

AN EQUILIBRIUM MODEL FOR BUCHAN-TYPE METAMORPHIC ROCKS, SOUTH-CENTRAL MAINE

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ABSTRACT

Equilibrium relationships in andalusite-staurolite-cordierite-mica schists of the Buchan-type from south-central Maine have been investigated. Samples containing assemblages of eight to eleven minerals from compositionally distinctive beds and laminations of pelitic schist in a single outcrop were studied by electron probe methods. The proximity of samples enables one to consider that the values for external parameters (P , T , μ_3) are the same over the sample area.

K_D' values for Mg-Fe distribution between contacting cordierite and biotite in all samples are identical, within experimental error. This equality indicates a close approach to chemical equilibrium.

Two models for equilibrium are considered. In the first model each lamination is treated as a closed system, and the maximum number of determining components is taken as eleven (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , FeO , MnO , MgO , CaO , Na_2O , K_2O and H_2O). Thus, laminations associated with three different beds, and containing eleven minerals should be invariant at arbitrary external conditions. However, analyses of individual grains of a mineral species within each lamination are not identical, and a plot of

$$\left(\frac{X_{\text{MgO}}}{X_{\text{FeO}}}\right)_{\text{biotite}} \text{ versus } \left(\frac{X_{\text{MgO}}}{X_{\text{FeO}}}\right)_{\text{cordierite}}$$

from these laminations does not define a unique point. These observations indicate the inadequacy of this model.

In the second model the rock is considered to consist of compositionally distinct equilibrium mosaics of discrete grain clusters. Compositions of individual mineral grains belonging to two- and three-grain clusters were examined. Different compositions of individual grains of the same mineral situated in different clusters in close proximity (4-6 mm) is consistent with this model. However, because a plot of

$$\left(\frac{X_{\text{MgO}}}{X_{\text{FeO}}}\right)_{\text{biotite}} \text{ versus } \left(\frac{X_{\text{MgO}}}{X_{\text{FeO}}}\right)_{\text{cordierite}}$$

for these clusters does not define a unique point, the number of mineral species contained in a mosaic must be less than the number of determining components. By uniting the chemical data from contacting minerals, a seven component system is found to be adequate to describe the phase relationships within the mosaics.

The compositions of coexisting ilmenite and magnetite suggest that the temperature was $\sim 500^\circ\text{C}$ and the $f(\text{O}_2)$ for the sample analyzed was $\sim 10^{-24}$ bars.

GENERAL STATEMENT

Rocks identified as the Waterville Formation (Osberg, 1968) in south-central Maine (Figure 1) have been recrystallized by a Buchan-type metamorphism. In this paper the degree to which chemical equilibrium has been attained by the mineral associations in the Waterville Formation is examined and thermodynamic models representing large-volume equilibrium and mosaic equilibrium are considered.

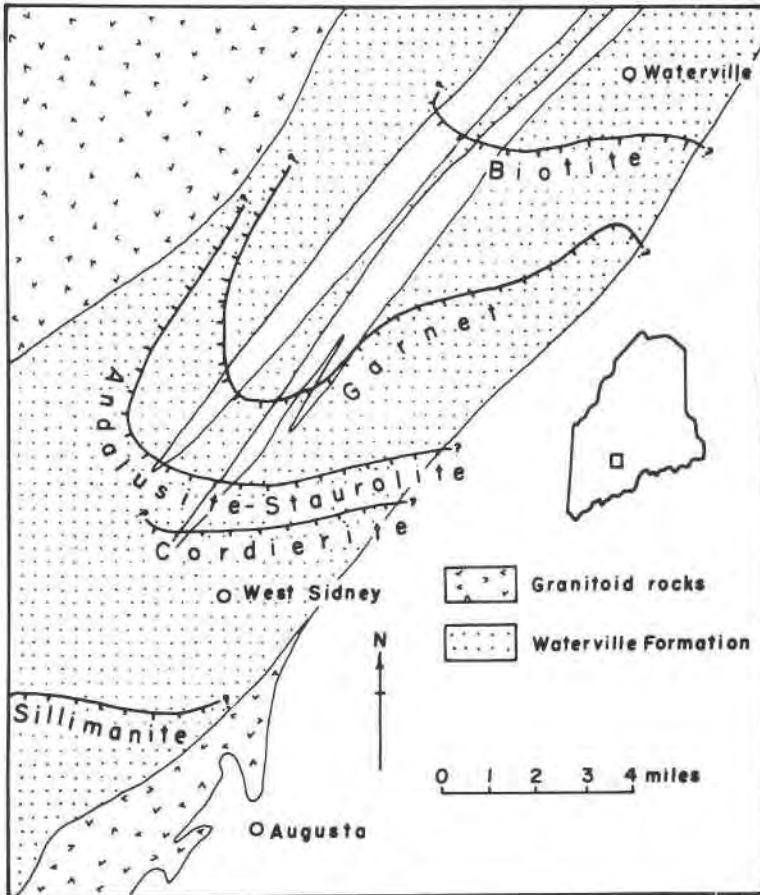


FIG. 1. Location and geologic map of the Waterville Formation south-central Maine.

At low grade the Waterville Formation consists of quartz, plagioclase, muscovite, and chlorite. Within the area studied (Figure 1) the metamorphic grade increases southward, and biotite, garnet, andalusite-staurolite, cordierite, and sillimanite isograds have been mapped.

