

**MINERAL EQUILIBRIA IN QUARTZ LEUCOAMPHIBOLITES
(QUARTZ – GARNET – PLAGIOCLASE – HORNBLLENDE CALC-SILICATES)
FROM SOUTHEASTERN BRITISH COLUMBIA, CANADA**

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ABSTRACT

Pods and lenses of leucoamphibolite a few meters in maximum dimension contain quartz (Qtz) – plagioclase (Pl) – hornblende (Hbl) – garnet (Grt) – epidote (Ep), with or without biotite (Bt). They occur within Late Precambrian clastic metasedimentary rocks of the Esplanade Range of southeastern British Columbia, and range in metamorphic grade from upper biotite zone to kyanite (Ky) zone (defined in pelitic rocks). Mineral equilibria using the database of Berman provide estimates of metamorphic pressure (P), temperature (T), and fluid compositions. These estimates can be compared to those from coexisting pelitic rocks to provide a check on consistency. Grt–Bt Mg–Fe exchange geothermometry suggests temperatures ranging from 530 to 580°C at 7 kbar. The lack of kyanite in leucoamphibolites suggests a maximum P of about 7–8 kbar. Pl–Qtz–Ep–Grt assemblages without calcite suggest H₂O-rich fluid compositions [generally $X(\text{H}_2\text{O}) > 0.8$]. For $a(\text{H}_2\text{O}) = 1.0$, Grt–Ep–Pl–Qtz–H₂O equilibria produce calculated temperatures near 565°C at 7 kbar. Although there is considerable overlap, estimates of P and T from the leucoamphibolites do not agree very well with estimates from nearby pelites. On the basis of natural occurrences, other investigators have suggested a miscibility gap and near-constant activity of anorthite over the range An_{40–90}. Electron-microprobe spot analyses in our study indicate that plagioclase compositions near ~An₄₀ and ~An₉₀ occur within single grains and within single samples. Other samples have compositions concentrated near either An₄₀ or An₉₀ or compositions with An_{≤40}. These results are consistent with petrological studies reported by other researchers.

Keywords: mineral equilibria, metamorphic plagioclase, pressure, temperature, fluid composition, amphibolite, Esplanade Range, British Columbia.

SOMMAIRE

Des lentilles de leucoamphibolite quartzifère mesurant quelques mètres en dimensions maximales contiennent l'assemblage quartz (Qtz) – plagioclase (Pl) – hornblende (Hbl) – grenat (Grt) – épidote (Ep), avec ou sans biotite (Bt). On les trouve dans une séquence de roches métasédimentaires tardi-précambriennes de la chaîne Esplanade, dans le sud-est de la Colombie-Britannique. Ces roches montrent un degré de métamorphisme allant de la zone à biotite supérieure à la zone à kyanite (Ky), définies dans les roches pélitiques. Les équilibres parmi les minéraux, étudiés avec la banque de données de Berman, mènent à une estimation de la pression (P), la température (T), et la composition de la phase fluide au cours du métamorphisme. On peut comparer ces estimés avec les valeurs dérivées des roches pélitiques coexistantes afin de vérifier la concordance interne des variables. La géothermométrie fondée sur l'échange Fe–Mg entre Grt et Bt indique un intervalle de températures allant de 530 à 580°C à 7 kbar. L'absence de kyanite dans les leucoamphibolites fait penser que la pression maximale était d'environ 7–8 kbar. Les assemblages à Pl–Qtz–Ep–Grt sans calcite indiquent une phase fluide riche en H₂O [$X(\text{H}_2\text{O})$ en général supérieur à 0.8]. Pour une valeur de $a(\text{H}_2\text{O})$ égale à 1.0, l'équilibre Grt–Ep–Pl–Qtz–H₂O mène à une température calculée près de 565°C à 7 kbar. Quoiqu'il y ait passablement de croisement, les estimations de P et de T faites à partir des leucoamphibolites ne concordent pas très bien avec celles dérivées des échantillons de pélite avoisinants. À la lumière des exemples naturels, d'autres chercheurs ont proposé l'existence d'une lacune de miscibilité et une activité de l'anorthite presque constante sur l'intervalle An_{40–90}. Les résultats de nos analyses à la microsonde électronique indiquent la présence de compositions près de An₄₀ et de An₉₀ à l'intérieur de cristaux et au sein d'un même échantillon. Dans d'autres échantillons, la composition du plagioclase est concentrée près de An₄₀ ou An₉₀, ou bien sa teneur en An est inférieure à 40%. Ces résultats concordent avec les études pétrologiques d'autres chercheurs.

Mots-clés: équilibre minéral, plagioclase métamorphique, pression, température, composition de la phase fluide, chaîne Esplanade, Colombie-Britannique.

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INTRODUCTION

Mineral assemblages in metamorphosed pelitic rocks have long been used in pressure–temperature petrogenetic grids (*e.g.*, Carmichael 1978) and in mineral equilibria to estimate pressure and temperature (*e.g.*, Ghent 1976). In this paper, we compare estimates of pressure, temperature, and fluid composition in some less common hornblende-bearing metasedimentary rocks in the Esplanade Range of southeastern British Columbia with results derived from nearby pelitic rocks. We also examine the phase relations of some metamorphic plagioclase.

GEOLOGICAL SETTING AND PREVIOUS WORK

The Windermere Series (Late Precambrian) in the Esplanade Range consists of metasedimentary rocks with lesser amounts of metabasalts. These rocks range in metamorphic grade from the biotite zone (greenschist facies) to the staurolite–kyanite zone (amphibolite facies, Fig. 1), defined in pelitic rocks. Details of the mapping of the pelitic isograds are presented in Ghent (1975). Metamorphic rocks in the Esplanade Range and adjacent areas have been the subject of several petro-

logical and isotopic studies (Jones 1972, Jones & Ghent 1971, Ghent & De Vries 1972, Ghent 1975, Ghent & O'Neil 1985, Gal & Ghent 1990). Limited geochronological studies indicate that metamorphism occurred in the Late Mesozoic (Ghent & McKee 1975). The metamorphic isograds have an outcrop pattern suggesting folding, but detailed structural and stratigraphic studies indicate that the relief on the isograds is dominantly primary (Fig. 1). The Windermere rocks are folded into a major premetamorphic syncline with a gentle northward plunge, suggesting little variation in structural depth.

