed different REE patterns from mantles and rims, showing steep and positively-sloping HREE-enriched patterns with $\text{Yb/Dy} = 24 \pm 0.3$ (2σ) without a positive Ce anomaly (Fig. 1.6a). A core with similar REE patterns as mantles and rims also exists (Fig. 1.6a). As shown in Figures 1.4, 1.6b, 1.6c, and Table 1.4, no correlation between rim REE patterns, ages, and distance from the vein was detected.



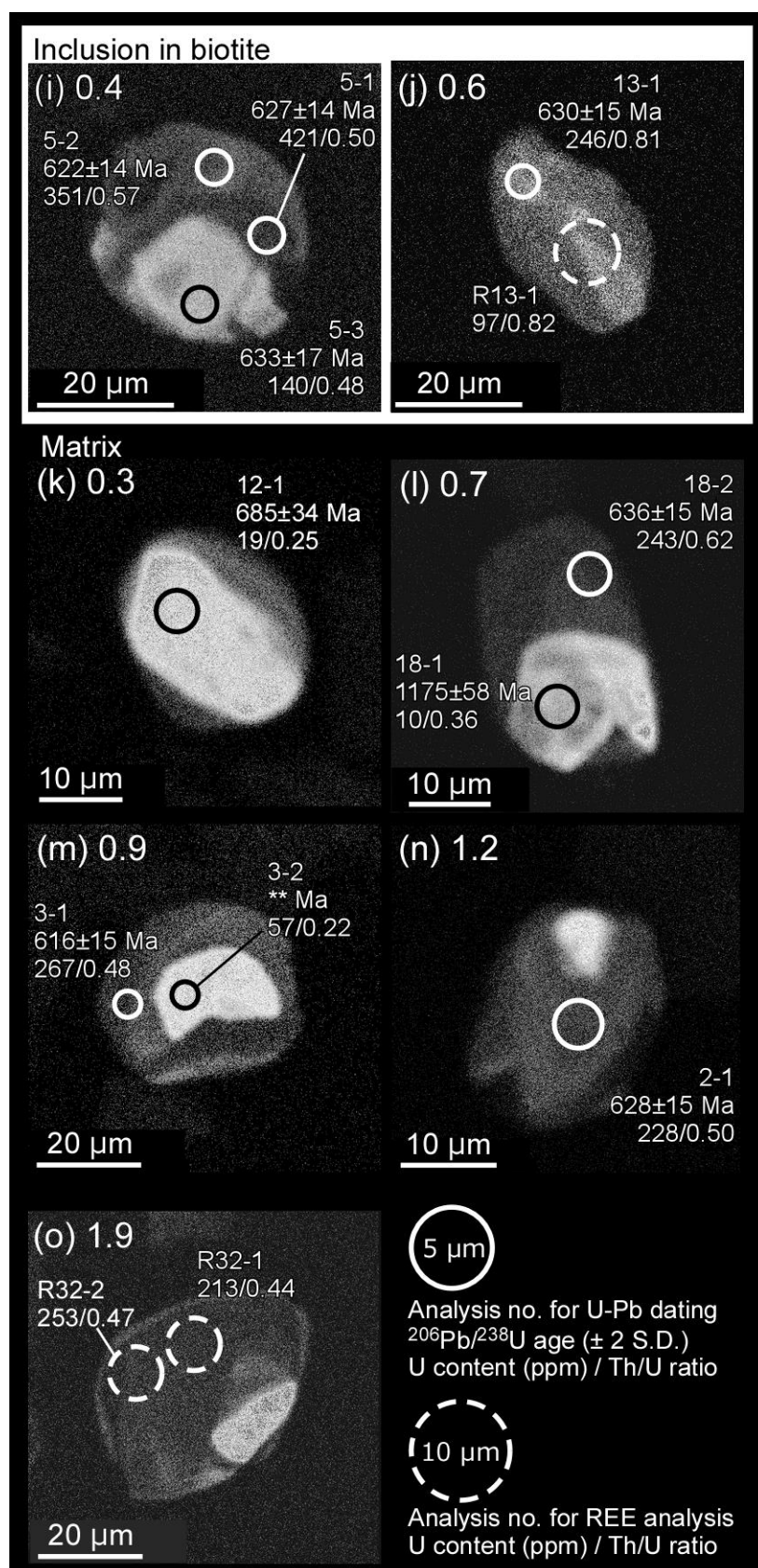


Figure 1.4. The CL images of zircon with analytical results of zircon. Numbers next to alphabets

in parentheses represent the distance from the Grt-Hbl vein center [cm] where each zircon grain occurs. Circles represent pits for LA-ICPMS U-Pb dating (5 μm in diameter). From the top to the bottom, numbers next to the circle represent analysis number, $^{206}\text{Pb}/^{238}\text{U}$ ages ± 2 S.D. error [Ma], U concentration [ppm] and Th/U ratio. ‘*’ represents concordance for the analysis point is out of 95-105 %. Dotted circles represent pits for LA-ICPMS REE analysis (10 μm in diameter). From the top to the bottom, numbers next to the dotted circle are analysis number, U concentration [ppm] and Th/U ratio. (a)-(c) Zircon included in garnet. (d) Zircon included in orthopyroxene. (e) Zircon included in hornblende. (f)-(h) Zircon included in plagioclase. (i)-(j) Zircon included in biotite. (k)-(o) Zircon present in the matrix.

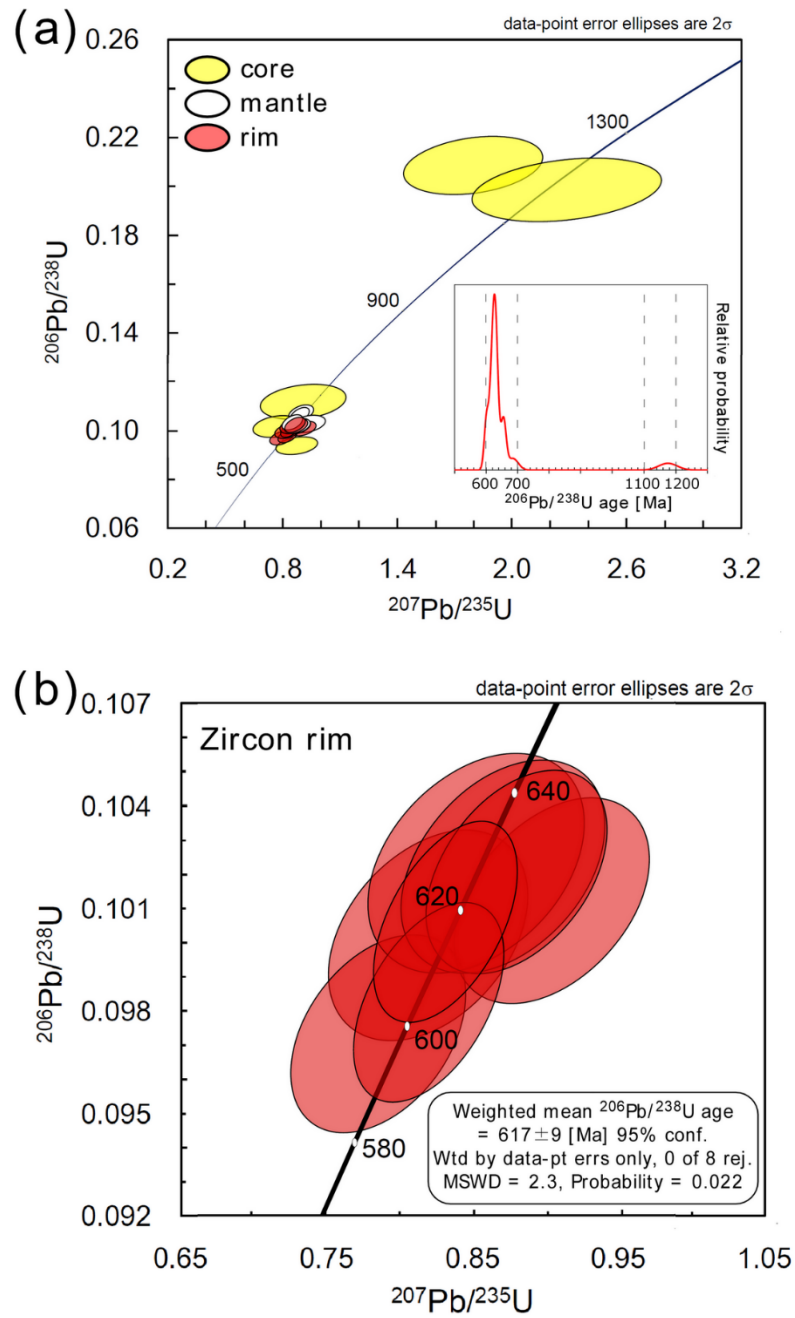


Figure 1.5. The results of LA-ICPMS U-Pb dating of zircon constructed using *Isoplot* v.4.13

(Ludwig, 2008). (a) U-Pb concordia plot for all zircon domains and a relative probability diagram for analysis points with 95-105 % concordance. (b) U-Pb concordia plot for rims of zircon.

Table 1.3. Summary of the results of LA-ICPMS U-Pb zircon dating

Analysis number	Distance from the vein center (cm)	$^{207}\text{Pb}/^{235}\text{U}$	2σ	$^{206}\text{Pb}/^{238}\text{U}$	2σ	r	$^{207}\text{Pb}/^{206}\text{Pb}$	2σ	
02C 2-1	Rim	1.2	0.8523	0.0596	0.1023	0.0026	0.367	0.06042	0.00393
02C 12-1	Core	0.3	0.9026	0.1833	0.1121	0.0058	0.255	0.05841	0.01147
02C 3-1	Rim	0.9	0.8199	0.0549	0.1002	0.0025	0.376	0.05934	0.00368
02C 3-2	Core	0.9	0.7623	0.0994	0.1020	0.0036	0.273	0.05418	0.00679
02C 18-1	Core	0.7	2.2830	0.4050	0.2000	0.0107	0.302	0.08281	0.01401
02C 6-1	Rim	0.2	0.7862	0.0481	0.0973	0.0024	0.397	0.05858	0.00329
02C 6-2	Rim	0.2	0.8704	0.0562	0.1022	0.0025	0.386	0.06175	0.00368
02C 6-3	Core	0.2	0.8679	0.0895	0.0941	0.0030	0.312	0.06688	0.00655
02C 5-1	Rim	0.4	0.8794	0.0500	0.1021	0.0024	0.419	0.06249	0.00323
02C 5-2	Rim	0.4	0.9031	0.0538	0.1012	0.0025	0.408	0.06471	0.00352
02C 5-3	Rim	0.4	0.9254	0.0758	0.1031	0.0029	0.342	0.06509	0.00501
02C 1-1	Mantle	1.0	0.8903	0.0538	0.1075	0.0027	0.424	0.06008	0.00329
02C 1-2	Core	1.0	1.7940	0.2983	0.2100	0.0098	0.281	0.06196	0.00989
02C 13-1	Mantle	0.6	0.8589	0.0442	0.1027	0.0025	0.475	0.06063	0.00275
02C 10-1	Mantle	0.4	0.8829	0.0412	0.1067	0.0025	0.511	0.06003	0.00241
02C 19-1	Rim	1.2	0.8203	0.0414	0.0983	0.0024	0.482	0.06055	0.00268
02C 18-2	Mantle	0.7	0.8451	0.0440	0.1038	0.0025	0.470	0.05908	0.00271
02C 17-1	Rim	0.2	0.8317	0.0396	0.1006	0.0024	0.503	0.05995	0.00247

Table 1.3. Summary of the results of LA-ICPMS U-Pb zircon dating (continued)

Analysis number	$^{206}\text{Pb}/^{238}\text{U}$		$^{207}\text{Pb}/^{235}\text{U}$		$^{207}\text{Pb}/^{206}\text{Pb}$		Concordance		U		Th		Th/U		Pb	
	age (Ma)	2 σ	age (Ma)	2 σ	age (Ma)	2 σ	(%)	(ppm)	2 σ	(ppm)	2 σ	(ppm)	2 σ		(ppm)	2 σ
02C 2-1	Rim	628	15	626	33	619	147	100	228	29	116	14	0.50	0.02	25	3
02C 12-1	Core	685	34	653	103	545	499	105	19	2	5	1	0.25	0.01	2	0
02C 3-1	Rim	616	15	608	31	580	141	101	267	34	130	16	0.48	0.02	29	4
02C 3-2	Core	626	21	575	59	378	310	109	57	7	13	2	0.22	0.01	6	1
02C 18-1	Core	1175	58	1207	134	1265	372	97	10	1	4	0	0.36	0.02	2	0
02C 6-1	Rim	599	14	589	28	552	127	102	367	47	201	24	0.54	0.02	39	5
02C 6-2	Rim	627	15	636	31	666	133	99	281	36	149	18	0.52	0.02	31	4
02C 6-3	Core	580	18	634	50	834	219	91	86	11	31	4	0.35	0.01	9	1
02C 5-1	Rim	626	14	641	27	691	114	98	421	54	215	26	0.50	0.02	47	6
02C 5-2	Rim	622	14	653	29	765	119	95	351	45	201	24	0.57	0.02	39	5
02C 5-3	Rim	633	17	665	41	777	171	95	140	18	68	8	0.48	0.02	16	2
02C 1-1	Mantle	658	16	647	29	607	123	102	162	47	163	33	0.99	0.10	20	6
02C 1-2	Core	1229	53	1043	115	673	384	118	9	3	4	1	0.41	0.04	2	1
02C 13-1	Mantle	630	15	630	24	626	101	100	246	71	203	41	0.81	0.08	29	8
02C 10-1	Mantle	653	15	643	22	605	89	102	306	89	306	61	0.98	0.10	39	11
02C 19-1	Rim	604	14	608	23	623	98	99	271	79	119	24	0.43	0.04	28	8
02C 18-2	Mantle	636	15	622	24	570	103	102	243	70	154	31	0.62	0.06	28	8
02C 17-1	Rim	618	14	615	22	602	92	101	309	90	166	33	0.53	0.05	33	9

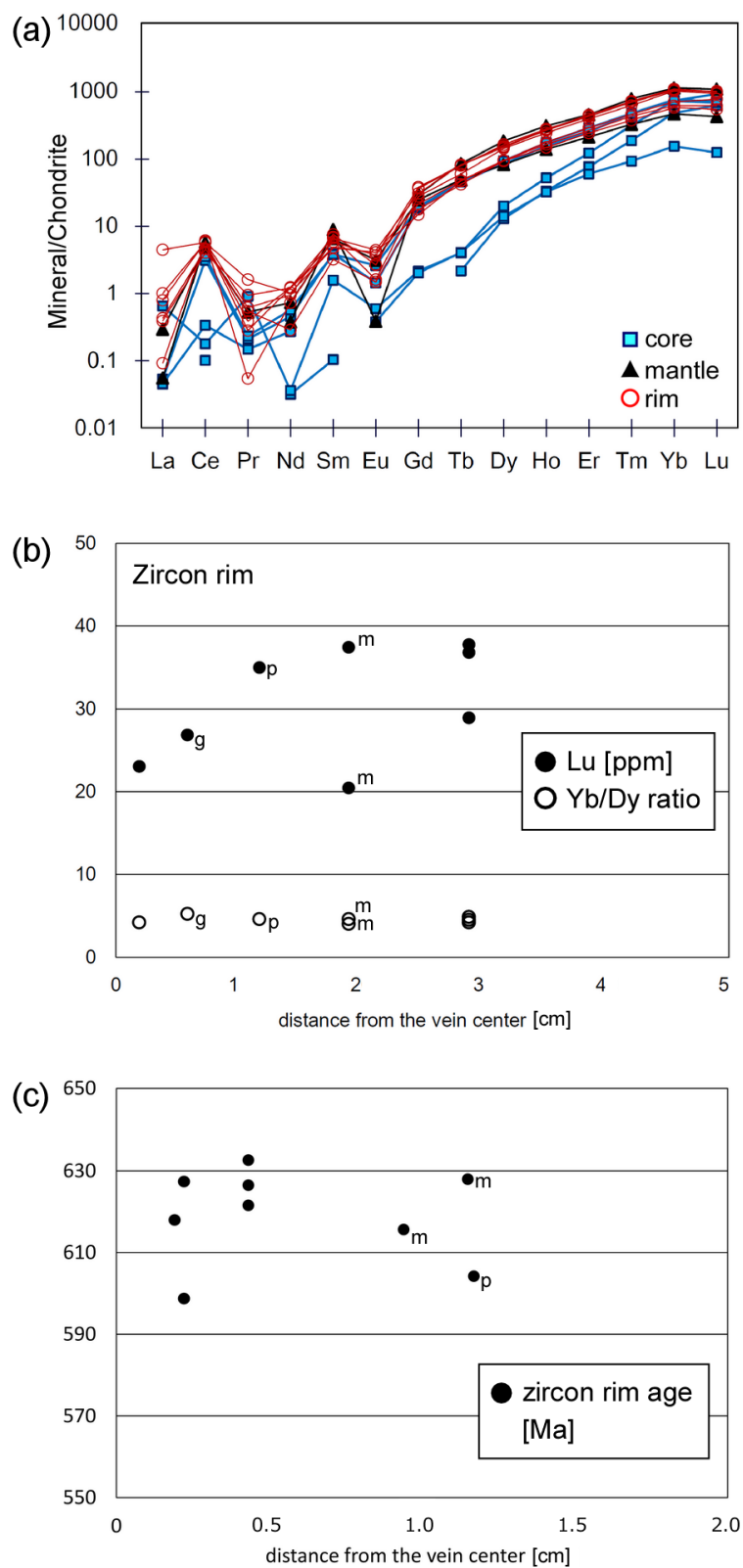


Figure 1.6. (a) Chondrite-normalized REE patterns of zircon. Zircon rims show similar REE

pattern. The REE patterns of zircon cores vary depending on the analysis points. Some cores and mantles show similar REE patterns to the rims. (b) Lutetium concentrations and Yb/Dy ratios of zircon rims with a distance from the vein center. REE compositions of zircon rims are constant with a distance from the vein. (c) $^{206}\text{Pb}/^{238}\text{U}$ ages of zircon rim with a distance from the vein center. The rim ages are constant with a distance from the vein. (b), (c) ‘g’: zircon included in Ca-poor garnet domain, ‘p’: zircon included in Na-richer plagioclase rim, ‘m’: matrix zircon.

Table 1.4. Rare earth element concentrations [ppm] of zircon determined by LA-ICPMS.

Analysis number	121002	121002	121002	121002	121002	121002	121002	121002	121002	121002	121002	121002	121002	121002	121002	121002	121002
	CR17-1	CR14-1	CR10-1	CR10-2	CR13-1	CR1-1	CR1-2	CR19-1	CR32-1	CR32-2	CR42-1	CR42-2	CR42-3	CR26-1			
	Rim	Core	Core	Mantle	Rim	Mantle	Core	Rim	Rim	Rim	Rim	Rim	Rim	Rim	Core		
Distance from the vein center	0.2	0.2	0.4	0.4	0.6	1.0	1.0	1.2	1.9	1.9	2.9	2.9	2.9	2.9	4.0		
Y	412	167	378	729	449	336	101	613	368	670	666	450	646	107			
La	0.1	0.2	0.0	0.0	b.d.	0.1	b.d.	0.0	0.2	b.d.	0.3	1.6	0.4	0.0			
Ce	3.8	0.2	2.9	5.5	3.4	4.6	0.1	5.4	4.4	5.8	5.5	5.4	5.5	0.3			
Pr	0.1	0.1	0.0	b.d.	0.0	0.1	b.d.	0.1	0.1	0.0	0.1	0.2	0.0	0.0			
Nd	0.8	0.0	0.3	0.3	0.4	0.5	0.0	0.9	0.2	0.5	0.7	0.7	0.8	0.2			
Sm	1.1	0.4	0.9	2.0	0.9	1.5	0.0	1.6	0.7	1.5	1.7	1.1	1.3	b.d.			
Eu	0.3	0.1	0.1	0.0	0.2	0.3	0.0	0.1	0.1	0.4	0.2	0.4	0.3	0.0			
Gd	6.4	0.7	5.5	9.0	5.9	7.4	b.d.	8.4	5.3	9.3	10.9	4.5	11.4	0.6			
Tb	2.7	0.2	2.6	4.8	2.6	2.8	0.1	3.4	2.4	4.7	4.5	2.7	4.6	0.2			
Dy	35.7	7.5	31.4	69.0	35.1	30.7	4.8	53.6	34.9	57.5	61.0	35.3	56.0	5.3			
Ho	13.8	4.4	13.0	25.8	14.5	11.7	2.8	20.3	12.4	22.8	23.3	14.9	22.2	2.7			
Er	64.5	29.8	61.2	111	70.5	51.8	18.8	96.0	59.2	110	104	70.7	104	14.6			
Tm	15.0	11.0	16.6	27.4	16.5	11.4	6.6	21.8	13.1	25.1	24.7	16.1	24.3	3.3			
Yb	151	178	177	275	184	114	117	247	141	266	257	172	254	37.6			
Lu	23.0	34.4	25.6	40.7	26.9	15.9	23.3	35.0	20.4	37.4	36.8	28.9	37.7	4.7			
Hf	6759	9976	8776	10423	5710	8154	8823	9252	7496	9646	9457	7833	9463	11101			
Th	81.1	2.8	88.3	107	79.7	127	2.3	93.2	94.5	119	90.7	78.8	88.8	4.0			
U	151	14.2	93.3	188	97.4	141	10.7	186	213	253	154	175	158	12.4			

1.6. Discussion

1.6.1. Host minerals of Zr

Using the Zr concentrations of minerals and the modal amount of minerals in rock slices 1-4 prepared parallel to the Grt-Hbl vein, the contribution of each mineral to the whole-rock Zr concentration is estimated (Fig. 1.7, Tables 1.1, and 1.2). Garnet and hornblende account for about 16% of the whole-rock Zr in the vein itself and the rest of Zr resides in zircon. In the wall rock, 3-5% of the whole-rock Zr resides in garnet and hornblende, and most of the whole-rock Zr is stored in zircon (Fig. 1.7). Therefore, Zr in this sample mostly resides in zircon irrespective of the distance from the vein (Fig. 1.7). Since this kind of calculation often accompanies a about $\pm 20\%$ error (e.g., Scambelluri et al., 2006; Marocchi et al., 2010; Xiong, et al., 2014), our results are acceptable. Our results for the host mineral of Zr are consistent with Fraser et al. (1997), who studied mafic granulites from the Lützow-Holm Complex, East Antarctica. Hermann (2002) showed that more than 90% of whole-rock Zr is contained in zircon in eclogites from Dora-Maira massif, Western Alps. The present study also confirmed that zircon is the most important sink mineral of Zr in the mafic gneiss collected from the granulite terrane.

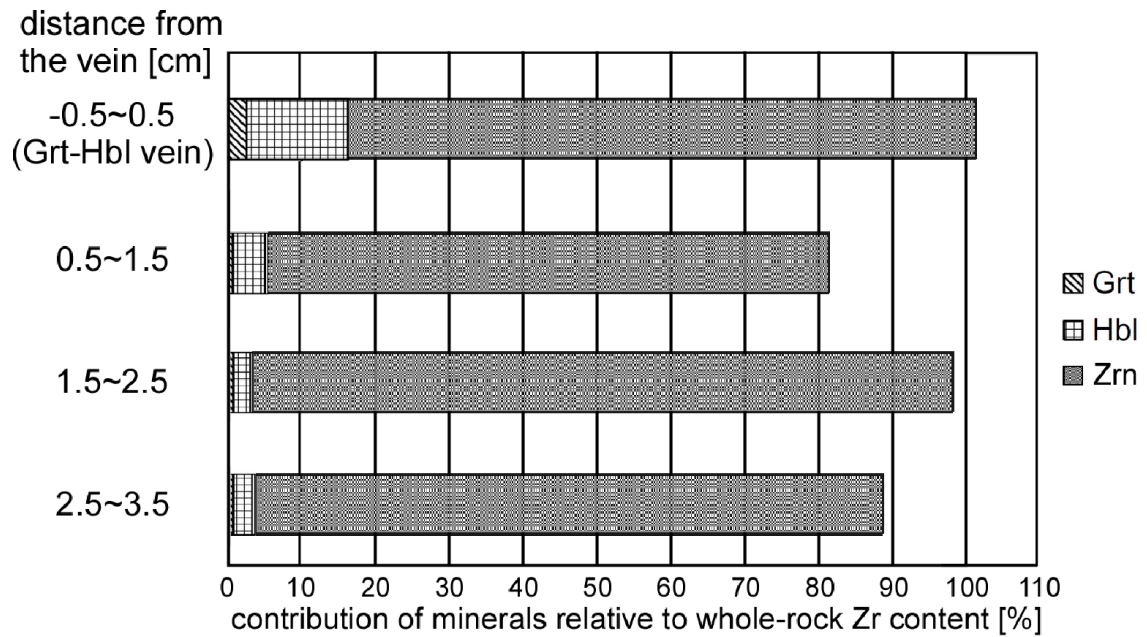


Figure 1.7. Zirconium distribution among the minerals in sample TK2009121002C, shown as a function of the distance from the Grt-Hbl vein. The whole rock Zr contents of each zones were obtained from the whole-rock Zr analysis by ICPMS, which was compared with the total Zr contents in each mineral calculated from the modal amount of minerals and Zr contents of each mineral determined by LA-ICPMS analyses (Tables 1.1 and 1.2). Garnet, hornblende, and zircon are shown in this figure, because they are recognized as host mineral of Zr. Zircon is the main host mineral of Zr irrespective of the distance from the vein. Although ilmenite could be an additional carrier of Zr (Degenhard, 1957), it is not considered here because of its low modal amount and low Zr concentration.

