## A comparative study of geothermometers and geobarometers in pelitic schists from south-central Maine

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#### Abstract

Pelitic schists from a Buchan-type metamorphic terrain contain eight independent geothermometer/geobarometers. Three pairs of fluid-independent geothermometer/geobarometers record lithostatic pressures consistent with  $3500\pm200$  bars. Fluid-independent geothermometers are mutually consistent and record a N-S temperature gradient in the area ranging from a mean of 460°C in the garnet zone to a mean of 550°C in the sillimanite zone. Fluid-dependent geothermometers record temperatures that are systematically higher than those recorded by fluid-independent geothermometers. The discrepancy is due to a combination of imprecise laboratory calibration of mineral equilibria and to conditions of  $p_{H_2O} < P_{total}$  during metamorphism. The mole fraction of  $H_2O$  in the metamorphic fluid was variable, and generally ranged between values of ~0.5 and 1. Temperature and pressure estimates based on mineral equilibria in pelitic schists are in good agreement with temperature and pressure estimates based on mineral equilibria in metamorphosed carbonate rocks from the same area.

#### Introduction

One goal of metamorphic petrology is to estimate the pressure-temperature conditions during metamorphic events and to estimate the compositions of fluids in equilibrium with mineral assemblages in different rock types. Laboratory calibration of mineral equilibria in the past two decades has permitted determinations of pressure, temperature, and fluid composition to become more numerous and to apply to increasingly varied mineral associations; specific, selected examples include studies by Cheney and Guidotti (1979), Ghent (1975), Hutcheon (1979), Jones (1972), and Rice (1977a,b).

The purpose of this study is twofold. First, geothermometer/geobarometers were used to estimate pressure-temperature conditions during metamorphism of pelitic schists in a Buchan-type terrain in south-central Maine. Sample density is sufficient to contour a map of the terrain with isotherms based on the biotite-garnet geothermometer. Second, because pelitic schists in the study area contain eight different laboratory-calibrated geothermometer/geobarometers, intercomparisons of independently-calculated pressures and temperatures can be made with the aim of evaluating the merit of individual thermometers. Samples of pelitic schist selected for study contain one or more of the following geothermometer/ geobarometers: biotite-garnet; garnet-plagioclasequartz-aluminum silicate; garnet-cordierite-sillimanite-quartz; muscovite-quartz-plagioclase-aluminum silicate; muscovite-quartz-microcline-sillimanite; staurolite-quartz-garnet-aluminum silicate; cordierite-garnet; and plagioclase-microcline. In addition, metamorphosed carbonate rocks from the same area contain a variety of geothermometers: calcite-dolomite; plagioclase-calcite-zoisite-quartzgarnet; plagioclase-calcite-zoisite-quartz-amphibole-diopside; plagioclase-calcite-zoisite-quartzbiotite-amphibole-microcline; and plagioclase-calcite-zoisite-quartz-muscovite-microcline. Calculated values of pressure, temperature, and fluid composition, derived from mineral assemblages in the metacarbonates, have been previously reported (Ferry, 1976b; 1978; 1980).

#### Geological setting

Samples were collected from the Silurian Waterville Formation in south-central Maine (Fig. 1). The Waterville Formation is composed of interbedded shale, argillaceous sandstone, and argillaceous carbonate rock and their metamorphic equivalents. Compositional layering is on a scale of 1–8 cm. The



Fig. 1. Sketch map of study area in south-central Maine. DSv: Vassalboro Formation; Sw: Waterville Formation; stippled areas: quartz monzonite stocks. Dash-dot line is the stratigraphic boundary between Waterville and Vassalboro Formations. Dashed lines are isograds based on mineral assemblages in pelitic schists: st.-and. = staurolite + andalusite; st.-cor. = staurolite + cordierite (hachures on high-grade side of isograd). The three features labeled "a" are isolated occurrences of rocks with staurolite + cordierite and are bounded by a staurolite + cordierite isograd. Numbers identify sample locations. Data from Osberg (1968, 1971, 1974b, personal communication); Barker (1964); Ferry (1976a, 1978).

age of the rocks, as well as the lack of reaction textures among minerals, suggests that the rocks were subjected to one metamorphic episode (corresponding to the Devonian Acadian Orogeny). Metasediments are folded into tight isoclinal folds with axes trending NE-SW. Porphyroblasts crosscut schisto-

sity, which indicates that metamorphism followed all or almost all deformation. With reference to pelitic schists, the grade of metamorphism varies from chlorite through sillimanite zones. A single rock containing sillimanite and microcline was collected. In the southern portion of the study area, metasediments are intruded by synmetamorphic quartz monzonite stocks. The stratigraphy, structural geology, and metamorphism of the pelitic schists have been discussed in more detail by Osberg (1968, 1971, 1974a,b); the metamorphism of the carbonate rocks has been studied by Ferry (1976a,b; 1978; 1979b; 1980); the petrology of the granitic rocks has been investigated by Barker (1964) and Ferry (1978, 1979a). Isograds in Figure 1 in part represent unpublished material kindly supplied by P. H. Osberg.

## Methods of investigation

Approximately 200 samples of pelitic schist were collected; locations of samples described in this report are diagrammed in Figure 1. Mineral assemblages were identified by petrography. An assemblage of minerals was judged to be in equilibrium by the same criteria listed by Ferry (1976a) with the following exception: if a 2.5cm-diameter circular thin section contained aluminum silicate and/or staurolite, then all minerals within the section were assumed to be in equilibrium with aluminum silicate and/or staurolite. Compositions of minerals were obtained at the following electron microprobe facilities: (1) Geophysical Laboratory; data were collected with an automated MAC microprobe, and were reduced on-line by the method of Bence and Albee (1968)

with correction factors of Albee and Ray (1970); (2) The Lunar and Planetary Laboratory, University of Arizona; data were collected with an automated ARL microprobe, and were reduced on-line with the same procedures as at the Geophysical Laboratory; (3) Department of Chemistry, Arizona State University; data were collected with a manual Cameca microprobe, and were reduced with the FRAME data reduction program (a ZAF correction scheme) at the A.S.U. microprobe facility. Limited duplication of analyses indicates that analytical results of identical material obtained at different facilities are not significantly different.

## Mineralogy and mineral chemistry

All samples contain biotite and quartz as well as various combinations of muscovite, chlorite, garnet, plagioclase, staurolite, cordierite, andalusite, sillimanite, microcline, calcite, epidote, calcic amphibole, apatite, graphite, ilmenite, and pyrrhotite.

