INTERGROWN CALCIC AND Fe–Mg AMPHIBOLES
FROM THE WONGWIBINDA METAMORPHIC COMPLEX, N.S.W., AUSTRALIA

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ABSTRACT

Hornblende–cummingtonite and actinolite–cummingtonite (or grunerite) pairs in sillimanite–orthoclase–zone amphibolites and quartzites of the Wongwibinda Complex occur as composite grains showing a variety of intergrowths. Coarse homoaxial intergrowths probably developed by simultaneous primary crystallization of the amphiboles during prograde metamorphism. Fine lamellar intergrowths are due to exsolution upon cooling. Irregular patchy intergrowths are probably also exsolution products, having formed either directly or by intragranular reorganization of exsolved lamellae. A close approach to chemical equilibrium between the coexisting amphiboles is indicated by relative uniformity in the amphibole compositions within domains of uniform host-rock chemistry, and by reasonable regularity in the distributions of major elements. The pairs of intergrown amphiboles clearly define the miscibility gap between the calcic and Fe–Mg amphibole series for the P–T conditions of final exsolution and equilibration. There appears to have been little difference in the solubilities of cummingtonite in hornblende and actinolite, whereas the solubility of actinolite in cummingtonite was greater than that of hornblende. Calculated pre-exsolution actinolite compositions suggest, by comparison with the experimentally determined cummingtonite–actinolite solvus, that metamorphism peaked at about 650°C and $P(H_2O) > 3\frac{1}{2}$ kbar. This is consistent with the conditions indicated by mineral assemblages and evidence of incipient melting in pelitic and psammitic schists, namely 650–700°C and 2–4 kbar $P(H_2O)$. However, anomalies in present and pre-exsolution compositions of the coexisting cummingtonites suggest that further study of the effects of variables such as pressure and chemical composition on the amphibole solvus will be necessary before coexisting calcic and Fe–Mg amphiboles can be used as reliable geothermometers.

SOMMAIRE

Dans les amphibolites et quartzites de la zone

métamorphique à sillimanite et orthose du complexe Wongwibinda, on trouve des associations hornblende–cummingtonite et actinote–cummingtonite (ou grunerite) sous forme de grains montrant une variété d'intercroissances. Des groupements homoaxes en gros grains sont probablement d'origine primaire, résultant d'une cristallisation simultanée des amphiboles au cours d'un métamorphisme progressif. Des groupements finement lamellaires indiquent une démixtion pendant le refroidissement. Des intercroissances en taches irrégulières sont probablement aussi des produits de démixtion, soit directement, soit à la suite d'une réorganisation intragranulaire de fines lamelles exsolvées. Les amphiboles en présence se trouvaient dans un état proche de l'équilibre chimique, ainsi qu'en témoignent l'uniformité relative des compositions amphiboliques à l'intérieur de domaines où le chimisme de la roche-mère est lui-même uniforme et une certaine régularité dans le partage des éléments essentiels. Les paires d'amphiboles accouplées définissent clairement la lacune de miscibilité entre les amphiboles calciques et ferromagnésiennes pour les conditions de pression et de température de l'exsolution et de l'équilibration finales. La cummingtonite semble avoir été presque également soluble dans la hornblende et dans l'actinote, tandis que l'actinote était, plus que la hornblende, soluble dans la cummingtonite. En regard du solvus cummingtonite–actinote déterminé expérimentalement, les compositions calculées de l'actinote avant la démixtion font penser que le métamorphisme a atteint son maximum d'intensité aux environs de 650°C, avec $P(H_2O) > 3.5$ kbar. Ces conditions sont aussi celles que l'on déduit des assemblages de minéraux et de la fusion incipiente observée dans les schistes cristallins pélitiques et psammitiques, à savoir: 650–700°C et $P(H_2O) = 2$–4 kbar. Toutefois, certaines anomalies observées dans les compositions, actuelle et d'avant la démixtion, des cummingtonites indiquent qu'une étude plus approfondie des effets de la pression et de la composition chimique sur le solvus sera nécessaire avant que les amphiboles ferromagnésiennes et calciques accouplées ne puissent servir de géothermomètres.

(Traduit par la Rédaction)

INTRODUCTION

Chemical data on pairs of coexisting amphiboles are important for the information they provide on the miscibility gaps between amphibole series, and for the possible use of element distributions in estimating physical conditions of crystallization. The association of hornblende and cummingtonite or grunerite in metamorphic rocks, especially amphibolites and iron formations, is not unusual; chemical analyses of coexisting pairs are fairly numerous (*e.g.*, Vernon 1962, Klein 1968, Bonnichson 1969, Kisch & Warnaars 1969, Robinson & Jaffe 1969, Ross *et al.* 1969, Leake 1972, Stout 1972, Hietanen 1973, Immega & Klein 1976, Bostock 1977). The association of actinolite and cummingtonite or grunerite appears to be less common; most of the analyzed pairs are from the metamorphosed iron-formations of North America (*e.g.*, Mueller 1960, Klein 1968, Bonnichson 1969, Ross *et al.* 1969, Simmons *et al.* 1974, Immega & Klein 1976).

Coexisting calcic and Fe–Mg amphiboles commonly form intergrowths for which various origins have been proposed. These include (i) simultaneous primary growth of the two amphiboles, (ii) replacement of one amphibole by the other, (iii) overgrowth of one amphibole around the other, and (iv) exsolution of the intergrown phases from a primary homogeneous amphibole. The exsolution origin of amphibole intergrowths has been strongly emphasized lately by Jaffe *et al.* (1968), Ross *et al.* (1968, 1969), Robinson *et al.* (1969), Papike *et al.* (1973), Gittos *et al.* (1974), Immega & Klein (1976) and others.

Cameron (1975) has investigated experimentally the actinolite–cummingtonite solvus for compositions with Mg/Fe = 1 at 2 kbar $P(H_2O)$ and $f(O_2)$ defined by the FMQ buffer. However, quantitative experimental information is lacking on the influence of variations in $P(H_2O)$, $f(O_2)$, Mg/Fe ratio and other components (*e.g.*, Al, Na, Mn, Fe^{3+}) on the extent of solid solution between coexisting amphiboles. At present, the effects of factors such as these must be inferred from analytical data on natural amphibole pairs. There has been no experimental study of the hornblende–cummingtonite solvus.

Mueller (1960, 1961, 1962), Kisch & Warnaars (1969) and Bostock (1977) have found the distribution of Mg and Fe between coexisting calcic and Fe–Mg amphiboles to be non-ideal. Kisch & Warnaars suggested that the Mg–Fe distribution may perhaps be used as an indicator of metamorphic conditions within the limits of specific parageneses, but a useful correlation between the distribution coefficient and P–T conditions has not been established.

