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CHLORITOID-PARAGONITE-PYROPHYLLITE AND STILPNOMELANE-BEARING ROCKS NEAR BLACKWATER MOUNTAIN, WESTERN ROCKY MOUNTAINS, BRITISH COLUMBIA

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ABSTRACT

Metasedimentary rocks of the Middle Cambrian Chancellor Formation near Blackwater Mountain, British Columbia, contain paragonite–chloritoid assemblages and locally contain pyrophyllite. Rocks of more mafic composition interlayered with the aluminous metasediments contain stilpnomelane–biotite. Calcite (± dolomite) is present in most rocks, and calcite–dolomite geothermometry suggests a metamorphic temperature near 345°C, which is consistent with the stability of pyrophyllite + quartz, at $P(H_2O) = P_{\text{total}} = 5$ kbars, that is, $310 < T < 415°C$. Mineral assemblages containing paragonite + chloritoid + calcite + dolomite could have equilibrated under slightly lower temperatures or slightly different (more CO_2-rich) composition of the fluid phase (or both) than those rocks that contain chlorite + albite + calcite + dolomite.

Keywords: metamorphism, chloritoid, pyrophyllite, stilpnomelane, T-$X(CO_2)$ diagrams, geothermobarometry, British Columbia.

SOMMAIRE

Les roches métasédimentaires de la Formation Chancellor, d'âge cambrien moyen, provenant de près de la montagne Blackwater, en Colombie-Britannique, contiennent l'assemblage de paragonite + chloritoïde avec, par endroits, de la pyrophyllite. Des roches de composition mafique, interlitées avec les métasédiments hyperalumineux, contiennent stilpnomélane + biotite. La calcite (± dolomite) est présente dans la plupart des roches. L'application géothermométrique de l'assemblage calcite–dolomite indique une température métamorphique d'environ 345°C, ce qui concorde avec le champ de stabilité de pyrophyllite + quartz à une valeur de $P(H_2O) = P_{total} = 5$ kbars, c'est-à-dire $310 < T < 415°C$. Les assemblages contenant paragonite + chloritoïde + calcite + dolomite pourraient témoigner soit d'une température légèrement inférieure, soit d'une phase fluide légèrement enrichie en CO_2, en comparaison des roches ayant chlorite + albite + calcite + dolomite.

(Traduit par la Rédaction)

Mots-clés: métamorphisme, chloritoïde, pyrophyllite, stilpnomélane, diagrammes T - $X(CO_2)$, géothermobarométrie, Colombie-Britannique.

INTRODUCTION

Aluminous mineral assemblages such as pyrophyllite + paragonite are useful in the estimation of peak metamorphic conditions in the lower grades of metamorphism (*e.g.*, Zen & Thompson 1974). Unfortunately, these mineral assemblages are relatively uncommon and as yet have not been well documented in the Rocky Mountain Fold and Thrust Belt, particularly in the western Rocky Mountains, where argillaceous and carbonate rocks of Lower Paleozoic to Late Precambrian age typically show pervasive slaty cleavage. In this paper, we document the occurrence of aluminous mineral assemblages, including chloritoid–paragonite–pyrophyllite, associated with more mafic assemblages containing stilpnomelane.

Although recognized on maps as a distinct geological unit, the western part of the Rocky Mountain Fold and Thrust Belt has clear structural and metamorphic affinities with the rocks of the Omineca Crystalline Belt to the west. For example, Craw (1978) reported that Lower Paleozoic to Late Precambrian rocks of the Park Ranges, British Columbia, were metamorphosed to sillimanite-zone conditions. These rocks are in contact along the Purcell Fault with rocks of the Omineca Crystalline Belt and were once part of a contiguous metamorphic complex.

Cruickshank & Ghent (1978) reported on chloritoid–paragonite assemblages in the Late Precambrian Horsethief Creek Group, approximately 50 km west of the area described in this paper. They examined metasedimentary rocks of Late Precambrian age near Lake Louise, Alberta, but found quartz–muscovite–chlorite assemblages with no aluminous assemblages.

The Blackwater Mountain area lies approximately 50 km northwest of Golden, British Columbia (Fig. 1) and was the subject of a structural and stratigraphic study by Ferri (1984). The rocks range in age from Late Precambrian to Middle Cambrian and belong to the Miette Group, Gog Group, and Chancellor Formation (Fig. 1).

