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COMPLEX EXSOLUTION IN GLAUCOPHANE FROM TILLOTSON PEAK, NORTH-CENTRAL VERMONT

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ABSTRACT

Complex exsolution microstructures in zoned glaucophane from blueschists at Tillotson Peak, north-central Vermont, have been studied using transmission and analytical electron microscopy (TEM, AEM). In all cases, the exsolution lamellae are sub-microscopic, ranging from 5 to 100 nm in thickness, and are coherently intergrown with the host. Abundant cummingtonite exsolution lamellae developed in Ca–Fe–Mg-rich zones in glaucophane, nearly parallel to (28 $\bar{1}$) and (28 $\bar{1}$) planes of the amphibole structure (space group $C2/m$). The observed orientations differ from more common “100” and “ $\bar{1}01$ ” exsolution lamellae in clin amphiboles and are optimal phase boundaries. AEM analyses indicate that Ca is preferentially partitioned into the cummingtonite lamellae, producing metastable, high-Ca cummingtonite compositions that lie well within the cummingtonite–actinolite miscibility gap. In many cases, narrow, periodic lamellae of actinolite have subsequently exsolved from the metastable cummingtonite lamellae along (100). Calculations of dimensional misfit and elastic strain energy using EPLAG indicate that the formation of “100” actinolite lamellae within the cummingtonite lamellae results in a highly non-optimal phase boundary between glaucophane and actinolite. Evidence for this is seen by high strain contrast in TEM images at the interfaces between actinolite and glaucophane. The periodic nature of this secondary exsolution microstructure can be explained as the result of the minimization of the total elastic strain energy associated with the glaucophane – cummingtonite – actinolite intergrowth. Evidence has also been found for multiple stages of exsolution involving winchite, cummingtonite, and actinolite, leading to complex, metastable, five-amphibole assemblages.

Keywords: glaucophane, cummingtonite, actinolite, blueschist, exsolution, transmission electron microscopy, analytical electron microscopy, strain energy, microstructure.

SOMMAIRE

Nous avons utilisé la microscopie électronique par transmission et la microscopie analytique pour étudier les microstructures complexes dues à l'exsolution dans des cristaux zonés de glaucophane provenant de schistes bleus de Tillotson Peak, dans la partie centre-nord du Vermont. Dans tous les cas, il s'agit de lamelles d'exsolution submicroscopiques, entre 5 et 100 nm en épaisseur, qui sont cohérentes avec l'amphibole hôte. Il y a une abondance de lamelles de cummingtonite dans les zones riches en Ca, Fe et Mg de la glaucophane, presque parallèles aux plans (28 $\bar{1}$) et (28 $\bar{1}$) dans la structure de l'amphibole (groupe spatial $C2/m$). Les orientations observées diffèrent des plans “100” et “ $\bar{1}01$ ”, qui semblent plus répandus, et seraient dues à une optimisation énergétique à l'interface. Les résultats d'analyses chimiques en microscopie montrent que le Ca est

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réparti de préférence dans les lamelles de cummingtonite, menant à des compositions métastablement enrichies en Ca et ainsi situées bien en dedans de la lacune de miscibilité entre cummingtonite et actinote. Dans plusieurs cas, des lamelles étroites et périodiques d'actinote sont apparues suite à une exsolution le long de (100) dans ces lamelles de cummingtonite. Nos calculs de discordance dimensionnelle et de l'énergie due à la déformation élastique, effectués avec le logiciel EPLAG, indiquent que la formation de lamelles "100" d'actinote dans les lamelles de cummingtonite mène à une interface fortement non optimale entre glaucophane et actinote. C'est ce qui explique le contraste frappant dans les images produites par transmission, dû à la distorsion des réseaux à l'interface entre actinote et glaucophane. La périodicité de cette microstructure d'exsolution secondaire résulterait de la minimisation de l'énergie totale due à ces distorsions dans l'intercroissance de glaucophane, de cummingtonite et d'actinote. Nous documentons aussi la présence de stades multiples d'exsolution impliquant winchite, cummingtonite et actinote, qui ont mené à la formation, dans ces roches, d'assemblages complexes et métastables de cinq amphiboles.

(Traduit par la Rédaction)

Mots-clés: glaucophane, cummingtonite, actinote, schistes bleus, exsolution, microscopie électronique par transmission, microscopie électronique analytique, énergie due à la déformation, microstructure.

INTRODUCTION

Exsolution involving various members of different amphibole series has been the subject of much study over the past 30 years. As a result, miscibility relations among calcic and ferromagnesian amphiboles (including orthoamphiboles) are relatively well understood [see reviews by Ghose (1981) and Robinson *et al.* (1982)]. Although less attention has been paid to the alkali amphiboles with respect to exsolution, exsolution microstructures involving alkali and ferromagnesian amphiboles have been reported by Klein (1966, 1968), Robinson *et al.* (1971), Ghose *et al.* (1974), Shau *et al.* (1993), and Smelik & Veblen (1989, 1991). Exsolution involving alkali and calcic amphiboles has been reported by Smelik & Veblen (1989, 1992).

Klein (1966, 1968) and Robinson *et al.* (1971) discussed mutual exsolution of magnesio-arfvedsonite and manganian cummingtonite from the metamorphosed Wabush Iron Formation in Labrador. The paper by Robinson *et al.* is notable in that it presented the basic theory for a two-dimensional optimal phase boundary between intergrown chain silicates. Ghose *et al.* (1974) and Shau *et al.* (1993) demonstrated fine-scale exsolution structures in Mn-rich alkali amphiboles from the manganese mines at Tirodi, Maharashtra, India. The latter authors presented analytical electron microscopy (AEM) data consistent with exsolution between manganian winchite (a sodic-calcic amphibole) and sodian manganian cummingtonite (nomenclature of Leake 1978). These above-mentioned studies all describe lamellar orientations near (100) and ($\bar{1}01$) planes of the host for the $C2/m$ unit-cell setting. These orientations are consistent with the "exact phase boundary theory" of Robinson *et al.* (1971, 1977) for exsolved clin amphiboles.

The papers by Smelik & Veblen (1989, 1991, 1992) reported the first-observed occurrences of exsolution lamellae in typical glaucophane from blueschist

and eclogite assemblages. These exsolution microstructures consist of fine-scale lamellar precipitates of cummingtonite in two newly documented orientations, nearly parallel to the (28 $\bar{1}$) and (28 $\bar{1}$) planes of the host ($C2/m$ unit-cell setting), and narrow curved lamellae of a Ca-rich amphibole nearly parallel to (100) and (201). All these orientations also are the result of considerations of the optimal phase boundary, as discussed by Smelik & Veblen (1991, 1992).

In this paper, we elaborate further on immiscibility relations among glaucophane, cummingtonite and actinolite, and discuss complex exsolution microstructures that suggest multiple-stage and multiple-phase exsolution processes in Ca-Fe-Mg-rich glaucophane from blueschists near Tillotson Peak, north-central Vermont.

SAMPLE DESCRIPTION AND EXPERIMENTAL TECHNIQUE

The samples of glaucophane used in this study were collected from blueschist assemblages near Tillotson Peak, north-central Vermont. Evidence for high-pressure, low-temperature metamorphism at Tillotson Peak was first described by Laird (1977). Laird & Albee (1981a) presented results of detailed electron-microprobe analyses of the blueschist mineral assemblage, which includes three different amphiboles: glaucophane, barroisite, and actinolite – actinolitic hornblende. In their companion paper (Laird & Albee 1981b), they suggested that the glaucophane-bearing assemblages formed during two periods of growth of metamorphic minerals (O1, O2), during the Taconic Orogeny in the Middle Ordovician [see Laird & Albee (1981a, b) for details of geological history]. These mineral assemblages are considered to be evidence of subduction-zone tectonics that accompanied the closing of the Proto-Atlantic (Iapetus) Ocean.

The present samples were collected from outcrops along the trail to Tillotson Pond, described by Bothner

& Laird (1987, their locality 1, p. 397). These samples of two-amphibole mafic schist contain the mineral assemblage epidote + garnet + glaucophane + actinolite + quartz + chlorite + carbonate + Fe-oxide $\pm$ white mica $\pm$ titanite. In petrographic thin sections, the glaucophane and actinolite show complex intergrowth relationships, including rimming of one amphibole by the other, and optically continuous intergrowths. Many of the glaucophane grains are zoned, with a darker blue core. Samples for transmission and analytical electron microscopy (TEM–AEM) were prepared by ion-milling selected areas of petrographic thin sections. Electron microscopy was performed with a Philips EM420 transmission electron microscope operated at 120 keV and equipped with a SuperTwin (ST) objective lens (spherical aberration coefficient $C_s = 1.2$ mm, chromatic aberration coefficient $C_c = 1.2$ mm). For high-resolution TEM (HRTEM) imaging, the diameter of the objective aperture either matched the point resolution of the microscope (0.30 nm) or was smaller, in order to eliminate irrelevant high-frequency information from the images.

Energy-dispersion X-ray spectra were obtained with an EDAX SiLi detector and processed with a Princeton Gamma-Tech model 4000 analyzer. The calibration and standardization procedures are described by Livi & Veblen (1987).

DISTRIBUTION, MORPHOLOGY, AND ORIENTATION OF EXSOLUTION LAMELLAE

The exsolution lamellae in the glaucophane, like those described by Smelik & Veblen (1991) in glaucophane from nearby eclogites, are submicroscopic, *i.e.*, smaller than the resolution of the petrographic microscope. When examined using TEM, the glaucophane was found to contain abundant exsolution lamellae of another amphibole (Fig. 1A). Furthermore, narrow, periodic lamellae of a third amphibole have exsolved in some of the lamellae (Fig. 1B). As shown in Figure 1, the primary lamellae are narrow, reaching a maximum thickness of about 60–80 nm. The secondary lamellae are smaller, rarely exceeding 7.5 nm in width. Note also in Figure 1B that the

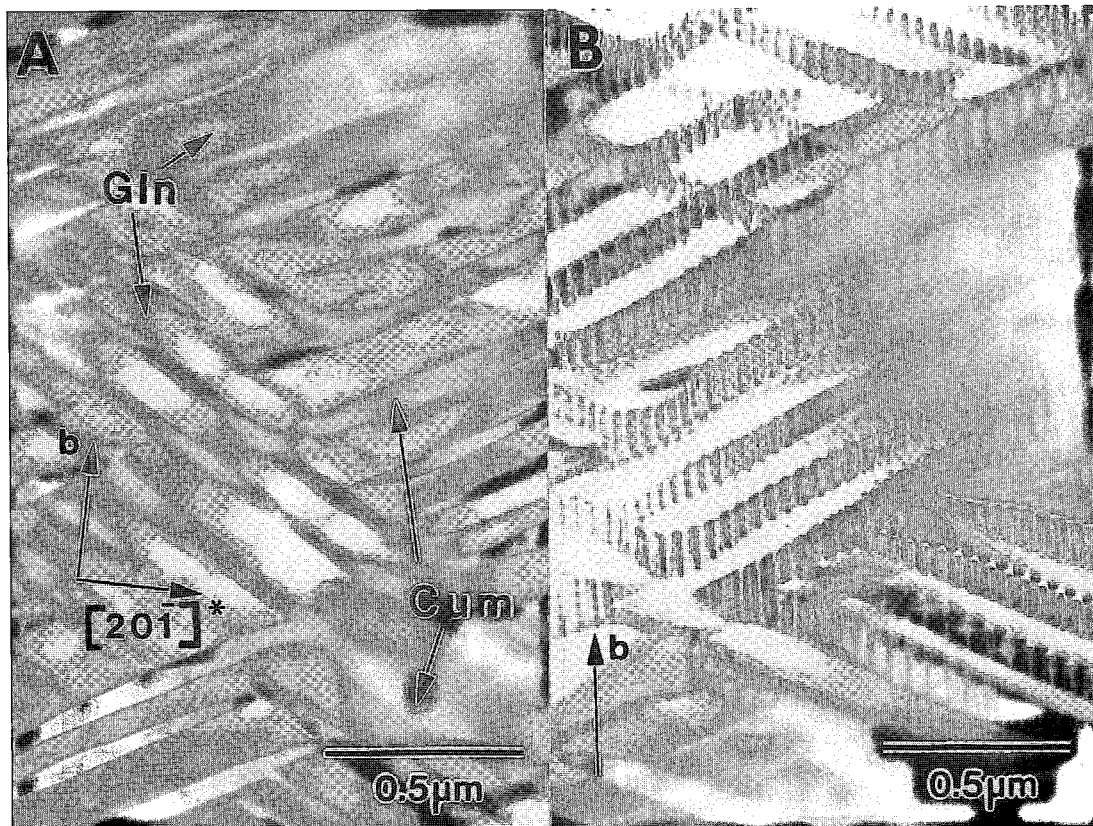


FIG. 1. Bright-field TEM images of exsolved glaucophane. (A) View down [102] zone showing primary lamellae of cummingtonite nearly parallel to (281) and (281) planes of the glaucophane. AEM shows the cummingtonite to be very rich in Ca. (B) A different area showing secondary exsolution of narrow lamellae of actinolite inside the cummingtonite lamellae. The microstructure has a distinct periodicity. Electron beam is near [101].

secondary lamellae have grown in a different orientation and are periodic.

