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THE DEVELOPMENT OF CARBONATE-BEARING BIOTITE ISOGRAD ASSEMBLAGES FROM TETE JAUNE CACHE, BRITISH COLUMBIA, CANADA

R. H. PINSENT* AND D. G. W. SMITH
Department of Geology, University of Alberta, Edmonton, Canada

ABSTRACT

Eight samples of Upper Proterozoic metasediment were analyzed following a structural study across the biotite isograd northeast of Tête Jaune Cache. Seven pelite and pelitic psammite samples show a restricted range in both their Al/(Mg+Fe) and Mg/(Mg+Fe) ratios. Somewhat similar values were obtained from the eighth sample, a calcareous pelite.

Microprobe analyses show that the muscovites associated with biotite and chlorite have a consistent yet anomalous composition: they are enriched in Al and Na, and depleted in Mg and Fe. Thus they have a low phengite content, and are similar to staurolite-almandine, or even kyanite-almandine subfacies muscovites reported from elsewhere. In contrast, the coexisting biotites and chlorites have compositions which are normal for the observed metamorphic grade.

Two ferromagnesian carbonates, ankerite and siderite, seem to have equilibrated with the silicate assemblage. Partition equilibria favour depletion of the silicate system in Fe and Mg, and, as the muscovite structure allows flexibility in the Al/(Mg + Fe) ratio, its composition is affected. The range of rock compositions able to crystallize biotite, above the level of the isograd, is thought to have been enlarged by the influence of carbonate on the muscovite composition.

The presence of ankerite coexisting with calcite and siderite in at least 5 of the samples permits temperature estimates to be made using the carbonate geothermometer (Rosenberg 1967). The temperatures of 340-370°C obtained are reasonable but are subject to some uncertainty due to the presence of minor Mn in the carbonates and the possible effects of variations in P_{H_2O} among samples during crystallization.

INTRODUCTION

In recent years data have become available on the mineralogical and mineral-chemical changes that occur in lower greenschist facies metasediments (Mather 1970; Wenk 1970; Butler 1967; Brown 1967). Emphasis has been placed on the coexising phyllosilicate phases which characterize the lower greenschist facies. Studies which involve additional phases (below the garnet isograd), are comparatively rare. Chinner (1967) discussed the significance of chloritoid, and Brown (1967, 1971) presented data on actinolite and stilpnomelane. The purpose of this paper is to present data on the influence of ferromagnesian carbonates on coexisting micas at the level of the biotite isograd, and to present an example of the application of the ankerite geothermometer (Rosenberg 1967).

THE AREA

Tête Jaune Cache lies in the Rocky Mountain Trench (Fig. 1). This feature separates the Omenica Crystalline Belt and the Foreland Thrust-and-Fold Belt (represented here by the Cariboo and Rocky Mountains, respectively) of the Columbian Orogen of the Canadian Cordillera (Wheeler *et al.* 1972). At this latitude the oldest rocks in the Rocky Mountains, which are well-exposed for some 15 km east of Tête Jaune Cache, along the valley of the Fraser River, belong to the upper Precambrian Miette Group. This is a succession of metamorphosed, poorly sorted, commonly graded, interbedded psammitic and pelitic rocks that originated as sediments deposited along the western edge of the North American Craton. Deformation and greenschist facies metamorphism, the intensities of which increase southwestwards, occurred in Mesozoic time.

SAMPLE SUITE

Eight samples were selected for detailed study from a suite collected along a 5 km stretch of the Canadian National Railway line between Rearguard Station and the level crossing at Tête Jaune Cache (Fig. 1). The sample traverse starts about 1.5 km southwest of the biotite isograd and extends approximately at right angles to the trend of the isograd. The mineralogy is characteristic of the biotite-muscovite-chlorite-quartz-albite subfacies of greenschist facies metamorphism (see Table 5). A small increase in metamorphic grade might be expected from sample 1 in the northeast to sample 8 in the southwest.

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*Present address: Department of Geological Sciences, University of Durham, Durham, England.