1.6.2. Zircon included in the minerals affected by the Grt-Hbl vein formation

The Ca-poor domains of garnet are abundant near the vein (Fig. 1.3c), suggesting that these domains recrystallized under the effect of Cl-rich fluid or melt when the Grt-Hbl vein was formed. Development of Na-richer plagioclase rims near the vein (Fig. 1.3d) also suggests that this part of the plagioclase, at least, is affected by the Cl-rich fluid or melt infiltration. Therefore, zircon grains presently included in Ca-poor domains of garnet and Na-richer plagioclase rims could have been the matrix phase during the Cl-rich fluid or melt infiltration, and entrapped in the garnet or plagioclase when the Grt-Hbl vein was formed. Thus, zircon included in these domains can be regarded similarly as zircon in the matrix (Figs. 1.4 and 1.6). Zircon grains marked by ‘g’ and ‘p’ in Figures 6b and 6c represent such grains.

1.6.3. Evaluation of Zr as an immobile element

In order to evaluate the appropriateness of Zr as an immobile element, it is necessary to investigate whether Zr was added or lost during the Grt-Hbl vein formation. The continuous gneissose structure from the wall rock to the vicinity of the vein center (Fig. 1.3e) suggests that most of the Grt-Hbl vein originated from the wall rock gneiss. However, the modal composition of the minerals in the vein itself is significantly different from that of the wall rock. Therefore, it is highly possible that at least part of the vein was not formed from the wall rock. It is also possible

that volume change occurred during the vein formation. On the other hand, the modal amounts of constituent minerals of the wall rock are almost constant irrespective of the distance from the vein. Therefore, it would be better to evaluate the vein itself and the wall rock separately.

First, the wall rock parts (0.5–3.5 cm away from the vein center) are discussed. Whole-rock Zr concentrations are almost constant in the wall rock (Table 1.1). Both modal amounts and Zr concentrations of garnet and hornblende are also constant irrespective of the distance from the vein (Fig. 1.3g). These observations imply that Zr addition from the Grt-Hbl vein into the wall rock or Zr loss out of the wall rock into the vein did not occur during the vein formation. Rims of zircon present in the wall rock show constant Th/U ratios, REE concentrations, REE patterns and U-Pb ages irrespective of a distance from the vein (Figs. 1.4-1.6). The grain size of zircon in the wall rock is also constant. Zircon rims did not give younger U-Pb ages than the timing of granulite facies metamorphism reported by previous studies in the study area (e.g., Adachi et al., 2013b). Moreover, there are no microstructures in zircon implying resorption and/or overgrowth (Fig. 1.4), and re-equilibrium textures of zircon formed in aqueous fluids or melts as reported in Geisler et al. (2007) are also not found. These observations suggest that the zircon grains in the wall rock were not significantly affected, both chemically and microstructurally, by the Grt-Hbl vein formation. Zirconium in other host minerals (garnet and hornblende) did not move significantly because the Zr concentrations and modal amounts of these minerals are constant in the wall rock

(Figs. 1.3 and 1.7). Therefore, Zr would be described as immobile in the wall rock during the Grt-Hbl vein formation.

Next, behavior of zircon and Zr in the vein itself is discussed. More than about 85% of the whole-rock Zr in the vein is hosted in zircon. There is no significant difference in grain size and microstructure between zircon in the Grt-Hbl vein and in the wall rock (Fig. 1.4). The zircon rims in the vein show similar ages, Th/U ratios, REE concentrations and REE patterns to zircon rims in the wall rock (Figs. 1.4-1.6). Therefore, zircon in the vein was also not significantly resorbed and overgrown during the Grt-Hbl vein formation.

On the other hand, whole-rock Zr concentration in the vein is slightly lower than that in the wall rock (Table 1.1). In addition to this difference, garnet and hornblende host about 15% of the whole-rock Zr in the vein, and this percentage is higher than in the wall rock (Fig. 1.7 and Table 1.1). There can be several possible interpretations to explain these observations. The first interpretation is to consider the closed system behavior of Zr. The whole-rock Zr concentration in the vein decreased because of a volume increase in the vein itself and that Zr addition/loss did not occur, while minor redistribution of Zr between zircon and other minerals took place. In this case, Zr in the vein can be dealt as immobile.

Addition of low Zr content material to the vein, or removal of Zr-bearing material from the vein can also account for the observation above, and this corresponds to open system behavior of

Zr in the vein. In both cases, Zr can be regarded as a mobile element in the vein, and the estimated Zr removal from the vein may reach up to about 10% (Table 1.1) in the present case.

Zirconium has been assumed as being an immobile element during dehydration reactions such as at the transition from the blueschist facies to the eclogite facies (e.g., Gao et al., 2007). However, it is reported that zircon, the most important sink mineral of Zr, might be altered by Cl-bearing fluid under high-*T* metamorphism (Dunkley, 2010). Detailed analysis of Zr-bearing minerals in this study made it clear that zircon is not altered even during the Grt-Hbl vein formation potentially caused by the Cl-rich fluid or melt infiltration under upper amphibolite facies condition, and Zr can be dealt as immobile in the wall rock during the Grt-Hbl vein formation. Therefore, in most of the rocks in which zircon is the major host of Zr, as attempted in this study, observing the presence or absence of zircon resorption/recrystallization through combined microstructural and chemical approaches will help evaluate whether Zr could become an appropriate ‘immobile element’ or not.

References

- Adachi, T., Hokada, T., Osanai, Y., Nakano, N., Baba, S. and Toyoshima, T. (2013a) Contrasting metamorphic records and their implications for tectonic process in the central Sør Rondane Mountains, eastern Dronning Maud Land, East Antarctica. Geological Society London, 383, 113-133.
- Adachi, T., Osanai, Y., Hokada, T., Nakano, N., Baba, S. and Toyoshima, T. (2013b) Timing of metamorphism in the central Sør Rondane Mountains, eastern Dronning Maud Land, East Antarctica: Constrains from SHRIMP zircon and EPMA monazite dating. Precambrian Research, 234, 136-160.
- Ague, J. (2003) Fluid infiltration and transport of major, minor, and trace elements during regional metamorphism of carbonate rocks, Wepawaug Schist, Connecticut, USA. American Journal of Science, 303, 753-816.
- Ague, J.J. and Van Haren, L.M. (1996) Assessing metamorphic mass and volume changes using the bootstrap, with application to deep crustal hydrothermal alteration of marble. Economic Geology, 91, 1169-1182.
- Asami, M., Osanai, Y., Shiraishi, K. and Makimoto, H. (1992) Metamorphic evolution of the Sør Rondane Mountains, East Antarctica. In Recent Progress in Antarctic Earth Science. (Yoshida, Y., Kaminuma, K. and Shiraishi, K. Eds.). Terra Scientific Publishing Company,

Tokyo, 7–15.

Ayers, J.C. and Watson, E.B. (1991) Solubility of apatite, monazite, zircon, and rutile in supercritical aqueous fluids with implications for subduction zone geochemistry.

Philosophical Transactions of the Royal Society of London Series A, 335, 365-375.

Degenhardt, H. (1957) Untersuchungen zur geochemischen Verteilung des Zirkoniums in der Lithosphäre. *Geochimica et Cosmochimica Acta*, 11, 279-300 (in German with English abstract).

Dill, H.G. (2010) The “chessboard” classification scheme of mineral deposits: Mineralogy and geology from aluminum to zirconium. *Earth-Science Reviews*, 100, 1-420.

Dunkley, D.J. (2010) Textural diagnosis of zircon re-equilibration by fluids and melts during high-T metamorphism. *Geochimica et Cosmochimica Acta*, 74, A252.

Fraser, G., Ellis, D. and Eggins, S. (1997) Zirconium abundance in granulite-facies minerals, with implications for zircon geochronology in high-grade rocks. *Geology*, 25, 607-610.

Gao, J., John, T., Klemd, R. and Xiong, X. (2007) Mobilization of Ti-Nb-Ta during subduction: Evidence from rutile-bearing dehydration segregations and veins hosted in eclogite, Tianshan, NW China. *Geochimica et Cosmochimica Acta*, 71, 4974-4996.

Geisler, T., Schaltegger, U. and Tomaschek, F. (2007) Re-equilibration of zircon in aqueous fluids and melts. *Elements*, 3, 43-50.

- Grant, J.A. (1986) The isocon diagram- a simple solution to Gresens' equation for metasomatic alteration. *Economic Geology*, 81, 1976-1982.
- Grantham, G.H., Macey, P.H., Horie, K., Kawakami, T., Ishikawa, M., Satish-Kumar, M., Tsuchiya, N., Graser, P. and Azevedo, S. (2013) Comparison of the metamorphic history of the Monapo Complex, northern Mozambique and Balchenfjella and Austhamaren areas Sør Rondane, Antarctica: Implications for the Kuunga Orogeny and the amalgamation of N and S. Gondwana. *Precambrian Research*, 234, 85–135.
- Harlov, D.E. and Dunkley, D.J. (2011) Experimental high-grade alteration of zircon using alkali- and Ca-bearing solutions. *Mineralogical Magazine*, 77, 980.
- Hermann, J. (2002) Allanite: thorium and light rare earth element carrier in subducted crust. *Chemical geology*, 192, 289-306.
- Higashino, F., Kawakami, T., M. Satish-Kumar, Ishikawa, M. and Grantham, G.H. (2013a) Multi-stage Cl-rich fluid activity and behavior of REE-bearing minerals in a Neoproterozoic granulite terrane. *Mineralogical Magazine*, 77, 1298.
- Higashino, F., Kawakami, T., M. Satish-Kumar, Ishikawa, M., Maki, K., Tsuchiya, N., Grantham, G.H. and Hirata, T. (2013b) Chlorine-rich fluid or melt activity during granulite facies metamorphism in the Late Proterozoic to Cambrian continental collision zone- An example from the Sør Rondane Mountains, East Antarctica. *Precambrian Research*, 234, 229-246.

- Hirata, T. and Kon, Y. (2008) Evaluation of analytical capability of NIR femtosecond laser ablation-inductively coupled plasma mass spectrometry. *Analytical Sciences*, 24, 345-353.
- Hirata, T. and Nesbitt, R.W. (1995) U-Pb Isotope Geochronology of Zircon: Evaluation of the Laser Probe-Inductively Coupled Plasma Mass Spectrometry Technique. *Geochimica et Cosmochimica Acta*. 59, 2491-2500.
- Iizuka, T. and Hirata, T. (2004) Simultaneous determinations of U-Pb age and REE abundances of zircon crystals using ArF Excimer laser ablation-inductively coupled plasma-mass spectrometry equipped with a Chicane ion lens system. *Geochemical Journal*, 38, 229-241.
- Ishikawa, M., Kawakami, T., M. Satish-Kumar, Grantham, G.H., Hokazono, Y., Saso, M. and Tsuchiya, N. (2013) Late Neoproterozoic extensional detachment in eastern Sør Rondane Mountains, East Antarctica: Implications for the collapse of East African Antarctic Orogen. *Precambrian Research*, 234, 247-256.
- Jacobs, J. and Thomas, R.J. (2004) Himalayan-type indenter-escape tectonics model for the southern part of the late Neoproterozoic-early Paleozoic East African-Antarctic orogeny. *Geology*, 32, 721-724.
- Kretz, R. (1983) Symbols for rock-forming minerals. *American Mineralogist*, 68, 277-279.
- Li, Z.L., Chen, H., Yang, S., Tainosho, Y., Shiraishi, K. and Owada, M. (2007) Fluid components in accessory minerals of Pan-African granitoids in the Sør Rondane Mountains, East

- Antarctica. Journal of Zhejiang University SCIENCE A, 8, 1004-1010.
- Ludwig, K.R. (2008) User's Manual for Isoplot 3.70. A geological toolkit for Microsoft Excel. Berkeley Geochronology Center Special Publication No. 4 (revision of August 26, 2008).
- Marocchi, M., Hermann, J., Tropper, P., Bargossi, G.M. and Mair, V. (2010) Amphibole and phlogopite in "hybrid" metasomatic bands monitor trace element transfer at the interface between felsic and ultramafic rocks (Eastern Alps, Italy). Lithos, 117, 135-148.
- Meert, J. (2003) A synopsis of events related to the assembly of eastern Gondwana. Tectonophysics, 362, 1-40.
- Mori, Y., Nishiyama, T. and Yanagi, T. (2007) Chemical mass balance in a reaction zone between serpentinite and metapelites in the Nishisonogi metamorphic rocks, Kyushu, Japan: Implications for devolatilization. Island Arc, 16, 28-39.
- Olsen, S.N. and Grant, J.A. (1991) Isocon analysis of migmatization in the Front Range, Colorado, USA. Journal of Metamorphic Geology, 9, 151-164.
- Osanai, Y., Nogi, Y., Baba, S., Nakano, N., Adachi, T., Hokada, T., Toyoshima, T., Owada, M., Satish-Kumar, M., Kamei, A. and Kitano, I. (2013) Geologic evolution of the Sør Rondane Mountains, East Antarctica: Collision tectonics proposed based on metamorphic processes and magnetic anomalies. Precambrian Research, 234, 8-29.
- Rubin, J.N., Henry, C.D. and Proce, J.G. (1993) The mobility of zirconium and other "immobile"

elements during hydrothermal alteration. *Chemical Geology*, 110, 29-47.

Sakata, S., Hattori, K., Iwano, H., Yokoyama, T.D., Danhara, T. and Hirata, T. (2014)

Determination of U-Pb Ages for Young Zircons using Laser Ablation-ICP-Mass Spectrometry Coupled with an Ion Detection Attenuator Device. *Geostandards and Geoanalytical Research*, 38, 409-420.

Scambelluri, M., Hermann, J., morten, L. and Rampone, E. (2006) Melt- versus fluid-induced

metamorphism in spinel to garnet wedge peridotites (Ulten Zone, Eastern Italian Alps): clues from trace element and Li abundances. *Contributions to Mineralogy and Petrology*, 151, 372-394.

Shiraishi, K. and Kojima, S. (1987) Basic and intermediate gneisses from the western part of the

Sør Rondane Mountains, East Antarctica. *Proceedings of the NIPR symposium on Antarctic Geosciences*, 1, 129-149.

Shiraishi, K., Asami, M., Ishizuka, H., Kojima, H., Kojima, S., Osanai, Y., Sakiyama, T.,

Takahashi, Y., Yamazaki, M. and Yoshikura, S. (1991) Geology and metamorphism of the Sør Rondane Mountains, East Antarctica. In *Geological Evolution of Antarctica* (Thomsom, M.R.A., Crame, J.A. and Thomson, J.W. Eds.). Cambridge University Press, Cambridge, 77–82.

Shiraishi, K., Dunkley, D.J., Hokada, T., Fanning, C.M., Kagami, H. and Hamamoto, T. (2008)

- Geochronological constraints on the Late Proterozoic to Cambrian crustal evolution of eastern Dronning Maud Land, East Antarctica: a synthesis of SHRIMP U-Pb age and Nd model age data. *Geological Society of London*, 308, 21–67.
- Taylor, R.J.M., Clark, C., Fitzsimons, I.C.W., Santosh, M., Hand, M., Evans, N. and McDonald, B. (2014) Post-peak, fluid-mediated modification of granulite facies zircon and monazite in the Trivandrum Block, southern India. *Contributions to Mineralogy and Petrology*, 168, 1-17.
- Toyoshima, T., Osanai, Y., Baba, S., Hokada, T., Nakano, N., Adachi, T., Otsubo, M., Ishikawa, M. and Nogi, Y. (2013) Sinistral transpressional and extensional tectonics in Dronning Maud Land, East Antarctica, including the Sør Rondane Mountains. *Precambrian Research*, 234, 30-46.
- Tsuchiya, N., Ishikawa, M., Satish-Kumar, M., Kawakami, T., Kojima, H., Kaiden, H., Miura, H., Suganuma, Y., Abe, M., Sasaki, D., Chiba, M., Okada, Y., Hashizume, F., Grantham, G. and Gorris, S. (2012) Report on geological fieldwork in the Sør Rondane Mountains, Eastern Dronning Maud Land, 2009-2010 (JARE-51). *Antarctic Record*, 56, 295–379.
- Whitbread, M.A. and Moore, C.L. (2004) Two lithogeochemical approaches to the identification of alteration patterns at the Elura Zn-Pb-Ag deposit, Cobar, New South Wales, Australia: use of pearce Element Ratio analysis and Isocon analysis. *Geochemistry: Exploration*,

Environment, Analysis, 4, 129-141.

Xiong, Q., Zheng, J.-P., Griffin, W.L., O'reilly, S.Y. and Pearson, N.J. (2014) Pyroxenite dykes in orogenic peridotite from North Qaidam (NE Tibet, China) track metasomatism and segregation in the mantle wedge. *Journal of Petrology*, 55, 2347-2376.

Yamasaki, S. (1996) Inductively coupled plasma mass spectrometry. In *Mass Spectrometry of Soils* (Boutton, T. and Yamasaki, S. Eds.). Marcel Dekker, New York, 459-491.

Yamasaki, S., Takeda, A., Nunohara, K. and Tsuchiya, N. (2013) Red soils derived from limestone contain higher amounts of trace elements than those derived from various other parent materials. *Soil Science and Plant Nutrition* 59, 692-699.

Supplementary materials

Table S1. Analytical condition for in situ U-Pb dating by LA-ICPMS.

Laser ablation system	
Instrument	NWR Femto (New Wave Research, Fremont USA)
Cell type	Two volume cell I
Laser wave length	260 nm
Pulse duration	<130 fs
Fluence	1.4 J/cm ²
Repetition rate	8 Hz
Ablation pit size	5 µm
Sampling mode	Single hole drilling
Pre-cleaning	1 shot with 10 µm
Carrier gas	He gas and Ar make-up gas combined outside ablation cell
He gas flow rate	0.60 l/min. Activated charcoal filter was used to reduce the Hg background (Hirata et al., 2005)
Ar make-up gas flow rate	0.70 - 0.80 l/min
Ablation duration	10 seconds
Signal smoothing device	Enabled (Tunheng and Hirata, 2004)
ICP Mass Spectrometer	
Instrument	Nu PlasmaII HR-MC-ICP-MS (Nu Instruments, Wrexham, U.K.)
RF power	1300 W
Data reduction	Integration of total ion counts per single ablation. Signals obtained from first few seconds were not used for data reduction, and next signals obtained from 5 seconds were integrated for further calculations.
Detection mode	Multiple collector mode
Monitored isotopes	²⁰² Hg, ²⁰⁴ (Hg + Pb), ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb, ²³² Th, ²³⁸ U
Integration time per peak	5 seconds for ²⁰² Hg, ²⁰⁴ (Hg + Pb), ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb, ²³² Th, ²³⁸ U
Total integration time per reading	0.2 seconds
Formation rate of ²³² Th ¹⁶ O	0.2%
Th/U relative sensitivity	Apparent ²³² Th/ ²³⁸ U ratio = 0.88 for continuous rastering of NIST SRM612

Table S1. (continued)

Data processing	
Gas blank	Gas blank counts obtained before and after 6 times measurements of primary standard samples and 15 times measurements of unknown or secondary standard samples
Calibration strategy	91500 zircon was used in correction for Pb/U fractionation and NIST SRM 610 was used in correction for Pb/Pb fractionation and calculation of Pb, Th, and U concentrations as primary standard samples. AS-3 (1099.1 ± 0.5 Ma, Schmitz et al., 2003) and OD-3 (33.0 ± 0.1 Ma, Iwano et al., 2013) were used as secondary's for quality control
Normalization values	$^{206}\text{Pb}/^{238}\text{U} = 0.1792$ (91500, Wiedenbeck et al., 1995), $^{207}\text{Pb}/^{206}\text{Pb} = 0.9096$, $^{206}\text{Pb}/^{204}\text{Pb} = 17.045$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.504$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.964$ (NIST SRM 610, Jochum et al., 2008), U content = 457.1, Th content = 450.6, Pb content = 413.3 (NIST SRM 610, Pearce et al., 1997)
Common-Pb correction	Not made
Uncertainties	Ages and isotope ratios are quoted at 2 SD absolute, propagation is by quadratic addition. Repeatability of primary standard and counting statistics of measured isotope are propagated (Sakata et al., 2014)
Quality control/validation	AS-3 : Weighted ave. $^{206}\text{Pb}/^{238}\text{U}$ age = 1102 ± 17 Ma (95% conf., MSWD = 3.4, n = 11, in 11 sessions), $^{207}\text{Pb}/^{235}\text{U}$ age = 1103 ± 16 Ma (95% conf., MSWD = 2.4, n = 11, in 11 sessions), OD-3 : Weighted ave. $^{206}\text{Pb}/^{238}\text{U}$ age = 33.14 ± 0.72 Ma (95% conf., MSWD = 2.4, n = 11, in 11 sessions), $^{207}\text{Pb}/^{235}\text{U}$ age = 33.1 ± 2.7 Ma (95% conf., MSWD = 3.5, n = 11, in 11 sessions)

Table S2. Analytical condition for in situ REE analyses by LA-ICPMS.

<i>In situ</i> REE analysis of zircon	
Laser ablation system	
Instrument	NWR femto (ESI, Portland, US)
Laser wave length	260 nm
Fluence	1.5 J/cm ²
Repetition rate	8 Hz
Ablation spot size	10 µm
Pre-cleaning	15 µm
Ablation duration	10 seconds
ICP Mass Spectrometer	
Instrument	iCAP-Qc
Data reduction	Integration of total ion counts per single ablation. Signals obtained from first few seconds were not used for data reduction, and next signals obtained from 5 seconds were integrated for further calculations.
Formation rate of ²³² Th ¹⁶ O	1.5-2.0%
Data processing	
Gas blank	Gas blank counts obtained between primary standard samples, secondary standard samples and unknown samples.
Calibration strategy	NIST SRM 610 was used as a primary standard sample. NST SRM 612 and 91500 zircon were used as secondary standards for quality control.
internal standard	²⁹ Si

Table S2. (continued)

<i>In situ</i> REE analysis of other minerals	
Laser ablation system	
Instrument	NWR-193 laser-ablation system (ESI, Portland, US)
Laser wave length	193 nm
Fluence	2.2 J/cm ²
Repetition rate	5 Hz
Ablation spot size	25 µm
Pre-cleaning	35 µm
Ablation duration	30 seconds
ICP Mass Spectrometer	
Instrument	iCAP-Qc
Data reduction	Integration of total ion counts per single ablation. Signals obtained from first few seconds were not used for data reduction, and next signals obtained from 5 seconds were integrated for further calculations.
Formation rate of ²³² Th ¹⁶ O	1.6-1.8%
Data processing	
Gas blank	Gas blank counts obtained between primary standard samples, secondary standard samples and unknown samples.
Calibration strategy	NIST SRM 610 was used as a primary standard sample. NST SRM 612 and 91500 zircon were used as secondary standards for quality control.
internal standard	²⁹ Si

Part 2: A possible process of brine infiltration constrained from mass transfer and chemical zonings within a grain to a hand specimen scale

2.1. Introduction

Fluid phase is responsible for mass and heat transfer, deformation of rocks, and changing of melting temperature (e.g., Helgeson, 1964; Sibson, 1994; Johannes and Holtz, 1996; Ague, 2003; Thompson, 2010). Among various kinds of fluids, importance of brine has been increasingly recognized due to its transport capacity (e.g., Newton et al., 1998; Harlov, 2012). Experimental studies and natural sample observations revealed that NaCl- and KCl-bearing brine coexists with CO₂-rich fluid and, different from CO₂-rich fluid, brine dissolves various major and accessory minerals at the mid- to lower-crustal *P-T* conditions (e.g., Newton et al., 1998; Shmulovich and Graham, 2004; Newton and Manning, 2010; Tropper et al., 2011). In addition to this, brine has low wetting angle and low viscosity (Watson and Brenan, 1987; Holness, 1997). This can result in large-scale mass transfer without partial melting (e.g., Newton et al., 1998; Harlov, 2012).

Apart from fluid inclusions, halite and sylvite inclusions and Cl-rich minerals have been suggested as evidence of brine and Cl-rich fluid (e.g., Van Reenen and Hollister, 1988; Kullerud,

1995; Markl and Bucher, 1998). In interpreting the significance of Cl-rich hydrous minerals, it is important to note that high Cl concentration in hydrous minerals is not a direct evidence of brine but an indicator of $f_{\text{HCl}}/f_{\text{H}_2\text{O}}$ ratio in the fluid (e.g., Munoz, 1992).

Composition of the continental crust is different depending on the depth (e.g., McLennan, 2001). Lithium, Be, B, Na, Si, P, K, As, Rb, Sr, Y, Zr, Nb, Mo, Sn, Cs, Ba, REE, Ta, W, Tl, Pb, Bi, Th and U concentrations increase from the lower towards the upper crust (e.g., Taylor and McLennan, 1985; McLennan, 2001). Brine in the lower crust would have a potential to play a role in upward transfer of these trace elements (e.g., Thompson and Connolly, 1992; Newton and Manning, 2010; Tropper et al., 2011; Touret and Huizenga, 2011).

In subduction zones, recycling of elements is observed as some trace elements in fluids trapped in a subducting slab. Such elements are released from the hydrous phases, and then trigger subduction-zone magmatism (e.g., Peacock, 1990; Tatsumi and Eggins, 1995). As a part of this cycle, trace element compositions in fluids in subduction zones are successfully estimated, using brine inclusions with daughter crystals, multiphase solid inclusions (MSIs), and mineral compositions combined with partition coefficients between minerals and fluids (e.g., Philippot and Selverstone, 1991; Ferrando et al., 2005, 2009; Hermann et al., 2006; Scambelluri et al., 2010). Among these previous studies, Philippot and Selverstone (1991) revealed a transport capacity of brine focusing on element recycling from the subducting slab into the

mantle wedge using trace element-rich brine inclusions in eclogitic veins.

