

Garnet-biotite geothermometry of a pelitic gneiss from the Lützow-Holm Complex in Skallen, East Antarctica: Constraints on retrograde metamorphism

Takeshi Ikeda

¹ *Department of Earth and Planetary Sciences, Graduate School of Science,
Kyushu University, 33 Hakozaki, Fukuoka 812-8581
E-mail: ikeda@geo.kyushu-u.ac.jp*

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Abstract: A garnet-rich pelitic gneiss was examined to estimate retrograde conditions of the Lützow-Holm Complex in Skallen, East Antarctica. Porphyroblastic grains of garnet show a chemical zoning of an outward decrease in Mg/Fe, and include biotite, plagioclase and quartz. Local depletion in Mg/Fe of garnet is recognized where garnet is in contact with biotite occurring as inclusions and in the matrix. A pair of garnet-biotite geothermometry and garnet-plagioclase-sillimanite-quartz (GASP) geobarometry were applied to garnet rim and matrix biotite that are not in contact with each other, which demonstrates a retrograde condition of 5.6 kbar and 760°C. Pairs of garnet and adjacent biotite yield temperatures of *ca.* 660°C at a nominal pressure of 6 kbar irrespective of whether biotite occurs in the matrix or as inclusions, which represents the closure temperature for the Fe-Mg exchange reaction between garnet and biotite.

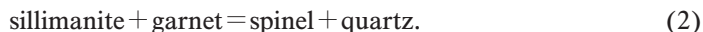
key words: garnet-biotite geothermometry, retrograde metamorphism, granulite facies, Skallen, Lützow-Holm Complex

1. Introduction

Metamorphic conditions of the Lützow-Holm Complex upgrade southwestward from amphibolite facies to granulite facies (Hiroi *et al.*, 1983, 1987). The granulite facies area is widely distributed on the southern coast of Lützow-Holm Bay. The following reactions are responsible for progressive change in mineral assemblages of calcsilicate and pelitic gneisses, respectively, as summarized by Hiroi *et al.* (1991):



and



Hiroi *et al.* (1987) determined the pressure of reaction (1) as 6.5–7.5 kbar by combining temperature of 810°C in the northern areas of the granulite facies, estimated by Yoshida and Aikawa (1983), Katsushima (1985), Motoyoshi (1986) and Suzuki (1986). Motoyoshi *et al.* (1985) defined the reaction (2) in Skallen, *ca.* 30 km south of reaction

(1), based on the fact that both spinel and quartz occur in the matrix, but they are not in direct contact with each other.

Recent works have discovered the mineral assemblages occurring as inclusions in garnet that are indicative of higher grades than the matrix assemblages, *i.e.*, sapphirine + quartz from Rundvågshetta (Yoshimura *et al.*, 2003) and spinel + quartz from Skallevikshalsen (Kawakami and Motoyoshi, 2004); both conditions are higher-grade than those defined by the reaction (2). Kawakami and Motoyoshi (2004) consider that the reversal of reaction (2) is responsible for the absence of spinel in the matrix. These lines of evidence suggest that the mineral assemblages as well as chemical composition of minerals in the matrix may not represent those at the peak metamorphism. The assumption accepted implicitly to estimate peak metamorphic conditions, that the cores of the matrix minerals preserve composition at peak metamorphism, is open to question, and its validity should be verified.

This study describes the mode of occurrence and chemical composition of minerals of a garnet-rich pelitic gneiss from Skallen. Conventional garnet-biotite geothermometry and garnet-sillimanite-quartz-plagioclase (GASP) geobarometry provide the retrograde pressure-temperature conditions of the sample and the closure temperature for the Fe-Mg exchange reaction between garnet and adjacent biotite.

2. Geological setting

The geology and petrology of Skallen have recently been reviewed by Osanai *et al.* (2004), so only a brief account is given here. Skallen is underlain mainly by pelitic and quartzofeldspathic gneisses that intercalate with thin layers of mafic gneisses (Yoshida *et al.*, 1976; Osanai *et al.*, 2004). The reaction (2) was defined at Skallen, as described before (Motoyoshi *et al.*, 1985). The metamorphic conditions were estimated to be 820°C, 4.1–6.5 kbar (Yoshida and Aikawa, 1983), 730°C, 6.3 kbar (Suzuki, 1983) and 810°C, 7.7–10.8 kbar (Motoyoshi, 1986), all of which were based on geothermobarometry. T. Tsunogae calculated temperature over 1000°C for a mafic granulite based on the garnet-orthopyroxene geothermometer of Pattison *et al.* (2003) (Osanai *et al.*, 2004), which suggests that Skallen may have undergone ultra-high temperature metamorphism. Michibayashi *et al.* (2004) found elongated garnets that were plastically deformed, which is indicative of high strain in local.