This paper deals with intergrown hornblende–cummingtonite and actinolite–cummingtonite (or grunerite) pairs from amphibolites and quartzites of the Wongwibinda complex, northern New South Wales, Australia. The Wongwibinda complex, described by Binns (1966), is a relatively small north-northwest-trending belt of metamorphic rocks 27 km long and up to 11 km wide, situated in the Nambucca Block about 65 km northeast of Armidale (Fig. 1). It provides a progression, from west to east, from incipiently metamorphosed greywackes and mudstones through metagreywackes and phyllites to high-grade schists and migmatites bordering a syntectonic granodiorite that probably forms the core of the complex. The mineralogical characteristics of the terrain suggest low-pres-
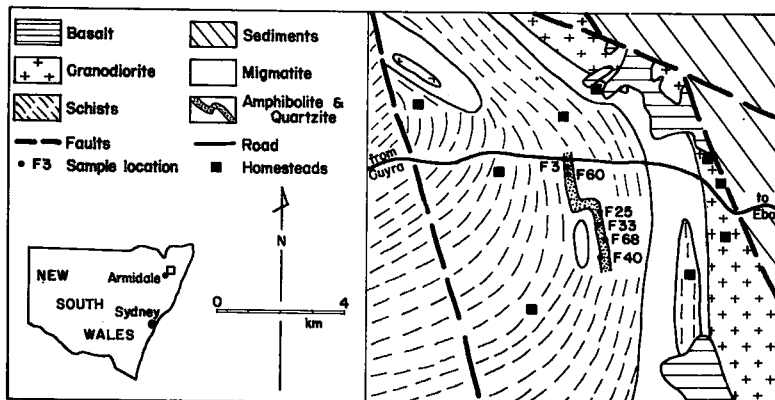

FIG. 1. Geological sketch map of part of the Wongwibinda complex (after Binns 1966), showing sample locations.

sure, Abukuma-type metamorphism. Andalusite is absent from the lower-grade schists, probably because they are not sufficiently aluminous, but cordierite is common and almandine garnet is generally restricted to the highest-grade schists. Staurolite and kyanite are absent. The maximum grade attained was that of the upper amphibolite facies. This is suggested by the occurrence of sillimanite + orthoclase and the absence of muscovite in pelitic schists, and by the absence of orthopyroxene in basic rocks. K–Ar biotite ages suggest 250 m.y. as the age of metamorphism (Binns & Richards 1965); current Rb–Sr studies indicate a complex metamorphic history extending over a considerable period of time.

THE HOST ROCKS

The amphibolites and quartzites in which the amphibole intergrowths occur are very minor components of the Wongwibinda complex. These rocks have been found in only one position in the metamorphic sequence, i.e., close to, and on the high-grade side of, the sillimanite–orthoclase isograd. They occur as several thin (<15 m wide) bands and lenses conformably interbanded with pelitic and psammitic schists, and extending discontinuously at least 3.5 km along strike (Fig. 1). The metamorphic isograds seem to parallel the trend of the amphibolite and quartzite outcrops; hence, the samples containing the analyzed amphibole pairs seem to have been metamorphosed under fairly uniform P–T conditions, although they were collected at widely separated localities over a distance of 3 km.

The amphibolites are tentatively interpreted as derivatives of basaltic lavas. They contain plagioclase (An_{35}–An_{90}) + hornblende ± diopside ± cummingtonite (+ ilmenite ± sphene ± quartz ± biotite ± K-feldspar). Cummingtonite occurs fairly rarely, and only in relatively Ca-poor, diopside-free varieties.

The quartzites are regarded as derivatives of impure cherts. They are mostly massive or weakly banded rocks composed mainly of medium-grained granoblastic quartz and minor amounts (<5%) of garnet, calcic amphibole and opaque oxides. Locally, mineralogical banding is prominent. Layers composed mainly of quartz alternate with quartz-poor layers containing various assemblages of Fe-rich silicates, including almandine, cummingtonite–grunerite, ferroactinolite, ferrohornblende, ferrosalite, Fe-biotite and (less commonly) Fe-chlorite, epidote, ferrohypersthene, calcite and plagioclase.

Magnetite and ilmenite are common accessories. Individual Fe-silicate bands vary from <1 mm up to about 10 mm in thickness, and the banding is interpreted as original bedding. The Fe-silicate assemblages closely resemble those found in moderate- to high-grade metamorphosed iron-formations, and they are believed to represent chemically precipitated Fe-silicate or Fe-carbonate layers in the original chert.

AMPHIBOLE TEXTURES

The coexisting amphiboles occur occasionally as discrete xenoblastic or subidioblastic prisms, but composite grains exhibiting a variety of intergrowth styles are more common (Fig. 2). These intergrowths can be broadly classified as follows:

(i) *Fine lamellar intergrowths.* Both amphiboles commonly contain fine lamellae of the other. These lamellae are strictly oriented parallel to ($\bar{1}$01) and (100) of the host (assuming $C2/m$ space-group symmetry). Those parallel to ($\bar{1}$01) are normally <1μ to 5μ wide, but may range up to about 10μ; the (100) lamellae are mostly <1μ in width. The spacing between lamellae may be uniform or irregular. They mostly extend with constant thickness across the entire width or length of the host grain but some are wedge-shaped, originating at a grain boundary or twin composition plane and gradually tapering off within the host. With the optical microscope it was not possible to
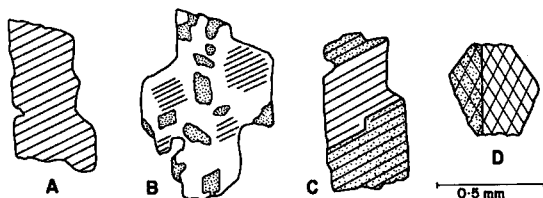

FIG. 2. Sketches illustrating the styles of intergrowth between coexisting calcic and Fe–Mg amphiboles from the Wongwibinda complex. (A) Fine exsolution lamellae of calcic amphibole parallel to ($\bar{1}$01) in cummingtonite. (B) Patches (stippled) and fine exsolution lamellae of calcic amphibole in cummingtonite. Note depletion of exsolution lamellae around the patches. (C) Coarse intergrowth between calcic amphibole (stippled) and cummingtonite, comprising broad bands parallel to ($\bar{1}$01). Both amphiboles contain ($\bar{1}$01) lamellae of the other. (D) Coarse intergrowth between calcic amphibole (stippled) and cummingtonite, with the interface parallel to (100). (The fine ruled lines represent (110) cleavage traces). Sections A–C are parallel to (010); section D is perpendicular to the c axis.

detect growth ledges (cf., Gittos et al. 1974). Measurements of the width and spacing of lamellae show that they may comprise up to about 15 vol. % of a grain, with no obvious relationship between variations in lamellae abundance and the identity of the host phase.

