

## GEOOTHERMOMETRY AND GEOBAROMETRY OF PELITIC ROCKS, UPPER KYANITE AND SILLIMANITE ZONES, MICA CREEK AREA, BRITISH COLUMBIA

EDWARD D. GHENT, CLIFFORD C. KNITTER,  
ROBERT P. RAESIDE AND MAVIS Z. STOUT

*Department of Geology and Geophysics, University of Calgary, Calgary, Alberta T2N 1N4*

### ABSTRACT

Temperatures have been estimated using garnet-biotite assemblages for pelitic rocks of the Mica Creek area, British Columbia. These rocks are in the upper-kyanite to K-feldspar-sillimanite zones. The estimates range from 560 to 790°C (Ferry & Spear calibration) and 540 to 700°C (Thompson calibration). Some of the higher-temperature estimates are inconsistent with muscovite-plagioclase-quartz-sillimanite stability limits. Some of these inconsistencies are due to compositional deviations in garnet and biotite from the ideal Fe-Mg binary system. The rims of many garnet grains show evidence of retrograde exchange of Mg and Fe with adjacent biotite. Pressure estimates, based upon garnet-plagioclase- $Al_2SiO_5$ -quartz equilibria, range from  $6.1 \pm 0.8$  kbar (upper kyanite zone) to  $7.2 \pm 0.8$  (K-feldspar-sillimanite zone); since these values are not significantly different, there is no evidence for a change in pressure with metamorphic grade.

*Keywords:* geothermometry, geobarometry, phase equilibria, metamorphism, British Columbia.

### SOMMAIRE

On détermine la température de formation d'assemblages grenat + biotite pour des roches pélitiques de la région de Mica Creek (Colombie-britannique). Ces roches, qui vont de la partie supérieure de la zone à disthène jusqu'à la zone à feldspath potassique + sillimanite, varient de 560 à 790° (calibration de Ferry & Spear) ou de 540 à 700°C (calibration de Thompson). Quelques résultats qui indiquent une température élevée sont incompatibles avec les limites de stabilité de l'assemblage muscovite + plagioclase + quartz + sillimanite. Dans certains cas, l'incompatibilité est due au fait que la composition du grenat et celle de la biotite s'écartent du système binaire Fe-Mg idéalisé. Dans de nombreux cas, la bordure des cristaux de grenat montre des effets d'un échange rétrograde de Mg et de Fe avec des cristaux de biotite contigus. L'équilibre grenat + plagioclase +  $Al_2SiO_5$  + quartz donne une approximation de la pression: celle-ci

varie de  $6.1 \pm 0.8$  kbar (à la partie supérieure de la zone à disthène) à  $7.2 \pm 0.8$  kbar pour la zone à feldspath potassique + sillimanite. Ces valeurs ne diffèrent pas de façon significative: on ne peut donc pas conclure que la pression soit ici fonction du degré de métamorphisme.

(Traduit par la Rédaction)

*Mots-clés:* géothermométrie, géobarométrie, équilibre des phases, métamorphisme, Colombie-britannique.

### INTRODUCTION

Metamorphic rocks in the Mica Creek area of British Columbia range in metamorphic grade from upper-garnet zone to K-feldspar-sillimanite zone. The protoliths were dominantly clastic rocks with minor algal limestones and locally thick bodies of mafic volcanic rocks (Simony *et al.* 1980). Isograds mapped in pelitic rocks are: 1) first appearance of staurolite + kyanite, 2) disappearance of staurolite + muscovite + quartz, 3) first appearance of abundant migmatite, 4) first appearance of sillimanite, 5) appearance of K-feldspar with muscovite + quartz + sillimanite and 6) disappearance of stable muscovite + quartz (Simony *et al.* 1980; see Fig. 1). The disappearance of staurolite + muscovite + quartz in the stability field of kyanite indicates that the metamorphism belongs to bathozone 5 of Carmichael (1978). Metamorphic rocks in the Park Ranges from east of the Purcell fault were metamorphosed at lower pressures, as suggested by the coexistence of staurolite + muscovite + sillimanite and the scarcity of migmatite (for maps, see Craw 1978, Simony *et al.* 1980).

Rocks of the Blue River area, which lie to the west of the Mica Creek area, contain staurolite + muscovite + sillimanite assemblages, suggesting that they were metamorphosed at lower pressures than were the rocks of the Mica Creek area (for a geological map, see Pell &



## SOURCES OF THERMODYNAMIC DATA

Thermodynamic constants used in this paper are listed in Table 1. The general expression is  $\Delta G_{T,P} = 0 = \Delta H^\circ - T\Delta S^\circ + RT \ln f(\text{H}_2\text{O}) + RT \ln K_a + RT \ln K_\gamma + (P-1) \Delta V_s$ , where  $G_{T,P}$  is the change in Gibbs free energy at P and T,  $\Delta H^\circ$  is the change in standard enthalpy at T and one bar, T is temperature in Kelvin,  $\Delta S^\circ$  is the change in standard entropy at T and one bar, R is the gas constant,  $f(\text{H}_2\text{O})$  is the fugacity of  $\text{H}_2\text{O}$ ,  $K_a$  is the activity product for the solids,  $K_\gamma$  is the activity-coefficient product for the solids, P is the pressure in bars and  $\Delta V_s$  is the volume change for the solids in the reaction. The sources of the data are given in Table 1.