The interfaces between the primary lamellae and host are nearly planar, and HRTEM images indicate that all lamella–host interfaces are coherent (Fig. 2). Selected-area electron diffraction (SAED) analysis combined with conventional (CTEM) imaging techniques indicate that the primary lamellae occur in two symmetrically related orientations, as shown in Figure 1A. These irrational orientations, nearly parallel to $(28\bar{1})$ and (281) planes of the host, have been discussed in detail by Smelik & Veblen (1991), who demonstrated that they represent optimal phase boundaries between the cummingtonite and glaucophane lattices. The compositions and unit-cell parameters derived from AEM and SAED indicate, as expected, that these lamellae are $C2/m$ cummingtonite [using the nomenclature of Leake (1978)]. These cummingtonite lamellae, however, differ significantly in Ca content from cummingtonite lamellae reported by Smelik & Veblen (1991).

The orientation of the interfaces between the secondary lamellae (Fig. 1B) and the glaucophane host is constrained by the orientation of the primary lamellae (“ $28\bar{1}$ ” and “ 281 ”). HRTEM images and SAED patterns, on the other hand, show that the interfaces between the secondary lamellae and the cummingtonite are nearly parallel to (100) (Fig. 2). This orientation is more common for exsolution lamellae in clinoamphiboles and can be calculated by the “exact phase boundary” theory of Robinson *et al.* (1971, 1977).

The highest density of precipitates generally occurs in the core of the glaucophane grains, suggesting that the grains show primary chemical zoning. Optical examination also revealed zoning that may be due to higher Fe^{3+} content in the core (Bancroft & Burns 1969). Evidence for primary chemical zoning in these glaucophane samples, leading to different patterns of exsolution for different parts of a single crystal of glaucophane, will be discussed more fully below.

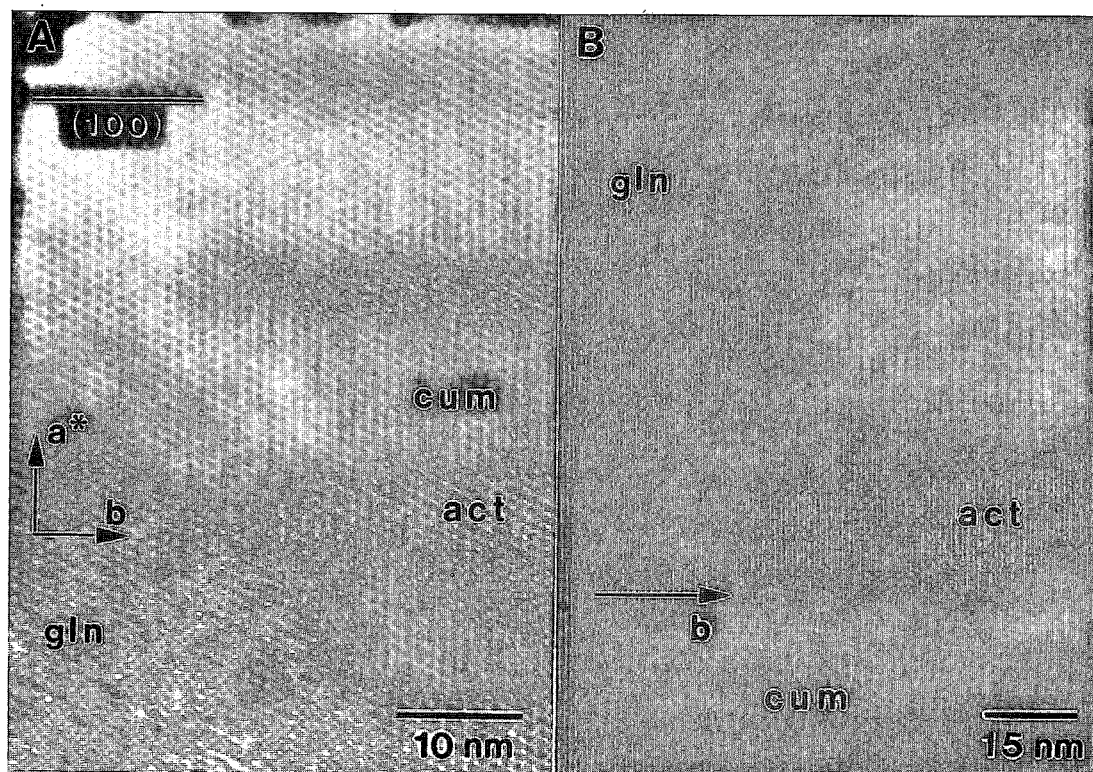


FIG. 2. HRTEM images of interfaces between lamellae. (A) Coherently intergrown glaucophane, cummingtonite, and actinolite viewed down the c axis. The boundary between the exsolved cummingtonite lamella and glaucophane is near $(28\bar{1})$, whereas the interface between the actinolite and cummingtonite is near (100) . (B) A one-dimensional HRTEM image of an exsolved lamella of cummingtonite taken with the beam near $[405]$. There is very little distortion of the (020) lattice fringes across the “ 100 ” actinolite–cummingtonite boundary.

TABLE 1. REPRESENTATIVE RESULTS OF AEM ANALYSES OF LAMELLAE OF HIGH-Ca CUMMINGTONITE

Sample # Spectrum #		VTP1-K TK14B	VTP1-K TK16B	VTP1-K TK20B	VTP1-F TPF14B	VTP1-J IJ17B	VTP1-I TI35B	VTP1-I TI36B	VTP1-I TI74B
tetrahedral	Si	7.79	7.92	8.02	7.87	7.87	7.88	7.92	7.99
	Al	0.21	0.08	0.00	0.13	0.13	0.12	0.08	0.01
	total T-site	8.00	8.00	8.02	8.00	8.00	8.00	8.00	8.00
octahedral M1,M2,M3	Al	0.12	0.10	0.15	0.12	0.16	0.05	0.12	0.11
	Ti	0.01	0.02	0.00	0.00	0.00	0.01	0.00	0.01
	Mg	4.00	3.69	3.68	3.99	3.94	3.83	3.90	3.84
	Fe ²⁺	0.87	1.19	1.17	0.89	0.90	1.11	0.97	1.04
	total M1-M3	5.00	5.00	5.00	5.00	5.00	5.00	4.99	5.00
M4	Ca	0.51	0.58	0.60	0.71	0.48	0.51	0.59	0.51
	Na	0.18	0.27	0.26	0.01	0.30	0.16	0.21	0.12
	Fe ²⁺	1.27	1.11	1.12	1.27	1.22	1.31	1.17	1.35
	Mn	0.03	0.04	0.02	0.01	0.00	0.02	0.03	0.02
	total M4	1.99	2.00	2.00	2.00	2.00	2.00	2.00	2.00
A site	Na	0.22	0.15	0.00	0.01	0.27	0.20	0.14	0.00
	K	0.04	0.06	0.00	0.01	0.00	0.00	0.02	0.00
	total A site	0.26	0.21	0.00	0.02	0.27	0.20	0.16	0.00
Mg/(Mg + Fe ²⁺)		0.652	0.616	0.616	0.649	0.649	0.613	0.645	0.616

Amphibole formula based on normalization to 23 O atoms and assuming all Fe as FeO.

AMPHIBOLE CHEMISTRY

High-Ca cummingtonite

Using a fine probe (10–20 nm), AEM analyses of all the intergrown amphiboles were carried out. Since the lamellae are quite narrow, their X-ray spectra usually contained small contributions from the surrounding host. In some cases, this effect was minimized when the specimen-stage tilt for an optimum analytical orientation coincidentally brought the lamellae into an edge-on orientation with respect to the electron beam. The AEM analyses for the primary (unexsolved) lamellae (Fig. 1A) indicate that the

cummingtonite is significantly enriched in Ca compared to normal cummingtonite and lamellae in glaucophane from nearby eclogites (Smelik & Veblen 1991) (Table 1).

Single-crystal X-ray-diffraction studies (Ghose 1961, Fischer 1966, Finger 1969) and Mössbauer spectroscopic analyses (Bancroft *et al.* 1967a, b, Hafner & Ghose 1971) have indicated that for most ferromagnesian amphiboles in the cummingtonite-grunerite series, Fe²⁺ is strongly ordered at the M4 site, and there is very little Fe³⁺ present. The structural formulae of the cummingtonite lamellae, therefore, have been calculated on a 23-oxygen basis assuming all Fe to be present as Fe²⁺ (Table 1). Idealized site-

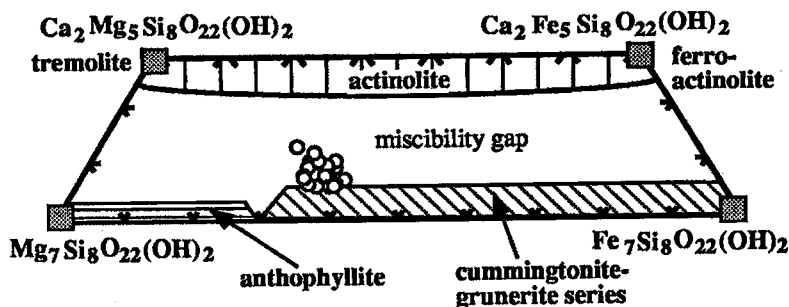


FIG. 3. Amphibole quadrilateral diagram (Robinson *et al.* 1982, p. 45) showing compositions of primary lamellae of cummingtonite. These compositions are rich in the actinolite component and fall within the miscibility gap between the calcic and ferromagnesian amphiboles, suggesting that these compositions are metastable. This excessive Ca content led to the secondary exsolution of narrow lamellae of actinolite.

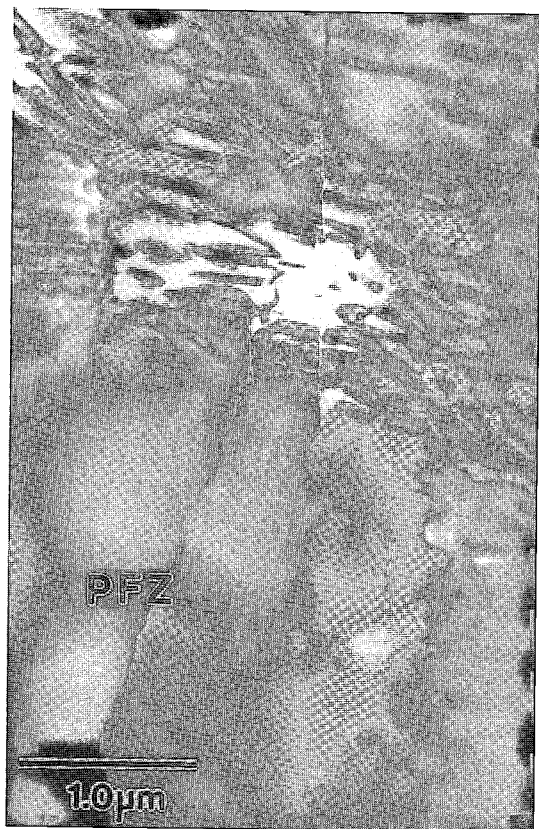


FIG. 4. Low-magnification bright-field TEM image showing evidence of primary chemical zoning in the glaucophane. The areas at the top and right contain many exsolved lamellae of cummingtonite. Next to these areas is a region with no precipitates (precipitate-free zone, PFZ). There is no grain boundary between the exsolved and unexsolved areas.

assignments of cations were made using the methods of Robinson *et al.* (1982). The average $\text{Mg}/(\text{Fe}^{2+} + \text{Mg})$ ratio for the cummingtonite is 0.632. Twenty-eight AEM analyses, including those in Table 1, are plotted on the amphibole quadrilateral (Fig. 3); the Ca contents for these lamellae are seen to be unusually high, ranging from 0.389 to 0.818 atoms per formula unit (pfu), with an average of 0.552 Ca atoms pfu. As far as we know, no cummingtonite with a Ca content this high has been reported in the literature (*cf.* Robinson *et al.* 1982, Table 2, p. 21). From Figure 3, it is evident that these compositions are metastable and lie well within the actinolite – cummingtonite miscibility gap.

AEM analyses of the exsolved lamellae of cummingtonite indicate that the metastable solid-solution has segregated into narrow lamellae of Ca-poor cummingtonite and actinolite, as discussed below.

TABLE 2. REPRESENTATIVE RESULTS OF AEM ANALYSES OF LAMELLAE OF GLAUCOPHANE HOST FROM BETWEEN CUMMINGTONITE LAMELLAE

Sample #		VIP1-I	VIP1-I	VIP1-J	VIP1-J	VIP1-K	VIP1-K	VIP1-F	VIP1-I
Spectrum #		TI13B	TI68B	IJ24B	IJ35B	TK15B	TK16B	TPF12B	TI54B
tetrahedral	Si	7.98	7.94	8.00	7.90	7.94	7.94	7.79	7.90
	Al	0.02	0.06	0.00	0.10	0.06	0.06	0.21	0.10
	total T-site	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
octahedral M1,M2,M3	Al	1.54	1.38	1.55	1.37	1.72	1.41	1.21	1.45
	Ti	0.00	0.00	0.01	0.01	0.00	0.00	0.02	0.01
	Cr	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00
	Mg	2.14	2.32	2.11	2.31	2.14	2.29	2.41	2.29
	Fe ²⁺	1.31	1.30	1.32	1.31	1.13	1.30	1.36	1.25
	total M1-M3	4.99	5.00	5.00	5.00	4.99	5.00	5.01	5.00
M4	Ca	0.14	0.23	0.16	0.15	0.10	0.33	0.26	0.20
	Na	1.64	1.65	1.73	1.66	1.73	1.50	1.45	1.53
	Fe ²⁺	0.22	0.12	0.10	0.19	0.16	0.17	0.28	0.26
	Mn	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.01
	total M4	2.00	2.00	2.00	2.00	1.99	2.00	2.00	2.00
A site	Na	0.09	0.33	0.12	0.34	0.06	0.13	0.40	0.15
	K	0.02	0.00	0.03	0.03	0.01	0.01	0.02	0.02
	total A site	0.11	0.33	0.15	0.37	0.07	0.14	0.42	0.17
Mg/(Mg + Fe ²⁺)		0.584	0.621	0.596	0.606	0.625	0.610	0.594	0.603

Amphibole formula based on normalization to 23 O atoms and assuming all Fe as FeO.