Andalusite- and sillimanite-bearing rocks contain mineral assemblages with the richest variety of geothermometer/geobarometers. Compositional parameters of muscovite, biotite, garnet, plagioclase, and staurolite in these rocks therefore are summarized in relative completeness in Table 1. Table 2 summarizes the composition of biotite and garnet in rocks that

Trenting	Fample	Domain		Garnet			Bio	otite		Plagio	lase	Muscovi	te	Staurolite	A1_SiO_
Number	Number	Number	Fe/(Fe+Mg)	XCa	Mn	X <sub>Fe</sub>	Fe/(Fe+Mg)	X <sub>Ti</sub>	X <sub>A1</sub>	Xan	Xab	Na/(Na+K)	X <sub>Al</sub>	X <sub>Fe</sub>	25
							0.50/	0.010	0 161	0 305	0 695	0 192	0.951	_	А
56	A	1	0.884	0.0471	0.146	0.713	0.524	0.019	0.101	0.505	0.075	0.175		0.845	A
56	A	2	0.902	0.0459	0.137	0.737	-		- 151	0 206	0 612	0 166	0 948	0.826	A
246	A	1	0.883	0,0615	0.146	0.700	0.508	0.025	0.151	0.380	0.012	0.100	0.943	0.020	S
388	A	1	0.866	0.0216	0.203	0.687	0.575	0.048	0,164	0.155	0.831	0.000	0.945	0 821	S
663	А	1	0.860	0.0648	0,139	0.679	0.507	0.034	0.169	0.465	0.534	0.112	0.930	0.021	19 <b>11</b>
		<b>.</b> 10	0 972	0.0527	0 181	0 668	0.507	0.039	0.183	0.347	0.652	0.126	0.929	0.830	S
666	A	1	0.072	0.0527	0.172	0.643	0 444	0 034	0.178	0.424	0.572	0.150	0.916		S
674	A	1	0.828	0.0508	0.175	0.640	0.407	0.041	0 188	0 242	0.753	0.085	0,926	-	S
675	-4	1	0.855	0.0306	0.210	0.649	0.497	0.052	0 188	0 223	0.775	0,085	0.924	-	S
675	-5	1	0.831	0.0318	0.241	0.604	0.473	0.052	0.161	0.343	0.655	0.114	0.943	2	S
905	A	1	0.859	0.0570	0.168	0.000	0.492	0.045	0.101	0.945	0.055	0.1.1			
						0.017	0 500	0.024	0 156	0 3/4	0 648	0 123	0.933	<b>1</b>	A
917	A	1	0.887	0.0545	0.137	0./1/	0.529	0,034	0.150	0.544	0,505	0 137	0 944	0 764	A
919	С	1	-	-	-		0.429	0.027	0.154	0.403	0.751	0.175	0 9/8	-	S
925	A	1	0.880	0.0301	0.208	0.670	-	-	-	0.240	0.751	0.175	0.940	0 799	S
925	A	2	0.858	0.0290	0.186	0.674	0.485	0.034	0.166			0 100	0 022	0.60%	۵
928	в	1	0.863	0.0497	0.147	0.694	0.505	0.038	0,162	0.325	0.6/4	0.122	0.932	0.094	
05.0			0 000	0 0357	0 119	0 761	0 542	0.031	0.152	0,192	0.805	0.251	0.954	0,828	A
953	A	5	0.900	0.0357	0.119	0.701	0.520	0.032	0.160	0.431	0.568	0,135	0.921	0.831	A
960	A	1		-	0 111	0 705	0.520	0.053	0 152	0.156	0.842	0.130	0,931	(#C)	S
969	В	1	0.901	0.0190	0.111	0.785	0.617	0.030	0.173	0.354	0 636	0.126	0.934	0.835	A
980	A	1	0.893	0.0579	0.123	0.731	0.517	0.030	0.151	0.342	0.657	0 155	0.945	0.795	A
1001	A	1	0,865	0.0524	0.144	0.695	0.484	0.028	0.151	0.042	0.057	01233			
1006	Δ	1	0 877	0.0552	0.151	0.696	0.486	0.034	0.170	0.354	0.645	0.117	0.927	0.819	A
1010	A .	1	0.881	0 0488	0.183	0.677	0.536	0.029	0,192	0.384	0.615	0.153	0.932	0.833	A
1104	-1	î	0.896	0,0189	0.075	0.811	0.576	0.044	0.157	0.093	0.906	0.200	0.946	0.844	S

Table 1. Compositional parameters of minerals in aluminum-silicate-bearing assemblages

For garnet:  $X_i = i/(Fe+Mg+Mn+Ca)$ ; for biotite and muscovite:  $X_i = i/(Fe+Mg+Mn+Ti+Al^{VI})$ ; for staurolite:  $X_{Fe} = Fe/(Fe+Mg+Mn)$ . Sample location numbers refer to Figure 1. A = andalusite; S = sillimanite.

Sample	C	mat					10007		-
Number	Fe	X.	X	Fe	X	X	1000 <i>ln</i> a	T <sub>F-S</sub>	T <sub>G-A</sub>
	(Fe+Mg)	Ca	Mn	(Fe+Mg)	Ti	AL			
5B32	0,900	0.078	0.291	0.521	0.034	0.154	9.128	460	508
5B43	0,926	0.057	0.211	0.619	0.035	0.121	10,609	479	452
16A	0.875	0.039	0.272	0.470	0.037	0.174	8 898	472	518
18A	0.882	0.084	0.271	0.474	0.028	0 144	8 896	460	518
2 3A	0.872	0.062	0.147	0.477	0.029	0.169	9.228	487	504
24A	0.846	0.074	0.204	0.452	0.036	0.165	7,916	520	566
25A	0.850	0.108	0.398	0.424	0,049	0.135	7.104	479	612
26A	0.874	0,056	0.161	0.480	0.033	0.181	9,175	485	506
27A	0.889	0.186	0.268	0.444	0.036	0.123	8.751	415	525
34A	0.890	0.120	0.423	0.457	0.031	0.179	7.811	424	571
37A	0,896	0.138	0.444	0.448	0.031	0.147	8.224	402	550
38A	0.899	0.182	0.303	0.456	0.028	0.163	8.573	402	533
39A	0.921	0.111	0.288	0.527	0.030	0.162	10.032	405	472
42C	0.884	0.095	0.346	0.494	0.048	0.141	8.193	475	552
44A	0,852	0,095	0.224	0.445	0.036	0.140	8,117	498	555
46A	0.907	0.227	0.303	0.488	0.040	0.132	8.416	410	541
47A	0.896	0.124	0.186	0.486	0.029	0,129	9.765	437	482
48A	0.888	0.161	0,328	0,444	0.029	0.154	11.792	417	414
52A	0.878	0.288	0,368	0.429	0.035	0.128	6.400	425	660
53A	0.929	0.059	0,160	0.617	0.030	0.175	10.765	462	446
133A	0,883	0.073	0.285	0.470	0.028	0.147	9.015	453	513
134A	0.871	0.125	0,304	0.423	0.033	0.138	8.438	434	539
141A	0.888	0.070	0.311	0.469	0.030	0.161	9.055	440	511
154A	0.939	0.047	0.229	0.628	0.031	0,189	10.994	436	439
160A	0.914	0.157	0.423	0.377	0.029	0.145	10,432	308	458
161A	0.872	0.145	0.310	0.431	0.030	0.144	8.018	440	560
161B	0.883	0.105	0.403	0.449	0.030	0.162	8.005	433	561
187A	0.908	0.044	0.278	0.524	0,026	0.174	IO.175	441	467
191A	0.887	0.149	0.422	0.428	0.036	0.163	7.900	405	567
192A	0,909	0.137	0.315	0.521	0.030	0.143	8,914	435	517
200A	0.913	0.061	0.331	0.526	0.039	0,160	9.827	428	480
215A	0.895	0.046	0.248	0.502	0.035	0.165	9,692	455	485
215B	0.880	0.073	0.215	0.464	0.025	0.151	9.376	454	498
218B	0.882	0.036	0.246	0.487	0.030	0.168	9.253	473	503
221A	0.893	0.049	0.180	0.486	0.025	0.164	10,196	444	466
239A	0.877	0.054	0.211	0.492	0.026	0,161	8,974	491	515
242A	0.902	0.079	0.177	0,535	0.025	0.183	9.512	469	492
256A	0.889	0.065	0.174	0.507	0.031	0.164	9.536	476	491
260A	0.897	0.095	0.350	0,505	0.030	0.130	8.759	452	524
261A	0.888	0.160	0.368	0.428	0.029	0.142	8,347	402	544
263A	0.856	0.271	0.307	0,405	0.036	0.136	6.244	447	671
264A	0.881	0.226	0.272	0.455	0.039	0.106	7.795	443	572
267A	0.890	0.059	0.123	0.506	0.025	0.188	9.784	472	482
521A	0.887	0.065	0.093	0.511	0.027	0.152	10,003	486	473
521B	0 873	0 064	0 152	0.480	0.067	0 126	0 765	1.99	482