(ii) *Patchy intergrowths.* Both amphiboles may enclose irregular patches of the other. These patches are variable in their size, shape and distribution within the host. A few show roughly planar boundaries parallel to ($\bar{1}$01) or (100).

(iii) *Coarse intergrowths.* The coexisting amphiboles may be coarsely intergrown in composite 'twin-like' crystals comprising two to five broad bands, each about 0.05 to 0.25 mm wide. The interfaces between adjacent bands are more or less planar, occasionally stepped planar, and mostly parallel to (101), less commonly parallel to (100), and rarely parallel to (010). Interfaces parallel to (100) commonly coincide with a simple twin composition plane. The coarse intergrowths are developed commonly between hornblende and cummingtonite, but very rarely between actinolite and cummingtonite.

In all varieties of intergrowths the boundaries between phases are optically and chemically sharp. The two intergrown phases extinguish simultaneously and, at first sight, cleavage traces seem continuous across the interfaces. However, detailed examination of the coarse intergrowths suggests that (110) cleavage traces and (100) lamellae may be deflected by up to 3° across interfaces parallel to ($\bar{1}$01), consistent with the observations of Jaffe et al. (1968). Nevertheless, the intergrown phases evidently share an approximately continuous lattice and may be regarded as essentially coherent.

The different types of intergrowths are believed to have formed variously by simultaneous primary metamorphic growth of the two amphiboles, by exsolution of one phase from the other during cooling, and perhaps by subsequent intragranular reorganization of the exsolved phase.

Fine regular lamellae oriented parallel to ($\bar{1}$01) and/or (100) in amphiboles are widely interpreted as the result of exsolution during cooling (e.g., Jaffe et al. 1968, Ross et al. 1968, 1969; Robinson et al. 1969, Papike et al. 1973, Gittos et al. 1974, Immega & Klein 1976, and others); there is no evidence to suggest that this interpretation is not applicable to the fine lamellar amphibole intergrowths described above. It is not possible to deduce the exsolution mechanism(s) from the available evidence. The tapered lamellae may have nucleated hete-

rogeneously at grain boundaries and twin composition planes, but tapered lamellae are relatively rare and therefore should not be used as a basis for general inferences; homogeneous nucleation of the exsolved phases cannot be ruled out.

The irregular patches are probably also exsolution products because (i) exsolution lamellae are usually depleted or absent in the host in the vicinity of the patches, and (ii) the patches themselves normally lack exsolution lamellae. The ratio of inclusions (fine lamellae + patches) to the host phase seems to vary widely between individual grains even within a single thin section, which is perhaps inconsistent with an origin for both the lamellae and patches by unmixing of a homogeneous precursor. However, this variation is inconclusive as evidence against an exsolution origin because the patches are irregularly distributed within their hosts; therefore, most sections of individual grains probably give a misleading impression of the actual host-to-inclusion ratio. It is not certain whether the patches are the direct product of exsolution or the result of intragranular reorganization of exsolved lamellae.

The origin of the coarse intergrowths is problematical. Ross et al. (1969) have interpreted somewhat similar composite amphibole crystals as the result of intragranular reorganization of fine lamellar exsolution intergrowths. The present intergrowth textures provide some weak support for this interpretation because the outlines of a few of the larger patches (possibly reorganized exsolution lamellae) suggest that they may represent an intermediate stage in the development of coarse intergrowths. The relative proportions of the two amphiboles in the coarse intergrowths seem to vary widely, but this is not conclusive evidence against an exsolution + reorganization origin because random sections through such coarse intergrowths do not permit reliable estimations of the relative abundances of the component phases. However, an exsolution + reorganization origin for the coarse intergrowths seems unlikely because both components of these intergrowths commonly contain fine exsolution lamellae of the other, whereas the irregular patches very rarely contain fine lamellae. Ross et al. (1969) interpreted occasional fine lamellae in similar coarse intergrowths as relics of original exsolution lamellae that escaped reorganization, but the lamellae are sufficiently numerous and uniformly developed in the present coarse intergrowths to suggest that unmixing occurred, or at least continued, *after*

TABLE 1. ELECTRON MICROPROBE ANALYSES AND CATION PROPORTIONS FOR COEXISTING CALCIC AND
Fe-Mg AMPHIBOLES FROM THE WONGWIBINDA COMPLEX, N.S.W.

	HORNBLENDES			ACTINOLITES				Fe-Mg AMPHIBOLES						
Sample No.	F3	F68	F33	F25	F40	F40a*	F60	F3	F68	F33	F33a*	F25	F40	F60
Catalogue No.**	43968	43969	43970	43971	43972	43972	43973	43968	43969	43970	43970	43971	43972	43973
SiO$_2$	47.68	47.39	44.02	49.63	52.71	52.09	49.33	52.43	54.99	51.32	50.72	50.33	51.06	49.46
TiO$_2$	0.60	0.85	0.38	0.13	-	-	-	-	-	-	-	-	-	0.08
Al$_2$O$_3$	7.05	10.55	9.30	2.71	0.77	0.89	1.19	0.62	1.39	0.41	1.43	0.61	0.35	0.19
FeO#	16.38	8.92	22.57	23.54	18.07	18.97	26.87	25.75	15.93	29.64	29.62	31.01	23.73	34.72
MnO	0.15	0.16	0.65	1.06	3.53	4.54	2.90	0.61	0.51	2.34	2.24	3.18	8.53	6.80
MgO	12.76	16.62	7.92	8.91	11.81	11.69	5.81	16.09	22.91	12.50	11.74	9.37	11.43	5.66
CaO	10.44	10.52	10.74	10.35	10.52	8.78	10.23	1.09	1.01	0.90	1.74	2.24	1.91	1.23
Na$_2$O	1.16	1.35	1.66	0.54	0.20	0.30	0.37	0.24	-	0.37	0.45	0.24	0.20	0.22
K$_2$O	0.19	0.11	0.31	0.09	-	0.08	0.11	-	-	-	-	-	-	-
Sum	96.41	96.47	97.55	96.96	97.61	97.34	96.81	96.83	96.74	97.48	97.94	96.98	97.21	98.36
Fe$_2$O$_3$##	2.37	1.59	5.46	2.91	0.69	0.49	0.72	-	-	-	-	-	-	-
FeO##	14.25	7.49	17.66	20.92	17.45	18.53	26.22	25.75	15.93	29.64	29.62	31.01	23.73	34.72