TABLE 3. REPRESENTATIVE RESULTS OF AEM ANALYSES OF GLAUCOPHANE FROM PRECIPITATE-FREE ZONES

Sample # Spectrum #		VTP1-I 211B	VTP1-I 1116B	VTP1-J 1J28B	VTP1-J 1J41B	VTP1-J 1J30B	VTP1-J 1J29B	VTP1-F TF7B	VTP1-E TPE9B
tetrahedral	Si	7.88	7.93	7.97	7.98	7.87	8.00	7.78	7.88
	Al	0.12	0.07	0.03	0.02	0.13	0.00	0.22	0.12
	total T-site	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
octahedral M1,M2,M3	Al	1.64	1.61	1.69	1.60	1.41	1.48	1.47	1.62
	Ti	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	Cr	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00
	Mg	2.10	2.16	2.01	2.17	2.26	2.22	2.28	2.08
	Fe ²⁺	1.26	1.23	1.29	1.22	1.32	1.30	1.25	1.30
	total M1-M3	5.01	5.00	4.99	5.00	5.01	5.00	5.00	5.00
M4	Ca	0.26	0.33	0.13	0.13	0.37	0.28	0.30	0.23
	Na	1.68	1.56	1.80	1.73	1.51	1.55	1.41	1.61
	Fe ²⁺	0.06	0.11	0.07	0.14	0.10	0.16	0.28	0.16
	Mn	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00
	total M4	2.00	2.00	2.00	2.00	1.99	2.00	2.00	2.00
A site	Na	0.12	0.00	0.12	0.12	0.18	0.05	0.15	0.09
	K	0.02	0.01	0.01	0.02	0.03	0.01	0.01	0.01
	total A site	0.14	0.01	0.13	0.14	0.21	0.06	0.16	0.10
Mg/(Mg + Fe ²⁺)		0.614	0.616	0.597	0.614	0.614	0.603	0.598	0.588

Amphibole formula based on normalization to 23 O atoms and assuming all Fe as FeO.

Glaucophane

Both optical and TEM examination of the glaucophane shows it to be zoned. The primary chemical zoning led to some areas with abundant exsolution lamellae and other areas that are precipitate-free (Fig. 4). AEM analyses of the glaucophane were obtained from regions between cummingtonite lamellae, as well as from precipitate-free zones. Representative results of the AEM analyses of both types of glaucophane are presented in Tables 2 and 3.

In contrast to cummingtonite, glaucophane generally contains Fe³⁺ (Hawthorne 1981, 1983). Studies of various alkali amphiboles have shown that there is complete miscibility between glaucophane and magnesio-riebeckite, with Fe³⁺ readily substituting for Al in the M2 site (Miyashiro 1957, Borg 1967, Coleman & Papike 1968, Wood 1980). The optically visible darker blue core is also evidence of increased Fe³⁺ content in the glaucophane (Bancroft & Burns 1969). Furthermore, during the exsolution process, we would have expected little or no Fe³⁺ to partition into the cummingtonite structure, so that any Fe³⁺ present will be concentrated in the glaucophane. Using the renormalization schemes of Robinson *et al.* (1982), we made several estimates of Fe³⁺ content for the glaucophane compositions shown in Tables 2 and 3. In most cases, one or more of these techniques of recalculation yielded reasonable (though probably not true) estimates of Fe³⁺. Since ferric iron probably behaves like Al during the exsolution process, its absolute concentration is not significant, and none of the recalculated compositions are presented here.

From Tables 2 and 3, it may be seen that the com-

positions of the glaucophane host are very similar to the compositions of unexsolved glaucophane. The Mg/(Mg + Fe²⁺) ratio for both types of glaucophane is essentially the same, with an average value of 0.605. In general, the unexsolved glaucophane contains slightly more Ca than the host glaucophane. In view of this observation, and the high concentrations of Ca in the primary lamellae of cummingtonite (Table 1), it appears that there is strong partition of Ca into the cummingtonite lamellae during the first episode of precipitation. This resulted in compositions of cummingtonite lamellae that are metastable with respect to the miscibility gap between calcic and ferromagnesian amphiboles (Fig. 3); in many cases, a lower free-energy state was achieved by subsequent exsolution of narrow lamellae of actinolite.

Secondary lamellae

It was common for narrow lamellae of actinolite to exsolve from the lamellae of Ca-rich cummingtonite (Fig. 1B). The unmixing of the high-Ca, metastable cummingtonite takes place *via* one simple substitution, involving only the M4 site: Ca ↔ (Fe²⁺, Mg). The operation of this mechanism of substitution is evident from AEM data obtained from a lamella of partially exsolved cummingtonite (Fig. 5). The compositions in Figure 5 are shown in terms of the raw energy-dispersion (ED) spectra. The lower portion of the lamella is unexsolved and has a Ca content of about 0.63 atoms pfu. The ED spectrum 1, taken from a narrow lamella (in dark contrast) in the exsolved section, shows very little Ca if any, and probably represents the composition of cummingtonite that is much

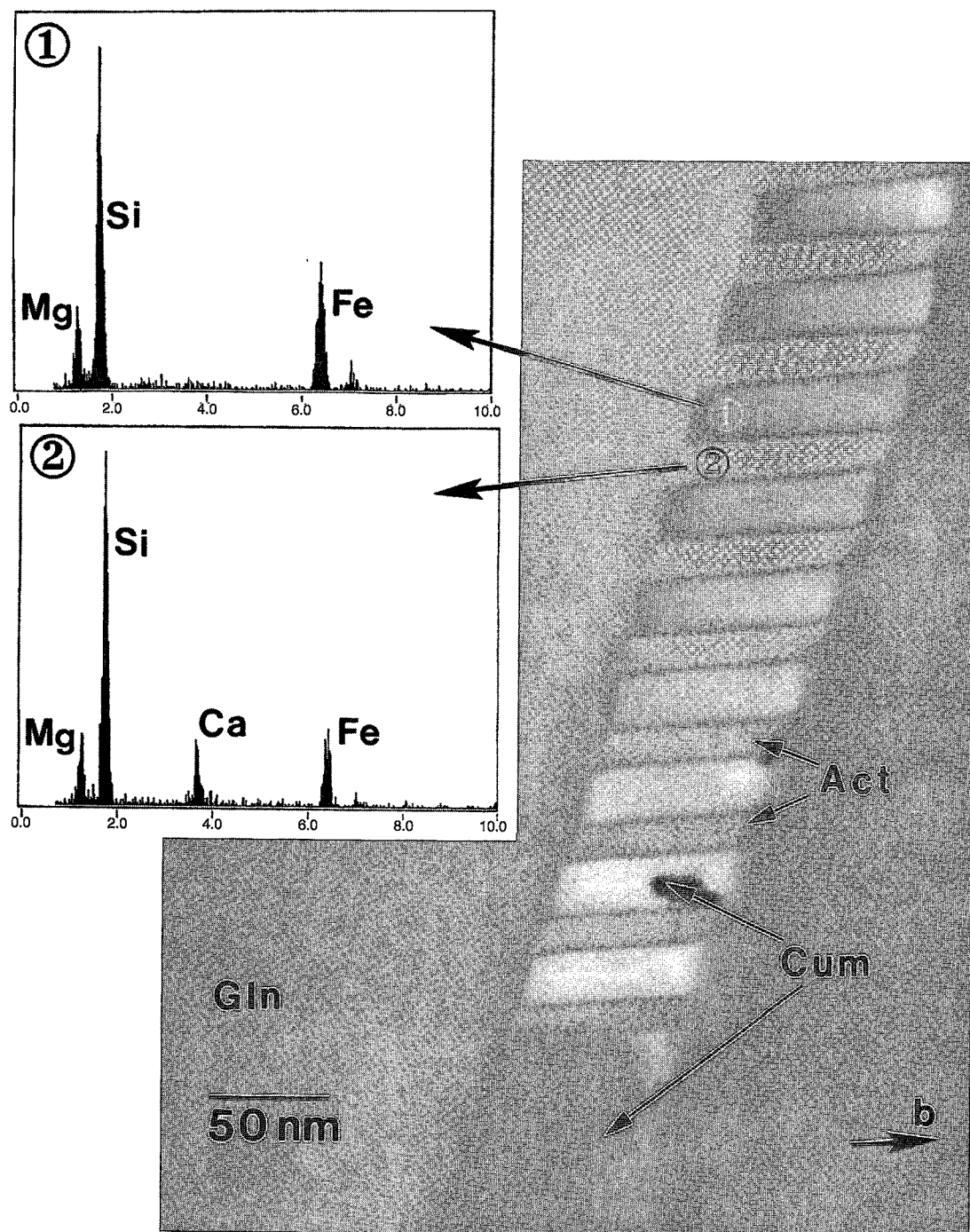


FIG. 5. Bright-field TEM image of a single lamella of partially exsolved cummingtonite. The unexsolved part of the cummingtonite is rich in Ca (~ 0.63 cations pfu). Also shown are two AEM spectra, taken from the exsolved part of the lamella. Spectrum 1 shows only Mg, Fe, and Si and represents a normal composition of cummingtonite. Spectrum 2, obtained from a "100" actinolite lamella, shows a significant increase in Ca, coupled with a slight decrease in Mg and a pronounced decrease in Fe. Area measurements of this lamella indicate that the exsolved portion of the lamella is approximately 40% actinolite and 60% cummingtonite. The electron beam is near [405].

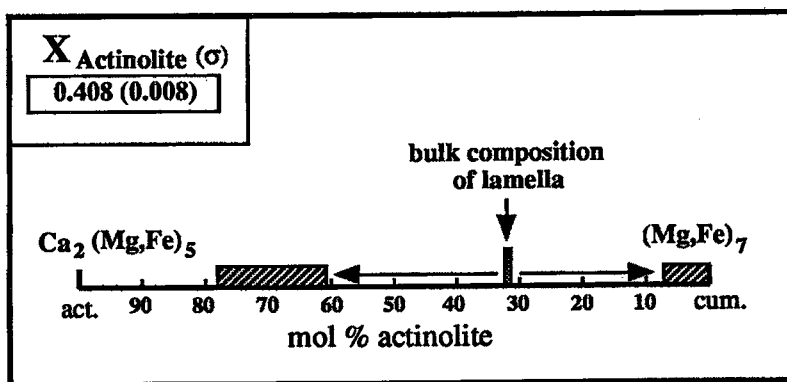


FIG. 6. Chemographic diagram along the actinolite - cummingtonite join showing the range of estimated compositions for actinolite and equilibrium cummingtonite from the exsolved lamella in Figure 5. The bulk composition of the lamella was averaged from five AEM analyses of the unexsolved part of the lamella.

closer to equilibrium. ED spectrum 2 was obtained from the adjacent lamella (in light contrast) and shows a significantly higher level of Ca, coupled with a slight decrease in Mg and a more dramatic decrease in Fe. This is the expected observation, since Fe^{2+} is usually ordered at *M4* (Ghose 1961, Fischer 1966, Bancroft *et al.* 1967a, b, Finger 1969, Hafner & Ghose 1971). Since these narrow "100" lamellae reach a maximum thickness of only about 7.5 nm, and are just beyond the spatial resolution of our AEM system, direct determination of their compositions was not possible. Despite this problem, an estimate of the actual compositions of actinolite and low-Ca cummingtonite was made using the following method.

The following analysis relies on three important assumptions. First, all interfaces between lamellae are assumed to be strictly planar. Although TEM images of the exsolution microstructure taken in different orientations show the detailed geometry of the interfaces to be rather complex, this assumption serves as a useful first approximation. Second, the AEM data for the unexsolved portion of the cummingtonite lamella are considered to represent the homogeneous, pre-exsolution composition for the entire lamella, including the exsolved portion. And third, the measured relative areas of "100" lamellae in the two-dimensional image are assumed to approximate the volume proportions of actinolite and low-Ca cummingtonite for the given exsolved lamella. With these assumptions in mind, the relative proportion of actinolite was estimated by carefully measuring the relative areas for each actinolite-cummingtonite pair in the exsolved section. For the lamella in Figure 5, this procedure resulted in an average fraction of actinolite, X_{act} , of 0.408. Knowing the relative proportions of actinolite and low-Ca cummingtonite and the bulk

composition of the lamella, it was a simple matter to apply the $\text{Ca} \leftrightarrow (\text{Fe}^{2+}, \text{Mg})$ exchange and estimate the compositions of the "100" lamellae. The resultant compositions are, of course, dependent upon how much Ca remained in the cummingtonite structure after unmixing. The ED spectrum (#1) presented in Figure 5 indicates very little or no Ca in the "100" cummingtonite lamella. The experimental study of Cameron (1975), on the actinolite - cummingtonite join [at $\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) = 0.5$], shows that the cummingtonite limb of the actinolite - cummingtonite solvus is very steep at temperatures between 400 and 500°C, with the Ca content of cummingtonite less than 0.20 cations pfu (10 mol % actinolite or Act_{10}). The estimates of Laird & Albee (1981a) for conditions of peak metamorphism in the Tillotson Peak area are $450 \pm 100^\circ\text{C}$ and 9 ± 2 kbar. Exsolution therefore occurred at or below these values.

