Canadian Mineralogist
Vol. 29. pp. 673-686 (1991)

ALGEBRAIC ANALYSIS OF THE BIOTITE–SILLIMANITE ISOGRAD IN THE FILE LAKE AREA, MANITOBA

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ABSTRACT

Mineral compositions from pelitic assemblages that straddle the sillimanite – biotite isograd in the File Lake area, Manitoba, have been examined using singular value decomposition and linear programming. If the rocks are modeled in a ten-component system, the mineralogy of individual assemblages can be interpreted as representing at least divariant equilibrium. A modification of Greenwood's (1967) technique of linear programming permits the identification of mass balances (crossing tie-lines in *n*-dimensional space) and also identifies the constituents that fail to balance where no mass balance exists. The isograd can be approximated by the reaction: St + Ms + Chl + Grt + Ilm = Pl + Qtz + Bt + Sil + H_2O. Metamorphic conditions are inferred to have been near 540°C and 330 MPa.

Keywords: electron-microprobe analyses, garnet, staurolite, biotite, muscovite, chlorite, metamorphism, algebraic analysis, File Lake Formation, Manitoba.

SOMMAIRE

La composition des minéraux des assemblages pélitiques qui chevauchent l'isograde sillimanite – biotite dans la région du lac File, au Manitoba, a fait l'objet d'une étude par décomposition de valeurs singulières et par programmation linéaire. Si les roches correspondent à des systèmes à dix composantes, la minéralogie des assemblages individuels peut résulter d'équilibres au moins bivariants. Une modification de la technique de programmation linéaire de Greenwood (1967) permet l'identification des équivalences des masses (le croisement de lignes d'attache dans un espace à *n* dimensions) et, en plus, les éléments qui sont en violation de l'équivalence des masses. La réaction isogradique serait: St + Ms + Chl + Grt + Ilm = Pl + Qtz + Bt + Sil + H_2O. Les conditions du métamorphisme auraient été près de 540°C et 330 MPa.

(Traduit par la Rédaction)

Mots-clés: analyses à la microsonde électronique, grenat, staurotide, biotite, muscovite, chlorite, métamorphisme, analyse algébrique, Formation de File Lake, Manitoba.

INTRODUCTION

A fundamental problem in metamorphic petrology is the identification of the underlying changes in phase compatibilities that result in the development of isograds (Thompson 1957). This has classically been done by the construction of petrogenetic grids using generalizations about assemblages and mineral compositions (*e.g.*, compilations in Philpotts 1990, Figure 17–11; Yardley 1989, Figures 3.11, 4.7). To be applicable to a number of field areas and simple enough to be useable, such grids usually model nature in terms of a small number of components. Rocks that don't quite "fit" these models are common, however, which leads to speculation that such rocks either do not represent equilibrium assemblages, or that additional components are required to adequately describe the natural occurrences. Following the pioneering work of Greenwood (1967, 1968), several investigators have attempted to resolve these questions for specific isograds using a variety of algebraic techniques (Fletcher 1971, Fletcher & Greenwood 1979, Pigage 1976, 1982, Lang & Rice 1985a, Fisher 1989).

This paper uses the SVD procedure suggested by Fisher (1989) and a new linear programming formulation of the *n*-dimensional tie-line problem that provides several advantages in investigations of this type. The results obtained in the study of the sillimanite – biotite isograd in pelitic rocks from the File Lake area in northern Manitoba indicate that: a) the assemblages above and below the isograd can be interpreted as divariant, and b) the isograd can be modeled by a discontinuous reaction in the ten-component system SiO_2–TiO_2–Al_2O_3–FeO–MnO–MgO–CaO–K_2O–Na_2O–H_2O. Pressure – temperature estimates show that this transition takes place near 540°C and 300 MPa, in concordance with the results of others on rocks from different settings.

GEOLOGICAL SETTING

The File Lake area in northern Manitoba (Fig.

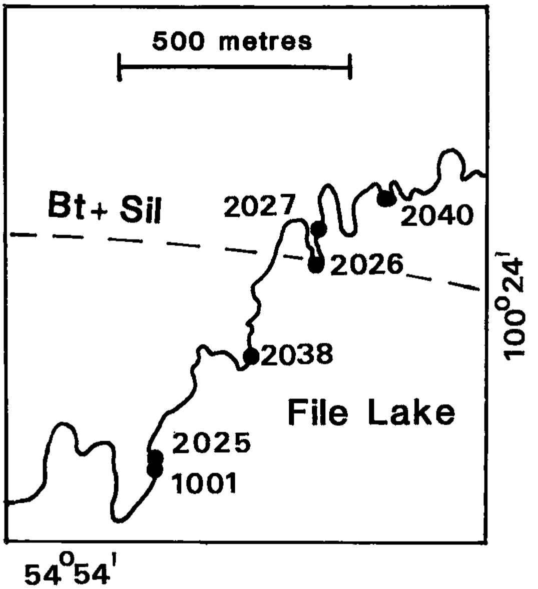

FIG. 1. Sample localities. Biotite–sillimanite isograd from this study and that of Bailes (1980).

1) lies within the Early Proterozoic Flin Flon metavolcanic belt. The area is partly underlain by the File Lake Formation of pelitic metasediments that preserve a prograde metamorphic sequence ranging from the chlorite – muscovite zone to the garnet – sillimanite – biotite zone (Bailes 1980). Regional metamorphic studies in the area have been summarized by Bailes & McRitchie (1978) and Gordon (1989).

The prograde appearance of aluminosilicate plus biotite in muscovite-bearing rocks has been mapped for 75 kilometers along strike east of File Lake (Froese & Gasparrini 1975, Froese & Moore 1980, Bailes 1980, 1985, Gordon & Gall 1982, Zaleski 1989). Pressure – temperature calibration of the isograd will therefore provide an important datum for reconstruction of the regional thermal history. This study also complements the detailed study of reaction mechanisms of Briggs & Foster (1989) and Foster (1991) in rocks from the File Lake area.

TABLE 1. MINERAL ASSEMBLAGES

Sample	Pl	Qtz	Bt	St	Grt	Chl	Ms	Ilm	Sil
1001	x	x	x	x	x	x	x	x	
2025A	x	x	x	x	x	x	x	x	
2038	x	x	x	x	x	x	x	x	
2026-2	x	x	x	x	x	x		x	x
2027	x	x	x	x		x	x	x	x
2040-2	x	x	x	x	x	x	x	x	x

Abbreviations are from Kretz (1983).

PETROGRAPHY AND MINERAL CHEMISTRY

The assemblages are shown in Table 1. Chlorite and muscovite, although ubiquitous, are not abundant. Trace amounts of apatite and tourmaline occur in all samples, and graphite is found in most.