CATION PROPORTIONS (23 oxygens)

	HORNBLENDES			ACTINOLITES				Fe-Mg AMPHIBOLES						
Si	7.080	6.798	6.676	7.566	7.861	7.840	7.771	7.862	7.835	7.864	7.755	7.877	7.877	7.892
Al^{iv}	0.920	1.202	1.324	0.434	0.135	0.158	0.221	0.110	0.165	0.074	0.245	0.113	0.064	0.036
Al^{vi}	0.314	0.583	0.339	0.053	-	-	-	-	0.069	-	0.012	-	-	-
Ti	0.067	0.092	0.043	0.015	-	-	-	-	-	-	-	-	-	0.010
Fe^{3+} ##	0.265	0.172	0.623	0.334	0.077	0.056	0.085	-	-	-	-	-	-	-
Fe^{2+} ##	1.770	0.899	2.240	2.667	2.177	2.332	3.454	3.229	1.898	3.799	3.787	4.059	3.062	4.633
Mn	0.019	0.019	0.083	0.137	0.446	0.579	0.387	0.077	0.062	0.304	0.290	0.422	1.115	0.919
Mg	2.824	3.553	1.790	2.024	2.625	2.622	1.364	3.596	4.865	2.855	2.675	2.185	2.628	1.346
Ca	1.661	1.617	1.745	1.691	1.681	1.416	1.727	0.175	0.154	0.148	0.285	0.376	0.316	0.210
Na	0.334	0.376	0.488	0.160	0.058	0.088	0.113	0.070	-	0.110	0.133	0.073	0.060	0.068
K	0.036	0.020	0.060	0.018	-	0.015	0.022	-	-	-	-	-	-	-
Si+Al^{iv}	8.000	8.000	8.000	7.996	7.996	7.998	7.992	7.972	8.000	7.938	8.000	7.990	7.941	7.928
Al^{vi}+Ti+Fe+Mn+Mg	5.259	5.318	5.120	5.230	5.325	5.589	5.291	7.147	7.048	7.215	7.183	7.114	7.180	7.186
Ca+Na+K	2.031	2.013	2.293	1.869	1.739	1.519	1.862							
Mg/(Mg+Fe^{2+})	0.615	0.798	0.444	0.431	0.547	0.529	0.283	0.527	0.719	0.429	0.414	0.350	0.462	0.225
Mn/(Mg+Fe^{2+}+Mn)	0.004	0.004	0.020	0.028	0.085	0.105	0.074	0.011	0.009	0.044	0.043	0.063	0.164	0.133
Ca/(Mg+Fe^{2+}+Ca)	0.266	0.266	0.302	0.265	0.259	0.222	0.264	0.025	0.022	0.022	0.042	0.057	0.053	0.034

F3:   Amphibolite. Andesine + hornblende + cummingtonite (+ ilmenite)
F68: Amphibolite. Bytownite + hornblende + cummingtonite (+ ilmenite + K-feldspar + biotite + quartz)
F33: Quartzite.   Quartz + garnet + hornblende + cummingtonite (+ ilmenite + magnetite ± biotite)
F25: Quartzite.   Quartz + garnet + actinolite + cummingtonite (+ ilmenite)
F40: Quartzite.   Quartz + garnet + actinolite + cummingtonite (+ magnetite ± apatite)
F60: Quartzite.   Quartz + garnet + actinolite + grunerite + ferrosalite
*   Discrete grains devoid of visible exsolution lamellae
**   Refers to the collection of the Geology Department, University of New England
#   Total Fe as FeO
Ferrous and ferric iron calculated; see text for explanation. The Fe$_2$O$_3$ contents of the
      Fe-Mg amphiboles are assumed to be negligible.

the development of the coarse intergrowths. Therefore, it is suggested that the coarse intergrowths may be the product of simultaneous primary homoaxial growth of the calcic and Fe–Mg amphiboles during prograde metamorphism. The ($\bar{1}01$), (100) and (010) lattice planes apparently provided coherent low-energy boundaries between the two phases.

AMPHIBOLE CHEMICAL ANALYSES

Six pairs of coexisting calcic and Fe–Mg amphiboles, representing a fairly wide range in Mg/Fe ratios and Mn contents, have been analyzed by electron microprobe. They comprise three hornblende–cummingtonite and three actinolite–cummingtonite (or grunerite) pairs. The investigation covered all types of intergrowth except exsolution lamellae narrower than about 3μ. The analyses and cation proportions (based on 23 oxygens) are presented in Table 1, where each analysis is the mean of 4 to 8 fairly uniform microprobe determinations. The Fe$_2$O$_3$ contents of the calcic amphiboles were calculated, largely by the method

of Papike *et al.* (1974). This method normally provides upper and lower limits for the Fe_2O_3 content; Papike (pers. comm.) recommends using the midpoint between these limits, a procedure that was followed for actinolite F25 and green hornblende F33. The calculation yields unique solutions for actinolites F40, F40a and F60. For the brown hornblendes F3 and F68 the calculated midpoint Fe_2O_3 values (4.72% and 4.96% respectively) are inconsistent with other data. The Fe_2O_3 contents shown in Table 1 for these two hornblendes were calculated from the host-rock Fe_2O_3 contents and modal analyses. This procedure yields Fe_2O_3 values well within the limits indicated by the calculation method of Papike *et al.*, and consistent with those obtained by wet-chemical analysis of three similar hornblendes separated from one-amphibole Wongwibinda amphibolites. The Fe_2O_3 contents of the Fe–Mg amphiboles were assumed to be negligible.

The amphiboles were generally found to˜be chemically uniform within domains of uniform host-rock chemistry. Thus in the massive amphibolites, the amphiboles show relatively little chemical variation at least throughout the area of a thin section, whereas in the banded quartzites they are uniform only within individual bands commonly less than 5 mm wide. This uniformity in amphibole compositions is usually maintained within these specified domains despite variations in the textural occurrence of the amphiboles. This suggests that the amphibole pairs have generally approached chemical equilibrium closely.