The Chancellor Formation is composed of slate, calcareous slate, argillaceous limestone, limestone, and dolomite. The aluminous assemblages occur in the basal part of the Chancellor Formation, northwest of Blackwater Mountain (Fig. 1). The lower part of the Chancellor Formation is repeated by a thrust fault near Felucca Mountain (Fig. 1); within the fault zone, spectacular veins of coarse-grained (1-5 cm)

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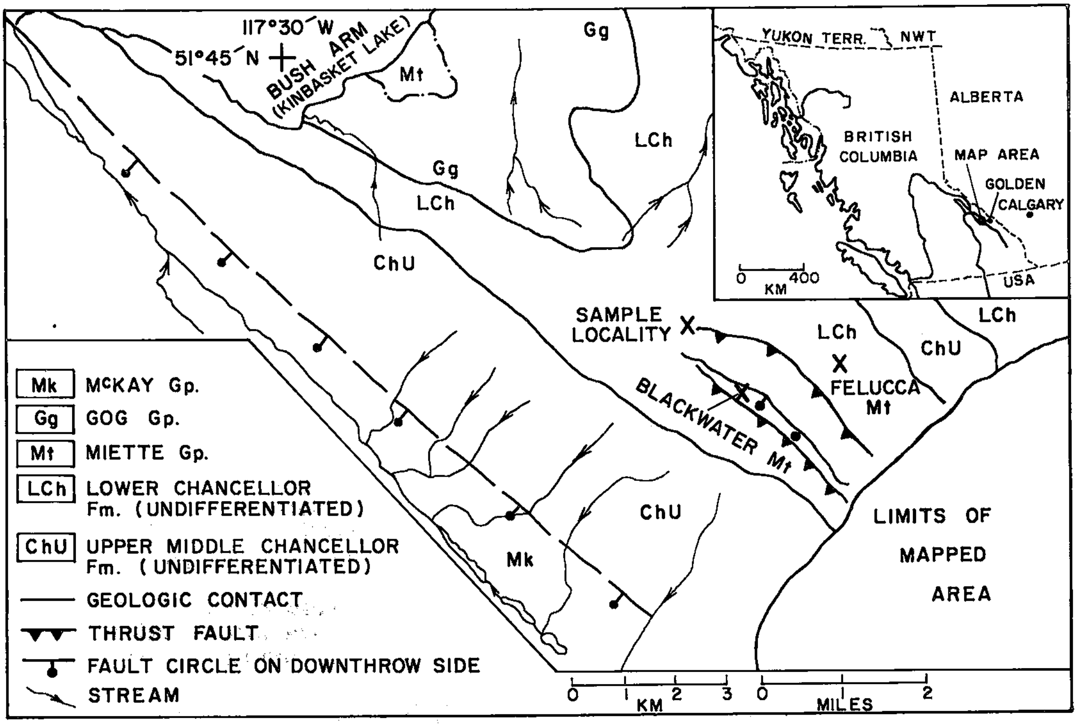

FIG. 1. Simplified geological map of the Blackwater Mountain area of British Columbia (after Ferri 1984), showing sample locations referred to in the text.

pyrophyllite occur. These veins formed after the principal phase of metamorphism.

PETROGRAPHY

The metasedimentary rocks considered in this paper contain three distinct mineral assemblages: one has chloritoid with paragonite and muscovite ± pyrophyllite, the second is characterized by stilpnomelane with biotite and albite, and the third lacks chloritoid or stilpnomelane but has moderately abundant colorless tourmaline (Table 1). All samples have one or two carbonate minerals and quartz.

TABLE 1. MINERAL ASSEMBLAGES IN ROCKS FROM BLACKWATER MOUNTAIN, BRITISH COLUMBIA

Mineral	84-FF -9	84-FF -10	84-FF -14	84-FF -16	84-FF -19	84-FF -20	F561
Cld		X	X			X	X
Dol	X	X	X			X	X
Cal		X		X	X		X
Ms		X	X			X	X
Pg		X	X			X	X
Prl							X
Chl	X			X	X		
Bt				X	X		
Stp				X	X		
Qtz	X	X	X	X	X	X	X
Pl	X			X	X		
Tur	X						
Rt			X	X	X	X	
Py			X		X		
Ilm				X			
Ttn				X			
Gr			X				

Mineral symbols (after Kretz 1983): Chd chloritoid, Dol dolomite, Cal calcite, Ms muscovite, Pg paragonite, Prl pyrophyllite, Chl chlorite, Bt biotite, Stp stilpnomelane, Qtz quartz, Pl plagioclase, Tur tourmaline, Rt rutile, Py pyrite, Ilm ilmenite, Ttn titanite, Gr graphite.