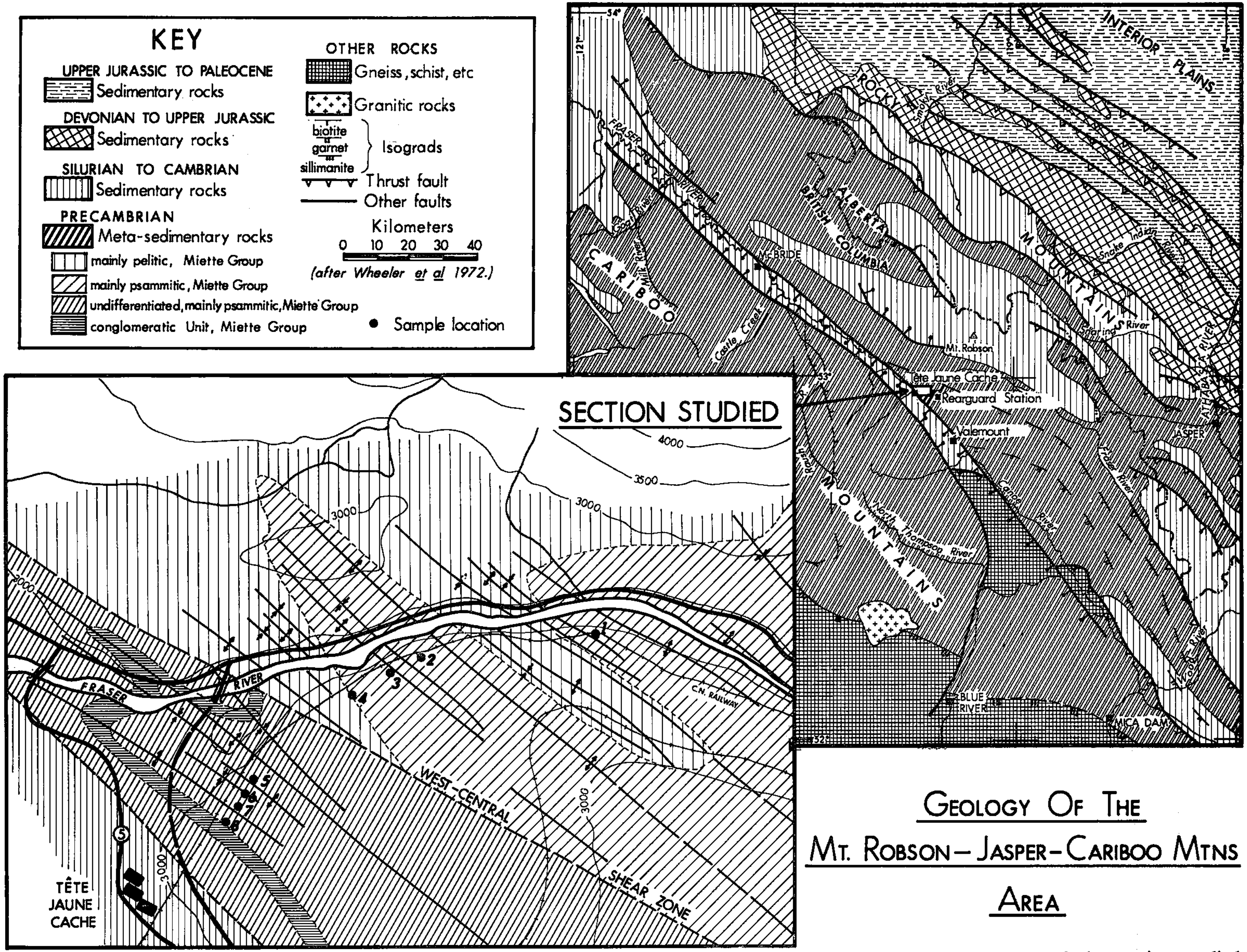

FIG. 1. Generalized geological map showing the positions of the biotite, garnet and sillimanite isograds and the location of the section studied.

Samples were selected for their compositional differences and varied mineralogy. With the exception of sample 8, a calcareous schist, they comprise a series based on differing proportions of feldspar and quartz clast content in the original clay matrix. Samples 4, 3 and 7 are now phyllitic and contain little quartz. Sample series 1, 5, 6, 2 represents a progressive increase in quartz into more psammitic rocks.

ANALYTICAL TECHNIQUES

Whole-rock analyses were made by classical wet-chemical techniques. Mineral compositions were obtained by wavelength dispersive analysis using an A. R. L. "EMX" electron probe operated at 15 kV. A beam current integrating system eliminated the effects of short-term drift, and measurement of standard intensities, before and after specimen intensities, compensated for the effects of any longer-term drift. Natural minerals of accurately determined composition, together with a few simple oxides, sulphides and pure metals were used as standards. There was little or no indication of inhomogeneity (zoning, *etc.*) within individual mineral grains, but five scattered 20-second point counts were taken on each of five different grains to ensure that an average composition was obtained. The nominal 20-second counting times at a point, using a focused beam of <0.5 μm diameter and probe current of about 0.01 μA, produced no significant damage to the silicates, but caused considerable damage to carbonates, as evidenced by changing count rates with time; thus carbonates had to be kept moving beneath the beam. At the 99% confidence level, the maximum statistical relative counting errors on all the major elements (*e.g.* Si, Al, Fe, Mg and K in the micas) ranged between 0.5% and 2.0%, the smaller percentage errors in general being associated with the larger concentrations. Apparent concentrations were corrected for atomic number, absorption and characteristic fluorescence effects using the APL computer programme of Smith & Tomlinson (1970). Matrix corrections were in general very small. Fe was in all cases treated as Fe^{2+} for the purposes of calculating oxygen contents, *etc.*

In all instances analyses are presented here as weight per cent elements, rather than in the traditional fashion as oxides. One of several reasons why this procedure is followed is that most modern mineral analyses are performed with an electron microprobe and it is the concentration of an *element* that is measured. For analogous reasons, structural formulae are given as the proportions of the total number of cations, rather than being based on the calculated but not determined number of anions. With the present widespread availability of electronic calculators and computers, this presentation should not give rise to significant problems in making comparisons with analyses presented in the traditional manner. For the sake of uniformity and to avoid rounding errors in some cases, all analyses are given to two decimal places. However, it should be stressed that for many elements the second decimal place is not significant.

MINERAL CHEMISTRY

Muscovite

A dioctahedral white mica occurs in all analysed samples. Microprobe analyses and structural formulae are given in Table 1. The mica is intermediate in composition between muscovite *sensu stricto*, $K_2Al_4Si_6Al_2O_{20}(OH)_4$, and phengite, $(K,Na)_2Al_3R^{++}Si_7AlO_{20}(OH)_4$.

The phengite component of the mica, as inferred from the Al/(Mg+Fe) ratio, is related to the mineralogy of the rock. Muscovite from sample 1, which coexists with biotite but not chlorite, has a low ratio, while that from sample 2, which coexists with chlorite but not biotite, has a high ratio. Samples 3 to 7, which contain the assemblage muscovite-biotite-chlorite, yield muscovites with an intermediate Al/(Mg+Fe) ratio. Although sample 8 is not strictly comparable in terms of bulk rock composition, its muscovite has an Al/(Mg+Fe) ratio very similar to the main cluster (Fig. 2).

Brown (1967) noted that coexisting musco-

TABLE 1. PARTIAL MICROPROBE ANALYSES OF MUSCOVITES

Sample No.		1	2	3	4	5	6	7	8
	Si	21.97	21.87	21.92	22.10	21.64	21.22	22.23	21.51
	Ti	0.43	0.16	0.23	0.22	0.22	0.22	0.24	0.20
	Al	15.07	18.51	17.12	17.12	16.87	16.57	16.76	17.38
	Fe	3.61	1.15	1.99	2.05	2.22	2.29	2.28	2.49
	Mg	1.22	0.41	0.81	0.83	0.69	0.87	0.90	0.56
	Ca	0.00	0.02	0.00	0.00	0.03	0.01	0.00	0.06
	Na	0.13	0.86	0.45	0.48	0.50	0.49	0.36	1.30
	K	9.19	8.11	8.69	8.91	8.81	9.01	8.93	8.02
	Sr	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05
	Ba	0.66	0.63	0.68	0.48	0.82	0.61	0.73	0.99
	F	0.22	0.17	0.00	0.11	0.00	0.00	0.00	0.38
Numbers of cations calculated for a total of 14									
Z	Si,	6.404	6.209	6.294	6.296	6.261	6.194	6.348	6.117
	Al^{IV}	1.596	1.791	1.706	1.704	1.739	1.806	1.652	1.883
Y	Al^{VI}	2.976	3.679	3.411	3.373	3.341	3.229	3.330	3.262
	Ti	0.073	0.027	0.039	0.037	0.037	0.038	0.040	0.033
	Fe	0.529	0.164	0.288	0.294	0.324	0.336	0.328	0.356
	Mg	0.409	0.134	0.269	0.274	0.232	0.293	0.298	0.184
X	Na	0.046	0.298	0.158	0.167	0.177	0.175	0.126	0.452
	K	1.924	1.654	1.793	1.824	1.832	1.888	1.833	1.639
	Ba	0.039	0.037	0.040	0.028	0.049	0.036	0.043	0.058
Mg/(Mg+Fe) (mol.)		0.436	0.450	0.483	0.483	0.418	0.465	0.476	0.341
Al/(Mg+Fe) (mol.)		4.87	18.32	9.18	8.94	9.14	8.01	7.96	9.53
Total X*		2.012	1.991	1.994	2.022	2.060	2.102	2.004	2.153
Total Y		3.987	4.004	4.007	3.978	3.934	3.896	3.996	3.835
Total Z		8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000