FIELD RELATIONSHIPS, PETROGRAPHY,
AND MINERAL CHEMISTRY

Layers and lenses of quartz leucoamphibolites (quartz – garnet – plagioclase – hornblende calc-silicates) occur in southeastern British Columbia throughout the Late Precambrian Windermere Group and locally within the Lower Cambrian metasedimentary rocks. In the Esplanade Range (Fig. 1), these rocks occur within feldspathic psammites and grits, and range in thickness from less than 2.5 cm to about 0.6 m (Fig. 2). The rocks generally lack a strong directional

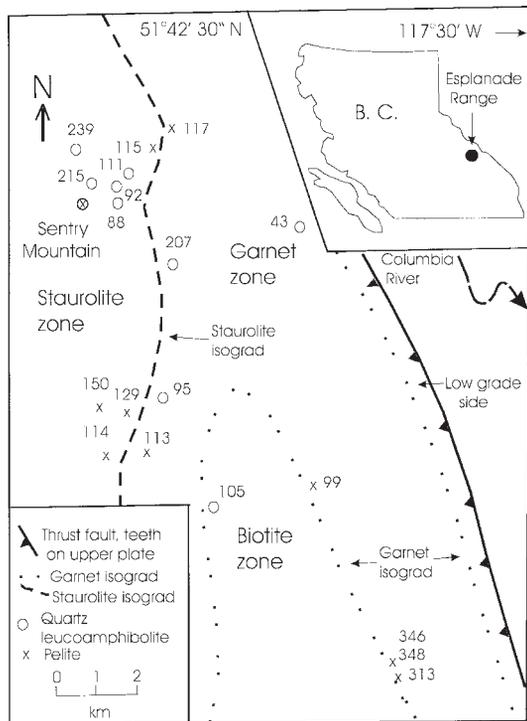


FIG. 1. Map of the Esplanade Range, British Columbia, showing metamorphic isograds in pelitic rocks, thrust faults, and sample localities.



FIG. 2. Outcrop photograph of quartz leucoamphibolite.

fabric (Fig. 2), and their textures are classified as granofelsic. Individual beds can be traced for distances as much as 15 m before they pinch out against metapsammite. On the basis of mineralogy, textures and the presence of trace amounts of calcite, we interpret these rocks to originally have been carbonate-bearing layers and nodules. The typical mineral assemblage in these rocks is hornblende – plagioclase – garnet – quartz – epidote. Some samples contain biotite, chlorite, titanite, calcite, and Fe–Ti oxides (Table 1; Ghent & De Vries 1972). Similar quartz leucoamphibolite pods occur in the Mica Creek area and in the Solitude Range, British Columbia (Gal & Ghent 1990).

These rocks are characterized by a high modal proportion of quartz (34–53%, Ghent & Devries 1972, p. 619). Garnet, hornblende, plagioclase, and epidote are rarely in direct contact, and the crystals are typically irregular in shape (Fig. 3; Ghent & De Vries 1972, p. 623). Because of the irregular shape of the crystals, particularly of garnet and plagioclase, it is difficult to do detailed studies of zoning and modeling of crystallization history. Representative results of electron-microprobe analyses are given in Table 2. The electron-microprobe analyses were done on an ARL SEMQ electron probe microanalyzer with nine wavelength-dispersion channels, housed at the Department of Geology and Geophysics, University of Calgary. Data were corrected according to the scheme of Bence & Albee (1968) using the programs of Nicholls & Stout (1988).

Compositions of garnet, epidote, and calcic amphibole

Grains of garnet show chemical zoning, both within crystals and among crystals in the same sample. The maximum range for spot analyses is: almandine (alm) 44 to 73 mol%, spessartine (sps) 5 to 17 mol%, pyrope (prp) 3 to 17 mol%, and grossular (grs) 8 to 34 mol%.

TABLE 1. MINERAL ASSEMBLAGES IN QUARTZ-BEARING LEUCOAMPHIBOLITES (CALC-SILICATE) SAMPLES, ESPLANADE RANGE, BRITISH COLUMBIA

sample	Grt	Amp	Pl	Bt	Ep	Other
CV-43 (G)	x	x	x		x	Ttn
CV-95 (G)	x	x	x	x	x	Chl–Ilm–Ttn
CV-105 (B)	x	x	x	x		Chl
CV-207 (G)	x	x	x	x	x	Chl–Ilm
CV-215 (S)	x	x	x		x	Ilm–Ttn
CV-239 (S)	x	x	x	x	x	Chl–Ilm–Ttn
GH-92 (S)	x	x	x			
GH-111 (S)	x	x	x		x	

Quartz is present in each sample. Abbreviations after Kretz (1983): Grt: garnet, Amp: Ca-amphibole, Pl: plagioclase, Bt: biotite, Ep: epidote, Rt: rutile, Ttn: titanite, Ilm: ilmenite, Chl: chlorite. (B): upper biotite zone; (G): garnet zone; (S): staurolite zone. x: present.

TABLE 2. REPRESENTATIVE COMPOSITIONS[§] OF MINERALS IN QUARTZ LEUCOAMPHIBOLITES FROM THE ESPLANADE RANGE, SOUTHEASTERN BRITISH COLUMBIA

Sample CV-95	Grt core	Grt rim	Bt	Amp	Pl	Ep	Ilm
SiO ₂ wt.%	36.96	37.37	37.48	41.32	59.93	38.76	-
TiO ₂	0.02	<0.02	0.96	0.62	n.a.	0.03	51.93
Al ₂ O ₃	20.53	21.36	17.40	16.94	25.51	28.42	-
FeO	31.18	28.62	19.03	17.35	n.a.	8.72 ^e	43.63
MnO	3.38	3.94	0.10	0.26	n.a.	0.03	1.53
MgO	1.66	1.77	10.88	7.67	n.a.	<0.03	0.08
CaO	5.96	7.25	0.04	11.95	7.86	23.75	n.a.
Na ₂ O	n.a.	n.a.	0.08	1.33	7.21	n.a.	n.a.
K ₂ O	n.a.	n.a.	9.80	0.29	0.04	n.a.	n.a.
F	n.a.	n.a.	0.62	0.21	n.a.	n.a.	-
H ₂ O	-	-	3.13	2.24	-	1.00	-
Sum	99.69	100.31	99.52*	99.74*	100.55	100.71	97.17
Number of atoms							
Si <i>apfu</i>	2.996	2.986	5.653	6.206	2.658	2.970	-
Al	0.004	0.014	2.347	1.794	1.333	0.030	-
Sum	3.000	3.000	8.000	8.000	3.991	3.000	-
Ti	0.001	0.000	0.109	0.008	-	0.002	1.015
Al	1.998	1.976	0.747	1.205	-	2.537	-
Fe ^{e+}	2.114	1.912	2.401	2.179	-	0.503 ^f	0.978
Mn	0.232	0.267	0.013	0.033	-	0.002	0.034
Mg	0.201	0.211	2.446	1.717	-	-	0.003
Ca	0.518	0.621	-	-	-	-	-
Sum C	5.023	5.009	5.716	5.142	-	3.044	1.015
Ca	-	-	0.006	1.923	0.373	1.950	0.800
Na	-	-	0.023	0.077	0.620	-	0.022
Sum B	-	-	-	2.000 ^a	0.995 ^a	1.95	0.822
Na	-	-	-	0.310	-	-	-
K	-	-	1.886 ^a	0.056	-	-	-
Sum A	-	-	1.930	0.366	-	-	-
Basis	-24 charge	-24 charge	-44 charge 4 OH ⁻	-46 charge 2 OH ⁻	-16 charge	-25 charge 1 OH ⁻	-6 charge

