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CALCULATION OF TEMPERATURE AND $X(CO_2)$ VALUES FOR TREMOLITE–K-FELDSPAR–DIOPSIDE–EPIDOTE ASSEMBLAGES

P.J. LeANDERSON
Department of Geological Engineering, Colorado School of Mines,
Golden, Colorado 80401, U.S.A.

ABSTRACT

The middle Proterozoic rocks in the southern part of the Grenville Province, southern Ontario, were metamorphosed and deformed during the Grenvillian orogeny. A study of calc-silicate isograds based on model equilibria demonstrates that the rocks in west central Limerick Township were metamorphosed to a range of grade corresponding to the first appearance of tremolite and diopside in the calcareous units. Five samples have assemblages corresponding to the mutual intersection of the following equilibria: 1) 5 phlogopite + 6 calcite + 24 quartz = 3 tremolite + 5 K-feldspar + 2 H_2O + 6 CO_2, 2) tremolite + 3 calcite + 2 quartz = 5 diopside + H_2O + 3 CO_2, 3) 2 zoisite + CO_2 = calcite + 3 anorthite + H_2O. Calculated intersection temperatures at 4000 bars range from 15°C higher to 142°C lower than those obtained for the same samples using the two-feldspar geothermometer of Whitney & Stormer (1977). Temperatures for assemblages corresponding to the intersection of equilibria 2) and 3) are reasonable, but those based on intersections involving the calcite–anorthite equilibrium are low by 45 to 142°C. This may be due either to erroneously high estimates of the activity of $CaAlAl_2Si_3O_{12}(OH)$ in epidote or to uncertainty in the position of equilibrium 3) in isobaric T–$X(CO_2)$ space. Assemblages in these samples and in those of Carmichael (1970) indicate that reaction 1) lies near the intersection of reactions 2) and 3). Based on this observation and the experimentally determined position of equilibria 2) by Hoschek (1973) and 3) by Skippen (1974), it is suggested that at temperatures greater than 400°C and pressures greater than 2 kbar, epidote is stable in metamorphic rocks if the $X(CO_2)$ of the fluid phase is less than 0.10 to 0.20, in contrast to a value of 0.03, determined experimentally by Johannes & Orville (1972).

Keywords: metamorphic petrology, phase equilibria, calculated temperatures, Grenville Province, Ontario, tremolite, diopside, epidote.

SOMMAIRE

Les roches d'âge Protérozoïque moyen du Sud de la province du Grenville, en Ontario, ont été métamorphisées et déformées pendant l'orogénèse Grenvillienne. Une étude des isogrades impliquant les calc-silicates et les équilibres modèles démontre que dans la partie centre–ouest du canton Limerick, les roches ont été métamorphisées à une intensité variable correspondant à la première apparition de la trémolite et de la diopside dans les calcaires. Cinq échantillons contiennent des assemblages qui correspondent à l'intersection mutuelle des équilibres suivants: 1) 5 phlogopite + 6 calcite + 24 quartz = 3 trémolite + 5 K-feldspath + 2 H_2O + 6 CO_2, 2) trémolite + 3 calcite + 2 quartz = 5 diopsite + H_2O + 3 CO_2 et 3) 2 zoisite + CO_2 = calcite + 3 anorthite + H_2O. La température d'intersection à 4000 bars varie de 15°C au-dessus à 142°C au-dessous des valeurs obtenues en utilisant les feldspaths coexistants dans les mêmes échantillons [géothermomètre de Whitney & Stormer (1977)]. Les températures qui correspondent à l'intersection des équilibres 2) et 3) sont raisonnables, mais celles que l'on obtient en utilisant une intersection avec l'équilibre calcite–anorthite sont inférieures par une marge de 45 à 142°C. Ceci refléterait soit une valeur trop élevée de l'activité de $CaAlAl_2Si_3O_{12}(OH)$ dans l'épidote, soit la position incertaine de l'équilibre 3) en termes de T–$X(CO_2)$. Les assemblages dans ces échantillons et ceux de Carmichael (1970) indiquent que la réaction 1) est située près de l'intersection de 2) et 3). A la lumière de cette observation et des déterminations expérimentales des équilibres 2) par Hoschek (1973), et 3) par Skippen (1974), il semble qu'à des températures supérieures à 400°C et à des pressions supérieures à 2 kbar, l'épidote soit stable dans les roches métamorphiques où la phase fluide possède une fraction molaire $X(CO_2)$ inférieure à 0.10–0.20 plutôt que 0.03, valeur déterminée expérimentalement par Johannes & Orville (1972).

(Traduit par la Rédaction)

Mots-clés: pétrologie métamorphique, équilibre des phases, températures calculées, province du Grenville, Ontario, trémolite, diopside, épidote.

INTRODUCTION

This paper presents the results of calculations performed on data for calc-silicate samples from Limerick Township, Ontario, 22 km south of Bancroft and 160 km northeast of

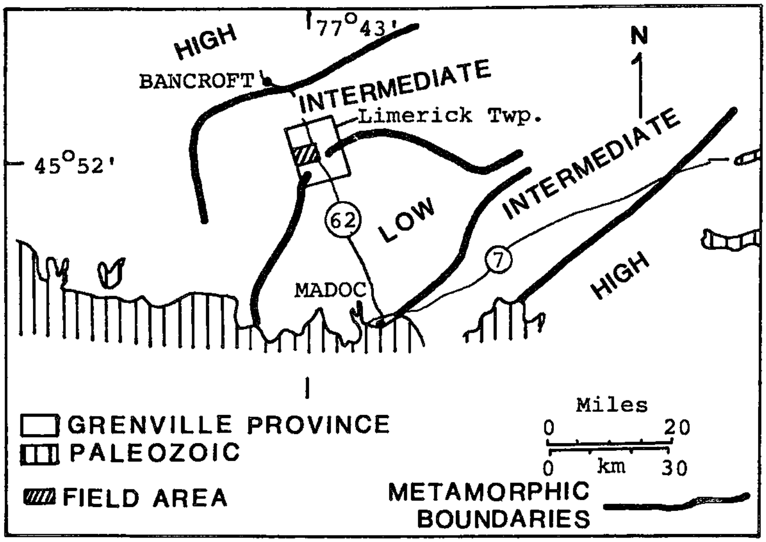

FIG. 1. The field area is located in Limerick Township, southern Ontario, 100 km northeast of Toronto (after Little *et al.* 1972).