* includes Ca & Sr

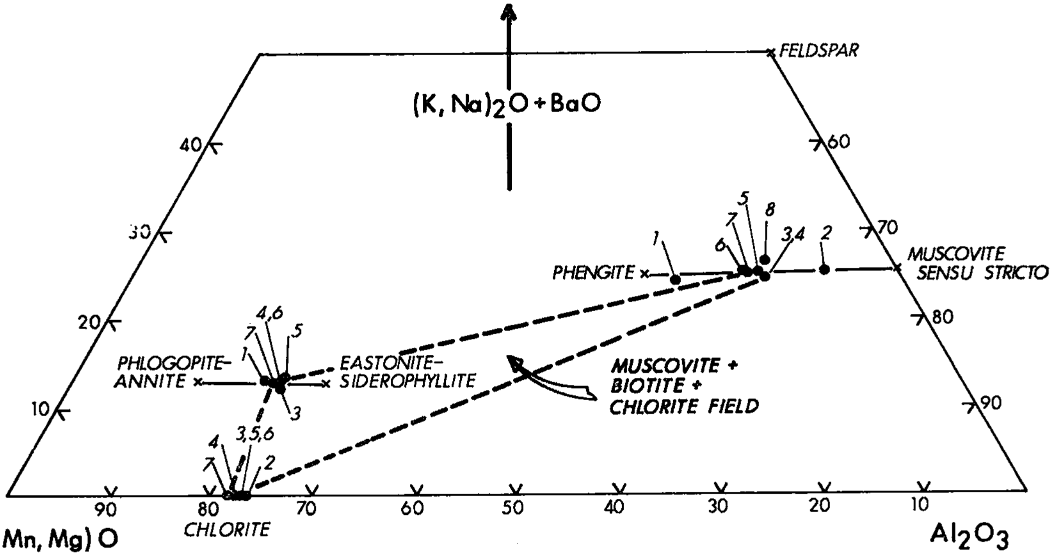

FIG. 2. Modified A-K-F plot showing the compositional variations for coexisting sheet silicates. Note that all Fe indicated by the microprobe analyses has been calculated as FeO.

vites and chlorites have few compositional controls other than whole-rock chemistry, in the absence of additional ferromagnesian phases. Thus, below the biotite isograd, the wide range of Al/(Mg+Fe) ratio possible in rocks of pelitic and semipelitic composition will be reflected in the compositions of the coexisting muscovites and chlorites. Above the isograd, the addition of biotite as a third phase imposes a restraint on the muscovite composition. According to Mather (1970), the mica must be the most phengitic acceptable under the prevailing conditions.

In comparison with Mather's data on ferromagnesian carbonate-free material, the Tête Jaune Cache muscovites have an appreciably lower phengite content at the same metamorphic

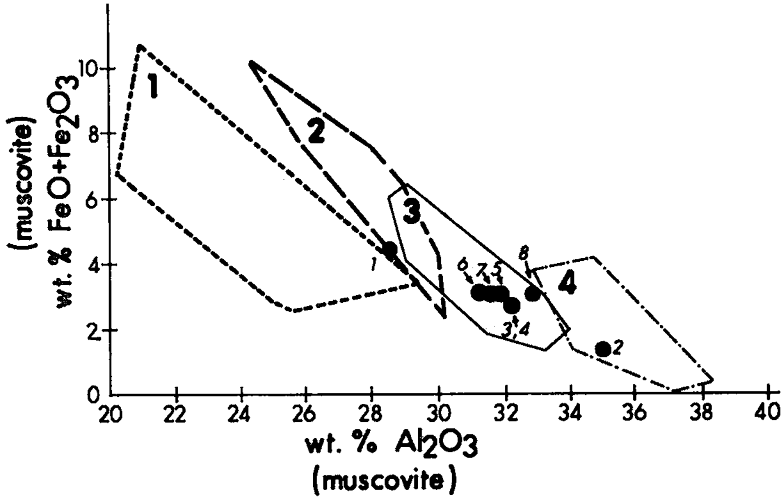

FIG. 3. Distribution of FeO + Fe_2O_3 and Al_2O_3 in phengitic muscovites as a function of metamorphic grade (after Butler 1967). 1 = blueschist facies; 2 = chlorite and biotite zones; 3 = almandine zone; 4 = staurolite and higher zones. Solid circles are data points from the present work. Note all Fe indicated by the microprobe analyses has been calculated as FeO.

grade. They are comparable in composition to muscovites collected by Lambert (1959) and Butler (1967) from higher metamorphic grades.

Butler (1967) found that fields of phengite content defined on the basis of $Al_2O_3/(FeO + Fe_2O_3)$ ratios could be correlated with metamorphic grade (Fig. 3). Cipriani (1971) established similar fields, based on cation content, which also reflect metamorphic grade (Fig. 4). He supported the suggestion of earlier workers that phengite content is reduced with increasing metamorphic grade and showed that the ratio of Al^{IV} to Si in the tetrahedral site increases with temperature, and that Al^{VI} replaces Mg and Fe in the octahedral site to restore charge balance. With respect to the paragenetic fields established by Butler and Cipriani (Figs. 3 and 4), all the Tête Jaune Cache muscovites are anomalous: the three-phase-field muscovites lie close to, or within, fields indicative of anything from kyanite-almandine-muscovite to almandine-staurolite subfacies. The regional geology of the area, and the nature of the coexising minerals, clearly preclude such conditions ever having been attained, and some other factor must be responsible for the anomalous composition of the muscovites.