The rocks contain a weak to moderately well-developed schistosity, which developed prior to and during the highest grade of metamorphism (Bailes 1980). In thin section, sparse flakes of

TABLE 2. ELECTRON-MICROPROBE DATA ON PLAGIOCLASE

	1001	2025A	2038	2026-2	2027	2040-2
SiO2	61.96	61.89	60.60	59.52	62.27	56.55
Al2O3	23.65	23.60	24.91	25.21	23.75	27.61
CaO	5.34	5.14	6.36	6.98	5.12	9.33
Na2O	8.78	8.83	8.11	7.78	8.92	6.19
K2O	0.05	0.10	0.05	0.04	0.06	0.18
Total	99.78	99.56	100.03	99.53	100.12	99.86
Number of ions on the basis of 16 positive charges						
Si	2.754	2.756	2.694	2.665	2.757	2.541
Al	1.239	1.239	1.305	1.330	1.239	1.462
Ca	0.254	0.245	0.303	0.335	0.243	0.449
Na	0.757	0.762	0.699	0.675	0.766	0.539
K	0.003	0.006	0.003	0.002	0.003	0.010
Weight percent end members						
An	26.49	25.50	31.55	34.63	25.40	46.28
Ab	74.29	74.72	68.62	65.83	75.48	52.38
Or	0.30	0.59	0.30	0.24	0.35	1.06
Total	101.08	100.81	100.47	100.70	101.23	99.72
Mole percent end members						
An	25.08	24.20	30.15	33.07	24.00	44.97
Ab	74.64	75.24	69.57	66.70	75.67	53.99
Or	0.28	0.56	0.28	0.23	0.33	1.03

All analyses are averages of rims in weight %.

TABLE 3. ELECTRON-MICROPROBE DATA ON BIOTITE

	1001	2025A	2038	2026-2	2027	2040-2
SiO2	35.51	35.13	35.00	37.11	35.14	34.97
TiO2	1.62	1.62	1.75	1.45	1.83	1.82
Al2O3	19.74	19.58	20.01	19.04	19.85	19.40
FeO	20.87	21.61	20.12	16.69	19.24	18.53
MnO	0.05	<0.04	<0.04	<0.04	0.06	0.06
MgO	9.27	9.65	9.59	12.79	10.07	10.32
CaO	0.03	0.02	0.03	<0.01	<0.01	0.07
BaO	0.23	0.24	0.27	0.30	0.38	0.34
Na2O	0.24	0.25	0.24	0.30	0.30	0.27
K2O	8.55	8.60	8.67	8.44	8.95	9.39
F	n.d.	n.d.	0.23	n.d.	0.25	0.21
H2O	3.70	3.08	3.88	3.63	3.68	4.47
Total	99.81	99.78	99.79	99.75	99.75	99.85
Tot-F	99.81	99.78	99.69	99.75	99.64	99.76
Number of ions on the basis of 44 positive charges, 4 OH						
Si	5.370	5.308	5.309	5.484	5.316	5.329
Al(iv)	2.630	2.692	2.691	2.516	2.684	2.671
	8.000	8.000	8.000	8.000	8.000	8.000
Ti	0.184	0.184	0.200	0.161	0.208	0.209
Al	0.888	0.794	0.887	0.800	0.855	0.814
Fe^2	2.639	2.731	2.552	2.063	2.434	2.362
Mn	0.006	0.000	0.000	0.000	0.008	0.008
Mg	2.090	2.173	2.168	2.817	2.271	2.344
	5.807	5.882	5.807	5.841	5.776	5.737
Ca	0.005	0.003	0.005	0.000	0.000	0.011
Ba	0.014	0.014	0.016	0.017	0.023	0.020
Na	0.070	0.073	0.071	0.086	0.088	0.080
K	1.649	1.658	1.678	1.591	1.727	1.825
	1.738	1.748	1.770	1.694	1.838	1.936
F	-----	-----	0.096	-----	0.120	0.101
OH	4.000	4.000	3.890	4.000	3.880	3.899
	4.000	4.000	4.000	4.000	4.000	4.000

All analyses are averages of rims in weight %.
n.d. = not determined.
Weight percent H2O estimated and iterated.

TABLE 4. ELECTRON-MICROPROBE DATA ON STAUROLITE

	1001	2025A	2038	2026-2	2027	2040-2
SiO2	26.61	26.52	26.90	27.04	26.86	26.80
TiO2	0.40	0.44	0.55	0.64	0.61	0.55
Al2O3	53.16	52.88	53.83	52.27	53.70	53.07
FeO	14.42	14.44	14.14	13.72	13.99	14.46
MnO	0.11	0.11	0.08	<0.06	0.16	0.32
MgO	1.45	1.50	1.67	2.12	1.79	2.00
H2O	2.00	2.00	2.00	2.00	2.00	2.00
Total	98.15	97.89	99.17	97.79	99.11	99.20
Number of ions on the basis of 47 positive charges, 2 OH						
Si	3.857	3.857	3.850	3.920	3.847	3.850
Ti	0.044	0.048	0.059	0.070	0.066	0.059
Al	9.082	9.064	9.081	8.932	9.065	8.985
Fe	1.748	1.756	1.693	1.664	1.676	1.737
Mn	0.014	0.014	0.010	0.000	0.019	0.039
Mg	0.313	0.325	0.356	0.458	0.382	0.428
OH	2.000	2.000	2.000	2.000	2.000	2.000

All analyses are averages of rims in weight %.

TABLE 5. ELECTRON-MICROPROBE DATA ON GARNET

	1001	2025A	2038	2026-2	2040-2
SiO2	36.72	36.74	36.99	37.49	36.97
TiO2	<0.03	<0.03	<0.03	<0.03	<0.03
Al2O3	21.08	20.36	20.78	20.87	20.74
FeO	36.70	36.80	36.56	35.99	32.21
MnO	2.21	2.17	1.45	0.09	4.91
MgO	2.21	2.26	2.73	3.92	2.90
CaO	1.27	1.23	1.43	1.88	2.18
Total	100.19	99.56	99.94	100.24	99.91
Number of ions on the basis of 24 positive charges					
Si	2.979	3.004	2.997	3.001	2.990
Al(iv)	0.021	0.000	0.003	0.000	0.010
	3.000	3.004	3.000	3.001	3.000
Ti	0.000	0.000	0.000	0.000	0.000
Al	1.994	1.962	1.981	1.969	1.967
Fe^2	2.490	2.516	2.477	2.409	2.179
Mn	0.152	0.150	0.099	0.006	0.336
Mg	0.267	0.275	0.330	0.468	0.350
Ca	0.110	0.108	0.124	0.161	0.189
	5.013	5.011	5.011	5.013	5.021
Mole fraction end members					
Alm	0.82	0.83	0.82	0.79	0.71
Spess	0.05	0.05	0.03	0.00	0.11
Pyr	0.09	0.09	0.11	0.15	0.11
Gros	0.04	0.04	0.04	0.05	0.06

All analyses are averages of rims in weight %.