However, two significant instances of intrasample variations in amphibole compositions have been detected. In sample F33 two distinct cummingtonite compositions were found; cummingtonite intergrown with hornblende shows lower Al and Ca contents than that occurring as discrete grains lacking visible exsolution lamellae (analyses F33 and F33a respectively, Table 1). Similarly, in sample F40 actinolite intergrown with cummingtonite has a higher Ca content than that forming discrete grains (analyses F40 and F40a, Table 1). In both these instances it is assumed that the compositions exhibited by the discrete grains (which may of course contain submicroscopic exsolution lamellae) represent or approach the original compositions of the amphiboles before unmixing, and that these compositions therefore did not equilibrate with the compositions of the unmixed phases with which they coexist. For the purposes of element distribution studies the presumed disequilibrium compositions (analyses F33a and F40a) have been disregarded.

TABLE 2. DISTRIBUTION COEFFICIENTS FOR COEXISTING CALCIC AND Fe-Mg AMPHIBOLES FROM THE WONGWIBINDA COMPLEX, N.S.W.

	$K_{D.Mg}$	$K_{D.Mn}$	$K_{D.Al}^{iv}$
Hornblende-cummingtonite pairs			
F3	1.43	0.40	9.3
F68	1.54	0.48	8.4
F33	1.06	0.45	21.1
Actinolite-cummingtonite pairs			
F25	1.41	0.43	4.0
F40	1.41	0.47	2.1
F60	1.36	0.52	6.2

$K_{D.Mg} = [X/(1-X)]^{Ca-am} \times [(1-X)/X]^{Fe-Mg-am}$, where

$X = Mg/(Mg+Fe^{2+})$.

Similarly, $K_{D.Mn}$ is based on $X = Mn/(Mg+Fe^{2+}+Mn)$,

and $K_{D.Al}^{iv}$ on $X = Al^{iv}/(Al^{iv}+Si)$.

ELEMENT DISTRIBUTIONS

Mg–Fe²⁺ distribution

In all six amphibole pairs the $Mg/(Mg+Fe^{2+})$ ratio is higher in the calcic amphibole than in the coexisting cummingtonite or grunerite. The Mg distribution coefficients (Table 2) for five of these pairs are fairly uniform, ranging from 1.36 to 1.54, whereas sample F33 gives a significantly lower value of 1.06. With the exception of F33, the $K_{D.Mg}$ values show a positive correlation with the $Mg/(Mg+Fe^{2+})$ ratios in both amphiboles (Fig. 3). A similar trend was found by Mueller (1960, 1961)
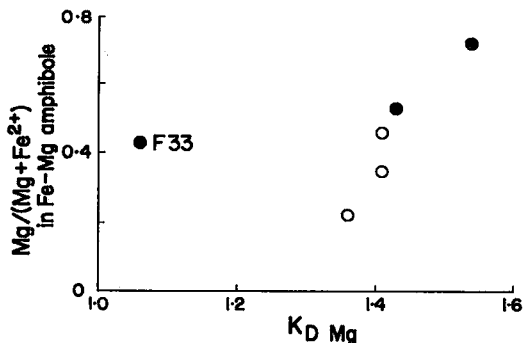

FIG. 3. Relation between the distribution of Mg between coexisting calcic and Fe–Mg amphiboles and the $Mg/(Mg+Fe^{2+})$ ratio in the Fe–Mg amphiboles. $K_{D.Mg}$ is similarly related to this ratio in the calcic amphiboles. Solid circles refer to hornblende–cummingtonite pairs; open circles refer to actinolite–cummingtonite pairs.

in the data on actinolite–cummingtonite pairs from the metamorphosed iron-formations of Québec. He attributed this feature to nonideal mixing in cummingtonite (cf., Mueller 1962).

Variations in $K_{D.Mg}$ values for coexisting calcic and Fe–Mg amphiboles have been attributed by several authors to selective substitution of Al (and perhaps Ti and Fe^{3+}) for Mg in the calcic amphibole (e.g., Kisch & Warnaars 1969, Stout 1972, Bostock 1977), but there are no clear correlations in the present data to support this hypothesis. The cause of the relatively low $K_{D.Mg}$ value in F33 is not obvious. It may be related to the high Al^{vi} + Ti + Fe^{3+} content of the hornblende, or, because of the possible influence of Al–Si substitutions on $Mg–Fe^{2+}$ substitutions (Ramberg 1952), to the anomalously high $K_{D.Al^{iv}}$ value for this pair (Table 2). Less probably, it may simply be the result of substantial underestimation of Fe_2O_3 in the hornblende.

Mn distribution

The Mn distribution coefficients are fairly uniform, ranging from 0.40 to 0.52 (Table 2). The distribution clearly illustrates the preference of Mn for the Fe–Mg amphibole structure. Bancroft et al. (1967) and Papike et al. (1969) have shown that Mn in cummingtonite is preferentially accommodated in the M_4 sites. In the calcic amphiboles the M_4 sites are largely occupied by Ca and Na, and Mn is forced into the less favorable M_1, M_2 and M_3 positions.

Conclusions

The reasonable uniformity in the $Mg–Fe^{2+}$ and Mn distributions supports the conclusion that a close approach to chemical equilibrium between the coexisting amphiboles has been achieved within the relatively small domains considered. It also seems that $Mg–Fe^{2+}$ distributions should not be used as indicators of crystallization temperatures without allowing for the influence of compositional factors on the distribution coefficients.

THE MISCIBILITY GAP BETWEEN THE CALCIC AND FE–MG AMPHIBOLE SERIES

The analyzed hornblendes and actinolites coexisting with Fe–Mg amphiboles show relatively low Ca contents (<1.75 cations per 23 oxygens), and high Al^{vi}+Ti+Fe+Mn+Mg contents (>5.23 cations per 23 oxygens, except F33) (Table 1). The large excess of Al^{vi}+Ti+Fe+Mn+Mg cations over the number required to fill the 5.0 available M_1, M_2

and M_3 positions implies substantial occupancy of the M_4 sites by some of these cations (principally Mn, Fe^{2+} and perhaps Mg), i.e., there is significant solid solution of the cummingtonite component in these calcic amphiboles. Nine hornblendes and actinolites from similar, closely associated one-amphibole assemblages from the amphibolites and quartzites of the Wongwibinda complex have been analyzed for comparison. These show higher Ca contents (1.77 – 1.93 cations per 23 oxygens), and lower Al^{vi}+Ti+Fe+Mn+Mg contents (5.00 – 5.24 cations per 23 oxygens). This indicates lower cummingtonite contents in the single calcic amphiboles than in those coexisting with Fe–Mg amphibole.