TABLE 2. PARTIAL MICROPROBE ANALYSES OF BIOTITE

Sample No.		1	3	4	5	6	7
	Si	16.72	17.07	16.84	16.24	16.83	17.03
	Ti	1.96	1.31	1.33	1.29	1.26	1.35
	Al	8.09	8.85	8.95	8.85	8.80	8.65
	Fe	20.63	19.45	19.87	20.52	19.41	19.38
	Mn	0.05	0.00	0.04	0.02	0.02	0.04
	Mg	4.18	4.68	4.56	3.87	4.50	4.97
	Na	0.03	0.04	0.05	0.05	0.04	0.04
	K	8.01	7.76	8.03	7.98	7.99	8.10
	Sr	0.03	0.02	0.03	0.03	0.02	0.03
	Ba	0.20	0.13	0.12	0.22	0.12	0.15
	P	0.02	0.02	0.01	0.00	0.01	0.01
	Cl	0.00	0.01	0.01	0.02	0.01	0.00
	F	0.15	0.22	0.27	0.18	0.20	0.12
Numbers of cations calculated for a total of 16							
Z	Si	5.647	5.700	5.603	5.562	5.666	5.647
	Al	2.353	2.300	2.397	2.438	2.334	2.353
Y	Al	0.491	0.776	0.703	0.717	0.750	0.632
	Ti	0.388	0.256	0.259	0.259	0.249	0.262
	Fe	3.504	3.266	3.324	3.534	3.286	3.232
	Mn	0.009	0.000	0.007	0.004	0.003	0.007
	Mg	1.629	1.806	1.752	1.532	1.749	1.905
X	Na	0.012	0.016	0.020	0.021	0.016	0.016
	K	1.943	1.862	1.919	1.914	1.932	1.930
	Ba	0.014	0.009	0.008	0.015	0.008	0.010
Mg/(Mg+Fe) (mol.)		0.317	0.356	0.345	0.302	0.347	0.371
Al/(Mg+Fe) (mol.)		0.554	0.606	0.611	0.623	0.612	0.581
Total X*		1.972	1.889	1.951	1.954	1.959	1.959
Total Y**		6.028	6.111	6.049	6.046	6.041	6.041
Total Z		8.000	8.000	8.000	8.000	8.000	8.000

Samples 2 and 8 do not contain biotite
* includes Sr; ** includes P.

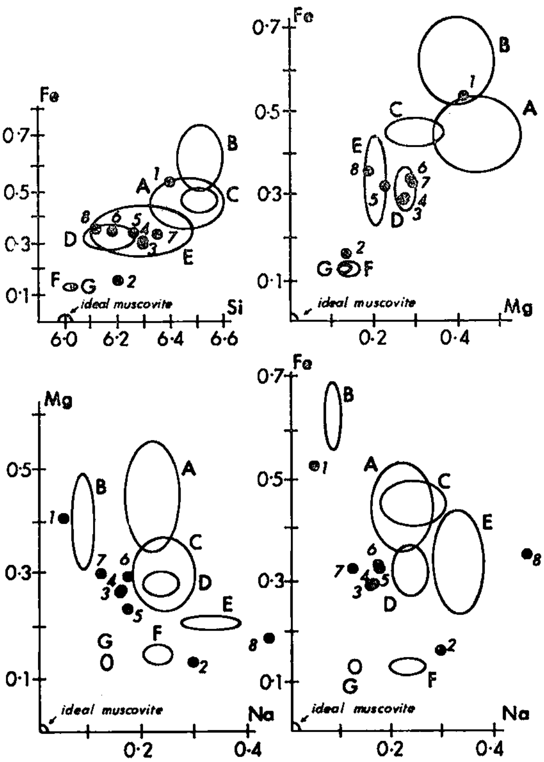

FIG. 4. Cation distribution plots for the Tête Jaune Cache muscovites. The fields A - G correspond respectively to quartz-albite-muscovite-chlorite subfacies; quartz-albite-epidote-biotite subfacies; quartz-albite-epidote-almandine subfacies; staurolite-almandine subfacies; kyanite-almandine-muscovite subfacies; sillimanite-almandine-muscovite subfacies and the orthoclase isograd. (Modified after Cipriani *et al.* 1971).

Below the biotite isograd, the phengite content of muscovites is largely governed by the partitioning of Mg, Fe and Al between the mica and the coexisting chlorite. The appearance at higher grades of metamorphism of additional ferromagnesian phases such as biotite, garnet and staurolite, disturbs the partition equilibria so that smaller proportions of Mg and Fe are incorporated as the phengite component of the white mica, which can therefore approach the composition of muscovite *sensu stricto* much more closely. In the Tête Jaune Cache rocks, samples 3 to 7 contain ankerite and, with the possible exception of sample 7, siderite. These carbonates together with iron and iron-titanium oxides which are present, influence the Mg/(Mg+Fe) and Al/(Mg+Fe) ratios in the coexisting minerals. In effect, they perform a similar role to biotite, garnet and staurolite present at higher metamorphic grades, and are thus responsible for the anomalous pattern of muscovite compositions relative to the trends found by Cipriani (1971) and Butler (1967).

Biotite

Biotite occurs in six of the analysed samples. In all rocks it coexists with muscovite and, with the exception of sample 1, with chlorite. Biotite analyses and structural formulae are given in Table 2, and are illustrated in Figure 2.

The biotites show an over-all consistency in composition. They are low in Na and Al, and high in Fe — characteristics normally associated with low-grade metamorphic biotites such as those reported by Lambert (1959) and Butler (1967). The position of the biotite apex of the muscovite-biotite-chlorite field in Figure 2 is close to that found by Mather (1970) for samples from the biotite isograd in a ferromagnesian carbonate-free environment.

The biotites, unlike the muscovites, are deficient in large alkali cations. The deficiency in '*X*' is apparently made up by an excess of smaller divalent cations. Both Na and Ba partition preferentially into muscovite.

Figure 5 illustrates the sympathetic relationship between the Mg/(Mg+Fe) ratio in the biotites and that in coexising phases, including ankerite and siderite.

Wenk (1970) found that coexisting muscovites and biotites change their Al^{VI} partition coefficient with increasing metamorphic grade: the ratio $K_D = Al^{VI}$ Musc./Al^{VI} Biot. decreases from 14 at low to 3 at high grades of metamorphism. Tête Jaune Cache samples give an average K_D value of 4.9, with little inter-sample variation. This low value is in line with the anomalous indication of high temperature of formation already discussed. Wenk also indicated that for greenschist facies rocks, total Al (muscovite)/total Al (biotite) should give a value of 1.61. The Tête Jaune Cache samples are close to this, with an average of 1.64. The total Al content is thus normally distributed, despite the anomalous distribution between Al^{VI} and Al^{IV} sites.