Given the estimated volume-proportion of actinolite (0.408), the composition of the "100" actinolite lamellae in Figure 5 would be pure $\text{Ca}_2(\text{Fe}^{2+}, \text{Mg})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ only if the bulk composition of the lamella contained 0.816 Ca cations pfu and the cummingtonite contained no Ca. The results of five AEM analyses of the unexsolved section show a range of 0.54 - 0.71 Ca pfu, with an average of 0.63 pfu. Figure 6 shows the ranges of calculated "100" actinolite and cummingtonite compositions from the exsolved portion, assuming a range of cummingtonite compositions from Act_0 to Act_7 [Act_7 obtained by extrapolating the Ca-poor limb of Cameron's (1975) solvus to 400°C]. The calculated compositions of "100" actinolite range from Act_{61} to Act_{78} (Fig. 6) and are considerably poorer in Ca than predicted by the experimental work of Cameron (1975). This procedure was carried out for several other lamellae and resulted

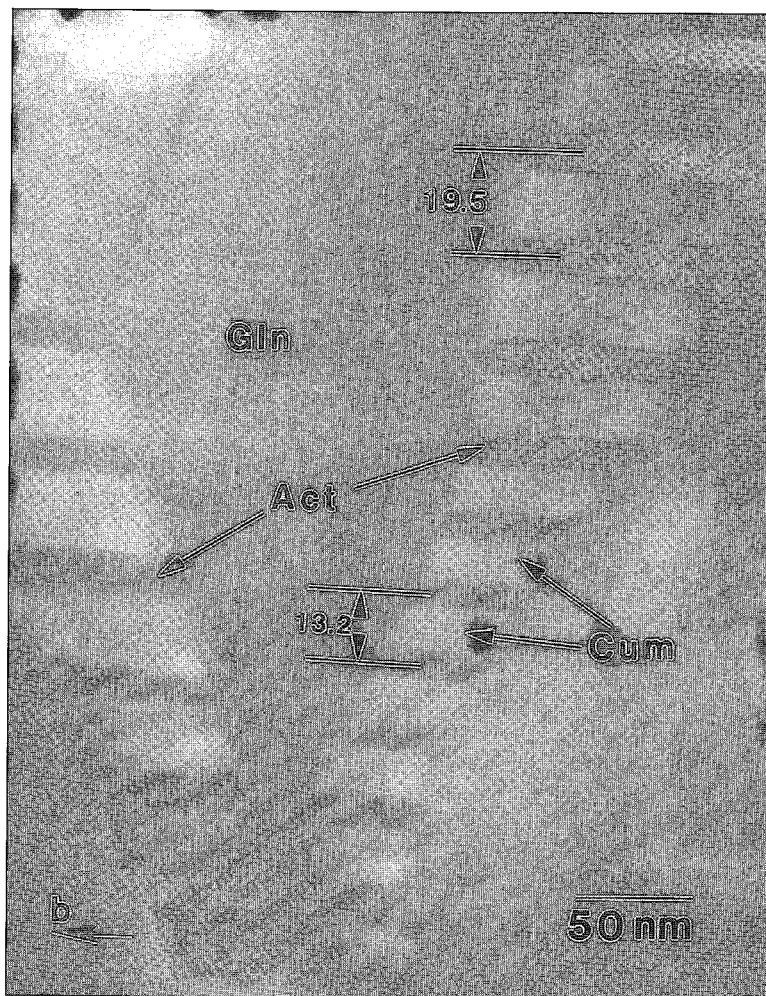


FIG. 7. Bright-field TEM image of two lamellae of fully exsolved cummingtonite. Where the parent lamella of cummingtonite is thinner, the periodicity and thickness of the "100" actinolite also are smaller, and *vice versa* for the thicker areas. Two measured periodicities are shown (in nm). These have been corrected for tilt. The electron beam is near [405].

in actinolite compositions ranging from Act_{100} to Act_{61} . For a few of these cases, including the example shown in Figures 5 and 6, the desired tilt for optimum take-off angle toward the energy-dispersion spectrum detector could not be achieved without drastically tilting the lamellae into an undesirable orientation. The AEM analyses, therefore, were obtained under less-than-optimum conditions, and may be prone to significant errors. We contend that these analytical errors plus possible measurement errors of areas may be responsible for the low calculated Ca contents for the "100" actinolite lamellae. On the other hand, it is possible that these narrow lamellae of actinolite really are

somewhat enriched in the cummingtonite component, similar to the case of actinolite described by Ross *et al.* (1969) from the Ruby Mountains, Montana.

LAMELLA PERIODICITY AND OPTIMAL PHASE-BOUNDARIES

From Figures 1B and 5, it is evident that the secondary exsolution of actinolite from the lamellae of metastable, high-Ca cummingtonite results in a distinctly periodic microstructure. The wavelength, λ , of the periodic lamellae of actinolite lamellae seems to be dependent upon the thickness and bulk composition

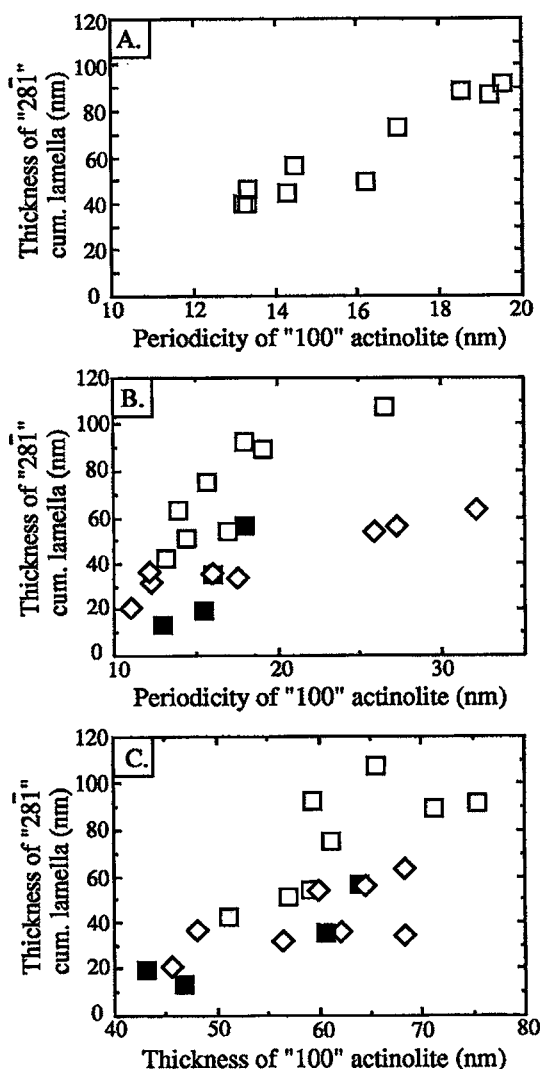


FIG. 8. Plots summarizing the relationships between actinolite periodicity, λ , and cummingtonite thickness for the exsolved lamellae of cummingtonite in the glaucophane. Open squares are for sample VTP1-K, filled squares for sample VTP1-F, and diamonds for sample VTP1-J. (A) Data from single lamella shown in Figure 7. (B) Thickness of cummingtonite *versus* periodicity of actinolite for all three samples. (C) Thickness of cummingtonite *versus* thickness of actinolite for all three samples.

of the host of lamella "281" cummingtonite.

The dependence of λ on changing thickness of the "281" cummingtonite lamellae is illustrated in Figure 7. This TEM image shows a fully exsolved

"281" cummingtonite lamella that has a considerable range of thickness over a small distance. Measurement of the spacing between the centers of the "100" actinolite lamellae, for different portions of this lamella, shows that λ increases as the lamella of "281" cummingtonite thickens. Two measured wavelengths (corrected for tilt), 13.2 nm for the narrow part and 19.5 nm for the thicker region, are indicated in Figure 7. In addition to λ increasing, the thickness of the "100" actinolite lamellae also increases with the thickening of the "281" cummingtonite lamella. These relationships are summarized for exsolved lamellae in three different samples in Figure 8. Detailed measurements of the relative areas of "100" lamellae in Figure 7 and several other cases show that the estimated volume-ratio between actinolite and low-Ca cummingtonite remains essentially constant, for a given lamella, regardless of the changing thickness of the host lamella. This suggests that the metastable lamellae of cummingtonite are indeed compositionally homogeneous and that during the second stage of precipitation, the thickness of the "100" lamellae (*i.e.*, the relative proportion of actinolite) in any given part of the host lamella depends in part upon the composition of the bulk lamella and associated equilibrium compositions at the P-T conditions of this process.

In attempting to understand why the lamellae are periodic, we will first consider the nature of the various interfaces between lamellae observed in the glaucophane. The three types of interfaces involved in this intergrowth are the "281" glaucophane – cummingtonite interface, the "100" actinolite – cummingtonite interface, and the "281" glaucophane – actinolite interface. The "281" and "281" boundaries between coherently intergrown glaucophane and primary lamellae of cummingtonite apparently are planes of best dimensional fit between the two monoclinic lattices (Smelik & Veblen 1991). These orientations of minimum two-dimensional lattice strain (or best fit) have been termed "optimal phase-boundaries" (OPBs) by Bollman & Nissen (1968). Results of calculations of three-dimensional misfit between unstrained structures of glaucophane and low-Ca cummingtonite were found to show good agreement with observed orientations for the glaucophane – cummingtonite intergrowth (Smelik & Veblen 1991). The fact that "281" and "281" boundaries occur for both low-Ca cummingtonite lamellae described by Smelik & Veblen (1991), as well as high-Ca cummingtonite lamellae (Fig. 1A), suggests that these orientations are not overly sensitive to small changes in unit-cell parameters. This is in contrast to calculated OPB results for exsolved actinolite – hornblende pairs from Wyoming, in which small changes in unit-cell parameters gave rise to a wide range of possible OPB orientations (Smelik *et al.* 1991).

The EPLAG program of Fleet (1982), used by Smelik & Veblen (1991), also was used in this study

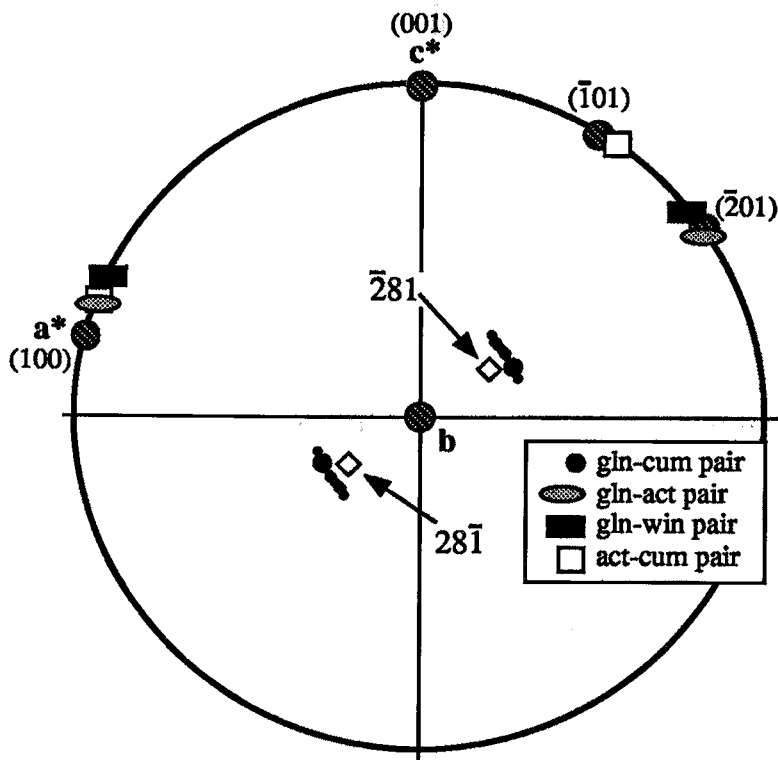


FIG. 9. Stereographic projection down *b* showing the results from EPLAG calculations for intergrown amphiboles using room-temperature, unstrained unit-cell parameters. Reference poles (100), (001), (010), ($\bar{1}01$) and ($\bar{2}01$) are shown by diagonally ruled circles. The poles for ($28\bar{1}$) and ($\bar{2}81$) are shown by diamonds. The filled circles are taken from Smelik & Veblen (1991) and show the location of the calculated optimal phase boundaries (OPBs) for intergrown cummingtonite – glaucophane. The OPB orientations for intergrown cummingtonite – actinolite are near (100) and ($\bar{1}01$), whereas the OPB orientations for intergrown glaucophane – actinolite and glaucophane – winchite are near (100) and ($\bar{2}01$). For the glaucophane – winchite pair, the cell of Maresch *et al.* (1982) was used.

for intergrown cummingtonite – actinolite and glaucophane – actinolite pairs. This version of EPLAG (EPLAG9) not only calculates the area misfit between normalized equivalent (*hkl*) planes in the two related lattices, but it also makes a quantitative estimate of elastic strain energy (ESE). Details of the three-dimensional OPB theory and a discussion of EPLAG were provided by Fleet (1982, 1984, 1986). It has been well documented that boundary planes near (100) and ($\bar{1}01$) represent not only OPBs, but in some cases “exact phase boundaries”, for intergrown calcic and ferromagnesian clinoamphiboles (Robinson *et al.* 1971). The exact phase-boundary theory of Robinson *et al.* (1971, 1977), which predicts these orientations, is based on the observation that the *b* axes of calcic and ferromagnesian amphiboles are virtually identical in length.