Over most of the area the number of phases in the rocks are few and the relationships between them do not give fruitful information for the purposes of this study. However, an outcrop in a small roadcut exposed at West Sidney (Figure 1) does provide an opportunity to investigate equilibrium relationships. The outcrop (Figure 2) contains six compositionally distinctive beds. Three beds contain associations of eleven relevant mineral species, whereas the others contain less than eleven.

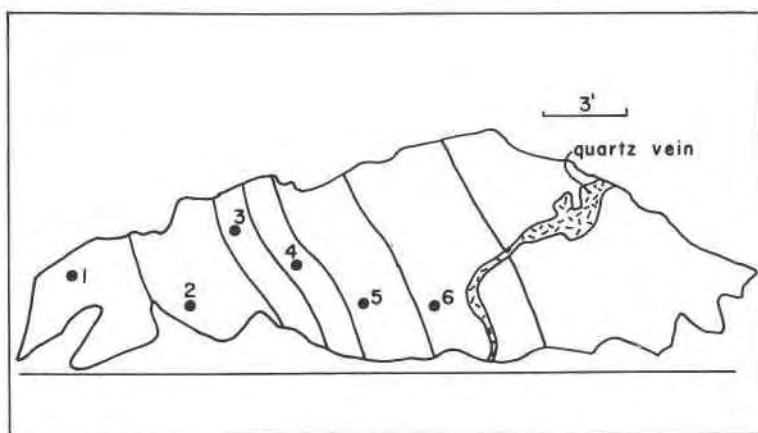


FIG. 2. Sketch of road-cut at West Sidney showing location of samples by circles. Numbers refer to beds.

PETROGRAPHY

Modes of each bed are presented in Table 1. A minimum of two thin sections were examined for each bed and the modes are the averages of 2000 point-counts per slide for all slides pertaining to a given bed.

The beds consist of thin laminations of quartzite and pelite, 1 mm to 3 cm thick. Many of the pelitic laminations contain all of the modal minerals. Commonly, garnet, staurolite, cordierite, andalusite, and chlorite are porphyroblastic, and although these minerals are mostly restricted to the pelite, they are locally developed in the quartzite laminations. In some cases a single porphyroblast extends across two or three laminations.

Optically, the micaceous minerals of the pelite define a schistosity that is essentially

TABLE 1. MODES OF BEDDING. SPECIMEN NUMBERS REFER TO BEDS IN FIGURE 2

Mineral	Modes					
	1	2	3	4	5	6
Quartz	34.6	25.6	51.3	23.6	42.2	32.6
Plagioclase	12.7	22.2	12.0	6.1	8.7	16.5
Muscovite	37.1	42.1	27.9	49.1	34.3	37.0
Biotite	6.7	—	0.2	4.0	11.6	7.5
Staurolite	2.5	7.9	6.1	2.0	1.5	3.9
Cordierite	4.4	—	—	11.2	tr	—
Andalusite	tr	—	0.6	tr	tr	tr
Garnet	0.4	1.0	0.7	1.3	1.0	1.4
Chlorite	1.7	1.3	1.2	2.7	0.7	1.1
Ilmenite						
Magnetite						

parallel to the laminations. Porphyroblasts interrupt the schistosity but show no helicitic structure. Textures indicative of alterations or reactions between grains were not observed, and, thus, the minerals appear to be in stable association. The following contacting associations were noted: biotite-chlorite-cordierite, biotite-chlorite-staurolite, chlorite-staurolite-cordierite, biotite-chlorite-andalusite, biotite-chlorite-garnet, biotite-cordierite-garnet, biotite-cordierite, biotite-staurolite, biotite-chlorite, biotite-garnet, garnet-staurolite, garnet-cordierite, andalusite-biotite, andalusite-chlorite, staurolite-chlorite cordierite-chlorite, and staurolite-cordierite. Quartz and muscovite are in close proximity in each association.

Quartz occurs as anhedral grains 0.03 to 0.14 mm in size and commonly exhibits undulatory extinction. The grains of quartz occur in a mosaic of generally rectangular forms in section. Inclusions of opaques and muscovite are rare, and muscovite and biotite embay quartz rather commonly.

Plagioclase was not positively identified in thin section, but diffractograms of quartz separates consistently display the 22.1° peak of plagioclase. It is untwinned and has approximately the refractive index of quartz. It probably makes up less than 3 percent of the rock.

Muscovite forms subhedral plates 0.05 to 0.9 mm across. The plates are preferentially oriented parallel to the schistosity. Grains of muscovite have simple contacts and contain few inclusions.

Biotite is subhedral. Grains have fair shape orientation, but it is not as good as that of muscovite. Biotite is pleochroic; α =colorless, β = γ =brown. Grains range from .08 to 0.4 mm in size. Quartz, muscovite, and opaques occur as inclusions, and commonly muscovite and chlorite embay biotite.

Staurolite forms subhedral to euhedral porphyroblasts, 1.3 to 3.9 mm in size. Crystals are commonly twinned on {232} and contain such an abundance of quartz, garnet, and opaque inclusions that they have a spongy appearance. Pleochroic colors are α =colorless, β =very light brown, and γ =yellowish brown.

Cordierite occurs as ameiboid grains, 2.3 to 11.4 mm across, that include quartz, biotite, muscovite, garnet, opaques, and chlorite. Included zircons are surrounded by pleochroic haloes with colors that range from colorless to yellow. Boundaries of cordierite crystals are penetrated by biotite, muscovite and chlorite. No twinning was observed in cordierite.