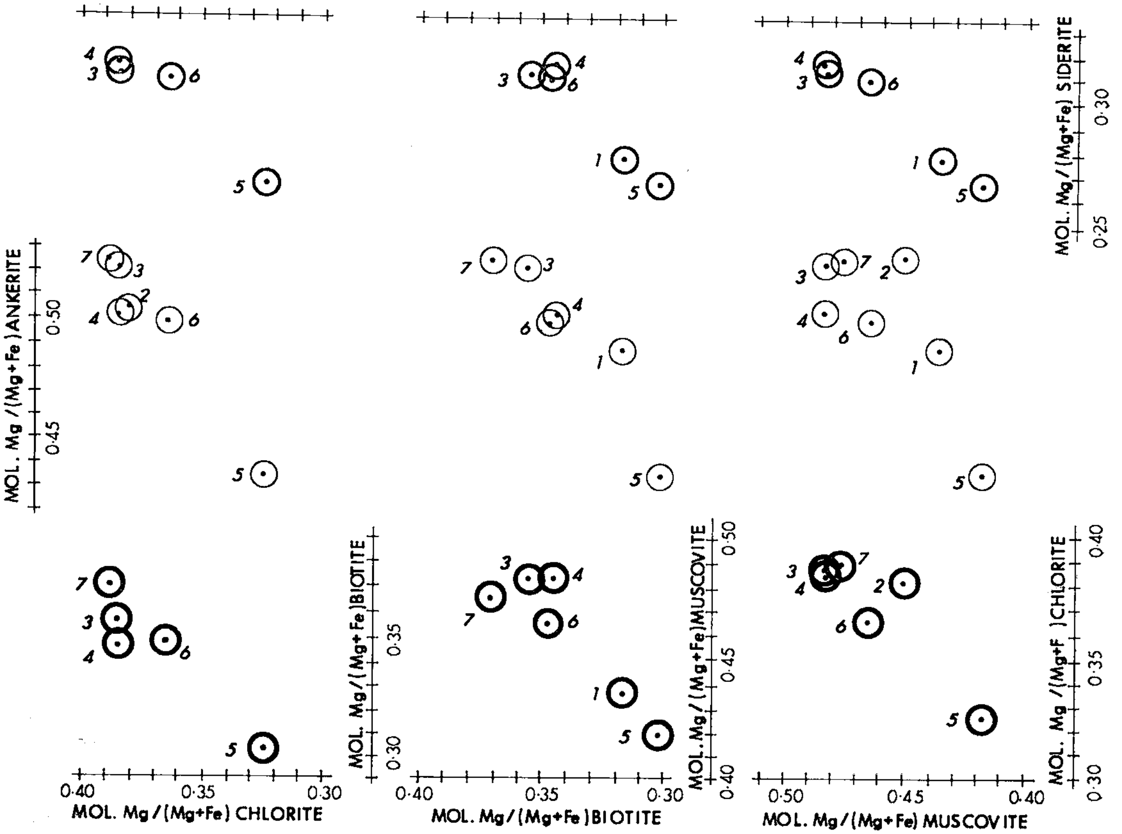

FIG. 5. Relationship of Mg/(Mg+Fe) ratios for the ferromagnesian minerals. Note that some of the scatter of data points from ideal lines may be related to variation in other minor elements such as Mn (see also Fig. 7).

Chlorite

Chlorite occurs in six of the analysed samples. In each it coexists with muscovite and, excepting sample 2, with biotite. Chlorite analyses and structural formulae are shown in Table 3. The chlorite in sample 6 is a brunsvigite, and the others are ripidolites (Deer *et al.* 1962). The chlorites are rich in Fe and Al, and are similar in most respects to lower greenschist facies chlorites described by Brown (1967) and Mather (1970). The chlorite population has a restricted range in composition and the position of the chlorite apex of the muscovite-biotite-chlorite field in Figure 2 is close to that found by Mather.

Carbonates

All analysed samples contain calcite and ankerite, and five of them also contain siderite. Siderite was not detected in sample 2 (a biotite-free schist); sample 7, which is otherwise normal; or sample 8, a calcareous schist. Carbonate analyses together with molecular percentages of the principal end-members are given in Table 4. Other than Mg, Fe and Ca, the only metal present in significant amounts is Mn. Entry of this element into ankerite and siderite has resulted in a marked depletion in the Mn contents of coexisting chlorites and biotites compared with the values for these minerals in the literature. Low Mn levels in biotite and chlorite in greenschist facies pelites may, therefore, be a useful pointer towards the presence of ankerite and/or siderite in the rocks.

Ankerites which coexist with calcite but not siderite in samples 2 and 8 are distinctive in having high $CaCO_3$ contents, and, in sample 8, notably high Mg/(Mg+Fe). Ankerites which coexist with calcite and siderite fall well within the ankerite field in Figure 6a and have a nearly constant $CaCO_3$ content. Mg/(Mg+Fe) varies within the range 0.525-0.435. The carbonates thus fall about midway between dolomite and ferroan dolomite, $CaFe(CO_3)_2$. Ankerite from sample 7 plots in the same position, and conceivably it may coexist with siderite although none was found in thin section.

TABLE 3. PARTIAL MICROPROBE ANALYSES OF CHLORITES

Sample No.		2	3	4	5	6	7
	Si	11.00	11.20	11.58	11.14	12.32	11.86
	Ti	0.04	0.00	0.04	0.03	0.00	0.00
	Al	11.79	11.33	11.34	11.62	11.52	10.85
	Fe	24.77	24.85	25.43	27.28	25.98	25.12
	Mn	0.09	0.04	0.07	0.08	0.06	0.10
	Mg	6.66	6.81	6.93	5.72	6.51	6.95
	Ca	0.01	0.01	0.01	0.03	0.02	0.00
	K	0.01	0.01	0.01	0.01	0.00	0.01
	Sr	0.00	0.02	0.01	0.02	0.06	0.01
	P	0.00	0.04	0.02	0.01	0.02	0.04
Numbers of cations calculated for a total of 20							
Z	Si	5.057	5.157	5.231	5.102	5.478	5.401
	Al	2.943	2.843	2.769	2.898	2.522	2.599
Y	Al	2.699	2.587	2.563	2.642	2.810	2.545
	Ti	0.011	0.000	0.011	0.008	0.000	0.000
	Fe	5.726	5.754	5.777	6.284	5.810	5.754
	Mn	0.021	0.009	0.016	0.019	0.014	0.023
	Mg	3.537	3.622	3.616	3.027	3.344	3.657
Mg/(Mg+Fe) (mol.)		0.382	0.386	0.385	0.325	0.365	0.389
Al/(Mg+Fe) (mol.)		0.609	0.579	0.568	0.595	0.583	0.547