Table 2. Compositional parameters of coexisting biotite and garnet from pelitic schists and temperatures (in °C) calculated from the Fe-Mg exchange equilibrium between biotite and garnet

Table 2. (continued)

Sample	G	arnet		B	iotite		10001100	T	ήr.
Number	Fe	X	X	Fe	X	x	10000000	F-S	G-A
110-12-01	(Fe+Mg)	~Ca	Mn	(Fe+Mg)	Ti	"A1			
	, <sub>0</sub> ,			(-+87					
522A	0,901	0.254	0.299	0.488	0.045	0.164	7.460	426	591
526A	0.904	0.200	0.339	0.511	0.038	0.177	7,538	439	587
527A	0.889	0.068	0.128	0.494	0.030	0.186	9.805	462	481
543A	0.892	0.217	0.262	0.479	0.039	0.135	9.388	483	497
659A	0.858	0.092	0.141	0.491	0.033	0.134	8.353	538	544
662A	0.859	0.028	0.270	0.429	0.038	0.165	8,959	465	515
665A	0.880	0.083	0.217	0.497	0.029	0.169	8.610	489	531
904A	0.831	0.084	0.051	0.404	0.021	0.111	9.361	495	498
906A	0.863	0 059	0 174	0.467	0.031	0 157	8 897	408	518
907A	0.907	0.040	0 086	0 544	0 041	0 150	11 188	463	433
50,11	0.707	0,040	0,000	O & Order	0.041	0.150	11.100	405	400
907B	0.898	0.046	0.109	0.521	0.052	0.133	10,929	466	441
909B	0.906	0.073	0.073	0.566	0.024	0.167	10.238	490	465
912A	0.895	0.267	0.155	0.522	0.045	0.126	7.765	475	574
913A	0.925	0.033	0.086	0,588	0.003	0.137	11.851	449	413
918A	0.878	0.220	0.222	0.451	0,054	0,123	8.040	446	559
919A	0.861	0.075	0.145	0.460	0.030	0.156	8,920	494	517
923A	0.884	0.126	0.247	0.523	0.049	0.153	7,972	507	563
924A	0.869	0.062	0.195	0.498	0.038	0.153	8.628	518	530
92.7A	0.877	0.084	0.168	0.499	0.025	0.169	8.727	499	526
930A	0.858	0.036	0.220	0.447	0.021	0.169	8.392	505	542
9314	0 881	0.040	0 193	0 / 83	0 029	0 163	9 612	471	488
932A	0.920	0.039	0.091	0.584	0.025	0 188	10 955	463	400
9/ 8A	0.918	0.048	0 155	0.576	0.062	0 139	11 124	461	440
950A	0.905	0.041	0.123	0.541	0.025	0.166	10.606	466	452
950B	0.911	0.041	0.055	0.558	0.028	0.175	11.113	462	435
0514	0.011	0.061	0 106	0 557	0 020	0 169	10.011	1.61	6.6.7
205 2D	0.911	0.041	0,104	0.557	0.030	0.100	10.911	404	441
9330	0.900	0.132	0.005	0.521	0.027	0.1/0	0.437	405	430
9596	0.009	0.132	0.219	0.521	0.030	0.149	0.571	491	243
10024	0.095	0.051	0.134	0.303	0.042	0,120	9.398	324	489
10024	0.070	0.040	0.201	0,404	0.031	0.130	9.304	480	497
1004A	0.859	0.026	0.201	0.452	0.032	0.166	9.074	490	510
1007A	0.868	0.070	0.157	0.456	0.028	0.174	9,123	474	508
1008A	0.888	0.062	0.148	0.514	0.032	0.177	9.452	487	495
1009A	0.877	0.042	0.153	0.496	0.025	0.199	9.113	495	509
1010B	0,928	0.170	0,293	0.505	0.027	0.168	10.102	367	470
1013A	0,862	0,262	0.339	0.364	0.032	0.133	7.073	396	614
1013B	0.898	0.127	0.382	0.463	0.032	0.154	8.625	411	531
1014A	0.890	0.047	0,155	0,586	0.062	0.158	8,977	568	515
1114A	0.881	0.070	0.188	0.499	0.028	0.163	9.043	488	512
1122A	0.920	0.052	0.232	0.562	0.028	0.169	10.458	441	457
						/			

1000lna from equation (9) of Goldman and Albee (1977);  $T_{P-S}$  from equation (7) of Ferry and Spear (1978);  $T_{G-A}$  from Goldman and Albee, p. 756.

lack aluminum silicate. Compositional parameters in Tables 1 and 2, with only a few exceptions, represent the average of 2–6 individual analyses obtained from mineral grains no further apart than 1.4 mm. Compositional parameters of garnets are with reference to their rims. For samples 56A and 925A, Table 1, mineral analyses are from two different 1.4mm-diameter circular domains in the same thin section.

## Geobarometry

Pressure during metamorphism was estimated in this study by four different mineral assemblages.