Andalusite forms glomeroblastic prisms 2.5 to 15.5 mm long, consisting of small euhedral needles. Quartz, biotite, and opaques are locally included in the glomeroblasts.

Garnet crystals are euhedral. Crystals measure 0.5 to 0.8 mm across. They are clear of inclusions and show no optical zoning.

Chlorite occurs as porphyroblasts that cut across the schistosity. Crystals are subhedral with generally simple contacts and measure 0.3 to 0.8 mm across. Chlorite is optically positive and has pleochroic colors ranging from colorless to very pale green. Inclusions within chlorite are quartz and opaques.

Opaques include ilmenite, magnetite, pyrite, and pyrrhotite. Ilmenite and magnetite were found in all beds, but pyrite and pyrrhotite were found in only two samples. Ilmenite is consistently the most abundant opaque. It occurs as euhedral hexagonal plates, approximately 0.03 mm across. Compositions judged from $2\theta_{(021)}\text{Fe}_{\text{K}\alpha_1}$ and $2\theta_{(116)}\text{Fe}_{\text{K}\alpha_1}$ and Lindsley's (1963) determinative curves are Ilm_{97} . Magnetite forms subhedral to anhedral grains. The cell dimension is $a = 8.40\text{\AA}$ which according to Lindsley's chart (1962) indicates a composition of Mg_{96} . Pyrrhotite occurs as irregular lens-shaped grains that lie in the schistosity. Pyrite is scarce relative to pyrrhotite. It forms subhedral to euhedral crystals commonly associated with pyrrhotite.

Non-opaque accessories include zircon, tourmaline, and apatite.

CHEMISTRY

Bulk samples from each bed were chemically analyzed and the results are posted in Table 2. Approximately 500 g of sample were pulverized by a jaw crusher and processed in a Spex-Mixer/Mill until the grains passed through a 325 mesh sieve. The sample was then reduced to 20 g by passing it repeatedly through a splitter. The samples were analyzed by the method of Shapiro and Brannock (1962) as modified by Shapiro (1967).

The compositions of the beds have been recalculated to mole-ratios and plotted on a Thompson projection (1957) in Figure 3. Before plotting the mole-ratios, iron was adjusted for titania in ilmenite and the molar amount of alumina was adjusted for soda and lime in oligoclase and lime in garnet. None of the points representing the different beds have identical compositions.

TABLE 2. CHEMICAL ANALYSES OF BEDS. NUMBERS, OTHER THAN G-2, REFER TO BEDS IN FIGURE 2

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	ΣFeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O ⁺	H ₂ O ⁻	P ₂ O ₅	Σ
G-2	69.2	0.5	15.4	2.4	N.D.	0.7	1.9	4.1	4.5	0.66	0.17	0.16	99.69
1	59.1	0.8	20.5	8.1	0.1	4.0	0.7	0.9	3.3	NA	NA	NA	97.50
2	58.1	0.8	19.4	7.4	0.1	3.5	0.6	0.9	3.6	NA	NA	NA	94.40
3	62.0	0.8	16.2	5.4	0.1	3.0	1.2	2.2	2.5	NA	NA	NA	93.40
4	53.4	1.0	20.9	9.8	0.1	5.2	0.5	0.7	3.9	NA	NA	NA	95.50
5	59.7	0.8	18.0	8.1	0.1	4.0	0.7	0.9	3.3	NA	NA	NA	95.60
6	55.9	0.9	20.3	7.8	0.1	4.3	0.8	1.3	3.9	NA	NA	NA	95.30

Analyst: P. H. Osberg.

Chemical analyses of contacting minerals in each bed were made using an Applied Research Laboratories EMX electron microprobe X-ray analyzer. The method of Bence and Albee (1968) was used to convert the data from the probe into weight percent. Primary standards were as follows: Si-quartz, Al-kyanite, Fe-hematite, Mn-rhodonite, Mg-pyrope, Ca-grossularite, and K-orthoclase. Analyses of minerals are presented in Table 3. Wet-chemical and probe analyses are shown for Sturbridge garnet and biotite standard to show comparative values. All standards and reference minerals are from a collection in the Hoffman Laboratory, Harvard University.

Except for garnet the minerals showed little chemical zoning. The rims of garnet are impoverished in MnO and enriched in FeO relative to the cores.

TEST FOR EQUILIBRIUM

One test for equilibrium consists of comparing distribution coefficients for exchangeable components between mineral pairs from beds of different bulk composition at the same set of external conditions. The derivation and the form of the equation for the distribution coefficient, K_D' , have been discussed by Kretz (1961, 1964) and Albee (1965).