Motoyoshi *et al.* (1985) discovered the inclusion minerals in garnet such as kyanite and staurolite as well as spinel + sillimanite, possible reaction products after staurolite. This suggests that garnet grew during the prograde pressure-temperature path passing through the transition from kyanite to sillimanite.

3. Sample description

3.1. Petrography

The sample described in this study, #I-181, was collected from a thin pelitic layer, 10 cm thick, intercalating with thin layers of mafic gneisses in the northern part of Skallen (69° 38' 53" S, 39° 25' 06" E). The sample consists of garnet, sillimanite, biotite, plagioclase, K-feldspar and quartz with minor apatite, ilmenite and monazite.

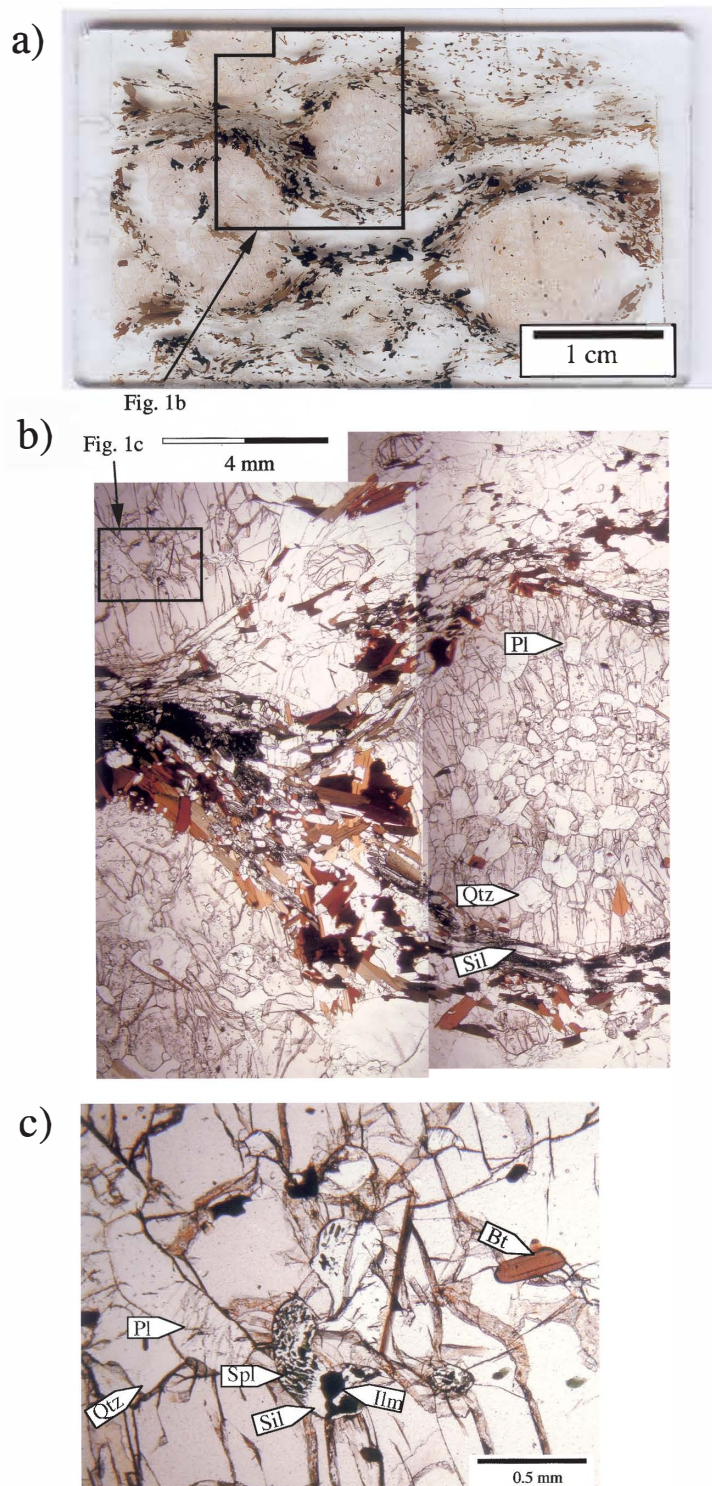


Fig. 1. a) Photograph of the thin section of the pelitic sample #I-181, showing voluminous garnet porphyroblasts, and biotite grains whose orientations are curved around garnet porphyroblasts. The thin section was prepared to be parallel to L_{m-1} and perpendicular to S_{m-1} . b) Photomicrograph of the boxed area of Fig. 1a in plane-polarized light. Garnet porphyroblasts contain many grains of plagioclase and quartz together with sporadic biotite. c) Photomicrograph of the boxed area of Fig. 1b in plane-polarized light, showing inclusions of symplectite that are composed of vermicular spinel embedded in sillimanite. Abbreviations: Bt, biotite; Ilm, ilmenite; Pl, plagioclase; Qtz, quartz; Sil, sillimanite; Spl, spinel.

Orthopyroxene is not present.

Preferred orientations of biotite and prismatic sillimanite in the matrix define foliation and mineral lineation, respectively (Fig. 1a, b). They correspond to S_{m-1} and L_{m-1} , formed at the earliest stage of deformation preserved in the matrix of the rocks in the