TABLE 6. ELECTRON-MICROPROBE DATA ON CHLORITE

	1001	2025A	2038	2026-2	2027	2040-2
SiO2	24.13	24.36	23.81	26.06	23.91	23.98
TiO2	0.07	0.06	0.08	0.21	0.09	0.13
Al2O3	23.51	23.34	23.68	22.23	23.80	23.67
FeO	26.92	26.85	25.60	21.74	24.68	22.94
MnO	0.04	0.04	<0.04	<0.04	0.09	0.19
MgO	13.85	13.82	14.24	17.75	15.01	16.46
CaO	0.01	<0.01	0.01	0.06	<0.01	<0.01
K2O	<0.02	0.12	<0.02	0.47	<0.02	<0.02
F	<0.05	<0.05	0.05	<0.05	0.05	<0.05
H2O	11.26	11.18	12.25	11.23	12.13	11.85
Total	99.79	99.77	99.76	99.75	99.77	99.22
Tot-F	99.79	99.77	99.74	99.75	99.75	99.22
Number of ions on the basis of 56 positive charges, 16 OH						
Si	5.075	5.119	5.040	5.336	5.029	5.015
Al(iv)	2.925	2.881	2.960	2.664	2.971	2.985
	8.000	8.000	8.000	8.000	8.000	8.000
Ti	0.011	0.009	0.013	0.032	0.014	0.020
Al	2.903	2.900	2.948	2.701	2.929	2.850
Fe^2	4.735	4.719	4.532	3.723	4.341	4.012
Mn	0.007	0.007	0.000	0.000	0.016	0.034
Mg	4.342	4.329	4.493	5.418	4.706	5.131
Ca	0.002	0.000	0.002	0.013	0.000	0.000
K	0.000	0.032	0.011	0.123	0.003	0.000
	12.000	11.996	11.999	12.010	12.009	12.047
F	0.000	0.000	0.033	0.000	0.033	0.000
OH	16.000	16.000	15.967	16.000	15.967	16.000

All analyses are averages of rims in weight %.
Weight percent H2O estimated and iterated.

TABLE 7. ELECTRON-MICROPROBE DATA ON MUSCOVITE

	1001	2025A	2038	2027	2040-2
SiO2	46.18	46.21	45.53	45.53	44.89
TiO2	0.33	0.34	0.41	0.44	0.35
Al2O3	36.35	35.63	36.41	37.25	34.43
FeO	1.08	1.12	1.04	1.02	2.50
MgO	0.48	0.49	0.57	0.43	0.56
CaO	<0.01	0.01	<0.01	<0.01	0.03
BaO	0.75	0.77	0.89	1.08	0.70
Na2O	1.42	1.39	1.25	1.58	1.09
K2O	9.10	9.24	9.40	9.08	10.13
F	n.d.	n.d.	0.06	<0.03	<0.03
H2O	4.07	4.64	4.15	3.31	5.15
Total	99.76	99.84	99.71	99.72	99.83
Tot-F	99.76	99.84	99.68	99.72	99.93
Number of ions on the basis of 44 positive changes, 4 OH					
Si	6.112	6.156	6.059	6.005	6.099
Al(iv)	1.888	1.844	1.941	1.995	1.901
	8.000	8.000	8.000	8.000	8.000
Ti	0.033	0.034	0.041	0.044	0.036
Al	3.783	3.750	3.769	3.795	3.612
Fe^2	0.120	0.125	0.116	0.112	0.284
Mg	0.095	0.097	0.113	0.085	0.113
	4.031	4.006	4.039	4.036	4.045
Ca	0.000	0.001	0.000	0.000	0.004
Ba	0.039	0.040	0.046	0.056	0.037
Na	0.364	0.359	0.323	0.404	0.287
K	1.536	1.570	1.596	1.528	1.756
	1.939	1.970	1.965	1.988	2.084
F	0.000	0.000	0.025	0.000	0.000
OH	4.000	4.000	3.975	4.000	4.000
	4.000	4.000	4.000	4.000	4.000

All analyses are averages of rims in weight %.
n.d. = not determined.
Weight percent H2O estimated and iterated.

TABLE 8. ELECTRON-MICROPROBE DATA ON ILMENITE

	1001	2025A	2038	2026-2	2027	2040-2
SiO2	0.17	<0.05	<0.05	0.05	<0.05	0.10
TiO2	51.78	52.03	52.23	51.90	51.60	46.86
FeO	46.65	46.87	46.84	46.02	46.65	50.16
MnO	0.39	0.43	0.27	0.66	0.74	0.69
MgO	0.38	0.18	0.43	0.39	0.26	0.34
CaO	0.21	<0.01	0.02	<0.01	0.01	0.09
Total	99.58	99.51	99.79	99.02	99.26	98.24

All analyses are averages in weight %.

TABLE 9. PRECISION IN THE RESULTS*

	Pl	Bt	St	Grt	Chl	Ms
SiO2	0.39	0.29	0.25	0.30	0.23	0.31
TiO2	----	0.03	0.02	0.01	0.01	0.01
Al2O3	0.39	0.31	0.54	0.38	0.33	0.45
FeO	----	0.14	0.11	0.18	0.17	0.04
MnO	----	0.02	0.02	0.09	0.03	0.02
MgO	----	0.06	0.03	0.04	0.08	0.02
CaO	0.03	0.01	0.01	0.02	0.01	0.01
BaO	0.05	0.06	----	----	0.04	0.08
Na2O	0.06	0.02	----	----	0.01	0.03
K2O	0.01	0.05	----	----	0.05	0.05
F	----	0.04	0.03	----	0.03	0.03

Symbols: Pl plagioclase, Bt biotite, St staurolite, Grt garnet, Chl chlorite, Ms muscovite (after Kretz 1983). * given at 1σ level (wt.%).

phyllosilicate cut the dominant foliation, but are identical in composition to the majority of grains that are parallel to the foliation. There is no textural evidence of disequilibrium in these samples.

Analyses were carried out on the ARL SEMQ electron microprobe at the University of Calgary. Within each polished section, the smallest area containing all minerals was selected for analysis. The individual mineral grains were examined for homogeneity, but only analyses from within approximately ten μm of grain boundaries were used for this study. Data-reduction procedures followed Nicholls & Stout (1988). The results of the analyses are presented in Tables 2 to 8. Table 9 gives the one-sigma error determined by propagation of counting errors in measurements of the calibration standards, background standards and the unknown.

Individual mineral grains do not show pronounced zoning. Plagioclase cores are generally less calcic than rims, but the compositional difference is usually less than 1 mol % An. Garnet rims are from zero to 3 mol % richer in almandine than cores, whereas spessartine, pyrope and grossular components show even less variability.

INITIAL SUBJECTIVE DECISIONS AND ASSUMPTIONS

The conclusions reached in this and similar studies are almost entirely dependent on three unavoidable and necessarily subjective decisions that must be made at the outset. Although these choices may appear obvious, it is important to understand their implications when interpreting the results of the mathematical manipulations.

A) *The systems assumed to be in equilibrium* are the rims of mineral grains within the smallest area containing all minerals in each polished thin section. This portion of each rock, *i.e.*, that portion of the minerals within approximately 10 μm of grain boundaries, is assumed to have retained equilibrium compositions. Microprobe-determined compositions of individual spots in this region are all within the one-sigma analytical errors tabulated in Table 9 and are hence indistinguishable.

The decision *not* to use the means of rim compositions from a number of areas within each polished section is important. In the context of this study, such averaged compositions cannot be satisfactorily interpreted in terms of thermodynamic equilibrium, which requires uniformity of compositions of phases. Using analytically indistinguishable compositions from a single small region maximizes the probability that assumption (A) is valid. The exceptions to this restriction are the ilmemite compositions in Table 8, which result from analyses averaged over several grains.

The algebraic tests described below attempt to find mass balances within and between the mineral compositions of individual assemblages. The interpretation of the results is based entirely on whether or not such mass balances can be found within compositional uncertainty. The larger uncertainties that would result from averaging mineral compositions over larger volumes of rock would make it easier to obtain mass balances; hence this definition of the equilibrium system has a major impact on the interpretations.

