Timing of attainment of the spinel + quartz coexistence in garnet-sillimanite leucogneiss from Skallevikshalsen, Lützow-Holm Complex, East Antarctica

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Spinel in direct contact with quartz is newly found in the Grt-Sil leucogneiss from Skallevikshalsen, Lützow-Holm Complex, East Antarctica. It is included in the outermost core of the garnet porphyroblast and is characterized by low ZnO content (2.77–3.83 wt%) and very low Cr₂O₃ content (0–0.09 wt%). Incorporation of 2.77–3.39 wt% ZnO stabilized the Spl + Qtz assemblage to lower temperatures for about 50 degrees. As a result, their coexistence can be attained around the peak *P-T* conditions of Skallevikshalsen. The occurrence of relic staurolite, kyanite and breakdown texture of staurolite to spinel and kyanite included in the garnet core suggests that prograde stage is preserved in the garnet core and breakdown of staurolite itself was attained in the kyanite stability field. The Spl + Qtz assemblage is included at outermost part of the garnet core, suggesting that outermost core of the garnet was formed near the peak metamorphic conditions. Decrease in anorthite content of plagioclase included in the garnet core from that found in the rock matrix suggests that decompression took place during garnet formation. Attainment of these reaction sequences requires clockwise *P-T* path as previously proposed for the Lützow-Holm Complex.

Introduction

The Lützow-Holm Complex (LHC) is one of the high-temperature metamorphic terrains with a notable clockwise *P-T-t* path, with prograde evolution of the complex better constrained than other high-grade terrains in East Antarctica (e.g. Harley and Hensen, 1990). Ultrahigh-temperature (UHT) conditions in the LHC have been previously reported from the southern part of the LHC, such as Rundvågshetta (Motoyoshi and Ishikawa, 1997) and Skallevikshalsen (Yoshimura et al., 2003).

Spinel + quartz assemblage is one of the diagnostic mineral assemblages suggesting UHT metamorphic conditions if ZnO and Cr₂O₃ contents in the spinel are significantly low, as they expands the stability field of Spl + Qtz to low-temperature side (e.g. Bohlen et al., 1986; Nichols et al., 1992; Ikeda, 1998; Shimura et al., 2002). It is important, therefore, to evaluate the effect of ZnO and Cr₂O₃ in spinel when we try to draw some information out from this assemblage. In this contribution, we newly report the occurrence of Spl + Qtz assemblage in the Grt-Sil leucogneiss from Skallevikshalsen. Spinel carries relatively

low ZnO (2.77–3.83 wt%) and very low Cr₂O₃ (0–0.09 wt%) contents. Spinel in direct contact with quartz is previously reported from Rundvågshetta (Motoyoshi et al., 1985), Botnnuten (Motoyoshi and Shiraishi, 1985; Motoyoshi, 1986) and Skallen (Motoyoshi, unpublished data) from the LHC. However, because the effect of ZnO and Cr₂O₃ contents in the spinel has not been quantitatively evaluated, stability of Spl + Qtz coexistence has not been well constrained. The aim of this report is to evaluate the effect of ZnO to the stability of Spl + Qtz assemblage first, and then combine it with textural constraints, such as order of inclusion entrapment into the garnet, to constrain timing when the Spl + Qtz coexistence was attained during the *P-T* evolution. We briefly report as well the staurolite breakdown texture and kyanite newly found as garnet inclusions in the Grt-Sil leucogneiss from Skallevikshalsen. Mineral abbreviations are after Kretz (1983).

Geological setting

Lützow-Holm Complex

The Lützow-Holm Complex is a Cambrian orogenic belt

bounded by the Late Proterozoic to Early Paleozoic Rayner Complex to the east and by the Late Proterozoic to Early Palaeozoic Yamato-Belgica Complex to the west (Shiraishi et al., 1992; 1994; 1997). Metamorphic grade changes progressively from upper amphibolite facies on the Prince Olav Coast to granulite facies in Lützow-Holm Bay (Hiroi et al., 1991). A thermal axis occurs at the southern end of Lützow-Holm Bay, around Rundvågshetta (Motoyoshi, 1986). Peak metamorphic conditions of around 1000°C and 11 kbar and subsequent isothermal decompression are reported from Rundvågshetta (Kawasaki et al., 1993; Motoyoshi and Ishikawa, 1997). The complex is considered to have experienced a 'clock-wise' P - T path, as indicated by the presence of prograde kyanite and staurolite as relic inclusions in garnet and plagioclase (Hiroi et al., 1983; Motoyoshi, 1986) and by reaction textures in ultramafic rocks (Hiroi et al., 1986). It has been agreed that rocks along the Prince Olav Coast experienced the reaction $St = Grt + Als + Spl + H_2O$ within the sillimanite stability field, whereas those from Lützow-Holm Bay experienced the reaction within the kyanite stability field (Hiroi et al., 1983; 1987). The timing of peak regional metamorphism is estimated by the U/Pb zircon dating by SHRIMP to be between 521 ± 9 and 553 ± 6 Ma (Shiraishi et al., 1992; 1994). It is also report-