On the other hand, in the deep continental crust as well, brine inclusions and MSIs are powerful tools to detect the presence of brine during orogenesis. However, even when brine inclusions and MSIs are not preserved, microstructures with Cl-rich minerals and appropriate partition coefficients between minerals and fluid would be used to detect former presence of brine and to constrain its composition. Therefore, the aim of this study is to propose a microstructural indicator implying a passage of brine in the deep crust and to estimate the brine composition from mineral chemistry affected by brine infiltration.

The Sør Rondane Mountains (SRM), East Antarctica is a high-grade metamorphic complex which can be traced for 200 km from east to west where the field distribution of Cl-rich hydrous minerals is reported (Li et al., 2007; Higashino et al., 2013; Part 1). In this study, passages of brine infiltration under upper amphibolite facies conditions are detected by focusing on addition and loss of alkali-chloride-rich fluid compatible elements in the vein and wall rock. Then, we discuss possible processes to form chemical zonings within a single grain to a hand specimen scale, preserved in minerals and wall rock around the passage. The capacity of mass transfer of brine is also implied. Mineral abbreviations are after Kretz (1983). In this study, Cl-rich hornblende and biotite represent ones containing more than 0.4 wt% Cl. Part 1 corresponds to Higashino et al. (2015).

2.2. Geological setting

The SRM (22°-28°E, 71.5°-72.5°S), eastern Dronning Maud Land, East Antarctica is dominated by granulite facies metamorphic rocks and granitoids (Shiraishi et al., 1991; Asami et al., 1992). It is thought to be a part of the collision zone between East and West Gondwana during the East African-Antarctic Orogen (Jacobs and Thomas, 2004). It is also interpreted to be in the hanging wall of a mega-nappe complex involving continental collision between northern and southern Gondwana (Grantham et al., 2013) during the Kuunga Orogeny of Meert (2003). The SRM is divided into the NE-terrane and the SW-terrane by a mylonite zone termed the Main Tectonic Boundary that dips gently to the north and northeast (Osanai et al., 2013) (Fig. 2.1). The NE-terrane rocks record clockwise *P-T* paths, and the SW-terrane rocks record anticlockwise *P-T* paths (Osanai et al., 2013). Ishikawa et al. (2013) mapped the existence of a SE-dipping ductile extensional shear zone named the Balchen detachment fault that structurally divides Balchenfjella into two metamorphic units (Fig. 2.1). From the point of view of metamorphism, the boundary between terrane that suffered the amphibolite facies metamorphism and the granulite facies metamorphism is termed the Sør Rondane Suture (SRS) shown in Fig. 2.1 (Osanai et al., 1992). The Main Shear Zone (MSZ) trends east-west and almost vertical, traversing the center of the SW-terrane in the SRM (Kojima and Shiraishi,

1986).

In northern Brattnipene, which belongs to the SW-terrane, metamorphic rocks are mainly classified into garnet-biotite gneiss, garnet-sillimanite-biotite gneiss, orthopyroxene-biotite gneiss, and hornblende-biotite gneiss (e.g., Shiraishi et al., 1997; Adachi et al., 2013a). The gneissose structure and lithological boundaries strike dominantly to the E-W and dip moderately to the S and SSW (e.g., Adachi et al., 2013a; Toyoshima et al., 2013). Peak metamorphic conditions in Brattnipene are estimated to be about 800 °C and 0.70-0.85 GPa (Shiraishi and Kojima, 1987; Adachi et al., 2013b), and an anticlockwise *P-T* path is inferred (Adachi et al., 2013b).

Previous studies on Cl-rich minerals are scarce in the SRM. Higashino et al. (2013) reported that the Cl-rich fluid or melt infiltration resulted in formations of Cl-rich biotite and apatite in pelitic gneisses from Balchenfjella, at the early stage of retrograde metamorphism near the peak-metamorphic condition of about 800 °C and 0.8 GPa (Fig. 2.1). In Part 1, on the other hand, we briefly reported the mode of occurrence of the Grt-Hbl vein from Brattnipene used in Part 2, and revealed that Zr can be dealt immobile during the Grt-Hbl vein formation. The Cl-rich mineral distribution can be traced for about 200 km from east to west in the SRM, both in pelitic gneisses (Higashino et al., 2013), and mafic gneisses (Part 1) along large-scale ductile shear zones. Magmatic hornblende has been reported to show relatively high halogen contents in

some granitoids, and hornblende from the Dufek granitoid shows 1.15-1.23 wt% F and 0.28-0.32 wt% Cl, and that from the Pingvinane granitoid shows 0.25-0.43 wt% F and 0.31-0.41 wt% Cl (Li et al., 2007).

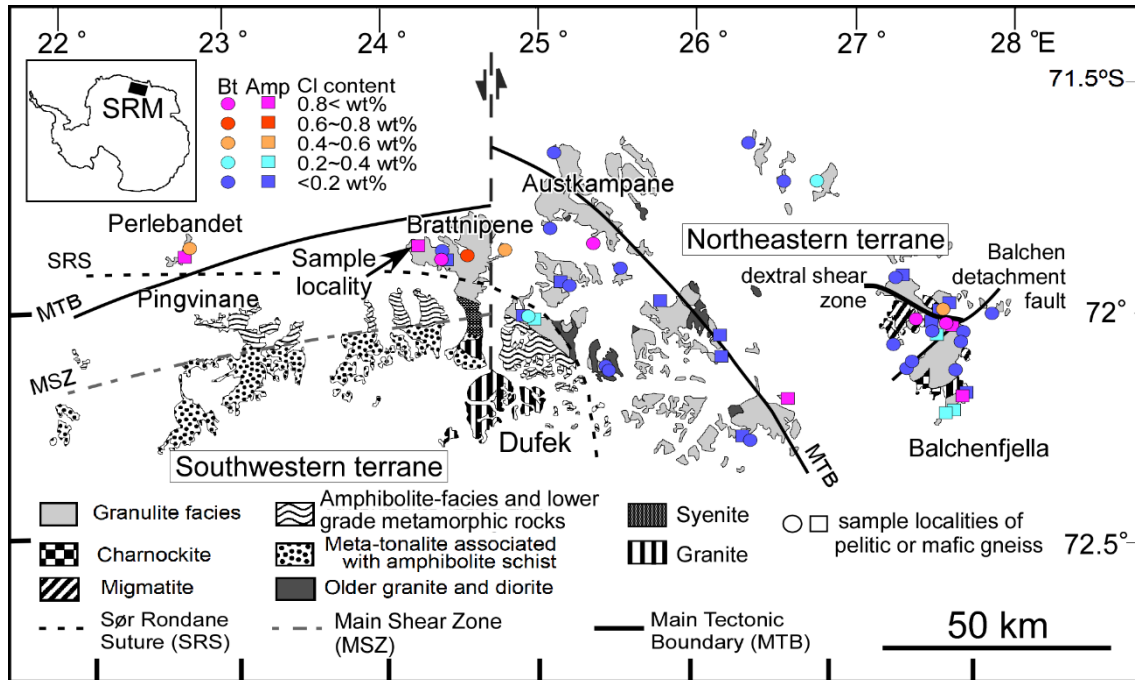


Figure 2.1. Simplified geological map of the Sør Rondane Mountains, East Antarctica (after

Shiraishi et al., 2008; Osanai et al., 2013; Toyoshima et al., 2013; Ishikawa et al., 2013).

The boundary between the NE and the SW Terranes is a mylonite zone termed the Main

Tectonic Boundary (Osanai et al., 2013). This map shows the wide distribution of the

pelitic and mafic gneisses containing Cl-rich biotite (circles) and/or amphibole (squares)

(data from Higashino et al., 2013; Part 1).

2.3. Analytical methods

Quantitative analyses and X-ray elemental mapping of minerals were performed using a JEOL JXA-8105 superprobe at Kyoto University. For quantitative analyses, counting time for the peak and backgrounds were 30 s and 15 s for Cl and P, 60 s and 30 s for F, and 10 s and 5 s for other elements, respectively. Further conditions for quantitative analyses and X-ray elemental mapping are summarized in Part 1.

The rock samples utilized in X-ray fluorescence (XRF) analysis were powdered in a tungsten-carbide mill at the Department of Geology and Mineralogy, Kyoto University. Loss on ignition was determined after heating at 950 °C for 24 hours using an electric furnace. Sample fusion and analysis by XRF was performed at the Graduate School of Environmental Studies, Tohoku University. A 1:2 ratio of powdered rock sample (1.8 g) and anhydrous lithium borate flux (3.6 g) was weighted into a Pt crucible and fused at 1200 °C to prepare a glass bead. Utilizing these glass beads, bulk rock major element compositions were determined by X-ray fluorescence (XRF) analysis using a PANalytical Epsilon 5 spectrometer. Concentration of bulk rock REE and trace elements was determined using solution inductively coupled plasma mass spectrometry (ICPMS) at Tohoku University (Yamasaki, 1996; Yamasaki et al., 2013). Detailed analytical conditions are described in Part 1.

In situ laser ablation- (LA-) ICPMS analyses of rare earth elements (REE) and trace element

concentrations of minerals were performed by an iCAP-Qc quadrupole-based ICPMS coupled with a NWR-193 ArF Excimer laser-ablation system at Kyoto University. Analytical condition for the LA-ICPMS analysis is summarized in Part 1.

2.4. Sample description

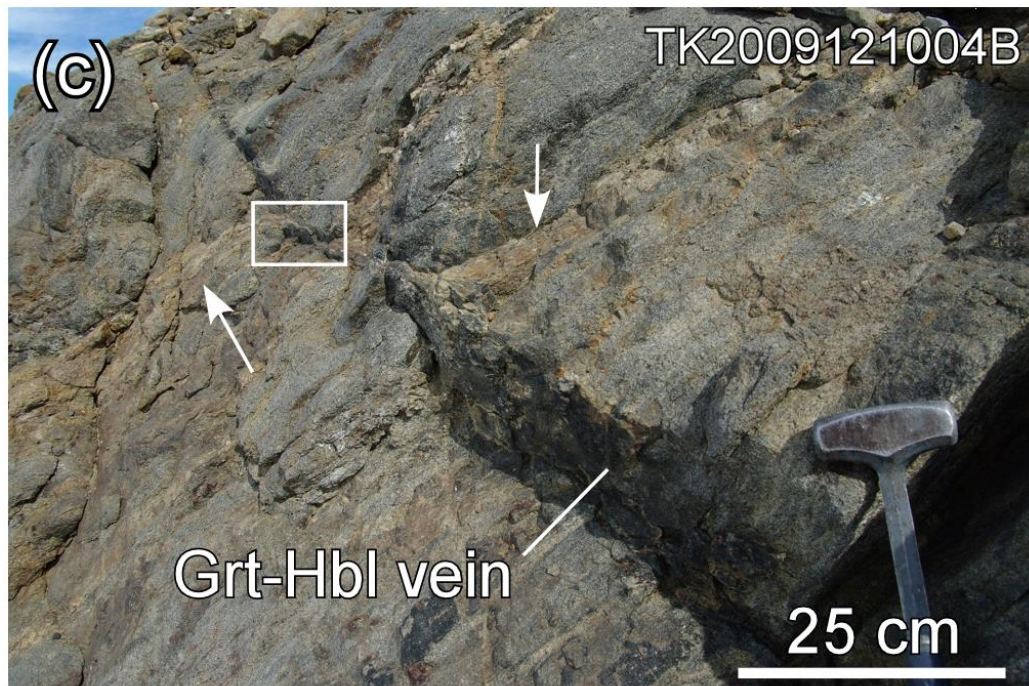
The sample used in this study (sample No. TK2009121002C) is a garnet-orthopyroxene-hornblende gneiss with about 1 cm-thick garnet-hornblende (Grt-Hbl) vein which discordantly cuts the gneissose structure (Fig. 2.2e), collected from Brattnipene during the summer season of the 51st Japan Antarctic Research Expedition (JARE 51, 2009-2010) (Tsuchiya et al., 2012). This vein is the same sample studied in Part 1. Similar veins are distributed within at least about 20 m thick layer (Fig. 2.2a). Such veins cut the gneissose structure randomly (Fig. 2.2b). One of these veins is about 2 m long and developed along a shear zone (Fig. 2.2c, d).

The Grt-Hbl vein mainly consists of coarse-grained garnet (7-10 mm) and hornblende, plagioclase, biotite, and quartz with minor amounts of apatite, zircon, sulfides, ilmenite, hematite, and secondary Fe-hydroxides. In the wall rock, orthopyroxene is present in addition to the mineral assemblage of the garnet-hornblende vein (Figs. 2.2g, 2.3, 2.4).

The biotite grains defining the gneissose structure are included in the vein-forming garnet

and hornblende, and continuous from the wall rock (Fig. 2.3a). This shows that the Grt-Hbl vein was originated from the wall rock. The boundary between coarse-grained Grt-Hbl assemblage and the wall rock is not sharp and straight. Therefore, the ‘Grt-Hbl vein’ in this study is defined as a 1 cm-thick plate in which all of the coarse-grained garnet and hornblende are included (Fig. 2.2g).





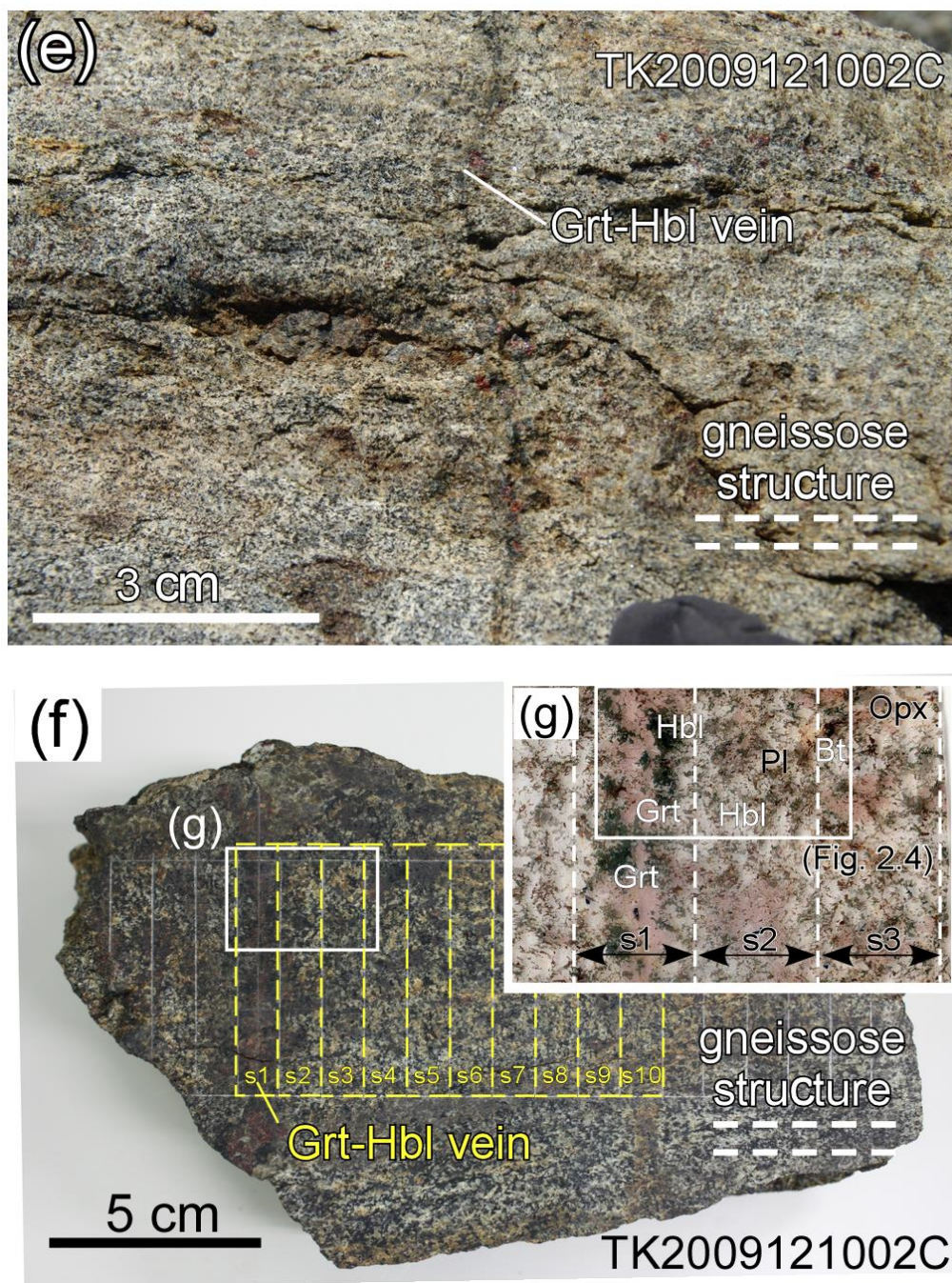
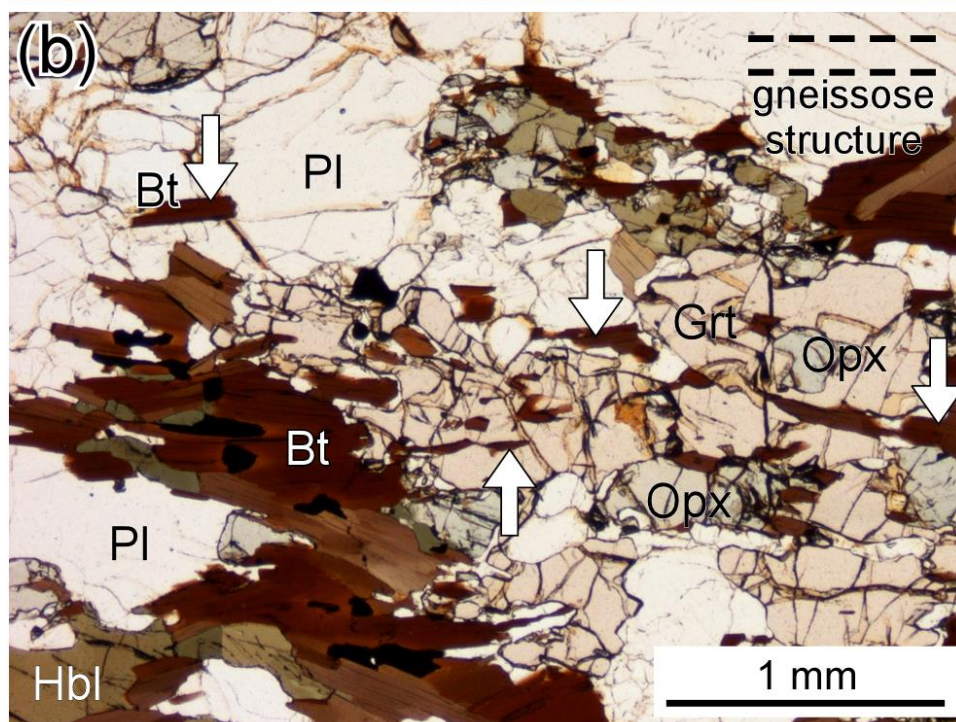
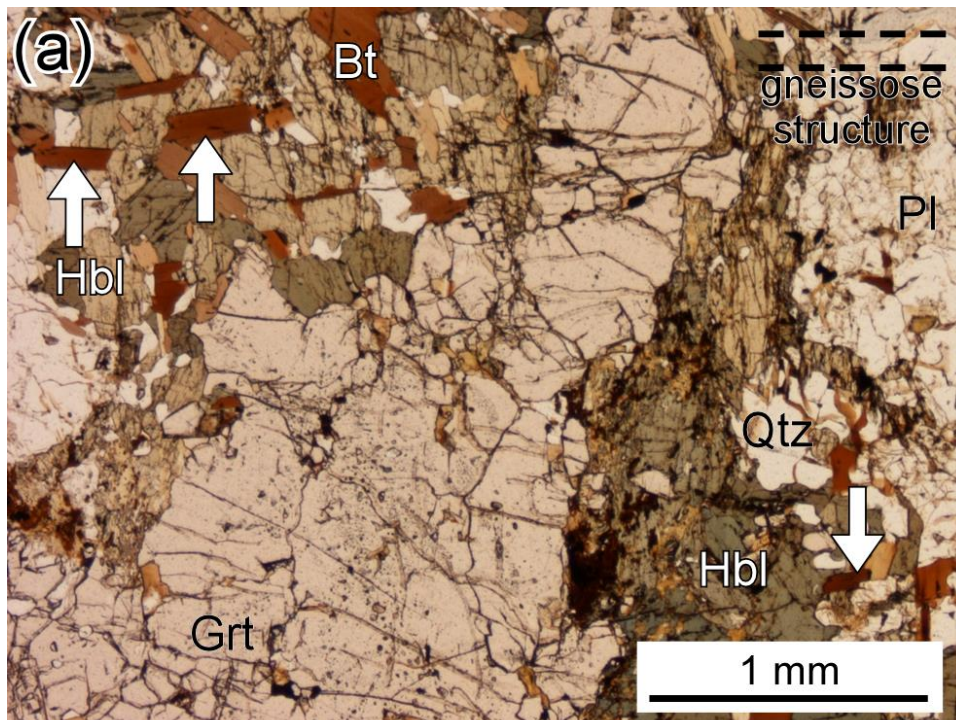


Figure 2.2. (a) Outcrop of sample TK2009121002 in Brattnipene. (b) Triangles indicate garnet-hornblende veins (dark color) that discordantly cut the gneissose structure in the outcrop shown in (a). Broken lines represent the gneissose structure. A hammer as a scale is 40 cm long. (c) Field occurrence of the Grt-Opx-Hbl gneiss collected from the sample

locality shown in Figs. 2.1 and in (a). A Grt-Hbl vein of about 1 cm-thick discordantly cuts the gneissose structure along a small dextral shear zone. The vein can be traced for at least about 2 m. Two white arrows indicate the same felsic layer with a displacement along the dextral shear zone. A boxed area indicates the area shown in (d). (d) Enlargement of the felsic layer indicated by arrows in (c) and the Grt-Hbl vein developed in the dextral shear zone. The felsic layer is deformed by the dextral shear zone. (e) Field occurrence of the Grt-Opx-Hbl gneiss sample TK2009121002C used in this study from the sample locality shown in (a). About 1 cm-thick Grt-Hbl vein discordantly cuts the gneissose structure (broken lines). (f) Slab photo of sample TK2009121002C. Slices shown by yellow broken lines (s1-s10) represent the zones utilized in the bulk rock analyses by XRF and ICPMS reported in Fig. 2.11 and Table 2.3. Broken lines represent the gneissose structure. Area of thin section photo in (g) is indicated by a white rectangle. (g) Photo of a whole thin section of the area shown in (f). A Grt-Hbl vein discordantly cuts the gneissose structure. The boxed area defined by solid lines in (g) represents the area of X-ray elemental maps shown in Fig. 2.4. Plane polarized light (PPL).



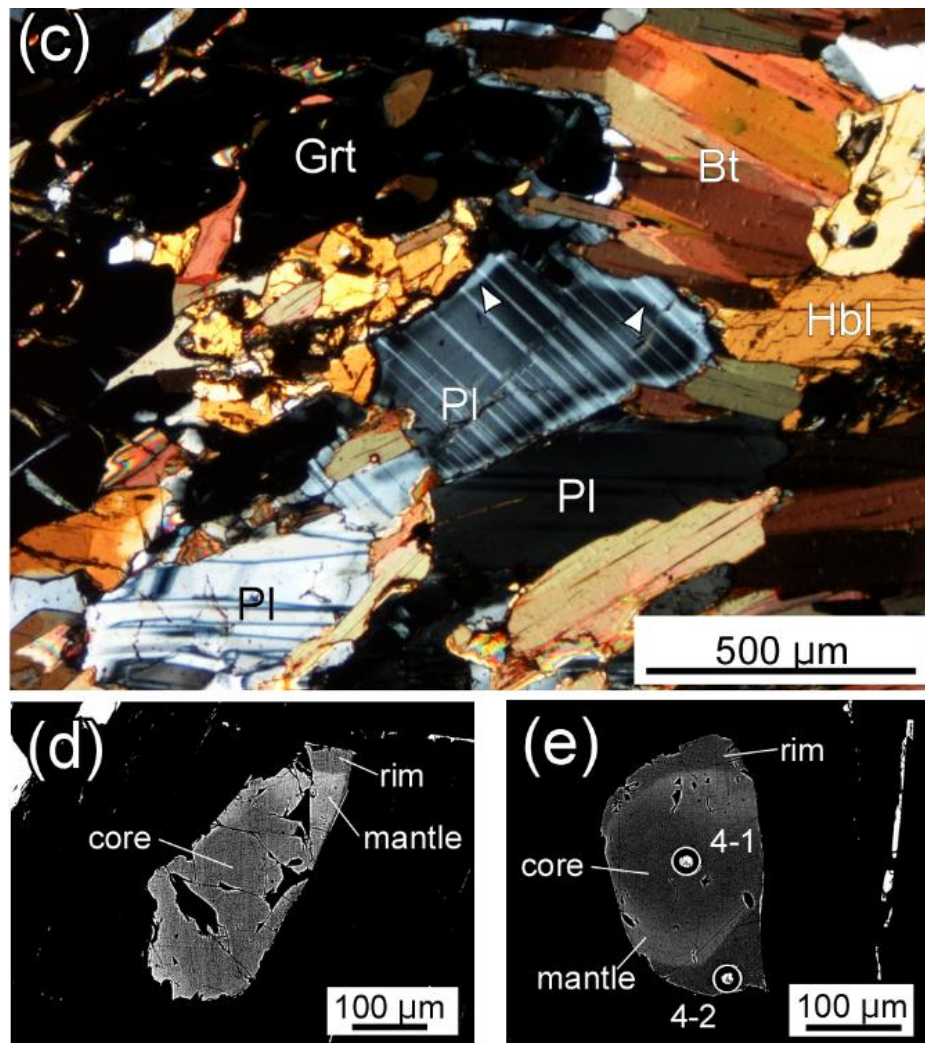


Figure 2.3. Thin section photos of sample TK2009121002C. (a) A photomicrograph showing a Grt-Hbl vein composed of coarser-grained garnet and hornblende than the wall rock. The vein is orthopyroxene-free. Note the continuous gneissose structure preserved as biotite arrangements included in the vein-forming garnet and hornblende. Broken lines represent the gneissose structure. PPL. (b) A photomicrograph of the wall rock about 4 cm away from the vein center. Orthopyroxene is present next to garnet and hornblende. Broken lines represent the gneissose structure. PPL. (c) A thin section photo of the wall rock about 1.5

cm away from the vein center. The mantle/rim boundary of plagioclase (white arrows) is clearly recognized under crossed polarized light. (d) The backscattered electron (BSE) image of apatite from about 1.3 cm away from the vein center. Dark rim, bright mantle, and dark core are recognized. The mantle/rim boundary is sharp, whereas the core/mantle boundary is gradual. (e) BSE image of apatite from about 0.5 cm away from the vein center. Circles represent pits for LA-ICPMS trace element analyses (25 μm). Numbers next to the circle represent analysis numbers given in Table 2.2.