Toronto (Fig. 1). The assemblages correspond to the intersections of two of the following equilibria: (1) 2 zoisite + CO_2 = calcite + 3 anorthite + H_2O, (2) 5 phlogopite + 6 calcite + 24 quartz = 3 tremolite + 5 K-feldspar + 2 H_2O + 6 CO_2 and (3) tremolite + 3 calcite + 2 quartz = 5 diopside + H_2O + 3 CO_2; the assemblages therefore lie at the intersection of isograds based on these equilibria.

Isograds based on model reactions have been termed reaction isograds (Winkler 1979). Each isograd is plotted between the location of the reactant and product assemblages and through the locations of the combined assemblages. Isograds mapped in calcareous rocks are based on univariant reactions that involve pure solid phases; they may be represented, at constant pressure, on $T\text{–}X(CO_2)$ diagrams (*e.g.*, Allen 1976, Ferry 1976, Rice 1977, LeAnderson 1978a, b, Williams-Jones 1973, 1981).

Assemblages that lie on an isograd are usually multivariant, owing to the presence of components in the minerals that are not considered in the pure phases of the model reaction. The effect of substitution of additional components on the position of equilibria in isobaric $T\text{–}X(CO_2)$ space (Skippen & Hutcheon 1974) and the sensitivity of the corresponding isograds to bulk composition (LeAnderson 1978a) have been semiquantitatively estimated.

An assemblage that corresponds to an isobaric invariant point in the model system contains subassemblages corresponding to the two or more model univariant equilibria that intersect at the invariant point. Temperature and $X(CO_2)$ values at the time of crystallization of such an assemblage can be obtained by calculating the displacement of any two of the intersecting equilibria (Allen 1976, Skippen & Carmichael 1977, Rice 1977, Crawford *et al.* 1979, LeAnderson 1978a, b).

The accuracy of the results of these calculations depends on the accuracy of the equilibrium constants, activities, estimated confining pressure, the fugacity coefficient employed and the extent to which the system approached equilibrium. It is difficult, and often not possible, to assess each of these factors independently. However, the validity of calculated $T\text{–}X(CO_2)$ values can be estimated by comparing them with independently obtained $T\text{–}X(CO_2)$ values for the same or adjacent samples. If it is concluded that the calculated $T\text{–}X(CO_2)$ values are reasonable, then they may be used to assist in the interpretation of the metamorphic conditions of the area from which they were collected.

GEOLOGY OF THE FIELD AREA

The samples examined in this study were collected from calc-silicate lenses in quartzofeldspathic schists that were intruded by the Thanet gabbro complex (Fig. 2) about 1200 *Ma* ago (Berger & York 1981). Both the schists and the intrusive body were deformed and

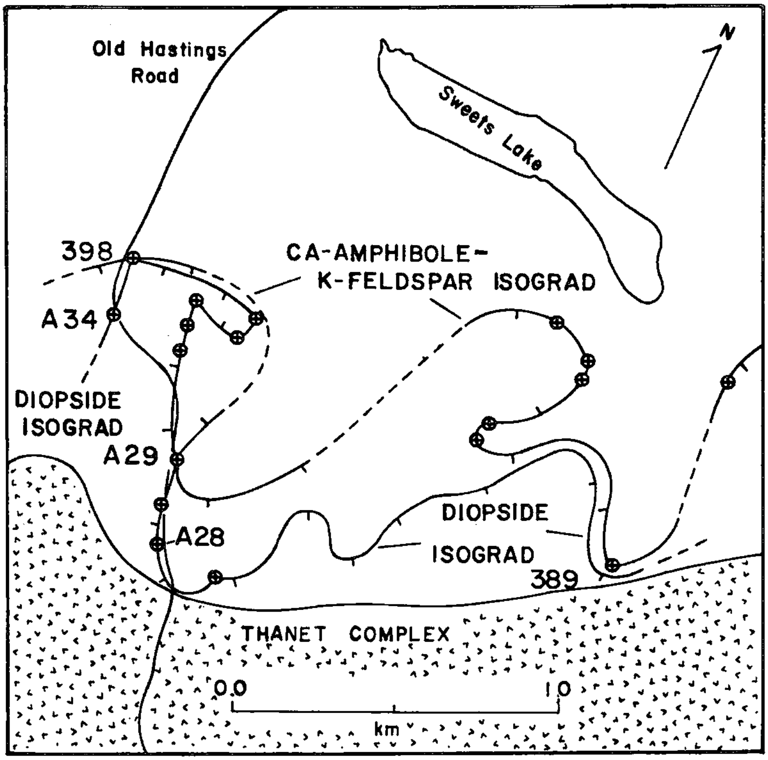

FIG. 2. The Ca-amphibole and diopside isograds near the Thanet gabbro complex. The isograds are dashed where inferred. Hatchures are shown on the high-grade side of each isograd. The plus-and-circle symbols indicate assemblages corresponding to both the reactant and product assemblages in the model reactions (see text). Samples used in the calculations are numbered.

metamorphosed during the Grenvillian orogeny. Isograds based on the reactions biotite + calcite + quartz = hornblende + K-feldspar, hornblende + calcite + quartz = diopside, and hornblende + K-feldspar + quartz = diopside + biotite were mapped adjacent to the Thanet complex (LeAnderson 1978a, b). The locations of the samples with respect to the hornblende–K-feldspar isograds and the gabbro are given in Figure 2.