TABLE 4. MICROPROBE ANALYSES (WT. %) OF CARBONATES

Sample No.		1	2	3	4	5	6	7	8
Calcites	Ca	39.55	39.79	39.67	39.63	39.54	39.97	39.86	37.79
	Fe	0.03	0.05	0.25	0.19	0.16	0.10	0.19	1.09
	Mg	0.10	0.02	0.04	0.03	0.03	0.02	0.03	0.35
	Mn	0.08	0.03	0.03	0.05	0.00	0.00	0.00	0.00
	Zn	0.00	0.06	0.06	0.07	0.00	0.00	0.00	0.01
	Sr	0.00	0.00	0.00	0.00	0.00	0.06	0.07	0.04
	C*	12.06	12.02	12.00	12.02	12.06	11.98	11.98	12.15
	O*	48.18	48.04	47.95	48.01	48.21	47.87	47.87	48.57
mol %	$CaCO_3$	99.36	99.68	99.26	99.32	99.58	99.68	99.46	96.47
	$FeCO_3$	0.06	0.09	0.44	0.33	0.30	0.18	0.35	2.01
	$MgCO_3$	0.44	0.08	0.15	0.14	0.12	0.07	0.11	1.46
	$MnCO_3$	0.14	0.05	0.06	0.09	0.00	0.00	0.00	0.00
	Mg/(Mg+Fe)	0.880	0.470	0.254	0.298	0.285	0.280	0.239	0.421
	Σ metal cations†	0.989	0.995	0.998	0.996	0.986	1.003	1.002	0.966
Ankerites		1	2	3	4	5	6	7	8
	Ca	19.90	20.91	20.01	20.35	20.07	20.05	20.03	20.94
	Fe	13.15	12.56	12.66	13.10	14.68	13.01	12.27	8.55
	Mg	5.44	5.55	6.02	5.75	4.30	5.64	5.92	7.48
	Mn	1.16	0.90	0.42	0.71	0.91	0.86	1.09	0.37
	Zn	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00
	Sr	0.12	0.02	0.06	0.03	0.06	0.00	0.00	0.02
	C*	12.06	12.04	12.17	12.21	11.88	12.08	12.15	12.54
	O*	48.21	48.11	48.66	48.77	47.47	48.26	48.54	50.10
mol %	$CaCO_3$	50.76	52.62	50.84	50.18	50.91	50.92	50.86	52.75
	$FeCO_3$	24.07	22.68	23.09	23.64	26.74	23.72	22.36	15.47
	$MgCO_3$	22.87	23.02	25.22	23.84	20.61	23.61	24.76	31.08
	$MnCO_3$	2.16	1.65	0.78	1.30	1.68	1.60	2.02	0.68
	Mg/(Mg+Fe)	0.487	0.504	0.522	0.502	0.435	0.499	0.525	0.668
	Σ metal cations	0.975	0.991	0.969	0.991	0.994	0.978	0.972	0.949
Siderites		1		3	4	5	6		
	Ca	0.36		0.37	0.38	0.47	0.43		
	Fe	35.78		34.85	35.04	36.30	34.96		
	Mg	5.96		6.91	7.08	5.77	6.88		
	Mn	1.79		1.06	1.04	1.39	1.85		
	Zn	n.d.		n.d.	0.01	n.d.	n.d.		
	Sr	n.d.		n.d.	0.00	n.d.	n.d.		
	C*	11.27		11.37	11.48	11.22	11.18		
	O*	45.02		45.43	45.89	44.85	44.70		
mol %	$CaCO_3$	0.97		1.00	1.01	1.27	1.12		
	$FeCO_3$	69.08		66.60	66.24	70.33	65.67		
	$MgCO_3$	26.43		30.34	30.75	25.64	29.67		
	$MnCO_3$	3.51		2.07	2.00	2.74	3.54		
	Mg/(Mg+Fe)	0.277		0.313	0.317	0.267	0.311		
	Σ metal cations	0.992		0.990	1.007	0.989	1.024		

* calculated values † on basis of one CO_3 n.d. not determined

Siderite compositions are much closer to the siderite-magnesite join than would be expected from the siderite field at 450°C as depicted by Rosenberg (1967) — Figure 6a. This suggests that the maximum $CaCO_3$ content of siderite decreases rapidly with falling temperature, assuming that Rosenberg's data for this field are accurate. Also, under the temperature/pressure conditions represented by this sample suite, the calcite field has shrunk to a very small fraction of its size at 450°C. Mg/(Mg+Fe) of the siderites fall within the range 0.317-0.267, and the pattern of Mg-Fe variation is similar to that in coexisting ankerite (Figs. 5 and 6). The total contents of Mg and Fe in coexisting calcites are so low that small inclusions and very minor analytical errors may mask a similar pattern.

The distribution of Mn between ankerite and siderite is dependent on the Mg/(Mg+Fe) ratios of these carbonates (Fig. 7). As the ratios increase, Mn shows a greater preference for siderite.

The carbonates have not only depleted the phyllosilicate system in Mg, Fe and Mn, but have also attained near-equilibrium partitioning of Mg and Fe amongst each other, and the micaceous phases (Fig. 5). The behaviour of Mn may account for some of the deviation from a simple and perfectly sympathetic relationship between each mineral pair.

CARBONATE GEOTHERMOMETER

Rosenberg (1967) studied sub-solidus relations between $CaCO_3$, $MgCO_3$ and $FeCO_3$ at temperatures from 350°C to 550°C. He found that the system was insensitive to total pressure (as $CO_2 + 2\%$ CO), within the experimental range 2-3 kb. Such temperatures and pressures are considered reasonable for lower greenschist facies conditions (Winkler 1967). Phase relations at 450°C, the lowest temperature studied *in detail* by Rosenberg, are shown in Figure 6a, along with compositional data from the Tête Jaune Cache carbonate assemblage.

Rosenberg found that the ordered solid-solution series $CaMg(CO_3)_2$-$CaFe(CO_3)_2$ in which ankerites lie, terminates at a three-phase ankerite-calcite-siderite field (Fig. 6a). He also found that the upper limit of Fe solubility in ankerite increases with temperature, and the ankerite compositions which are stable with calcite and siderite at experimentally determined temperatures are shown in Figure 6a. If the effective rock composition lies within the field 'C+A+S' in Figure 6a, minerals with compositions 'X', 'Y' and 'Z' will coexist at 450°C. Similarly, 'X_1', 'Y_1', and 'Z_1' delineate the field 'C+A+S' for the Tête Jaune Cache rocks on the basis of average value for samples 1, 3, 4, and 6 (Fig. 6b). Although Rosenberg's detailed data did not extend below 400°C, by extrapolation of the data from the ankerite composition (X), a temperature of about 350°C is obtained. The temperature suggested by sample 5 is higher, about 370°C. A further uncertainty surrounds both of these temperature estimates due to the presence of small amounts of Mn in the carbonates. The effective compositions of samples 2, 8 and possibly 7 lie within the 'C+A' field in Figure 6b, under the prevailing conditions, and no temperature estimates are possible.