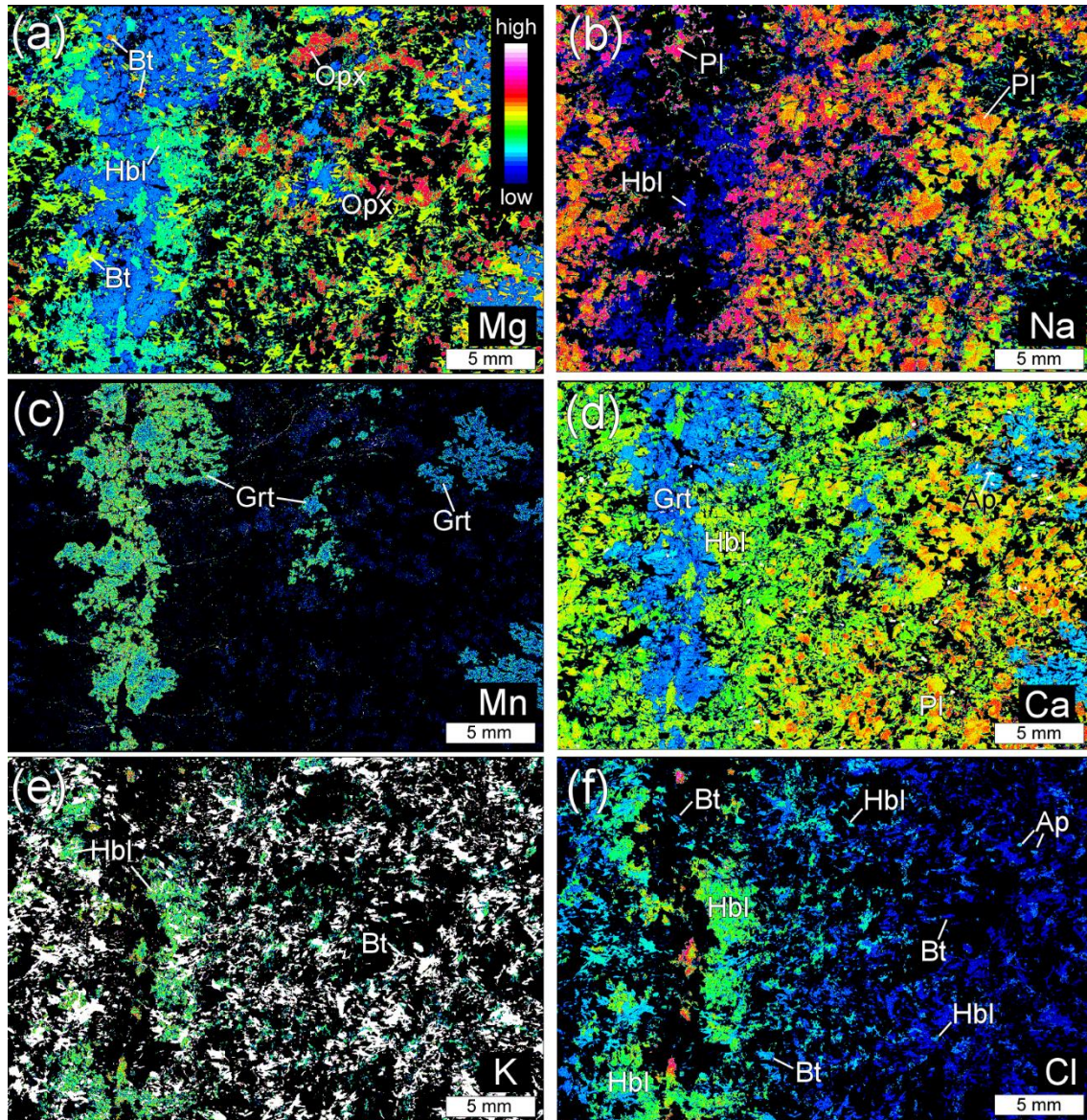


Figure 2.4. X-ray elemental maps of boxed area in Fig. 2.2g. (a) X-ray map of Mg shows that the Grt-Hbl vein is orthopyroxene-free. Shown in red is orthopyroxene except for several biotite grains in the vein. Shown in yellow, green, and blue are biotite, hornblende and garnet, respectively. (b) X-ray map of Na showing the development of Na-rich rim on plagioclase in the wall rock. Sodium-rich rim of plagioclase tends to become thinner with distance from the vein. Shown in greenish-yellow to pink is plagioclase, and shown in dark

blue is hornblende. (c) X-ray elemental map of Mn. Garnet present in and near the vein has a rim slightly enriched in Mn. The garnet away from the vein is unzoned, having similar Mn contents to the garnet core in the vein. Blue- to green-colored grains are garnet. (d) X-ray elemental map of Ca. The Ca content of plagioclase shows opposite trends to those of the Na content. Shown in white is apatite, orange to green is plagioclase, and blue is garnet. (e) X-ray elemental map of K. The K content of hornblende (green to blue) decreases away from the vein center. Shown in white is biotite. (f) X-ray elemental map of Cl. Chlorine contents of hornblende and biotite decrease away from the vein center.

2.5. Mineral description

2.5.1. Garnet

Garnet in the Grt-Hbl vein is coarser-grained (about 7-10 mm in diameter) than that in the wall rock with a diameter of less than 5 mm (Fig. 2.4). Garnet in the vein is zoned in terms of Ca and Mn (Figs. 2.4c, d, 2.5a). In the Grt-Hbl vein, garnet has Mn-rich rim and lower Ca domain (Fig. 2.4c, d), and they are not the same shape. With distance from the vein center, Mn-rich rim becomes thinner. Garnet about 2 cm away from the vein center is not zoned in Mn and Ca (Figs. 2.4, 2.5; Table 2.1). Major-element garnet compositions within a single grain are $\text{Alm}_{57-62}\text{Prp}_{19-25}\text{Grs}_{15-19}\text{Sps}_{2-3}$ and $X_{\text{Mg}} = 0.24-0.30$ in the vein and $\text{Alm}_{58-63}\text{Prp}_{20-24}\text{Grs}_{14-18}\text{Sps}_{2-3}$ and $X_{\text{Mg}} = 0.24-0.28$ in the wall rock (Part 1). Irrespective of distance from the vein, almandine increases, and pyrope slightly decreases rimward, respectively. The Mn-poor core is not zoned in Ca (Fig. 2.5b, c).

Garnet in the Grt-Hbl vein is not zoned in terms of trace elements and REE. It shows low concentration of trace elements as 34-44 ppm Sc, 10-20 ppm Y, and less than 3 ppm of REE (Fig. 2.5a; Table 2.2). Garnet about 1 cm away from the vein center in the wall rock is zoned in terms of Sc, Y, and Gd to Lu among REE. Concentrations of Y and Gd to Lu decrease from the garnet core (about 200 ppm Y, about 40 ppm Dy) to the rim (about 20 ppm Y, about 5 ppm Dy) (Fig. 2.5b). It locally has lower Sc content part (65-70 ppm) than the other parts (100-120 ppm).

A garnet grain about 2 cm away from the vein center has homogeneous Mn and Ca concentrations similar to the garnet at ca. 1 cm. The Sc, Y, and Gd to Lu concentrations decrease from the core (110-127 ppm Sc, 175-260 ppm Y, about 40 ppm Dy) to the rim (Sc = 60-80 ppm, Y = 3-78 ppm, Dy = 3-5 ppm) (Fig. 2.5c).

Garnet in the wall rock is not zoned in major elements, although it is zoned in trace elements and REE. On the contrary, garnet in the vein is zoned in major elements although it is not zoned in trace elements and REE (Fig. 2.5). Garnets in the wall rock show bell-shaped zoning in Y (Fig. 2.5). The Y-rich core includes biotite (0.45 wt% Cl, $X_{Mg} [=Mg/(Fe_{total} + Mg)] = 0.60$), and the mantle changing Y concentration includes biotite (0.37 wt% Cl, $X_{Mg}=0.61$), plagioclase (An_{60}) and orthopyroxene ($X_{Mg}=0.54-0.56$). The Y-poor rims in wall rock garnet have similar Y and REE concentrations to garnet in the Grt-Hbl vein, irrespective of distance from the vein. The Y-poor rim includes biotite (0.42 wt% Cl, $X_{Mg}=0.59$), plagioclase (An_{54-61}), orthopyroxene and quartz. Almost all inclusions are associated with cracks connected with the matrix.

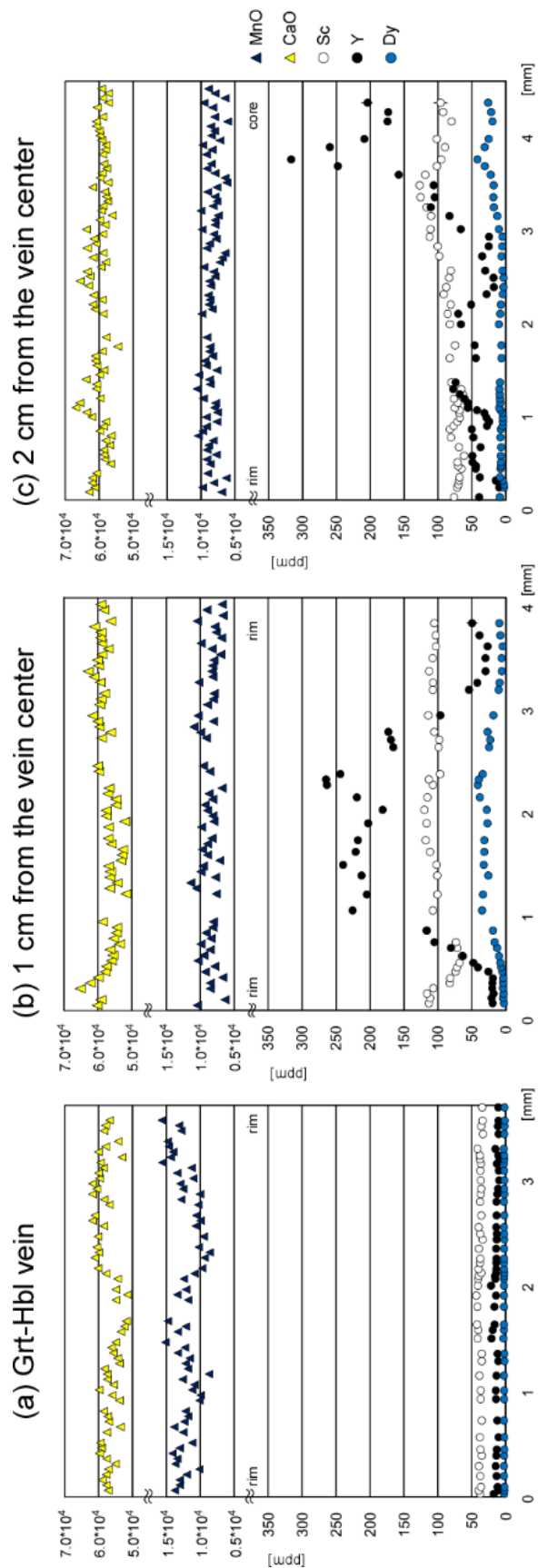


Figure 2.5. Compositional profile of garnet. Error bars are shown only on the rightmost analysis

point on each profile on (c), although most of them are within the size of symbols. (a)

Garnet grain composed of the Grt-Hbl vein, which has higher Mn and lower Ca

concentrations than the wall rock grains. (b) Garnet with a diameter of about 4 mm present

at about 1 cm from the vein center. Yttrium and Dy concentration shows bell-shaped

zoning. (c) Garnet with a diameter of about 1 cm present at about 2 cm from the vein center.

Yttrium and Dy concentration shows bell-shaped zoning. The profile represents rim (left)

to core (right).

Table 2.1. Representative mineral compositions from the Grt-Hbl vein and the wall rock (1 cm and 2 cm from the vein center). n.d.; not determined. b.d.; below detection limit.

analyses number	vein center										ca. 1 cm off the vein center										ca. 2 cm off the vein center																																																																																																																																																																																																																																																																																																																																																																																																								
	TK20091210					TK20091210					TK20091210					TK20091210					TK20091210					TK20091210					TK20091210																																																																																																																																																																																																																																																																																																																																																																																														
	OZC 2	OZC 7	Bt 3	Pl present in matrix	Ap 6	OZC 41	Grt core	Grt rim	Bt present in matrix	Pl present in matrix	Ap 6	OZC 42	Grt core	Grt rim	Bt present in matrix	Pl present in matrix	Pl mantle present in matrix	Pl rim present in matrix	Opx core present in matrix	Ap 16	OZC 46	Grt core	Bt present in matrix	Pl present in matrix	Pl mantle present in matrix	Pl rim present in matrix	Opx core present in matrix	Ap	OZC 51	Pl rim present in matrix	Opx core present in matrix	Ap 26																																																																																																																																																																																																																																																																																																																																																																																													
mineral	Grt core	Grt rim	Bt present in matrix	Pl present in matrix	Ap	Grt core	Grt rim	Bt present in matrix	Pl present in matrix	Pl mantle present in matrix	Pl rim present in matrix	Opx core present in matrix	Ap	Grt core	Grt rim	Bt present in matrix	Pl present in matrix	Pl mantle present in matrix	Pl rim present in matrix	Opx core present in matrix	Ap	Grt core	Bt present in matrix	Pl present in matrix	Pl mantle present in matrix	Pl rim present in matrix	Opx core present in matrix	Ap	Grt core	Bt present in matrix	Pl present in matrix	Pl mantle present in matrix	Pl rim present in matrix	Opx core present in matrix	Ap																																																																																																																																																																																																																																																																																																																																																																																										
SiO ₂	38.8	38.4	39.1	56.4	0.1	38.2	37.8	36.7	53.3	50.4	53.7	52.0	0.1	38.2	38.1	53.3	50.6	54.9	51.5	0.2	38.2	38.1	53.3	50.6	54.9	51.5	0.2	38.2	38.1	53.3	50.6	54.9	51.5	0.2																																																																																																																																																																																																																																																																																																																																																																																											
TiO ₂	0.1	0.1	0.7	0.1	n.d.	b.d.	0.1	4.9	0.2	b.d.	b.d.	b.d.	n.d.	b.d.	4.3	0.1	0.1	b.d.	0.1	n.d.	b.d.	b.d.	4.3	0.1	0.1	b.d.	0.1	n.d.	b.d.	4.3	0.1	0.1	b.d.	0.1	n.d.																																																																																																																																																																																																																																																																																																																																																																																										
Al ₂ O ₃	21.4	21.3	14.3	27.5	0.0	21.9	21.1	14.5	28.6	30.7	27.2	1.7	b.d.	21.3	14.2	28.8	30.8	27.7	1.9	b.d.	21.3	21.3	14.2	28.8	30.8	27.7	1.9	b.d.	21.3	21.3	14.2	28.8	30.8	27.7	1.9	b.d.																																																																																																																																																																																																																																																																																																																																																																																									
Cr ₂ O ₃	b.d.	b.d.	b.d.	b.d.	n.d.	0.1	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	n.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	n.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	n.d.	b.d.	b.d.	b.d.	b.d.	b.d.	n.d.																																																																																																																																																																																																																																																																																																																																																																																											
FeO	27.3	27.4	16.9	0.1	0.2	28.0	28.3	18.2	0.1	1.3	0.1	27.8	0.1	26.9	18.0	0.2	0.1	b.d.	28.8	0.0	28.0	28.3	18.2	0.1	0.1	0.1	28.8	0.0	26.9	18.0	0.2	0.1	b.d.	28.8	0.0																																																																																																																																																																																																																																																																																																																																																																																										
MnO	0.8	1.3	b.d.	b.d.	0.0	1.1	1.3	0.1	b.d.	b.d.	b.d.	0.4	0.0	1.0	0.1	b.d.	0.1	b.d.	0.2	0.1	1.1	1.3	0.1	b.d.	0.1	0.1	0.2	0.1	1.0	0.1	b.d.	0.1	b.d.	0.2	0.1																																																																																																																																																																																																																																																																																																																																																																																										
MgO	6.1	5.8	15.1	b.d.	0.1	6.1	5.4	12.3	b.d.	11.2	14.1	0.6	55.4	5.8	13.1	b.d.	11.9	14.1	18.3	0.1	6.1	5.4	12.3	0.2	17.9	0.0	5.8	18.3	5.8	13.1	b.d.	11.9	14.1	10.4	0.6	55.3																																																																																																																																																																																																																																																																																																																																																																																									
CaO	5.9	5.3	0.1	9.9	55.4	5.8	5.9	0.7	0.2	b.d.	b.d.	0.6	55.4	5.8	0.3	b.d.	0.2	b.d.	0.6	55.3	5.8	5.9	0.7	0.2	17.9	0.0	5.8	18.3	5.8	13.1	b.d.	11.9	14.1	10.4	0.6	55.3																																																																																																																																																																																																																																																																																																																																																																																									
BaO	b.d.	b.d.	0.2	b.d.	n.d.	b.d.	b.d.	0.1	5.0	3.5	5.4	b.d.	n.d.	b.d.	0.1	0.1	0.1	b.d.	0.1	n.d.	b.d.	0.1	0.1	0.1	0.1	0.1	0.1	n.d.	b.d.	0.3	b.d.	0.2	b.d.	0.1	b.d.	n.d.																																																																																																																																																																																																																																																																																																																																																																																									
Na ₂ O	b.d.	b.d.	0.1	5.7	b.d.	b.d.	b.d.	0.1	5.0	3.5	5.4	b.d.	n.d.	b.d.	0.1	0.1	0.1	b.d.	0.1	n.d.	b.d.	0.1	0.1	0.1	0.1	0.1	0.1	n.d.	b.d.	0.3	b.d.	0.2	b.d.	0.1	b.d.	n.d.																																																																																																																																																																																																																																																																																																																																																																																									
K ₂ O	b.d.	b.d.	9.0	0.1	b.d.	b.d.	b.d.	9.3	0.1	0.1	0.1	0.1	b.d.	b.d.	9.6	0.1	0.1	0.1	0.1	b.d.	b.d.	9.6	0.1	0.1	0.1	0.1	0.1	b.d.	b.d.	9.6	0.1	0.1	0.1	b.d.	0.1	b.d.	n.d.																																																																																																																																																																																																																																																																																																																																																																																								
F	b.d.	b.d.	0.7	n.d.	2.9	n.d.	n.d.	0.4	n.d.	n.d.	n.d.	n.d.	3.1	n.d.	0.4	n.d.	n.d.	n.d.	n.d.	3.0	n.d.	n.d.	0.4	n.d.	n.d.	n.d.	n.d.	3.0	n.d.	n.d.	0.4	n.d.	n.d.	n.d.	n.d.	3.0	n.d.	n.d.																																																																																																																																																																																																																																																																																																																																																																																							
Cl	n.d.	n.d.	1.1	n.d.	0.5	n.d.	n.d.	0.5	n.d.	n.d.	n.d.	0.3	n.d.	n.d.	0.5	n.d.	n.d.	n.d.	0.5	n.d.	n.d.	n.d.	0.5	n.d.	n.d.	n.d.	0.5	n.d.	n.d.	n.d.	0.5	n.d.	n.d.	n.d.	n.d.	0.5	n.d.	n.d.																																																																																																																																																																																																																																																																																																																																																																																							
O=Cl	n.d.	n.d.	0.3	n.d.	1.2	n.d.	n.d.	0.2	n.d.	n.d.	n.d.	1.3	n.d.	n.d.	0.2	n.d.	n.d.	n.d.	1.2	n.d.	n.d.	n.d.	0.2	n.d.	n.d.	n.d.	1.2	n.d.	n.d.	n.d.	0.2	n.d.	n.d.	n.d.	n.d.	1.2	n.d.	n.d.																																																																																																																																																																																																																																																																																																																																																																																							
P ₂ O ₅	n.d.	n.d.	0.3	n.d.	0.1	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	0.1	n.d.	n.d.																																																																																																																																																																																																																																																																																																																																																																																							
total (wt %)	100.5	99.5	96.9	98.9	101.7	101.3	100.1	97.3	98.5	99.0	98.4	100.4	100.5	99.7	98.2	99.1	99.5	98.7	101.4	99.7	98.2	98.2	98.2	98.2	98.2	98.7	101.4	101.2	99.7	98.2	99.1	99.5	98.7	101.4	101.2	99.7	98.2	99.1	99.5	98.7	101.4	101.2																																																																																																																																																																																																																																																																																																																																																																																			
number of O	12	12	22	8	25	12	12	22	8	8	8	6	25	12	12	22	8	8	8	6	25	12	12	22	8	8	8	6	25	12	22	8	8	8	6	25	12	22	8	8	8	6	25																																																																																																																																																																																																																																																																																																																																																																																		
Si	3.01	3.01	5.84	2.52	0.01	2.96	2.98	5.52	2.44	2.32	2.48	1.98	0.02	3.00	5.64	2.43	2.32	2.50	1.95	0.03	3.00	5.64	2.43	2.32	2.50	1.95	0.03	3.00	5.64	2.43	2.32	2.50	1.95	0.03	3.00	5.64	2.43	2.32	2.50	1.95	0.03	3.00	5.64	2.43	2.32	2.50	1.95	0.03																																																																																																																																																																																																																																																																																																																																																																													
Ti	0.01	0.00	0.07	0.00	n.d.	b.d.	0.01	0.55	0.01	b.d.	b.d.	b.d.	n.d.	b.d.	0.48	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d.	0.48	0.00	0.00	0.00	b.d.	0.00	n.d.	b.d

Table 2.2 (continued) Errors are 15–20 % for concentrations of 1000 ppm, 10–15 % for 10–100 ppm, and 5–10 % for less than 10 ppm.

Mineral	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Opx	Opx	Opx	Opx	Opx	Opx
analysis	5_7	5_19	6_11	7_11	8_16	8_5	9_11	10_8	5_9	6_9	7_9	8_3	9_10	10_3
number														
distance														
from the														
vein center														
[ppm]														
Li	55.4	50.7	23.5	23.8	22.0	21.6	22.8	26.1	3.2	4.4	2.2	3.4	3.4	2.8
P	25.8	15.9	26.7	28.9	43.5	39.1	24.9	20.9	50.4	52.0	61.0	54.3	39.6	44.3
Sc	11.1	9.6	19.0	25.9	17.3	16.6	19.3	17.5	28.7	92.0	105.2	53.7	55.8	66.4
V	485.4	497.9	697.3	770.0	605.3	648.2	654.8	895.2	108.7	133.1	92.1	118.0	135.1	126.1
Cr	68.4	74.4	63.9	189.6	60.8	94.5	76.4	209.8	33.3	39.7	25.9	32.7	30.2	33.6
Co	83.1	73.3	77.5	76.6	67.8	67.8	85.8	77.0	66.9	68.2	68.9	62.5	67.8	66.7
Ni	17.4	16.0	23.5	20.7	15.4	17.6	16.8	19.8	7.5	8.5	7.7	6.6	6.3	5.8
Cu	1.8	1.6	8.5	3.2	9.9	2.4	9.8	50.3	0.7	b.d.	b.d.	b.d.	7.2	b.d.
Zn	217.2	209.0	188.9	181.0	140.1	150.3	158.7	149.2	377.4	356.0	351.0	293.2	285.2	283.5
Ga	20.0	20.2	17.7	18.7	16.8	19.8	20.3	23.3	8.5	10.7	6.0	9.7	9.7	9.4
Ge	1.0	0.5	0.7	1.2	0.9	2.3	1.5	1.1	4.5	3.2	3.4	3.8	4.4	2.8
Rb	520.7	534.9	360.6	303.1	283.4	275.8	316.4	328.2	b.d.	0.1	b.d.	b.d.	0.1	0.1
Sr	16.8	20.3	4.5	5.8	2.9	5.8	5.1	4.1	b.d.	b.d.	b.d.	b.d.	0.3	b.d.
Y	0.3	0.3	0.1	0.1	b.d.	b.d.	b.d.	0.1	0.6	2.3	3.5	2.1	1.1	2.3
Zr	0.2	0.3	1.7	1.6	0.4	1.5	0.2	1.0	0.5	1.0	0.8	0.8	1.1	0.7
Nb	5.9	5.4	8.1	9.7	8.9	9.6	11.1	8.3	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Mo	0.9	1.1	0.2	0.4	0.2	b.d.	b.d.	b.d.	0.2	b.d.	0.3	b.d.	b.d.	b.d.
Ba	8581.9	5465.3	2973.4	2384.6	2492.8	2591.9	3394.1	2393.2	b.d.	b.d.	b.d.	b.d.	0.1	b.d.
La	0.1	0.1	b.d.	b.d.	b.d.	b.d.	0.1	b.d.	b.d.	0.1	0.1	b.d.	0.1	b.d.
Ce	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.0	b.d.	0.1	0.6	0.1	b.d.	0.1
Pr	b.d.	b.d.	0.0	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Nd	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.3	0.4	0.2	b.d.	0.2
Sm	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.1	b.d.	b.d.	b.d.
Eu	0.5	0.3	0.1	0.2	0.2	0.2	0.3	0.1	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Gd	7.2	3.6	1.0	0.4	1.0	0.6	b.d.	b.d.	b.d.	b.d.	0.3	b.d.	b.d.	b.d.
Tb	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.1	b.d.	b.d.	b.d.
Dy	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.4	0.7	0.2	0.3	0.2
Ho	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.1	b.d.	b.d.	0.1	0.1
Er	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.1	0.3	0.6	0.1	0.1	0.5
Tm	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.1
Yb	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.3	1.0	0.2	0.3	0.2
Lu	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.1	0.1	0.1	b.d.	b.d.
Pb	20.0	20.4	9.9	6.9	2.9	2.1	1.5	1.8	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Th	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.3	0.1	b.d.	b.d.
U	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.1	b.d.	b.d.	b.d.