B) *Phases in the model system* are plagioclase, quartz, biotite, staurolite, garnet, chlorite, muscovite, ilmenite and sillimanite, plus a fluid phase of unknown composition, taken to be H_2O. These minerals account for over 99% of the modes of the rocks. Whole-rock analyses of the File Lake Formation show an average of only 0.24 wt.% CO_2 and 0.20 wt.% P_2O_5 (Bailes 1980). The mass-balance calculations described below do not include B, C or P, so that the omission of tourmaline, graphite and apatite will not affect the results.

C) *Compositional variability of the phases* may be described in terms of SiO_2, TiO_2, Al_2O_3, total iron as FeO, MnO, MgO, CaO, K_2O, Na_2O and H_2O, present in the phases for which there are analytical data reported in Tables 2 to 8. Microprobe analyses give satisfactory totals when recalculated in terms of these oxides, and also produce satisfactory structural formulae. This is a minimum number of constituents. The less abundant cations Mn and Ti are known to affect mineral stabilities and hence cannot be excluded from consideration.

Determinations of Fe_2O_3 are not available for these samples. The calculations that follow thus contain the implicit assumption that the rocks were open to O_2, *i.e.*, any imbalance in O_2 between mineral compositions was compensated exactly by an appropriate gain or loss of O_2 to the coexisting fluid phase (Greenwood 1967, p. 480).

The ten oxides are the initial *constituents* from which the number of *components* may be determined numerically. Note that the number of components in the model system can be no greater than the lesser of a) the number of phases as determined by assumption (B) above, or b) the number of constituents, as determined by (C). The outcome of the phase-rule-based calculations below are thus largely constrained by these choices.

VARIANCE OF INDIVIDUAL ASSEMBLAGES ACCORDING TO THE PHASE RULE

A common assumption in metamorphic studies is that the minerals in an assemblage attained equilibrium under externally imposed, arbitrary pressure and temperature, and hence should represent divariant equilibrium. A permissive test of this assumption is the determination of the variance of an assemblage.

Brinkley (1946a, b) showed that the number of components, c, in a thermodynamic system is equal to the rank of the matrix of vectors that express the compositions of the p phases in terms of an initial set of constituents, in this paper, oxides. The phase-rule variance of a single assemblage, $f = c + 2 - p$, follows directly. As pointed out by Thompson (1988) and Fisher (1989), a variance of less than two is equivalent to a statement that a mass balance or mass balances can be written among some or all of the phase compositions of the assemblage.

For each assemblage studied here, there is thus a composition matrix formed of columns corresponding to the compositions of minerals in that assemblage, with the addition of columns corresponding to the ideal compositions of quartz, water, and sillimanite where appropriate. Determination of the ranks of these 10 by 10 or 10 by 9 matrices will therefore determine the number of independent components in each assemblage.

In this type of study, the initial subjective choices of constituents and phases determine the number of rows and columns in each composition matrix. The number of components in a model assemblage therefore cannot exceed the lesser of a) the number of rows (constituents); or b) the number of columns (phases) in that assemblage. The subjective choice of a smaller number of constituents or larger number of phases would result in a smaller phase-rule variance.

Compositions of minerals are not known perfectly, so that the problem becomes that of determining the rank of a matrix where its elements are subject to uncertainty. Least-squares (LSQ) techniques have commonly been used for this computation (Greenwood 1968, Fletcher 1971, Fletcher & Greenwood 1979, Pigage 1976, 1982, Lang & Rice 1985a). The LSQ approach attempts to find a linear dependency among the mineral compositions. If at least one such dependency exists, then the composition matrix cannot be of full rank.

A more direct technique is the use of singular value decomposition (SVD) to determine the rank of the matrix directly (*e.g.*, Noble & Daniel 1988, p. 342–343, Fisher 1989). SVD routines are readily available to perform the computation (*e.g.*, Press *et al.* 1989, Fisher 1989, The Mathworks 1989).

The application to petrological problems was introduced and clearly elucidated by Fisher (1989). Briefly, the procedure is to express a composition matrix as the product of three other matrices:

$$A = U \bullet W \bullet V^T \tag{1}$$

where U and V have orthogonal columns, and W is diagonal with nonnegative elements. U and W may be rectangular or square, depending on particular implementations of the SVD algorithm, but W always contains positive numbers known as the *singular values* of matrix A. They appear in order of decreasing magnitude. The rank of A is equal to the number of nonzero singular values. Matrices of lower rank that form the "best" approximations to A can be formed by setting the smaller nonzero singular values in W to 0.0, which leads to matrix W^*, then performing the multiplication:

$$A^* = U \bullet W^* \bullet V^T \tag{2}$$

Matrices A^* and A can then be compared to determine whether the matrix of reduced rank approximates the original matrix within analytical uncertainty. If this is the case, then for the assemblages studied here, the number of components of the modeled system would be less than the number of phases, and the phase-rule variance, less than 2.

Several investigators who have used LSQ methods to determine rank have weighted the composition matrices by multiplying by the inverse of the measurement-error covariance matrix (*e.g.*, Reid *et al.* 1979, Pigage 1982). This procedure homogenizes the influences of components with very different abundances. It should be noted, however, that a) there is no unanimity on the validity of applying statistical weighting to petrological models (see discussion in Le Maitre 1982, p. 103–105), and b) general weighting (scaling) strategies for linear problems are unreliable, hence "It is best to scale (if at all) on the basis of what the source problem proclaims about the significance of each a_{ij}" (Golub & Van Loan 1989, p. 125).

One argument against this type of weighting is that it is the major constituents that determine the stable assemblage in an equilibrium system. Weighting drastically increases the influence of minor constituents, although their abundances do not determine the presence and amounts of major phases. In this study, *unweighted* matrices were used in the numerical determination of rank.

The assemblages consist of either nine or ten phases described in terms of ten constituents. The approximate rank of each unweighted composition matrix was tested by SVD techniques as described

TABLE 10. MISFIT BETWEEN ORIGINAL COMPOSITION MATRICES AND MATRICES OF REDUCED RANK

	Pl	Bt	St	Grt	Chl	Ms	Ilm
1001							
MnO		**8.83**	**5.46**	-0.51	**-3.9**		-0.26
CaO	-0.33	**-9.3**		1.21	**6.16**	**8.72**	
Na2O	0.1	2.69				-1.68	
2025							
MnO		**9.35**	**5.69**	-0.53	**-4.33**		-0.28
CaO	-0.28	**-8.15**		1.03	**5.65**	**7.51**	
Na2O	0.08	2.21				-1.35	
2038							
MnO		**6.03**	**3.59**	-0.34	-2.65		0.82
CaO	-0.25	**-8.46**		1.07	**5.57**	**7.77**	
Na2O	0.1	**3.35**				-2.05	
2026-2							
CaO	0.29	0.02		**-3.58**	-0.99		
2027							
CaO	-0.7	**-19.95**			**12.54**	**19.59**	
Na2O	0.2	**5.76**			**-7.24**	**-3.77**	
2040-2							
MnO		2.96	-0.2	-0.01	-1.16		0.44
CaO	-0.16	**-14.11**		0.07	**8.25**	**13.04**	
Na2O	0.12	**10.76**				**-6.63**	

Results obtained by SVD calculations without row or column weighting. Units are multiples of one-sigma analytical errors in Table 9.

by Noble & Daniel (1988) and Fisher (1989), using routines in PC-MATLAB (The Mathworks 1989). For each assemblage, the difference between A^*, the matrix of rank one less than initial matrix A, was computed and compared on a term-by-term basis with the uncertainties shown in Table 9. Because ideal compositions were used for quartz, sillimanite and water, and because all minerals were not analyzed for all oxides, comparisons were restricted to matrix entries for which analytical uncertainty was measured.