In this paper the distribution of iron and magnesium between contacting pairs is analyzed in exchange reactions of the type

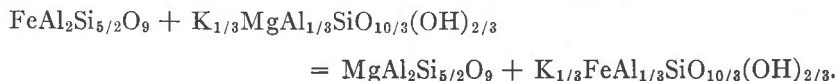


TABLE 3. CHEMICAL COMPOSITION OF MINERALS. NUMBERS REFER TO BEDS IN FIGURE 2

Standards		Biotite																	
		1		2		3		4			5		6						
Synthetic* Almandine	Synthetic Almandine (Probe)	a	b	a	a	a	b	a	b	c	d	a	b	a	b	a	b		
SiO ₂	36.2	36.7	38.0	37.8	36.6	35.3	37.7	37.3	38.7	37.4	36.5	36.2	36.9	38.1					
Al ₂ O ₃	20.5	20.9	18.3	20.6	20.8	20.2	20.3	19.8	20.5	20.8	20.3	20.8	20.5	20.1					
ΣFeO	43.3	43.4	13.6	18.4	19.3	18.7	18.6	18.2	18.4	18.2	19.0	18.9	18.2	17.8					
MnO	0.00	0.00	NA	0.13	0.13	0.13	0.13	0.14	0.14	0.14	0.13	0.14	0.13	0.13					
MgO	0.00	0.00	15.1	9.9	10.9	10.0	10.1	10.3	10.1	10.0	9.9	10.5	10.4	10.5					
K ₂ O	0.00	NA	9.00	8.7	8.3	8.8	8.9	8.9	9.0	8.9	8.7	8.8	8.7	8.9					
Σ	99.9	100.5	100.1	94.1	95.5	93.1	95.7	94.6	96.8	95.4	94.5	95.3	94.3	95.5					
MgO/FeO (Moles)		1.00-	0.98-	0.94-	0.98-	0.94-	0.96-	0.99-	0.96-	0.97-	0.92-	0.97-	1.00-	1.04-					
(95% confidence level)		1.03	1.00	0.98	1.03	0.98	0.99	1.02	0.99	0.99	0.93	1.00	1.04	1.07					

Standards		Garnet Rim						Chlorite				Cordierite					
		3		4		5		3		4		3		4		5	
1	a	a	b	a	b	a	a	a	a	a	a	b	b	d	a	a	b
21.6	25.1	35.8	38.0	24.9	36.0	23.3	23.2	45.1	45.8	44.1	46.2	44.1	46.2	44.1	44.1	44.1	46.0
54.2	55.0	21.1	22.2	54.3	21.0	25.0	23.5	34.6	34.6	34.3	34.3	34.3	34.3	34.3	33.5	33.5	34.5
14.8	14.8	31.7	32.3	14.8	31.2	23.5	23.5	7.7	7.9	7.9	7.7	7.9	7.7	7.7	8.2	8.2	7.5
0.8	0.8	8.0	9.5	0.7	8.7	0.15	0.23	0.5	0.5	0.4	0.6	0.5	0.5	0.5	0.5	0.5	0.5
2.1	2.1	2.7	2.9	2.0	2.8	14.6	14.7	8.2	8.1	8.3	8.4	8.3	8.4	8.1	8.3	8.1	8.3
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
96.5	97.8	99.3	104.9	96.7	99.7	86.6	85.1	96.1	96.9	95.0	97.2	94.4	96.8	94.4	94.4	94.4	96.8
0.24-	0.25-	0.14-	0.15-	0.24-	0.15-	1.09-	1.10-	1.89-	1.80-	1.85-	1.91-	1.74-	1.95-	1.74-	1.74-	1.74-	1.95-
0.26	0.26	0.15	0.16	0.25	0.16	1.13	1.13	1.94	1.86	1.89	1.96	1.79	2.01	1.79	1.79	1.79	2.01

* Synthetic Almandine standard and Biotite 4 standard contain respectively: T₂O₃ 0.00, 2.3; CaO 0.00, 0.33; Na₂O 0.00, 0.55; H₂O 0.00, 4.2.

The distribution coefficient may then be written

$$K_D' = \frac{X_{\text{MgO}}^{\text{cordierite}} X_{\text{FeO}}^{\text{biotite}}}{X_{\text{FeO}}^{\text{cordierite}} X_{\text{MgO}}^{\text{biotite}}}$$

The value of the distribution coefficient depends on temperature, pressure, chemical potential of water, concentrations of other exchangeable components, and deviations from ideality of solid solutions. The outcrop at West Sidney is sufficiently small that the external conditions ($T, P, \mu_{\text{H}_2\text{O}}$) can be considered constant. In addition to iron and magnesium, aluminum, manganese, and titanium are exchangeable components in the mineral pairs analyzed, but their effect on the ratio of magnesium and iron is probably small. Finally, the effect of non-ideality is regarded as approximately constant in each comparison because of the constancy of external conditions and the similarity of chemical compositions of the phases involved.

The resulting K_D' values are presented in Table 4. The similarity of values within pairs of contacting minerals indicates that at the time the chemistry was frozen into the rock mutual exchange of chemical components existed at least between contacting minerals. Such relationships suggest a close approach to equilibrium.

It might be argued that the Mg-Fe ratios in biotite, chlorite, cordierite, garnet, and staurolite change so little in response to changing external

TABLE 4. K_D' VALUES FOR CONTACTING MINERALS.
NUMBERS ARE THE SAME AS TABLE 3

Specimen	K_D' (cordierite/ biotite)	K_D' (staurolite/ biotite)	K_D' (garnet-rim/ biotite)	K_D' (chlorite/ biotite)
1a		.25		
1b	1.93			
2a	1.91			
3a			.15	1.11
3b	1.95			
4a				1.15
4b		.26		
4c			.16	
4d	1.98			
5a	1.91			
5b		.25		
6a	1.95		.16	
6b	1.93			

TABLE 5. COMPARISON OF K_D' FOR MINERAL PAIRS AT DIFFERENT METAMORPHIC GRADE

Location	K_D' (garnet rim-biotite)	K_D' (chlorite-biotite)
West Sidney	0.16	1.13
Comparison outcrop	0.13	1.02

conditions that their K_D' values are poor indicators of equilibrium. The average K_D' values for contacting chlorite-biotite and garnet rim-biotite from the outcrop at West Sidney compared with an outcrop in the low intensity part of the staurolite zone are tabulated in Table 5. These comparisons indicate that K_D' is sensitive to changes in metamorphic conditions.