[§] Results of electron-microprobe analyses. n.a.: not analyzed; * total minus oxygen equivalent of fluorine; also includes 0.26% BaO. x includes 0.015 Ba atoms; a: includes 0.002 K atoms. e: Fe as Fe₂O₃; f: Fe³⁺. Abbreviations after Kretz (1983).

The maximum compositional range within a single crystal is in CV-239, with the almandine component ranging from 48 to 61 mol%, and the grossular component ranging from 32 to 19 mol%. We used garnet edges for calculations of mineral equilibria. Crystal edges typically show minimum values of spessartine + grossular and maximum values of almandine and pyrope components.

Epidote shows a narrow range of composition, ranging from 9 to 16 mol% of the "pistacite" (Ps) component. The maximum compositional range within a single crystal is Ps₁₂ to Ps₁₆. Titanium contents range from 0.01 to 0.03 wt.% TiO₂, Mn, from 0.03 to 0.24 wt.% MnO, and Mg, from 0.03 to 0.14 wt.% MgO.

Calcic amphibole is typically high in Al, with values as high as 17.8 wt.% Al₂O₃. Titanium contents are usually near 0.10 wt.% TiO₂. Potassium contents are typically less than 0.3 wt.% K₂O, and Na contents are usually near 1.5 wt.% Na₂O. A comparison of these

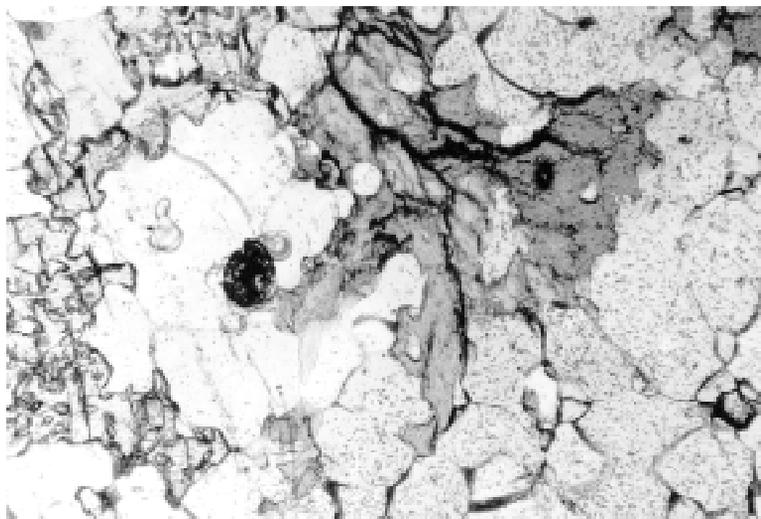


FIG. 3. Microphotograph of leucoamphibolite. Skeletal garnet at left side of photograph (high relief) and hornblende (dark-colored) at right side, set in a quartz matrix. Bottom of photograph is 1.4 mm long.

compositions with proposed correlations of calcic amphibole composition with pressure and temperature is rendered difficult by the fact that the published correlations are based upon calcic amphiboles from metabasites. One example indicates the difficulty. Ernst & Liu (1998) correlated the Ti and Al contents of the calcic amphibole with pressure and temperature. If we plot our data on their diagrams, we get implausible results. As an example, using the Ti content of the amphibole in Table 2 (CV-95, 0.92 wt.% TiO_2) and plotting it on their Figure 10 (p. 962) yields a temperature near 600°C at $P = 10$ kbar. The Al content, 16.9 wt.% Al_2O_3 , would indicate a pressure greater than 25 kbar (extrapolated) at a temperature of 550°C .

Plagioclase compositions

The interpretation of subsolidus phase relationships of plagioclase has been a long-standing problem for mineralogists and petrologists (*e.g.*, Smith 1974). Miscibility gaps between $\sim\text{An}_0$ and $\sim\text{An}_{25}$ (peristerite), between An_{66} and An_{87} (Hüttenlocher), and between An_{45} and An_{65} (Bøggild) have been documented. A temperature–composition phase diagram for plagioclase (*e.g.*, Spear 1993, p. 82) indicates that at temperatures less than about 800°C or so, there is a miscibility gap, referred to as the Voll gap. This gap suggests possible coexistence of oligoclase and anorthite at lower temperature. With increasing temperature, the oligoclase increases in anorthite content.

Grove *et al.* (1983, 1986) have argued that coexisting An_{39} and An_{88} near Thetford, Maine are a stable

equilibrium assemblage. This interpretation was based on Spear's evidence that plagioclase and amphibole were in cation-exchange equilibrium (Spear 1980). An exchange relation exists between anorthite (CaAl) and albite (NaSi) in plagioclase and tschermakite ($\text{CaM}_4^{\text{IVAl}}$) and glaucophane ($\text{NaM}_4^{\text{IVSi}}$). In our study, we have documented $\sim\text{An}_{40}$ and $\sim\text{An}_{90}$ within single grains (CV-43). Andesine ($\sim\text{An}_{40}$) typically occurs within the core of grains, and more calcic plagioclase ($\sim\text{An}_{90}$) occurs on the rims, but compositions near An_{40} also occur at grain margins and in small grains. No compositions near An_{66} were observed, but several compositions are in the range An_{58-62} . Other compositions determined by spot analyses are in the range An_{76-86} (Fig. 4). Spear (1980) also found andesine commonly in cores of grains and bytownite at the rims. Grove *et al.* (1983) interpreted intermediate compositions between An_{39} and An_{88} as mixtures. We examined a plot of tie lines connecting X_{NaM_4} (~ 0.1) in calcic amphibole rims against X_{an} (~ 0.90) in plagioclase rims. The tie lines for our samples cross those presented by Spear (1980), but there is a large uncertainty in the calculation of NaM_4 in a calcic amphibole, and the calcic amphiboles from British Columbia are different in composition from those considered by Spear (see discussion above).