The chloritoid-bearing rocks generally have a good foliation defined by finely intergrown muscovite and paragonite, locally outlined by graphitic material. The chloritoid occurs both as clusters of radiating prisms and as individual porphyroblasts from 0.4 to 2 mm long. Lamellar twinning and optical zoning, evident from patterns of inclusion and variable extinction under crossed polarizers, are common in chloritoid. Chloritoid is choked with fine-grained inclusions of quartz, carbonate, and opaque minerals. Some of the chloritoid is cut by veins and blebs of quartz and carbonate. Chloritoid porphyroblasts grew across the early foliation defined by oriented flakes of white mica and also across the later crenulation cleavage, suggesting that crystallization took place after deformation. Pyrophyllite is locally abundant and coarse grained in sample F561, but it is not commonly in contact with muscovite and paragonite.

The stilpnomelane-bearing samples lack foliation and contain randomly oriented bladed albite, and green stilpnomelane mainly in radiating clusters up to 2 mm long and 0.05 mm wide (Fig. 2). Calcite, quartz and albite are generally less than 1 mm in diameter. The chlorite is very fined grained and occurs in vermiform patches up to 1 mm long. Opaque minerals (ilmenite, rutile, ± titanite ± pyrite) are moderately abundant.

Colorless tourmaline occurs both as inclusions in ferroan dolomite and in the quartz–chlorite matrix. Tourmaline is up to 0.5 mm long and locally occurs as aggregates of crystals. Ferroan dolomite occurs as porphyroblasts up to 4 mm long. Quartz–feldspar veins locally cut across the foliation.

MINERALOGY

Chloritoid

A representative chemical composition of chloritoid is presented in Table 2. Complete sets of analytical data are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. These analytical data were collected on an 8-channel ARL-SEMQ electron-probe microanalyzer, using an online data-reduction system with Bence–Albee correction procedure (Bence & Albee 1968, Albee & Ray 1970). Although chloritoid porphyroblasts show optical zoning, chemical zoning within individual crystals is near the limits of analytical precision. Chloritoid from near Blackwater Mountain has a narrow range of Mg/(Mg + Fe) (atomic), ranging only from 0.125 to 0.153; Ti, Mn and Ca are low to below detection limits. For comparison, chloritoid from the Late Precambrian Horsethief Group in the Omineca Belt has a similar Mg/(Mg + Fe) value (0.13–0.14: Cruickshank & Ghent 1978); however, this chloritoid exhibits more pronounced zoning in Mn and Mg.

Chloritoid from the present study is nearly stoichiometric in Si and Al (Table 2) with 2.00 ± 0.03 Si atoms per formula unit and 4.00 ± 0.02 Al atoms per formula unit (Table 2). These data suggest little ferric iron in octahedral coordination. Ashworth & Evirgen (1984), Cruickshank & Ghent (1978), and Ghent *et al.* (1987) reached similar conclusions regarding the ferric iron content of chloritoid. The occurrence of ilmenite + graphite in several of the samples (Table 1) is consistent with a relatively low oxygen fugacity during metamorphism and relatively low ferric iron in chloritoid.

Pyrophyllite

A representative chemical composition of pyrophyllite is presented in Table 2. Most of the analyzed crystals contain detectable amounts of Fe, Mg, Ca, Na and K. Structural formulas calculated on the basis of 44 positive charges per formula unit suggest limited substitution of Al for Si in tetrahedral sites (Table 2). Deer *et al.* (1962b) suggested that there is limited substitution of Fe and Mg for Al in octahedral sites. They also suggested that Na and K may exist in the sites occupied by the same elements in muscovite and paragonite and they would compensate electrically for minor Si-for-Al substitution. This scheme would indicate solid solution between pyrophyllite and muscovite–paragonite. Presumably, Ca would play a similar role and would indicate solid solution toward margarite. Examination of the excess negative charge in the tetrahedral site, produced by Al-for-Si substitution, shows that it is much larger than the positive charge produced by the sum of the interlayer cations Na, K and Ca. One possible explanation is the substitution of small amounts of Mg and Fe into trioctahedral sites, which are normally vacant in pyrophyllite. Comparison of these results with published data in Deer *et al.* (1962b, p. 118) indicates that several of their analyzed specimens also have negative tetrahedral charges that are not simply compensated by positive charges from interlayer cations.