The elastic stiffness constants necessary for the present calculations were obtained from Alexandrov & Ryzhova (1961, published in Hawthorne 1983, Table 69, sample hornblende II). The cell parameters of the cummingtonite and glaucophane were obtained from Smelik & Veblen (1991), and the parameters of the actinolite cell were obtained from Ross *et al.* (1969, Table 4, sample HJ182–60). The reader should bear in mind that these calculations are made using room-temperature unit-cell data, and are based on the assumption that the unit cell expands more or less isotropically in an extrapolation to the temperatures of exsolution. The results from the EPLAG calculations are summarized in Figure 9 and Table 4. Table 4 presents the minima in area misfit and calculated ESE values for the three types of interfaces: glaucophane – cummingtonite (Type 1), cummingtonite – actinolite

TABLE 4. SUMMARY OF EPLAG RESULTS FOR INTERGROWN AMPHIBOLES

Interface Type	amphibole pair	D (°)	E (°)	misfit data (minimum orientation)	area misfit	normalized to "100" cum-act	ESE* $\times 10^4$ J/cm ³
Type 1	gln-cum	130	55	"281"	0.016	6.661	1.503
	gln-act	70	0	"100"	0.021	8.803	3.037
		125	0	"201"	0.021	8.699	3.276
Type 3	"281" (gln-act)	125	60	"281"	0.036	14.941	4.822
Type 2	cum-act	70	0	"100"	0.002	1.000	0.045
		145	0	"101"	0.003	1.351	0.031
	gln-win	65	0	"100"	0.010	4.230	0.900
		130	0	"201"	0.010	4.289	0.896

* Elastic stiffness coefficients from Alexandrov & Ryzhova (1961), as published in Hawthorne (1983, Table 69, sample hornblende II).

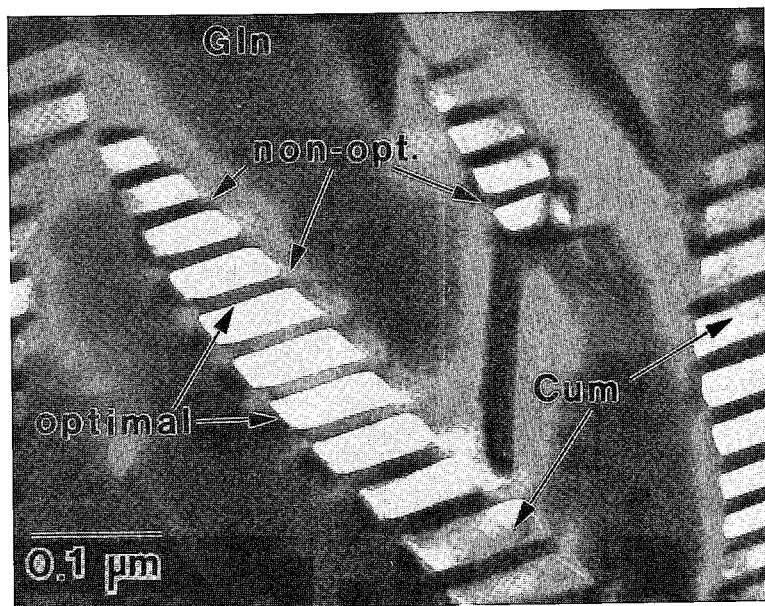


FIG. 10. Dark-field TEM image of lamellae of exsolved cummingtonite. Three different types of lamellar phase-boundaries are indicated. The "100" actinolite – cummingtonite and the "281" glaucophane – cummingtonite interfaces are optimal phase boundaries, whereas the "281" glaucophane – actinolite interface represents a non-optimal orientation for this intergrowth. There is high strain-contrast at the tips of the "100" actinolite lamellae, indicating a poor fit between the actinolite and glaucophane lattices.

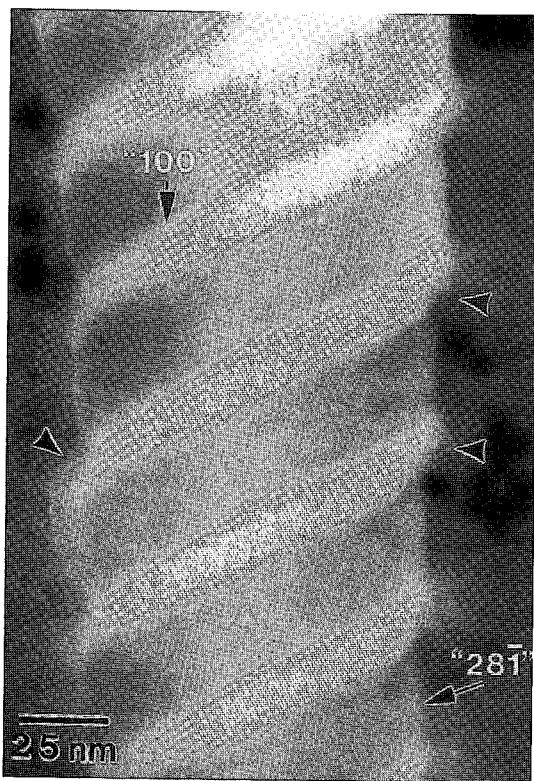


FIG. 11. One-dimensional HRTEM image of a large exsolved lamella of cummingtonite. "100" and "281" OPBs between cummingtonite – actinolite and cummingtonite – glaucophane, respectively, are labeled. The "281" glaucophane – actinolite boundary appears to be step-like, with a portion trying to adopt a "100" orientation (arrows), which was shown to be an OPB for this pair. This complex morphology may express one way in which the total strain energy at these locations is reduced. The electron beam is near [405].

(Type 2), and glaucophane – actinolite (Type 3). Both the cummingtonite – actinolite and the glaucophane – actinolite intergrowths show two minima in misfit, occurring near (100) and $(\bar{1}01)$, and (100) and $(\bar{2}01)$, respectively. From Figure 9, it may be seen that the actual orientations of the minima are several degrees away from these rational orientations. The data for the glaucophane – cummingtonite pair [near (281) and $(\bar{2}8\bar{1})$] are those reported by Smelik & Veblen (1991).

The calculations further show that "281" and $(\bar{2}8\bar{1})$ orientations for the glaucophane – actinolite interface represent a relatively high degree of lattice misfit and relatively high elastic strain energy, compared to the OPB orientations (Table 4). The differences are more clearly seen if the misfits are normalized to the "100" cummingtonite – actinolite minimum, which has the

lowest value of area misfit (Table 4, column 6). The high strain associated with the "281" glaucophane – actinolite interface can be seen especially well in TEM dark-field images, as illustrated in Figure 10. In this image, both the "281" and "100" optimal phase boundaries between glaucophane – cummingtonite and actinolite – cummingtonite are labeled, as well as the "281" non-optimal boundaries between actinolite and glaucophane. Note the strain contrast associated with the tips of the narrow "100" actinolite lamellae. This strain contrast can also be seen in certain bright-field images, depending upon specimen orientation (e.g., Fig. 1B). Close examination of this high-strain boundary suggests that the "281" interface is actually step-like, with the glaucophane – actinolite portion rotated so as to be closer to a "100" orientation (Fig. 11). This presumably helps to reduce the interfacial strain energy at these locations. As discussed below, the buildup in strain energy along the glaucophane – actinolite interface during growth of the "100" lamellae is considered to play an important role in the development of the periodicity of the lamellae, as well as being a limiting factor in the thickness of the actinolite lamellae.

MULTIPLE-PHASE, MULTIPLE-STAGE EXSOLUTION

In one sample, VTP1-K, which contains an exceptionally large grain of glaucophane containing several solid inclusions of quartz and titanite, a very complex exsolution microstructure was observed (Fig. 12). AEM of the various exsolved amphiboles suggests at least three stages of phase separation. The numerous lamellae of cummingtonite are separated into patches by several lamellae elongate parallel to the *b* axis. AEM of these areas shows them to be the sodic-calcic amphibole winchite. EPLAG calculations for intergrown glaucophane – winchite show that "100" represents one optimal phase boundary for this pair (Table 4, Fig. 9), which is consistent with the observations in Figure 12. The exsolution of Ca-rich amphibole lamellae from glaucophane, which adopted both OPB orientations ("100" and $(\bar{2}01)$), is discussed in detail by Smelik & Veblen (1992). Since the cummingtonite lamellae do not match up across the winchite areas, the exsolution of the "100" winchite from the Ca-rich glaucophane probably occurred first.

At some time after or during the late stages of winchite exsolution, metastable "281" and $(\bar{2}8\bar{1})$ lamellae of high-Ca cummingtonite exsolved in the regions between the "100" winchite lamellae. In Figure 12, these lamellae have the darkest contrast and contain up to 0.75 Ca cations pfu. Subsequent to this event, narrow, periodic "100" lamellae of actinolite and low-Ca cummingtonite exsolved within many of these lamellae, as discussed above.

The AEM data for amphiboles examined in this

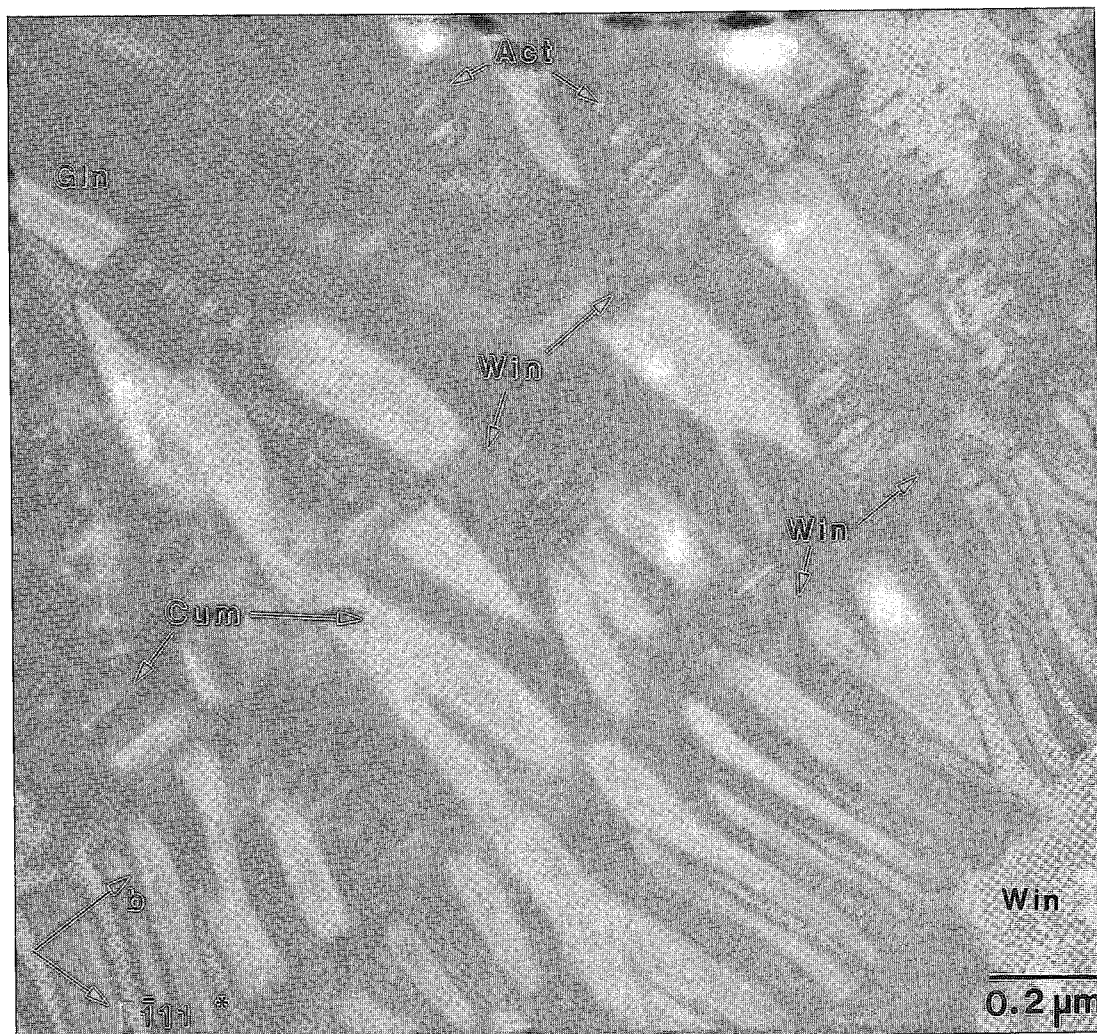


FIG. 12. Bright-field TEM image showing evidence for multiple-phase, multiple-stage exsolution in glaucophane. The first stage of exsolution involved "100" winchite lamellae. This was followed by the precipitation of "281" and "281" lamellae of metastable, high-Ca cummingtonite, some of which further exsolved narrow, periodic "100" lamellae of actinolite and low-Ca cummingtonite. This area records a complex history of exsolution, resulting in the metastable coexistence of five different amphiboles.

study are plotted in terms of calculated $M4$ contents in Figure 13. The outlines shown around the various types of amphibole do not represent stability fields but simply serve to group the analyses. The stippled boxes connected by tielines show the compositions of the five amphiboles (glaucophane, winchite, metastable Ca-rich cummingtonite, low-Ca cummingtonite, and actinolite) observed in Figure 12. The composition of low-Ca cummingtonite and actinolite was estimated as described earlier. Given the metastable nature of the Ca-rich cummingtonite, this five-amphibole assem-

blage does not represent an equilibrium assemblage, but instead records a complex history of exsolution for these samples.