Lützow-Holm Complex (Kawakami and Ikeda, 2004a, b; Ikeda and Kawakami, 2004). Garnet is abundant and occurs as porphyroblasts up to 1.5 cm in diameter. Garnet grains have cracks approximately perpendicular to the foliation, S_{m-1} (Fig. 1b). The biotite grains defining S_{m-1} change their orientation around garnet porphyroblasts, suggesting that the garnet growth continued until the formation of S_{m-1} foliation. Biotite is planar and is as coarse as 0.5 mm thick. A symplectitic relation of biotite with quartz, indicative of pseudomorphs after orthopyroxene, is not recognized.

Garnet porphyroblasts contain many rounded inclusions of plagioclase and quartz (Fig. 1b). Biotite also occurs sporadically as inclusions in garnet, suggesting that biotite was stable during the garnet growth. Garnet also includes symplectite composed of vermicular grains of spinel (hercynite) embedded in sillimanite together with ilmenite (Fig. 1c). This microstructure has been interpreted as being reaction products after staurolite by Motoyoshi *et al.* (1985).

3.2. Mineral chemistry

The chemical compositions of constituent minerals were determined using a scanning electron microscope (JEOL JSM-5800LV) combined with a Link ISIS analytical system at Kyushu University, under analytical conditions of 500 pA beam current, 20 kV accelerating voltage and 100 s livetime. Ferric contents in garnet estimated from stoichiometry are negligible and those in spinel and ilmenite are *ca.* 15% in atomic ratio of total iron. This implies a relatively low oxygen fugacity. Therefore this study regards biotite as ferric-free. Representative analyses of garnet, biotite and plagioclase are shown in Tables 1, 2 and 3, respectively.

Table 1. Representative analyses of garnet (12 oxygen basis).