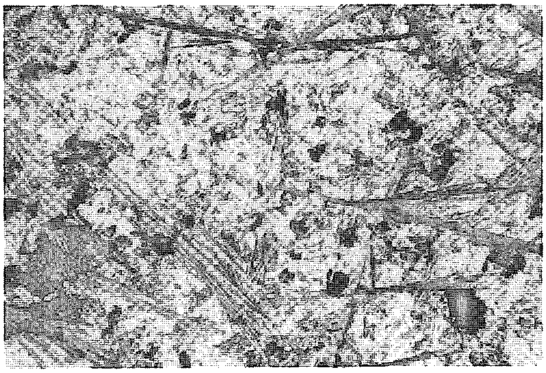

FIG. 2. Randomly oriented blades and radiating clusters of stilpnomelane in a matrix of albite, quartz, calcite, minor biotite, vermiform chlorite, and opaque phases (ilmenite and rutile). The dark, slightly curved stilpnomelane crystal at the top of the figure is 2 mm in length.

K-Na micas

Muscovite and paragonite have been identified by X-ray diffraction in all of the chloritoid-bearing rocks (Table 1). We were unable to obtain satisfactory electron-microprobe analyses of the coexisting micas because the grain size is clearly less than the spatial resolution of the electron microprobe. Cruickshank & Ghent (1978) also were unable to obtain electron-microprobe analyses of coexisting muscovite and paragonite because of the fine grain-size. Because the amount of "Na-phengite" type of sub-

TABLE 2. REPRESENTATIVE ELECTRON-MICROPROBE COMPOSITIONS OF MINERALS FROM BLACKWATER MT., B.C.

	F561	F561	F561	F561	84- FF-9	84- FF-9	8-4 FF-16	84- FF-16
	Cld[1]	Prl	Cal	Dol	Chl	Tur	Stp	Bt
SiO_2	24.14	65.89			27.89	36.67	48.33	37.34
TiO_2	<0.02	<0.02			0.51	0.11	0.03	2.02
Al_2O_3	40.82	28.41			27.76	36.41	6.03	14.06
Fe_2O_3[2]		0.12						
FeO	24.40		1.37	12.20	9.06	1.72	22.45	17.06
MnO	0.06	<0.06	0.09	0.19		<0.06	0.25	0.08
MgO	2.37	0.05	0.54	12.76	24.10	10.04	11.35	14.86
CaO	<0.01	0.06	54.17	29.41	0.02	0.36	0.31	0.20
BaO						<0.11	1.16	0.41
SrO			<0.05	<0.05				
Na_2O		0.10			0.02	1.90	0.03	0.02
K_2O		0.04			<0.01	<0.01	0.74	7.95
F						<0.08	<0.09	1.08
CO_2			44.00	44.61				
H_2O	7.00	5.11			10.48	11.06[3]	9.02	4.77
Total	98.79	99.78	100.17	99.17	99.84	99.27	99.70	99.85
Tot-F								99.40
				Number of Ions				
Si	2.006	7.947			5.235	5.96	8.00	5.684
^{IV}Al		0.053			2.765	6.04	1.18	2.316
		8.000			8.000	12.00		8.000
^{VI}Al	3.997	3.986			3.377	0.75		0.207
Ti					0.072	0.01		0.231
Fe^{3+}		0.011						
Fe^{2+}	1.695		0.038	0.335	1.422	0.23	3.11	2.172
Mn	0.004		0.003	0.005			0.03	0.010
Mg	0.293	0.009	0.027	0.625	6.743	2.37	2.80	3.372
Ca		0.008	1.933	1.035	0.004	0.06	0.05	0.033
Ba							0.08	0.024
Sr								
Na		0.023			0.007	0.58	0.01	0.006
K		0.006					0.16	1.544
F								0.520
CO_3			2.000	2.000				
OH	4.000	4.000			16.000			3.480

1. See Table 1 for mineral abbreviations; 2. Recalculated from FeO; 3. Includes B. Chl formula calculated on the basis of 24 positive charges, 4 OH; Prl calculated on the basis of 44 positive charges, 4 OH; Cal and Dol calculated on the basis of 4 positive charges, 2 CO_3; Chl calculated on the basis of 56 positive charges, 16 OH; Tur calculated on the basis of 16 cations without B; Stp calculated on the basis of 8 Si; Bt calculated on the basis of 44 positive charges, 4 (OH + F).

stitution is much less than the phengitic substitution in muscovite (*e.g.*, Guidotti 1984), we attempted to estimate the compositions of the micas by plotting the wt.% K_2O and Na_2O against other chemical variables. In theory, K should show a positive correlation with Mg + Fe, and a negative correlation with the number of Si atoms per formula unit and Na should show exactly the opposite relationship. These plots show a wide scatter, suggesting that the micas are inhomogeneous on the scale of the analysis, or that at least one other phase is involved. Composition of the K–Na micas can be recast into reasonable structural formulas, suggesting that the latter explanation is not the case.