Ferry (1980) did not find coexisting andesine and bytownite, but found evidence that compositions of $\sim\text{An}_{40}$ and $\sim\text{An}_{90}$ are strongly favored. We have found similar evidence in our study (Fig. 4). For example, sample CV-215 contains only bytownite–anorthite (An_{85-94}), whereas CV-95 contains oligoclase–andesine (cores An_{35-46} zoned to An_{23-26} , see Fig. 4).

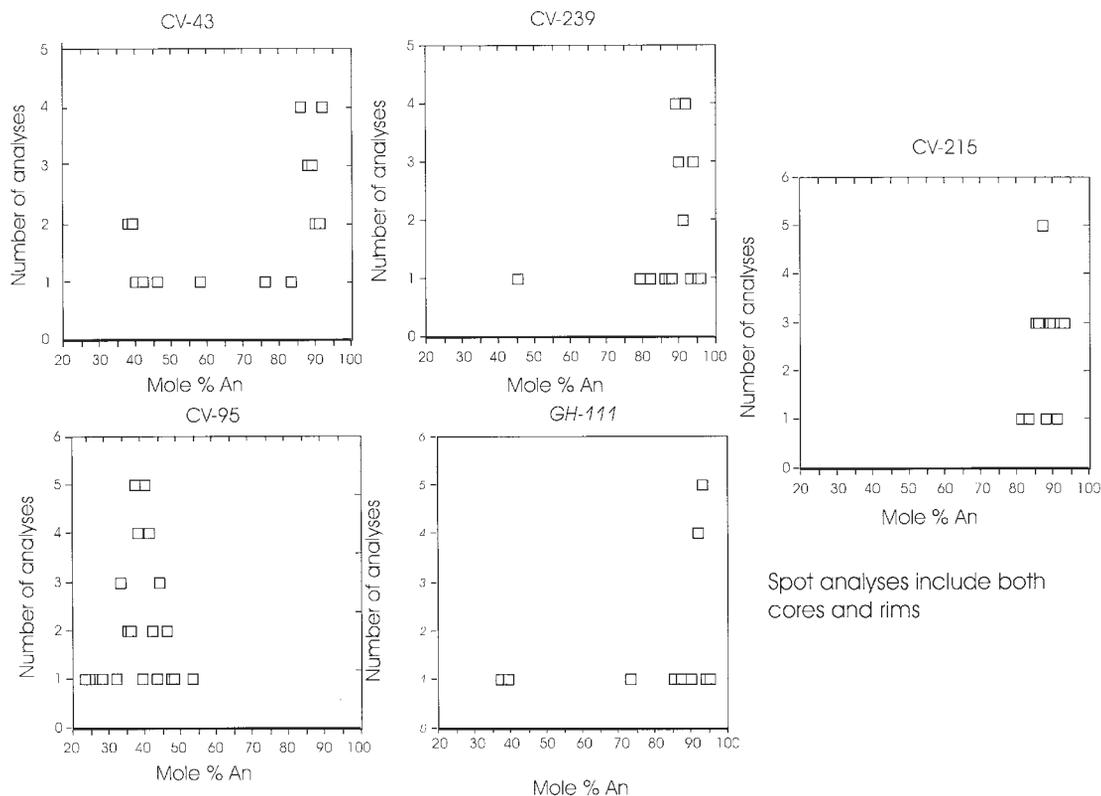


FIG. 4. Electron-microprobe results from spot analyses of plagioclase from quartz leucoamphibolites. Plot of number of analyses against anorthite in mole % for five samples.

PHASE EQUILIBRIA

Thermodynamic database

In the phase-equilibrium calculations, we have used the program of Brown *et al.* (1988) and the thermodynamic database of Berman (1988) for the phase components. The solution models used were: garnet: Berman (1990); plagioclase: Fuhrman & Lindsley (1988); biotite: McMullin *et al.* (1991); calcic amphibole: Mäder *et al.* (1994); epidote: $(1-3X_{\text{Fe}})$, where X_{Fe} is the mole fraction of Fe^{3+} in octahedral sites (Jenkins *et al.* 1985); titanite: $(X_{\text{Ca}}*X_{\text{Ti}})$; Ghent & Stout (1994), where X_{Ca} is the mole fraction of Ca in the 8-fold site, and X_{Ti} is the mole fraction of Ti in the octahedral site.

Activity-composition relations in plagioclase

Activity-composition relations in plagioclase have been determined by thermochemical studies and by analysis of plagioclase coexisting with various mineral assemblages at estimated pressures and temperatures.

Reviews of activity-composition relationships in plagioclase were made by Newton *et al.* (1980), Fuhrman & Lindsley (1988), Elkins & Grove (1990) and Holland & Powell (1992). These studies have emphasized the high structural-state (*i.e.*, disordered) plagioclase, *e.g.*, Newton *et al.* (1980). Rebbert & Rice (1997) recently reviewed activity-composition relations in plagioclase based upon plagioclase equilibria with a variety of coexisting minerals. None of the activity-composition relationships calculated at 550°C suggest a close approach to a constant value of the activity of anorthite between X_{an} 0.4 and ~0.9 (Fig. 5). In a section below, we examine the consequences of this disagreement on a calculation of mineral equilibria involving $X_{\text{an}} \approx 0.4$.

Discussion of critical mineral equilibria

Because of the variety of minerals present in the quartz leucoamphibolites, there are several pertinent phase-equilibria relationships. We discuss each of these in turn.

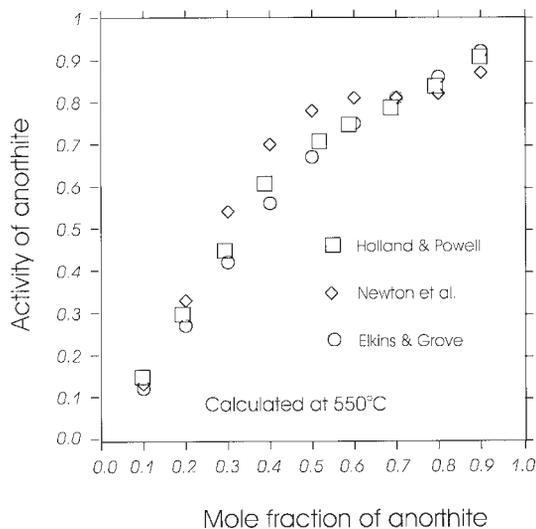


FIG. 5. Calculated activity–composition relations for plagioclase at 550°C, using various expressions for the Margules parameters.