The Fe–Mg amphiboles coexisting with calcic amphiboles contain 0.15 – 0.38 Ca cations, 0.00 – 0.13 Na cations, and 0.04 – 0.26 Al cations per 23 oxygens (Table 1), suggesting some solid solution of the calcic amphibole component. Four analyzed Fe–Mg amphiboles from similar one-amphibole assemblages from the Wongwibinda complex differ consistently only in their lower Ca contents (<0.06 cations per 23 oxygens).

To illustrate the amount of solid solution between the calcic and Fe–Mg amphibole series the analyzed amphiboles from one- and two-amphibole assemblages from the Wongwibinda complex have been plotted on the amphibole quadrilateral bounded by the end members $Ca_2Mg_5Si_8O_{22}(OH)_2$ (tremolite), $Ca_2Fe_5Si_8O_{22}(OH)_2$ (ferroactinolite), $Mg_7Si_8O_{22}(OH)_2$ (anthophyllite), and $Fe_7Si_8O_{22}(OH)_2$ (grunerite) (Fig. 4). Here the amphibole pairs define a miscibility gap between the calcic and Fe–Mg amphibole series similar to that determined ex-
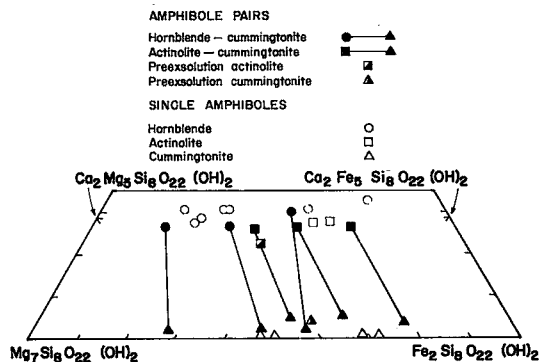

FIG. 4. Amphibole quadrilateral showing the compositions of calcic and Fe–Mg amphibole pairs (joined by tie lines) and single amphiboles from amphibolites and quartzites of the Wongwibinda complex.

perimentally by Cameron (1975) and inferred from natural amphibole pairs from other regions (*e.g.*, Klein 1968). The width of the miscibility gap in Figure 4 provides a measure of the maximum amount of solid solution possible between coexisting calcic and Fe–Mg amphiboles at the P–T conditions of exsolution and equilibration. The following discussion of the amphibole solvus is based essentially on the quadrilateral components (*i.e.* on Ca:Mg:Fe^{2+} proportions), though the possible influence of other cations is considered.

Five of the six calcic amphiboles coexisting with Fe–Mg amphibole contain 8±1.3 mol % cummingtonite in solid solution, irrespective of large variations in Mg/Fe ratio and contents of Al and Mn. Hornblende F33 apparently contains little or no cummingtonite component. The lack of consistent differences between the hornblendes and actinolites from two-amphibole assemblages in their present and exsolved cummingtonite contents suggests that the solubility of cummingtonite in calcic amphibole was either little affected by large variations in the Al content of the host phase (*cf.*, Papike *et al.* 1973, Immega & Klein 1976), or that the influence of the Al content was nullified by other factors, *e.g.*, variations in the Mg/Fe ratio or Mn content.

The Fe–Mg amphiboles coexisting with hornblende contain 8±0.7 mol % calcic amphibole in solid solution, whereas those coexisting with actinolite contain 12–20 mol % calcic amphibole. Therefore, the solubility of actinolite in Fe–Mg amphibole appears to be greater than that of hornblende at the P–T conditions of final equilibration in the Wongwibinda rocks.

The analyzed amphiboles from one-amphibole assemblages plot in the one-amphibole fields away from the projection of the inferred solvus in Figure 4, suggesting that these single amphiboles were undersaturated in the other amphibole component at the P–T conditions of final equilibration. This explains the absence of exsolution textures in the single amphiboles.

Cummingtonite F33a and actinolite F40a, which occur in two-amphibole assemblages as discrete grains devoid of visible exsolution lamellae, plot in the two-amphibole field in Figure 4. This suggests that these two discrete amphiboles may be relics of the original pre-exsolution amphiboles.

Cameron (1975) has studied experimentally the actinolite-cummingtonite solvus for compositions with Mg/Fe = 1 at P(H$_2$O) = 2 kbar and f(O$_2$) defined by the FMQ buffer. He suggested that the compositions of actinolites

with Mg/Fe $\sim$ 1 that coexist with cummingtonites can be used to estimate or put lower limits on metamorphic temperatures, provided the actinolite limb of the solvus is not significantly affected by small variations in pressure, Mg/Fe ratio and the content of other cations (*e.g.*, Na, Mn, Al, Fe^{3+}).

The cummingtonite content of the analyzed Wongwibinda actinolites with intermediate Mg/Fe ratios and intergrown with cummingtonite is roughly 8 mol %, suggesting, by comparison with Cameron's data (1975, Fig. 6), a temperature of exsolution and final equilibration of about 550°C. The higher cummingtonite content (22 mol %) of actinolite grains lacking visible exsolution lamellae (and hence interpreted as relics of the original actinolite) in sample F40 suggests that a temperature around 650°C was attained during metamorphism. Calculation of the original actinolite composition from the relative amounts of actinolite host and cummingtonite exsolution lamellae indicates an original cummingtonite content of about 15-20 mol %, and hence, a temperature of 600–650°C. This calculation is based on the observed host-to-lamellae ratio between 85:15 and 90:10 in grains showing little or no evidence of post-exsolution reorganization, and on the assumption that lamellae too fine for microprobe analysis are similar in composition to the analyzed lamellae. Similarly, calculation of the original composition of the cummingtonites containing actinolite exsolution lamellae (with a host-to-lamellae ratio of 85:15 to 90:10) suggests an original actinolite content of about 27–30 mol %.

Although the temperatures indicated by the actinolite compositions are not unreasonable, such extensive original solid solution between coexisting actinolites and cummingtonites (with intermediate Mg/Fe ratios) in pyroxene-free assemblages is inconsistent with the phase relations determined by Cameron (1975) (see Fig. 5). This discrepancy is presumably due to differences between the experimental system studied by Cameron and the natural systems provided by the Wongwibinda amphibolites and quartzites. The most obvious differences of likely significance are (i) components such as Al, Na and Mn, present in the natural samples but absent in the experimental system, and perhaps (ii) differences in pressure.