Mineral	PI			PI			PI			PI			Ap			Ap		
	5_15	5_11	6_8	7_1	8_14	9_16	10_10	1_1	2_1	4_1	4_2	5_1	6_1	8_2	9_1	10_3	Ap	
analysis number	4.7	5.0	0.7	0.4	0.1	2.7	0.6	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	
distance	37.4	99.5	76.1	84.4	43.7	55.8	53.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
from the vein center	9.8	8.3	5.0	6.0	10.1	10.0	10.9	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	
[ppm]	b.d.	0.2	b.d.	b.d.	0.3	b.d.	b.d.	2.5	4.0	1.7	2.5	3.6	2.6	3.5	2.9	3.9	2.7	
Li	3.9	10.5	16.1	b.d.	2.7	7.2	7.2	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	
P	0.2	0.1	0.2	0.5	0.3	b.d.	0.5	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	
Sc	b.d.	1.3	0.6	1.2	0.3	0.8	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	
V	0.1	0.8	0.9	1.1	0.9	1.0	1.4	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	
Cr	23.7	21.6	17.8	16.7	23.3	b.d.	5.1	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	
Co	b.d.	2.4	1.2	1.4	1.4	2.1	1.7	3.9	5.2	3.8	3.9	8.5	5.3	7.4	5.6	7.6	18.1	
Ni	0.1	0.2	0.1	0.1	0.2	0.2	0.1	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	
Cu	991.9	732.0	411.1	444.4	436.3	435.2	398.2	950	930	870	830	376	306	241	244	233	219	
Zn	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.2	12	78	10	12	223	287	224	185	148	500	
Ga	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	
Ge	0.5	b.d.	b.d.	0.5	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	
Ba	106.9	57.1	45.2	42.2	42.2	61.3	40.9	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	
La	6.7	8.4	7.0	9.7	7.2	8.5	10.5	743	1570	651	690	557	296	192	305	371	710	
Ce	6.3	9.5	10.7	15.7	10.1	17.6	19.8	1100	1570	980	1220	1247	835	660	785	846	1670	
Pr	0.4	1.0	0.8	1.4	0.7	1.6	2.0	98	163	108	147	198	125	98	110	108	279	
Nd	0.5	1.9	4.5	3.4	2.1	5.5	6.7	296	494	340	420	705	498	378	472	476	1292	
Sm	b.d.	b.d.	b.d.	0.4	b.d.	0.3	0.9	35	64	47	60	125	97	68	74	78	243	
Eu	0.5	0.6	1.1	1.4	0.8	0.7	0.6	9.7	11.5	7.6	9.5	13.9	8.8	7.2	6.7	7.7	222	
Gd	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	22	46	28	31	100	100	76	72	81	246	
Tb	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	1.3	4.1	1.6	2.0	9.9	10.9	8.3	7.6	7.9	25.3	
Dy	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	3.7	17.3	4.5	4.4	44.9	58.3	42.0	38.9	37.1	121.3	
Ho	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.5	3.1	0.3	0.4	10.0	12.3	7.7	7.3	6.9	20.9	
Er	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.6	7.2	0.5	0.6	18.9	22.2	17.0	13.7	11.6	43.6	
Tm	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.1	0.7	b.d.	b.d.	2.3	2.7	1.8	1.2	1.1	3.2	
Yb	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.1	3.1	b.d.	0.1	12.8	12.7	10.1	6.5	4.7	13.1</	

2.5.2. Hornblende

Hornblende in the wall rock is about 500 μm in diameter, and that in the Grt-Hbl vein is 1-2 mm in diameter. Hornblende is included in garnet and orthopyroxene, and often rimming garnet and orthopyroxene (Fig. 2.3a, b). Hornblende is also present as a matrix phase and some of them define the gneissose structure (Fig. 2.3b). Hornblende is homogeneous in major, trace elements, and REE composition within a grain. However, Cl and K concentrations of hornblende decrease with distance from the Grt-Hbl vein (Figs. 2.4, 2.6). Distance where the element concentration becomes constant from the vein center is about 1.6 cm for Cl and about 0.4 cm for K (Fig. 2.6) (Part 1 in this thesis). Magnesium content slightly increases and becomes constant at about 0.5 cm away from the vein. The X_{Mg} of hornblende is almost constant at $X_{\text{Mg}} = 0.50$, while X_{Mg} in the vein is slightly low ($X_{\text{Mg}} = 0.45$) (Fig. 2.6b).

Zinc, Rb, Sr, Ba, Pb and U concentrations of hornblende decrease with distance from the vein center and become constant at about 1.2 cm for Rb, Sr, and Ba, about 2 cm for Zn and U, and about 3.6 cm for Pb (Fig. 2.7; Table 2.2). Such decreasing trends of element concentration with distance from the vein are referred to as decreasing ‘diffusion-like’ profiles in this study, because the pattern is similar to those formed through diffusion process at a glance. On the other hand, Sc, Ce, Sm and Gd concentrations of hornblende gradually increase with distance from the vein, and become constant at about 1 cm for Sc, and about 1.5 cm for others (Fig. 2.7).

Concentrations of Nb and REE except for La have relatively large variations (Fig. 2.7).

However, their concentrations in the Grt-Hbl vein are low.

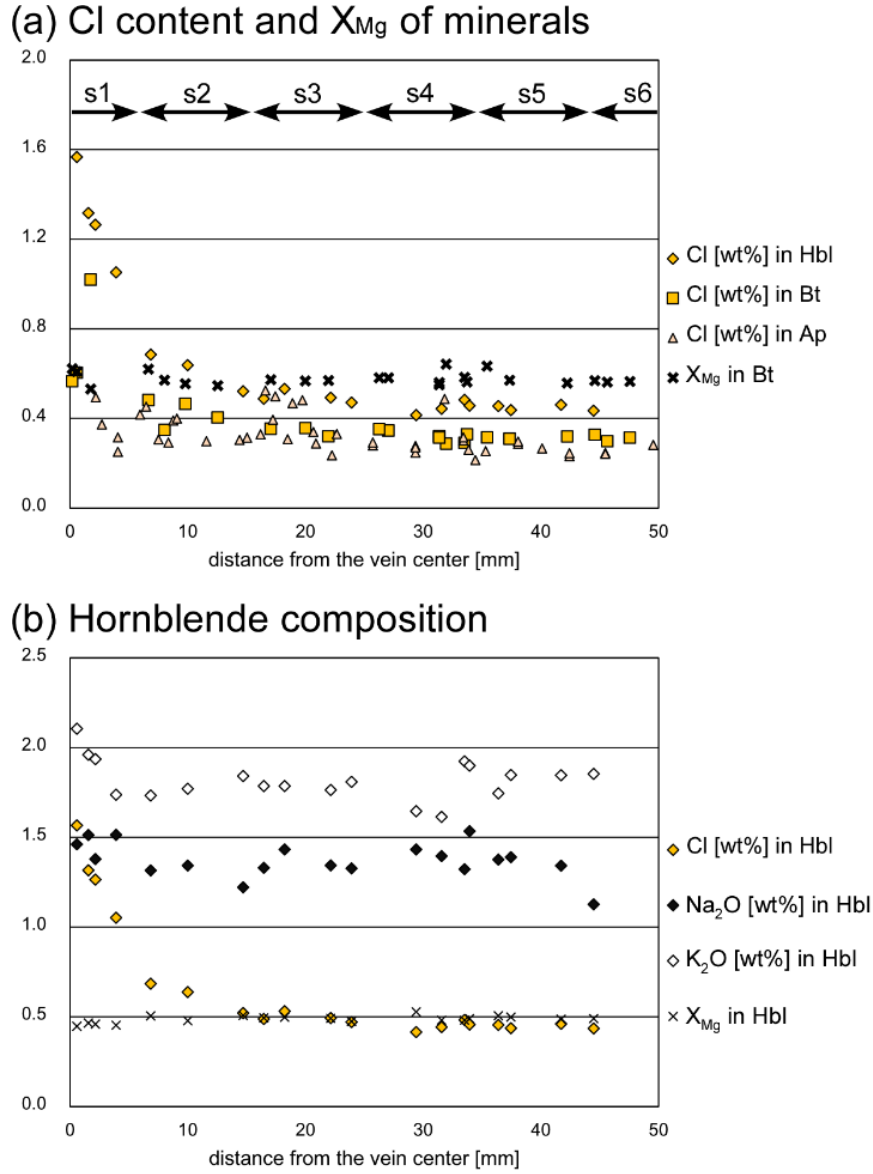
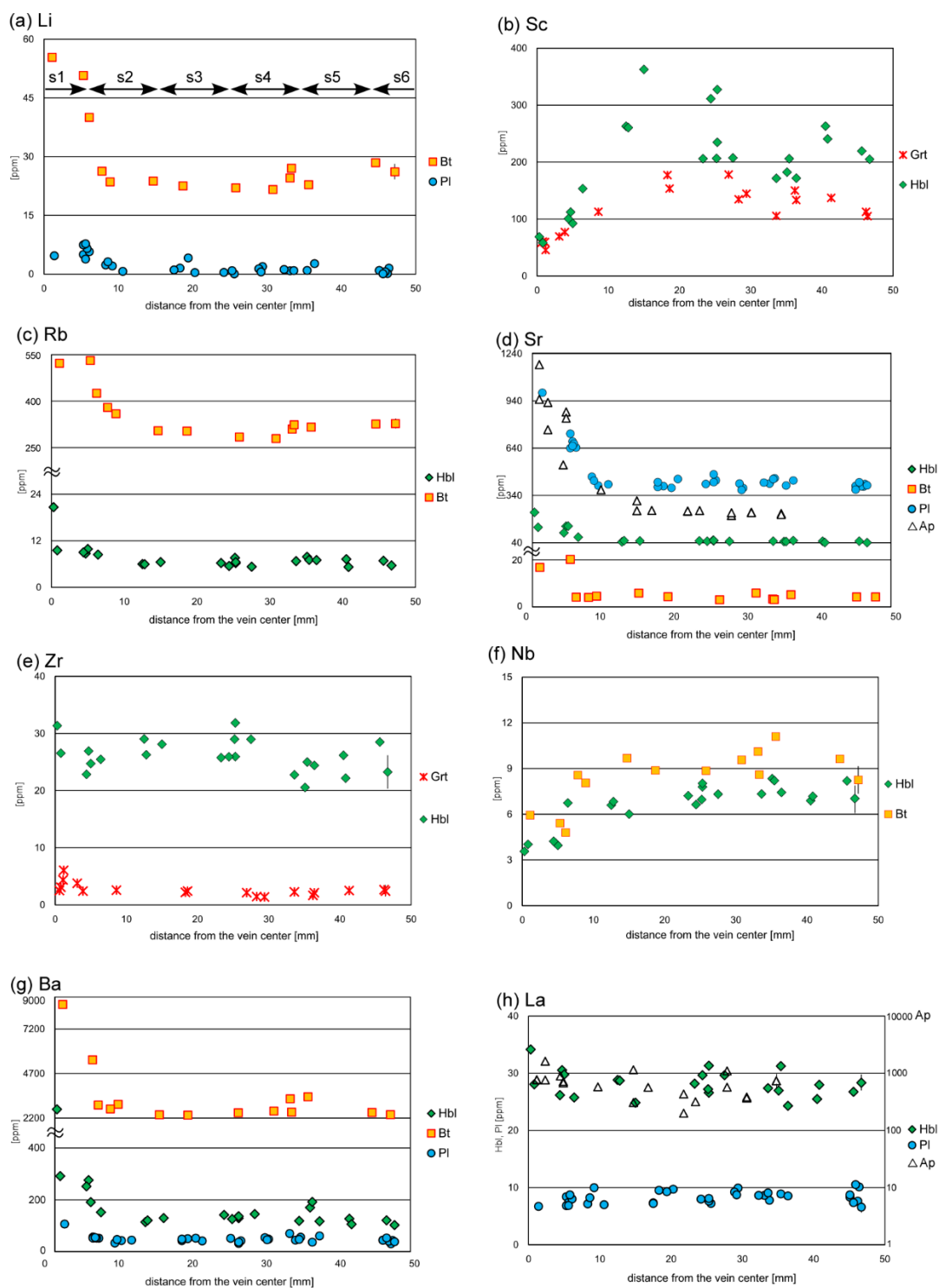


Figure 2.6. Change of hydrous mineral compositions in sample TK2009121002C as a function of distance from the vein center. (a) Chlorine contents of hornblende and biotite decrease away from the vein center, whereas X_{Mg} in biotite is almost constant. Chlorine content of apatite is constant as well. s1-s6 represent slices 1-6 shown in Fig. 2.2f. (b) Hornblende composition. Chlorine and K contents similarly decrease away from the vein center. Sodium content is almost constant, and X_{Mg} in the vein is low.



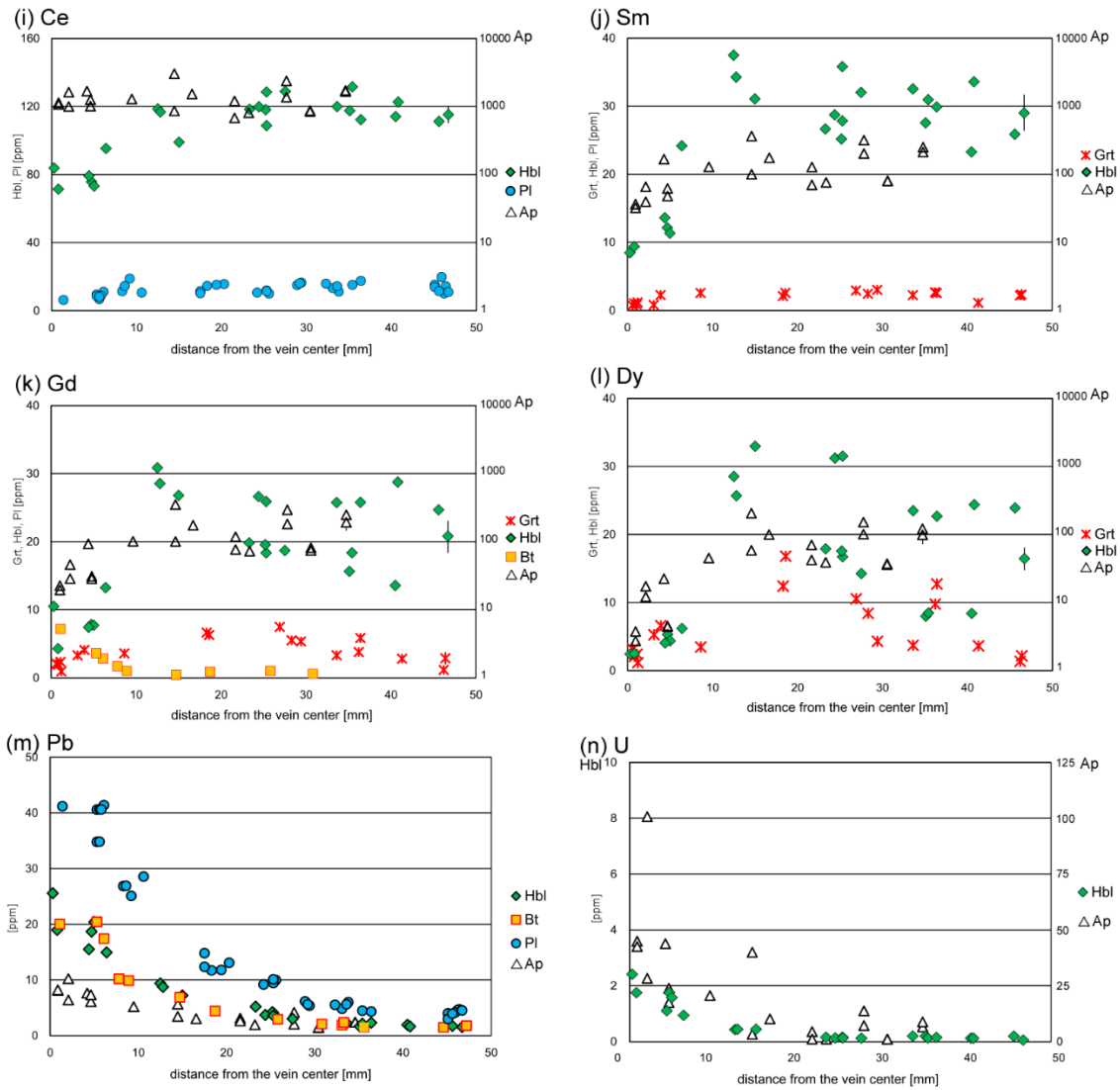


Figure 2.7. Change of trace element compositions of minerals in sample TK2009121002C as a

function of distance from the vein center. Error bars are shown only on the rightmost

analysis points of each element for each mineral. (a) Change of Li concentration of biotite

and plagioclase. Decreasing ‘diffusion-like’ profiles exist within about 1cm from the vein

center. s1-s6 represent slices 1-6 shown in Fig. 2.2f. (b) Scandium concentration of garnet

and hornblende. Garnet and hornblende near the vein have lower Sc concentration than

those in the wall rock. (c) Change of Rb concentration of hornblende and biotite. They become constant at about 1.2 cm away from the vein center. (d) Change of Sr concentration of hornblende, biotite, plagioclase, and apatite as a function of distance from the vein center. Strontium concentration of these three minerals shows decreasing ‘diffusion-like’ profiles with distance from the vein and becomes constant at about 1 cm from the vein center. (e) Zirconium concentration of garnet and hornblende is constant with distance from the vein center. (f) Change of Nb concentrations of hornblende and biotite. The increasing ‘diffusion-like’ trend becomes flat at about 1.5 cm away from the vein center. (g) Change of Ba concentrations of hornblende, biotite, and plagioclase. The decreasing ‘diffusion-like’ profiles are observed near the vein and become flat at about 1 cm from the vein center. (h) Lanthanum concentration of hornblende, plagioclase, and apatite are constant irrelevant to the distance from the vein center. (i) Cerium concentration of hornblende and plagioclase show increasing ‘diffusion-like’ profiles, whereas Ce content of apatite is constant. (j) Change of Sm concentration of garnet, hornblende, and apatite. Samarium concentration of hornblende shows an increasing ‘diffusion-like’ profile and the concentration becomes constant at about 1 cm from the vein center. (k) Change of Gd concentration of garnet, hornblende, biotite, and apatite. Hornblende and apatite show increasing ‘diffusion-like’ profiles, and biotite shows a decreasing ‘diffusion-like’ profile. (l) Change of Dy

concentration of garnet, hornblende, and apatite. Apatite shows an increasing 'diffusion-like' profile, whereas hornblende in the vein has low Dy concentration. Dy in garnet shows a parabolic profile. (m) Change of Pb concentration of hornblende, biotite, plagioclase, and apatite. Lead concentration of these three minerals decrease with a distance from the vein and become constant at about 3.6 cm from the vein center. (n) Change of U concentration of hornblende and apatite. Both minerals show decreasing 'diffusion-like' profiles.

2.5.3. Biotite

Biotite is present as inclusions in garnet cores and rims, orthopyroxene and plagioclase rims. It is also present as a matrix phase. Both define continuous gneissose structure (Fig. 2.3a, b). Biotite is not zoned within a grain in terms of major and trace elements. Major element compositions are shown in Fig. 2.8. Biotite included in garnet has slightly high concentration of Na (Fig. 2.8c). The Na-rich biotite included in garnet is present in the wall rock further than the point where Cl concentration becomes constant (Fig. 2.8c). Barium and Cl in biotite shows decreasing ‘diffusion-like’ profile from the Grt-Hbl vein to the wall rock irrespective of the mode of occurrence of biotite. The Ba concentration becomes constant at about 0.5 cm from the vein (Fig. 2.8b), and Cl concentration becomes constant at about 1.6 cm from the vein center (Fig. 2.6a). Irrelevant to distance from the vein, Ti, Al, and F concentrations and X_{Mg} [$=Mg/(Fe_{total} + Mg)$] are almost constant (Figs. 2.6, 2.8). Mg-Cl avoidance is slightly observed (Fig. 2.6).

The decreasing ‘diffusion-like’ profile with distance from the vein is observed for Li, Zn, Rb, Sr, Ba, Gd, and Pb, whereas increasing profile is observed for Nb (Fig. 2.7). Distances where these element concentrations in biotite become constant are about 1 cm for Li, Sr, Ba, and Gd, about 1.5 cm for Rb and Nb, about 2.5 cm for Zn, and about 3.6 cm for Pb (Fig. 2.7).

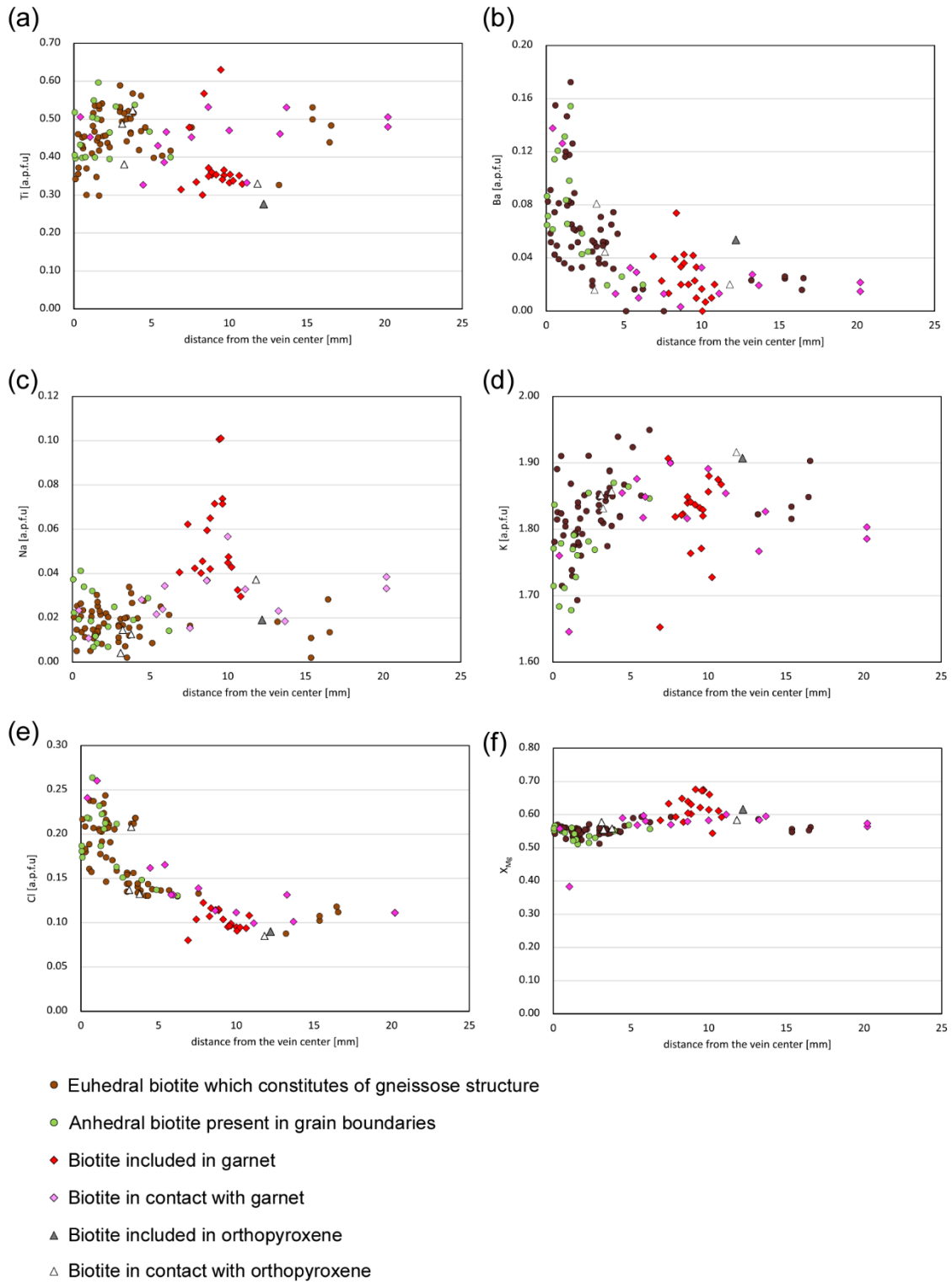


Figure 2.8. Compositional variation of biotite depending on its mode of occurrence. (a) Ti

(a.p.f.u) vs distance from the vein center. There is no correlation between mode of

occurrence and Ti concentrations. (b) Ba (a.p.f.u) vs distance from the vein center. Ba concentration decreases with distance from the vein irrespective of the mode of occurrence. (c) Na (a.p.f.u) vs distance from the vein center. Biotite included in garnet has higher Na concentration. (d) K (a.p.f.u) vs distance from the vein center. K concentration is flat with distance from the vein center. (e) Cl (a.p.f.u) vs distance from the vein center. Cl concentration decreases with distance from the vein irrespective of the mode of occurrence. (f) X_{Mg} vs distance from the vein center. Mg-Cl avoidance rule is slightly observed. Biotite included in garnet has high X_{Mg} values.