An important geothermometer based upon Fe–Mg exchange equilibrium is that between garnet and biotite (*e.g.*, Ferry & Spear 1978, Table 3, equation 1). One of the advantages of this equilibrium is that it can be compared with garnet–biotite Fe–Mg exchange geothermometry in nearby pelitic rocks.

Mäder *et al.* (1994) have empirically calibrated the Fe–Mg exchange between amphibole and garnet as a geothermometer (Table 3, equations 2 and 3). They suggested that the Fe–Mg exchanges between tremolite – “Fe-tremolite” (Fe-tremolite is not an IMA-recognized name) and Mg–Fe garnet and tschermakite – “Fe-tschermakite” (Fe-tschermakite also is not a recognized name) and Mg–Fe garnet are the most robust geothermometers.

These rocks do not contain a reaction assemblage that is both vapor-absent and pressure-sensitive. The equilibrium anorthite – grossular – Al_2SiO_5 – quartz (Table 3, equation 4), in the presence of garnet – plagioclase – quartz and the absence of kyanite, can be used to set a maximum possible limit on metamorphic pressure at a given temperature.

If an activity of H_2O is assumed, the equilibrium among anorthite, clinozoisite, grossular, quartz, and H_2O (Table 3, equation 5) can be used to estimate temperature at a given pressure.

A test of the reasonableness of the assumption that $a(\text{H}_2\text{O}) \approx 1.0$ can be made by calculation of a T – $X(\text{CO}_2)$ diagram at constant pressure. The occurrence of garnet, epidote, plagioclase and quartz, and the ab-

TABLE 3. CRITICAL PHASE-EQUILIBRIA REFERRED TO IN THIS PAPER

(1)	annite + pyrope = phlogopite + almandine
(2)	5 tremolite + 3 almandine = 5 “Fe-tremolite” + pyrope
(3)	tschermakite + almandine = “Fe-tschermakite” + pyrope
(4)	3 anorthite = grossular + 2 kyanite + quartz
(5)	4 clinozoisite + quartz = 5 anorthite + grossular + 2 H_2O
(6)	2 clinozoisite + CO_2 = 3 anorthite + calcite + H_2O
(7)	calcite + rutile + quartz = titanite + CO_2
(8)	2 clinozoisite + titanite = rutile + grossular + 2 anorthite + H_2O
(9)	2 clinozoisite + rutile + quartz = titanite + 3 anorthite + H_2O
(10)	grossular + 2 paragonite + 3 quartz = 3 anorthite + 2 albite + 2 H_2O
(11)	annite + 2 paragonite + 3 quartz = muscovite + almandine + 2 albite + 2 H_2O
(12)	2 paragonite + phlogopite + 3 quartz = pyrope + muscovite + albite + 2 H_2O
(13)	anorthite + 2 calcite + quartz = grossular + CO_2
(14)	2 clinozoisite + 5 calcite + 3 quartz = 3 grossular + 5 CO_2 + H_2O

Note that “Fe-tremolite” and “Fe-tschermakite” do not conform to the IMA-approved terminology of amphibole-group minerals.

sence of calcite, constrain the fluid’s composition to relatively high values of $X(\text{CO}_2)$ (Table 3, equation 6).

Less precise limits on pressure, temperature and fluid compositions can be made using equilibria involving Ti-bearing phases. For equilibria involving CO_2 (Table 3, equation 7), the lack of calcite + rutile in the presence of titanite + quartz sets a limit on $X(\text{CO}_2)$ at a given temperature and total pressure.

Estimation of P – T – $X(\text{H}_2\text{O})$

In the section that follows, we discuss the methods used to estimate P – T – $X(\text{H}_2\text{O})$ by presenting the details for one sample, CV-95 (garnet zone). Where possible, we compare our estimates with those derived from pelitic rocks (Tables 4, 5, and 6).

Garnet–biotite Fe–Mg exchange geothermometry for three pairs yields $530 \pm 10^\circ\text{C}$ (one standard deviation) at 7 kbar. This equilibrium has a dP/dT slope of about $5^\circ\text{C}/\text{kbar}$. The intersection of the P – T curves for equilibrium (4), $3 \text{ an} = \text{grs} + 2 \text{ ky} + \text{qtz}$, and for the garnet–biotite Fe–Mg exchange is 540°C and 7.6 kbar. The lack of kyanite in this sample suggests that this is the upper limit of metamorphic pressure at this temperature.

Garnet–hornblende Fe–Mg exchange suggests a temperature of about 570°C for equilibrium (2) and 550°C for equilibrium (3) at 7 kbar. These equilibria have a dP/dT slope of about $5^\circ\text{C}/\text{kbar}$.

For equilibrium (5), the estimated temperature is about 560°C at 7 kbar for $a(\text{H}_2\text{O}) = 1.0$.

We examined the equilibria on a T – $X(\text{H}_2\text{O})$ diagram (Fig. 6) for the assemblage plagioclase – garnet – epidote – quartz – fluid without calcite. Equilibrium (6) intersects other equilibria at $T = 535 \pm 25^\circ\text{C}$ and $X(\text{CO}_2) < 0.2 \pm 0.19$ at 7 ± 1 kbar [note $1 - X(\text{H}_2\text{O}) = X(\text{CO}_2)$, Fig. 6]. These results are consistent with the garnet–biotite Fe–Mg exchange geothermometry. The inference that these leucoamphibolite pods were originally car-

TABLE 4. SUMMARY OF PRESSURE – TEMPERATURE – FLUID COMPOSITION ESTIMATES USING PTAX

Sample	Eqn 1 T °C	Eqn 2 T °C	Eqn 3 T °C	Eqn 4 P kbar T °C	Eqn 5 T °C	Eqn 6 X(CO ₂) T °C	Eqn 7 X(CO ₂)
CV-43 (G)		480	485	<8.4 550	565	<0.2 570	<0.2
CV-95 (G)	530 ±10	570	550	<7.6 550	560	<0.2 535	<0.2
CV-105 (B)		565 ±60	580 ±55	<6.2 550			
CV-207 (G)	540 ±5	575 ±15	565 ±15	<8.8 550			
CV-215 (S)	545 ±5	465	425	<7.6 550	555	<0.3 555	<0.2
CV-239 (S)	580 ±5	535	535	<5.4 550	550	<0.5 540	<0.2
GH-92 (S)		550 ±10	570 ±20	<6.9 550			
GH-111 (S)		505	495	<6.8 550	535	<0.3 530	

Equations 1, 2, and 3 calculated at 7 kbar; Equation 4: maximum pressure at T; Equation 5 calculated at 7 kbar, $\alpha(\text{H}_2\text{O}) = 1.0$; Equation 6: $X(\text{CO}_2)$ at the specified temperature and 7 kbar total pressure; Equation 7: calculated at 550°C and 7 kbar total fluid pressure. (B): upper biotite zone, (G): garnet zone, (S): staurolite zone.

bonate-rich suggests that the initial metamorphic fluid could have been richer in CO₂, but that once all of the calcite or dolomite or both had been used up in reactions, the final composition of the fluid that equilibrated with these minerals would be H₂O-rich.