ed that a period between 520 and 500 Ma involved approximately 600°C of cooling, and approximately 23 km of relatively rapid exhumation at Rundvågshetta (Fraser et al., 2000).

Skallevikshalsen

Skallevikshalsen lies on the eastern coast of Lützow-Holm Bay, about 30 km northeast of Rundvågshetta (Fig. 1). Skallevikshalsen is underlain by layers of metamorphic rock including Opx-Hb brown gneiss, Grt-bearing leucogneiss (Grt-Sil leucogneiss and Grt-Bt felsic gneiss), marble, skarn and metabasite including Grt-2Px basic granulite. The gneisses are intruded by a number of granitic pegmatites (e.g. Yoshida et al., 1976). The Opx-Hb brown gneiss is the most common lithology. All the lithologies except the granitic pegmatites are strongly deformed. At least, two stages of deformation can be recognized from the fold interference patterns; early stage represented by the isoclinal fold with fold axis trending NNE-SSW to NE-SW and axial plane almost parallel to the chemical banding of surrounding rocks, and the second stage represented by tight to open fold with fold axis trending NNE-SSW to NE-SW and steeply-dipping axial plane (Kawakami and Ikeda, 2003). Boudinage structures

Figure 1. Geological map of Skallevikshalsen (after Yoshida et al., 1976). Sample locality of the Spl + Qtz bearing Grt-Sil leucogneiss is also shown.

Figure 2. (a) Field occurrence of Grt-Sil leucogneiss (light color) intercalated with Grt-2Px basic granulite (dark color). (b) Photomicrograph of Grt-Sil leucogneiss. Garnet porphyroblasts are around 5 cm in diameter and sillimanite defines the schistosity. Plane polarized light. (c) Backscattered electron image of the boxed part of (b). Spl + Qtz is included at the edge of the garnet core. Plagioclase inclusions are albite-rich in composition (An_5). (d) Ky + Spl + Bt inclusion in the garnet core. Relic staurolite is found in the kyanite inclusion, implying the reaction $St = Ky + Grt + Spl + H_2O$. (e) Backscattered electron image of Spl + Qtz, which is the enlargement of the boxed part of (c). Note that spinel is in direct contact with quartz. (f) Staurolite included in the core and the columnar sillimanite inclusion in the garnet rim. Crossed polarized light.

Figure 3. (a) Backscattered electron image of the garnet porphyroblast including plagioclase, kyanite, relic staurolite and breakdown product of staurolite ($Ky + Spl \pm Bt$ inclusion). (b) Chemical mapping of the garnet grain shown in (a) in terms of grossular content. The garnets can be divided into inclusion-rich core where higher grossular content is observed, and the rim including sillimanite. (c), (d) Chemical mapping of the garnet grain shown in Figure 2(c, f), respectively, in terms of grossular content. (e) Chemical mapping of the garnet grain shown in Figure 3(a, b) in terms of phosphorus. Discontinuous zoning and enrichment of phosphorus in the rim are observed. (f) Enlargement of the boxed part of Figure 2c. Backscattered electron image. Albite-rich plagioclase is intergrown with biotite flakes. This is the largest example of the albite-rich plagioclase inclusion.

possibly formed by the same high-strain deformation as the former isoclinal fold are observed throughout the area. The Grt-2Px basic granulite is commonly boudinaged and leucosome is filling the interboudin partitions. Recently, Yoshimura et al. (2003) estimated the peak metamorphic conditions of Skallevikshalsen to be 800–950°C and 7–10 kbar, based on various geothermobarometers. Yoshimura et al. (2003) also observed the chemical zoning of garnet and reported that it has an yttrium-rich core and phosphorus-rich rim. They considered that this chemical zoning was related to the growth of garnet during partial melting of the Grt-Sil leucogneiss, adopting the interpretation of Hiroi and Ellis (1994) and Hiroi et al. (1997).