## Biotite-garnet-andalusite-sillimanite

Four rock samples within 0.3 km of the mapped sillimanite isograd contain biotite and garnet (24A,

44A, 666A, 905A). It was assumed that pressuretemperature conditions at these four localities were identical to conditions at the sillimanite isograd. The assumption is necessary because no samples collected from the study area (and these four samples, in particular) contain both sillimanite and andalusite. The transition from andalusite- to sillimanite-bearing schists is abrupt, and coexisting aluminum silicates are found in rocks over a distance of only a few meters precisely on the mapped sillimanite isograd (P. H. Osberg, personal communication). Pressure was calculated from expressions 3 and 7, Table 3, describing the andalusite-sillimanite equilibrium and Fe-Mg exchange equilibrium between biotite and garnet and from compositions of minerals in the rocks (Tables 1 and 2). The calibration of biotitegarnet Fe-Mg exchange equilibrium by Ferry and

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₽	Relation	∆H (cal)	$\Delta \overline{S}$ (cal/deg)	$\Delta \overline{V}_{s}$ (cal/bar)	Source
1	muscovite quartz K-feldspar sillimanite steam $KA1_3Si_3O_{10}(OH)_2 + SiO_2 = KA1Si_3O_8 + A1_2SiO_5 + H_2O$	24,184	40.817	-0.113	Chatterjee and Johannes (1974)
2	muscovite quartz plagioclase and alusite steam NaAl $_3$ Si $_3$ O $_{10}$ (OH) $_2$ + SiO $_2$ = NaAlSi $_3$ O $_8$ + Al $_2$ SiO $_5$ + H $_2$ O	21,226	39.876	-0.068	Chatterjee and Froese (1975)
3	and alusite sillimanite $Al_2SiO_5 = Al_2SiO_5$	569	0.546	-0.039	Holdaway (1971)
4	garnet sillimanite quartz plagioclase $Ca_3Al_2Si_3O_{12} + 2Al_2SiO_5 + SiO_2 = 3CaAl_2Si_2O_8$	11,675	32.815	+1.301	Ghent (1976)
5	garnet and alusite quartz plagioclase $Ca_3Al_2Si_3O_{12} + 2Al_2SiO_5 + SiO_2 = 3CaAl_2Si_2O_8$	12,892	34.023	+1,225	Ghent (1976)
6	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	1,571,113	1837.668	-0.897	Hutcheon (1979)
7	$\begin{array}{llllllllllllllllllllllllllllllllllll$	12,454	4.662	+0.057	Ferry and Spear (1978)
8	staurolite quartz garnet and alusite steam 3 $\operatorname{Fe}_8\operatorname{Al}_3\operatorname{Si}_1\operatorname{S}^0_9\operatorname{H}_8$ + 25 $\operatorname{SiO}_2$ = 8 $\operatorname{Fe}_3\operatorname{Al}_2\operatorname{Si}_3\operatorname{O}_{12}$ + 46 $\operatorname{Al}_2\operatorname{SiO}_5$ + 12 $\operatorname{H}_2\operatorname{O}_5$	1,544,939	1812.552	+0.897	calculated from #3 & #6
9	muscovite quartz plagioclase sillimanite steam $NaAl_3Si_3O_{10}(OH)_2 + SiO_2 = NaAlSi_3O_8 + Al_2SiO_5 + H_2O_2$	21,795	40.422	-0.107	calculated from #2 & #3

Table 3. Thermodynamic parameters of various mineral equilibria pertinent to pelitic schists

Spear (1978) was used because it is the only calibration that explicitly accounts for the effect of pressure on the equilibrium. Calculated pressures are listed in Table 4. Errors on calculated pressure correspond to errors of  $\pm 0.005$  Fe/(Fe+Mg) in garnet and of  $\pm 0.01$ Fe/(Fe+Mg) in biotite (half the normal range in this parameter for groups of analyzed biotite and garnet in the same 1.4mm-diameter domain of a thin section) propagated through the pressure calculations.

## Garnet-plagioclase-quartz-andalusite-sillimanite

Samples 666A and 905A contain plagioclase, quartz, and sillimanite in addition to biotite and garnet. Pressure was calculated by simultaneously solving expressions 3 and 4, Table 3, describing the andalusite-sillimanite equilibrium and the garnetplagioclase-quartz-sillimanite equilibrium and from compositions of minerals (Table 1). Activity coefficients used for plagioclase components are those of Orville (1972). Ganguly and Kennedy (1974) suggest, from examination of mineral assemblages in rocks, that the activity coefficient of the grossular component in some garnets may be greater than one, and their conclusion is substantiated by experimental data on grossular-pyrope solid solutions (Hensen et al., 1975; Newton et al., 1977). The garnets whose compositions are summarized in Table 1, however, are poorly approximated by grossular-pyrope solid solutions. They are grossular-almandine-spessartine solid solutions with less than 11 mole percent pyrope component. If Fe and Mn mix in a similar fashion in garnet, then the garnets in Table 1 can be better approximated by almandine-grossular solid solutions. Experimental studies indicate that for almandinegrossular solid solutions with compositions similar to garnets in Table 1 at temperatures in the range 850°-1100°C, there is no evidence for the activity coefficient of the grossular component being different from one (Cressey et al., 1978). Cressey et al. did not present expressions to extrapolate their experimentallydetermined activity coefficients to the lower temperatures of metamorphism in the study area (450°-550°C). The activity of grossular was therefore estimated as the cube of the mole fraction of the grossular component. Numerically, the treatment of activity-composition relations for plagioclase and garnet used here is almost identical to an empirical activity coefficient product for the garnet-quartz-plagioclase-aluminum silicate equilibrium formulated by Ghent et al. (1979).

Calculated pressures are listed in Table 4. Errors on calculated pressure represent errors of  $\pm 0.01$  mole fraction anorthite component in plagioclase and of  $\pm 0.005$  mole fraction grossular component in garnet propagated through the pressure calculations. For assemblages containing plagioclase of composition  $X_{an}$ < 0.1, errors in calculated pressure caused by  $\pm 0.01$ error in  $X_{an}$  are much greater than  $\pm 250$  bars. Con-

		1			
_					
	Sample	P <sub>1</sub>	P 2	P <sub>3</sub>	
	Number	(+350)	$(\pm 250)$	$(\pm 950)$	
	Number	(=550)	(=250)	(	
	0/1	2101		1.5	
	Z4A	3494		10	
	44A	3182		2110	
	56A	-	-	3119	
	246A	_	-	2961	
	388A	-	-	3685	
	663A	-	~	3466	
	666A	3474	3396	3299	
	674A	-	-	2831	
	675-4	-		3095	
	675-5	-	<del>R</del> o	4084	
	9054	3263	3550	3915	
	9174	5205	5550	3174	
	0254		25.6	2573	
	0288			3725	
	9534	-		3362	
	<i>,,,,,</i> ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,			0001	
	969B	_	-	3219	
	980A	-	24	2731	
	1001A	-		3164	
	1006A	-	-	2721	
	1010A	-	-	2737	
	Mean	3503	3473	3270	
	esd	213	109	432	

 
 Table 4. Pressures (in bars) calculated from three geobarometers in pelitic schists

P<sub>1</sub> from biotite-garnet-andalusitesillimanite

P2 from garnet-plagioclase-quartzandalusite-sillimanite

P<sub>3</sub> from biotite-garnet-plagioclasequartz-aluminum silicate

sequently, only those rocks containing plagioclase of composition  $X_{an} > 0.1$  were used in obtaining estimates of pressure during metamorphism.