The sample contains titanite plus quartz and lacks calcite + rutile. For equilibrium (7), the calculated T–X(CO₂) diagram indicates $X(\text{CO}_2) < 0.2$ at 550°C and 7 kbar total fluid pressure. We attempted to use other equilibria involving Ti-bearing phases to set limits on P and T. The equilibria (8), 2 clinozoisite + titanite = rutile + grossular + 2 anorthite + H₂O, and (9), 2 clinozoisite + rutile + quartz = titanite + 3 anorthite + H₂O, yield inconsistent results on a P–T diagram with $\alpha(\text{H}_2\text{O}) = 1.0$. The assemblage lacks rutile, but rutile lies on the high-temperature side of equation (8) and on the low-temperature side of equation (9). This finding suggests that either the titanite is not in equilibrium with the other minerals or that the thermodynamic data are inaccurate.

Connolly & Cesare (1993) have suggested that a C–O–H fluid produced by the equilibration of H₂O and excess graphite must maintain the atomic ratio H/O of water, 2:1. H₂O is the dominant species relative to CO₂ and CH₄ at 550°C and 7 kbar for these restrictions (Connolly & Cesare 1993, Fig. 1a, p. 380). This inference is consistent with the estimates of H₂O/CO₂ for the binary system discussed above. In addition, ilmenite is the only Fe–Ti–O phase predicted to be stable with

quartz at T > 400°C and P < 10 kbar at oxygen fugacities calculated with the Connolly & Cesare model of excess graphite and the atomic ratio H/O of water, 2:1.

Application of INVEQ to estimation of pressure and temperature

In the INVEQ method (Gordon 1992, 1998, Gordon *et al.* 1994, Ghent & Gordon 2000), P and T estimates are found by finding the best-fit hyperplane to the partial molar free energies of all phase components rather than the traditional method of using a set of independent equilibria, *e.g.*, the approach of Berman (1990). The INVEQ approach has the advantage of providing a measure of misfit for each individual phase component and an easily computed region of confidence. This program calculates only vapor-absent equilibria. In Table 5, we report the calculated values of pressures and temperatures using the following phase components: quartz, anorthite, albite, pyrope, almandine, grossular, clinozoisite, tremolite, “Fe-tremolite”, tschermakite, “Fe-tschermakite”, pargasite, and “Fe-pargasite”. We calculated pressures and temperatures for CMASH (CaO–MgO–Al₂O₃–SiO₂–H₂O), CFMASH (with FeO), and NCFMASH (with Na₂O). The method of calculat-

TABLE 5. APPLICATION OF INVEQ TO QUARTZ LEUCOAMPHIBOLITES, ESPLANADE RANGE, SOUTHEASTERN BRITISH COLUMBIA

Sample	CMASH T °C, P bars (std dev T, P)	CFMASH T °C, P bars (std dev T, P)	NCFMASH T °C, P bars (std dev T, P)
CV-43	561, 6365 (44, 539)	460, 6663 (15, 524)	457, 7032 (14, 511)
CV-95	874, 8772 (51, 578)	546, 7289 (17, 567)	557, 6379 (16, 555)
CV-105	n.a.	627, 5562 (22, 917)	626, 5075 (21, 821)
CV-207	n.a.	565, 7059 (20, 948)	565, 6888 (19, 856)
CV-215	n.a.	467, 7864 (15, 539)	467, 7754 (14, 522)
CV-239	1093, 9890 (73, 520)	557, 9047 (18, 545)	556, 8890 (17, 527)
GH-92	n.a.	546, 5943* (19, 814)	544, 5809* (20, 755)
GH-111	1219, 10380 (77, 514)	519, 8992 (17, 548)	519, 8835 (15, 530)

CMASH: CaO–MgO–Al₂O₃–SiO₂–H₂O, F: FeO, N: Na₂O. Phase components are: grossular, pyrope, almandine, clinozoisite, tremolite, “Fe-tremolite”, tschermakite, “Fe-tschermakite”, pargasite, “Fe-pargasite”, albite, anorthite, and quartz. The standard deviation (std dev) is shown in parentheses. n.a.: not applicable, no epidote present. * For Gh-92, temperature, pressure estimates are the means of five sets of P, T, and Amp compositions. Note that “Fe-tremolite”, “Fe-tschermakite” and “Fe-pargasite” do not conform to the IMA-approved terminology of amphibole-group minerals.

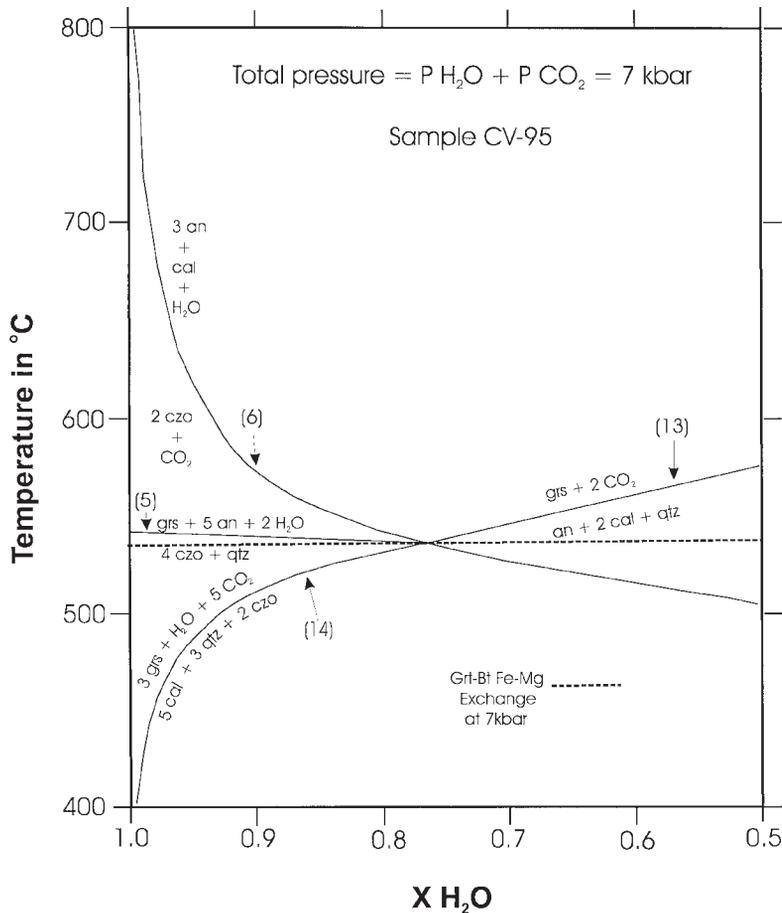


FIG. 6. Temperature- $X(H_2O)$ diagram at 7000 bars total fluid pressure. For sample CV95-1, the assemblage epidote - quartz - garnet - plagioclase - H_2O (fluid) and the lack of calcite constrain the equilibrium to lie along equilibrium (5) and at higher values of $X(H_2O)$ than 0.76.