Feldspar

Plagioclase has been detected in only two samples, associated with stilpnomelane–chlorite–biotite (Table 1). The plagioclase is nearly pure albite.

Biotite

Biotite occurs as light reddish brown irregular platy crystals (~0.1–0.15 mm) in two samples (Table 1) and is locally altered to chlorite and opaque minerals. Biotite is locally in contact with stilpnomelane, but there is no evidence suggesting a reaction relationship.

Biotite has a rather low sum of interlayer cations (Ca + Ba + Na + K), between 1.46 and 1.61, suggesting the possibility of low-temperature leaching of these cations (Table 2). Compared with low-grade biotite from the Late Precambrian metasedimentary rocks of the Esplanade Range, B.C. (Ghent 1975), this biotite has higher Ti, Ba, and Mg and lower Al (Table 2).

Chlorite

Chlorite occurs in only three samples (Table 1), and some of this chlorite is clearly in reaction relationship with other Fe-Mg phases. Patches of chlorite are locally penetrated by stilpnomelane needles, suggesting a possible reaction relationship (samples 85–FF–16 and –19). Chlorite is an alteration product of biotite, but none of this chlorite has been analyzed. Chlorite in 84–FF–9 occurs as isolated microporphyroblasts and appears to be a stable member of the mineral assemblage. Chlorite from Blackwater Mountain is slightly less aluminous (Table 2) than chlorite from the Esplanade Range and Blackwater Ridge (Ghent 1975, Cruickshank & Ghent 1978).

Stilpnomelane

Stilpnomelane apparently has not been reported previously from the Canadian Rocky Mountains. This occurrence is of interest because the stilpnomelane occurs in close proximity to Al-rich mineral assemblages.

Most of the stilpnomelane is green, but color changes from green to reddish brown occur over distances of a few mm, and, in a few instances, along the length of a single crystal. Color zoning has been reported by Brown (1971) in stilpnomelane from other areas; he attributed the brown color to oxidation of iron during weathering.

Compared to compositions listed by Brown (1971), stilpnomelane from Blackwater Mountain has a higher Mg/Fe value and lower amounts of K and Mn. Stilpnomelane from Blackwater Mountain has appreciable Ba (Table 2), and some crystals have measurable F (but neither element was determined by Brown).

Tourmaline

Colorless tourmaline is present in one sample (Table 1), in which it occurs as microporphyroblasts. The microprobe composition was normalized to 16 cations, omitting B (Table 2). The normalized cations are in reasonable agreement with the compositions given in Deer *et al.* (1962a). As Mg exceeds Fe and the mineral is colorless, it is classified as dravite. Colorless tourmaline is known in other greenschist-facies rocks, *e.g.*, in New Zealand, but few chemical data have been reported for such material.

Carbonate minerals

Carbonate minerals are present as porphyroblasts, and as granoblastic aggregates in the matrix and in veins in all samples examined in this study. The carbonate minerals are calcite and ferroan dolomite (X_{Fe} 0.28–0.24, Table 2). According to Reeder (1983), the term *ankerite* is reserved for the more Fe-rich phases along the join $CaMg(CO_3)_2$ – $CaFe(CO_3)_2$, and the term *ferroan dolomite* is used for less Fe-rich members of the solid solution.

Apparently not all of the carbonate minerals were in equilibrium at the peak conditions of metamorphism. For example, in sample F561, calcite coexisting with ferroan dolomite contains 0.027 atoms of Mg per formula unit, whereas calcite in 84–FF–10, which also coexists with ferroan dolomite, contains no detectable Mg.