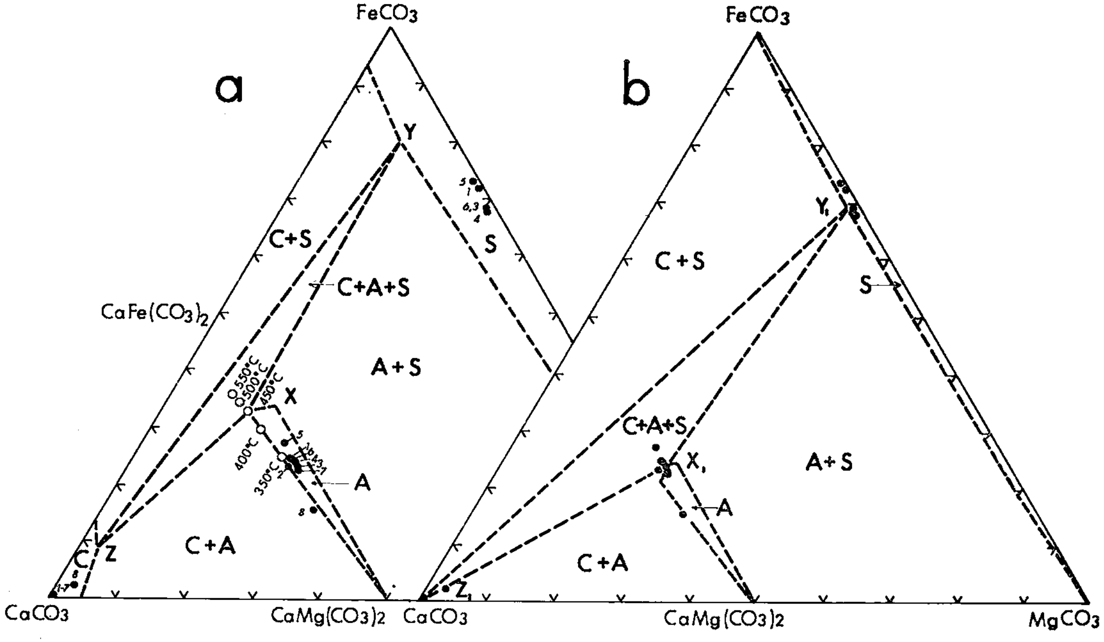

FIG. 6. Compositions of coexisting carbonates in sample 1-8 superimposed in (a) on subsolidus relations in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ at 450°C; also shown are the limiting ankerite compositions at temperatures ranging from 550°C to 350°C (after Rosenberg 1967). In (b) the inferred subsolidus relations for the Tête Jaune Cache samples are indicated. C = calcite solid solution, S = siderite solid solution and A = ankerite solid solution.

It is clear from Figure 6 that a small range of both ankerite and siderite compositions coexist with calcite and other ferromagnesian silicates (biotite, chlorite and muscovite). The observed Mg/(Mg + Fe) ratios increase in the order 5, 1, 6, 4, 3, (7) in the ankerites that coexist with two other carbonates. Clearly the range of ratios observed is not simply related to a small metamorphic grade increase that can be anticipated in the sample sequence 1-8; nor does the trend directly follow the whole-rock Mg/Mg + Fe) ratios, (Table 5); rather it corresponds more closely to the Si contents of the rocks which decrease in the order, 6, 5, 1, 4, 3, (7). This decrease reflects the modal proportions of clay matrix to quartz plus feldspar in the original sediment. Rosenberg's (1967) experimental work was on the pure carbonate system and is therefore not strictly applicable to natural situations in which other Fe, Mg-bearing minerals and a hydrous fluid phase are present. In particular, it can be anticipated that P_{H_2O} will have some effect on the minimum Mg/(Mg + Fe) ratio permitted in the ankerite, so that a small range of ankerite compositions corresponding to a range of P_{H_2O} may coexist with two other carbonates. No estimates of P_{H_2O} for these samples are available but it is possibly significant that the most hydrous, pelitic rocks, 4, 3 (& 7) lie at one end of the observed range whereas 5, a much more psammitic sample, lies at the other. Although the proportion of hydrous minerals will obviously not be related

TABLE 5. WHOLE-ROCK CHEMICAL ANALYSES

Sample No.	2	6	5	1	4*	3	7	8*
SiO_2	78.18	75.40	67.91	64.90	61.06	58.56	48.84	34.99
TiO_2	0.23	0.42	0.58	0.85	0.82	0.96	1.17	0.38
Al_2O_3	8.94	10.91	14.50	15.42	17.20	18.52	22.80	8.95
Fe_2O_3	0.71	0.23	0.75	1.13	1.54	1.43	3.09	1.12
FeO	2.34	2.75	3.02	5.06	5.60	5.51	5.12	1.97
MnO	0.06	0.06	0.07	0.04	0.07	0.09	0.08	0.18
MgO	0.94	1.25	1.24	2.12	2.08	2.19	3.12	1.86
CaO	1.98	1.14	1.72	0.53	0.02	0.65	1.15	24.65
Na_2O	1.30	1.79	2.42	0.92	0.48	1.69	0.68	0.46
K_2O	1.48	2.89	3.32	5.46	5.60	4.96	8.00	2.40
H_2O^-	0.09	0.10	0.08	0.04	0.18	0.05	0.13	0.15
H_2O^+	1.68	1.42	1.93	2.42	3.06	2.65	4.09	1.34
P_2O_5	0.61	0.14	0.14	0.11	0.10	0.10	0.25	0.27
CO_2	1.90	1.87	2.32	0.84	1.93	2.96	1.59	21.47
S					0.21			
S_2=O					0.05			
Total	100.44	100.37	100.00	99.84	99.90	100.32	100.11	100.19
Oxidation Ratio	21.45	7.00	18.26	16.73	19.84	18.93	35.19	33.84
Mg/(Mg+Fe) (mol.)	0.360	0.430	0.374	0.384	0.347	0.365	0.413	0.527
Al/(Mg+Fe)	2.707	2.965	3.461	2.205	2.267	2.439	2.387	2.004

* Analyses by A. Stelmach, Department of Geology, University of Alberta; other analyses by R.H. Pinsent

Mineral Assemblages:

1. Quartz, muscovite, biotite, albite, ankerite, siderite, calcite and ilmenite.
2. Quartz, muscovite, chlorite, albite, ankerite, calcite, ilmenite.
3. Quartz, muscovite, biotite, chlorite, albite, ankerite, siderite, calcite and ilmenite.
4. Quartz, muscovite, biotite, chlorite, ankerite, siderite, calcite and ilmenite.
5. Quartz, muscovite, biotite, chlorite, albite, ankerite, siderite, calcite and ilmenite.
6. Quartz, muscovite, biotite, chlorite, albite, ankerite, siderite, calcite and ilmenite.
7. Quartz, muscovite, biotite, chlorite, ankerite, calcite and ilmenite.
8. Quartz, muscovite, ankerite, calcite, chloritoid, rutile, hematite and magnetite.

Note: Most rocks have accessory minerals including one or more of: apatite, tourmaline, zircon and pyrite.