An estimation of load pressure at the time of metamorphism for this region can be made from the distribution of the aluminum silicate minerals and the Al_2SiO_5 phase diagram of Holdaway (1971). No aluminum silicate minerals were identified in the field area, but andalusite is found in northern Limerick Township approximately 10 km to the north-northeast (Lumbers 1969). Andalusite is also found 16 km to the southwest in central Lake Township, 8 km east of the kyanite–sillimanite isograd (D.M. Carmichael, pers. comm. 1973). This indicates that the pressure in central Lake Township probably was close to that of the triple point assemblage kyanite–sillimanite–andalusite. In the absence of more definitive data, it is assumed that the same pressure prevailed in the field area. The pressure of the aluminum silicate triple point determined by Holdaway is 3.76 ± 0.3 kbar at a temperature of 501°C ± 20°. Calorimetric work (Anderson *et al.* 1977) and a thermodynamic analysis of the aluminum silicate system (Day & Kumin 1980) support Holdaway's data. The pressure in the field area is therefore assumed to have been close to, but no higher than, 4000 bars. This pressure was assumed in the study.

In making calculations using results of chemical analyses of coexisting minerals, it is necessary to assume that the minerals were in equilibrium. The range of composition for each of the minerals analyzed in most samples in this study is usually greater than the reproducibility of the analyses. This suggests that adjacent grains of each mineral did not equilibrate with one another. Nevertheless, plots of analytical means for coexisting mineral pairs on diagrams showing mol fraction *versus* mol fraction and mol fraction *versus* distribution coefficient suggest that equilibrium between mineral pairs was closely approached; this hypothesis is supported by the presence of mosaic textures (LeAnderson 1978a, b). As well, the subsequent effect on the mean composition of each mineral is less than the range, owing to analytical reproducibility. The failure to attain equilibrium, therefore, does not affect the calculations, because only the mean compositions were used.

ANALYTICAL TECHNIQUES

Mineral analyses were obtained at Queen's University using an ARL–EMX electron microprobe equipped with an energy-dispersion detection system and a PDP–11 computer. The system was operated at an accelerating voltage of 1.50 kV and an emission current of 100 μA. Raw data were reduced using the Multiple Least Squares computer program (written by Northern Scientific for the PDP–11 computer) with the methods and constants of Bence & Albee (1968).

Oxide totals of 98–102% were considered acceptable for analyses of anhydrous minerals. Acceptable totals for the hydrous minerals were determined by subtracting the average water content of the mineral [from data listed by Deer *et al.* (1962a, b, c, 1963)] from the range 98–102%. The results of the chemical analyses are given in Table 1. Fluorine contents were not determined, and only semiquantitative Cl analyses were made (LeAnderson 1978a). The reproducibilities of the mol fractions of Al^{IV}, Mg, Ca, Na and K are less than or equal to 0.01 for the minerals studied, except for Ca in epidote (X_{Ca} = ± 0.02: LeAnderson 1978a).

EQUATIONS USED TO CALCULATE THE POSITION OF THE UNIVARIANT EQUILIBRIA IN ISOBARIC T-X(CO_2) SPACE

Equation (1) was used to calculate the position of equilibria (1), (2) and (3) in T–X (CO_2) space at 4000 bars; this equation was, in part, obtained from the data presented by Froese (1976). Standard states for the Gibbs free energy are defined as follows: CO_2 and H_2O: the ideal gas at 1 bar and the temperature at equilibrium. Solids: the pure phase at 1 bar and the temperature at equilibrium.

$$\log K = \frac{A}{T} + B + \frac{C(P-P^{\circ})}{T} \qquad \text{............(1)}$$

TABLE 1. MEAN CHEMICAL ANALYSES*

	K-feldspar					Plagioclase				
	A28(5)	A29(3)	A34(3)	389(3)	398(3)	A28(2)	A29(2)	A34(3)	389(3)	398(3)
SiO_2	64.2	64.4	64.8	63.7	64.2	59.1	61.8	62.4	63.4	60.7
TiO_2				0.2		0.1	0.1	0.1	0.1	0.1
Al_2O_3	18.7	18.7	18.7	18.4	18.3	26.4	23.6	24.1	23.2	25.2
Fe_2O_3										
FeO	0.1			0.1	0.1	0.2	0.2	0.2	0.1	0.2
MnO	0.1			0.2						
MgO		0.1				0.2	0.3	0.1		0.3
CaO						7.4	5.0	5.0	4.1	6.2
Na_2O	1.0	1.0	0.9	0.7	0.8	7.4	8.5	8.7	9.2	8.1
K_2O	15.6	15.2	15.4	15.6	15.5	0.1	0.1	0.2	0.1	0.2
Total	99.7	99.4	99.8	98.9	98.9	100.9	99.6	100.8	100.2	101.0
					Cation proportions					
Si	2.98	2.98	2.99	2.98	3.00	2.62	2.76	2.75	2.80	2.68
Ti				0.01		0.00	0.00	0.00	0.00	0.00
Al	1.02	1.00	1.02	1.02	1.01	1.38	1.24	1.25	1.21	1.31
Fe^{3+}										
Fe^{2+}	0.00			0.01	0.01	0.01	0.01	0.01	0.00	0.01
Mn	0.00			0.01						
Mg		0.01				0.01	0.01	0.01		0.02
Ca						0.35	0.24	0.24	0.19	0.29
Na	0.09	0.09	0.08	0.06	0.07	0.64	0.74	0.74	0.79	0.69
K	0.92	0.90	0.91	0.93	0.92	0.01	0.01	0.01	0.01	0.01