## GARNET-BIOTITE GEOTHERMOMETRY

The distribution of Fe and Mg between garnet and biotite has been used to estimate temperatures of metamorphism. Several calibrations of  $\ln K_D$  Mg-Fe ga-bi [ $K_D = (\text{Mg}/\text{Fe})^{\text{ga}} / (\text{Mg}/\text{Fe})^{\text{bi}}$ ] as a function of temperature and other variables have been published (Thompson 1976, Goldman & Albee 1977, Ferry & Spear 1978). Temperatures estimated for staurolite-kyanite-zone rocks from British Columbia, using the Thompson and Ferry & Spear calibrations, agree reasonably well with temperatures estimated from other geothermometers (Ghent *et al.* 1979). Ferry (1980) has demonstrated reasonable agreement between garnet-biotite geothermometry and other geothermometers for andalusite-sillimanite-grade pelitic rocks from Maine. Bohlen & Essene (1980) and Stoddard (1980), however, have presented evidence that garnet-biotite temperatures do not agree with other temperatures estimated for granulite-facies rocks from the Adirondacks. Hodges & Spear (1982) have presented evidence that the garnet-biotite Fe-Mg-exchange geothermometer is susceptible to re-equilibration during cooling and is most accurate in medium-grade metamorphic terranes. They suggest that it may yield unrealistically low temperatures for high-grade metamorphic terranes.

## GARNET ZONING AND GARNET-BIOTITE TEMPERATURES

One of the many problem in estimating metamorphic temperatures from the garnet-biotite Fe-Mg exchange geothermometer is the fact that most garnet grains show internal chemical zoning (*e.g.*, Tracy *et al.* 1976). The pattern of chemi-

cal zoning in garnet is a complex function of bulk-rock composition, the P-T history of the rock, rates of homogeneous diffusion within garnet and, possibly, the availability of metamorphic fluids during the stages of garnet growth (Tracy *et al.* 1976). Biotite grains co-existing with garnet are typically not chemically zoned. Because of the zoning problem in garnet, temperature estimates will necessarily carry an uncertainty in addition to that due to analytical uncertainty.

In a previous study of staurolite-kyanite-zone rocks, Ghent *et al.* (1979) analyzed garnet rims and adjacent biotite and showed that consistent and plausible temperatures could be estimated from the Fe-Mg exchange geothermometer as calibrated by Ferry & Spear (1978) and Thompson (1976). In a discussion of the high-grade metamorphic rocks from Massachusetts, Tracy *et al.* (1976) presented an interpretation of garnet-interior zoning as due to prograde continuous reaction and rim zoning as due to retrograde continuous reactions. They argued that where the rock contains very little garnet or the retrograde outer rims of garnet are narrow (and there are no other abundant Fe-Mg-Mn phases), the matrix biotite may have been close to an infinite reservoir, and the biotite Fe/Mg ratio could not have increased substantially from what it was earlier. In this case,  $K_D$  determined from a garnet interior and matrix biotite should give a substantially correct estimate of prograde temperatures.

In a study of garnet compositions from garnet, staurolite and cordierite zones in British Columbia, Woodsworth (1977) showed that the higher-grade garnet crystals are very weakly zoned; he proposed that originally zoned garnet crystals were homogenized at higher temperatures. He also pointed out the possibility that the Mg/Fe ratio of the garnet could be modified by exchange with another Mg-Fe phase during homogenization.

In the present study, we sampled garnet in contact with biotite grains and measured compositional profiles across a number of garnet grains. Compared to lower-grade garnet, Mn content generally is low, and zoning, where present, is weak and typically reversed, *i.e.*, Mn is relatively depleted in grain cores and enriched in grain margins (Table 2). These data suggest homogenization of originally zoned garnet. Mg/Fe ratios in garnet, however, were not completely homogenized; there are significant differences in  $\ln K_D$  values for garnet cores-matrix biotite versus  $\ln K_D$  values for garnet rims - matrix biotite (Table 2). The presence of re-

TABLE 2. ESTIMATES OF PRESSURE AND TEMPERATURE FOR PELITIC ROCKS, UPPER KYANITE TO SILLIMANITE ZONES, MICA CREEK, BRITISH COLUMBIA

Sample No.	Mineral	ln Kd	ln Ks	XMn	XCa	XTi	XAl	T1	T2	P	Zone
1 - 12	ga core	-1.27	-5.23	.02	.02			695	790	8.4	K
	ga rim	-1.62	-5.23	.07	.02			590	620	5.6	
	bi					.04	.22				
7 - 8	ga core	-1.37	-4.65	.02	.05			660	740	8.3	K
	ga rim	-1.62	-4.65	.03	.05			590	625	6.3	
	bi					.04	.23				
11 - 3	ga core	-1.81	-2.90	.00	.15			540	560	7.0	K
	ga rim	-1.46	-3.50	.00	.13			635	700	9.1	
	bi					.02	.22				
13 - 1	ga core	-1.42	-2.86	.02	.09			645	725	10.1	K
	ga rim	-1.81	-3.39	.06	.09			540	560	6.2	
	bi					.05	.25				
30 - 17	ga core	-1.44	-6.82	.05	.03			640	690	4.8	K
	ga rim	-1.52	-5.43	.05	.05			615	665	6.0	
	bi					.03	.22				
CK-77-192	ga bi	-1.58	-5.41	.04	.03			600	635	5.4	K
1 - 6	ga core	-1.39	-5.94	.04	.04			655	715	5.6	KS
	ga rim	-1.32	-4.10	.08	.08			680	770	9.3	
	bi					.05	.19				
4 - 9	ga core	-1.48	-4.90	.05	.07			630	690	6.6	KS
	ga rim	-1.51	-4.65	.03	.08			620	670	6.8	
	bi					.06	.15				
7 - 1	ga core	-1.30	-4.81	.03	.07			685	775	8.3	KS
	ga rim	-1.54	-4.93	.06	.08			610	655	6.1	
	bi					.06	.16				
22 - 3	ga core	-1.71	-3.52	.05	.10			565	595	7.0	KS
	ga rim	-1.76	-3.68	.06	.08			550	575	6.5	
	bi					.05	.14				
24 - 8	ga core	-1.89	-3.09	.04	.16			520	535	6.3	KS
	ga rim	-1.75	-2.99	.04	.16			555	585	7.4	
	bi					.06	.20				
CK-77-80	ga bi	-1.71	-5.23	.03	.05			565	585	4.8	KS
CK-77-132	ga bi	-1.62	-4.73	.03	.02			590	625	5.9	KS
CK-77-139	ga bi	-1.63	-4.41	.01	.03			585	620	6.3	KS
CK-77-158	ga bi	-1.74	-4.30	.08	.07			555	580	5.7	KS
CK-77-164	ga bi	-1.68	-4.14	.03	.07			575	605	6.4	KS
CK-77-168	ga bi	-1.65	-3.98	.08	.06			580	615	6.8	KS
GM-73-104	ga core	-1.37		.05	.03			660			KS
	ga rim	-1.64	-5.63	.07	.03			585	610	4.5	
	bi					.04	.17				
GM-73-105	ga core	-2.08		.03	.11			480			KS
	ga int	-1.52		.05	.07			615			
	ga rim	-1.54		.06	.07			620			
	bi					.03	.17				
GM-73-106	ga core	-1.35		.04	.05			670			KS
	ga rim	-1.60	-4.74	.07	.05			595	630	6.1	
	bi					.05	.14				
6 - 1	ga bi	-1.45	-5.02	.07	.04			635	695	6.7	MS