#### Biotite-garnet-plagioclase-quartz-aluminum silicate

Eighteen samples from the study area contain the assemblage biotite-garnet-plagioclase-quartzaluminum silicate. Pressure was calculated from expressions 4, 5, and 7 (Table 3) describing the garnetplagioclase-quartz-aluminum silicate equilibrium and Fe-Mg exchange equilibrium between biotite and garnet and from compositions of minerals in the rocks (Table 1). Assumed mixing properties of minerals were as described above. Calculated pressures are listed in Table 4. Errors on calculated pressure correspond to errors in garnet, plagioclase, and biotite composition (as described above) propagated through the pressure calculations.

#### Garnet-cordierite-sillimanite-quartz

A single sample (666A) contains the assemblage garnet-cordierite-sillimanite-quartz, in which cordierite has the composition Fe/(Fe+Mg) = 0.338. Newton and Wood (1979) present diagrams from which pressure can be estimated for occurrences of garnet-cordierite-sillimanite-quartz providing that the composition, Fe/(Fe+Mg), of cordierite and  $p_{H_{2O}}$ are known. Because  $p_{H_{2O}}$  is an unknown variable, the mineral assemblage in sample 666A can be used only to estimate a range of metamorphic pressures. The range is 3300-4500 bars with lower and upper limits corresponding to conditions of  $p_{H_{2O}} = 0$  and  $p_{H_{2O}} =$  $P_{Total}$ , respectively.

## Discussion of calculated pressures

The assemblage biotite-garnet-andalusite-sillimanite and garnet-plagioclase-quartz-andalusite-sillimanite are inherently more accurate geobarometers than the assemblage biotite-garnet-plagioclasequartz-aluminum silicate. The error analysis is substantiated by the estimated standard deviations (esd s) of the three groups of calculated pressures. All calculated pressures corroborate a pressure of 3500±300 bars previously calculated (Ferry, 1976b) from the assemblage calcic amphibole-calcitequartz-diopside-biotite-microcline at pressure-temperature conditions of the andalusite-sillimanite equilibrium. Pressures calculated here are also consistent with the presence of muscovite and sillimanite in the quartz monzonite stocks (Ferry, 1978). In the discussion of geothermometry that follows, the pressure of metamorphism in the study area will be taken as 3500 bars.

#### Geothermometry

Temperature during metamorphism was estimated in this study by eight different geothermometers.

#### **Biotite-garnet**

Almost all samples contain biotite and garnet, and their compositions are summarized in Tables 1 and 2. Tables 2 and 5 list temperatures recorded by Fe-Mg exchange between biotite and garnet as calibrated both by Ferry and Spear (1978) and Goldman and Albee (1977). Errors on calculated biotite-garnet temperatures are roughly  $\pm 25^{\circ}$ C, corresponding to errors propagated through the calibrations of  $\pm 0.01$ Fe/(Fe+Mg) in biotite and  $\pm 0.005$  Fe/(Fe+Mg) in garnet.

Temperatures reported in Table 5 are only for

Sample	Bio0	Gar.*	_						
Number	T <sub>G-A</sub>	TES	TG-P-A-Q	TM-Q-A-P	<sup>T</sup> C,Di	<sup>T</sup> C,Ga	T misc.		
	0 11	1-0		_	_				
	GARNET ZONE								
5843	452	479					459+		
53A	446	462		2	12	<u> </u>	459 +		
154A	439	436	*	-	-				
242A	492	469	-				-		
913A	413	449		2	-	-			
0214	1.00	471							
932A	400	4/1							
1122A	457	441			1	÷.			
Mean	453	459	7.5	1		-	459 <sup>†</sup>		
esd	26	15	-	-	1241	-			
		ST	AUROLITE-AN	DALUSITE Z	ONE				
234	50%	497							
564	497	407	520	540		70	2		
215B	498	454	549	340					
218B	503	473					-		
221A	466	444		2	2	20			
239A	515	491			(#1)	5#15			
246A	492	493	522	535	-	170	57		
250A	491	476	2 <b>—</b> 2	12	-				
26/A	482	472	() <del>,</del> = :	. <del></del>		-	3		
52 IA	4/3	480	0.53	1.17		-	10 C		
521B	482	488	- <b>4</b>	-		-20	-		
527A	481	462	-	-	-				
906A	518	498			525	499			
907A	433	463		2			12 I.		
907B	441	466	20 <del>0</del> 5	÷			$\approx$		
DOOR	1.65	400							
9095	400	490	0.00		551	=	14		
9190	JII	494	() <del>-</del> -()	541	551	542	*		
925A	531	531	584	551	551	344			
930A	542	505	-	-	-		- Q		
950A	452	466	-			-			
950B	435	462	-	-		-	-		
951A	441	464	-				÷#		
953A	400	482	489	545		2	1		
ענוע	430	405		-	-		-		
960A		~	-	542		-	-		
980A	474	476	516	554		2	2		
1004A	510	490	-		$\sim$	201	2		
1006A	496	484	526	562	-	2 <b>7</b> .5	8		
1007A	508	474	•		٠	-	3		
10094	500	405							
10104	535	490	575	541	•	(H) (	*		
LULUA	222	101	212	241	<u></u>		2		
Mean	487	482	534	546	546**	531**	-		
esd	30	20	33	8	12	20			

biotite-garnet pairs in which the mole fractions of

the grossular component and grossular + spessartine

components are less than 0.1 and 0.3, respectively.

For these mineral pairs of restricted composition, agreement between calculated temperatures is generally good. For biotite-garnet pairs with garnets con-

taining greater than 0.1 mole fraction grossular or

greater than 0.3 mole fraction grossular + spessartine

components, the Ferry-Spear calibration usually re-

sults in a lower calculated temperature, caused by the

Table 5. Temperatures (in °C) calculated from various geothermometers in pelitic schists and metacarbonate rocks

#### Table 5. (continued)

Sample Number	BioC	Gar.*	T <sub>G-P-A-Q</sub>	T <sub>M-Q-A-P</sub>	T <sub>C,Di</sub>	<sup>T</sup> C,Ga	T <sub>misc</sub> ,
		STA	UROLITE-CO	RDIERITE ZO	DNE		
26A	506	485	1	2			2
904A	498	495		÷:	-		H:
917A	490	506	523	559	548	-	÷:
924A	530	518	121	20	-	-	2
927A	526	499		÷.		×	*
928B	531	543	531	567	-	-	
963A	489	524		2		-	<u> </u>
1001A	511	512	530	552	-	-	÷:
1114A	512	488	100	71	27.0		
Mean	510	508	528	559	548**	508**	H:
esd	16	19	4	8			<b>1</b>
			SILLIMAN	IITE ZONE			
24A	566	520		-		-	-
659A	544	538	-	-	517	-	-
663A	549	553	554	545	-	1	2
666A	532	521	533	559	-	-	515-525 TT
674A	580	550	594	539	531	2	
675-4	564	553	580	602	-	561	-
675-5	607	585	549	605	-	561	-
905A	539	537	512	562	542	520	-
969B	481	571	590	581	-	-	23
1014A	515	568		8	-	*	<del>))</del> :
1104-1	463	534	-	564	-	2	2
Mean	540	548	559	570	543**	52 7**	515-525++
esd	42	21	31	24	23	25	-
		SII	LIMANITE-K	FELDSPAR ZO	ONE		
388A	524	565	554	627	3 <b>7</b> .0		662 <sup>§</sup> 505 <sup>§§</sup>