Whether or not the values of K_D' at West Sidney were established by prograde or retrograde reactions is unknown, *i.e.*, whether or not the chemistry was frozen in at the climax of metamorphic conditions or at some set of conditions slightly below the climax. It is reasoned, in either case, that the common values of K_D' for parts of coexisting minerals from rocks of differing bulk composition indicates a close approach to equilibrium in volumes at some scale

THERMODYNAMIC MODELS

Having demonstrated that the mineral associations approach chemical equilibrium, the question arises as to the thermodynamic model that is consistent with the mineral relationships. Two models are considered. The first is a "large volume model" in which a lamination constitutes the system, and the second is a "mosaic model" in which clusters of grains are considered to constitute the system.

Large volume model. In considering the "large volume model", three beds are of interest: 1, 4, and 5. In these beds individual laminations contain all of the modal minerals and, in the case of 4 and 5, the probe analyses of minerals were all from single layers.

These beds have slightly different bulk compositions (Table 2, Figure 3), and modal analyses (Table 1) indicate that each contains eleven relevant minerals including ilmenite and magnetite. Following Korzhinskii (1959, p. 62) at fixed external conditions (T , P , $\Sigma\mu_i$) the phase rule reduces to the form

$$f = c_i - p$$

where

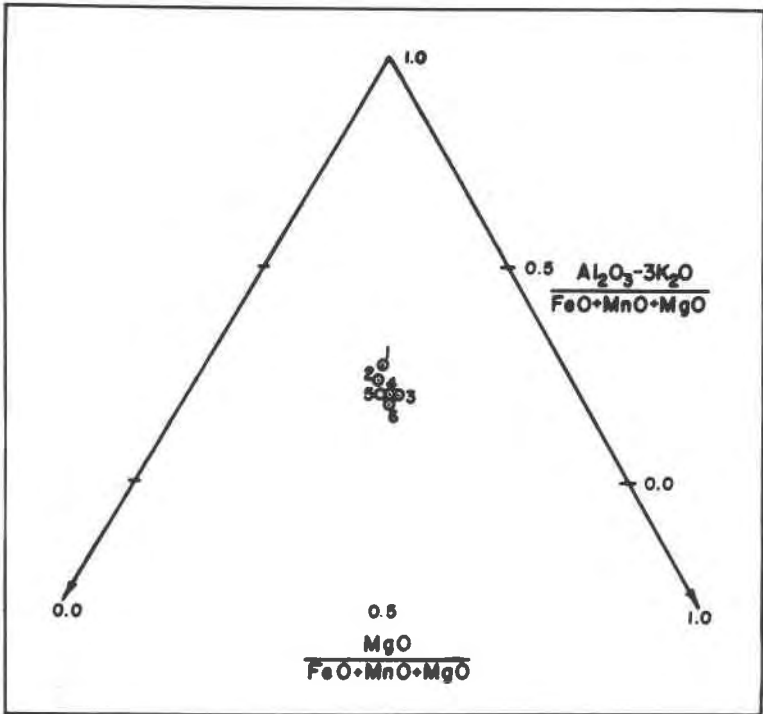


FIG. 3. Bulk compositions of beds.

f = number of degrees of freedom
 c_i = number of buffered components
 p = number of phases.

In these laminations (in beds 1, 4, and 5), if the assemblages of eleven minerals are considered to be in equilibrium, the number of buffered components must be at a minimum eleven. Because there is no *a priori* way of knowing which components are buffered, the simplest procedure is to parcel out the buffered components among the major rock forming oxides— SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , FeO , MnO , MgO , CaO , Na_2O , K_2O , and H_2O . To satisfy the minimum requirement of the eleven phase assemblages, all of the major oxides are used, and water must be considered buffered. These circumstances suggest that these laminations with eleven phases as systems have zero degrees of freedom at constant T , P , $E\mu_j$, and consequently the phase relationships are determined completely by the eleven major oxides. It is doubtful that trace amounts of other components would materially affect the ratios of the major components.

The possibility that the assemblages of eleven minerals contain non-reactive phases, phases stabilized by additional components, or represent phases involved in an incompleting reaction must be considered. Because garnet is zoned it might be thought to be a nonreactive phase. Although diffusion between the inner parts of the crystal and its environment is obviously difficult, the rims of garnets are reactive as shown by the change in values of K_D' between garnet rims and contacting biotite with metamorphic grade (see table 5). The presence of zinc might stabilize staurolite and thus reduce by one the number of phases that are determined by the major rock forming oxides. This question was not studied, but it is questionable that a trace amount of zinc in the rock serves to stabilize up to eleven modal percent of staurolite. Finally, the absence of reaction rims between minerals and the occurrence of the same phase assemblage at other outcrops seems to argue against the notion that the assemblage represents an incomplete reaction.