verse Mn zoning, often with a sharp increase in Mn content near garnet rims, also suggests the possibility of retrograde reactions (*cf.*, Woodsworth 1977).

Temperatures estimated were from Thompson (1976, Fig. 1-B, p. 429) and from the calibration of Ferry & Spear (1978). For the Ferry & Spear calibration, we substituted component

SM-76-1	ga core	-1.52	-5.09	.04	.08			615	660	6.0	MS
	ga rim	-1.73	-5.09	.04	.08			560	580	4.7	
	bi					.08	.15				
CK-77-202	ga	-1.53	-4.16	.02	.07			615	660	7.2	MS
	bi					.03	.15				
GM-78-1	ga		-4.35	.06	.06						MS
	bi	-1.34				.08	.15	670	755	8.7	
	bi incl	-1.68				.08	.14	575	600	6.1	
GM-78-20	ga		-4.49	.06	.03						MSF
	bi	-1.34				.09	.12	670	755	8.4	
	bi incl	-1.64				.09	.12	585	615	6.1	
3-8	ga core	-1.51	-4.70	.05	.05			620	670	6.7	MSF
	ga rim	-1.39	-4.58	.04	.05			655	730	7.9	
	bi					.04	.14				
40-10	ga core	-1.41	-4.88	.01	.07			650	715	7.2	MSF
	ga rim	-1.86	-5.90	.02	.05			530	530	2.9	
	bi					.09	.06				
GM-78-3	ga			.04	.04						MSF
	bi	-1.47				.08	.14	630			
	bi incl	-1.74				.07	.14	555			
3-10	ga core	-1.38	-5.07	.08	.05			660	730	7.1	SF
	ga rim	-1.44	-4.28	.08	.06			640	705	7.9	
	bi					.06	.16				
39-14	ga core	-1.38	-5.07	.06	.04			660	730	7.1	SF
	ga rim	-1.85	-4.97	.07	.04			530	540	4.2	
	bi					.07	.13				
43-10	ga core	-1.26	-5.53	.03	.04			700	790	7.3	SF
	ga rim	-1.60	-5.78	.04	.03			595	625	4.5	
	bi					.06	.13				

ga core = garnet core; ga int = garnet interior; ga rim = garnet rim; bi = biotite; bi incl = biotite included in garnet  
 In  $K_D$  and In  $K_S$  defined in text,  $X_{Mn} = Mn/(Mn+Ca+Fe+Mg)$  atoms

$X_{Ca} = Ca/(Ca+Mn+Fe+Mg)$  atoms  $X_{Ti} = Ti/\text{sum octahedral atoms}$   $X_{Al} = Al/\text{sum of octahedral atoms}$

$T_1$  = Temperature estimated from Thompson calibration (see text)

$T_2$  = Temperature estimated from Ferry and Spear calibration combined with garnet-plagioclase  $Al_2SiO_5$ -quartz

P = pressure estimated from garnet-plagioclase- $Al_2SiO_5$ -quartz and Ferry Spear calibration

K = kyanite zone; KS = near kyanite-sillimanite isograd; MS = muscovite-sillimanite zone; MSF = muscovite-sillimanite-K-feldspar zone; SF = sillimanite-K-feldspar zone

activities into equilibrium (6) and equilibrium (1) or (2) (Table 1) and solved these equations simultaneously for P and T.

Upper-kyanite-zone samples show quite variable temperature estimates both for garnet core - biotite and for garnet rim - biotite (Table 2). One sample (11-2) shows garnet rim - biotite temperature estimates higher than those for garnet core - biotite. The range in garnet rim - biotite temperatures is 540 to 635°C (Thompson calibration) and 560 to 700°C (Ferry & Spear calibration), which seems rather large for upper-kyanite-zone samples from a relatively restricted area. The average estimated temperatures and standard deviations for the upper-kyanite-zone samples are  $595 \pm 30^\circ\text{C}$  (Thompson calibration) and  $635 \pm 50^\circ\text{C}$  (Ferry & Spear calibration). Ghent *et al.* (1979, p. 877) estimated a standard deviation of  $\pm 15^\circ\text{C}$  due to analytical uncertainty in the garnet-biotite geothermometer (see also Ferry & Spear 1978, p. 117). The observed standard deviations

indicate that the variation is likely due to factors other than analytical uncertainty. This point will be discussed in more detail later.

Samples near the kyanite-sillimanite isograd also show quite variable garnet core - biotite and garnet rim - biotite temperatures (Table 2, Fig. 1). The range in estimated temperatures for 14 samples is over 100°C (Table 2, Fig. 1). Six samples from a restricted area (CK-77-80 to CK-77-168, Table 2, Fig. 1) show a relatively narrow estimated temperature range, 555 to 590°C (Thompson calibration) and 585 to 625°C (Ferry & Spear calibration). For these samples, garnet was sampled a least 100  $\mu\text{m}$  from the edge of the grains. Garnet rim - biotite temperatures estimated for these rocks are lower by 50 to 100°C or more (Knitter 1979).