For each assemblage, rows containing values of $A^* - A$ greater than one sigma are shown in units of one sigma in Table 10. In every case, the rows corresponding to CaO and either Na_2O or MnO contain one or more terms greater than three times the corresponding standard deviation (shown in boldface).

The values in Table 10 are much larger than the analytical uncertainties; hence the model matrices are not adequate representations of the composition matrices, and the composition matrices have ranks equal to the number of minerals in the corresponding assemblages. This means that the phase-rule variance of each model assemblage must be at least two, consistent with the usual assumption that mineral assemblages in regionally metamorphosed rocks represent divariant equilibrium.

The dependence of this conclusion on the initial subjectively chosen constituents in each mineral is profound. If the initial subjective constraints were modified such that MnO, CaO, and Na_2O were *not* included in the model phases where they occur in small quantities, matrices A^* would be indistinguishable from the corresponding matrices A, and the conclusion would be that all assemblages are monovariant. In this case, the rightmost column of each matrix V would represent the one-dimensional null space of the corresponding A^*, and could be interpreted as a mass balance corresponding to a univariant equilibrium.

We believe that our choice of constituents is sound. As a matter of interest, however, the mass balances that would result from the modified problem are presented below, using mineral abbreviations from Kretz (1983). For samples 1001, 2025 and 2038 from below the isograd, the mass balance is:

$$\text{Grt} + \text{Chl} + \text{Ms} + \text{Ilm} = \text{Pl} + \text{Qtz} + \text{Bt} + \text{St} + H_2O$$

Samples above the isograd have different assemblages, and hence the mass balances differ. They are:
for sample 2026-2:

$$\text{Pl} + \text{Qtz} + \text{Bt} + \text{St} = \text{Grt} + \text{Chl} + \text{Ilm} + \text{Sil} + H_2O,$$

for sample 2027:

$$\text{Ms} + \text{St} + \text{Chl} + \text{Ilm} = \text{Pl} + \text{Qtz} + \text{Bt} + \text{Sil} + H_2O,$$

and for sample 2040-2:

$$\text{Ms} + \text{St} + \text{Grt} + \text{Chl} + \text{Ilm} = \text{Pl} + \text{Qtz} + \text{Bt} + \text{Sil} + H_2O.$$

DIFFERENCES IN EXTERNALLY IMPOSED CONDITIONS ACROSS THE ISOGRAD

Greenwood (1967) provided the analytical formulation for "deciding whether the mineralogy of one rock differs from another because of some difference in their bulk compositions or because of some difference in the physical conditions of their formation." The solution to this problem depends on the premise that at given values of two externally imposed variables (such as pressure and temperature), any particular bulk composition has a *unique* state at equilibrium (*i.e.*, the amounts and compositions of phases). This is not universally true (*e.g.*, Berry 1990), but for the macroscopic systems encountered in geology, an exception is virtually impossible. Zen (1966, p. 7-9), for example, used an equivalent statement as a necessary "fundamental axiom" to establish geometric rules for construction of phase diagrams.

The test thus reduces to the search for a hypothetical bulk composition that can be expressed as a positive combination of the mineral compositions in each assemblage. This is equivalent to the search for a mass balance between the two assemblages. If any such mass balance is found to exist, then a bulk composition exists that can be represented by two distinct sets of phase compositions. The postulate of uniqueness then requires that the two assemblages must have equilibrated under different externally imposed conditions. Note that the bulk compositions, and hence modes of the assemblages, are not important in these calculations; only the mineral compositions are.

Although this procedure is commonly described as the search for a balanced "reaction" between mineral assemblages, it is important to note that the successful identification of such a mass-balance relationship does not demonstrate that a particular chemical process acted, nor does it imply that the mass balance corresponds to a univariant equilibrium relationship between the two assemblages in the model system. Note also that failure to find a mass-balance relationship implies only that the two assemblages do not share any bulk compositions. It is permissive, not diagnostic, of equilibration under the same conditions.

The simplest mathematical statement of the mass-balance condition is:

$$\begin{array}{ll} \sum_{j=1}^{m} a_{ij}\cdot x_j - \sum_{j=m+1}^{m+n} a_{ij}\cdot x_j = 0 & i=1,2,\ldots,c \\ x_j \ge 0 & j=1,2,\ldots,m+n \\ \sum_{j=1}^{m} x_j = 1 & \end{array} \tag{3}$$

where a_{ij} is the weight % of constituent i in phase j, x_j is the unknown weight fraction of phase j in the sought-after mass balance, c is the number of constituents in the system, and m, n are the number of phases in the respective assemblages.

The inequalities in (3) express the requirement that the unknown weight fractions have nonnegative values, which will ensure that if the mass balance can be found, it is also physically attainable. In order to exclude the trivial solution (all $x_j = 0$) and to specify a unique set of mass-balance coefficients, an additional restriction, such as the equation normalizing the values of x_j for one assemblage, is required.

Following Greenwood's (1968) paper, most investigators have used LSQ approaches to this problem (Fletcher 1971, Fletcher & Greenwood 1979, Pigage 1976, 1982, Lang & Rice 1985a). Standard LSQ algorithms do not permit inclusion of the inequality and normalization equations in (3); hence LSQ methods commonly include an iterative step to determine whether a solution can be found with correct signs for each set of x_j values. The linear programming (LP) approach originally proposed by Greenwood (1967) avoids these problems, however; furthermore, the recent increase in availability of inexpensive spreadsheet programs and computer codes for the solution of such problems (Press *et al.* 1989), make the use of linear programming techniques relatively simple.

As with the determination of the variance of a single assemblage, uncertainties in mineral compositions must be taken into account. Greenwood's (1967) formulation included the uncertainty terms explicitly in the inequalities. His inequalities (20) and equations (22) can be rearranged as:

$$\begin{array}{ll} \sum_{j=1}^{m} (a_{ij}-\delta_{ij})\cdot x_j - \sum_{j=m+1}^{m+n} (a_{ij}+\delta_{ij})\cdot x_j \le 0 & i=1,2,\ldots,c \\ \sum_{j=1}^{m} (a_{ij}+\delta_{ij})\cdot x_j - \sum_{j=m+1}^{m+n} (a_{ij}-\delta_{ij})\cdot x_j \ge 0 & i=1,2,\ldots,c \\ x_j \ge 0 & j=1,2,\ldots,m+n \\ \sum_{j=1}^{m} x_j = 1 & \\ \sum_{j=m+1}^{m+n} x_j = 1 & \end{array} \tag{4}$$

where the notation is the same as (3), and δ_{ij} is the uncertainty in the analysis of constituent i in phase j.

This form of Greenwood's statement of the problem can be easily compared with (3) above. The nominal compositions of minerals are permitted to vary within their known uncertainties, thus expanding the equation into two inequalities. If there are nontrivial solutions to (4), they will define an infinite set of x_j values satisfying the inequalities.

A system of inequalities cannot be "solved" in the sense of giving a unique solution, but LP algorithms can be used to (a) determine whether the inequalities are consistent or *feasible*, and (b) maximize or minimize a linear function (*objective function*) of the unknown values of x_j. Using this formulation, a number of objective functions, usually the weight fractions of each phase, are maximized in turn. If a feasible solution is found, then an infinite number of hypothetical mass-balances exist, and the solution to any particular problem provides one of them.