	Biotite			Epidote			Ca-amphibole				
	A29(5)	389(4)	398(3)	A28(3)	A34(4)	389(3)	A28(5)	A29(6)	A34(5)	389(4)	398(3)
SiO_2	37.0	35.7	37.1	38.8	37.9	37.7	47.6	48.1	42.3	40.8	46.8
TiO_2	1.5	1.6	2.0	0.4	0.4	0.4	0.5	0.4	0.7	0.7	0.6
Al_2O_3	15.5	16.4	15.2	29.0	23.7	24.7	9.2	7.7	12.0	13.0	8.5
Fe_2O_3				6.8	13.9	12.2					
FeO	19.2	24.9	20.0				15.2	15.7	19.7	23.5	17.5
MnO	0.1	0.4	0.2		0.1		0.1	0.1	0.1	0.6	0.1
MgO	12.6	7.6	11.5		0.1	0.1	11.7	12.3	8.9	5.5	10.7
CaO	0.2	0.1		23.6	22.5	22.8	12.2	12.0	11.5	11.0	11.7
Na_2O	0.4	0.2	0.1	0.1	0.3	0.1	0.9	1.2	1.3	1.5	0.9
K_2O	9.0	9.1	9.4		0.1	0.1	0.9	0.9	1.6	1.6	1.0
Total	95.5	96.0	95.5	98.7	99.0	98.1	98.3	98.4	98.1	98.2	97.8
					Cation proportions						
Si	2.81	2.78	2.83	2.98	2.99	2.98	6.94	7.06	6.43	6.26	6.98
Ti	0.08	0.10	0.12	0.02	0.02	0.03	0.05	0.04	0.08	0.08	0.07
Al	1.39	1.50	1.37	2.63	2.20	2.29	1.58	1.33	2.14	2.51	1.49
Fe^{3+}				0.39	0.82	0.74					
Fe^{2+}	1.22	1.62	1.28				1.85	1.93	2.49	3.02	2.18
Mn	0.00	0.02	0.02		0.01		0.01	0.01	0.01	0.08	0.01
Mg	1.43	0.88	1.30		0.01	0.01	2.54	2.69	2.02	1.26	2.38
Ca	0.02	0.01		1.94	1.90	1.92	1.91	1.89	1.88	1.81	1.87
Na	0.06	0.03	0.01	0.01	0.05	0.02	0.25	0.34	0.41	0.45	0.26
K	0.87	0.90	0.92		0.01	0.01	0.17	0.17	0.21	0.31	0.19

	Calcite					Diopside			
	A28(4)	A29(2)	A34(3)	389(6)	398(3)	A28(10)	A29(7)	A34(5)	398(13)
SiO_2						52.8	52.2	51.9	52.4
TiO_2						0.4	0.4	0.3	0.3
Al_2O_3						0.8	0.5	1.8	0.7
Fe_2O_3									
FeO	0.5	0.5	0.8	0.8	0.7	11.4	11.0	11.0	12.5
MnO				0.2				0.1	
MgO	0.3	0.2	0.4	0.2	0.3	11.2	11.3	11.1	10.6
CaO	51.8	47.8	51.2	50.4	51.6	23.4	23.0	22.2	22.9
Na_2O			0.2			0.2	0.3	0.5	0.3
K_2O			0.3			0.1	0.2	0.1	0.1
Total	52.6	48.5	52.9	51.6	52.6	100.3	98.9	99.0	99.8
				Cation proportions					
Si						1.99	2.00	1.98	1.99
Ti						0.01	0.01	0.01	0.01
Al						0.04	0.02	0.08	0.03
Fe^{3+}									
Fe^{2+}	0.01	0.01	0.01	0.01	0.01	0.36	0.35	0.35	0.40
Mn				0.00				0.00	
Mg	0.01	0.00	0.01	0.00	0.01	0.63	0.64	0.63	0.60
Ca	0.95	0.96	0.94	0.95	0.95	0.95	0.94	0.91	0.93
Na			0.00			0.01	0.02	0.04	0.02
K			0.00			0.00	0.01	0.00	0.00

* Chemical data are rounded to the first decimal place. Cation proportions are rounded to the second decimal.

$$A = -\frac{\Delta H^\circ}{2.303R} \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

$$B = \frac{\Delta S^\circ}{2.303R} \cdots\cdots\cdots\cdots\cdots\cdots (3)$$

$$C = -\frac{\Delta V_s}{2.303R} \cdots\cdots\cdots\cdots\cdots\cdots (4)$$

Log K may be calculated if values of A, B and C are known and if the activities of components in the solid phases are estimated or calculated. The A, B and C values used are listed in Table 2. The calculated positions of the three equilibria in T–$X(CO_2)$ space at a pressure of 4000 bars are shown in Figure 3.

It was assumed that $P(CO_2) + P(H_2O) = P_{Total}$. Williams-Jones (1973) calculated the effects of other gas species on the sum $P(CO_2) + P(H_2O)$ in the presence of graphite and the buffers pyrite–pyrrhotite and magnetite–iron. He found that displacement of the curves due to the reduced species was less than the uncertainty in their position due to width of the experimentally determined equilibrium brackets, except for assemblages in equilibrium with an H_2O-rich gas phase. The temperature of equilibrium of such assemblages may therefore be dependent on the concentration of gas species other than H_2O and CO_2.