A test for the adequacy of the "large volume model" is to compare the compositional invariability of phases from beds of different bulk composition. This comparison can readily be made on a diagram in which the Mg-Fe ratios of contacting minerals are plotted. For invariant conditions this plot should define a unique point, whereas if the conditions are not invariant, the coordinates for contacting minerals should lie along a curve. Figure 4 shows the plots for contacting biotite-garnet rims, biotite-staurolite, biotite-chlorite, and biotite-cordierite. The uncertainty of the

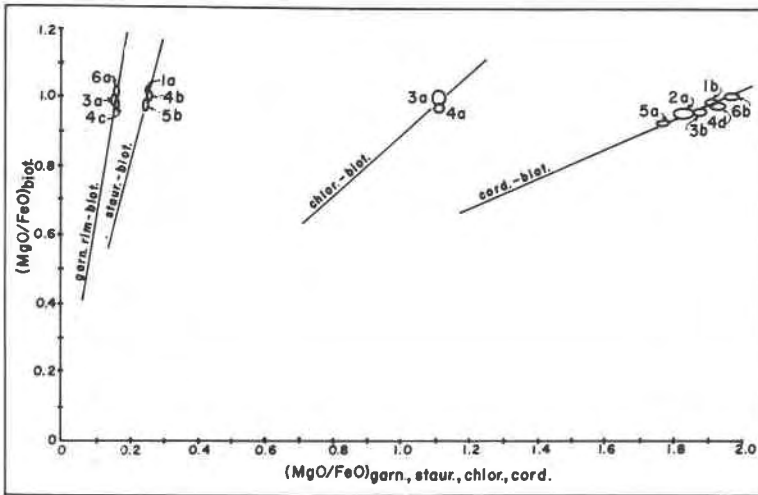


FIG. 4. Plot of MgO/FeO for biotite against MgO/FeO for minerals in contact with biotite. Ellipses show precision at 95% confidence level.

values at the 95 percent confidence level is indicated by the dimensions of the ellipses.

The plot of the MgO-FeO ratios for contacting biotite and cordierite is instructive. It is obvious that the coordinates for these minerals from laminations in beds 1, 4, and 5 are not the same, and in fact they differ by an amount far greater than any conceivable error in analysis. Although phase considerations suggest that these laminations are compositionally invariant, the plot indicates that they are not. This contradiction leads the writer to judge the "large volume model" inadequate.

Mosaic model. In the "mosaic model" the rock is thought to consist of grain clusters that have bulk compositions that may differ from that of adjacent grain clusters. Exchange of chemical species between adjacent clusters is incomplete, but the external conditions are uniform for all clusters.

A test for the "mosaic model" would be to show that the compositions of a particular mineral varied from point to point in the rock. Because biotite is the dominant Mg-Fe mineral in all samples, a comparison of the MgO-FeO ratios of biotite from different parts of a lamination should show the validity of the model.

MgO-FeO ratios of selected biotites along a ten millimeter traverse are shown in Figure 5. The precision of the ratios at the 95 percent confidence level is represented by the lengths of the line-segments. A staurolite crystal occupies the left margin of the traverse, followed by a biotite-concentration, a cordierite porphyroblast, a muscovite-rich seam, and a quartz-rich layer as indicated. The MgO-FeO ratios of biotite vary from point to point along the traverse.

The variation in MgO-FeO ratio from biotite grain to biotite grain indicates the existence of compositional realms. This compositional variation coupled with the existence of equilibrium partitions indicates a condition of mosaic equilibrium.

Compositional realms are apparently controlled by the growth of porphyroblasts that as they grow extend their compositions over large volumes of rock. In their growth the porphyroblasts replace certain minerals in the rock, incorporating some chemical constituents and exchanging others with neighboring minerals, the exchange partitions being a function of the factors of state. Diffusion within porphyroblasts is generally faster than diffusion through multicrystalline volumes of rock, and, therefore, chemical constituents that diffuse out of the porphyroblast into the environment tend to be concentrated in a selvage of minerals immediately adjacent to the porphyroblasts.

Porphyroblasts seeded in different parts of the rock may have slightly

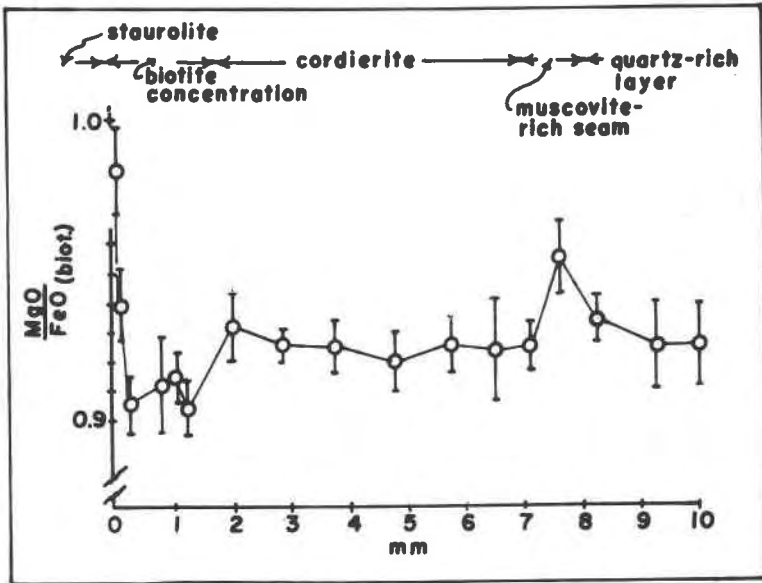


FIG. 5. MgO/FeO for biotite along a 10 mm traverse. Mineralogy is indicated at top of diagram. Five segments indicate precision at 95% confidence level. Data are from beds 5.

different compositions because of initial differences in bulk chemistry. As a consequence, the compositions of corresponding paired porphyroblasts and selvage minerals may differ from place to place in the rock.