 $T_{G-A}$  from biotite-garnet, calibration of Goldman and Albee (1977)  $T_{F-S}$  from biotite-garnet, calibration of Ferry and Spear (1978)  $T_{G-P-A-Q}$  from garmet-plagioclase-aluminum silicate-quartz (Chent, 1976)

- ${}^{T}_{\rm M-Q-A-P}$  from muscovite-quartz-aluminum silicate-plagioclase (Cheney and Guidotti, 1979)
- <sup>T</sup>C, Di from amphibole-alcite-quartz-zoisite-plagioclase-diopside in metacarbonate rocks from same outcrop (Perry, 1978; 1980)
- ${}^{T}{}_{C,Ga}$  from calcite-quarts-zoisite-plagioclase-garmet in metacarbonate rocks from same outcrop (Ferry, 1978; 1980).

- <sup>T</sup>misc. miscellaneous geothermometers: + calcite-dolomite in metacarbonate rocks from same outcrop (Ferry, 1976b; 1979b) ++ garmet-cordierite (Thompson, 1976; Holdaway and
  - Lee, 1977)
  - § muscovite-quartz-sillimanite-Kfeldspar

§§ plagioclase-Kfeldspar (Ferry, 1978,

\* Samples are included only if for garnet  $X_{Ca}^{<0.10}$  and  $X_{Ca}^{+X}Mn^{<0.30}$ 

\*\* Mean temperatures represent the mean of all carbonate samples collected within the appropriate zone

well-documented effect of garnet composition on the biotite-garnet Fe-Mg exchange equilibrium. No restriction of samples was made on the basis of biotite composition because the composition of biotite from rocks of the study area is relatively constant. For example, while for garnets  $X_{Ca}$  and  $X_{Mn}$  are in the range 0.019–0.288 and 0.055–0.444, respectively,  $X_{Ti}$  and  $X_{Al}$  for biotites are in the much narrower range 0.019–0.067 and 0.106–0.199, respectively. Although the Goldman–Albee calibration qualitatively corrects for these compositional effects in the proper manner, quantitatively the calibration may over-correct for them. For example, high-calcium garnets such as in samples 52A and 1013A appear to record anomalously high temperatures, calculated from the Goldman–Albee calibration, for garnet-zone metamorphic conditions.

Samples in Table 5 are arranged by zone, where a zone corresponds to the area in Figure 1 between the isograd bearing the zone's name and the next mapped isograd at higher grades. Sample 388A is a single sample containing sillimanite and microcline. Although no sillimanite + K-feldspar isograd was mapped in the area, sample 388A would lie in a sillimanite + K-feldspar zone. The biotite-garnet temperatures indicate a regular increase in temperature with increasing metamorphic grade. Average temperatures in each of the zones (Ferry-Spear calibration) are: garnet zone, 459°C; staurolite-andalusite zone, 482°C; staurolite-cordierite zone, 508°C; sillimanite zone, 548°C; sillimanite + K-feldspar zone, 565°C.

Biotite-garnet temperatures in Table 5 (Ferry-Spear calibration) were plotted on a map of the area where each sample was collected (Fig. 2). The plotted data were contoured with 475°, 500°, and 550°C isotherms. The sillimanite isograd at 3500 bars represents a 520°C isotherm (Holdaway, 1971). Only three samples are inconsistent with the three isotherms based on the biotite-garnet geothermometer. Although the position of individual isotherms in Figure 2 is modestly uncertain due to the  $\pm 25^{\circ}$ C error associated with each measured value of temperature, the pattern of isotherms, if only considered as approximately correct, illustrates some general characteristics of physical conditions in the area during metamorphism. First, the mapped isotherms indicate a regional N-S temperature gradient that is perturbed only slightly by the granitic stocks. Second, comparison of isograds in Figure 1 with isotherms in Figure 2 indicates that isograds, at least in a general way, are isotherms. The northward deflection of isograds in the central portion of the study area (especially well displayed by the garnet and staurolite-andalusite isograds) indeed outlines a corridor of rocks that were hotter than rocks immediately to the west

or east. Osberg (1974a) has convincingly argued, however, that small-scale irregularities in the mapped isograds are likely due to local variations in the compositions of metamorphic fluids.

#### Garnet-plagioclase-quartz-aluminum silicate

Eighteen samples contain garnet, plagioclase, quartz, and aluminum silicate. Table 5 lists temperatures recorded by this geothermometer/geobarometer at 3500 bars pressure. Temperatures were calculated from expressions 4 and 5 in Table 3 (derived from equations in Ghent, 1976) and from mineral compositions in Table 1. Assumed mixing properties of minerals were identical to those discussed previously. Errors on calculated temperatures are roughly  $\pm 25^{\circ}$ C, corresponding to an error of  $\pm 0.01$ mole fraction anorthite component in plagioclase and an error of ±0.005 mole fraction of grossular component in garnet propagated through the temperature calculations. For reasons discussed above, only assemblages containing plagioclase of composition  $X_{\rm an} > 0.1$  were used in obtaining estimates of metamorphic conditions from the assemblage garnetplagioclase-quartz-aluminum silicate.

Comparison of temperatures calculated from garnet-quartz-plagioclase-aluminum silicate with temperatures calculated from biotite-garnet indicates that garnet-plagioclase-quartz-aluminum silicate temperatures are systematically higher than calculated biotite-garnet temperatures. The systematic difference, however, with one exception, is well within the  $\pm 25$ °C error associated with each temperature estimate. Both geothermometers appear to record temperatures that are in good agreement considering their estimated errors.

The garnet-plagioclase-quartz-aluminum silicate geothermometer records that temperature during metamorphism in the sillimanite and sillimanite + K-feldspar zones was greater than temperature in the staurolite-andalusite and staurolite-cordierite zones, in harmony with calculated biotite-garnet temperatures. The garnet-plagioclase-quartz-aluminum silicate geothermometer, however, detects no significant difference in metamorphic temperatures between the sillimanite and sillimanite + K-feldspar zones and between the staurolite-andalusite and staurolite-cordierite zones. The lack of detected differences is not surprising, considering the error associated with the garnet-plagioclase-quartz-aluminum silicate geothermometer and the small temperature



Fig. 2. Paleotemperatures from Table 5 recorded by the biotite-garnet geothermometer (Ferry-Spear calibration). Isotherms at 475°, 500°, and 550°C are drawn from plotted temperatures. Isotherm at 520°C is the sillimanite isograd. Other features same as in Fig. 1.

differences between the two pairs of zones recorded by the biotite-garnet geothermometer.