A disadvantage of this approach is that failure to find a feasible solution causes most algorithms to return an "infeasible" flag without providing information as to which constituents are failing to balance. An alternative formulation that avoids this problem is presented here:

$$\begin{array}{ll} \sum_{j=1}^{m} a_{ij}\cdot x_j - \sum_{j=m+1}^{m+n} a_{ij}\cdot x_j + s_i^{+} - s_i^{-} = 0 & i=1,2,\ldots,c \\ \sum_{j=1}^{m} x_j = 1 & \\ x_j \ge 0 & j=1,2,\ldots,n+m \\ s_i^{+} \ge 0 & i=1,2,\ldots,c \\ s_i^{-} \ge 0 & i=1,2,\ldots,c \end{array} \tag{5}$$

where s_i^+ and s_i^- are new variables that account for any imbalance in constituent i. Note that linear programming algorithms ensure that at most only one of s_i^+ or s_i^- will appear in the solution for each i.

This statement of the problem is a simple extension to (3), forcing each of the i equations to be satisfied exactly. For each constituent i, the value of either s_i^+ or s_i^- provides the amount by which the mineral compositions fail to satisfy the mass balance.

If the objective function is chosen as:

$$\text{Minimize} \qquad \sum_{i=1}^{c} (s_i^+ + s_i^-) \tag{6}$$

then linear programming algorithms will return a single solution that may include nonzero values of some s_i^+ / s_i^- and as well as x_j.

For any particular i, nonzero s_i^+ or s_i^- values in the solution will give the amounts by which the mineral compositions fail to balance for particular constituents. These values can then be compared with the imbalance permitted by the propagation of analytical error for constituent i predicted by the values of x_j and the known values of the uncertainties in the analytical results:

$$\sqrt{\sum_{j=1}^{m+n} (x_j \epsilon_{ij})^2} \qquad i=1,2,\ldots,c \qquad 7)$$

where ϵ_{ij} is the known one-sigma analytical uncertainty of constituent i in phase j.

If s_i^+ or s_i^- is less than (7), then the equation for constituent i balances within the predicted uncertainty. If, on the other hand, s_i^+ or s_i^- is greater than (7), then there is no permissible mass-balance. In contrast to the other methods, this formulation of the problem results in the identification of the constituent(s) that fail to balance.

There are nine possible combinations of assemblages formed by pairing each sample from below with each sample from above the isograd. Each of these pairs was tested using measured compositions and the formulation given by (5) and (6), and the simplex routine in Press *et al.* (1989). Because the compositional data have only two significant digits following the decimal place, an equation was considered to balance if the right-hand side was less than 0.005 weight %. Quartz and a fluid phase containing H_2O are assumed to be present in both assemblages, hence neither SiO_2 nor H_2O was included in the mass-balance equations. The solutions that minimize the imbalances are presented in Table 11.

Only 2025A = 2026–2 and 2038 = 2026–2 require an additional term in order to attain a mass balance. In both cases, CaO fails to balance. The amounts of CaO required are much higher than the error permitted by (7), even if $\epsilon_{\mathrm{CaO}_j}$ is taken as three times the one-sigma errors in Table 8. These pairs of assemblages clearly differ in bulk composition sufficiently that no conclusion can be drawn about differences in their conditions of formation.

The remaining pairs do show mass-balance relationships, however, which demonstrates that the isograd is due to a change in externally imposed conditions, pressure or temperature (or both).

UNDERLYING REACTIONS AND EQUILIBRIA

Although it is tempting to equate mass balances obtained between different assemblages to reactions or phase equilibria, such correlations can be misleading. This can be illustrated by the simplified situation shown in Figure 2. A three-component system has four phases of interest, all of which show solid solution. Under some initial conditions of pressure and temperature, phases **a**, **b**, and **d** are stable in assemblages **abc** and **abd**; at different pressure and temperature, the equilibrium compositions of **a**, **b**, **c** and **d** have shifted to **A**, **B**, **C** and **D**, respectively, and the stable assemblages have become **ACD** and **BCD**. At some intermediate conditions, a univariant reaction has caused the

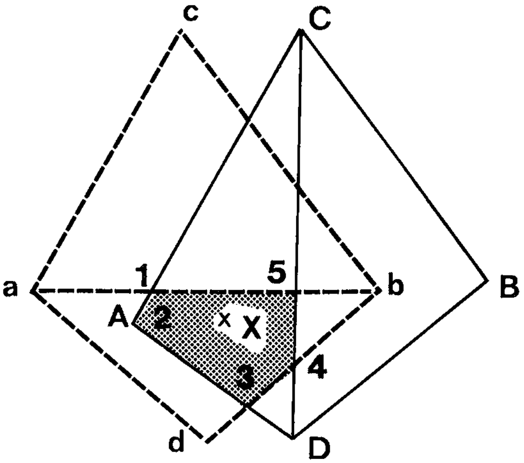

FIG. 2. Assemblages from a hypothetical three-component system with solid solution and discontinuous equilibrium. Only one of the algebraically determined four-phase mass balances between ensemble **abcd** and ensemble **ABCD** corresponds to the discontinuous equilibrium. Numbers refer to the mass balances: 1) **a** + **b** = **A** + **C**, 2) **a** + **b** + **d** = **A**, 3) **b** + **d** = **A** + **D**, 4) **b** + **d** = **C** + **D**, and 5) **a** + **b** = **C** + **D**.

TABLE 11. RESULTS OF LINEAR PROGRAMMING CALCULATIONS TO DETERMINE MASS BALANCES BETWEEN ASSEMBLAGES ABOVE AND BELOW THE ISOGRAD

1001 = 2026-2
0.0143 Pl + 0.0244 Chl + 0.1072 Grt + 0.0057 St + 0.8388 Ilm =
0.0161 Pl + 0.1469 Grt + 0.8369 Ilm

1001 = 2027
0.3079 Pl + 0.2213 Chl + 0.0437 Grt + 0.2927 Ms + 0.1855 Ilm =
0.3397 Pl + 0.2970 Bt + 0.1877 St + 0.1755 Ilm

1001 = 2040-2
0.0350 Pl + 0.2374 Grt + 0.0008 Ms + 0.7525 Ilm =
0.0499 Pl + 0.0235 Chl + 0.0489 Grt + 0.8314 Ilm + 0.0463 Sil

2025A = 2026-2
0.0511 Chl + 0.6393 St + 0.2974 Ilm + ***0.1073 CaO*** =
0.0007 Bt + 0.0571 Grt + 0.6465 St + 0.2956 Ilm

2025A = 2027
0.1335 Chl + 0.0133 Grt + 0.8520 Ms + 0.0497 Ilm =
0.0048 Pl + 0.1836 Bt + 0.6878 Ms + 0.0813 St + 0.0425 Ilm

2025A = 2040-2
0.0127 Pl + 0.2416 Grt + 0.0002 Ms + 0.7765 Ilm =
0.0181 Pl + 0.0145 Chl + 0.0531 Grt + 0.8621 Ilm + 0.0522 Sil

2038 = 2026-2
0.0367 Chl + 0.7872 St + 0.1560 Ilm + ***0.0505 CaO*** =
0.0002 Bt + 0.0288 Grt + 0.8158 St + 0.1553 Ilm

2038 = 2027
0.2644 Bt + 0.1924 Chl + 0.0375 Grt + 0.5481 Ms + 0.0093 Ilm =
0.0124 Pl + 0.5241 Bt + 0.3040 Ms + 0.1594 St

2038 = 2040-2
0.0045 Pl + 0.1791 Grt + 0.3961 Ms + 0.4540 Ilm =
0.0253 Pl + 0.0338 Bt + 0.3358 Ms + 0.1006 St + 0.5044 Ilm

Measured compositions from Tables 2 to 8 and inequalities (5), described in the text, were used to find mass balances between assemblages. Coefficients are weight fractions. Imbalances occur only for CaO (bold italics) and can be compared with the error permitted by the analytical uncertainties in Table 9 and the coefficients in the equations.