DISCUSSION

Mechanisms of exsolution

"281" lamellae. With the exception of the complicated area shown in Figure 12, and other samples showing only Ca-rich lamellae (Smelik & Veblen

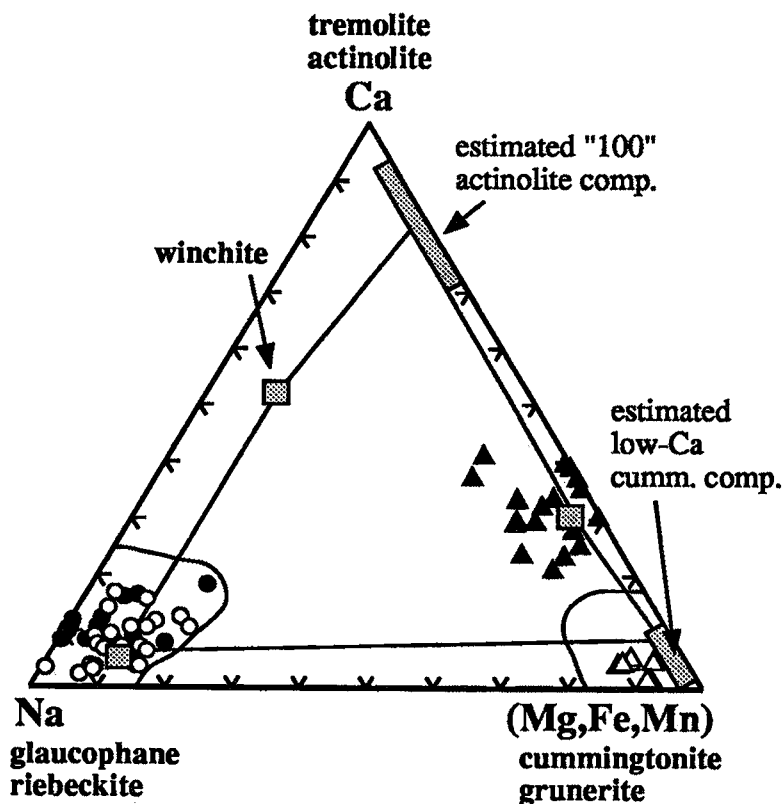


FIG. 13. Triangular diagram showing amphibole compositions in terms of calculated $M4$ occupancies for glaucophane and associated exsolved phases from Tillotson Peak. Circles indicate compositions of both exsolved (open) and unexsolved (filled) glaucophane. Filled triangles represent the compositions of lamellae of metastable, high-Ca cummingtonite. Empty triangles are lamellae of low-Ca cummingtonite from Smelik & Veblen (1991). Stippled boxes connected by tie-lines show the compositions of the five coexisting amphiboles shown in Figure 12. Actinolite and cummingtonite compositions from exsolved cummingtonite lamellae were estimated, as described in the text.

1992), the first stage of precipitation in these glaucophane samples was the formation of "281" and "281" cummingtonite lamellae. In most cases, this cummingtonite is unusually rich in Ca and is metastable (Fig. 3). This observation indicates a strong partition of Ca from the initial Ca-Fe-Mg-rich glaucophane host into the cummingtonite during initial phase-separation. The most common mechanism of exsolution seems to have been homogeneous nucleation and growth, although evidence of heterogeneous nucleation of lamellae on dislocations and (010) chain-width errors also were observed.

The primary chemical substitution operating during the first stage of the exsolution can be expressed ideally as: $M4Na, M2(Al, Fe^{3+}) \leftrightarrow M4(Fe^{2+}, Mg), M2(Mg, Fe^{2+})$. This coupled substitution does not consider any Ca.

The strong partitioning of Ca into cummingtonite during exsolution is unexpected. Since Na and Ca are nearly the same size, one might expect the Ca to remain behind in the larger $M4$ site of glaucophane, rather than forcing its way into the smaller $M4$ site of the cummingtonite structure during exsolution. The coexisting pairs of alkali and ferromagnesian amphiboles of Klein (1966, 1968) and Black (1973), in fact, do show preferential Ca partitioning into the alkali amphibole; these occurrences, however, are very Al-poor and Fe^{3+} -rich, and the alkali amphibole is somewhat deficient in Na. In the present case, calcium may favor cummingtonite over glaucophane partly because of imbalance of electrostatic charges resulting from divalent Ca ions (in $M4$) surrounded by increasing numbers of trivalent Al ions in the $M2$ sites of glaucophane.

phane during the exsolution of cummingtonite. Further support for this is evident in the evaluation of root-mean-square (RMS) deviations from Pauling's (1960) neutrality principle for various compositions in glaucophane (Hawthorne 1978). His results indicate that an increase of the mean valence in $M4$, as would occur with additional Ca, leads to an increase of the RMS deviation, rendering high-Ca glaucophane relatively unstable. The observations in the present study support Hawthorne's conclusions and emphasize the importance of local bond-strength requirements in controlling cation order in amphiboles.

In addition, the high-temperature (270°C) crystal-structure refinement of a manganian cummingtonite by Sueno *et al.* (1972) revealed that at elevated temperatures, the $M4$ cations are significantly displaced away from the octahedral strip to positions more similar to those of $M4$ cations in calcic amphiboles. Although the high-Ca cummingtonite lamellae are clearly metastable (Fig. 3), the partitioning of Ca into the cummingtonite may be somewhat enhanced by distortion of $M4$ polyhedra at the elevated temperatures of this process.

"100" actinolite-cummingtonite lamellae. At some time after the precipitation of the "281" and "281" lamellae of Ca-rich cummingtonite, a second stage of exsolution began in which secondary lamellae exsolved within the metastable lamellae. The most striking feature of this second stage is the periodic nature of the intergrowth. The cause of this periodicity has been briefly discussed above in terms of considerations of the optimal phase boundary for the

three coherently intergrown amphiboles and will be explored further here.

A periodic exsolution-induced microstructure like this initially calls to mind a mechanism of spinodal decomposition. However, TEM observations of lamellae that are partially exsolved (Fig. 5) and more random distributions of "100" lamellae (Fig. 14) argue against this mechanism of exsolution. Spinodal decomposition normally involves a compositional modulation that occurs throughout the entire crystal, resulting in a pervasive exsolution-induced texture (Champness & Lorimer 1976). If this mechanism operated in the present case, one would expect *all* of the lamellae to be completely exsolved, not just some of them. Since the microstructure is free of dislocations (Fig. 2), the dominant mechanism appears to be one of homogeneous nucleation and growth. The driving force for nucleation is the decrease in free energy, ΔG_{volume} , associated with the formation of a two-phase intergrowth from a metastable homogeneous phase. For classical processes of nucleation, there are two main free-energy terms that inhibit the formation of a nucleus, $\Delta G_{\text{surface}}$ and ΔG_{strain} . For processes of coherent exsolution, the surface-energy term is generally small, whereas the strain-energy term contributes significantly to the activation-energy barrier and also controls the orientation of the exsolution lamellae (Cahn 1961, 1962, 1968, Willaime & Brown 1974, Robin 1974, Champness & Lorimer 1976, Putnis & McConnell 1980, Fleet 1982). The magnitude of the interfacial strain energy depends upon the actual degree of lattice mismatch across the coherent interface and the elastic properties of

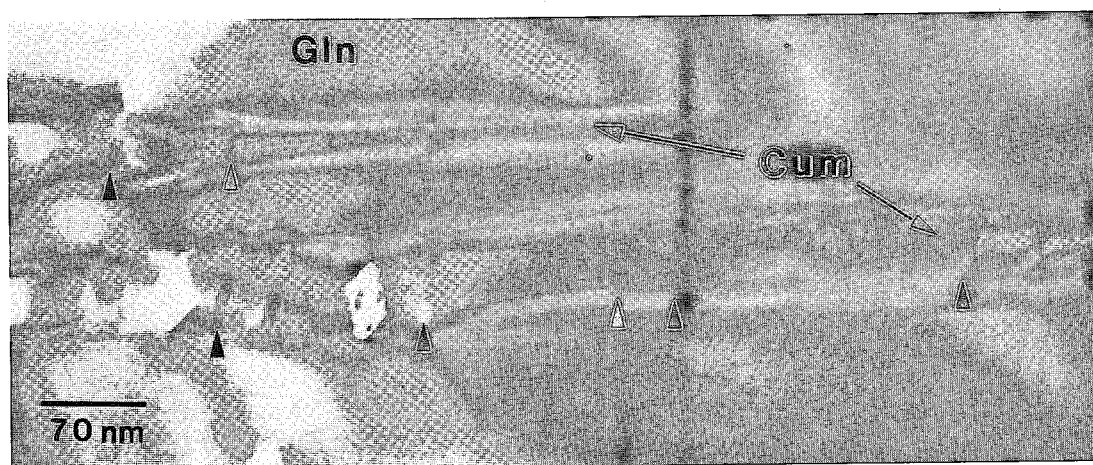


FIG. 14. Bright-field TEM image illustrating random distribution of "100" actinolite lamellae in a Ca-rich "281" cummingtonite lamella. This texture suggests multiple, simultaneous nucleation events throughout the parent lamella. The electron beam is nearly parallel to [001].

the intergrown phases. Robinson *et al.* (1971, 1977) have shown for quadrilateral amphiboles and pyroxenes that with the proper amount of lattice rotation (which can be substantial), an exact match in lattices at lamellar interfaces can be achieved, assuming the *b* axes of host and lamellae are equal in length. This "exact phase boundary" theory is applicable in the present case. If the HRTEM images shown in Figure 2 are viewed at a low angle parallel to the (020) fringes, it is evident that there is very little rotation in the lattice (about *c*) and virtually no distortion of the fringes across the "100" actinolite – cummingtonite interface. This observation suggests that there is an excellent, if not exact, match between the lattices of actinolite and cummingtonite, which implies a very low strain-energy at these locations. Additional evidence for low strain-energy across this interface can be seen in the very low elastic-strain energy and area-misfit values calculated by EPLAG for the actinolite – cummingtonite interface (Table 4).

The situation for the "281" actinolite – glaucophane interface is considerably different, however. Results of lattice misfit and ESE calculations presented above (Table 4) indicate that the ESE for this interface is about two orders of magnitude higher than that of the actinolite – cummingtonite boundary. After the nucleation of the "100" actinolite lamellae, during the very early stages of growth, each newly formed lamella of actinolite is only a few unit cells wide. The high-strain "281" glaucophane – actinolite interface, therefore, is very small in area, and thus the magnitude of the elastic strain-energy is also probably small. This, plus the excellent fit of the lattices and low ESE along the "100" cummingtonite – actinolite interface, suggest that owing to the small barrier in activation energy, nucleation of the actinolite occurs relatively easily. Once each lamella of actinolite has nucleated, further growth is controlled by the diffusion rates of Ca and (Fe,Mg) to and from the interface.

Energy-minimization model and periodicity

It is important to note that after the nucleation of an actinolite lamella, and as it coarsens, the dimensions of the "100" interfaces remain constant, whereas the "281" boundaries increase in area. The elastic-strain energy associated with the "100" boundaries therefore remains essentially constant, whereas the strain energy at the tips of the "100" lamellae will increase. To consider the effects of strain energy on the development of this periodic microstructure, we present a simplified model that demonstrates that the total interfacial elastic-strain energy associated with this three-amphibole intergrowth may be minimized at certain values of the spacing of actinolite lamellae (λ), and further we show that this equilibrium spacing increases with increasing thickness of the "281" parent lamella.

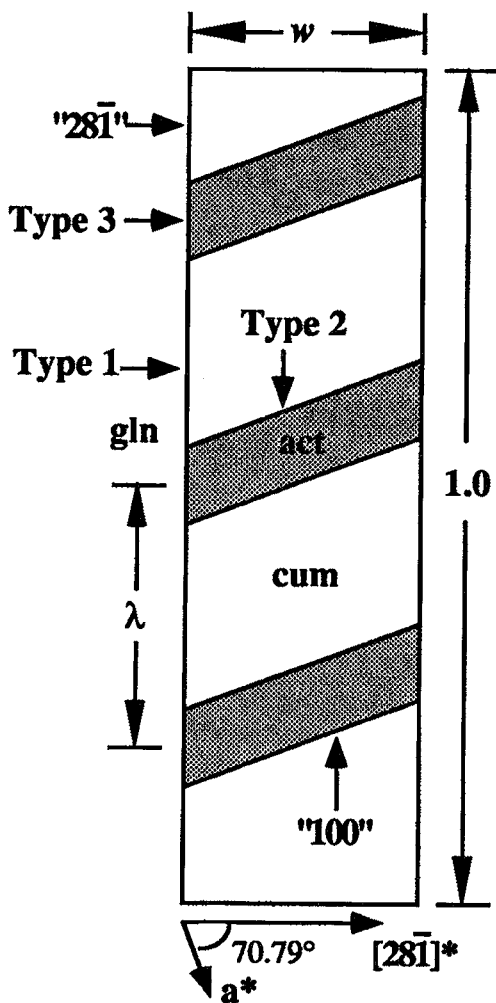


FIG. 15. Schematic diagram showing the initial parameters for the energy minimization model. This view, down [018], shows both the "281" primary cummingtonite lamella and the secondary "100" actinolite lamellae in edge-on orientations. The three types of lamella interfaces and their orientations are indicated. λ refers to the periodicity of "100" actinolite, and w is the thickness of the primary "281" lamella. For the calculations, a unit length and unit depth of the primary lamella are assumed. All interfacial elastic strain energies were calculated using room-temperature unit-cell data.