## Muscovite-quartz-plagioclase-aluminum silicate

Twenty samples contain muscovite, quartz, plagioclase, and aluminum silicate. Table 5 lists temperatures recorded by this geothermometer calculated at 3500 bars pressure. Temperatures were calculated from mineral composition data in Table 1 and from expressions 2 and 9 (Table 3), following the scheme of Cheney and Guidotti (1979). The activity of paragonite in muscovite solid solutions was estimated from mixing parameters of Chatterjee and Froese (1975), corrected for octahedral Fe, Mn, Mg, and Ti in the manner of Ferry (1976b) and Cheney and Guidotti (1979). Metamorphic temperatures calculated from the muscovite-quartz-plagioclase-aluminum silicate geothermometer represent maximum possible temperatures, because the geothermometer has been applied with the assumption  $p_{\rm H_2O} = P_{\rm total}$ . Indeed, while muscovite-quartz-plagioclase-aluminum silicate temperatures in Table 5 are generally similar to both biotite-garnet and garnet-plagioclase-quartz-aluminum silicate temperatures, the muscovite-quartz-plagioclase-aluminum silicate geothermometer records temperatures systematically higher than the other two.

Because it is uncertain whether  $p_{H_2O} = P_{total}$  during metamorphism in the study area, temperatures recorded by the muscovite-quartz-plagioclase-alumi-

num silicate geothermometer are of uncertain significance. Nevertheless, the geothermometer does record an increase in metamorphic temperature from staurolite-andalusite through sillimanite + K-feldspar zones, in harmony with the other geothermometers. In fact, the  $\sim$ 80°C difference between mean temperatures in the staurolite-andalusite and sillimanite + K-feldspar zones recorded by the assemblage muscovite-quartz-plagioclase-aluminum silicate matches a similar difference in mean temperatures recorded by the assemblage biotite-garnet.

## Muscovite-quartz-microcline-sillimanite

A single sample (388A) contains muscovite, quartz, microcline, and sillimanite. Microcline has composition Or<sub>0.889</sub>Ab<sub>0.111</sub>, and compositional parameters of muscovite are listed in Table 1. Table 5 lists a temperature calculated from the observed assemblage with mineral composition data; expression 1 in Table 3; mixing properties for muscovite of Chatterjee and Froese (1975), corrected for octahedral Fe. Mg, Mn, and Ti in muscovite; mixing parameters of Bachinski and Muller (1971); and the assumption  $p_{\rm H_{2}O} = P_{\rm total} = 3500$  bars. The calculated temperature represents an upper bound on temperature and is approximately 100°C higher than temperatures calculated from geothermometers that are independent of  $p_{\rm H,0}$ . Comparison of the temperature calculated from the muscovite-quartz-microcline-sillimanite geothermometer with other calculated temperatures indicates that  $p_{H_{2}O} < P_{total}$  during metamorphism at location 388.

## Plagioclase-microcline

Sample 388A contains plagioclase and microcline. Compositions of feldspars, when referred to equation (9) of Ferry (1978), record a metamorphic temperature of  $505^{\circ} \pm 30^{\circ}$ C (Table 5). The estimated error corresponds to errors of  $\pm 0.01 X_{ab}$  in both feldspars propagated through the calculation of temperature. Considering the estimated errors associated with the different geothermometers, the plagioclase-microcline temperature is marginally consistent with temperatures calculated from other  $p_{H_2O}$ -independent geothermometers in the same rock. The K-feldspar in sample 388A, however, probably did not initially crystallize as a triclinic phase (microcline) but inverted from a monoclinic phase on cooling (Thompson and Waldbaum, 1969). The 505°C temperature recorded by plagioclase-microcline pairs is lower than temperatures recorded by other geothermometers in the rock, possibly because it represents a cooling temperature related to the monoclinic-triclinic inversion.

#### Garnet-cordierite

A single sample (666A) contains garnet (see Table 1 for composition) and cordierite with Fe/(Fe+Mg) = 0.338. Although experimental work by Newton and Wood (1979) indicates that Fe-Mg exchange between garnet and cordierite is not temperature-sensitive, Thompson (1976) and Holdaway and Lee (1977) have presented garnet-cordierite Fe-Mg exchange geothermometers. The temperature recorded by Fe-Mg exchange between garnet and cordierite is 515°C from Thompson's calibration and 525°C from the calibration of Holdaway and Lee. The two calibrations, judging from the data from which they were derived, are probably accurate to only approximately ±50°C. The garnet-cordierite Fe-Mg exchange temperatures, calculated for sample 666A, therefore are in surprisingly good agreement with temperatures calculated from other geothermometers in the same sample. Because garnet and cordierite were found in only one sample, this study, however, does not provide any information bearing on whether Fe-Mg exchange between garnet and cordierite is temperature-dependent or not.

## Staurolite-quartz-garnet-aluminum silicate

Eleven samples contain staurolite, quartz, garnet, and aluminum silicate. Compositions of staurolite and garnet in the assemblage in the eleven samples are listed in Table 1. The temperature of equilibrium among the four minerals in each sample was calculated from mineral composition data, expressions 6 and 8 in Table 3 (derived from equations of Hutcheon, 1979), and the assumption  $p_{H_{2}O} = P_{total} = 3500$ bars. Calculated temperatures ranged from 673°-679°C, 140°-200° in excess of temperatures calculated from other geothermometers in the same rocks. Such high calculated temperatures could be due to conditions of  $p_{\rm H_2O} < P_{\rm total}$  during metamorphism. Further calculations, however, demonstrate that if the staurolite-quartz-garnet-aluminum silicate geothermometer records temperatures similar to temperatures recorded by  $p_{\rm H,o}$ -independent geothermometers in the same specimens, then unlikely conditions of  $p_{\rm H,O} \sim 10^{-4}$  existed during the metamorphic event. The equilibrium among staurolite, quartz, garnet, and aluminum silicate is only approximately located in pressure-temperature space. The unreasonably high temperatures recorded by the staurolite-quartzgarnet aluminum silicate geothermometer, as calibrated in Table 3, are most likely explained by the imprecise experimental location of the equilibrium among Fe-staurolite, quartz, almandine, and sillimanite as a function of temperature and pressure (see Hutcheon, 1979 and Ghent *et al.*, 1979 for further discussion).

## Andalusite-sillimanite

The sillimanite isograd in Figures 1 and 2 corresponds to the equilibrium between andalusite and sillimanite, which occurs at 520°C at 3500 bars (Holdaway, 1971). The sillimanite isograd therefore represents a 520°C isotherm. The configurations of other isotherms in Figure 2 are consistent with the sillimanite isograd as a 520°C isotherm. Considering the  $\pm 25$ °C uncertainty in temperatures plotted in Figure 2, no individual temperature in the figure is in conflict with this temperature.