Analytical procedures

Chemical composition of minerals was determined by

WDS (JOEL JXA-8800M) at the National Institute of Polar Research (NIPR). Analytical conditions were 15 kV accelerating voltage, 8 nA probe current and 10–20 seconds counting time for each element with a focused <1 µm beam under which sodium is not evaporated. ZAF correction was applied and natural and synthesized oxides were used as standards for the analysis (e.g. Hokada, 2001). Chemical mapping of the garnets were performed in Research Institute of Natural Sciences, Okayama University of Science. Whole-rock chemistry of the rocks were determined by the XRF analysis with Rigaku simultaneous X-ray spectrometer system 3550 at Kyoto University. The analytical procedure follows that of Goto and Tatsumi (1994).

Table 1. Representative compositions of constituent minerals of Grt-Sil leucogneiss

Sample no.	011804c	011804c	011804c	011804c	011804c	011804c	011804d
Mineral	Spl*	Spl**	St	Grt rim	Grt core	Pl in matrix	Pl in Grt
SiO ₂	0.07	0.04	26.05	39.52	39.47	60.30	57.35
TiO ₂	0.02	0.02	1.47	b.d.	0.06	b.d.	0.05
Al ₂ O ₃	61.13	61.60	56.03	22.37	22.48	25.05	27.46
Cr ₂ O ₃	0.02	0.58	0.10	b.d.	b.d.	b.d.	0.02
FeO	28.68	22.01	10.39	29.25	30.00	0.06	0.45
ZnO	2.87	9.32	1.48	b.d.	b.d.	b.d.	b.d.
MnO	0.03	0.07	b.d.	0.32	0.45	b.d.	b.d.
MgO	7.83	7.55	2.92	8.00	7.25	b.d.	b.d.
CaO	b.d.	b.d.	b.d.	1.06	2.16	7.11	9.48
Na ₂ O	0.10	0.33	0.08	b.d.	b.d.	7.45	6.09
K ₂ O	b.d.	b.d.	b.d.	b.d.	b.d.	0.16	0.36
Total	100.74	101.52	98.52	100.55	101.88	100.16	101.28
Si	0.00	0.00	3.65	3.03	3.01	2.68	2.55
Ti	0.00	0.00	0.15	b.d.	0.00	b.d.	0.00
Al	1.97	1.99	9.26	2.02	2.02	1.31	1.44
Cr	b.d.	0.01	0.01	b.d.	b.d.	b.d.	0.00
Fe	0.66	0.50	1.22	1.88	1.91	0.00	0.02
Zn	0.06	0.19	0.15	b.d.	b.d.	b.d.	b.d.
Mn	0.00	0.00	b.d.	0.02	0.03	b.d.	b.d.
Mg	0.32	0.31	0.61	0.91	0.82	b.d.	b.d.
Ca	b.d.	b.d.	b.d.	0.09	0.18	0.34	0.45
Na	0.01	0.02	0.02	b.d.	b.d.	0.64	0.52
K	b.d.	b.d.	b.d.	b.d.	b.d.	0.01	0.02
Total	3.01	3.03	15.08	7.96	7.98	4.99	5.00
$X_{Mg} [=Mg/(Mg+Fe)]$	0.33	0.38	0.33	0.33	0.30	-	-
An [=Ca/(Ca+Na+K)]	-	-	-	-	-	34.2	45.3

Spinel and staurolite are inclusions in garnet.

* Spinel coexisting with quartz.

** Spinel coexisting with kyanite.

b.d., below detection limit.

Table 2. Whole-rock chemistry of Grt-Sil leucogneiss and Grt-2Px basic granulite

Sample	011803	011804
	Grt-2Px basic granulite	Grt-Sil leucogneiss
SiO ₂	52.48	61.12
TiO ₂	2.19	1.02
Al ₂ O ₃	14.32	23.77
Fe ₂ O ₃ *	17.33	8.23
MnO	0.23	0.09
MgO	4.24	1.78
CaO	9.16	0.75
Na ₂ O	0.19	0.71
K ₂ O	0.20	2.90
P ₂ O ₅	0.31	0.07
Total	100.65	100.45
$X_{Mg} [=Mg/(Fe_{total}+Mg)]$	0.33	0.30

* Total Fe as Fe₂O₃.