TABLE 2. EQUILIBRIUM CONSTANTS[1] AT 1 BAR

Equilibrium[2]		A	B	C
1a)	$5Ph + 6Cc + 24Q = 3Tr + 5Kf + 2H_2O + 6CO_2$	-37300	72.764	0.808
1b)	$5Ph + 6Cc + 24Q = 3Tr + 5Kf + 2H_2O + 6CO_2$	-41607	78.24	0.808
1c)	$5Ph + 6Cc + 24Q = 3Tr + 5Kf + 2H_2O + 6CO_2$	-32609	67.09	0.808
2a)	$Tr + 3Cc + 2Q = 5Di + H_2O + 3CO_2$	-12486	27.95	0.5152
2b)	$Tr + 3Cc + 2Q = 5Di + H_2O + 3CO_2$	-12840	27.45	0.5152
2c)	$Tr + 3Cc + 2Q = 5Di + H_2O + 3CO_2$	-9925	26.08	0.5152
3)	$2Zo + CO_2 = Cc + 3An + H_2O$	-320	2.60	-0.3463

1. Constants in the equation $\log K = \frac{A}{T} + B + \frac{C(P-P^\circ)}{T}$.
2. Sources of data: 1a) Hoschek (1973); 1b) and 1c) are the upper and lower limits of equilibrium 1a), respectively. 2a) Skippen (1974); 2b) and 2c) are the upper and lower limits of equilibrium 2a), respectively. 3) Johannes & Orville (1972).

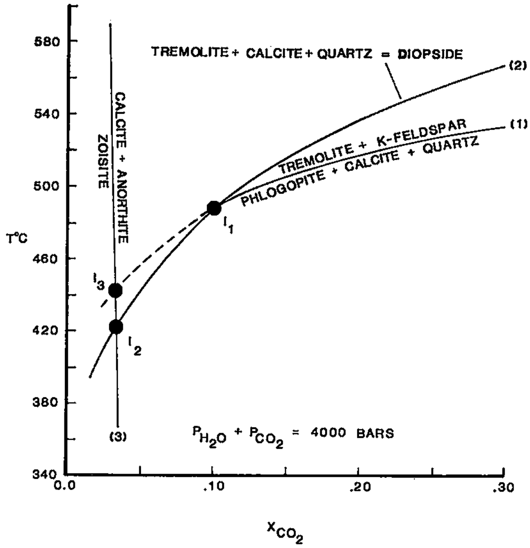

FIG. 3. The position of the tr–Kf (1), dp (2) and cc–an (3) equilibria in the system $CaO–MgO–K_2O–Al_2O_3–SiO_2–CO_2–H_2O$ in T–$X(CO_2)$ space at 4000 bars pressure. Invariant points are labeled. Additional equilibria present at the invariant points are not shown for the sake of clarity.

It is assumed that H_2O and CO_2 mix ideally. Kerrick & Slaughter (1976) calculated the position of the equilibria 3 dolomite + 4 quartz + H_2O = talc + 3 calcite + 3 CO_2 and calcite + quartz = wollastonite + CO_2 in T–$X(CO_2)$ space at 0.5 and 1.0 kbar according to two methods: (1) assuming ideal mixing of H_2O and CO_2 and using the fugacity coefficients for pure H_2O of Burnham *et al.* (1969) and CO_2 of Burnham & Wall (unpubl. data) and (2) using the fugacity coefficients of Ryzhenko & Malinin (1971) for non-ideal mixtures of H_2O and CO_2. Both equilibria lie at higher temperatures for a given $X(CO_2)$ when ideal mixing is assumed in comparison with temperatures calculated assuming nonideal mixing. For each equilibrium, the $X(CO_2)$ difference between the curves calculated assuming ideal mixing and those assuming nonideal mixing decreased as high and low values of $X(CO_2)$ were approached and as the pressure was increased. At $X(CO_2)$ about 0.20, the difference between the two is approximately 10°C at 1 kbar for both the talc + calcite and wollastonite equilibria. The assumption that CO_2 and H_2O mix ideally at 4000 bars probably has little effect on these calculations where $X(CO_2)$ is less than about 0.20, because the error introduced is approximately equal to the uncertainty in the position of equilibrium (1) and is much less than the uncertainty in the position of equilibrium (2) (Table 2).

Fugacities of pure H_2O and pure CO_2 were calculated at the equilibrium temperature and at a pressure of 4000 bars using the CO_2 fugacity coefficient data of Burnham & Wall (with permission of the authors through D.M. Carmichael) and the H_2O fucacity coefficient data of Burnham *et al.* (1969).

EQUILIBRIUM CONSTANTS USED IN THE CALCULATIONS

Published equilibrium constants are available for equilibrium (1) (Hoschek 1973, Hewitt 1975). A plot of $\Delta H°_r$ *versus* 1/T (K^{-1}) (Moore 1976) shows that 1) $\Delta H°_r$ for the data of Hoschek is constant over a temperature range of 490 to 640°C and 2) it is therefore thermodynamically self-consistent. However, the calculated $\Delta H°_r$ for the data of Hewitt (1975) over a measured temperature range of 450 to 640°C is not constant but varies linearly with 1/T, indicating that the data are thermodynamically inconsistent (Moore 1976, Skippen & Carmichael 1977). Therefore, the equilibrium constant of Hoschek (1973) is used in this study (Table 2).

The equilibrium constants of Skippen (1974) and Slaughter *et al.* (1975) for equilibrium (2) are in good agreement (Slaughter *et al.* 1975). The data of Skippen are used in this study. The upper and lower limits of uncertainty given by Skippen (1974) have been used to calculate the uncertainty in the position of equilibrium (2) at 4000 bars (Table 2).

When the above data are used at 4000 bars, equilibria (1) and (2) intersect. According to the rules of Schreinemakers (Zen 1966), equilibrium curve (1) should be stable only on the high $X(CO_2)$ side of the intersection (Fig. 3).