ing variances for P and T quoted in the tables is discussed in Ghent & Gordon (2000), and uses a default *a priori* estimated error of $\pm 1 \text{ kJ}$ for each phase component. For sample GH-92, we obtained results on five different sets of plagioclase, garnet, and hornblende compositions and calculated a mean and standard deviation with the P and T calculated from INVEQ. These values can be compared with the results of Fe-Mg exchange thermometry between garnet and hornblende calculated from the same five datasets using PTAX (the program of Brown *et al.* 1988). For the PTAX calculations, the results from equations (2) and (3) are: 550 ± 10 and $570 \pm 20^{\circ}\text{C}$, respectively. The values from INVEQ are, for NCFMASH $546 \pm 19^{\circ}\text{C}$ and for CFMASH, $544 \pm 20^{\circ}\text{C}$. The upper limit on pressure calculated from PTAX is 6.9 kbar at 550°C , and the

results from INVEQ are, for NCFMASH, $5.9 \pm 0.8 \text{ kbar}$, and for CFMASH, $5.8 \pm 0.8 \text{ kbar}$.

A comparison of the P - T values using PTAX and INVEQ results calculated with either CFMASH and NCFMASH shows that the latter two are within the variance. To make comparisons, we can extrapolate the PTAX estimates to the pressure estimated from INVEQ for each sample, using a typical gradient of 5°C/kbar . There is no systematic difference between the estimates based upon the different methods, but it must be emphasized that we did not estimate pressure directly using PTAX.

A comparison of the results of PTAX and INVEQ for the same dataset and phase components of CV-43 is presented in Figure 7. Only stable equilibria from PTAX are plotted. Note the large number of intersections for

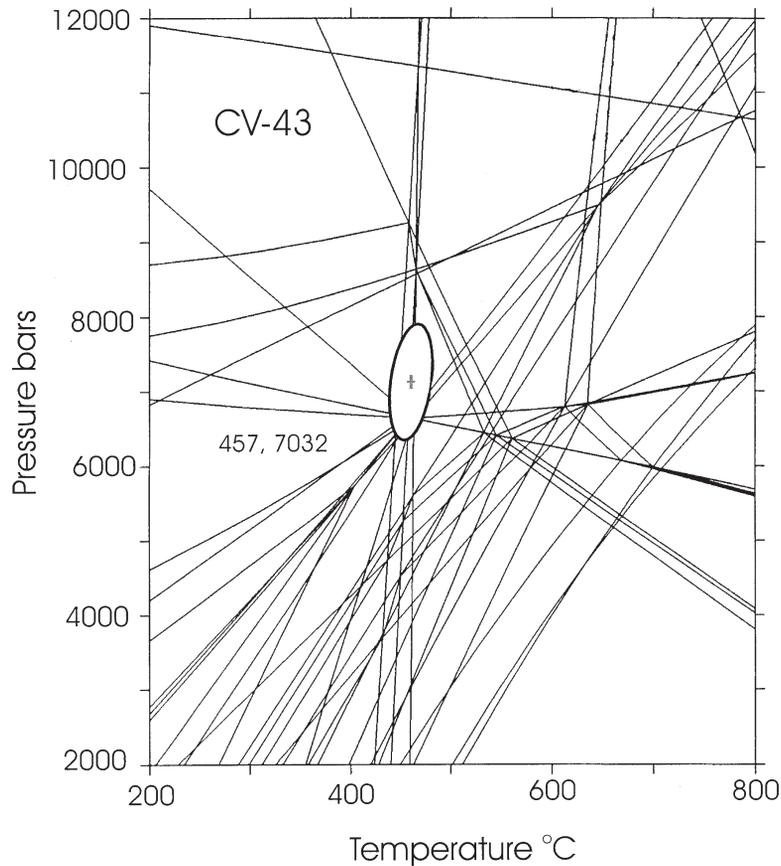


FIG. 7. Plot of INVEQ P-T estimates against those estimated from PTAX. Lines in P-T space are stable equilibria calculated from PTAX. Point at 457°C and 7032 bars is calculated from INVEQ for the same phase components. Ellipse is 68.3% confidence limits using a default uncertainty of ± 1 kJ for each phase component. See text for discussion.

the PTAX calculations, which are extremely difficult to interpret. The estimated P and T and the associated error ellipse are generated by INVEQ with the aforementioned uncertainty of ± 1 kJ for each phase component. This provides a more realistic estimate of the uncertainty than does an average of the intersections (see Berman 1991).

PTX COMPARISONS

P-T-X(H₂O) estimates for pelites from the Esplanade Range are presented in Table 6. Pressures and temperatures have been estimated from garnet-plagioclase-muscovite-biotite-quartz equilibria (*e.g.*, Ghent & Grover 1995). Fluid compositions have been estimated using the following equilibria: (10) grs + 2 paragonite (prg) + 3 qtz = 3 an + 2 ab + 2 H₂O; (11) annite (ann) +

2 prg + 3 qtz = muscovite (ms) + alm + 2 ab + 2 H₂O; (12) 2 prg + phlogopite (phl) + 3 qtz = prp + ms + ab + 2 H₂O (Table 3). There is a poor correlation of Fe-Mg garnet-biotite exchange temperatures with metamorphic grade (see also Ghent & Valley 1998). The estimated range of temperature from the garnet "isograd" to the staurolite "isograd" is about 75°C (Spear 1993, p. 355).