Petrography of the Spl + Qtz bearing Grt-Sil leucogneiss

The Grt-Sil leucogneiss is intercalated with, and contains lens of the Grt-2Px basic granulite (Fig. 2a). The Grt-Sil leucogneiss is remarkably dry, consisting of garnet, sillimanite, plagioclase, K-feldspar, quartz, and subordinate amounts of rutile, ilmenite and zircon. Myrmekite is locally observed, and apatite is almost absent. Biotite, chlorite and muscovite are locally present as retrograde products replacing garnet and sillimanite. Sillimanite defines the stretching lineation trending NNE-SSW to NE-SW on the schistosity that is parallel to the compositional layering.

Garnet is *ca.* 5 mm in diameter and has inclusion-rich core and inclusion-poor rim (Figs. 2b, c and 3a). Chemical mapping of the garnet grains reveals that zoning in almandine and spessartine components is not clear, whereas weak zoning in pyrope and grossular components is present. The general trend that core is rich in grossular component and poor in pyrope component than the rim can be observed (Fig. 3b-d). Grossular content is low around the sillimanite inclusions even if it is included in the garnet core (Fig. 3c). In order to check that samples used in this study show the same zoning characteristics with that observed in Yoshimura et al. (2003), chemical mapping in phosphorus was performed as well. As a result, our sample also showed discontinuous zoning, and the rim was enriched in phosphorus (Fig. 3e). Inclusions

found in the garnet core are kyanite, sillimanite, biotite, rutile, spinel, plagioclase, quartz and staurolite (Figs. 2c and 3a). Spinel is commonly included with kyanite, and some of such kyanite crystals further include relic staurolite (Fig. 2d). Spinel crystals of this kind show high ZnO contents (Table 1). Rarely, spinel in direct contact with quartz is included at the outermost core of the garnet (Fig. 2e). It shows relatively low ZnO content of 2.77–3.83 wt% and very low Cr₂O₃ content (0–0.09 wt%; see Table 1). Plagioclase included in the core is An₄₂₋₄₅ whereas that in the rock matrix is An₃₃₋₃₄ (Table 1). They are *ca.* 500 μ m in diameter. Albite-rich plagioclase inclusions (An₅) are found around the spinel + quartz inclusion, and are commonly 20–30 μ m in diameter. Such an albite-rich plagioclase is intergrown with tiny biotite flakes (Fig. 3f). Biotite is commonly formed at the boundary between garnet and albite-rich plagioclase. Inclusions in the garnet rim are, if present, mostly sillimanite. Aluminosilicate in the core is commonly kyanite when accompanied with spinel but sillimanite alone is also included in the core. Sillimanite in the core is prismatic and that in the rim is fibrous or columnar under the thin section parallel to the stretching lineation, and normal to the schistosity (Fig. 2f). The difference in crystal orientation between sillimanite included in the core and that included in the rim implies two stages of sillimanite formation. Cordierite has not been found in the rock.

The result of whole-rock chemical analysis of the Spl + Qtz bearing Grt-Sil leucogneiss and Grt-2Px basic granulite is given in Table 2. Low P₂O₅ content is concordant with the rare occurrence of apatite. Whole rock X_{Mg} (= 0.30) is almost the same with that of garnet (0.30–0.33), the dominant mafic mineral in the matrix.

Discussion

Presence of staurolite inclusions in the garnet core and absence of staurolite both in the garnet rim and in the rock matrix suggests that staurolite broke down during prograde metamorphism. Since quartz is present as an inclusion in the garnet core, some of the staurolite may have experienced the reaction:

The kyanite + spinel inclusion in the garnet core implies that breakdown of staurolite itself occurred within the kyanite stability field via the reaction

as Hiroi et al. (1983; 1987; 1991) pointed out in the high-

Figure 4. A P - T diagram showing the P - T path of Grt-Sil leucogneiss from Skallevikshalsen. Part of the P - T path of Rundvågshetta (Motoyoshi and Ishikawa, 1997) is also shown for comparison. Reactions lines cited in the figure are as follows. a, Richardson (1968) (FASH); b, Hiroi et al. (1994); c, Nichols et al. (1992) (FASZn); d, Nichols et al. (1992) (MASZn); e, Huckenholz et al. (1981); f, Harley and Hensen (1990) and Bertrand et al. (1991); g, Holdaway (1971); h, Johannes and Holtz (1996).