analyzed point	interior not in contact with biotite inclusions			interior in contact with biotite inclusions						rim adjacent to biotite		rim not in contact with biotite	
	Grt 12	Grt 13	Grt 27	Grt 14	Grt 15	Grt 16	Grt 18	Grt 22	Grt 25	Grt 4	Grt 17	Grt 2	Grt 7
SiO ₂	38.36	38.04	36.86	37.84	37.57	37.60	38.28	36.31	36.54	37.06	37.45	37.45	37.74
Al ₂ O ₃	21.06	21.51	21.06	21.38	21.23	21.28	21.26	20.77	20.70	20.88	21.15	20.87	21.60
FeO	31.99	31.58	32.23	32.04	33.26	33.29	32.68	32.10	32.76	33.23	35.72	33.91	32.87
MnO	0.30	0.41	0.29	0.41	0.41	0.40	0.39	0.23	0.37	0.50	0.67	0.58	0.37
MgO	7.54	7.44	6.60	7.09	6.29	6.05	6.67	6.17	6.06	5.70	4.90	5.74	6.57
CaO	1.01	1.13	1.85	1.02	1.29	1.23	1.14	1.55	1.67	1.08	1.05	1.00	1.04
total	100.26	100.11	98.89	99.78	100.05	99.85	100.42	97.13	98.10	98.45	100.94	99.55	100.19
Si	3.003	2.980	2.949	2.982	2.974	2.981	3.003	2.959	2.959	2.987	2.973	2.991	2.972
Al	1.943	1.986	1.986	1.986	1.981	1.989	1.966	1.995	1.975	1.983	1.979	1.964	2.005
Fe	2.094	2.069	2.157	2.112	2.202	2.208	2.144	2.188	2.218	2.240	2.371	2.265	2.165
Mn	0.020	0.027	0.020	0.027	0.027	0.027	0.026	0.016	0.025	0.034	0.045	0.039	0.025
Mg	0.880	0.869	0.787	0.833	0.742	0.715	0.780	0.750	0.731	0.685	0.580	0.683	0.771
Ca	0.085	0.095	0.159	0.086	0.109	0.104	0.096	0.135	0.145	0.093	0.089	0.086	0.088
total cation	8.025	8.026	8.058	8.026	8.035	8.024	8.015	8.043	8.053	8.022	8.037	8.028	8.026

The analyzed points Grt 7 and Grt 2 have maximum and minimum Mg/Fe values among the garnet rims not in contact with biotite, respectively.

Table 2. Representative analyses of biotite (22 oxygen basis).

analyzed point	inclusions in garnet					matrix adjacent to garnet		matrix not in contact with garnet	
	Bt 6	Bt 7	Bt 8	Bt 10	Bt 11	Bt 2	Bt 9	Bt 3	Bt 12
SiO ₂	36.04	35.38	35.48	35.21	34.68	35.35	35.70	35.14	34.03
TiO ₂	4.26	5.40	5.62	4.68	4.15	4.32	4.99	4.61	5.31
Al ₂ O ₃	16.98	16.77	16.84	16.82	16.69	16.27	16.21	16.65	16.20
FeO	14.70	14.22	14.59	14.89	12.54	15.97	18.48	17.84	19.02
MgO	12.29	12.34	12.15	11.81	13.15	11.73	10.35	10.48	9.47
Na ₂ O	0.38	0.92	0.49	0.43	0.73	0.53	0.48	0.43	0.59
K ₂ O	10.03	9.56	9.91	10.00	9.43	9.53	9.62	9.79	9.61
total	94.68	94.59	95.08	93.84	91.37	93.70	95.83	94.94	94.23
Si	5.435	5.338	5.335	5.377	5.376	5.423	5.415	5.374	5.294
Ti	0.483	0.613	0.636	0.538	0.484	0.499	0.569	0.530	0.621
Al	3.018	2.982	2.985	3.028	3.049	2.942	2.898	3.001	2.970
Fe	1.854	1.794	1.835	1.902	1.626	2.049	2.344	2.282	2.475
Mg	2.763	2.776	2.724	2.689	3.039	2.683	2.340	2.389	2.196
Na	0.111	0.269	0.143	0.127	0.219	0.158	0.141	0.128	0.178
K	1.930	1.840	1.901	1.948	1.865	1.865	1.861	1.910	1.907
total cation	15.594	15.612	15.559	15.609	15.658	15.619	15.568	15.614	15.641

The analyzed points Bt 3 and Bt 12 have maximum and minimum Mg/Fe values among the matrix biotites not in contact with garnet, respectively.

Table 3. Representative analyses of plagioclase (8 oxygen basis).