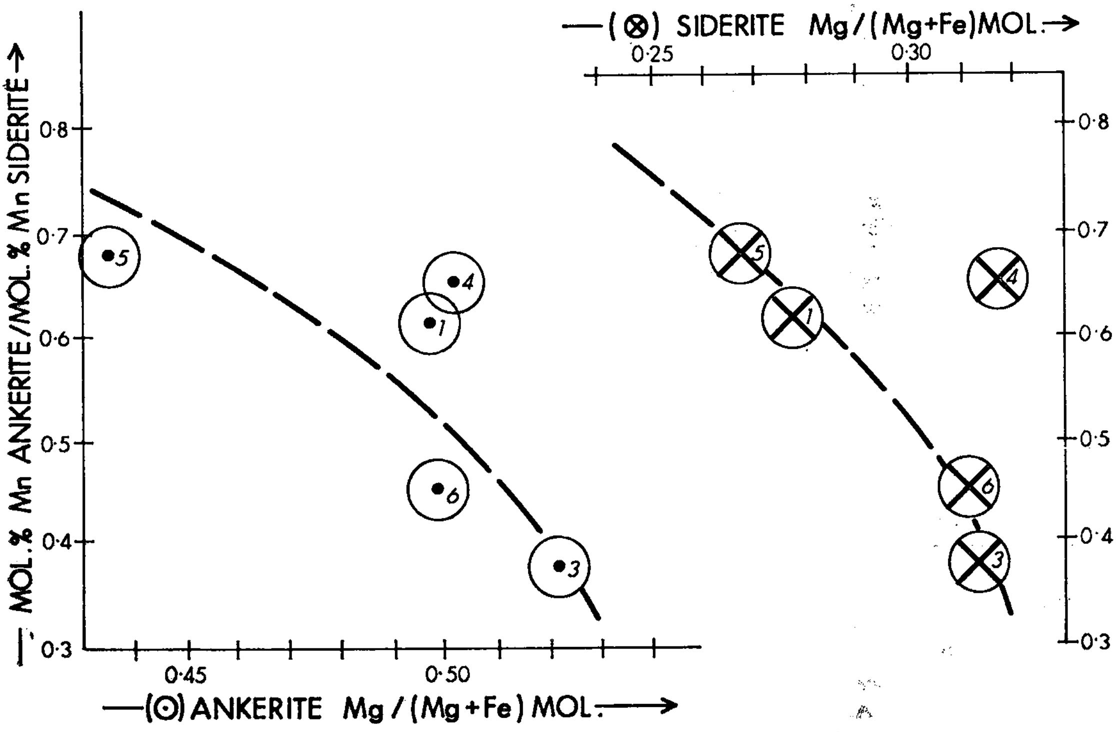

FIG. 7. Influence of Mg/(Mg+Fe) ratio on the distribution of Mn between ankerite and siderite. Dashed curves are visual estimates of best-fit variation trends.

simply to P_{H_2O}, the observed trend suggests that as X_{H_2O} increases, the maximum amount of Fe permitted in the ankerite decreases.

Winkler (1967) estimated temperatures of about 450° - 470°C for the onset of biotite formation, which suggest that values based on the carbonate geothermometer are low. However, data on fractionation of carbon and oxygen isotopes and Mg between coexisting calcite and dolomite obtained by Sheppard & Schwarcz (1970), suggest biotite isograd temperatures of about 295°C on the basis of the maximum temperature indicated for the chlorite zone. In the present work, the uncertainties in temperature estimates due to the Mn contents of natural assemblages and the possible effects of X_{H_2O} are difficult to estimate but are considered unlikely to exceed ± 50°C.

BIOTITE ISOGRAD

The use of a biotite isograd based on the first appearance of this mica in rocks of poorly defined pelitic composition was challenged by Mather (1970), on the grounds that prograde metamorphic biotite is found commonly in rocks of greywacke composition appreciably below the classical isograd. The present data support this observation, and Jones & Ghent (1970) also indicated that early biotite is of common occurrence in the upper Proterozoic metasediments of Western Canada.

Biotite formation is dependent on the whole-rock composition, the chlorite-grade mineralogy, and metamorphic grade. The apparent absence of K-feldspar from Miette Group sediments, other than in a few pebble conglomerate horizons, has been attributed by Charlesworth *et al.* (1967) to a period of albitization. This is inferred to predate biotite-grade metamorphism (Pinsent 1971), and the following biotite-forming reaction is suggested for samples 3-7:

phengitic muscovite$_1$ + chlorite$_1$ → less phengitic muscovite$_2$ + biotite + chlorite$_2$ (+H_2O) (1)

Textural evidence (Pinsent 1971), suggests that the intimately associated "chlorite$_1$ + phengitic muscovite$_1$" assemblage completely recrystallised to the biotite-grade mineralogy.

The absence of chlorite in sample 1 is a function of whole-rock composition, and the following reaction suggested by Ernst (1963), is inferred:

phengitic muscovite$_1$ + chlorite →
less phengitic muscovite$_2$ + biotite (2)

Similarly, the absence of biotite in sample 2 is attributable to the Al-rich nature of the rock composition after allowance has been made for components forming non-micaceous minerals such as quartz, albite and carbonates. Under the prevailing conditions biotite could not be generated.

Mather (1970) suggested that once the muscovite-biotite-chlorite field is established (Fig. 2), it will increase in size as the "muscovite" apex of the field is depleted in phengite and approaches the composition of muscovite *sensu stricto*, with increase in grade. The position of the muscovite apex on the phengite-muscovite join for the Tête Jaune Cache samples is anomalous, as has been noted, and the whole-rock compositional range capable of producing the muscovite-biotite-chlorite assemblage is enlarged. Sediments which would retain their chlorite-grade mineralogy in a ferromagnesian carbonate-free environment in fact have crystallized biotite at the level of the isograd.

The presence of ankerite and siderite above the isograd is itself unusual (Winkler 1967). Dolomite and magnesite, and so presumably their Fe-bearing counterparts ankerite and siderite, are normally unstable in association with quartz above the isograd. The two reactions which limit their stability are divariant, and the carbonate stability is much enhanced by a high mole fraction CO_2 in the fluid phase (Winkler 1967). Either the rocks at Tête Jaune Cache had a very high mole fraction CO_2 in the fluid phase, or the isograd temperature was lowered by the interference of carbonate with the muscovite chemistry.

CONCLUSIONS

This study shows that ankerite and siderite in biotite-isograd metasediments influence the composition of the coexisting muscovite. The apparent ability of these phases to deplete silicates in Fe and Mg has led to the formation of Al-rich white micas with compositional characteristics more similar to those reported for muscovites from the kyanite-almandine-muscovite and almandine-staurolite subfacies of regional metamorphism. Stability of an Al-rich muscovite at the biotite isograd has enlarged the whole-rock compositional range within which the assemblage muscovite-biotite-chlorite is formed.

The carbonate geothermometer (Rosenberg 1967), based on Fe content of ankerite coexisting with calcite and siderite, indicates temperatures in the range 350-370°C for the biotite isograd. However, the presence of minor Mn in the carbonates as well as possible variations in P_{H_2O} from sample to sample at the time of crystallisation of the present assemblages, introduce some uncertainty in these figures.

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