Equilibrium (3) has been investigated experimentally by Johannes & Orville (1972), and their equilibrium constant was used to calculate the position of this equilibrium curve. The upper and lower limits on the position of the curve are not known but reported to be large (Johannes & Orville, pers. comm. 1973 through D.M. Carmichael). The preliminary data of Allen & Fawcett (1980) on the position of this curve are in good agreement with those of Johannes & Orville (1972), although Allen's & Fawcett's data indicate that the curve may lie at slightly higher $X(CO_2)$ values than indicated by Johannes & Orville [$0.05 < X(CO_2) < 0.11$ at 500°C and 500 bars (Allen & Fawcett 1980), compared with 0.03 at 500°C and 4000 bars (Johannes & Orville 1972)].

The equilibrium curve of Johannes & Orville lies at an $X(CO_2)$ value lower than that of the intersection of equilibria (2) and (3) at 4000 bars, and therefore intersects only equilibrium (2) (Fig. 3).

ACTIVITY MODELS USED IN THE CALCULATIONS

The position of equilibria (1), (2) and (3) in T–$X(CO_2)$ space at 4000 bars in the presence of additional components in the minerals has been determined by estimating the activities of end-member components in the minerals and solving equation (5):

$$\log K = \frac{A}{T} + B' + \frac{C(P-P°)}{T} \quad \ldots\ldots\ldots (5)$$

Equation (5) is obtained from equation (1) by the addition of activity terms for the solids to the *B* term (Trommsdorff & Evans 1972):

$$B' = B + \log\left[\frac{(a_A)^a(a_B)^b}{(a_C)^c(a_D)^d}\right] \quad \ldots\ldots\ldots\ldots (6)$$

The *A* and *C* terms are unchanged.

Activity-coefficient data for end-member components in mineral solid solutions are not usually available, but assuming ideal mixing, it is generally possible to construct such models. However, in many cases several models can be constructed without advance knowledge of which is most accurate. It is therefore possible to calculate several temperatures and $X(CO_2)$ values for two given equilibria using one set of equilibrium constants.

Activities have been estimated for the phases involved based on knowledge of substitutions in the various lattice sites of the minerals, using the Temkin or cationic model (Temkin 1945). According to this model, "the activity is equal to the products of powers of the atomic fractions of elements in the appropriate lattice sites, the exponent of each atomic fraction being equal to the number of atoms in the formula" (Froese 1973). For example, for the potassium and magnesium sites in biotite, the expressions (K) and $(Mg/3)^3$ are used, where K and Mg represent the numbers of ions in the mineral analysis.

A modified form of the Temkin model is used where the coupled substitution of Al in the tetrahedral and octahedral sites is required to maintain electrostatic neutrality in Ca-amphibole and biotite. Fe^{2+} substitutes for Mg^{2+} in the octahedral sites and is coupled to Al^{IV}. The Fe^{3+} contents are not known; total iron has been calculated as FeO. The substitution units are therefore $Al^{IV}(Al^{VI}) \rightleftharpoons SiMg$. The Si term is dropped in the activity expressions because the activity of Si depends almost exclusively on the Al^{IV} concentration, which is coupled to Al^{VI} (Carmichael *et al.* 1974, Skippen & Carmichael 1977).

The activity models are presented in Table 3. In tremolite, there is a vacant *A* site in the mineral structure, but in hornblende some of these vacancies are filled with Na and K. To be consistent, the vacant site and the Ca site are treated separately. The activity of the vacant site is therefore 1–Na–K, and the activity of the Ca site is $(Ca/2)^2$.

The number of ions in the mineral analyses of calcite is low, between 0.96 and 0.98 (Table 1). The reason for this is unknown. The activity of $CaCO_3$ in calcite has therefore been obtained by normalizing the Ca content (X_{Ca}) to 1.00.

It is not necessary to construct an activity model for anorthite in plagioclase because activity-coefficient data are available (Orville 1972). The activity of $CaAl_2Si_2O_8$ in plagioclase is calculated directly using the expression $a = X\gamma$, where γ, the activity coefficient, is 1.276 for plagioclase of the compositional range of these samples (Table 1).

The end member for epidote is $Ca_2AlAl_2Si_3O_{12}(OH)$. Because the data for the equilibrium constant for equilibrium (3) pertain to the orthorhombic form zoisite and the observed mineral phase is monoclinic epidote, an error will be introduced in the calculations that is proportional to the free-energy change from the former to the latter. However, this error is probably less than 15° (Ghent & de Vries 1972).

TABLE 3. ACTIVITY MODELS OF "PURE" END MEMBERS IN MINERALS

$a^{Biotite}_{KMg_3AlSi_3O_{10}(OH)_2} = (K)\ (Mg/3^3)\ (OH/2)^2$

$a^{Ca\text{-}amphibole}_{Ca_2Mg_5Si_8O_{22}(OH)_2} = (1\text{-}Na\text{-}K)\ (Ca/2)^2\ (Mg/5)^5\ (OH/2)^2$

$a^{Calcite}_{CaCO_3} = (X_{ca}) = Ca/(Ca + Mn + Fe + Mg)$

$a^{K\text{-}feldspar}_{KAlSi_3O_8} = (X_K) = K/(K + Na + Ca + Mn + Fe + Mg)$

$a^{Plagioclase}_{CaAl_2Si_2O_8} = X\gamma,\ X = An = (Ca + Mn + Mg)/(Ca + Mn + Mg + Na + K)$
$\gamma = 1.276$, Orville (1972)

$a^{Epidote}_{Ca_2AlAl_2Si_3O_{12}(OH)} = (Ca/2)^2(1\text{-}Fe^{3+}\text{-}Mn)\ (Si/3)^3$

$a^{Diopside}_{CaMgSi_2O_6} = (Ca)\ (Mg)\ (Si/2)^2$

Al is present in three sites in epidote: *M*(1), *M*(2) and *M*(3). It is assumed that Fe^{3+} and Mn substitute for Al in the *M*(3) site only (Dollase 1972); X_{Al} for the *M*(1) and *M*(2) sites equals 1.0 and is not included in the expression.