Papike *et al.* (1973) and Immega & Klein (1976) suggested that the solubility of cummingtonite in calcic amphibole *decreases* with increasing Al content in the latter phase. Although the present study has not confirmed this conclusion, the available evidence suggests
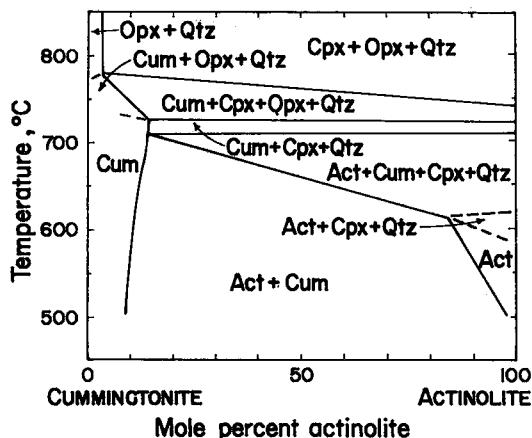
FIG. 5. Experimental phase diagram for the pseudo-binary join $Mg_{3.5}Fe_{3.5}Si_8O_{22}(OH)_2 - Ca_2Mg_{2.5}Fe_{2.5}Si_8O_{22}(OH)_2$ + excess H_2O at P(fluid) = 2 kbar and $f(O_2)$ defined by the FMQ buffer (after Cameron 1975).

that components such as Al, Na and Mn are not likely the cause of the observed *increased* solid solution (relative to Cameron's results) between the coexisting amphiboles.

Hence, the relatively narrow pre-exsolution miscibility gap inferred from the analytical data on the Wongwibinda amphibole pairs may be due to metamorphism at $P(H_2O)$ higher than that employed by Cameron (*i.e.*, > 2 kbar). Papike *et al.* (1973) and Cameron (1975) reached a similar conclusion regarding the large amounts (up to 50 vol. %) of exsolved cummingtonite found in calcic amphiboles in metamorphosed iron-formations of Montana. Their conclusion is consistent with the P–T conditions of metamorphism inferred for the Montana iron-formations from associated pelitic assemblages, namely 650–750°C and 4–6 kbar $P(H_2O)$ in the Tobacco Root Mountains area, and slightly lower temperature or higher pressure in the Carter Creek area of the Ruby Mountains (Immega & Klein 1976).

However, the precise explanation for this proposed influence of increased $P(H_2O)$ on the miscibility gap between the calcic and Fe–Mg amphibole series is not perfectly clear. Cameron (1975) assumed that variations in pressure have no effect on the solvus itself. He suggested that increased $P(H_2O)$ should raise the upper boundary of the two-amphibole field in Figure 5 to higher temperatures, thereby exposing more of the solvus and allowing increased solid solution of cummingtonite in calcic amphibole.

This explanation adequately accounts for the estimated original compositions and paragenesis

of the Wongwibinda actinolites. If the upper boundary of Cameron's two-amphibole, pyroxene-free field is raised by only 30°C, projection of the actinolite limb of the solvus to higher temperatures suggests that actinolite (Mg/Fe ~ 1) with up to 20 mol % cummingtonite in solid solution would be stable in pyroxene-free assemblages (as in samples F25 and F40) at about 650°C. An increase of 30°C in the upper boundary of the two-amphibole, pyroxene-free field requires an increase in $P(H_2O)$ of 1½–3 kbar above that employed by Cameron (*i.e.*, $P(H_2O)$ > 3½ kbar) assuming, by analogy with the experimental data on amphibole stability summarized by Ernst (1968), a $P(H_2O)$–T gradient of 1 kbar/10–20°C for the actinolite breakdown curve above 2 kbar $P(H_2O)$. Thus, the estimated original content of up to 20 mol % cummingtonite in the Wongwibinda actinolites in pyroxene-free assemblages is consistent with peak metamorphism at about 650°C and $P(H_2O)$ > 3½ kbar.

However, the relatively high original actinolite contents (27–30 mol %) of the cummingtonites coexisting with actinolite are not so easily explained by simply raising the upper boundary of the two-amphibole field within geologically reasonable limits of temperature and water vapor pressure, unless the slope of the cummingtonite limb of the solvus on Cameron's T–composition diagram starts to decrease markedly at temperatures not much above 700°C (Fig. 5). Furthermore, even if the solubility of actinolite in cummingtonite does increase more rapidly with increasing temperature above 700°C, the present and original actinolite contents of the Wongwibinda cummingtonites are inconsistently high compared with the cummingtonite contents of the coexisting actinolites, if the amphibole solvus determined by Cameron (1975) is applicable to the Wongwibinda rocks. This suggests that the solvus itself may be affected by increased $P(H_2O)$, although this proposal is inconsistent with the minimal influence of pressure on the analogous pyroxene solvus at temperatures up to 900°C (Mori & Green 1975). However, the possibility that the solvus may be affected by variations in pressure (or, for that matter, by variations in composition) casts doubt on the P–T conditions of metamorphism inferred above from the actinolite compositions; an independent assessment of these conditions is necessary.

P–T CONDITIONS OF METAMORPHISM

Pelitic schists associated with the two-am-

phibole-bearing rocks of the Wongwibinda complex locally contain garnet, cordierite and sillimanite which appear, on textural evidence, to be related by the divariant reaction: cordierite⇌ garnet + sillimanite + quartz. However the garnet–cordierite geothermometer-geobarometer of Currie (1971), Hensen & Green (1973) and Thompson (1976) has failed to satisfactorily establish the P–T conditions of metamorphism, probably because of the high Mn contents of the garnets (Weisbrod 1973). Thus, for a pelitic schist sample with Mg/(Mg + Fe) = 0.741 in cordierite and 0.168 in garnet containing 10–13% MnO, the temperature indicated by Currie's calibration (940°C at 6.6 kbar) is unreasonably high for amphibolite-facies rocks, whereas Hensen's & Green's and Thompson's calibrations suggest P–T conditions in the kyanite field despite the widespread occurrence of sillimanite as the stable Al_2SiO_5 polymorph.

However, the maximum possible pressure can be estimated from the experimental data of

Currie (1971) and Hensen & Green (1973), or from the garnet–cordierite phase relations calculated by Thompson (1976) and Holdaway & Lee (1977). If a temperature of 600–800°C is assumed, the absence of garnet from Mn-poor pelitic schists containing cordierite with Mg/(Mg + Fe) ratios around 0.6 suggests a maximum pressure of 6 kbar according to Currie's data (curve 1, Fig. 6), or 8 kbar according to Hensen's & Green's data. The phase relations calculated by Thompson and by Holdaway & Lee tend to support the maximum pressure estimate derived from Currie's data. The suggestion that pressure did not exceed 6 kbar is not inconsistent with the occurrence of garnet in relatively Mn-rich pelitic schists because Mn substitution stabilizes Fe–Mg garnets at pressures significantly lower than those determined by Currie (1971) and Hensen & Green (1971, 1972) for Mn-free systems (Weisbrod 1973).