DISTRIBUTION OF Fe, Mg AND Mn BETWEEN COEXISTING SILICATES

The distribution coefficient K_D can be defined as $[Fe/(Mg+Mn)]^a/[Fe/(Mg+Mn)]^b$, where *a* and *b* are two distinct minerals. For biotite–chlorite, including all core, middle and rim analyses, K_D varies from 0.92 to 0.98, indicating little fractionation of Fe relative to Mg and Mn. For rocks of similar metamorphic grade, Brown (1971) found K_D Bt–Chl = 1.1. For biotite and stilpnomelane, K_D ranges from 0.56 to 0.64, which is also similar to values found by Brown (1971). Stilpnomelane and chlorite show similar values of K_D (0.57–0.66) to those shown by stilpnomelane and biotite. The ratio Mn/(Fe + Mg) is largest in stilpnomelane, followed by chlorite, and then biotite, which is similar to the results of Brown (1971). The available data on the distribution of Fe, Mg and Mn among biotite, stilpnomelane, and chlorite are consistent with a close approach to equilibrium during metamorphism.

PRESSURE – TEMPERATURE – FLUID COMPOSITION CONDITIONS ATTENDING METAMORPHISM

It is extremely difficult to estimate metamorphic pressure for the Blackwater Mountain area, because of the lack of geobarometers. Craw (1978) estimated pressures at nearly 5 kbars in the Park Ranges, about 50 km north of the study area. L. Gal (pers. comm. 1988) has estimated pressure for staurolite-kyanite-bearing rocks to be near 5 kbars in the area a few km north of the study area. For the present study, we tentatively estimate 5 kbars as the metamorphic pressure for the Blackwater Mountain area.

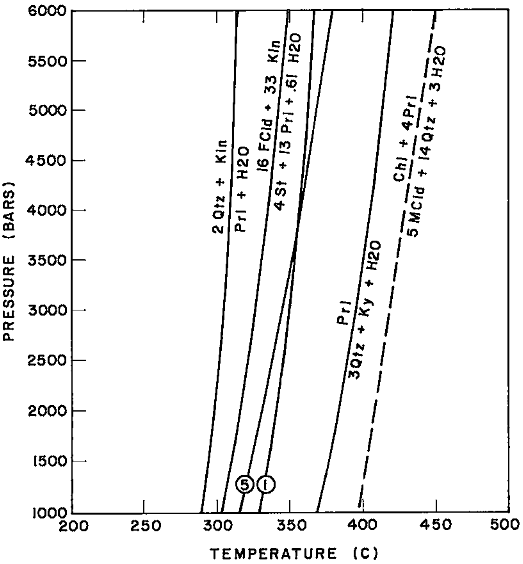

FIG. 3. Pressure–temperature diagram for the system $FeO–Al_2O_3–SiO_2–H_2O$ calculated from the program GEOCALC. Numbered equilibria are: (1) 3 Kln = Prl + 2 Ky + 5 H_2O; (5) 8 FCld + 10 Prl = 2 St + 35 Qtz + 14 H_2O. Dashed curve is metastable. Abbreviations (after Kretz 1983): Qtz quartz, Kln kaolinite, Prl pyrophyllite, Ky kyanite, St staurolite, FCld Fe-rich chloritoid, MCld Mg-rich chloritoid, Chl chlorite.

A pressure–temperature diagram for the system $FeO–Al_2O_3–SiO_2–H_2O$ (Fig. 3) was calculated using the thermodynamic data-base of Berman *et al.* (1985) and B. Patrick & R.G. Berman (pers. comm. 1986) and the programs in GEOCALC written by Perkins *et al.* (1986). Pyrophyllite from sample F561 is relatively pure (Table 2); other aluminous phases such as kyanite and kaolinite tend also to be relatively pure in nature (*e.g.*, Deer *et al.* 1962b, Albee & Chodos 1969). Consequently, these equilibrium curves can be applied to the Blackwater Mountain occurrence without correction for solid solution. The presence of pyrophyllite + quartz and the lack of kyanite suggest that the temperature did not exceed about 415°C at 5 kbars. The lack of kaolinite, for $P(H_2O) = P_{total}$, suggests a *minimum* temperature near 310°C at 5 kbars (Fig. 3).

The phase relations involving Fe-rich chloritoid, quartz, staurolite, pyrophyllite, kaolinite, and fluid also are presented in Figure 3. The thermodynamic properties of chloritoid and staurolite are subject to large uncertainties (Berman *et al.* 1985, B. Patrick & R.G. Berman, pers. comm. 1986). Because of these uncertainties we will neglect the small effect of Fe–

Mg partitioning on chloritoid–staurolite phase relations [*e.g.,* Albee (1972)]. The apparently stable occurrence of pyrophyllite with chloritoid in one sample (Table 1) suggests a maximum temperature near 375°C at 5 kbars. It should be noted, however, that the calculated field of stability for Fe-rich chloritoid + quartz is inconsistent with the occurrence of chloritoid + sillimanite in some metamorphic terranes (*e.g.,* Milton 1986). In addition, the calculated position of the equilibrium, chlorite ($X_{Mg} = 0.48$) + pyrophyllite = Mg-rich chloritoid ($X_{Mg} = 0.14$) + quartz + H_2O, is metastable with respect to the curve for the maximum stability of pyrophyllite (see below for a definition of X_{Mg} and activity models).