analyzed point	inclusions in garnet						matrix	
	Pl 6	Pl 8	Pl 10	Pl 11	Pl 13	Pl 14	Pl 3	Pl 12
SiO ₂	59.64	59.46	59.02	57.83	58.75	60.03	59.87	60.21
Al ₂ O ₃	24.35	24.57	25.05	25.74	25.32	25.20	23.92	24.35
FeO			0.24					0.27
CaO	6.51	6.28	6.88	7.90	7.43	6.82	5.56	6.33
Na ₂ O	7.52	7.43	7.42	6.68	7.09	7.53	8.03	8.09
K ₂ O	0.61	0.61	0.70	0.36	0.16	0.61	0.17	
total	98.63	98.35	99.31	98.51	98.75	100.19	97.55	99.25
Si	2.696	2.692	2.660	2.624	2.652	2.674	2.723	2.701
Al	1.297	1.311	1.330	1.376	1.347	1.323	1.282	1.288
Fe	0.000	0.000	0.009	0.000	0.000	0.000	0.000	0.010
Ca	0.315	0.305	0.332	0.384	0.359	0.325	0.271	0.304
Na	0.659	0.652	0.648	0.588	0.621	0.650	0.728	0.704
K	0.035	0.035	0.040	0.021	0.009	0.035	0.010	0.000
total cation	5.002	4.995	5.019	4.993	4.988	5.007	4.994	5.007

Garnet grains represent an outward decrease in $\text{Mg}/(\text{Fe} + \text{Mg})$ (Fig. 2). MnO is less than 1.0 wt%. Most grains contain CaO less than 1.0 wt%, but some grains contain CaO up to 2.0 wt% where the CaO content decreases toward the rim. Local depletion in $\text{Mg}/(\text{Fe} + \text{Mg})$ is recognized in a zone *ca.* 0.03 mm thick adjacent to the matrix biotite and, in some cases, around the biotite grains occurring as inclusions (Fig. 2). Such features are, in contrast, not recognized in the vicinity of quartz and plagioclase occurring as matrix and inclusion minerals. Therefore the composition at the rim varies significantly depending on whether the rim is in contact with biotite or not.

Biotite included in garnet has higher Al content and $\text{Mg}/(\text{Fe} + \text{Mg})$ than biotite in the matrix (Fig. 3). A biotite grain in the matrix that is in contact with garnet is depleted in Ti and enriched in $\text{Mg}/(\text{Fe} + \text{Mg})$ as compared with biotite not in contact with garnet.