The minimum possible pressure of metamorphism may be estimated from the development of sillimanite (rather than andalusite) from the breakdown of muscovite + quartz with increasing metamorphic grade in the pelitic schists of the Wongwibinda complex. This suggests a pressure not less than 2 kbar (Fig. 6) according to Holdaway's (1971) determination of the andalusite–sillimanite inversion curve and to various investigations of the muscovite + quartz breakdown (e.g., Evans 1965, Althaus et al. 1970, Day 1973, Chatterjee & Johannes 1974). Higher minimum pressures may be inferred from other determinations of the andalusite-sillimanite phase relations; e.g., the results of Althaus (1967) and of Richardson et al. (1969) suggest minimum pressures of 2½–3 kbar and about 4 kbar, respectively. Thus, mineral assemblages in the pelitic schists of the Wongwibinda complex suggest a metamorphic pressure in the range 2–6 kbar.

The usual absence of muscovite and the presence of sillimanite + orthoclase in pelitic schists associated with the two-amphibole-bearing rocks allows a lower limit to be placed on the temperature of metamorphism. This lower limit is defined by the breakdown of muscovite + quartz, which occurs at about 620°C at 2 kbar, increasing to about 720°C at 6 kbar, where $P(H_2O) = P$ (total) (e.g., Althaus et al. 1970) (see Fig. 6). If $P(H_2O) < P$(total), the muscovite + quartz breakdown curve is displaced towards lower temperatures, e.g., by about 50°C if $P(H_2O) = 0.5 P$ (total) (Kerrick 1972), and the lower-temperature limit for metamorphism of the two-amphibole-bearing rocks is reduced accordingly.
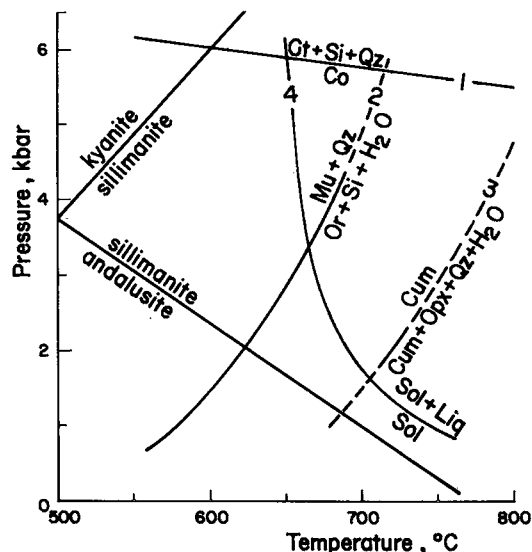
FIG. 6. Experimental phase relations relevant to metamorphism of the two-amphibole-bearing amphibolites and quartzites of the Wongwibinda complex. Al_2SiO_5 equilibria after Holdaway (1971). (1) cordierite ⇌ garnet + sillimanite + quartz, where Mg/(Mg + Fe) = 0.6 (Currie 1971). (2) muscovite + quartz ⇌ K-feldspar + Al_2SiO_5 + H_2O (Althaus et al. 1970). (3) Fe–Mg amphibole ⇌ Fe–Mg amphibole + orthopyroxene + quartz + H_2O, where Mg/(Mg + Fe) = 0.5 and $f(O_2)$ is defined by the FMQ buffer (inferred from Popp et al. 1977). (4) minimum melting curve for metagreywackes (Winkler 1976).

The maximum possible temperature of metamorphism may be estimated from the absence of orthopyroxene in cummingtonite-bearing rocks. Orthopyroxene occurs rarely in the quartzites, but is restricted to those bearing grunerite with $Mg/(Mg + Fe) < 0.30$, rather than cummingtonite. At 2 kbar $P(H_2O)$, Fe–Mg amphiboles with intermediate Mg/Fe ratios begin to break down to orthopyroxene + quartz at about 720°C where $P(H_2O) = P$ (total) and $f(O_2)$ is defined by the FMQ buffer (Popp *et al.* 1977). The breakdown temperatures at higher pressures are not known, but a value exceeding 800°C at 6 kbar $P(H_2O)$ is perhaps likely (curve 3, Fig. 6).

The pelitic and psammitic schists associated with the two-amphibole-bearing amphibolites and quartzites locally contain very small granitic segregations, their first appearance, with increasing metamorphic grade, in the Wongwibinda complex. Although these segregations have not been analyzed, they seem to approximate minimum melting compositions, and therefore suggest that the relevant minimum melting temperature may have been reached, but not significantly exceeded, at this locality. If these segregations are in fact the product of incipient melting, their appearance here, slightly on the high-grade side of the sillimanite–orthoclase isograd, permits a more precise estimate of the P–T conditions of metamorphism in the associated two-amphibole-bearing rocks. Comparison (Fig. 6) of the minimum melting curve for metagreywackes similar to the Wongwibinda schists (Winkler 1976, p. 316) with the muscovite + quartz breakdown curve (Althaus *et al.* 1970) suggests a pressure of 2–3½ kbar and a temperature of roughly 650–700°C, where $P(H_2O) = P(total)$.

If $P(H_2O) < P$ (total), displacement of the melting curve to higher temperatures, and of the muscovite + quartz breakdown curve to lower temperatures means that a higher total pressure may be inferred. However there is no reason to suppose that $P(H_2O)$ was significantly less than P (total); therefore, metamophism of the two-amphibole-bearing rocks and related schists probably occurred at about 2–4 kbar and 650–700°C.

CONCLUSIONS

P–T conditions of metamorphism (650°C and $P(H_2O) > 3½$ kbar), inferred from a comparison of the original composition of actinolites coexisting with cummingtonite with Cameron's (1975) experimental data, are broadly consistent with those indicated by mineral assemblages and evidence of incipient melting in pelitic and psammitic schists (650–700°C and $P(H_2O) = 2–4$ kbar). However, the present and original compositions of the coexisting cummingtonites seem anomalous, suggesting that the effects of variables such as $P(H_2O)$, Mg/Fe ratio and contents of other cations (*e.g.*, Al, Na, Mn) on the miscibility gap between calcic and Fe–Mg amphiboles are not yet well understood. Further work on synthetic and natural systems is necessary before the compositions of coexisting amphiboles can be used as reliable indicators of P–T conditions of crystallization.

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