In the present study, it is necessary to assume that X_{OH} equals 1.00 for biotite and Ca-amphibole, because only semiquantitative Cl and no F analyses were obtained. The validity of this assumption has been tested by calculating the displacements of the curves for Carmichael's (1970) samples (for which Cl and F were determined), assuming $X_{OH} = 1.00$, and then using X_{OH} values that take into account the Cl and F contents of the minerals (LeAnderson 1978a). The temperature difference resulting from the assumption that X_{OH} equals 1.00 is less than or equal to 10°C for all three samples. It is therefore assumed that the "error" introduced for the samples of this study is negligible, because it is likely that the partitioning of Cl and F between the minerals is similar in the samples from both areas. The activities are given in Table 4.

RESULTS

The accuracy of the calculated temperatures can be evaluated only if reliable independent mineralogical evidence is available. An estimate of the accuracy of the calculated temperatures for this study has been determined by calculating temperatures for four of Carmichael's samples (1970) that contain some of the same assemblages as the samples in the present study. These temperatures were then compared with independently estimated temperatures based on the aluminum silicates present in nearby pelitic rocks (Table 5). An additional check on the calculated temperatures for the samples of this study was obtained (Table 6) using the two-feldspar geothermometer of Whitney & Stormer (1977). However, this does not constitute an independent check of the temperatures, because the analytical data for plagioclase and microcline are involved in both sets of calculations.

The temperatures calculated for the samples whose assemblages correspond to the intersec-

TABLE 4. CALCULATED ACTIVITIES OF END MEMBERS[1]

	A110	A500	A545	A144	A28	A29
$a^{\text{Biotite}}_{KMg_3AlSi_3O_{10}(OH)_2}$	0.087	0.358	0.070	0.189		0.094, + .008, -.006
$a^{\text{Ca-amphibole}}_{Ca_2Mg_5Si_8O_{22}(OH)_2}$	0.003	0.172	0.002	0.253	0.012 ± .005	0.024, + .006, -.005
$a^{\text{Calcite}}_{CaCO_3}$	0.978	0.955	0.957	0.940	0.990, + .001, -.010	0.990, + .010, -.011
$a^{\text{K-feldspar}}_{KAlSi_3O_8}$	0.946	0.918	0.931	0.891		0.900 ± .02
$a^{\text{Plagioclase}}_{CaAl_2Si_2O_8}$	0.221	0.439	0.363		0.454, +.025, -.026	
$a^{\text{Epidote}}_{Ca_2AlAl_2Si_3O_{12}(OH)}$	0.106	0.133	0.183		0.563, +.071, -.065	
$a^{\text{Diopside}}_{CaMgSi_2O_6}$				0.730	0.593, +.022, -.017	0.602, +.016, -.028

	A34	398	389
$a^{\text{Biotite}}_{KMg_2AlSi_3O_{10}(OH)_2}$		0.075, +0.004, -0.006	0.023, ± 0.002
$a^{\text{Ca-amphibole}}_{Ca_2Mg_5Si_8O_{22}(OH)_2}$	0.005, ± .001	0.014, ± 0.005	0.0004, ± 0.000
$a^{\text{Calcite}}_{CaCO_3}$	0.979, +.011, -.010	0.979, +0.011, -0.010	0.990, ± 0.010
$a^{\text{K-feldspar}}_{KAlSi_3O_8}$		0.929, ± 0.02	0.930, ± 0.02
$a^{\text{Plagioclase}}_{CaAl_2Si_2O_8}$	0.332, +.028, -.026		0.245, +0.025, -0.026
$a^{\text{Epidote}}_{Ca_2AlAl_2Si_3O_{12}(OH)}$	0.152, +.029, -.021		0.235, +0.009, -0.012
$a^{\text{Diopside}}_{CaMgSi_2O_6}$	0.562, +.027, -.026	0.552, +0.021, -0.025	

[1] The chemical analyses for samples A144, A500, A545, A110 are given in Carmichael (1970). The analyses for samples A28, A29, A34, 398, 389 are given in Table 1. The ± values for the samples of this study represent the ranges of the calculated activities due to the analytical reproducibility. (LeAnderson 1978a).

tion of equilibria (1) and (2) (invariant point I_1, Fig. 3) range from 0 to 69°C lower than the independently estimated (sample A144, Table 5) and calculated (A29 and 398, Table 6) temperatures.

The calculated temperatures for five of the six samples whose assemblages correspond to the intersection of equilibria (1) and (2) with equilibrium (3) range from 45 to 142°C lower than the estimated or calculated temperatures used for comparison (samples A110, A545 and A500, Table 5; A28 and 389, Table 6). Based on these comparisons, only A34 (Table 6) gives a reasonable temperature.

It appears that reasonable temperatures can be calculated for assemblages corresponding to invariant point I_1 using these activity models, equilibrium constants and assumptions, although they may be low by 50 to 75°C. On the other hand, temperatures calculated for assemblages corresponding to invariant points I_2 and I_3 can be expected to be low by at least 50°C, and perhaps by as much as about 150°C.

DISCUSSION

Three principal sources of error may contribute to the low values that result when equilibrium (3) is involved: 1) the true value lies within the range of reproducibility of the chemical analyses; 2) the calculated positions of equilibria (1) and (2) are in error; 3) the calculated position of equilibrium (3) lies at too low an $X(CO_2)$ value over the temperature range in question.