The parameters for the model are shown schematically in Figure 15, which illustrates a view parallel to [018] showing a single, exsolved "281" lamella. Both the "281" and the "100" interfaces are in an edge-on orientation with respect to the viewing direction. Note that the "100" interface makes an angle of 70.79° with the "281" interface [angle between (100) and (281)].

Assuming a unit-length section of the primary “281” lamella and unit depth, the interfacial areas A between the individual lamellae (ind) can be expressed as follows:

$$\begin{aligned}\text{Type 1 (gln-cum): } A_{1,\text{ind}} &= 2\lambda(1 - X_{\text{act}}) \\ \text{Type 2 (act-cum): } A_{2,\text{ind}} &= 2(w/\sin 70.79) = 2.118w \\ \text{Type 3 (act-gln): } A_{3,\text{ind}} &= 2\lambda X_{\text{act}}\end{aligned}$$

where w is the thickness of the “281” parent lamella, X_{act} is the fraction of actinolite in the “281” lamella, λ is the periodicity of actinolite lamellae, and the factor 2 is introduced because each lamella has two interfaces. The total areas of Type-1 and -3 interfaces are dependent only on the proportion of actinolite in the lamella (X_{act}), whereas the total area of Type-2 interfaces is the product of the individual area and the number of actinolite lamellae ($1/\lambda$). The expressions for the total areas are given below:

$$\begin{aligned}\text{Type 1: } A_{1,\text{tot}} &= 2(1 - X_{\text{act}}) \\ \text{Type 2: } A_{2,\text{tot}} &= 2(w/\sin 70.79)/\lambda = 2.118w/\lambda \\ \text{Type 3: } A_{3,\text{tot}} &= 2X_{\text{act}}\end{aligned}$$

For consideration of the elastic strain energy, assume that the total interfacial elastic strain energy is the sum of the individual interfacial elastic strain energies. In order to calculate the increase in strain energy with increasing interfacial area, we first define a nominal strain energy, $E_{o,n}$, per unit area for each type of interface (1–3), as the areas go to zero. The total strain energy for each type of interface, in the limit as the areas approach zero, is therefore the product of the nominal strain energy and the total interface area:

$$\begin{aligned}\text{Type 1: } E_{\text{tot},1} &= 2(1 - X_{\text{act}})E_{o,1} \\ \text{Type 2: } E_{\text{tot},2} &= 2.118wE_{o,2}/\lambda \\ \text{Type 3: } E_{\text{tot},3} &= 2X_{\text{act}}E_{o,3}\end{aligned}$$

We also assume that as the area of a given interface becomes larger (*i.e.*, as the lamella grows), there is a term that reflects excess strain energy, E_{ex} , that also increases (see, for example, Gotoh & Fukuda 1989, Christian 1975). If we assume that E_{ex} increases as the square of the area [similar to the energy of a dislocation, which increases proportionally to b^2 (Nabarro 1967)], then we can write E_{ex} for the three types of interfaces as:

$$\begin{aligned}\text{Type 1: } E_{1,\text{ex}} &= K_1E_{o,1}[2\lambda(1 - X_{\text{act}})]^2 \\ \text{Type 2: } E_{2,\text{ex}} &= K_2E_{o,2}[2.118w]^2 \\ \text{Type 3: } E_{3,\text{ex}} &= K_3E_{o,3}[2\lambda X_{\text{act}}]^2\end{aligned}$$

where K_1 , K_2 , and K_3 are proportionality constants; $E_{o,1}$, $E_{o,2}$, and $E_{o,3}$ are the nominal interfacial strain energies, and the remaining terms in each expression are the individual interface areas given above. The

total excess strain energies can then be determined by multiplying the above expressions by $1/\lambda$, the number of actinolite lamellae, as shown below:

$$\begin{aligned}\text{Type 1: } E_{1,\text{ex}(\text{tot})} &= K_1E_{o,1}[2\lambda(1 - X_{\text{act}})]^2 [1/\lambda] \\ \text{Type 2: } E_{2,\text{ex}(\text{tot})} &= K_2E_{o,2}[2.118w]^2 [1/\lambda] \\ \text{Type 3: } E_{3,\text{ex}(\text{tot})} &= K_3E_{o,3}[2\lambda X_{\text{act}}]^2 [1/\lambda]\end{aligned}$$

For a general case, where all the specific interfacial strain energies increase as the squares of their areas, the total interfacial strain energy can be expressed as the sum of the total nominal strain energies and the total excess strain energies:

$$E_{\text{tot}} = \sum_{n=1}^n E_{\text{tot},n} + \sum_{n=1}^n E_{\text{ex},n}$$

For the three-amphibole intergrowth modeled in Figure 15, the expanded expression for the total interfacial strain energy is given by:

$$\begin{aligned}E_{\text{tot}} &= \{2(1 - X_{\text{act}})E_{o,1} + \\ &K_1E_{o,1}[2\lambda(1 - X_{\text{act}})]^2 [1/\lambda]\} + \\ &\{2.118wE_{o,2}/\lambda + K_2E_{o,2}[2.118w]^2 [1/\lambda]\} + \\ &\{2X_{\text{act}}E_{o,3} + K_3E_{o,3}[2\lambda X_{\text{act}}]^2 [1/\lambda]\}.\end{aligned}\quad (1)$$

Assuming the values of $E_{o,n}$ can be represented by the EPLAG calculations, and X_{act} can be measured from TEM images, this equation reduces to one with the general form

$$E_{\text{tot}} = C_1 + C_2w/\lambda + C_3w^2/\lambda + C_4\lambda$$

where the C_n are constants, and the only variables are the primary lamellar thickness, w , and the actinolite lamellar spacing, λ . Provided the C_n are positive, a function of this type will always have a minimum. Substituting in equation (1) the estimates of elastic strain energy [Table 4, $E_{o,1} = 1.503$, $E_{o,2} = 0.0448$, and $E_{o,3} = 4.822 (\times 10^4 \text{ J/cm}^2)$] for the nominal interfacial energies, and letting X_{act} equal 0.408 (see Figs. 5 and 6), results in the following expression, in terms of w and λ :

$$\begin{aligned}E_{\text{tot}} &= 5.714 + 0.0949w/\lambda + 0.201K_2w^2/\lambda + \\ &(2.107K_1 + 3.211K_3)\lambda.\end{aligned}\quad (2)$$

The values of the proportionality constants K_1 , K_2 , and K_3 are unknown, but their actual values will not change the general shape of the function. Our goal is to examine how the equilibrium lamellar spacing, λ , changes, as the thickness of the primary “281” lamella, w , increases. Assuming that the K factors are all 1.0, and arbitrarily letting $w = 0.8$, results in the following expression:

$$E_{\text{tot}} = 5.714 + 0.2046/\lambda + 5.318\lambda.\quad (3)$$

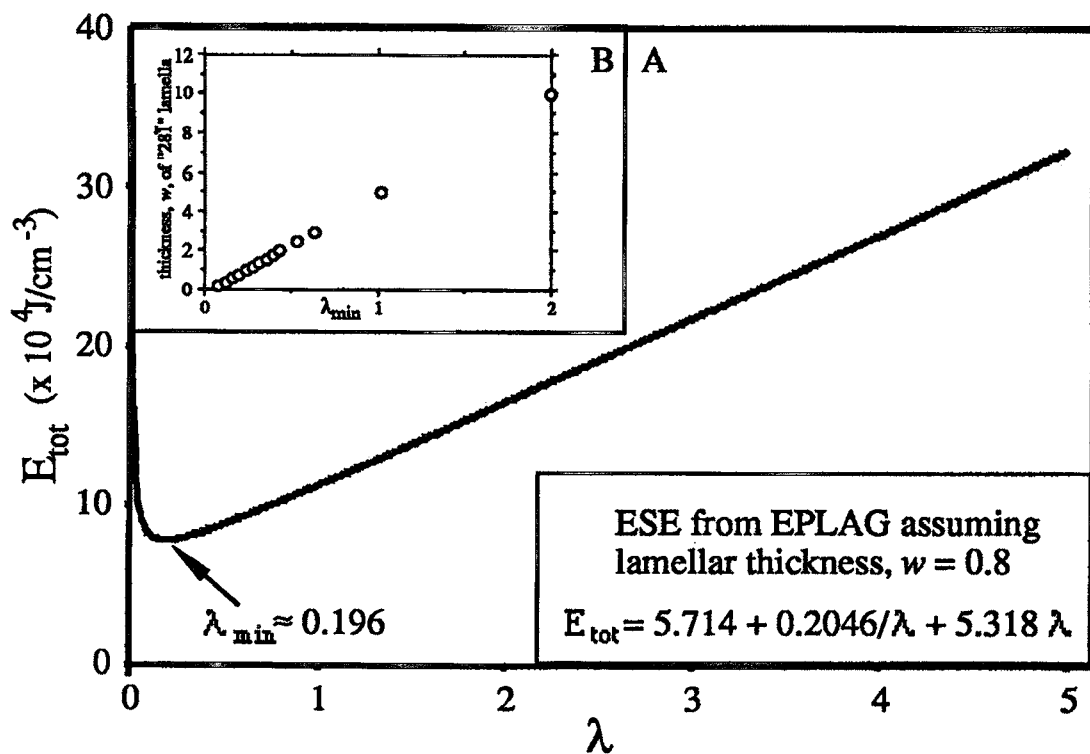


FIG. 16. (A) Plot of total interfacial energy, E_{tot} , versus "100" actinolite periodicity, λ , calculated from the model described in text (eqn. 3) for a value of the thickness of a "281" primary lamella, w , of 0.8 (arbitrary units). The minimum energy falls at a λ value of about 0.196. (B) Plot of thickness of "281" primary lamella, w , versus λ_{min} . As w increases, λ_{min} increases, similar to the result shown in Fig. 8A.

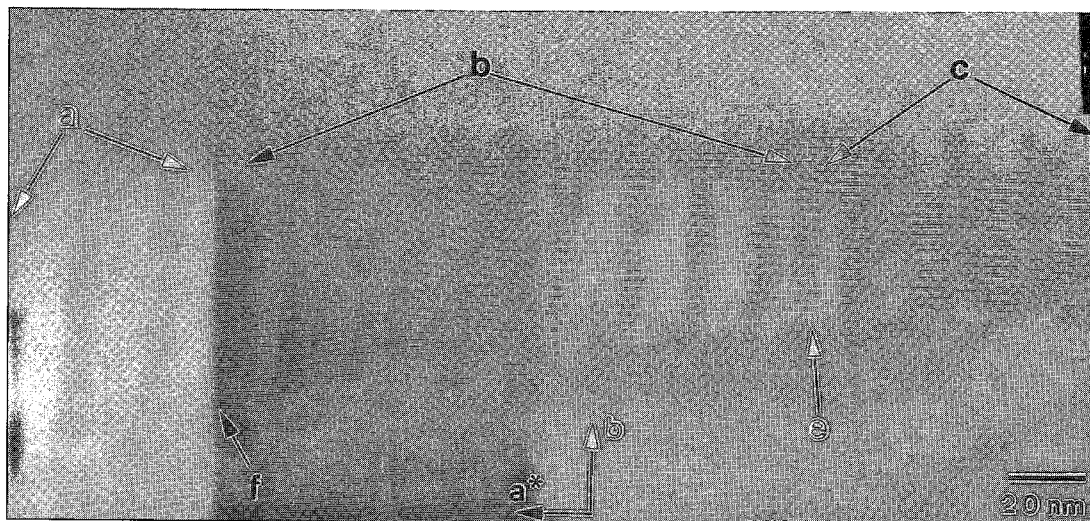


FIG. 17. Bright-field TEM image of an exsolved lamella of cummingtonite showing evidence for three separate exsolution-fronts. The three distinct segments of periodicity are bracketed by arrows and labeled "a", "b", and "c". Exsolution front "a" met "b" at location "f", and front "b" met "c" at "e". Where the fronts converged with one another, they were out of phase, resulting in narrower "100" actinolite lamellae at the intersections. It is likely that this texture developed owing to simultaneous nucleation and growth of actinolite at several locations within a single lamella. Electron beam is parallel to c.

This function is plotted in Figure 16A and shows a minimum at a λ value of approximately 0.196. This value of λ , then, represents the equilibrium spacing for which the total elastic strain energy of the intergrowth is minimized, for the given starting conditions. If we make the same calculation assuming a thicker "281" lamella, say $w = 1.6$, the energy minimum falls at $\lambda \approx 0.354$. These calculated results compare well with the TEM observations plotted in Figure 8A.