2.5.4. Plagioclase

Plagioclase is compositionally zoned and is constituted from core (An_{50-60}), mantle (An_{60-70}), and rim (An_{48-60}) (Figs. 2.4b, 2.9). The core-mantle boundary is gradual, whereas the mantle-rim boundary is sharp (Figs. 2.4b, 2.9). The range of An content does not vary as a function of distance from the vein (Fig. 2.9). Sodium-rich rim of plagioclase becomes thinner with distance from the vein (Fig. 2.4) (Part 1 in this thesis).

Plagioclase in the vein contains about 2-6 ppm Li, about 500-650 ppm Sr, about 40-60 ppm Ba, and about 20-30 ppm Pb (Fig. 2.9a; Table 2.2). Plagioclase about 1.6 cm away from the vein center contains about 2 ppm Li, about 300-450 ppm Sr, about 30-40 ppm Ba, and about 10-20 ppm Pb. It is slightly zoned in terms of Sr, and Pb within a single grain, showing gradual increase from the core to the rim (Fig. 2.9b). At about 3 cm away from the vein center, plagioclase contains about 1 ppm Li, about 280-380 ppm Sr, about 20-45 ppm Ba, and 5-10 ppm Pb (Fig. 2.9c). Plagioclase is not zoned in trace element except for that at 1.6 cm from the vein center. Trace element zoning within a grain, if any, is not correlated with zoning in An content.

Decreasing ‘diffusion-like’ profiles with distance from the vein are observed for Li, Sr, Ba, and Pb. Distances where these elements become constant are about 1 cm for Li, Sr, and Ba, and about 3.6 cm for Pb (Fig. 2.7). The compositional change within a single grain is almost negligible compared to that observed as a function of distance from the vein center.

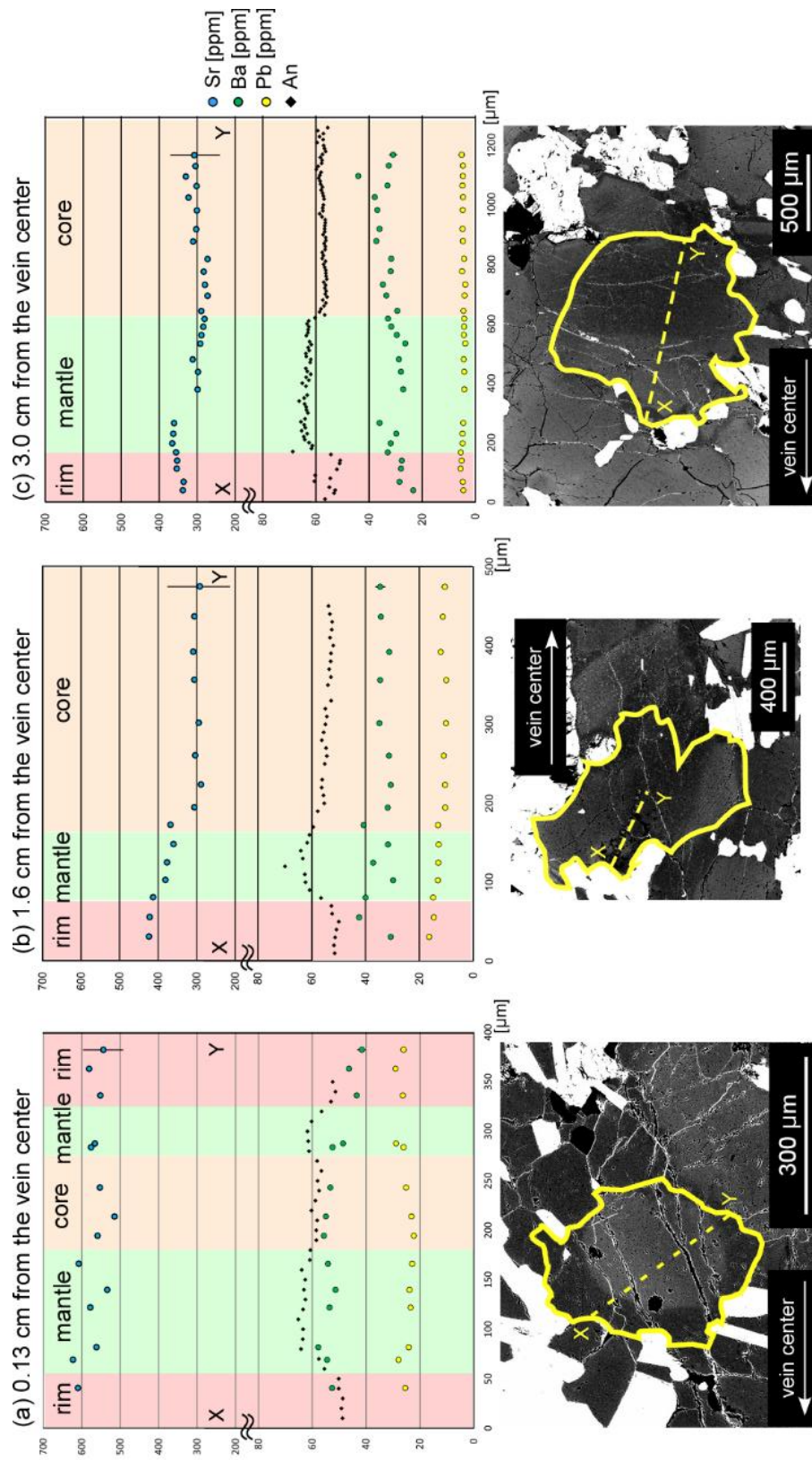


Figure 2.9. Compositional profile of plagioclase along the yellow broken line (X-Y) in the BSE

image. Relationships between An content and trace element concentration within a single grain are shown. Error bars are shown only on the rightmost analysis point on each zoning profile. Yellow solid lines in the BSE images represent the plagioclase outline. (a) Plagioclase present at 0.13 cm from the vein center. (b) Plagioclase present at 1.6 cm from the vein center. Rimward increase of Sr to the opposite side of the vein is observed. (c) Plagioclase present at 3 cm away from the vein center. Compositional variation within a single grain is smaller than that with distance from the vein center.

2.5.5. Orthopyroxene

Orthopyroxene is not present in the Grt-Hbl vein and present in the wall rock as isolated grains and as inclusions in garnet (Figs. 2.3b, 2.4a). Orthopyroxene in the wall rock includes plagioclase and biotite. In the vicinity of the vein, orthopyroxene is often surrounded by hornblende and biotite, whereas isolated orthopyroxene becomes dominant with distance from the vein center. Orthopyroxene is not zoned, and the composition is $\text{Al}_2\text{O}_3 = 1.7 \text{ wt\%}$ and $X_{\text{Mg}} = 0.54$ at about 1 cm from the vein center, and $\text{Al}_2\text{O}_3 = 1.9 \text{ wt\%}$ and $X_{\text{Mg}} = 0.53$ at about 2-3 cm, respectively. Although almost all the element concentrations in orthopyroxene are almost constant with distance from the vein, Zn content gradually decreases and becomes constant at about 3 cm from the vein center (Table 2.2).

2.5.6. Apatite

Apatite grains share similar microstructural features between matrix ones and inclusions. Their microstructure does not vary as distance from the vein. Apatite zoning can be recognized as dark core, bright mantle, and dark rim in the BSE image (Fig. 2.3d, e). The core-mantle boundary is gradual, whereas the mantle-rim boundary is sharp as in the case of plagioclase (Figs. 2.3d, e, 2.9). There is a tendency that the rim of apatite contains higher Ga, Ge, Y, REE, Pb, Th and U than the core and the mantle (Table 2.2). The variation in Y, REE, Pb, and U

concentrations within a single grain is almost negligible compared to the compositional variation observed as a ‘diffusion-like’ profile with distance from the vein (Fig. 2.7).

Decreasing ‘diffusion-like’ profile from the vein to the wall rock is observed in Sr, Pb, and U. These element concentrations become constant at about 1.5 cm away from the vein center for Sr, about 3.5 cm for Pb, and about 2 cm for U (Fig. 2.7). On the other hand, apatite in the vein has lower Y and REE concentrations except for La and Ce than that in the wall rock (Table 2.2).

2.6. Bulk rock compositional variation as distance from the vein

Slices of the studied sample (1 cm thick) were prepared parallel to the Grt-Hbl vein (Fig. 2.2c, d) (Part 1): slice 1 is the garnet-hornblende vein itself (-0.5-0.5 cm from the vein center) and slice 2 to 10 are the wall rocks of 1 cm thick from 0.5-1.5 cm to 8.5-9.5 cm, respectively (Fig. 2.2d).

Using powdered samples of each slice, bulk rock compositions for each slice were determined by XRF and ICPMS (Table 2.3). Concentration of both major and trace elements except for P, Cr, Cu, and Pb are almost constant in the wall rock slices. Slice 1, the Grt-Hbl vein, has the highest Fe₂O₃, MnO, Li, Sc, Ge, Y, Ba, REE, Th, and U concentrations, and has the lowest SiO₂, TiO₂, Al₂O₃, CaO, Na₂O, K₂O, P, Cu, Ga, Rb, and Nb concentrations among 10 slices (Table 2.3). Most of all, Fe₂O₃, MnO, Li, P, Cr, Cu, Ge, Y, Nb, Ba, REE, and U

concentrations seem to have large difference from that in the wall rocks. Addition and loss of elements in and around the Grt-Hbl vein are discussed in the discussion section.

Table 2.3. Bulk rock compositions of slices 1 to 10 determined by XRF and ICPMS analyses.

n.d.; not determined.

sample	Slice 1 Grt-Hbl vein	Slice 2	Slice 3	Slice 4	Slice 5	Slice 6	Slice 7	Slice 8	Slice 9	Slice 10
major elements [wt%]										
SiO ₂	43.7	46.4	45.8	45.9	45.7	46.3	46.2	46.5	47.0	46.7
TiO ₂	0.8	1.1	1.1	1.0	1.0	0.9	1.0	1.0	0.9	0.9
Al ₂ O ₃	17.2	19.3	18.9	19.0	19.1	19.0	18.8	19.0	19.1	19.2
Fe ₂ O ₃ (total)	19.5	13.5	14.2	14.0	14.3	14.1	14.3	13.7	13.5	13.7
MnO	0.5	0.2	0.2	0.1	0.2	0.2	0.2	0.1	0.2	0.2
MgO	6.0	5.7	6.1	6.2	6.1	5.9	6.0	5.9	5.8	5.7
CaO	6.8	7.3	7.1	7.2	7.3	7.4	7.3	7.4	7.4	7.2
Na ₂ O	2.1	2.5	2.7	2.3	2.3	2.4	2.5	2.5	2.6	2.9
K ₂ O	1.3	2.0	2.1	2.1	2.0	1.8	1.9	1.9	1.8	1.8
LOI	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	98.0	97.9	98.0	97.8	98.0	98.0	98.1	98.0	98.1	98.4
trace elements [ppm]										
Li	14.1	8.9	6.3	6.3	4.0	7.5	6.8	6.2	4.6	5.3
P	280	727	626	675	676	685	843	995	399	682
Sc	48.6	39.4	44.4	41.5	43.0	38.8	42.1	40.9	34.6	39.4
V	267	261	222	268	255	222	229	267	223	234
Cr	9	19	23	24	15	86	115	27	16	58
Cu	40	172	627	71	101	188	159	366	78	106
Zn	104	135	137	127	109	143	105	109	107	99
Ga	16.2	18.7	18.9	18.9	17.7	17.6	18.7	18.9	18.7	18.0
Ge	28.6	18.9	21.2	19.8	19.3	18.7	19.9	19.8	18.0	17.8
Rb	40.3	69.7	58.9	56.9	52.8	44.4	48.6	50.3	43.3	42.2
Sr	276	296	224	229	219	226	238	254	236	238
Y	21.7	16.2	17.1	15.7	16.3	15.9	17.7	16.5	15.6	14.9
Zr	45.6	53.2	55.1	57.6	58.5	47.2	36.8	56.8	52.0	53.1
Nb	944	1785	1538	1167	1889	1738	1611	1503	915	1708
Ba	1084	808	671	677	626	567	608	647	600	604
La	14.1	10.5	9.6	9.9	9.5	9.7	10.8	11.1	10.5	10.3
Ce	27.9	20.3	20.7	21.5	20.8	20.9	23.1	23.7	22.0	21.6
Pr	3.4	2.5	2.6	2.7	2.7	2.6	2.8	2.9	2.7	2.6
Nd	14.8	11.3	11.5	11.9	11.5	11.7	12.0	12.4	11.1	11.1
Sm	3.9	3.3	3.3	3.3	3.0	3.0	3.3	3.3	3.0	2.9
Eu	1.2	1.0	1.1	1.1	1.0	1.0	1.1	1.1	1.0	1.0
Gd	3.9	3.6	3.6	3.3	3.1	3.1	3.4	3.2	3.0	2.8
Tb	0.8	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.6	0.6
Dy	4.3	3.6	3.6	3.3	3.3	3.2	3.4	3.2	3.3	3.0
Ho	1.0	0.9	0.9	0.8	0.8	0.8	0.9	0.8	0.8	0.8
Er	2.6	2.0	2.2	2.0	2.0	1.9	2.2	1.9	1.8	1.9
Tm	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.3
Yb	2.5	1.9	2.1	1.7	1.9	1.8	2.0	1.8	1.7	1.7
Lu	0.6	0.5	0.5	0.5	0.4	0.5	0.5	0.4	0.4	0.5
Pb	12.0	19.3	55.0	7.0	5.8	4.3	4.0	21.8	7.0	5.3
Bi	1.2	1.3	1.5	1.2	1.1	1.1	1.2	1.2	1.2	1.1
Th	3.2	3.1	3.1	3.0	3.0	3.0	3.0	3.0	3.0	3.0
U	0.7	0.5	0.2	0.1	0.0	0.0	0.1	0.1	0.1	0.1

2.7. Discussion

2.7.1. The Grt-Hbl vein formation through brine infiltration

2.7.1.1. Evidence for the Grt-Hbl vein formation through an open system process

Whether bulk rock compositions are balanced or not between the vein and the wall rocks can tell the mechanism of vein formation (Oliver and Bons, 2001). In the case of balanced bulk rock compositions, the vein would be formed as pressure- or kinetically dependent closed system segregation veins in which transfer of soluble components from wall rock to the vein leaves behind a residual selvage. On the other hand, the unbalanced compositions would mean that the vein formed through an open system process with the addition and loss of elements (Oliver and Bons, 2001).

In order to detect changes of bulk rock compositions with distance from the vein center in more detail, modal amount of minerals and bulk rock composition in 0.25 cm-thick slices parallel to the vein were determined based on X-ray elemental maps and electron microprobe data of the minerals in each parts (Fig. 2.10a). That is, slices 1-4 were further divided into 0.25 cm-thick slices (termed ‘subslices’ hereafter). Modal amount of garnet, orthopyroxene, hornblende, biotite, plagioclase (separated into mantle + core, and rim parts), quartz, and apatite were determined. Although this sample contains accessory minerals such as zircon, pyrite, and ilmenite, they were neglected because they were too tiny to be recognized under the present

analytical conditions of X-ray elemental mapping. The studied Grt-Hbl vein itself has clearly different modal amount of minerals from the wall rock, and has higher Fe_2O_3 (FeO) and lower SiO_2 contents than the wall rock subslices (Fig. 2.10b; Table 2.3), although bulk rock compositions of the wall rocks (slices 2-10) are almost constant outside the vein (slice 1). The bulk rock compositions for major elements in the vein and in the vicinity of the vein are unbalanced, especially in SiO_2 and FeO (Fig. 2.10b; Table 2.3). Therefore, this suggests that the studied Grt-Hbl vein was formed through an open system process with addition and loss of elements.

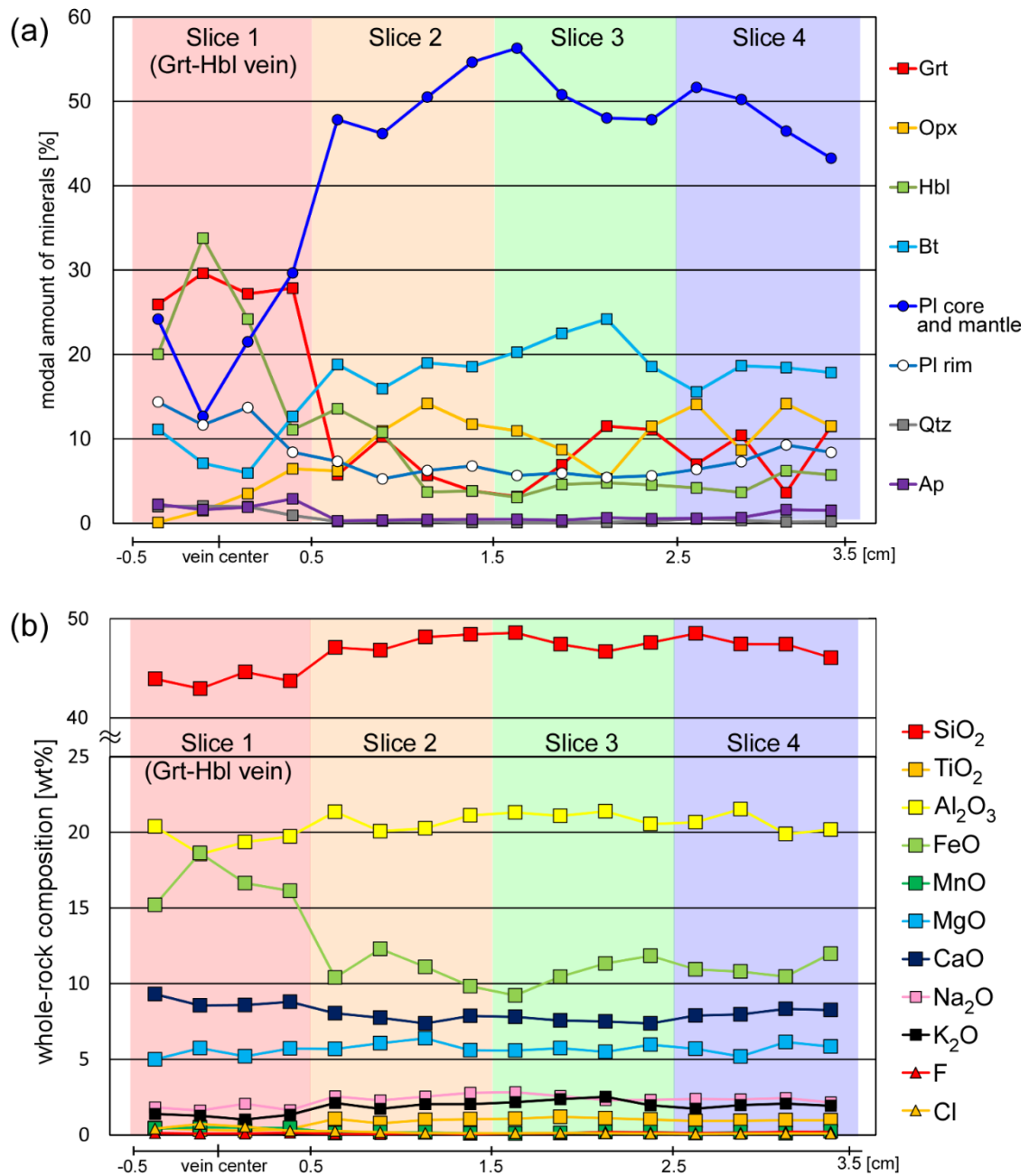


Figure 2.10. (a) Change of modal amount of minerals (vol%) in each subslice with distance from the vein center, calculated from X-ray elemental mapping. Modal amount of garnet, hornblende, quartz and apatite is high and that of orthopyroxene, plagioclase and biotite is low at Slice 1 (corresponds to the Grt-Hbl vein itself). (b) Changes of bulk rock

composition (wt%) with a distance from the vein center. Calculated by using the modal amount of minerals shown in (a), with density of each minerals and the mineral compositions of each Slice. Concentration of SiO_2 and FeO is notably different in the vein and becomes constant in Slices 2-4.

2.7.1.2. Brine infiltration implied by the elements added to the Grt-Hbl vein and its wall rock

Since the continuous gneissose structure is preserved as biotite arrangements, and such biotite is included in the vein-forming garnet and hornblende, the Grt-Hbl vein is likely to have been formed by infiltration of fluid or melt into a thin crack, and the vein itself was formed from the wall rock (Fig. 2.3a). Based on detailed geochemical evaluation of Zr behavior in the studied sample, Zr is shown to be immobile in the wall rocks (Part 1). Zirconium may be mobile in the vein to some extent, but the maximum amount of Zr removal from the vein may reach up to ~ 10% only (Part 1). Therefore, Zr would be used as an immobile element to evaluate the mass movement based on the bulk rock chemical variation during the Grt-Hbl vein formation, following the method suggested by Ague (2003). Fractionation mass change value (τ) (Ague, 2003) is used to examine mass addition/loss. Using element i as an immobile element, the ratio (r) between concentration of i within the altered domain (C'_i) and the concentration of i within the reference domain (C^0_i) represents volume change value.

$$r = C'_i / C^0_i$$

Using r value, the fractionation mass change value (τ) for element j is calculated as

$$\tau = r (C^0_j / C'_j) - 1$$

The fractionation mass change values shown in Fig. 2.11 reveal that Fe, Mn, Li, Sc, Cu, Rb,

Ba, REE, Pb, and U were added to the vein and to the wall rock. Elements such as Li, Cu, Rb, Ba, Pb and U are incorporated in alkali-chloride-rich fluid rather than melt and chloride-free-fluid (Keppler, 1996; Keppler and Wyllie, 1990; Borchert et al., 2009, 2010; Kawamoto et al., 2014; Webster et al., 1989). Decreasing ‘diffusion-like’ profile of Cl and K in biotite and decreasing Na-rich rim width of plagioclase from the vein would imply that NaCl and KCl infiltrated from the vein into the wall rock (Figs. 2.4b, f, 2.6a). Therefore, the Grt-Hbl vein was probably formed by the infiltration of brine, not by the infiltration of Cl-bearing melt.

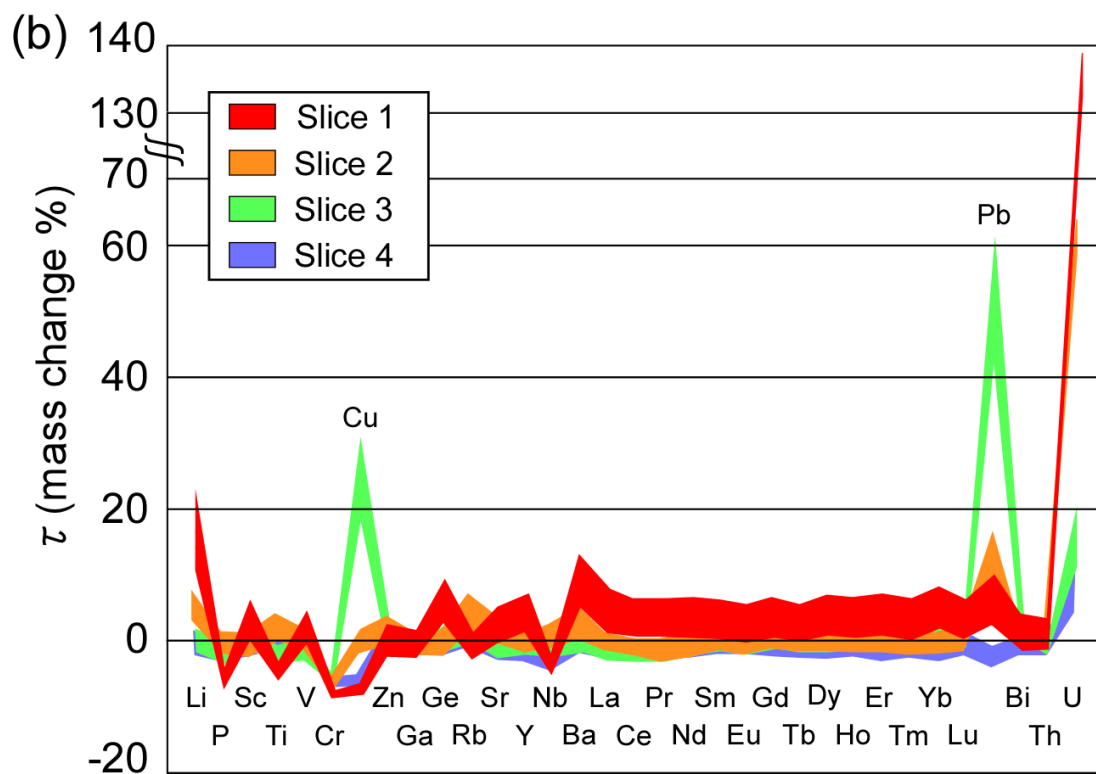
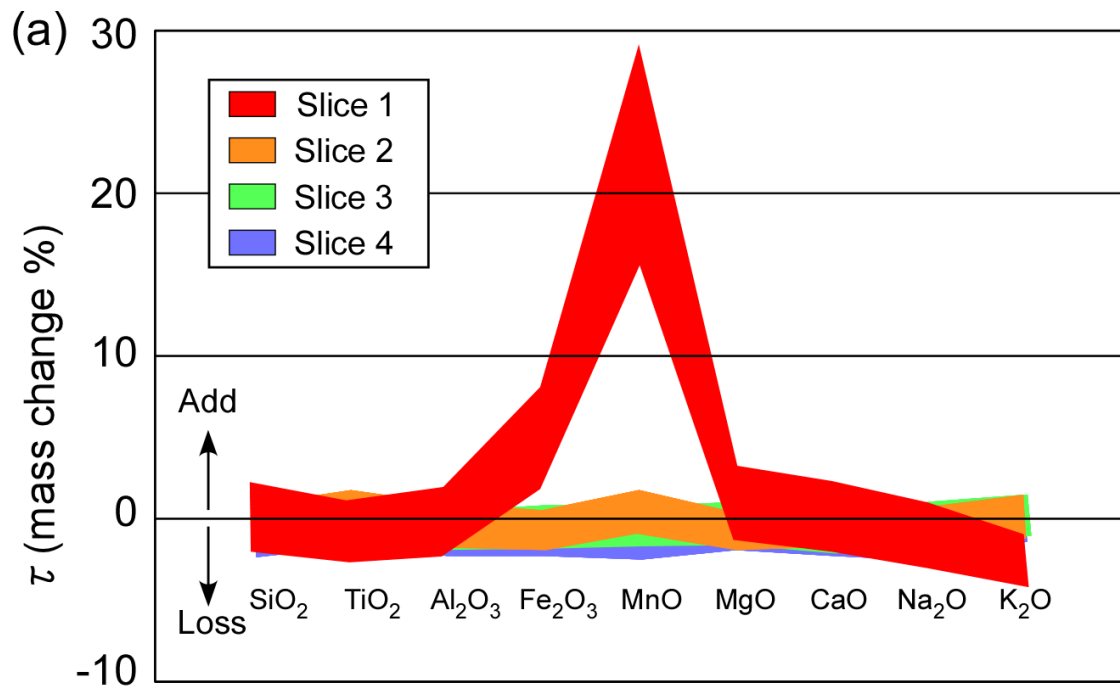


Figure 2.11. The fractional mass change values (τ) with a distance from the vein based on the

equation of Ague (2003). Bulk rock compositions of rock slices prepared as distance from the vein (Slices 1-10) are used in this calculation. Volume change is taken into account. Average Zr concentration in slices 5-10 is used as an immobile reference species (Fig. 2.2d). Thickness of each pattern reflects errors, including variation of Zr concentration in slices 5-10 (2σ) and maximum amount of Zr removal in slice 1 implied in Part 1. (a) Mass change values for major elements determined by XRF analyses. Iron and Mn are added to the Grt-Hbl vein. (b) The τ value for trace elements and REE. Lithium, Cu, Rb, Ba, Pb and U which tend to be incorporated in fluids rather than melts are added to the Grt-Hbl vein and the wall rock.