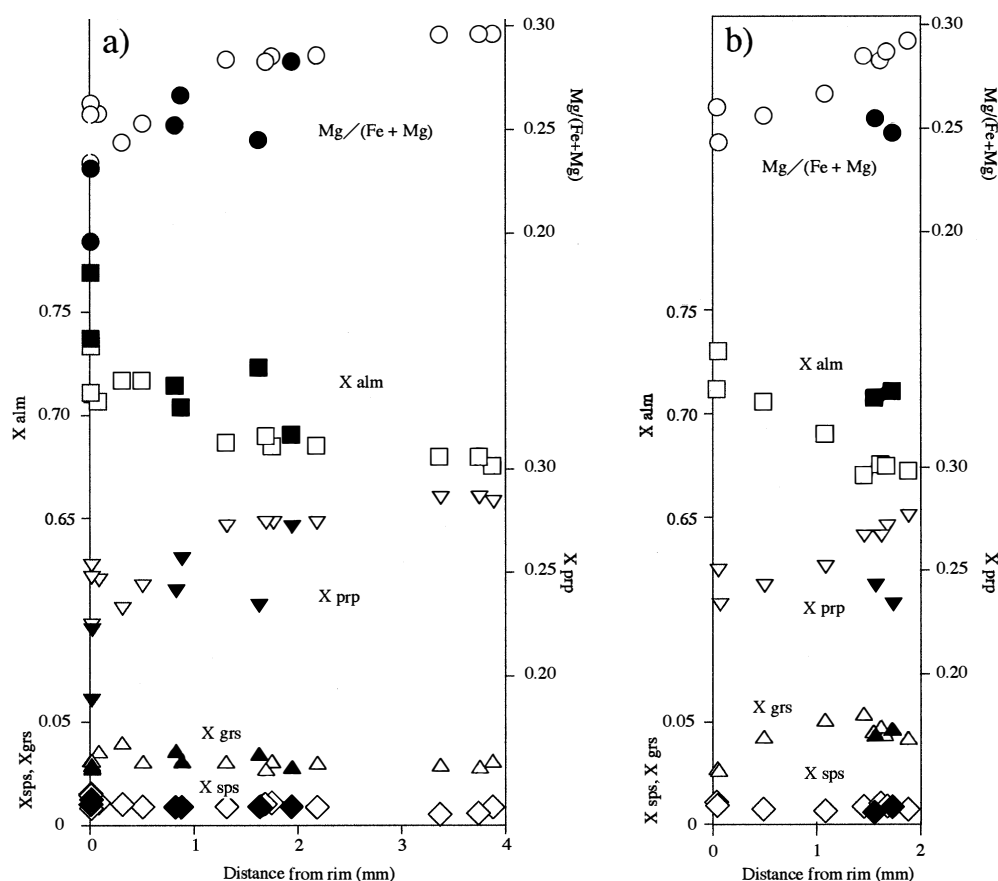


Fig. 2. Composition of garnet as a function of distance from the periphery of the grains : a) and b) are profiles of grains at the centre and upper left in Fig. 1b, respectively. Solid symbols represent composition in contact with biotite occurring either as inclusions or in the matrix. Open symbols show composition of garnet that is not in contact with biotite. Abbreviations: alm, almandine; grs, grossular; prp, pyrope; sps, spessartine.

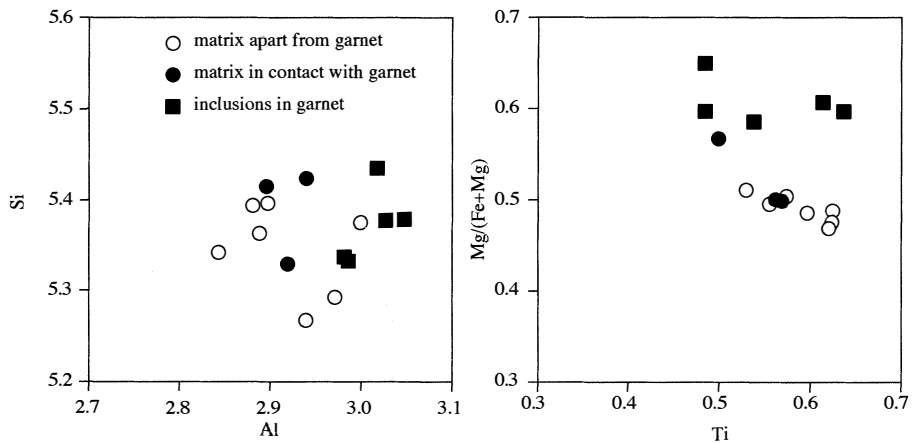


Fig. 3. Composition of biotite with respect to Si vs. Al and Ti vs. $Mg/(Fe+Mg)$ based on 22 oxygen.

Anorthite content of plagioclase in the matrix is 27–30 mol% in contrast to 30–46 mol% for plagioclase included in garnet. Sillimanite is nearly pure Al_2SiO_5 with ferric content less than 1.0 wt%. Spinel occurring as symplectite in garnet contains ZnO up to 6.0 wt% and has $Mg/(Fe+Mg)$ of ca. 0.3.

4. Discussion

4.1. Closure temperature for the Fe-Mg exchange reaction between garnet and adjacent biotite

Local enrichment and depletion in $Mg/(Fe+Mg)$ of matrix biotite and rim garnet, respectively, that are in contact with each other can be well explained by the retrograde re-equilibration in terms of the Fe-Mg exchange reaction between garnet and adjacent biotite. However, some analyses of garnet and biotite do not show such deviations, as shown in Figs. 2 and 3. The extent to which this deviation is significant would depend on which mineral is dominant in the effective volume for the exchange reaction. That is, if the effective bulk composition approximates the composition of original biotite, the composition of biotite would not change significantly in contrast to the garnet composition that would change during retrograde metamorphism, and *vice versa*. Figure 4 plots the pairs of Mg/Fe values of garnet and adjacent biotite, together with the Mg/Fe ranges of matrix biotite and rim garnet that are not in contact with each other. It is clear that rim garnet is depleted in Mg/Fe when it is in contact with matrix biotite having similar composition to the matrix biotites not in contact with garnet. This can be accounted for as the local effective bulk composition being close to the matrix biotite. The Ti-poor biotite is enriched in Mg/Fe, and the adjacent garnet rim has similar composition to the rim not in contact with biotite (Figs. 3 and 4). Such a Ti-poor biotite adjacent to the garnet rim was possibly formed at the expense of garnet, as is common in high-grade metamorphic rocks (*e.g.*, Ikeda, 1991). The formation of biotite at the expense of garnet rim requires the effective bulk composition to be close to