For 11 samples from the higher-grade metamorphic zones, with one exception (3-8), garnet rim - biotite temperatures are lower than garnet interior - biotite temperatures. This

suggests retrograde Fe–Mg exchange between biotite and garnet rims during cooling. For the higher-grade metamorphic zones, the range in estimated temperatures is 615–700°C (Thompson calibration) and 660 to 790°C (10 samples, Ferry & Spear calibration). The mean temperatures and standard deviations are  $650 \pm 25^\circ\text{C}$  (Thompson calibration) and  $715 \pm 45^\circ\text{C}$  (Ferry & Spear calibration).

#### DISCUSSION OF GARNET–BIOTITE TEMPERATURES

There are two points to discuss: 1) the variation in estimated temperatures within a given metamorphic zone, and 2) the accuracy of the calibrations of the garnet–biotite Fe–Mg exchange geothermometer.

The estimated maximum variation in temperature along the kyanite–sillimanite isograd is  $20^\circ\text{C}$  (see Ghent *et al.* 1980 for a discussion). This estimated variation is far less than that in estimated temperatures based on garnet–biotite geothermometry. All samples contain quartz–muscovite–biotite–garnet–plagioclase–kyanite (sillimanite)–ilmenite. The garnet and biotite show some variation in composition (Table 2), but there is no significant correlation between Mn and Ca content of garnet, Ti and  $\text{Al}^{\text{VI}}$  content of biotite and the estimated temperature of equilibration. We conclude that the large variations in temperature for samples along the kyanite–sillimanite isograd are the products of a) real variations in closure temperatures for Mg–Fe exchange along the isograd, b) analytical uncertainty, and c) sampling of garnet domains that were not in equilibrium with matrix biotite and that consequently yield erroneous temperatures.

Because of the large variation in estimated temperatures for the samples described in this study, it will be extremely difficult to determine the precise geometry of isothermal surfaces in this terrane using garnet–biotite geothermometry. The problem is compounded by the fact that the isograds have been folded (Simony *et al.* 1980, Ghent *et al.* 1980). Folding of the kyanite–sillimanite isograd is clearly demonstrated by the coincidence of sillimanite-zone outliers with the hinges of  $F_3$  folds (Fig. 1; Ghent *et al.* 1980). The essentially parallel pattern of outcrop of the staurolite-out and muscovite–quartz–K-feldspar–sillimanite isograds does not reflect the  $F_3$  folding; however, these isogradic surfaces initially had steep dips, and the folding would be detected only if the  $F_3$  fold were of very large amplitude.

To discuss the accuracy of the calibrations of the garnet–biotite geothermometer, we next compare these temperature estimates to those based upon another equilibrium that is temperature-dependent.

#### MICA–QUARTZ–FELDSPAR– $\text{Al}_2\text{SiO}_5$ EQUILIBRIA

In pelitic rocks at metamorphic grades below the disappearance of muscovite + quartz, a common mineral assemblage is K–Na–mica–quartz–plagioclase–kyanite (sillimanite)  $\pm$  K-feldspar. This assemblage can be modeled by the following equilibria:

- 3) paragonite + quartz = albite +  $\text{Al}_2\text{SiO}_5$  +  $\text{H}_2\text{O}$
- 5) muscovite + quartz =



Reaction numbers are those given in Table 1.

Ghent (1975) and Ghent *et al.* (1979) showed that, if an estimate of  $P_s$  and  $T$  could be made, substitution of activities of paragonite in muscovite–paragonite crystalline solutions and of albite component in albite–anorthite crystalline solutions allows an estimation of  $f(\text{H}_2\text{O})$ , the fugacity of  $\text{H}_2\text{O}$ .

In the present paper we compare garnet–biotite estimates of temperature with the maximum temperature at which K–Na–mica–quartz–plagioclase–kyanite (sillimanite)–fluid would be stable. For these estimates we set  $P(\text{H}_2\text{O}) = P_s = 6$  kbar and use the thermodynamic data given in Table 1. The temperatures have been estimated using two models for the activity of paragonite component in K–Na–mica. The first model sets  $a_{\text{pa}}^{\text{mi}} = \gamma_{\text{pa}}^{\text{mi}} \cdot X_{\text{Na}}^{\text{mi}}$  where  $a_{\text{pa}}^{\text{mi}}$  is the activity of paragonite (pa) in K–Na–mica (mi),  $\gamma_{\text{pa}}^{\text{mi}}$  is the activity coefficient of paragonite in K–Na–mica, and  $X_{\text{Na}}^{\text{mi}}$  is the mole fraction of Na in K–Na–mica [ $X_{\text{Na}}^{\text{mi}} = \text{Na}/(\text{Na} + \text{K})$ ]. The activity coefficient of paragonite component is estimated from the equations of Eugster *et al.* (1972). The second model sets  $a_{\text{pa}}^{\text{mi}} = (\gamma_{\text{pa}}^{\text{mi}} \cdot X_{\text{Na}}^{\text{mi}}) \cdot (X_{\text{Al}^{\text{VI}}}^{\text{mi}})^2$ , where  $X_{\text{Al}^{\text{VI}}}^{\text{mi}}$  is the mole fraction of Al in octahedral sites [=  $\text{Al}^{\text{VI}}/(\text{Al}^{\text{VI}} + \text{Fe} + \text{Mg} + \text{Ti})$ ]; all other symbols have the same definition. The octahedral Al content is an estimate of “phengite” substitution and assumes coupling of (Mg, Fe)-for-Al substitution in octahedral sites with Si-for-Al substitution in tetrahedral sites (see Ghent *et al.* 1979). Because we have no quantitative data on the activity coefficient of octahedral Al in K–Na–mica, we treat it as an ideal solution. This model will displace equilibrium (3) to higher temperatures at constant pressure. Compared to data

for other solid solutions where Mg and Fe substitute for Al in octahedral sites, we would predict a positive deviation from ideality for this substitution. If, for example, we set  $\gamma_{Al_i}^{ml} = 1.10$ , the temperature estimate at 6 kbar would be reduced by about 10°C. Consequently, the maximum temperature estimate probably lies between temperatures estimated from the model with no "phengite" correction and the model with "phengite" correction using an ideal model for octahedral Al.