# Mineral assemblages in metamorphosed carbonate rocks

Metamorphosed carbonate rocks contain numerous geothermometers: zoisite-calcite-plagioclasequartz-garnet; zoisite-plagioclase-calcite-quartzamphibole-diopside; zoisite-calcite-plagioclasequartz-biotite-amphibole-microcline; and zoisitecalcite-plagioclase-quartz-muscovite-microcline. Temperatures recorded by these geothermometers have been reported previously (Ferry, 1976b; 1978; 1980). The assemblages zoisite-calcite-plagioclasequartz-garnet and zoisite-calcite-plagioclasequartz-amphibole-diopside are the commonest, and temperatures recorded by these two geothermometers are listed in Table 5 when they occur in carbonate rocks collected from the same sample localities as were the pelitic schists. Agreement between temperatures calculated from geothermometers in metacarbonate rocks and geothermometers in pelitic schists is good: usually within 20°C and in all cases within 60°C. Table 5, in addition, lists the mean temperatures recorded by all analyzed samples containing zoisite-calcite-plagioclase-quartz-garnet and zoisite-calcite-plagioclase-quartz-amphibolediopside in the staurolite-andalusite, staurolite-cordierite, and sillimanite zones. Considering errors in measurement and considering that metacarbonate and pelitic rocks were generally collected from different sample locations, there are no significant differences between mean temperatures in the stauroliteandalusite, staurolite-cordierite, and sillimanite zones estimated from geothermometers in pelitic schists and mean temperatures estimated from geothermometers in metacarbonate rock in the same zone.

#### Calcite-dolomite

At location 5 (Fig. 1) seven samples of carbonate rock containing calcite and dolomite were collected. The average temperature recorded by the calcite– dolomite pairs is  $459^{\circ} \pm 20^{\circ}$ C (Ferry, 1979b). Temperature was also estimated from a single calcite– dolomite pair in carbonate rock at location 53. Temperature estimated from calcite–dolomite pairs is in excellent agreement with temperature estimated from rocks containing biotite and garnet from the same outcrops (Table 5).

#### Discussion of calculated temperatures

Considering errors in values of temperature estimated by each geothermometer, there is, with two exceptions, good agreement among the various calculated temperatures. The first exception is muscovitequartz-microcline-sillimanite, which records too high a temperature, probably because  $p_{H_2O} < P_{total}$ when this assemblage attained equilibrium. The second exception is staurolite-quartz-garnet-aluminum silicate, which records temperatures that are too high, probably because of imprecise laboratory calibration of the geothermometer. Temperatures estimated from the muscovite-quartz-plagioclase-aluminum silicate-fluid equilibrium have a tendency to be somewhat higher than temperatures recorded by fluid-independent equilibria, probably because of conditions of  $P_{H_{2}O} < P_{total}$  at some sample locations during metamorphism. The consistency in estimated temperatures argues for a close approach towards thermal and chemical equilibrium during metamorphism of pelitic schists in the study area.

#### Fluid composition

The mole fraction of H<sub>2</sub>O in the fluid phase during metamorphism was estimated for 21 samples containing muscovite, quartz, plagioclase, and aluminum silicate (Table 6). Values of  $X_{\rm H_2O}$  in Table 6 were calculated from expressions 2 and 9 in Table 3, mineral composition data (Table 1), and the assumption of ideal mixing of H<sub>2</sub>O in the fluid. Pressuretemperature conditions of the equilibrium were taken as 3500 bars and the temperature recorded by biotite-garnet pairs in each sample (Table 5). Because  $dX_{\rm H_2O}/dT$  is large for the muscovite-quartzplagioclase-aluminum silicate-fluid equilibrium at high values of  $X_{\rm H_2O}$ , errors on calculated  $X_{\rm H_2O}$  are also large. The temperatures recorded by the biotite-gar-

Table 6. Mole fraction of  $H_2O$  in the metamorphic fluid calculated from the muscovite-quartz-plagioclase-aluminum silicate-fluid equilibrium at 3500 bars pressure and at the temperature recorded by the biotite-garnet geothermometer in the same specimen (Ferry-Spear calibration)

Sample Number	т( <sup>о</sup> с)	x <sub>H2</sub> 0	
56A	508	0.71	
246A	493	0.64	
388A	565	0.51	
663A	553	1.09	
666A	521	0.68	
674A	550	1.12	
675-4	553	0.62	
675-5	585	0.80	
905A	537	0.78	
917A	506	0.59	
919C	494	0.31	
925A	531	0.81	
928B	543	0.81	
953A	482	0.49	
960A	506	0.54	
969B	571	0.89	
980A	476	0.43	
1001A	512	0.71	
1006A	484	0.44	
1010A	531	0.89	
1104-1	534	0.72	

net geothermometer are uncertain by ±25°C, and this temperature uncertainty translates into a  $\pm 0.2$ uncertainty in values of  $X_{H_{2}O}$  listed in Table 6. When uncertainty in mineral compositions are also considered, it is evident that tabulated values of  $X_{\rm H,O} > 1$ are not significantly different from 1; values of  $X_{\rm H,O}$ in the range  $0.7 < X_{H_{2}O} < 1$ , similarly, are not distinguishable from 1. Nevertheless, half the tabulated values of  $X_{\rm H,O}$  are less than 0.7, indicating that  $p_{\rm H,O}$ was definitely less than  $P_{\text{total}}$  during metamorphism of a substantial number of pelitic schists. It is unlikely, however, that  $p_{\rm H_2O} < 0.5 P_{\rm total}$  in any but a very few samples. Although calculations summarized in Table 6 document conditions of  $p_{\rm H_2O} < P_{\rm total}$ , the uncertainty of the  $X_{H_2O}$  values impedes accurate quantitative assessment of such conditions.

Osberg (1974a) has argued that variable conditions of  $p_{\rm H_2O} < P_{\rm total}$  during metamorphism of pelitic schists is the most reasonable explanation of unusual patterns of mapped isograds in the area, such as those in Figure 1. Calculated results in Table 6 support Osberg's conclusion: although results are uncertain to  $\pm 0.3$  (after consideration of errors in  $X_{\rm H_2O}$  caused by errors in both temperature and mineral composition), they indicate (a) that  $p_{\rm H_2O}$  was variable during metamorphism of the pelitic schists and (b) that  $p_{\rm H_2O} < P_{\rm total}$ , at least at some locations in the metamorphic terrain.

Table 6 shows a positive correlation between calculated temperature and  $X_{\rm H_2O}$ . Such a correlation is not surprising, because  $dX_{\rm H_2O}/dT$  is large and positive for the muscovite-quartz-plagioclase-aluminum silicate-fluid equilibrium at high values of  $X_{\rm H_2O}$ . The observed correlation between calculated temperature and  $X_{\rm H_2O}$  may be taken as evidence that mineral assemblages in pelitic schists (muscovite-quartzplagioclase-aluminum silicate, in particular) buffer the composition of metamorphic fluids with which they are in equilibrium. Buffering of the composition of fluids by mineral assemblages in metamorphosed carbonate rocks from the study area has already been documented (Ferry, 1976a).

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