2.7.1.3. Interpretation of chemical zonings and microstructures in minerals

Among the minerals in the wall rock, plagioclase show microstructural change in terms of major elements as a function of distance from the vein. The plagioclase rim thickness decreases with distance from the vein, showing that the rim alone is affected by the brine infiltration. Therefore, it is reasonable to consider that the core and mantle preserve the major element composition before brine infiltration (Figs. 2.4b, 2.9). However, a complete change of trace element composition in plagioclase from the original one is suggested by the decreasing/increasing ‘diffusion-like’ profile of trace elements with distance from the vein (Fig. 2.7).

Garnet also has characteristic trace element zoning. Garnet in the wall rock has bell-shaped zoning in Y, although garnet in the vein shows flat Y zoning (Fig. 2.5). Low-Y rim of garnet in the wall rock shows similar Y concentration with garnet in the vein (Fig. 2.5). This implies that the low-Y rims of garnet in the vein and in the wall rock are coeval, resulted from the recrystallization during brine infiltration. Figure 2.4c shows that Mn-poor garnet cores in the vein are not affected by brine. The low-Y rim of garnet partly corresponds with Mn-rich rim (Fig. 2.5). Higher modal amount of garnet in the vein than the wall rock suggests that at least the garnet with low-Y and high-Mn compositions was formed by the brine infiltration (Figs. 2.4, 2.5).

Biotite grains which constitute the gneissose structure also show the ‘diffusion-like’ profile in Cl and other elements (Figs. 2.6a, 2.7, 2.8). This probably resulted from the compositional change of biotite without changing its microstructure during brine infiltration. Biotite grains included in garnet have slightly high Na concentrations (Fig. 2.8c). It is possible that such Na-rich biotite was already present before the brine infiltration, because garnet including Na-rich biotite preserves prograde Y zoning. However, such garnet grains are present beyond the distance where Cl concentration of biotite becomes constant. In addition, almost all biotite inclusions are associated with cracks connected with the matrix and Cl concentration of biotite included in garnet constitutes ‘diffusion-like’ profile. Therefore, whether biotite included in garnet was affected by brine infiltration or cannot be clearly determined.

There would be at least two stages of hornblende formation. Hornblende that constitutes the gneissose structure with biotite would be already present before the brine infiltration (Fig. 2.3b). On the other hand, hornblende in the Grt-Hbl vein is considered to be newly formed by the brine infiltration (Fig. 2.3a). Both hornblendes constitute ‘diffusion-like’ profile in trace elements (Fig. 2.7), implying that hornblendes in the wall rocks are compositionally affected by the brine infiltration irrespective of mode of occurrence.

Modal amount of orthopyroxene is clearly high as distance from the vein (Fig. 2.10a). Orthopyroxene in the wall rock near the vein are surrounded by hornblende and biotite,

implying the hydration reactions during the brine infiltration.

Although compositional change with distance from the vein is not observed in quartz, modal amount of quartz is high in the Grt-Hbl vein (Fig. 2.10a). This might suggest that quartz is formed during the vein formation by brine infiltration.

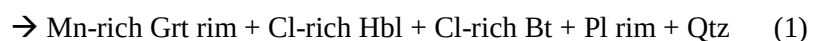
Zoning of apatite is recognized in BSE images. The core-mantle boundary is gradual, whereas the mantle-rim boundary is sharp as in the case of plagioclase (Fig. 2.3d, e). Apatite present in the matrix is commonly in contact with plagioclase rim. This might imply that the apatite rim is possibly affected by the brine infiltration as well as plagioclase rim, although Cl concentration of apatite is low (Fig. 2.6a).

2.7.1.4. Possible reaction on the brine infiltration

According to the interpretation of microstructure and mineral compositions, the brine infiltration changed compositions of Mn-poor garnet to Mn-rich, Cl-poor hornblende to Cl-rich, Cl-poor biotite to Cl-rich, plagioclase core and mantle to rim. In addition to the compositional change, orthopyroxene was consumed in the vein and quartz was formed (Fig. 2.10a).

Therefore, change in mineral assemblage between the Grt-Hbl vein and the wall rock suggests that the reaction as follows took place.

Mn-poor Grt core + Opx + Hbl + Bt + Pl (core + mantle) + brine



2.7.1.5. *P-T* conditions for the brine infiltration

Figure 2.8 implies that biotite changed its composition on the brine infiltration. Therefore, *P-T* conditions for the brine infiltration were estimated using minerals present in the Grt-Hbl vein; Mn-rich garnet domain, hornblende and biotite which are not in contact with garnet, and Na-richer plagioclase rim. The reason choosing this mineral assemblage is to avoid the effect of retrograde Fe-Mg exchange between garnet and biotite/hornblende that results in lower-*T* estimate. On the other hand, Mg-Cl avoidance in biotite possibly results in higher-*T* estimates. Therefore, we selected biotite grain in the vein which constitutes the gneissose structure, and which is not in contact with garnet in order to estimate maximum *P-T* conditions for the brine infiltration. The garnet-biotite geothermometer (Holdaway, 2000) and the garnet-biotite-plagioclase-quartz (GBPQ) geobarometer (Wu et al., 2004) yielded about 800 °C, 0.57 GPa. On the other hand, the garnet-hornblende Fe-Mg geothermometer (Ravna, 2000) and the garnet-hornblende-plagioclase-quartz (GHPQ) geobarometer (Kohn and Spear, 1990) yielded about 680 °C, 0.69 GPa. Biotite in this sample is more likely affected by Mg-Cl avoidance than hornblende (Figs. 2.6; 2.8g, f), and thus the geothermobarometer using biotite could be less reliable.

In contrast, *P-T* conditions for the wall rock formation can be estimated using mineral compositions not affected by the brine infiltration. Mineral composition beyond the point where

major and trace elements become constant possibly predates the Grt-Hbl vein formation and is possibly less affected by the brine infiltration (Fig. 2.7). Therefore, utilizing mineral compositions about 15 cm away from the vein where isolated orthopyroxene is still preserved and effect of brine infiltration is small, the *P-T* conditions are estimated to be about 750-790 °C and 0.70-0.86 GPa from the same geothermobarometers presented above. In addition, garnet-orthopyroxene geothermometry (Harley, 1984) gave temperature around 750 °C. Therefore, the Grt-Hbl vein was possibly formed during the early stage of retrograde metamorphism at about 680 °C, 0.69 GPa, implying upper amphibolite facies metamorphism.

The mineral assemblage in the Grt-Hbl vein and the wall rock can be modeled by the Na₂O-K₂O-CaO-FeO-MgO-Al₂O₃-SiO₂-H₂O system. As shown in the modified A'F'M' diagram projected from biotite, plagioclase, quartz, and H₂O (Fig. 2.12), bulk rock composition of the Grt-Hbl vein is different from that of the wall rock. Tie lines between garnet and hornblende in the vein and in the wall rock are subparallel (Fig. 2.12). Two-phase stability field for garnet and hornblende is located on the Fe-rich side of three-phase stability field of garnet-orthopyroxene-hornblende assemblage in the A'F'M' diagram of upper amphibolite facies (Spear, 1995), suggesting that not only temperature decrease but also bulk rock compositional change towards Fe-rich side decomposes orthopyroxene, and Grt + Hbl assemblage becomes stable. Similar geometry in modified A'F'M' diagram (Fig. 2.12) suggests

that the Grt + Hbl assemblage was formed due to change in bulk rock composition caused by the brine infiltration. Addition of Fe by brine infiltration (Fig. 2.11a) supports the formation of Grt + Hbl assemblage under upper amphibolite facies P - T conditions. This is consistent with P - T estimates for the vein formation.

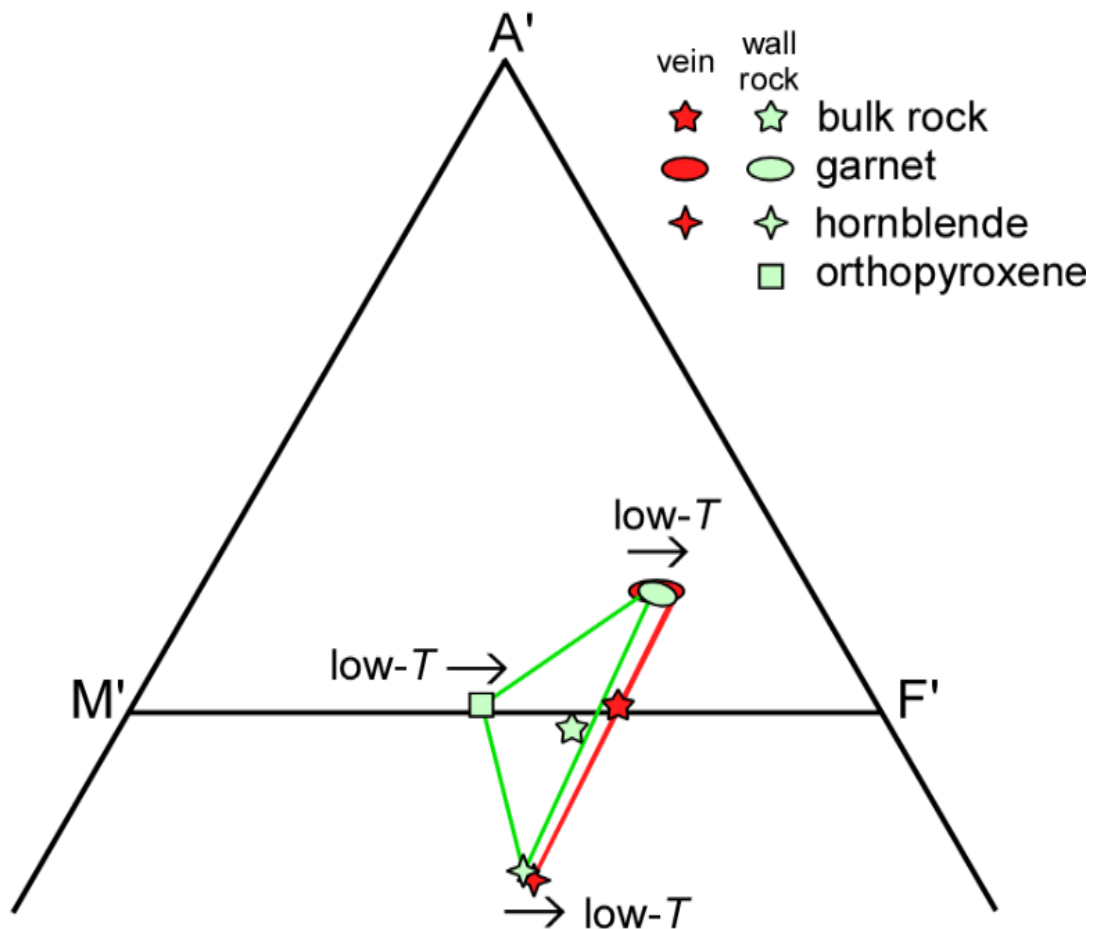


Figure 2.12. Modified A'F'M' diagram projected from biotite, plagioclase, quartz, and H₂O.

Biotite and plagioclase compositions used for the projection are those in the wall rock;

$A' = \text{Al}_2\text{O}_3\text{-CaO-Na}_2\text{O-1.3K}_2\text{O}$, $F' = \text{FeO-3.0K}_2\text{O}$, $M' = \text{MgO-2.2K}_2\text{O}$. Garnet, hornblende,

and bulk rock compositions in the Grt-Hbl vein are shown in red, and those in the wall rock

are shown in green. Ellipses for garnets represent compositional variations within a grain.

Each mineral composition from the vein is Fe-richer than that from the wall rock.

2.7.2. Formation process of mineral microstructures related to brine infiltration

It is noted that the core and mantle in terms of An content preserve the composition before brine infiltration (Figs. 2.4b, 2.9), although trace element content does not show the same zoning with An content (Fig. 2.7). Sharp mantle/rim boundary in plagioclase implies that the plagioclase rim was formed by distribution-reprecipitation process or by overgrowth. Diffusion process to form the rim is not likely because NaSi-CaAl interdiffusion coefficient, which is in the order of 10^{-31} m²/s at 700 °C (e.g., Grove et al., 1984) is too small to form plagioclase rims of a few 100 µm-width. NaSi-CaAl interdiffusion takes more than 10^6 Myr for several tens of µm diffusion distance. On the other hand, lattice diffusion coefficients for Sr, Ba, and Pb in plagioclase are known to be in the order of 10^{-22} - 10^{-24} m²/s at 700 °C (e.g., Cherniak and Watson, 1994; Cherniak, 1995; Cherniak, 2002). Therefore, high temperature duration at 700 °C for 1 Myr can result in flat trace element zoning, irrespective of mechanism of the plagioclase rim formation. In this section, we discuss possible process to form plagioclase rims and to form ‘diffusion-like’ chemical profiles in the wall rock.

2.7.2.1. Possible process of plagioclase rim formation

Dissolution-reprecipitation process is possible to form sharp mantle/rim boundary shown in Fig. 2.7. In this case, brine is likely to have been present in grain boundaries and reacted with plagioclase surface. Brine probably made the grain boundaries wet, and induced

dissolution-reprecipitation of plagioclase rim. This would result in changing brine composition in the grain boundaries due to the incorporation of trace elements into the plagioclase rims.

2.7.2.2. Possible mechanism for ‘diffusion-like’ profile formation

Distances where ‘diffusion-like’ profiles of trace element concentrations become constant are dependent on elements, and not on mineral species (Fig. 2.7). Trace element composition in plagioclase would be completely changed from the original one. Lithium, Sr and Ba contents becomes constant at about 1 cm. Rb, U, Pb and Sc become constant at about 1.5 cm, 2.5 cm, 3.6 cm, and 2 cm, respectively (Fig. 2.7; Table 2.2). Strontium and Pb concentration shown in Fig. 2.9b represents that their compositional change is slightly recognized with distance from the grain boundary in addition to distance from the vein. This suggests that trace element compositional change proceeded mainly along the grain boundaries towards inside the grains. Therefore, grain boundary diffusion of trace elements or infiltration of brine along grain boundaries is proposed as a possible mechanism for the formation of ‘diffusion-like’ profile followed by the plagioclase rim formation.

First, we assume grain boundary diffusion as a mechanism. Grain boundaries would have been wet as implied by the plagioclase rim formation process discussed above. Distances where ‘diffusion-like’ profile becomes constant may correspond to diffusion distance of each element along the grain boundaries (Fig. 2.7). Therefore, ‘diffusion-like’ profile formed by grain

boundary diffusion was accompanied by plagioclase rim formation. Although wet grain boundary diffusion coefficients for trace elements shown in Fig. 2.7 are not known, a previous study shown that grain boundary diffusion coefficient is more than 4 orders of magnitude greater than lattice diffusion coefficient (e.g., Joesten, 1991). Therefore, 2 orders of magnitude greater distance for grain boundary diffusion than lattice diffusion would be consistent with the difference of the diffusion coefficient between lattice and grain boundary diffusions. The ‘diffusion-like’ profile is in the order of a few cm, and zoning in the plagioclase grain is in the order of several hundred microns (Figs. 2.7, 2.9). This would support that ‘diffusion-like’ profile is formed by grain boundary diffusion process.

Secondly, we consider the case of brine infiltration. In this case, brine composition needs to change as distance from the vein. However, because diffusion of elements in fluid would be fast, it might be difficult to preserve such chemical gradient.

Taken together, the most possible processes that formed microstructures in the wall rock of the garnet-hornblende vein is grain boundary diffusion along wet grain boundaries, followed by brine-induced dissolution-reprecipitation process at the grain boundaries, and finally, lattice diffusion that mainly affected trace elements (Fig. 2.13). It is reasonable to consider that minerals other than plagioclase are also affected by the same processes.

High temperature duration (t_d) postdating vein formation deduced from the diffusion profile

recorded at the boundary between plagioclase core and mantle would be estimated to be $\log t_d = 0.3 \pm 2.5/-1.7$ Myr (2σ ; MSWD = 3.2, probability = 0.042), using lattice diffusion coefficient of Ba (dry), Sr (dry) and Pb (dry) in An_{60} at about 700 °C (Cherniak and Watson, 1994; Cherniak, 1995; Cherniak, 2002). The NaSi-CaAl intrerdiffusion distance under dry condition at 700 °C for 0.3 Myr is estimated to be about 0.0008 μm in the case of An_{80} (Grove et al., 1984). The seemingly sharp boundary between plagioclase rim and mantle shown in Fig. 2.3c supports the small contribution of diffusion postdating recrystallization of the plagioclase rim (Fig. 2.9).

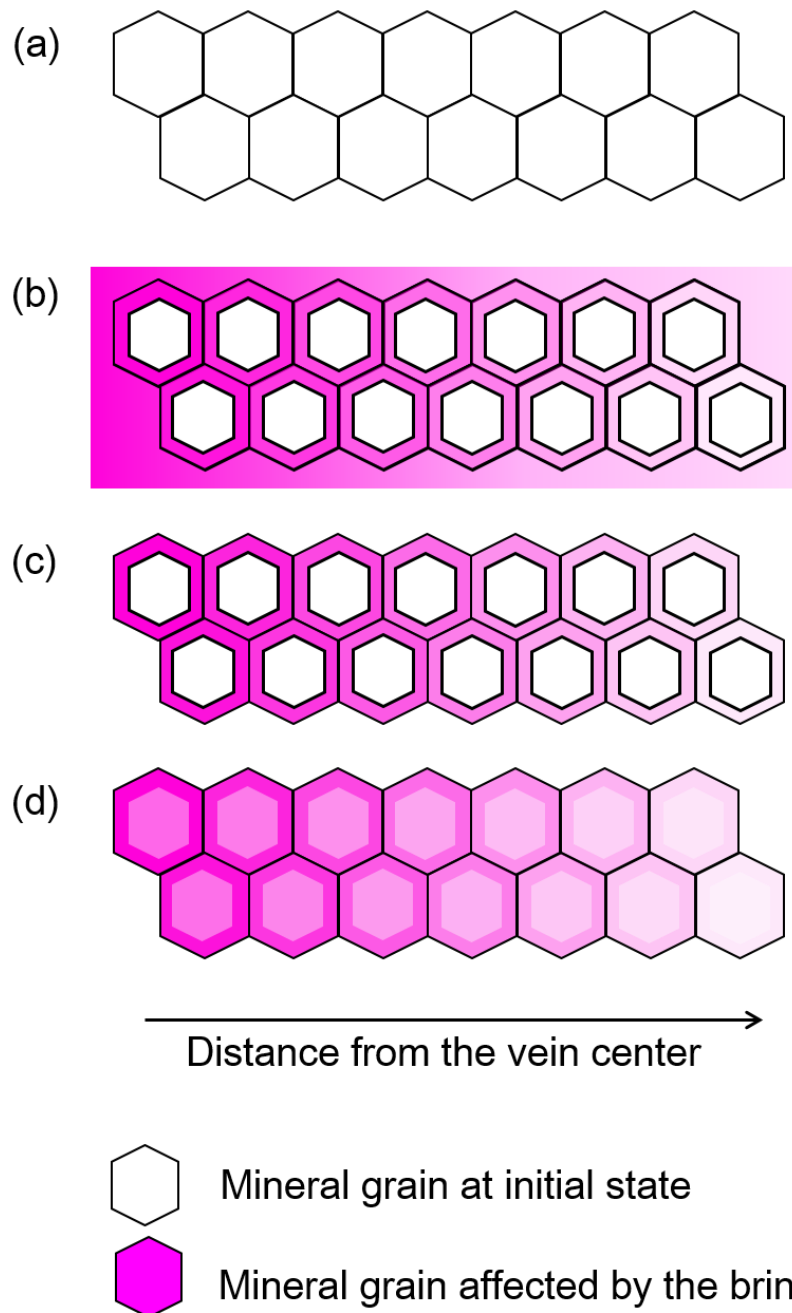


Figure 2.13. Illustration showing the microstructural evolution of the wall rock minerals

(plagioclase as an example) during brine infiltration. (a) Initial state in the wall rock. (b)

Grain boundary diffusion under wet condition and/or incorporation of trace elements into

the plagioclase rims from the brine form compositional variation in the grain boundary

with distance from the vein center. Brine infiltrated into grain boundary induces dissolution-reprecipitation, resulting in the rim formation. (c) Sharp core/rim boundary produced by dissolution-reprecipitation process. (d) Lattice diffusion in wall rock minerals proceeds and the boundary between core/rim becomes ambiguous.

2.7.3. Brine composition and implications for a microstructural evidence of brine

Trace element composition of the brine can be calculated using the published mineral/fluid partition coefficients ($D_{\text{mineral/fluid}}$). Concentration of trace element i in minerals in the vein center can be obtained by extrapolating ‘diffusion-like’ profile to distance = 0 in Fig. 2.7. This concentration of element i and partition coefficients $D_{\text{Amp/fluid}}^i$ determined for 0.5 m NaCl fluid at 900 °C, 2.0 GPa (Brenan et al., 1995a) may be applied to estimate the composition of element i in the brine, keeping in mind the difference in P - T conditions and brine composition. The value of $D_{\text{Amp/fluid}}^i$ is 1.7 for Sr, 0.5 for Ba, 0.1 for Pb, and 0.4 for U, respectively (Brenan et al., 1995a). This calculation results in the brine composition of 86 ppm Sr, 1893 ppm Ba, 249 ppm Pb, and 4 ppm U (Table 2.4). On the other hand, Zr and REE concentration in the brine can be calculated as < 1 ppm (Table 2.4), using $D_{\text{Grt/fluid}}^i$ values at 900 °C, 2.0 GPa (Brenan et al., 1995b) and at 900 °C, 5.0 GPa (Stalder et al., 1998). Yttrium concentration in the brine is calculated as about 1 ppm using $D_{\text{Ap/fluid}}^Y$ in John et al. (2008).

Figure 2.14 shows these calculated brine compositions in the middle to lower crust normalized to primordial mantle. Shaded region in Fig. 2.14 represents a calculated fluid composition in equilibrium with majorite (Scambelluri et al., 2010) and a broken line represents a calculated fluid composition at blueschist/eclogite transition (Hermann et al., 2006) in subduction zone environment. Both of these previous studies estimated fluid composition using mineral compositions and partition coefficients between mineral and fluid at 1000 °C, 6 GPa

(Scambelluri et al. 2010) and 700 °C, 3 GPa (Hermann et al., 2006), respectively. Comparing the estimated brine composition in the middle to lower crust (this study) with those in the subduction and mantle conditions by Hermann et al. (2006) and Scambelluri et al. (2010), the brine in the crust shows similar enrichments in concentration of fluid compatible elements and particular depletion of Zr and REE. This indicates that movement of the brine has potential to enrich the middle crust with Ba, Pb, and U (Fig. 2.14). Although Hermann et al. (2006) and Scambelluri et al. (2010) do not point to the presence of halogen in the fluids, Philippot and Selverstone (1991) reports the trace-element-rich aqueous brine in eclogitic veins. Using fluid inclusions with daughter minerals, high solubility of Na, K, Ca, Mg, Fe, Zr, Ti, P, Ba, Ce, La, Th, and S species in the brine is indicated (Phillipot and Selverstone, 1991). Among these elements, Zr, La, Ce, and Th in the fluid are reported to be immobile in Hermann et al. (2006), and Zr and Ce are likely to be immobile in this study as well (Fig. 2.14). Barium, Pb, U, Ce, Sr, Zr, Sm, and Y are reported to increase their concentrations from the lower towards the upper crust (e.g., Taylor and McLennan, 1985; McLennan, 2001). Therefore, this study implies that the brine in the middle to the lower crust can potentially transport Ba, Pb, and U upwards. It would be necessary, however, to consider an error derived from the partition coefficients of different *P-T* conditions from about 700 °C, 0.7 GPa. Further experiments to determine partition coefficients between minerals and fluids in appropriate *P-T* conditions and mineral species would help

constrain the element transport by brine in the crustal conditions.