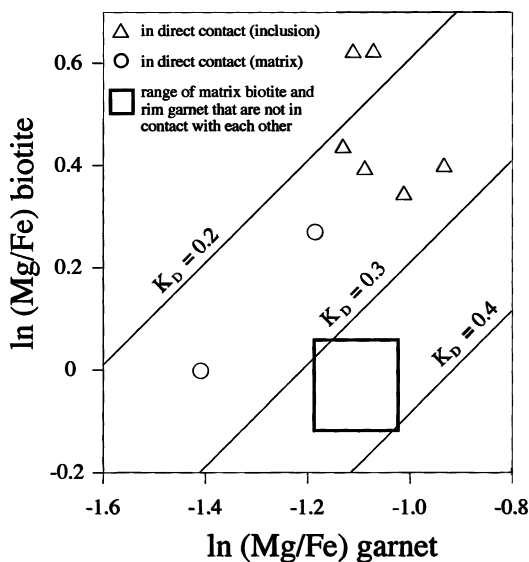


Fig. 4. Plot of natural logarithms of Mg/Fe of garnet and biotite. The lines represent isopleths in terms of the distribution coefficient K_D , where K_D is defined as $(\text{Mg/Fe})^{\text{garnet}}/(\text{Mg/Fe})^{\text{biotite}}$. The box represents the ranges in composition of rim garnet and matrix biotite that are not in contact with each other. The analyses of garnet and biotite having maximum and minimum Mg/Fe values are shown in Tables 1 and 2, respectively.

that of original garnet, which agrees with the observation.

Local depletion in Mg/Fe is recognized also in the interior of garnet around biotite inclusions, as described before, suggesting that the biotite inclusions also underwent retrograde re-equilibration. This indicates that the composition of inclusion biotite was changed during retrograde metamorphism. Pairs of garnet and adjacent biotite show distribution coefficients K_D , defined as $(\text{Mg/Fe})^{\text{garnet}}/(\text{Mg/Fe})^{\text{biotite}}$, similar to each other, ranging from 0.18 to 0.27 irrespective of whether biotite occurs as inclusions in garnet or in the matrix (Fig. 4). This suggests that the exchange reaction between garnet and adjacent biotite did not proceed below a specific temperature for a wide range in compositions of garnet and biotite.

This study examined several garnet-biotite geothermometers to estimate the closure temperature for the exchange reaction in the sample #I-181. The geothermometer of Holdaway (2000) applied to garnet and adjacent biotite yields temperatures that range from 620 to 700°C, assuming a nominal pressure of 6 kbar (Table 4). Estimated temperatures based on Thompson (1976), Perchuk and Lavrent'eva (1983) and Dasgupta *et al.* (1991) are up to 30°C higher or lower than those of Holdaway (2000). This study considers, therefore, the closure temperature for the Fe-Mg exchange reaction to be *ca.* 660°C. All these calibrations take the Al content of biotite into account by using either the natural compositions of biotite, aluminous biotite for experiments or thermodynamic considerations. In contrast, the two models of Indares

Table 4. Estimated retrograde temperatures using the geothermometer of Holdaway (2000). Pressure is assumed to be 6 kbar except for the last four calculations that employ the geobarometer of Koziol and Newton (1988). $K_D = (Mg/Fe)^{garnet} / (Mg/Fe)^{biotite}$.

occurrences	pair of analyses	K_D	T (°C)	P (kbar)
inclusion biotite and adjacent interior garnet	Bt 6 - Grt 14	0.265	696	
	Bt 7 - Grt 16	0.209	642	
	Bt 8 - Grt 15	0.227	657	
	Bt 10 - Grt 18	0.257	687	
	Bt 11 - Grt 22	0.183	626	
	Bt 11 - Grt 25	0.176	619	
matrix biotite and adjacent rim garnet	Bt 9 - Grt 17	0.245	670	
	Bt 2 - Grt 4	0.234	668	
* matrix biotite and rim garnet that are not in contact with each other	Bt 3 - Grt 7 - Pl 12	0.340	753	5.76
	Bt 12 - Grt 7 - Pl 12	0.401	797	6.40
	Bt 3 - Grt 2 - Pl 12	0.288	706	4.81
	Bt 12 - Grt 2 - Pl 12	0.340	745	5.38

* Garnet and biotite having maximum and minimum Mg/Fe values in this occurrence are paired.