We compare garnet-biotite temperatures based upon the Thompson and Ferry & Spear calibrations with *maximum* possible temperatures based upon K-Na-mica-quartz-feldspar- $Al_2SiO_5$  equilibria (Table 3). Temperature estimates for sillimanite-zone samples using the Ferry & Spear temperature estimates are generally higher than temperature estimates based on K-Na-mica-quartz-feldspar- $Al_2SiO_5$  with no "phengite" correction. Four of these garnet-biotite temperature estimates exceed temperature estimates based on K-Na-mica-quartz-feldspar- $Al_2SiO_5$  with phengite correction. Only one of the garnet-biotite temperature estimates using the Thompson calibration exceeds the K-Na-mica-quartz-feldspar- $Al_2SiO_5$  temperature estimates (Table 3). The total spread of garnet-biotite temperatures is from 580 to 740°C for the Ferry & Spear calibration and from 555 to 670°C for the Thompson calibration. The higher temperature estimate (740°C) is clearly outside the upper stability limit of the associated muscovite<sub>ss</sub> + quartz for  $P(H_2O) = P_s$ .

For six samples from a restricted area near the kyanite-sillimanite isograd (CK-77-80 to CK-77-168, Tables 2, 3, Fig. 1), the estimated temperature range is 585 to 610°C (no phengite correction) and 605° to 635°C (with phengite correction). These estimates suggest that, for these samples from a restricted area, there was little variation in metamorphic temperature or  $f(H_2O)$ . The mica-quartz- $Al_2SiO_5$ -feldspar- $H_2O$  equilibria cannot strictly be used as a geothermometer unless we can make independent estimates of  $P_s$  and  $f(H_2O)$ . In addition, for  $P(H_2O) = P_s$  at higher pressures and temperatures, equilibria involving paragonite crystalline solution + quartz + albite crystalline solution +  $Al_2SiO_5$  +  $H_2O$  will be metastable with respect to equilibria involving an  $H_2O$ -saturated silicate melt (Thompson & Tracy 1979). The upper stability limit of Ca-bearing muscovite-K-bearing anorthite-quartz for  $P(H_2O) = P_s$  is near 695°C and 5.2 kbar; this limit is clearly exceeded by some of the garnet-biotite temperature estimates (Tables 2, 3).

TABLE 3. COMPARISON OF TEMPERATURES ESTIMATED FROM GARNET-BIOTITE EQUILIBRIUM WITH UPPER PARAGONITE-QUARTZ-ALBITE- $Al_2SiO_5$  EQUILIBRIA

Sample	T(F&S)	T(Th)	T(1)	T(2)
GM 73 104	615	585	615	635
105	600	570	610	635
106	630	595	640	640
GM 78 1	735	670	690	730
bi inclusion	595	570		
GM 78 3a	685	635	695	720
bi inclusion	580	555		
GM 78 20	740	670	670	710
SM 76 1	580	560	665	690
CK 77 80	590	565	590	610
CK 77 132	620	590	610	635
CK 77 139	615	585	595	615
CK 77 158	580	555	595	620
CK 77 164	600	575	585	605
CK 77 168	610	580	585	610
CK 77 192	635	600	600	615
CK 77 202	655	615	590	600

F&S = temperature estimated from Ferry and Spear calibration at 6 kbar

Th = temperature estimated from Thompson calibration (1976, p. 429)

T1 = upper limit on temperature at 6 kbar ( $P_{H_2O} = P_s$ )

for paragonite-quartz-albite- $Al_2SiO_5$  equilibria no "phengite" correction.

T2 = same as condition for T1 except "phengite" correction applied. See table.

#### EFFECTS OF DEVIATION OF COMPOSITION FROM BINARY FE-MG SYSTEM ON GARNET-BIOTITE GEOOTHERMOMETRY

Compositional deviations from the ideal Fe-Mg system will affect temperatures estimated from the garnet-biotite geothermometer (*e.g.*, Goldman & Albee 1977, Ferry & Spear 1978). Samples from the upper-kyanite through muscovite-feldspar-sillimanite zones in the Mica Creek area contain the mineral assemblage quartz-muscovite-biotite-plagioclase-garnet- $Al_2SiO_5$ -ilmenite (Table 2) and samples from the K-feldspar-sillimanite zone contain K-feldspar-sillimanite instead of muscovite (Table 2). Because the mineral system would be saturated with  $SiO_2$ ,  $Al_2SiO_5$  and a Ti-bearing phase, any variation in the concentrations of these elements should be a function of P, T and other intensive variables rather than the bulk concentration of these elements in the mineral system.

Tracy (1978) pointed out that biotite from sillimanite-zone rocks in Massachusetts contains appreciable octahedral Ti and does not conform precisely to trioctahedral stoichiometry. Both Thompson (1976) and Goldman & Albee (1977) suggested that for large quantities of Ti in biotite, a correction should be made to the temperature estimated using  $\ln K_D$  for the ideal binary Fe-Mg system. Goldman & Albee (1977) suggested that, for a given Ti content in biotite, the temperature estimate based upon  $\ln K_D$  for the Fe-Mg binary system should be reduced. Higher-grade biotite from the Mica Creek area generally contains more Ti than lower-grade biotite; some of these samples yield garnet-biotite estimates of temperature that are

higher than maximum temperatures estimated from K–Na–mica–quartz– $\text{Al}_2\text{SiO}_5$ –plagioclase– $\text{H}_2\text{O}$  equilibria.