NUMBER OF DETERMINING COMPONENTS

Because mosaic equilibrium was established in these rocks, the total mineral assemblage of a lamination is in disequilibrium, and the total number of phases is undoubtedly greater than the maximum number possible for the smaller equilibrium volumes. The question of the maximum number of phases, and therefore the number of determining components, contained within an equilibrium mosaic has not been answered, mainly because (1) most compositional realms contain less than the maximum number of phases, and (2) the plane of the thin section nearly always shows fewer than the number of minerals that makes up the compositional realm. However, some insight into the maximum number of minerals (and therefore the number of determining components) can be obtained by studying the compositional relationships between contacting minerals belonging to many equilibrium mosaics. With this information it should be possible to piece together a phase diagram consistent with the observed relationships. We are looking for the minimum number of com-

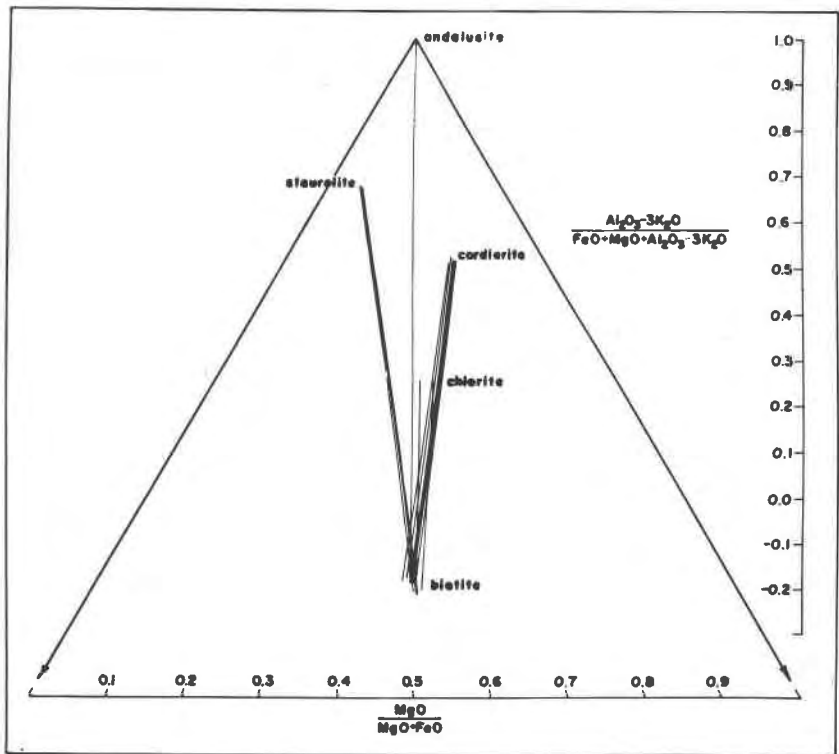


FIG. 6. Thompson projection showing tie-lines between chemically analysed mineral pairs. Data are for minerals that appear in Table 3.

ponents required in the constructions of a consistent diagram, *i.e.*, a diagram in which phase polyhedra do not intersect.

Figure 6 shows tie-lines connecting compositionally analyzed mineral pairs. Optical observations of contacting minerals indicate the existence of additional tie-lines as follows: andalusite-chlorite, chlorite-cordierite, chlorite-staurolite, and cordierite-staurolite. Garnet, although not plotted, has tie-lines extending to all minerals shown in Figure 6. The andalusite-biotite tie line intersects both the staurolite-chlorite and the staurolite-cordierite tie lines. In addition the andalusite-chlorite tie-line intersects that of staurolite-cordierite. Because these mineral pairs exhibit equilibrium partitions, the intersecting tie-lines indicate a need to consider chemical components other than those specified in the Thompson projection.

Garnet contains a relatively high percentage of MnO, and a consideration of this oxide does separate the intersecting tie-lines in Figure 6. The

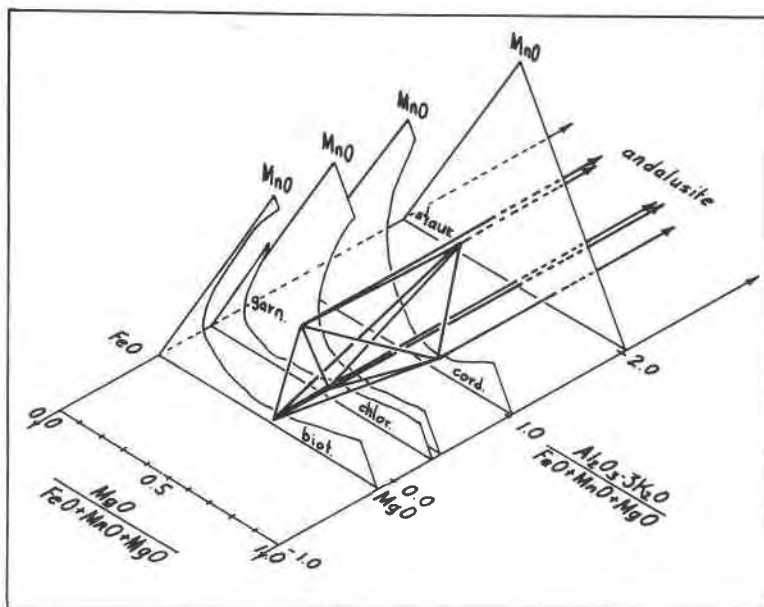
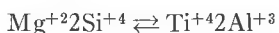
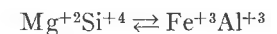


FIG. 7. Modified Thompson projection showing the separation of tie-lines that results when MnO is considered as a component.