and Martignole (1985) provide temperatures *ca.* 100°C lower than the above methods even though they also consider the effect of Al and Ti in biotite. This feature has been clearly demonstrated by Dasgupta *et al.* (1991) when biotite has X_{Al}^{vi} lower than 0.1; the X_{Al}^{vi} of biotite in #I-181 ranges from 0.03 to 0.08. This discrepancy may be ascribed to the models of Indares and Martignole (1985) that assume a specific substitution to introduce Al and Ti into biotite, as suggested by Nakamura (1996), which requires the interaction parameter, $W_{MgAl}-W_{FeAl}$, to be much higher than those proposed by Dasgupta *et al.* (1991) and Holdaway (2000).

4.2. Retrograde pressure-temperature condition

The mineral assemblage preserved in the matrix may be described in terms of the reaction,



This reaction predicts that the Mg/Fe of garnet and its modal amount increase with increasing temperature. The depletion of Mg/Fe at the outer part of the garnet grain can be ascribed to the reversal of reaction (3) during retrograde metamorphism in which garnet was consumed to produce biotite. The core of garnet is, therefore, most likely to preserve the composition at higher temperatures than the rim.

The assumption of the homogeneous matrix biotite representing the composition at peak metamorphism cannot be adopted for a garnet-rich sample, which is the object of this study (*cf.* Tracy *et al.*, 1976). The matrix biotite may have been initially equilibrated with garnet having the composition now preserved at its core. The garnet in the sample shows an outward decrease in Mg/Fe in a zone 2 mm thick from the periphery and has a modal amount larger than biotite. Therefore the volume of garnet

whose composition was modified with decreasing temperature would not be negligible compared with the volume of matrix biotite. This suggests that biotite in the matrix probably does not preserve the composition at peak metamorphism but has significantly changed its composition. It is difficult to assess how large a volume of biotite has changed composition to produce garnet rim during retrograde metamorphism. Therefore we cannot estimate the composition of biotite that was equilibrated with the garnet core.

In contrast, garnet rim and matrix biotite that are not in contact with each other represent a small range of compositional variations that have not been explained so far (Fig. 4). It is possible to consider that the matrix biotite was re-equilibrated with the garnet rim under retrograde conditions. This suggests that the equilibrium domain involves sillimanite, quartz and plagioclase occurring in the matrix between garnet and matrix biotite not in contact with garnet. This assemblage enables us to employ the GASP geobarometer together with the garnet-biotite geothermometer.

Pairing maximum and minimum Mg/Fe values of garnet and biotite that are not in contact with each other provides the maximum and minimum estimates of the retrograde condition. The geothermometer of Holdaway (2000) was used again, combined with the GASP geobarometer of Koziol and Newton (1988). The estimated conditions range from 710 to 800°C and from 4.8 to 6.4 kbar (Table 4). We regard the mid value of the range, 760°C, 5.6 kbar, as the retrograde condition that the sample #I-181 has preserved. The obtained temperatures are significantly higher than the temperatures based on garnet and adjacent biotite. Use of Ghent (1976) as a geobarometer yields pressures negligibly higher, by less than 0.3 kbar.

The decompressional retrograde paths of the Lützow-Holm Complex have been proposed mainly based on microstructural analyses of the garnet-consuming reactions (e.g., Hiroi *et al.*, 1986; Motoyoshi and Ishikawa, 1997; Fraser *et al.*, 2000). Even though the peak metamorphic condition of Skallen is still controversial, the retrograde condition obtained in this study is clearly lower both in temperature and pressure than the conditions, 810°C and 7.7–10.8 kbar, estimated by Motoyoshi (1986), who carefully chose mineral compositions at a higher-grade stage. The retrograde path connecting these two conditions is consistent with the decompressional path.

5. Conclusions

The pelitic gneiss examined in this study contains garnet that shows an outward decrease in Mg/Fe. The condition under which the rims of garnet and matrix biotite were equilibrated is estimated to be 760°C, 5.6 kbar. The garnet core has probably been equilibrated at higher temperatures, thus the estimated condition is that of retrograde metamorphism. The Fe-Mg exchange reaction between garnet and adjacent biotite has proceeded under still lower temperatures and ceased at *ca.* 660°C, providing a closure temperature of the reaction for this sample.

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