Goldman & Albee (1977) suggested that for a given octahedral Al( $\text{Al}^{\text{VI}}$ ) in biotite, the temperature estimate based upon  $\ln K_D$  for the ideal Fe–Mg binary system should be increased. A plot of  $\ln K_D$  versus  $X_{\text{Al}^{\text{VI}}}$  in biotite for Mica Creek rocks shows a poor correlation;  $X_{\text{Al}^{\text{VI}}}$  is generally lower in the higher-grade rocks.

Goldman & Albee (1977) and Ganguly (1979) both suggested that for Fe–Mg exchange geothermometers, a correction for high Ca and Mn contents of garnet should be made. Examination of the data in Table 3 indicates that garnet from lower-grade samples generally contains slightly more Ca and Mn than that from higher-grade samples, but there is a significant overlap in the composition of garnet as a function of metamorphic grade.

In summary, deviations from the ideal Fe–Mg binary system will likely lead to inaccurate estimates of temperature using garnet–biotite geothermometry. Quantitative estimates of the effects of other elements on Fe–Mg exchange between garnet and biotite are needed; relevant experimental determinations of phase equilibria and thermochemical studies are currently in progress (e.g., Albrecht & Hewitt 1981).

#### PRESSURE ESTIMATES BASED UPON GARNET–PLAGIOCLASE– $\text{Al}_2\text{SiO}_5$ –QUARTZ EQUILIBRIA

The pressure during metamorphism can be estimated from the equilibrium (Ghent 1976, Ghent *et al.* 1979)



Using a value of  $\ln K_s = 4.61 \pm 0.46$  ( $\ln K_s = 3 \ln X_{\text{gr}}^{\text{Ca}} - 3 \ln X_{\text{an}}^{\text{Al}}$ ) for the kyanite–sillimanite isograd from several metamorphic areas, Ghent *et al.* (1979, p. 878) estimated a value of  $\ln K_T = 3 \ln \gamma_{\text{gr}}^{\text{Ca}} - 3 \ln \gamma_{\text{an}}^{\text{Al}} = -0.92$ . This value is close to that estimated by Newton & Haselton (1981) using activity coefficients from experimental phase-equilibria and thermochemistry.

A plot of  $\ln K_s$  against  $\ln K_D$  shows no strong correlation, suggesting that pressure of metamorphism does not increase with increasing temperature of metamorphism. The estimation of pressure using garnet– $\text{Al}_2\text{SiO}_5$ –plagioclase–quartz is dependent upon the estimate of metamorphic temperature; a T uncertainty of  $\pm 15^\circ\text{C}$ , with analytical uncertainties of  $\pm 1$

mol% an and  $\pm 1$  mol% gr, leads to an uncertainty of  $\pm 1.6$  kbar (2 standard deviations). Consequently, the uncertainties discussed in the section on garnet–biotite geothermometry must be propagated in the pressure calculations.

#### CALCIUM ZONING IN GARNET AND PLAGIOCLASE

In an earlier paper, Ghent (1976) suggested that calcium zoning in individual garnet and plagioclase grains is systematically related. Typically, plagioclase grains show “reverse” zoning, with calcium enrichment in the rims relative to cores, and garnet grains show lower calcium in rims relative to cores (Table 2). Since garnet and plagioclase are the dominant calcium-bearing minerals in a metamorphosed pelite, the correlation of zoning profiles suggests communication of calcium between the coexisting minerals. The interpretation of calcium zoning in terms of pressure and temperature of crystallization was discussed by Ghent (1976). The rims of adjacent garnet and plagioclase were assumed to have equilibrated at a given pressure and temperature, and the phases were saturated with quartz and  $\text{Al}_2\text{SiO}_5$ . Use of this model has yielded a reasonably consistent set of pressure estimates for staurolite–kyanite-zone rocks from Mica Creek, British Columbia (Ghent *et al.* 1979). Temperatures estimated for these rocks were based upon garnet–biotite geothermometry (Ghent *et al.* 1979). In the present study, higher-grade rocks show evidence of retrograde exchange of Mg, Fe, and Mn among garnet, biotite and other phases. In some samples, we have used the garnet interior Mg–Fe compositions as the best estimate of maximum temperature conditions. It is not clear which portion of a nearby plagioclase grain should be considered to be in equilibrium with interiors of garnet grains. Not only must there have been equilibrium distribution of calcium between garnet interiors and plagioclase, but also the phases must be saturated with quartz and  $\text{Al}_2\text{SiO}_5$ . This latter point can be demonstrated for garnet and plagioclase rims but not for garnet and plagioclase interiors. A second problem is the nature of retrograde reactions between garnet and plagioclase. A drop in temperature at constant pressure should produce calcium enrichment in the garnet relative to plagioclase. The reaction is complicated by the necessity of coupled Na, Si substitution for Ca, Al in plagioclase, indicating the participation of at least one additional phase. If there is not saturation with quartz and  $\text{Al}_2\text{SiO}_5$  at a given pressure and temperature, the ratio of anorthite in plagio-

close to grossular in garnet will not be buffered and this ratio consequently will not provide a good indication of P, T conditions.

VARIATION IN  $\ln K_s$  AND PRESSURE WITH METAMORPHIC GRADE

Estimates of mean values and standard deviations for  $\ln K_s$  for the different metamorphic zones are: kyanite zone  $-4.5 \pm 1.1$ , near kyanite-sillimanite isograd  $-4.6 \pm 0.8$ , and muscovite-sillimanite zone and higher grade  $-4.8 \pm 0.4$ . These calculations suggest that there is no significant difference in  $\ln K_s$  as a function of metamorphic grade. A difference in temperature of about  $70^\circ\text{C}$  from the kyanite zone to the muscovite-sillimanite and higher-grade zones would produce a pressure difference of about 1 kbar, which is near the standard deviation of the mean values of  $\ln K_s$ .