The range of temperatures due to the analytical reproducibility is given in Table 6. The temperatures obtained for four of the five

TABLE 5. CALCULATED TEMPERATURE AND X_{CO_2} VALUES FOR FOUR SAMPLES OF CARMICHAEL (1970)

Sample No.	Intersecting Reactions	Estimated T°
A110	Calcite-Anorthite & Ca-amphibole-K-feldspar	450°-475°
A144	Diopside & Ca-amphibole-K-feldspar	510°-550°
A545	Calcite-Anorthite & Ca-amphibole-K-feldspar	550°-575°
A500	Calcite-Anorthite & Ca-amphibole-K-feldspar	575°-650°

Calculated Temperature and X_{CO_2} Values

	A110	A144	A545	A500
T°C, X_{CO_2}	415,0.03	525,0.11	425,0.05	495,0.13

Difference between calculated & estimated temperatures

A110	A144	A545	A500
≈-45°	≈0°	≈-45°	≈-115°

The calculated temperature and X_{CO_2} values for four samples of Carmichael (1970) are presented along with the estimated temperature (LeAnderson 1978a) based on the position of the samples with respect to the kyanite-sillimanite isograd.

TABLE 6. CALCULATED TEMPERATURE AND X_{CO_2} VALUES FOR THE SAMPLES OF THIS STUDY

Obtained by calculating the displacement of the reaction curves

Sample No.	The Two Intersecting Reactions
A29 & 398	Tremolite-K-feldspar and Diopside
A28 & A34	Calcite-Anorthite and Diopside
389	Calcite-Anorthite & Tremolite-K-feldspar

	A28	A29	A34
T°C	380±25	445±5	495,+10,-55
X_{CO_2}	.01,+.01, -.003	.03,+.01, -.00	.04,+.05, -.02

	389	398
T°C	370±30	440,+10-0
X_{CO_2}	.01,+.01, -.003	.03,+.00, -.01

Temperatures obtained using the two-feldspar geothermometer

	A28	A29	A34
T°C	522,+21,-22	514,+21,-20	480±18

	389	398
T°C	435,+22,-23	464,+20,-21

Difference between the calculated temperatures

	A28	A29	A34
T°C	-142	-69	+15

	389	398
T°C	-65	-24

The ± values refer to the range of possible temperature and X_{CO_2} values owing to the analytical reproducibility.

samples using the two-feldspar geothermometer do not lie within the ranges of the temperatures calculated by displacement of the equilibrium curves. Therefore, this cannot explain the difference between the temperatures.

Calculated temperatures for invariant point I_1 agree reasonably well with the temperatures used for comparison. It is only where equilibria (1) and (2) are used in conjunction with equilibrium (3) that unreasonably low temperatures result. If the positions of equilibria (1) and (2) are responsible for the low values where they intersect equilibrium (3), then invariant point I_1 would have to lie at an $X(CO_2)$ less than 0.11, the $X(CO_2)$ value of their intersection (Fig. 2). If I_1 lies near equilibrium (3) at about 490°C at 4000 bars and $X(CO_2) = 0.03$, reasonable temperatures would be obtained for assemblages corresponding to all three intersections. However, equilibrium (2) would then lie about 30°C above the upper experimental bracket given by Skippen (1974). The close agreement between Skippen (1974) and Slaughter *et al.* (1975) for the position of this equilibrium indicates that this is not a likely possibility (Slaughter *et al.* 1975). This agreement suggests that the problem, at least in part, lies in the calculated position of equilibrium (3).

Mineralogical evidence indicates that, for rocks with the bulk composition of those in the field areas of Carmichael (1970) and in this study, reaction (3) lies near the intersection of reactions (1) and (2). Samples A110, A545, A500 and 389 contain the assemblage that corresponds to I_3. Reaction curve (3) for these samples must lie at an $X(CO_2)$ value greater than that of I_1 for this assemblage to be stable (Fig. 3). The assemblages in samples A29, 398 and A144 correspond to I_1 and contain calcite and plagioclase but not epidote. Reaction curve (3) for these assemblages must lie at $X(CO_2)$ values less than that of I_1. This indicates that reaction curve (3) commonly lies near, and can be found at, $X(CO_2)$ values either higher or lower than invariant point I_1 and that the stable assemblage formed depends on the relative displacements of these reaction curves due to solid solutions in the minerals. Consequently, there appear to be two possible explanations for the low temperatures. The relative position of equilibrium curve (3) as shown in Figure 3 is correct. It is displaced farther to the right than indicated here either because lower activity values of $Ca_2AlAl_2Si_3O_{12}(OH)$ occur in epidote than can be obtained using the activity model in Table 3 or because the model equilibrium curve (3) lies near I_1 (or both).

CONCLUSIONS

Temperature values calculated for assemblages corresponding to the intersection of the tremolite–K-feldspar and diopside equilibria, using the stated equilibrium constants, activity models and assumptions, appear to be reasonable, although they may be low by as much as 50 to 75°C. However, temperatures calculated for assemblages corresponding to the intersection of the calcite–anorthite equilibrium curve with the tremolite–K-feldspar and diopside equilibria are usually low by 50 to 150°C. This may be due either to calculated activities of $Ca_2AlAl_2Si_3O_{12}(OH)$ in epidote that are too high or to an error in the calculated position of the calcite–anorthite equilibrium (or both). At present, it cannot be determined which of the two possibilities is correct. It is apparent from the mineral assemblages, however, that the calcite–anorthite reaction curve lies near the intersection of the tremolite–K-feldspar and diopside reaction curves. Assuming that the tremolite–K-feldspar and diopside equilibria intersect at low $X(CO_2)$ values, which is indicated by the experimentally determined equilibrium constants, epidote is restricted to coexisting with fluid compositions less than about 0.10 to 0.20 $X(CO_2)$ at temperatures greater than perhaps 400°C and pressures greater than perhaps 2 kbar; this is in agreement with the conclusions of Allen & Fawcett (1980) and Bird & Helgeson (1981). It also suggests that if the position of the calcite–anorthite equilibrium (Johannes & Orville 1972) is in error, it lies within about 0.10 $X(CO_2)$ of its true position over the temperature range of 350 to 600°C at 4000 bars.

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