Geothermometers are generally lacking at this grade of metamorphism, and this is the case for the Blackwater Ridge area. Only one calcite–dolomite pair appears to have been in equilibrium under metamorphic conditions (Table 2) and was considered suitable for geothermometry. Application of the experimental and computed phase-equilibria relationships of Powell *et al.* (1984) to the data for F561 yields an estimate of 345°C. Application of equation (31) in Anovitz & Essene (1987) yields 315°C.

Fluid compositions attending metamorphism can be estimated from mineral equilibria. The mineral equilibria at 5 kbars, shown in Figure 4, were calculated using the program GEOCALC. The applicability of the algorithm for calculation of nonideal mixing of H_2O and CO_2 (Kerrick & Jacobs 1981) is limited to temperatures greater than 350°C. For equilibria between calcite and dolomite, the expression for activity of $MgCO_3$ in calcite of Gordon & Greenwood (1970) is used.

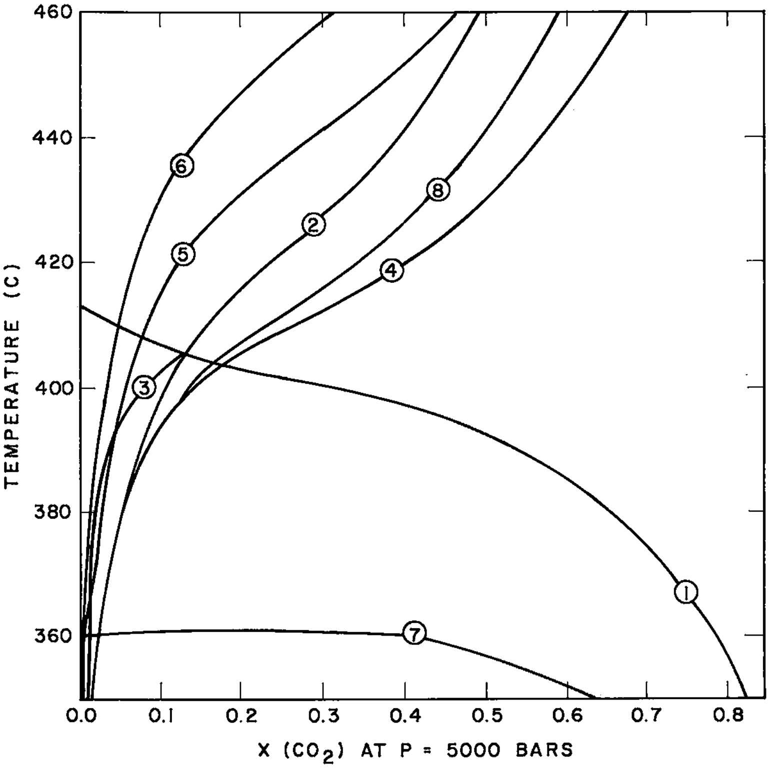

FIG. 4. Temperature – mole fraction of CO_2 plot at a constant total pressure of 5 kbars for part of the system K_2O–Na_2O–FeO–MgO–CaO–Al_2O_3–SiO_2–H_2O–CO_2 calculated from the program GEOCALC. Equilibria are: (1) Prl = Ky + 3 Qtz + H_2O; (2) Mrg + CO_2 = 2 Ky + Cal + H_2O; (3) Mrg + Qtz + CO_2 + H_2O = Prl + Cal; (4) Chl + 5 Cal + Qtz + 5 CO_2 = 5 Dol + Prl + 3 H_2O; (5) Chl + 5 Cal + Ab + 5 CO_2 = 5 Dol + Pg + 3 Qtz + 3 H_2O; (6) Chl + Phl + 8 Cal + 8 CO_2 = Ms + 8 Dol + 3 Qtz + 4 H_2O; (7) 8 FCld + 10 Prl = 2 St + 33 Qtz + 14 H_2O; (8) Chl + 4 Cal + 4 CO_2 = 4 Dol + 2 Qtz + MCld + 3 H_2O. Abbreviations (after Kretz 1983) as in Figure 3; in addition, Dol dolomite, Cal Calcite, Phl phlogopite, Ms muscovite, Pg paragonite, Ab albite, Mrg margarite.