This interpretation is borne out by the mean estimates of pressure and standard deviations. These values are: kyanite zone  $6.1 \pm 0.6$  kbar, near kyanite-sillimanite isograd  $6.1 \pm 0.8$  kbar, and muscovite-sillimanite zone and higher grade  $7.2 \pm 0.8$  kbar. These pressure estimates are based on garnet-biotite temperatures using the Ferry & Spear calibration. If the Thompson calibration were used, the estimated pressures would be reduced (Fig. 2). For example, for  $\ln K_s = -4.5$  and  $T = 630^\circ\text{C}$ ,  $P = 6.3$  kbar; a reduction in temperature to  $600^\circ\text{C}$  would reduce P to 5.8 kbar. The conclusions regarding essentially constant pressure in the different metamorphic zones, however, would not change.

Although metamorphic temperatures generally increase from the staurolite-kyanite zone south to the sillimanite-K-feldspar zone (Table 3, Fig. 1), the metamorphic pressure remains nearly the same. This is consistent with the structural and stratigraphic data, which suggest little change in the postmetamorphic structural level. This is in contrast with the cross section from the staurolite-kyanite isograd north to Foster Creek (Simony *et al.* 1980, Ghent *et al.* 1979), where the postmetamorphic southerly plunge produces exposure of deeper and deeper levels.

CONCLUSIONS

1) Temperatures estimated from garnet-biotite geothermometry generally agree with maximum limits of temperature estimated from the maximum stability of muscovite-plagioclase-quartz. In some sillimanite-zone rocks, temperature estimates based upon the Ferry & Spear calibra-

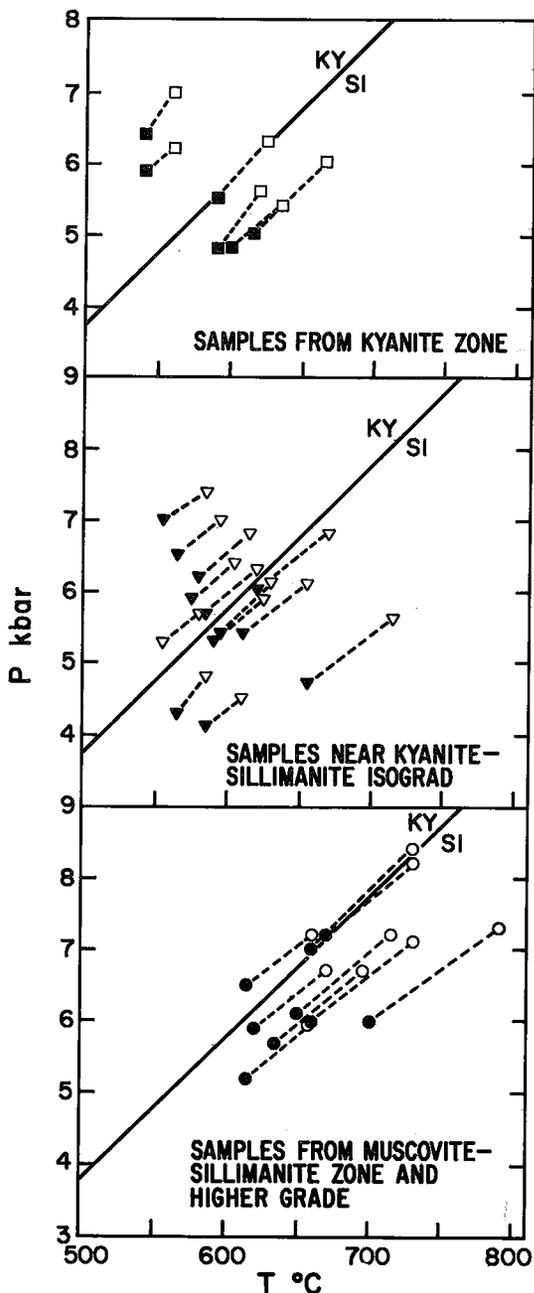


FIG. 2. Pressure-temperature diagrams showing estimated temperatures and pressures based on garnet-biotite and garnet-plagioclase- $\text{Al}_2\text{SiO}_5$ -quartz equilibria. Filled symbols are temperatures based on Thompson calibration; open symbols are temperatures based on Ferry & Spear calibration.

tion are higher than maximum stability limits of associated muscovite-plagioclase-quartz. The effects of compositional deviations from this ideal Fe-Mg binary system must be quantitatively corrected to make accurate estimates of temperature of metamorphism.

2) Garnet-biotite temperature estimates are difficult to make in the higher-grade rocks owing to chemical zonations of garnet. In sillimanite-zone rocks, the rim of a garnet crystal typically shows retrograde exchange of Mg, Fe and Mn with biotite and other phases.

3) Pressure estimates based upon garnet-plagioclase- $\text{Al}_2\text{SiO}_5$ -quartz show no significant variation with increasing metamorphic grade. This is consistent with the structural cross-section, which suggests that there is no significant postmetamorphic structural plunge in the southern end of the Mica Creek area.

#### ACKNOWLEDGEMENTS

The writers thank P.S. Simony of the University of Calgary for supplying some of the samples used in this study. We appreciate the constructive criticisms of M.L. Crawford, L.S. Hollister and J. Nicholls. Mrs. Vicki Roberts kindly typed the final manuscript. Ghent acknowledges financial support from NSERC Operating Grant A-4379 and EMR Research Contract 119-4-81.