A plot of P-T estimates for leucoamphibolites and pelites is presented in Figure 8. Since there are no direct estimates of pressure for the leucoamphibolites, we have plotted temperature estimates for garnet-biotite Fe-Mg exchange geothermometry at 7 kbar and have averaged the two estimates of temperature for Fe-Mg garnet-hornblende exchange geothermometry and, for clarity, plotted them at 7.2 kbar. The temperature estimates for the pelites do not show a consistent increase from the garnet zone to the staurolite zone, but they generally

TABLE 6. ESTIMATES OF PRESSURE, TEMPERATURE, AND FLUID COMPOSITION FOR PELITIC ROCKS, ESPLANADE RANGE, BRITISH COLUMBIA

Sample no.	Pressure, kbar	T, °C	X(H ₂ O)
CV-99 (G)	8.6	565	0.5
CV-113 (G)	8.5	575	0.4
CV-114 (S)	8.8	630	0.6
CV-150 (S)	7.7	555	0.5
GH-115 (S)	6.3	560	0.5
GH-117 (G)	9.1	625	0.9
Gh-129 (S)	7.6	545	0.4
JH-313 (G)	7.5	525	0.2
JH-346 (G)	8.1	515	0.2
JH-348 (G)	7.7	520	0.2

X(H₂O) is [1 - X(CO₂)]. See text for explanation of the calculations.

give higher temperatures than the temperatures estimated from the leucoamphibolites. Pressure estimates from the pelites are generally higher than the maximum possible pressures estimated from the lack of kyanite in leucoamphibolites (Fig. 8, Table 4).

We can compare closely spaced samples directly. As an example, leucoamphibolite CV-95 gives garnet-biotite Fe-Mg temperature of $530 \pm 10^\circ\text{C}$ at 7 kbar, and pelite CV-113 gives a temperature of 575°C at 8.5 kbar. Garnet-hornblende Fe-Mg temperatures are 570 and 560°C (7 kbar), respectively, and equilibrium (5) gives 560°C at 7 kbar and $a(\text{H}_2\text{O}) = 1.0$. Fluid compositions estimated for CV-95 have $X(\text{H}_2\text{O}) > 0.8$, but equilibria (10), (11), and (12) for CV-113 give $X(\text{H}_2\text{O}) = 0.4$ at 575°C and 8.5 kbar total pressure. The problem of estimating $X(\text{H}_2\text{O})$ in medium-grade pelites has been discussed elsewhere (*e.g.*, Ghent & Grover 1995). The

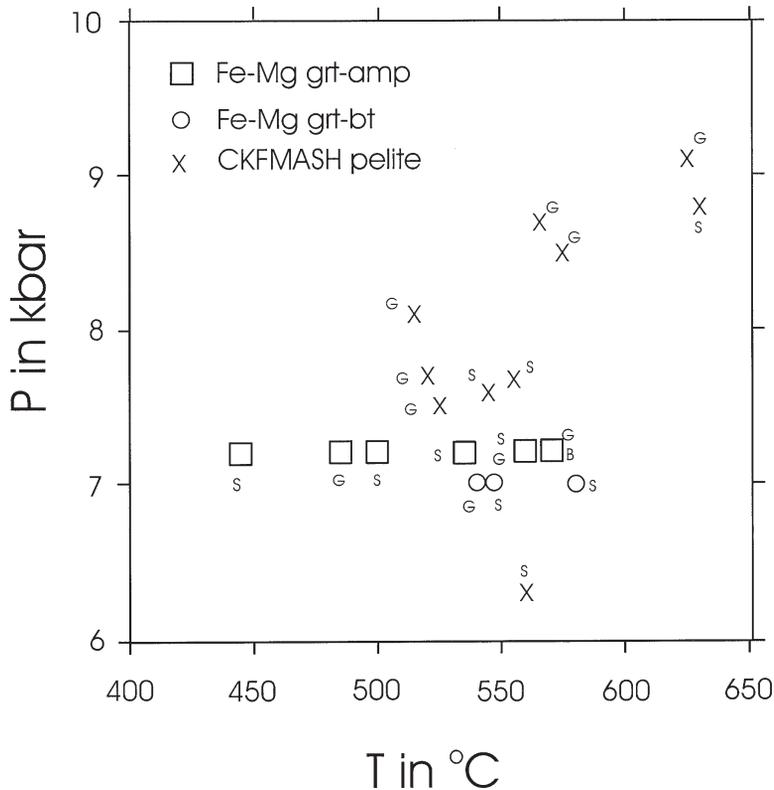


FIG. 8. Pressure-temperature plot of results from Fe-Mg exchange in garnet-biotite and garnet-hornblende for leucoamphibolites against CKFMASH mineral equilibria for pelites.

calculation of equilibria (10), (11) and (12) is very sensitive to temperature and thermodynamic properties of the phase components. For example, if the temperature were about 600°C, the value of $X(\text{H}_2\text{O})$ would increase to near 0.8. Making the enthalpy of formation from the elements at 298 K and 1 bar, $H_{f,298}^\circ$, of paragonite more positive by 2 kJ would increase $X(\text{H}_2\text{O})$ to near 0.7.

CONCLUSIONS

For the quartz leucoamphibolites from the Esplanade Range, garnet–biotite Fe–Mg exchange geothermometry suggests a temperature ranging from 520 to 580°C at 7 kbar, and garnet–hornblende Fe–Mg exchange geothermometry suggests temperatures ranging from 425 to 580°C. There is no systematic increase in metamorphic temperature with increasing grade based upon pelitic metamorphic zones. The lack of kyanite in the leucoamphibolites suggests a maximum P of about 7–8 kbar. Plagioclase – quartz – epidote – garnet assemblages without calcite suggest H_2O -rich fluid compositions [generally $X(\text{H}_2\text{O}) > 0.8$]. This inference is consistent with an interpretation of the field relations. The leucoamphibolites occur as small bodies within large volumes of quartz-rich metasedimentary rocks; any CO_2 produced during metamorphism would be greatly diluted by the large quantities of H_2O from dehydration reactions in the quartz-rich metasedimentary rocks. For $a(\text{H}_2\text{O}) = 1.0$, calculation of garnet – epidote – plagioclase – quartz – H_2O equilibria results in temperatures between 535 to 565°C at 7 kbar. On the basis of natural occurrences, other investigators have suggested a miscibility gap and near-constant activity of anorthite over the range An_{40-90} . Electron-microprobe spot analyses in our study indicate that plagioclase compositions near $\sim\text{An}_{40}$ and $\sim\text{An}_{90}$ occur within single grains and within single samples. Other samples have compositions concentrated near either An_{40} or An_{90} or compositions with An contents ≤ 40 mol%.

Temperatures estimated from pelitic rocks are generally higher than those from the leucoamphibolites, but there is no systematic increase in temperature with increasing metamorphic grade based upon the metamorphic zones. Fluid compositions estimated for the pelites are systematically lower in $X(\text{H}_2\text{O})$ than those from leucoamphibolites, and are lower than those estimated from C–H–O equilibria for consistent values of $f(\text{O}_2)$.

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