It is important to emphasize that whereas these calculated values of λ are dimensionless, the model clearly illustrates that the thicker the primary "281" lamellae, the greater the equilibrium spacing of the "100" actinolite lamellae should be, to minimize overall elastic strain energy (Fig. 16B). Furthermore, if the primary "281" lamellae do not have a constant thickness, the equilibrium spacing of the "100" actinolite lamellae should adjust to maintain a minimum strain-energy configuration. These model results are consistent with TEM images showing changes in the periodicity of "100" actinolite lamellae with changing "281" thickness (Figs. 7, 8), and they suggest that the periodicity is the result of strain. This minimization of total strain energy leading to a periodic microstructure is similar to the common observation of periodic transformation-induced twins in exsolved alkali feldspars, which is also the result of minimization of strain energy during the monoclinic–triclinic transformation in the Ab-rich feldspar lamellae (e.g., Willaime & Gandais 1972, Brown & Parsons 1984, Waldron & Parsons 1992).

Although the periodic exsolution-induced microstructure in these amphiboles looks strikingly similar to periodic twinning in alkali feldspars, the mechanisms of nucleation and growth seem to be quite different. TEM images of partially exsolved lamellae (Figs. 5, 12) suggest that each "100" actinolite lamella coarsens to considerable size before the next one nucleates. Viewed in this manner, this process behaves like an exsolution front moving through each metastable lamella, with the location of the next site of nucleation probably being influenced by the strain-energy field at the exsolution front, and the concentration gradient away from the last "100" interface through the metastable portion of the lamella. As discussed earlier, the activation-energy barrier for nucleation of the "100" actinolite lamellae may be relatively small. If this is true, then one might expect multiple episodes of nucleation within a single parent lamella. There is abundant evidence that this has occurred in these samples (Figs. 14, 17). Figure 17 illustrates a fully exsolved lamella viewed down [001]. Three distinct segments of periodicity can be discerned ("a", "b", and "c"), which suggests three initial episodes of nucleation. The three exsolution fronts came together at locations "e" and "f". It is evident that where the different exsolution fronts converged with one another, they were out of phase, and nar-

rower lamellae of actinolite grew in the out-of-phase regions.

CONCLUSIONS

The results from this study indicate that the glaucophane from Tillotson Peak, north-central Vermont, records a complex history of exsolution. Primary chemical zoning, involving Ca, Fe, and Mg enrichment, has given rise to two- and, locally, three-stage exsolution. The optimal phase-boundaries (i.e., minimization of strain energy) seem to control the orientation relationships of the various amphibole lamellae during all stages of exsolution. Calcium is partitioned in a step-wise manner, first into metastable "281" and "281" cummingtonite lamellae, and finally into narrow "100" actinolite lamellae within the cummingtonite lamellae. The second episode of exsolution formed a periodic microstructure that seems largely to be controlled by buildup in strain energy at the non-optimal phase boundaries between glaucophane and actinolite. The periodicity represents a minimization of the total elastic strain energy for the intergrowth. To our knowledge, this is the first example of strain-induced periodic exsolution lamellae in silicates. These results, combined with previous results by Smelik & Veblen (1989, 1991, 1992), emphasize the complexities of exsolution processes and microstructures that are possible in glaucophane.

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REFERENCES

- ALEKSANDROV, K.S. & RYZHOVA, T.V. (1961): The elastic properties of rock-forming minerals: pyroxenes and amphiboles. *Izv. Akad. Nauk SSSR, Ser. Geofiz.* **9**, 1339–1344 (in Russ.).
- BANCROFT, G.M. & BURNS, R.G. (1969): Mössbauer and absorption spectral study of alkali amphiboles. *Mineral. Soc. Am., Spec. Pap.* **2**, 137–148.

- _____, _____ & MADDOCK, A.G. (1967a): Determination of the cation distribution in the cummingtonite – grunerite series by Mössbauer spectra. *Am. Mineral.* **52**, 1009-1026.
- _____, MADDOCK, A.G. & BURNS, R.G. (1967b): Applications of the Mössbauer effect to silicate mineralogy. I. Iron silicates of known crystal structure. *Geochim. Cosmochim. Acta* **31**, 2219-2246.
- BLACK, P.M. (1973): Mineralogy of New Caledonian metamorphic rocks. II. Amphiboles from the Ouégoa District. *Contrib. Mineral. Petrol.* **39**, 55-64.
- BOLLMAN, W. & NISSEN, H.-U. (1968): A study of optimal phase boundaries: the case of exsolved feldspars. *Acta Crystallogr.* **A24**, 546-557.
- BORG, I.Y. (1967): Optical properties and cell parameters in the glaucophane – riebeckite series. *Contrib. Mineral. Petrol.* **15**, 67-92.
- BOTHNER, W.A. & LAIRD, J. (1987): Structure and metamorphism at Tillotson Peak, north-central Vermont. In *Guidebook for Field Trips in Vermont*, Vol. 2 (D. S. Westerman, ed.). 79th Ann. Meet., New England Intercollegiate Geol. Conf. (Montpelier, Vermont), 383-405.
- BROWN, W.L. & PARSONS, I. (1984): The nature of potassium feldspar, exsolution microtextures and development of dislocations as a function of composition in perthitic alkali feldspars. *Contrib. Mineral. Petrol.* **86**, 335-341.
- CAHN, J.W. (1961): On spinodal decomposition. *Acta Metall.* **9**, 795-801.
- _____. (1962): On spinodal decomposition in cubic crystals. *Acta Metall.* **10**, 179-183.
- _____. (1968): Spinodal decomposition. *Trans. Metall. Soc. AIME*, **242**, 166-180.
- CAMERON, K.L. (1975): An experimental study of actinolite – cummingtonite phase relations with notes on the synthesis of Fe-rich anthophyllite. *Am. Mineral.* **60**, 375-390.
- CHAMPNESS, P.E. & LORIMER, G.W. (1976): Exsolution in silicates. In *Electron Microscopy in Mineralogy* (H.-R. Wenk, ed.). Springer-Verlag, Berlin (174-204).
- CHRISTIAN, J.W. (1975): *The Theory of Transformations in Metals and Alloys, Part I* (2nd ed.). Pergamon Press, Oxford.
- COLEMAN, R.G. & PAPIKE, J.J. (1968): Alkali amphiboles from the blueschists of Cazadero, California. *J. Petrol.* **9**, 105-122.
- FINGER, L.W. (1969): The crystal structure and cation distribution of a grunerite. *Mineral. Soc. Am., Spec. Pap.* **2**, 95-100.
- FISCHER, K.F. (1966): A further refinement of the crystal structure of cummingtonite, $(\text{Mg,Fe})_7(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$. *Am. Mineral.* **51**, 814-818.
- FLEET, M.E. (1982): Orientation of phase and domain boundaries in crystalline solids. *Am. Mineral.* **67**, 926-936.
- _____. (1984): Orientation of feldspar intergrowths: application of lattice misfit theory to cryptoperthites and e-plagioclase. *Bull. Minéral.* **107**, 509-519.
- _____. (1986): Lattice-misfit theory and transformation twinning in alkali feldspar. *Can. Mineral.* **24**, 615-623.
- GHOSE, S. (1961): The crystal structure of a cummingtonite. *Acta Crystallogr.* **14**, 622-627.
- _____. (1981): Subsolidus reactions and microstructures in amphiboles. *Rev. Mineral.* **9A**, 325-372.
- _____, FORBES, W.C. & PHAKEY, P.P. (1974): Unmixing of an alkali amphibole (tirodite) into magnesiorichterite and magnesioriebeckite. *Ind. J. Earth Sci.* **1**, 37-42.
- GOTOH, Y. & FUKUDA, H. (1989): Interfacial energy of the bcc(110)/fcc(111) interface and energy dependence on its size. *Surface Sci.* **223**, 315-325.
- HAFNER, S.S. & GHOSE, S. (1971): Iron and magnesium distribution in cummingtonites $(\text{Fe,Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$. *Z. Kristallogr.* **133**, 301-326.
- HAWTHORNE, F.C. (1978): The crystal chemistry of the amphiboles. IX. Polyvalent-cation ordering in clinoamphiboles. *Can. Mineral.* **16**, 521-525.
- _____. (1981): Crystal chemistry of the amphiboles. *Rev. Mineral.* **9A**, 1-102.
- _____. (1983): The crystal chemistry of the amphiboles. *Can. Mineral.* **21**, 173-480.
- KLEIN, C., JR. (1966): Mineralogy and petrology of the metamorphosed Wabush iron formation, southwestern Labrador. *J. Petrol.* **7**, 246-305.
- _____. (1968): Coexisting amphiboles. *J. Petrol.* **9**, 281-330.
- LAIRD, J. (1977): *Phase equilibria in mafic schist and the polymetamorphic history of Vermont*. Ph.D. thesis, California Institute of Technology, Pasadena, California.
- _____ & ALBEE A.L. (1981a): High-pressure metamorphism in mafic schist from northern Vermont. *Am. J. Sci.* **281**, 97-126.
- _____ & _____ (1981b): Pressure, temperature, and time indicators in mafic schist: their application to reconstructing the polymetamorphic history of Vermont. *Am. J. Sci.* **281**, 127-175.
- LEAKE, B.E. (1978): Nomenclature of amphiboles. *Am. Mineral.* **63**, 1023-1053.

- LIVI, K.J.T. & VEBLEN, D.R. (1987): "Eastonite" from Easton, Pennsylvania: a mixture of phlogopite and a new form of serpentine. *Am. Mineral.* **72**, 113-125.
- MARESCH, W.V., MEDENBACH, O. & RUDOLPH, A. (1982): Winchite and the actinolite – glaucophane miscibility gap. *Nature* **296**, 731-732.
- MIYASHIRO, A. (1957): The chemistry, optics and genesis of the alkali amphiboles. *J. Fac. Sci. Univ. Tokyo, Sec. II*, **11**, 57-83.
- NABARRO, F.R.N. (1967): *Theory of Crystal Dislocations*. Clarendon Press, Oxford, U.K.
- PAULING, L. (1960): *The Nature of the Chemical Bond* (3rd ed.). Cornell University Press, Ithaca, New York.
- PUTNIS, A. & MCCONNELL, J.D.C. (1980): *Principles of Mineral Behaviour*. Elsevier, New York.
- ROBIN, P.-Y.F. (1974): Stress and strain in cryptoperthite lamellae and the coherent solvus of alkali feldspars. *Am. Mineral.* **59**, 1299-1318.
- ROBINSON, P., JAFFE, H.W., ROSS, M. & KLEIN, C., JR. (1971): Orientations of exsolution lamellae in clinopyroxenes and clinoamphiboles: consideration of optimal phase boundaries. *Am. Mineral.* **56**, 909-939.
- _____, ROSS, M., NORD, G.L., JR., SMYTH, J.R. & JAFFE, H.W. (1977): Exsolution lamellae in augite and pigeonite: fossil indicators of lattice parameters at high temperature and pressure. *Am. Mineral.* **62**, 857-873.
- _____, SPEAR, F.S., SCHUMACHER, J.C., LAIRD, J., KLEIN, C., EVANS, B.W. & DOOLAN, B.L. (1982): Phase relations of metamorphic amphiboles: natural occurrence and theory. *Rev. Mineral.* **9B**, 1-227.
- ROSS, M., PAPIKE, J.J. & SHAW, K.W. (1969): Exsolution textures in amphiboles as indicators of subsolidus thermal histories. *Mineral. Soc. Am., Spec. Pap.* **2**, 275-299.
- SHAU, YEN-HONG, PEACOR, D.R., GHOSE, S. & PHAKEY, P.P. (1993): Submicroscopic exsolution in Mn-bearing alkali amphiboles from Tirodi, Maharashtra, India. *Am. Mineral.* **78**, 96-106.
- SMELIK, E.A., NYMAN, M.W. & VEBLEN, D.R. (1991): Pervasive exsolution within the calcic amphibole series: TEM evidence for a miscibility gap between actinolite and hornblende in natural samples. *Am. Mineral.* **76**, 1184-1204.
- _____, & VEBLEN, D.R. (1989): A five-amphibole assemblage from blueschists in northern Vermont. *Am. Mineral.* **74**, 960-964.
- _____, & _____ (1991): Exsolution of cummingtonite from glaucophane: a new orientation for exsolution lamellae in clinoamphiboles. *Am. Mineral.* **76**, 971-984.
- _____, & _____ (1992): Exsolution of Ca-amphibole from glaucophane and the miscibility gap between sodic and calcic amphiboles. *Contrib. Mineral. Petrol.* **112**, 178-195.
- SUENO, S., PAPIKE, J.J., PREWITT, C.T. & BROWN, G.E. (1972): Crystal structure of high cummingtonite. *J. Geophys. Res.* **77**, 5767-5777.
- WALDRON, K.A. & PARSONS, I. (1992): Feldspar microtextures and multistage thermal history of syenites from the Coldwell Complex, Ontario. *Contrib. Mineral. Petrol.* **111**, 222-234.
- WILLAIME, C. & BROWN, W.L. (1974): A coherent elastic model for the determination of the orientation of exsolution boundaries: application to the feldspars. *Acta Crystallogr.* **A30**, 316-331.
- _____, & GANDAIS, M. (1972): Study of exsolution in alkali feldspars: calculation of elastic stresses inducing periodic twins. *Phys. Stat. Sol. A* **9**, 529-539.
- WOOD, R.M. (1980): Compositional zoning in sodic amphiboles from the blueschist facies. *Mineral. Mag.* **43**, 741-752.

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