#### REFERENCES

- ALBRECHT, J. & HEWITT, D.A. (1981): Substitutions in synthetic Ti-biotites. *Geol. Soc. Amer. Abstr. Program* 13, 393.
- BOHLEN, S.T. & ESSENE, E.H. (1980): Evaluation of coexisting garnet-biotite, garnet-clinopyroxene, and other Mg-Fe exchange thermometers in Adirondack granulites. *Geol. Soc. Amer. Bull.* 91, 695-719.
- BURNHAM, C.W., HOLLOWAY, J.R. & DAVIS, N.F. (1969): Thermodynamic properties of water to 1000°C and 10,000 bars. *Geol. Soc. Amer. Spec. Pap.* 132.
- CARMICHAEL, D.M. (1978): Metamorphic bathozones and bathograds: a measure of the depth of post-metamorphic uplift and erosion on the regional scale. *Amer. J. Sci.* 278, 769-797.
- CHATTERJEE, N.D. & FROESE, E. (1975): A thermodynamic study of the pseudobinary join muscovite-paragonite in the system  $\text{KAlSi}_3\text{O}_8$ - $\text{NaAlSi}_3\text{O}_8$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{H}_2\text{O}$ . *Amer. Mineral.* 60, 985-993.
- CRAW, D. (1978): Metamorphism, structure and stratigraphy in the southern Park Ranges, British Columbia. *Can. J. Earth Sci.* 15, 86-98.
- EUGSTER, H.P., ALBEE, A.L., BENCE, A.E., THOMPSON, J.B., JR. & WALDRAUM, D.R. (1972): The two-phase region and excess mixing properties of paragonite-muscovite crystalline solutions. *J. Petrology* 13, 147-179.
- FERRY, J.M. (1980): A comparative study of geothermometers and geobarometers in pelitic schists from south-central Maine. *Amer. Mineral.* 65, 720-732.
- & SPEAR, F.S. (1978): Experimental calibration of the partitioning of Fe and Mg between biotite and garnet. *Contr. Mineral. Petrology* 66, 113-117.
- GANGULY, J. (1979): Garnet and clinopyroxene solid solutions and geothermometry based on Fe-Mg distribution coefficient. *Geochim. Cosmochim. Acta* 43, 1021-1029.
- GHEENT, E.D. (1975): Temperature, pressure and mixed volatile equilibria attending metamorphism of staurolite-kyanite-bearing assemblages, Esplanade Range, British Columbia. *Geol. Soc. Amer. Bull.* 86, 1654-1660.
- (1976): Plagioclase-garnet- $\text{Al}_2\text{SiO}_5$ -quartz: a potential geobarometer-geothermometer. *Amer. Mineral.* 61, 710-714.
- , ROBBINS, D.B. & STOUT, M.Z. (1979): Geothermometry, geobarometry, and fluid compositions of metamorphosed calc-silicates and pelites, Mica Creek, British Columbia. *Amer. Mineral.* 64, 874-885.
- , SIMONY, P.S. & KNITTER, C.C. (1980): Geometry and pressure-temperature significance of the kyanite-sillimanite isograd in the Mica Creek area, British Columbia. *Contr. Mineral. Petrology* 74, 67-73.
- GOLDMAN, D.S. & ALBEE, A.L. (1977): Correlation of Mg/Fe partitioning between garnet and biotite with  $^{18}\text{O}/^{16}\text{O}$  partitioning between quartz and magnetite. *Amer. J. Sci.* 277, 750-767.
- HODGES, K.V. & SPEAR, F.S. (1982): Accuracy vs. reliability of element partitioning geothermometers and geobarometers. *Amer. Mineral.* 67, (in press).
- HOLDAWAY, M.J. (1971): Stability of andalusite and the aluminum silicate phase diagram. *Amer. J. Sci.* 271, 97-131.
- KNITTER, C.C. (1979): *Metamorphism and Structure of the Soards Creek Area, British Columbia*. M.Sc. thesis, Univ. Calgary, Calgary, Alta.

- NEWTON, R.C. & HASELTON, H.T. (1981): Thermodynamics of the garnet-plagioclase- $\text{Al}_2\text{SiO}_5$ -quartz geobarometer. In *Thermodynamics of Minerals and Melts* (R.C. Newton, A. Navrotsky & B.J. Wood, eds.), Springer-Verlag, New York.
- PELL, J. (1981): Metamorphism in the southern Cariboo Mountains, British Columbia. *Geol. Assoc. Can./Mineral. Assoc. Can. Program Abstr.* 6, 46.
- & SIMONY, P. (1981): Stratigraphy, structure, and metamorphism in the southern Cariboo Mountains, British Columbia. *Geol. Surv. Can. Pap.* 81-A, 227-230.
- SIMONY, P.S., GHENT, E.D., CRAW, D., MITCHELL, W. & ROBBINS, D.B. (1980): Structural and metamorphic evolution of northeast flank of Shuswap complex, southern Canoe River area, British Columbia. *Geol. Soc. Amer. Mem.* 153, 445-461.
- SPANG, J.H., SIMONY, P.S. & MITCHELL, W.J. (1980): Strain and folding mechanisms in a similar style fold from the northern Selkirks of the Canadian Cordillera. *Tectonophys.* 66, 253-267.
- STODDARD, E.F. (1980): Metamorphic conditions at the northern end of the northwest Adirondack Mountains. *Geol. Soc. Amer. Bull.* 91, 589-616.
- THOMPSON, A.B. (1976): Mineral reactions in pelitic rocks. I. Prediction of P-T-X(Fe-Mg) phase relations. II. Calculation of some P-T-X(Fe-Mg) phase relations. *Amer. J. Sci.* 276, 401-454.
- & TRACY, R.J. (1979): Model system for anatexis of pelitic rocks. II. Facies series melting and reactions in the system  $\text{CaO-KAlO}_2\text{-NaAlO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ . *Contr. Mineral. Petrology* 70, 429-438.
- TRACY, R.J. (1978): High grade metamorphic reactions and partial melting in pelitic schist, west-central Massachusetts. *Amer. J. Sci.* 278, 150-178.
- , ROBINSON, P. & THOMPSON, A.B. (1976): Garnet composition and zoning in the determination of temperature and pressure of metamorphism, central Massachusetts. *Amer. Mineral.* 61, 762-775.
- WOODSWORTH, G.J. (1977): Homogenization of zoned garnets from pelitic schists. *Can. Mineral.* 15, 230-242.

Received September 1981, revised manuscript accepted April 1982.