If the mineral assemblages in the Blackwater Mountain area equilibrated under nearly isothermal-isobaric conditions, it is possible that the variation in mineral assemblages was controlled by the composition of the fluid phase attending metamorphism. It should be pointed out, however, that at lower temperatures, the equilibrium curves tend to cluster at the H_2O-rich end of the diagram, making the discrimination difficult (Fig. 4). The coexistence of pyrophyllite with calcite and quartz, and the lack of margarite and kyanite (F561, Table 1), suggest a fluid composition having $X(CO_2)$ less than 0.8 at 350°C (Equilibria 1 and 3, Fig. 4). The same sample contains dolomite and lacks chlorite, suggesting that $X(CO_2)$exceeded ~0.02 at 350°C (Equilibrium 4, Fig. 4). This calculation was made using a chlorite composition X_{Mg} of 0.48 (where X_{Mg} equals the number of Mg atoms per formula unit divided by the number of octahedrally coordinated atoms per formula unit) and an activity of the clinochlore $[Mg_5Al_2Si_3O_{10}(OH)_8]$ component in chlorite given by $(X_{Mg})^6$. The stable occurrence of chloritoid + pyrophyllite and the lack of staurolite are consistent with these estimates of fluid composition, *i.e.*, $X(CO_2)$ was less than 0.6 at 350°C.

Several samples contain mineral assemblages consistent with either slightly higher temperature or different fluid composition. As all samples were collected from a single continuous cliff section over 200 m in vertical extent, it seems unlikely that peak metamorphic temperatures could have varied by more than a few degrees C. A common mineral assemblage is dolomite + calcite + chloritoid + quartz (*e.g.*, 84–FF–10, Table 1). These samples lack chlorite, suggesting that $X(CO_2)$ exceeded ~0.01 at 350°C (Equilibrium 8, Fig. 4). Equilibrium 8 was calculated using the activity of the clinochlore component in chlorite given above and the activity of Mg-rich chloritoid given by $X_{Mg} = 0.14$, where X_{Mg} is the mole fraction of Mg in octahedrally coordinated sites in chloritoid (Table 2). The same samples contain paragonite and lack albite, suggesting from Equilibrium 5 (Fig. 4) that $X(CO_2)$ exceeded ~0.01 at 350°C. Because of the lack of accurate analytical data on the paragonite, we used data for pure paragonite in these calculations. In contrast, several samples contain calcite + chlorite + albite and lack paragonite and chloritoid (Table 1, *e.g.*, 84–FF–19). These rocks could have equilibrated at slightly higher temperatures (see above discussion) or with slightly more H_2O-rich fluid compositions (or both). The assemblage biotite + calcite + chlorite + dolomite + quartz occurs in two samples (Table 1), and these rocks lack muscovite. Equilibrium 6 suggests that these rocks also could have equilibrated under slightly higher temperatures or with more H_2O-rich fluids (or both). This calculation was made with an activity of the phlogopite component in biotite set equal to $(X_{Mg})^3$, where X_{Mg} is the mole fraction of Mg in the octahedrally coordinated site in biotite (Table 2). The close proximity of these equilibrium curves in T-$X(CO_2)$ space and the lack of accurate and precise temperature estimates mean that we cannot clearly distinguish the relative roles of temperature and fluid composition in the equilibration of the assemblages of metamorphic minerals.

CONCLUSIONS

The strong bulk-composition effects make difficult the comparison of these occurrences of chloritoid, pyrophyllite, biotite and stilpnomelane to those in other areas. For example, Frey (1974) reported chloritoid within the stability field of pyrophyllite in Liassic phyllites in the Alps; the absence of pyrophyllite was attributed by Frey to the low Al content of these rocks, because the assemblage chloritoid + pyrophyllite is common in the aluminous rocks of Devonian age. In the Liassic rocks, biotite first appears at higher grades than the first appearance of chloritoid. Frey & Wieland (1975) reported very fine-grained chloritoid in Mesozoic phyllites of the Aar Massif, Central Alps, where the assemblage pyrophyllite + chlorite is stable very near the first appearance of stilpnomelane. Clearly, the stability field of pyrophyllite + chlorite has been exceeded in the present study-area (Fig. 3).

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