grade parts of the Lützow-Holm Complex. Although P - T location of the reaction (2) is difficult to determine, we use the reaction line of Richardson (1968) and that in Hiroi et al. (1994) for reference (Fig. 4). Yoshimura et al. (2003) estimated the peak P - T conditions of Skallevikshalsen to be 800–950°C, 7–10 kbar based on various geothermobarometers. Using the composition of plagioclase (An₄₂₋₄₅) included in the garnet core (Fig. 2c) and adjacent garnet core composition, GASP geobarometer (Ghent, 1976) gives the pressure of 7.5–9.0 kbar at 900°C, which is concordant with the peak P - T conditions. The ZnO-poor spinel coexisting with quartz included at the outermost core of the garnet is the evidence that the reaction

possibly proceeded. The effect of Cr₂O₃ is not significant in the present case because the spinel contains very low concentration of Cr₂O₃. Only the effect of ZnO in the spinel, therefore, is considered in the reaction (3) and shown in Figure 4, using observed compositions of garnet and

spinel (Table 1), and thermodynamic data of Nichols et al. (1992). Spl + Qtz assemblage is stabilized to lower temperature by the addition of 2.77–3.39 wt% ZnO to the spinel for about 50 degrees. As a result, the reaction (3) can be attained around the peak P - T conditions of Skallevikshalsen (Fig. 4). Because Spl + Qtz assemblage is not present in the rock matrix, back reaction of the reaction (3)

is plausible to have taken place.

Although mesoscopic structure implying the former presence of melt such as boudin necks or shear zones filled with leucosome is not found in the Grt-Sil leucogneiss, partial melting of the Grt-Sil leucogneiss is possible in Skallevikshalsen because most part of the P - T path discussed in this paper is well above the solidus of the pelitic rocks (Fig. 4). Hiroi and Ellis (1994) and Hiroi et al. (1997) performed the chemical mapping of garnet from Sri Lankan granulite on yttrium and phosphorus and considered that phosphorus-poor core of the garnet was

formed during partial melting whereas phosphorus-rich rim was formed through subsequent solidification and phosphate saturation of the melt. They proposed that phosphorus zoning in garnet can be a effective tool to infer the former presence of partial melting (Hiroi and Ellis, 1994; Hiroi et al., 1997). Spear and Kohn (1996) showed that discontinuous chemical zoning of phosphorus in garnet can be formed through muscovite dehydration melting without the participation of phosphate minerals. Yoshimura et al. (2003) considered that yttrium and phosphorus zoning in garnet from Grt-Sil leucogneiss of Skallevikshalsen were formed through the garnet growth during partial melting. Garnet grains shown in Figures 2 and 3 were enriched in phosphorus at the rim (Fig. 3e). We consider, therefore, that the Grt-Sil leucogneiss described in this study experienced partial melting as well. Sillimanite bearing garnet rim belongs to high phosphorus and low grossular part, suggesting that they were formed through subsolidus reactions, possibly during decompression.

Combining the reaction sequences discussed above, i.e., (i) crossing the reaction (1) and (2), (ii) attainment of peak metamorphic conditions (Yoshimura et al., 2003) followed by the attainment of Spl + Qtz coexistence at near peak conditions, (iii) crossing the reaction (4), and (iv) post peak decompression, we obtain a clockwise P - T path as proposed in Hiroi et al. (1991). Because the peak P - T conditions used in this study are different from that of Hiroi et al. (1991), we modified the P - T path in this respect. However, it is qualitatively the same as Hiroi et al. (1991) except that retrograde path go through the Spl + Qtz stability field at near metamorphic peak conditions. Result of chemical mapping in phosphorus implies that (i)-(iii) occurred in the presence of melt and reactions (1) and (2) are potentially melting reactions.

The albite-rich plagioclase (An_5) inclusions in the garnet (Fig. 3e) may be explained by considering the presence of melt during the garnet growth. Presence of the melt is supported by the phosphorus-poor nature of the garnet core where the albite-rich plagioclase inclusions are found. If we assume the coexistence of the albite-rich plagioclase with kyanite, garnet and quartz, the GASP geobarometer (Ghent, 1976) gives pressure of 15–21 kbar at 700–900°C, which is not concordant with the coexistence with Spl + Qtz inclusion. We consider, therefore, that the albite-rich plagioclase was not stable as a solid phase but possibly precipitated from a melt trapped in the garnet. Such an albite-rich melt probably coexisted with plagioclase (An_{42-45}) included in the garnet core, and the subsequent garnet growth trapped the plagioclase and the melt separately. In the course of post-peak decompression (Fig. 4), the melt possibly crystallized within the

garnet to form albite-rich plagioclase (An_5). Biotite intergrown with plagioclase may be the product formed through the reaction between trapped melt and surrounding garnet.

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