A–B tie-line to become unstable with respect to the **C–D** tie-line.

Consider two samples consisting of an assemblage with bulk composition **x**, with assemblage **abd**, and one with bulk composition **X**, with assemblage **ACD**. The two phase diagrams clearly intersect, and an infinite number of mass balances between the assemblages can be obtained from within the shaded area. Because this is a three-component system, the usual algebraic techniques would essentially examine all four-phase combinations selected from **a**, **b**, **c**, **d**, **A**, **B**, **C** and **D**. The mass balances obtained would correspond to hypothetical equilibria:

1) **a** + **b** = **A** + **C**
2) **a** + **b** + **d** = **A**
3) **b** + **d** = **A** + **D**
4) **b** + **d** = **C** + **D**
5) **a** + **b** = **C** + **D**

Of these, only the last bears any relationship to the actual univariant equilibrium responsible for the topological differences between the phase diagrams.

The situation in ten dimensions is very likely much worse. It is not difficult to imagine a circumstance in which tie-line **C–D** would fall completely outside of **abcd**, in which case, none of the algebraically obtained mass-balances would correspond to the underlying univariant equilibrium.

Whereas algebraic techniques may not identify an actual reaction or equilibrium, they may be used to test reactions proposed on other grounds. In the File Lake area, field and petrographic observations (Bailes & McRitchie 1978, Bailes 1980, this study) indicate that the prograde appearance and increase in abundance of sillimanite coincide with a decrease in modal chlorite, muscovite and staurolite. This is commonly observed in metamorphosed pelitic rocks (*e.g.*, Guidotti 1974, Lang & Rice 1985a, b). In the model KFMASH system, this reaction is attributed to the univariant equilibrium:

$$\text{Chl} + \text{Ms} + \text{St} = \text{Qtz} + \text{Sil} + \text{Bt} + H_2O \qquad (8)$$

To extend this model reaction to the File Lake assemblages, it is necessary to consider the additional phases plagioclase, garnet, and ilmenite. The problem is to attempt to find mass balances among analyzed minerals that preserve the six-component equilibrium above and contain the additional constituents and phases.

For this aspect of the study, Greenwood's formulation of the problem, given in (4) above, was used. To ensure that the mass balances would result in sillimanite as a product phase, a linear programming problem was set up for each of the nine pairs of assemblages with the objective function:

$$Maximize\ x_{sillimanite} \qquad (9)$$

Although all pairs produced feasible mass-balances, only two provided solutions that contain equilibrium (8) as a subset. The results were:

1001 = 2040-2
0.5569 Ilm + 0.0128 Chl + 0.0659 Grt + 0.2828 St + 0.0825 Ms =
0.6208 Ilm + 0.0147 Pl + 0.0788 Bt + 0.2788 Sil + 0.0069 H_2O

2037 = 2038
0.1301 Pl + 0.3363 Chl + 0.0241 St + 0.4966 Ms + 0.0128 Ilm = 0.1658 Pl + 0.0048 Qtz + 0.5152 Bt + 0.2709 Sil + 0.0433 H_2O

If these mass balances have any relationship to actual "reactions", plagioclase is a product and garnet a reactant. The role of ilmenite is unclear. This result is in accordance with the processes inferred by Bailes (1980) for this area, by Guidotti (1974) for pelitic schists in the Rangely area, Maine, and by Lang & Rice (1985a) for assemblages at Snow Peak, northern Idaho.

PRESSURE–TEMPERATURE CONDITIONS OF THE ISOGRAD

It is not our intention in this study to evaluate the numerous calibrations of exchange equilibria relevant to pelitic rocks. We decided to estimate pressure–temperature conditions using the publicly available PTAXSS program and data-base (Berman & Brown 1988) that is part of the GE0-CALC system (Berman *et al.* 1987).

Estimates of pressure and temperature were based on the simultaneous solution of the Gibbs free energy equations corresponding to H_2O-free equilibria among appropriate end-members in the data-base. This can be done with GE0-CALC by examining intersections of the pressure–temperature curves corresponding to equilibria between mineral end-members for which there are reference-state data. The end members used were: almandine (alm), annite (ann), anorthite (an), clinochlore (chl), grossular (grs), muscovite (ms), phlogopite (phl), pyrope (prp), β-quartz (βqtz), sillimanite (sil) and staurolite (st).

The version of the GE0-CALC data-base utilized was NOV89.RGB, which uses the thermochemical data of Berman (1988, 1990), the activity model for garnet of Berman (1990), and the activity model for biotite of Indares & Martignole (1985). These data are consistent with the experiments of Ferry & Spear (1978). The muscovite–paragonite activity model of Chatterjee & Froese (1975) and the plagioclase mixing model of Furhman & Lindsley (1988) also were adopted. The formula for end-member clinochlore used in the data-base is $Mg_5Al_2Si_3O_{10}(OH)_8$; hence we adopted a single-site, coupled-substitution model (Chernosky *et al.* 1988). The activity of clinochlore was estimated by:

$$a^{CHLORITE}_{CLINOCHLORE} = \left[\frac{x(^{IV}Mg)}{6} \Big/ \frac{5}{6}\right]^5 \cdot \left[\frac{x(^{IV}Al)}{6} \Big/ \frac{1}{6}\right]^1 .$$

The activity of the iron end-member of staurolite, computed as

$$a^{STAUROLITE}_{Fe\text{-}STAUROLITE} = [x(Fe^{2+})]^4 ,$$

from the staurolite formula in the data-base, gave $Fe_4Al_{18}Si_{7.5}O_{44}(OH_4)$.

Although in the assemblages studied here there are as many as 32 possible equilibria between the chosen end-members, the number of linearly independent equilibria is much smaller. All equilibrium curves can be generated from linear combinations of a particular set of independent equilibria. For each assemblage, the number of linearly independent equilibria is equal to the rank of the matrix formed of all possible equilibria (Jouguet 1921), or equivalently, the rank of the null space of the composition matrix of end-member compositions (Aris 1965, Thompson 1982, 1988).

The stoichiometry of the end members used in this study is such that three independent equilibria suffice to generate all equilibria in assemblages 1001, 2025A, 2038, and 2026-2, and four independent equilibria suffice for assemblage 2040–2. Because assemblage 2027 does not contain garnet, it defines only one equilibrium, hence was excluded from further consideration.