In this study, we suggest that ‘diffusion-like’ profile of Cl and decreasing rim width of plagioclase with sharp mantle/rim boundary with distance from the vein (Figs. 2.4, 2.6) would become a potential tool to detect the presence of brine in the mid- to lower-crustal environment. Dissolution-reprecipitation microstructure in minerals coexisting with Cl-bearing minerals without nearby ‘diffusion-like’ profiles, would characterize formally wet grain boundaries by brine. Field mapping of these microstructures has a potential to unravel the large-scale distributions and movement of brine in the lower crust of the continental collision zones. Examining brine movement in the crust might reveal large-scale elemental transports comparable to those in the subducting oceanic crust.

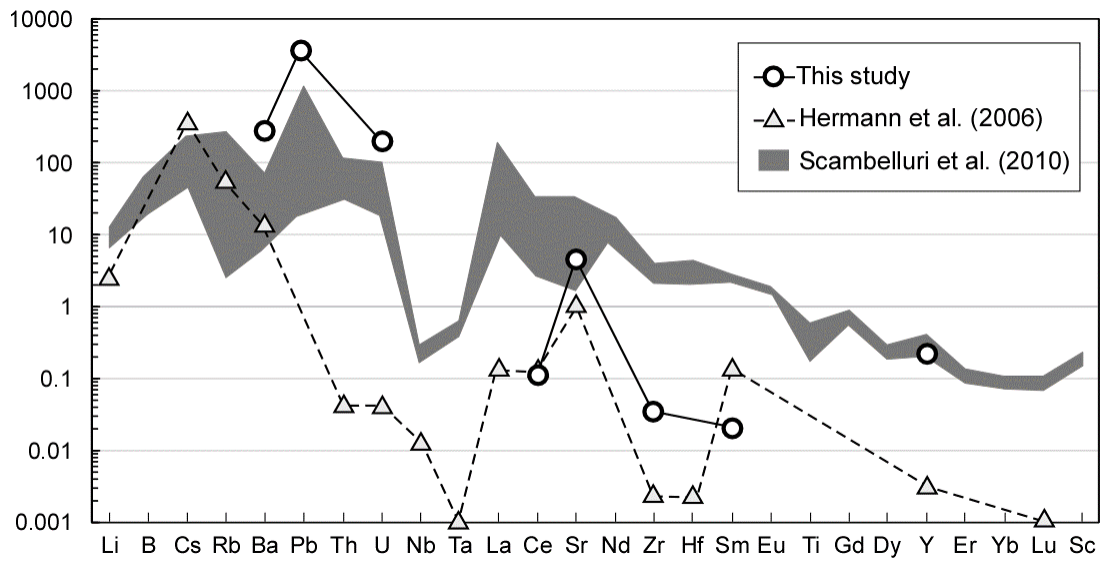


Figure 2.14. Trace element patterns of calculated brine composition normalized to primitive mantle of McDonough et al. (1992). Circles with solid lines represent the brine composition calculated based on partition coefficients between fluid and minerals by Brenan et al. (1995a, b), Stalder et al. (1998), and John et al. (2008). Shaded region represents a fluid composition in equilibrium with majorite estimated by Scambelluri et al. (2010) and triangles with a broken line represent calculated fluid compositions at the blueschist/eclogite transition (Hermann et al., 2006). The brine in this study would be more capable of transporting trace elements than the fluid reported in Hermann et al. (2006).

Table 2.4. Calculated brine composition [ppm]. The values of trace element concentration of minerals were obtained from extrapolating ‘diffusion-like’ profile towards the Grt-Hbl vein center.

Mineral data from trace element analyses			Calculated brine composition		
	Mineral	extrapolation concentration in the Grt-Hbl vein	initial concentration	$D_{\text{Mineral/fluid}}$	Reference
Sr	Amp	146	86	1.7	Brenan et al. (1995a)
Ba	Amp	965	1893	0.5	Brenan et al. (1995a)
Y	Ap	10	1.0	10	John et al. (2008)
Zr	Grt	2.8	0.4	7.8	Stalder et al. (1998)
Ce	Grt	0.1	0.2	0.5	Brenan et al. (1995b)
Sm	Grt	0.9	0.01	100	Brenan et al. (1995b)
Pb	Amp	20	249	0.1	Brenan et al. (1995a)
U	Amp	1.4	4.1	0.4	Brenan et al. (1995a)

References

- Adachi, T., Hokada, T., Osanai, Y., Nakano, N., Baba, S., Toyoshima, T. 2013a. Contrasting metamorphic records and their implications for tectonic process in the central Sør Rondane Mountains, eastern Dronning Maud Land, East Antarctica. Geological Society London, 383, 113-133.
- Adachi, T., Osanai, Y., Hokada, T., Nakano, N., Baba, S., Toyoshima, T. 2013b. Timing of metamorphism in the central Sør Rondane Mountains, eastern Dronning Maud Land, East Antarctica: Constrains from SHRIMP zircon and EPMA monazite dating. Precambrian Research, 234, 136-160.
- Ague, J. 2003. Fluid infiltration and transport of major, minor, and trace elements during regional metamorphism of carbonate rocks, Wepawaug Schist, Connecticut, USA. American Journal of Science 303, 753-816.
- Asami, M., Osanai, Y., Shiraishi, K., Makimoto, H. 1992. Metamorphic evolution of the Sør Rondane Mountains, East Antarctica. In: Recent Progress in Antarctic Earth Science (Yoshida, Y., Kaminuma, K., Shiraishi, K. Eds.). Terra Scientific Publishing Company, Tokyo, 7-15.
- Borchert, M., Wilke, M., Schmidt, C., Rickers, K. 2009. Partitioning and equilibration of Rb and Sr between silicate melts and aqueous fluids. Chemical Geology 259, 39-47.

- Borchert, M., Wilke, M., Schmidt, C., Cauzid, J., Tucoulou, R. 2010. Partitioning of Ba, La, Yb and Y between haplogranitic melts and aqueous solutions: An experimental study. *Chemical Geology* 276, 225-240.
- Brenan, J.M., Shaw, H.F., Ryerson, F.J., Phinney, D.L. 1995a. Mineral-aqueous fluid partitioning of trace elements at 900 °C and 2.0 Gpa: Constraints on the trace element chemistry of mantle and deep crustal fluids. *Geochimica et Cosmochimica Acta* 59, 3331-3350.
- Brenan, J. M., Shaw, H. F., Ryerson, F. J. 1995b. Experimental evidence for the origin of lead enrichment in convergent-margin magmas. *Nature* 378, 54-56.
- Cann, J.R. 1982. Rayleigh fractionation with continuous removal of liquid. *Earth and Planetary Science Letters* 60, 114-116.
- Cherniak, D.J. 1995. Diffusion of lead in plagioclase and K-feldspar: an investigation using Rutherford Backscattering and Resonant Nuclear Reaction Analysis. *Contributions to Mineralogy and Petrology* 120, 358-371.
- Cherniak, D.J. 2002. Ba diffusion in feldspar. *Geochimica et Cosmochimica Acta* 66, 1641-1650.
- Cherniak, D.J., Watson, E.B. 1994. A study of strontium diffusion in plagioclase using Rutherford Backscattering Spectroscopy. *Geochimica et Cosmochimica Acta* 58,

5179-5190.

Ferrando, S., Frezzotti, M. L., Dallai, L., Compagnoni, R. 2005. Multiphase solid inclusions in UHP rocks (Su-Lu, China): remnants of supercritical silicate-rich aqueous fluids released during continental subduction. *Chemical Geology* 223, 68-81.

Ferrando, S., Frezzotti, M. L., Petrelli, M., Compagnoni, R. 2009. Metasomatism of continental crust during subduction: the UHP whiteschists from the Southern Dora - Maira Massif (Italian Western Alps). *Journal of Metamorphic Geology* 27, 739-756.

Grantham, G.H., Macey, P.H., Horie, K., Kawakami, T., Ishikawa, M., Satish-Kumar, M., Tsuchiya, N., Graser, P., Azevedo, S. 2013. Comparison of the metamorphic history of the Monapo Complex, northern Mozambique and Balchenfjella and Austhamaren areas Sør Rondane, Antarctica: Implications for the Kuunga Orogeny and the amalgamation of N and S. Gondwana. *Precambrian Research*, 234, 85–135.

Grove, T.L., Baker, M.B., Kinzler, R.J. 1984. Coupled CaAl-NaSi diffusion in plagioclase feldspar: Experiments and applications to cooling rate speedometry. *Geochimica et Cosmochimica Acta* 48, 2113-2121.

Harley, S.L., 1984. An experimental study of the partitioning of Fe and Mg between garnet and orthopyroxene. *Contributions to Mineralogy and Petrology* 86, 359-373.

Harlov, D.E. 2012. The potential role of fluids during regional granulite-facies dehydration in

the lower crust. *Geoscience Frontiers* 3, 813-827.

Helgeson, H. C. 1964. *Complexing and hydrothermal ore deposits*. MacMillan.

Hermann, J., Spandler, C., Hack, A., Korsakov, A. V. 2006. Aqueous fluids and hydrous melts in high-pressure and ultra-high pressure rocks: implications for element transfer in subduction zones. *Lithos*, 92, 399-417.

Higashino, F., Kawakami, T., M. Satish-Kumar, Ishikawa, M., Maki, K., Tsuchiya, N., Grantham, G.H., Hirata, T. 2013. Chlorine-rich fluid or melt activity during granulite facies metamorphism in the Late Proterozoic to Cambrian continental collision zone- An example from the Sør Rondane Mountains, East Antarctica. *Precambrian Research* 234, 229-246.

Higashino, F., Kawakami, T., Tsuchiya, N., Satish-Kumar, M., Ishikawa, M., Grantham, G.H., Sakata, S., Hattori, K., Hirata, T. 2015. Geochemical behavior of zirconium during Cl-rich fluid or melt infiltration under upper amphibolite facies metamorphism – A case study from Brattnipene, Sør Rondane Mountains, East Antarctica. *Journal of Mineralogical and Petrological Sciences* 110, 166-178.

Holdaway, M.J., 2000. Application of new experimental and garnet Margules data to the garnet-biotite geothermometer. *American Mineralogist* 85, 881-892.

Hollister, L.S. 1966. Garnet zoning: An interpretation based on the Rayleigh fractionation model.

Science 154, 1647-1651.

Holness, M.B. 1997. Surface chemical controls on pore-fluid connectivity in texturally equilibrated materials. In: Fluid Flow and Transport in Rocks. (Jamtveit, B., Yardley, B.W.D. Eds.). Chapman and Hall, London, 149-169.

Ishikawa, M., Kawakami, T., Satish-Kumar, M., Grantham, G.H., Hokazono, Y., Saso, M., Tsuchiya, N. 2013. Late Neoproterozoic extensional detachment in eastern Sør Rondane Mountains, East Antarctica: Implications for the collapse of East African Antarctic Orogen. *Precambrian Research*, 234, 247-256.

Jacobs, J., Thomas, R.J. 2004. Himalayan-type indenter-escape tectonics model for the southern part of the late Neoproterozoic-early Paleozoic East African-Antarctic orogeny. *Geology*, 32, 721-724.

Joesten, R. 1991. Grain-boundary diffusion kinetics in silicate and oxide minerals. In: Diffusion, atomic ordering and mass transport: Selected problems in geochemistry (Ganguly, J. Eds.). Springer, New York, 345-395.

Johannes, W., Holtz, F. 1996. Petrogenesis and experimental petrology of granitic rocks. Springer-Verlag. Berlin, Heidelberg.

John, T., Klemm, R., Gao, J. Garbe-Schönberg, C. D. 2008. Trace-element mobilization in slabs due to non steady-state fluid-rock interaction: constraints from an eclogite-facies

- transport vein in blueschist (Tianshan, China). *Lithos*, 103 1-24.
- Kawamoto, T., Mibe, K., Bureau, H., Reguer, S., Mocuta, C., Kubsky, S., Thiaudière, D., Ono, S., Kogiso, T. 2014. Large-ion lithophile elements delivered by saline fluids to the sub-arc mantle. *Earth, Planets and Space* 66, 61.
- Keppler, H. 1996. Constraints from partitioning experiments on the composition of subduction-zone fluids. *Nature* 380, 237-240.
- Keppler, H., Wyllie, P.J. 1990. Role of fluids in transport and fractionation of uranium and thorium in magmatic processes. *Nature* 348, 531-533.
- Kohn, M.J., Spear, F.S., 1990. Two new geobarometers for garnet amphibole, with applications to southern Vermont. *American Mineralogist* 75, 89-96.
- Kojima, S., Shiraishi, K. 1981. Note on the geology of the western part of the Sør Rondane Mountains, East Antarctica. *Memoirs of National Institute of Polar Research, Special Issue* 43, 116-131.
- Kretz, R. 1983. Symbols for rock-forming minerals. *American Mineralogist* 68, 277-279.
- Kullerød, K. 1995. Chlorine, titanium and Barium-rich biotites: factors controlling biotite composition and the implications for garnet-biotite geothermometry. *Contributions to Mineralogy and Petrology* 120, 42-59.
- Li, Z.L., Chen, H., Yang, S., Tainosho, Y., Shiraishi, K., Owada, M. 2007. Fluid components in

- accessory minerals of Pan-African granitoids in the Sør Rondane Mountains, East Antarctica. *Journal of Zhejiang University SCIENCE A*, 8, 1004-1010.
- Markl, G., Bucher, K. 1998. Composition of fluids in the lower crust inferred from metamorphic salt in lower crustal rocks. *Nature* 391, 781-783.
- McDonough, W. F., Sun, S. S., Ringwood, A. E., Jagoutz, E., Hofmann, A. W. 1992. Potassium, rubidium, and cesium in the Earth and Moon and the evolution of the mantle of the Earth. *Geochimica et Cosmochimica Acta* 56, 1001-1012.
- McLennan, S. M. 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochemistry, Geophysics, Geosystems* 2 (4).
- Meert, J. 2003. A synopsis of events related to the assembly of eastern Gondwana. *Tectonophysics*, 362, 1-40.
- Munoz, J. L. 1992. Calculation of HF and HCl fugacities from biotite compositions: revised equations. *Geological Society of America, Abstracts with Programs* 24, A221.
- Newton, R.C., Manning, C.E. 2010. Role of saline fluids in deep - crustal and upper - mantle metasomatism: insights from experimental studies. *Geofluids*, 10, 58-72.
- Newton, R.C., Aranovich, L.Ya., Hansen, E.C., Vandenheuvel, B.A. 1998. Hypersaline fluids in Precambrian deep-crustal metamorphism. *Precambrian Research* 91, 41-63.
- Oliver, N.H.S., Bons, P.D. 2001. Mechanisms of fluid flow and fluid-rock interaction in fossil

metamorphic hydrothermal systems inferred from vein-wallrock patterns, geometry and microstructure. *Geofluids* 1, 137-162.

Osanai, Y., Shiraishi, K., Takahashi, Y., Ishizuka, H., Ttainosho, Y., Tsuchiya, N., Sakiyama, T.,

Kodama, S. 1992. Geochemical characteristics of metamorphic rocks from the central Sør Rondane Mountains, East Antarctica. *Recent Progress in Antarctic Earth Science* (Yoshida, K., Kaminuma, K., and Shiraishi, K. Eds.). National Institute of Polar Research, 17-27.

Osanai, Y., Nogi, Y., Baba, S., Nakano, N., Adachi, T., Hokada, T., Toyoshima, T., Owada, M.,

Satish-Kumar, M., Kamei, A., Kitano, I. 2013. Geologic evolution of the Sør Rondane Mountains, East Antarctica: Collision tectonics proposed based on metamorphic processes and magnetic anomalies. *Precambrian Research*, 234, 8-29.

Peacock, S. A. 1990. Fluid processes in subduction zones. *Science* 248, 329-337.

Philippot, P., Selverstone, J. 1991. Trace-element-rich brines in eclogitic veins: implications for fluid composition and transport during subduction. *Contributions to Mineralogy and Petrology* 106, 417-430.

Putnis, A., Austrheim, H. 2010. Fluid-induced processes: metasomatism and metamorphism. *Geofluids* 10, 254-269.

Pyle, J.M., Spear, F.S. 1999. Yttrium zoning in garnet: Coupling of major and accessory phases

during metamorphic reactions. *Geological Materials Research* 1, 1-49.

Ravna, E.K., 2000. Distribution of Fe²⁺ and Mg between coexisting garnet and hornblende in synthetic and natural systems: an empirical calibration of the garnet-hornblende Fe-Mg geothermometer. *Lithos* 53, 265-277.

Rayleigh, J.W.S. 1896. Theoretical considerations respecting the separation of gases by diffusion and similar processes. *Philosophical Magazine* 42, 493-498.

Scambelluri, M., Van Roermund, H.L., Pettke, T. 2010. Mantle wedge peridotites: fossil reservoirs of deep subduction zone processes: inferences from high and ultrahigh-pressure rocks from Bardane (Western Norway) and Ulten (Italian Alps). *Lithos* 120, 186-201.

Shiraishi, K., Kojima, S. 1987. Basic and intermediate gneisses from the western part of the Sør Rondane Mountains, East Antarctica. *Proceedings of the NIPR symposium on Antarctic Geosciences* 1, 129-149.

Shiraishi, K., Asami, M., Ishizuka, H., Kojima, H., Kojima, S., Osanai, Y., Sakiyama, T., Takahashi, Y., Yamazaki, M., Yoshikura, S. 1991. Geology and metamorphism of the Sør Rondane Mountains, East Antarctica. In *Geological Evolution of Antarctica* (Thomsom, M.R.A., Crame, J.A. and Thomson, J.W. Eds.). Cambridge University Press, Cambridge, 77-82.

- Shiraishi, K., Osanai, Y., Ishizuka, H., Asami, M. 1997. Geological map of the Sør Rondane Mountains, Antarctica. Antarctic Geological Map Series, Sheet 35, scale 1:250 000. National Institute of Polar Research, Tokyo.
- Shiraishi, K., Dunkley, D. J., Hokada, T., Fanning, C. M., Kagami, H., Hamamoto, T. 2008. Geochronological constraints on the Late Proterozoic to Cambrian crustal evolution of eastern Dronning Maud Land, East Antarctica: a synthesis of SHRIMP U-Pb age and Nd model age data. Geological Society, London, Special Publications, 308, 21-67.
- Shmulovich, K.I., Graham, C.M. 2004. An experimental study of phase equilibria in the systems $\text{H}_2\text{O}-\text{CO}_2-\text{CaCl}_2$ and $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ at high pressures and temperatures (500-800 °C, 0.5-0.9 GPa): geological and geophysical applications. Contributions to Mineralogy and Petrology 146, 450-462.
- Sibson, R. H. 1994. Crustal stress, faulting and fluid flow. Geological Society, London, Special Publications 78, 69-84.
- Spear, F. S. 1995. Metamorphic phase equilibria and Pressure-Temperature-time paths. Mineralogical Society of America, 799 pages.
- Stalder, R., Foley, S. F., Brey, G. P., Horn, I. 1998. Mineral-aqueous fluid partitioning of trace elements at 900–1200 °C and 3.0–5.7 GPa: new experimental data for garnet, clinopyroxene, and rutile, and implications for mantle metasomatism. Geochimica et

Cosmochimica Acta, 62, 1781-1801.

Tatsumi, Y., Eggins, S. 1995. Subduction Zone Magmatism. Blackwell, Cambridge. 211 pp.

Taylor, S. R., McLennan, S. M. 1985. The continental crust: its composition and evolution.
Blackwell Scientific Pub., Palo Alto, CA.

Thompson, A.B. 2010. Perspectives on metamorphic processes and fluids. Elements 6, 142-143.

Thompson, A. B., Connolly, J. A. 1992. Migration of metamorphic fluid: some aspects of mass
and heat transfer. Earth-Science Reviews 32, 107-121.

Touret, J.L.R., Huizenga, J.M. 2011. Fluids in granulites. The Geological Society of America
Memoir 207, 25-37.

Toyoshima, T., Osanai, Y., Baba, S., Hokada, T., Nakano, N., Adachi, T., Otsubo, M., Ishikawa,
M., Nogi, Y. 2013. Sinistral transpressional and extensional tectonics in Dronning Maud
Land, East Antarctica, including the Sør Rondane Mountains. Precambrian Research, 234,
30-46.

Tropper, P., Manning, C.E., Harlov, D.E. 2011. Solubility of CePO₄ monazite and YPO₄
xenotime in H₂O and H₂O–NaCl at 800 °C and 1GPa: implications for REE and Y
transport during high-grade metamorphism. Chemical Geology, 282, 58-66.

Tsuchiya, N., Ishikawa, M., Satish–Kumar, M., Kawakami, T., Kojima, H., Kaiden, H., Miura,
H., Suganuma, Y., Abe, M., Sasaki, D., Chiba, M., Okada, Y., Hashizume, F., Grantham,

- G., Goreris, S. 2012. Report on geological fieldwork in the Sør Rondane Mountains, Eastern Dronning Maud Land, 2009–2010 (JARE–51). *Antarctic Record*, 56, 295–379.
- Van Reenen, D.D., Hollister, L.S. 1988. Fluid inclusions in hydrated granulite facies rocks, southern marginal zone of the Limpopo Belt, South Africa. *Geochimica et Cosmochimica Acta* 52, 1057-1064.
- Watson, E.B., Brenan, J.M. 1987. Fluids in the lithosphere, 1. Experimentally-determined wetting characteristics of CO₂-H₂O fluids and their implications for fluid transport, host-rock physical properties, and fluid inclusion formation. *Earth and Planetary Science Letters* 85, 497-515.
- Webster, J. D., Holloway, J. R., Hervig, R. L. 1989. Partitioning of lithophile trace elements between H₂O and H₂O+ CO₂ fluids and topaz rhyolite melt. *Economic Geology* 84, 116-134.
- Wu, C., Zhang, J., Ren, L., 2004. Empirical garnet-biotite-plagioclase-quartz (GBPQ) geobarometry in medium- to high-grade metapelites. *Journal of Petrology* 45, 1907-1921.
- Yamasaki, S. 1996. Inductively coupled plasma mass spectrometry. In: *Mass Spectrometry of Soils*. (Boutton, T., Yamasaki, S. Eds). Marcel Dekker, New York, 459-491.
- Yamasaki, S., Takeda, A., Nunohara, K., Tsuchiya, N. 2013. Red soils derived from limestone contain higher amounts of trace elements than those derived from various other parent

materials. Soil Science and Plant Nutrition 59, 692-699.

Conclusions

Part 1 in this study revealed that modal analysis of the wall rock minerals combined with the quantitative determination of their Zr contents reveals that most of the whole-rock Zr resides in zircon whereas ~ 5% is hosted in garnet and hornblende. The Zr concentration of garnet and hornblende is constant irrespective of the distance from the vein. In addition to this, zircon rim ages and rare earth patterns are constant with distance from the vein, as well. All of these detailed observations on zircon support that zircon is little dissolved or overgrown, and that Zr is not added nor lost during the Grt-Hbl vein formation. Therefore, Zr can be described as an appropriate ‘immobile element’ during the Grt–Hbl vein formation in the wall rock, and also in the vein itself with 10% error.

In Part 2, the mass balance analysis based on the bulk rock chemical variation with a distance from the vein revealed that Li, Cu, Rb, Ba, Pb, and U were added to the wall rock of the vein. Addition of these fluid compatible elements suggests that the Grt-Hbl vein was formed by the brine infiltration, meaning that a passage of brine in the crust was detected. The *P-T* conditions for the vein formation was estimated to be ca. 700 °C, 0.7 GPa. The added element concentrations in this rock forming minerals show decreasing ‘diffusion-like’ profiles with distance from the vein and distances where the trace element concentrations become constant are dependent on elements,

and not on mineral species. As a possible process to form the chemical zonings, grain boundary diffusion and brine-induced dissolution-reprecipitation process were suggested. This results in changing brine composition with distance from the vein, and dissolution-reprecipitation process incorporated trace element from the brine into minerals. These process was followed by the lattice diffusion of trace element within wall rock minerals, whereas plagioclase zoning in An component was preserved because of NaSi-CaAl interdiffusion. In addition, trace element concentration of the brine was estimated using published partition coefficients, although these concentrations would include errors resulting from consistence of *P-T* conditions with this sample. This reveals that the brine has potential to enrich the middle crust with Ba, Pb, and U rather than the aqueous fluid liberated at the blueschist to eclogite facies transition. Therefore, the brine has potential to enrich the middle to upper crust with Ba, Pb, and U.

Overall, the passage and process of brine advection under upper amphibolite facies *P-T* conditions are successfully explained. This study suggests that combination of a plagioclase zoning possibly formed by dissolution-reprecipitation process and Cl-bearing minerals could be an indicator for brine infiltration. This new indicator would be a powerful tool to understand a brine behavior even in samples without clear passage of brine and without brine inclusions.

Acknowledgements

This thesis has been conducted at Department of Geology and Mineralogy, Graduate School of Science, Kyoto University under the supervision of Dr. Tetsuo Kawakami. I would like to express my appreciation to Dr. Kawakami for opening my door to join Petrology Lab and JARE geology group. I could not have written this thesis without his daily discussion, support and encouragement.

I would also like to thank Prof. Takao Hirajima and attendees of petrology seminars for daily discussion, Prof. Takafumi Hirata, Dr. Shuhei Sakata and Mr. Kentaro Hattori for LA-ICPMS analyses, and Prof. Noriyoshi Tsuchiya for bulk rock analyses. Fruitful discussions through ‘Nishi-Higashi’ Seminars and Conference Meetings improved my understanding of earth science.

I am grateful to numerous people in my life.