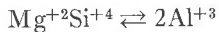
MnO-content of the minerals is as follows: andalusite < biotite = chlorite < cordierite < staurolite < garnet. These chemical relationships are shown on a modification of the Thompson projection similar to that employed by Drake (1969). In Figure 7 the vertical axis is $\text{Al}_2\text{O}_3\text{-}3\text{K}_2\text{O}/\text{FeO} + \text{MnO} + \text{MgO}$ and triangles of composition with apices FeO, MnO, and MgO are erected on the plane of projection. This geometric modification serves to move the compositions of cordierite and staurolite off the projection plane, thereby separating the intersecting tie-lines.

Such a manipulation, however, does not alleviate the problem of crossing tie-lines in the immediate vicinity of biotite in Figure 6. In this diagram the biotite in contact with cordierite has larger $\text{Al}_2\text{O}_3\text{-}3\text{K}_2\text{O}/\text{FeO} + \text{MgO}$ and smaller $\text{MgO}/\text{FeO} + \text{MgO}$ values than does the biotite that contacts staurolite. On the other hand, biotite contacting chlorite has values of $\text{Al}_2\text{O}_3\text{-}3\text{K}_2\text{O}/\text{FeO} + \text{MgO}$ and $\text{MgO}/\text{FeO} + \text{MgO}$ that in some cases approach those of biotite associated with cordierite and in other cases those of biotite associated with staurolite. These relationships can be explained by either of the following solid solutions in biotite:



The writer favors the second possibility because although Ti enters staurolite, it does not enter into cordierite, and consequently the biotite associated with cordierite should be Ti-rich relative to the biotite associated with staurolite. This circumstance causes the biotite contacting cordierite to have higher values of $\text{Al}_2\text{O}_3\text{-}3\text{K}_2\text{O}/\text{FeO}+\text{MgO}$ and lower values of $\text{MgO}/\text{FeO}+\text{MgO}$ than does biotite contacting staurolite.

When MnO is considered to be a component, the biotite solid solution



can explain the chemistry of biotite contacting cordierite and staurolite. However, it cannot explain the chemistry of biotite associated with chlorite. These assumptions cause some of the chlorite-biotite tie-lines to cross the surface containing the cordierite-biotite tie-lines.

An alternative interpretation explaining the crossing tie-lines in the vicinity of biotite (Figure 6) is that mosaics consisting of a given mineral pair were frozen in at external conditions that differed from those at which other mosaics consisting of different mineral pairs were frozen in. This interpretation is rejected on the basis that mosaics consisting of a triad of minerals, for example a biotite crystal that contacts both garnet and cordierite (see Tables 4, 3a, and 6a) has a biotite composition that is homogeneous within the limits of the experimental technique. Moreover, the K_D' values for biotite and the other two minerals of the triad are comparable to those for mosaics consisting only of mineral pairs.

These relationships suggest that the number of determining components is seven (SiO_2 , TiO_2 , Al_2O_3 , FeO , MnO , MgO , and K_2O). Water is considered mobile.

TEMPERATURE AND FUGACITY OF OXYGEN

The existence of ilmenite and magnetite in the rocks at West Sidney allows an estimate of the temperature of the equilibrium to be made using the method of Lindsley (1963). The temperature estimates of this method are somewhat uncertain. Because of the small grain size of both ilmenite and magnetite and because of the scarcity of magnetite, the compositions are averages of grain separates. There is no guarantee that the compositions are those of contacting magnetite and ilmenite.

The $2\theta_{(116)}$ and $2\theta_{(024)}$ lines for ilmenite and the cell edge for magnetite were measured using a 114.6 mm Debye-Scherrer camera. The value for the cell edge of magnetite was determined using Talyor and Sinclair's (1945) and Nelson and Riley's (1945) extrapolations. Applying these values to Lindsley's graphs (1962, 1963) leads to compositions of Ilm_{97} and Mag_{96} . Utilizing the $f(\text{O}_2)$ projections of Lindsley (1963), the

compositional coordinates indicated lie in the lower left corner. Extrapolating Lindsley's data for these compositions indicates that the temperature was approximately 500°C. The $f(\text{O}_2)$ average specific to this sample was of the order of 10^{-24} bars, but might vary from sample to sample.

SUMMARY

Although beds contain up to eleven minerals, chemical relationships indicate that the minerals are not all in mutual equilibrium. Instead, compositional realms have been established within which local equilibrium exists. A minimum of seven determining components is necessary to describe the phase relationships within the mosaics. The compositions of coexisting ilmenite and magnetite suggest that the temperature at equilibrium was $\approx 500^\circ\text{C}$.

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