In general, the computed equilibria for any one assemblage are inconsistent, *i.e.*, they do not define a single pressure and temperature. Examination of the results indicates that the problem arises from inconsistency between equilibria involving muscovite on the one hand and those involving clinochlore and staurolite on the other. The only equilibria that do not involve muscovite, clinochlore, or staurolite are the garnet – biotite Fe–Mg exchange:

$$\text{alm} + \text{phl} = \text{prp} + \text{ann} \qquad \text{(A)}$$

and the sillimanite – quartz – grossular – anorthite equilibrium:

$$\text{sil} + \beta\text{qtz} + \text{grs} = 3\ \text{an} \qquad \text{(B)}$$

Equilibrium (A) can be determined in five of the samples, hence it was chosen as the first independent equilibrium to examine.

In samples from below the isograd (1001, 2025A, and 2038), equlibrium (A) and all chlorite- and staurolite-free equilibria are linearly dependent and hence intersect at a single point. One of these:

$$\text{alm} + \text{grs} + \text{ms} = 3\ \text{an} + \text{ann} \qquad \text{(C)}$$

was thus chosen as the second of the three independent equilibria. Similarly, a number of muscovite-free equilibria intersect (A) at a unique pressure, and

$$6\ \text{st} + 45\ \beta\text{qtz} + 5\ \text{prp} + 24\ \text{grs} = 8\ \text{alm} + 72\ \text{an} + 3\ \text{chl} \qquad \text{(D)}$$

was chosen as the third independent equilibrium.

Assemblages from above the isograd include equilibrium (B), as well as a single muscovite-free, biotite-free equilibrium involving the minimum number of end members:

$$6\ \text{st} + 21\ \beta\text{qtz} + 5\ \text{prp} = 8\ \text{alm} + 3\ \text{chl} + 48\ \text{sil} \qquad \text{(E)}$$

hence this also was used in the calculations.

The sensitivity of the results to uncertainties in mineral compositions was estimated by repeated calculations with the weight % of each constituent varying by two standard deviations from its nominal value. The maximum uncertainty in temperature of equilibration of a single assemblage, as determined from (A), was ± 15°C, whereas the maximum uncertainty in pressure of a single assemblage, as determined from (B), was ± 30 MPa.

The pressures and temperatures defined by these equilibria are plotted in Figure 3. The temperatures determined for samples 2038 and 2026–2 are inconsistent with the assumed increase of temperature across the isograd, but lie within the uncertainty from analytical measurement, giving a median of 540°C. Pressures determined by chlorite- and staurolite-bearing equilibria are uniformly in the andalusite field and hence suspect, not a surprising result, given the approximations used for activities of these end members. Muscovite-bearing equilibria are most consistent with equilibrium (B), and the two give a median pressure of 330 MPa.

These results are comparable with the work of other investigators on similar assemblages from rocks metamorphosed at higher pressures. For example, in the study of Lang & Rice (1985b), assemblages containing plagioclase + quartz + biotite + staurolite + garnet + muscovite + chlorite + kyanite were estimated to have experienced pressures near 600 MPa at temperatures near 525°C. The conditions determined at File Lake are consistent with their results and suggest that temperatures recorded by the biotite – sillimanite isograd are between 500°C and 550°C throughout the pressure range 300 to 600 MPa.

CONCLUSIONS

Algebraic techniques have been applied to mineral compositions obtained from assemblages that straddle the sillimanite – biotite isograd in the File Lake area. If the rocks are modeled in a ten-component system, the mineralogy of individual samples can be interpreted as representing at least divariant equilibrium. The isograd can be approximated by the reaction:

$$\text{St} + \text{Ms} + \text{Chl} + \text{Grt} + \text{Ilm} = \text{Pl} + \text{Qtz} + \text{Bt} + \text{Sil} + \text{H}_2\text{O}$$

Metamorphic conditions are inferred to have been near 540°C and 330 MPa.

ACKNOWLEDGEMENTS

It will be obvious to the reader that the approach taken in this paper owes its origin to Hugh Greenwood's innovations in the quantitative study of metamorphic rocks. We express our profound thanks to Hugh, not only for his excellent contributions to science, but also for his kindness and generosity as a teacher, colleague, and friend.

Alan Bailes kindly furnished air photographs and led several field trips to the File Lake area. Steve Jackson, Eva Zaleski, and Julie Jackson provided able field assistance during sample

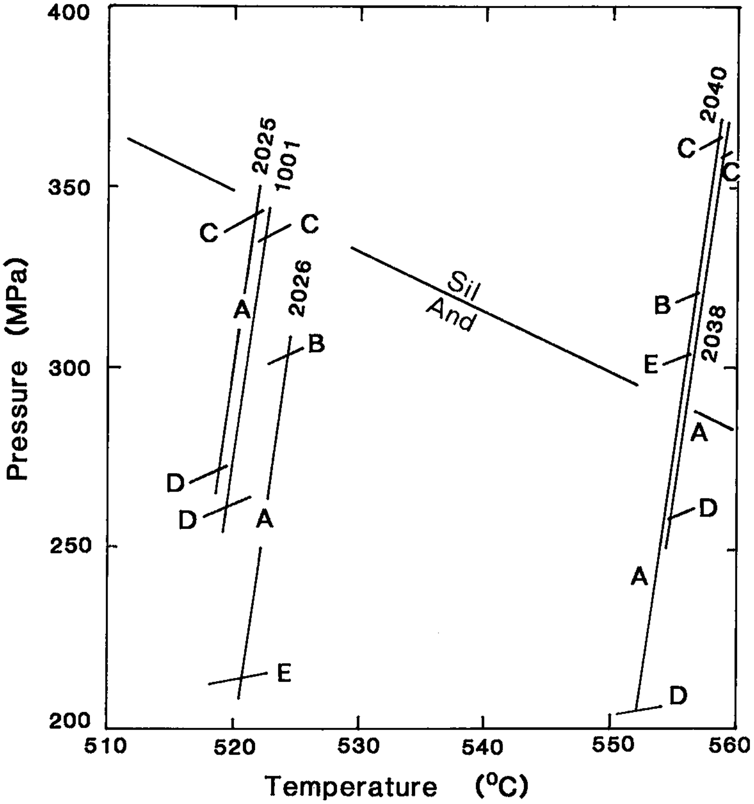

FIG. 3. Pressure–temperature conditions for samples (numbers) obtained from GE0-CALC (Berman *et al.* 1987). Letters refer to equilibria (A) to (E) discussed in text. For each sample, pressure–temperature conditions from equilibrium (A), alm + phl = prp + ann, are the near-vertical lines. For clarity, pressure–temperature conditions obtained from the equilibria: B) sil + βqtz + grs = 3 an, C) alm + grs + ms = 3 an + ann, D) 6 st + 45 βqtz + 5 prp + 24 grs = 8 alm + 72 an + 3 chl, and E) 6 st + 21 βqtz + 5 prp = 8 alm + 3 chl + 48 sil, are shown as short lines where they intersect the corresponding equilibrium (A).

collection. Rob Berman generously supplied beta versions of GE0-CALC software and date-base. Many enjoyable discussions with Jim Nicholls, Rob Berman and Eva Zaleski helped clarify the ideas expressed in this paper. We are very appreciative of the perceptive and constructive reviews by Howard Day, George Fisher, and Charles Guidotti. The research was supported by a University of Calgary Research Grant, a Lithoprobe grant and NSERC grant GP0046219 to TMG, and NSERC grant A4379 to EDG. This is Lithoprobe Publication 214.

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Received November 6, 1990, revised manuscript accepted February 14, 1991.