RELATIONSHIPS BETWEEN CELL PARAMETERS AND CHEMICAL COMPOSITIONS OF MONOCLINIC AMPHIBOLES

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ABSTRACT

Chemical analyses of amphiboles have been collected, and variation of relatively pure members plotted on a series of eight compositional quadrilaterals; an attempt has been made to avoid lumping by distinguishing Fe^{2+}, Mg, Fe^{3+} and Al as independent chemical variables. Magnesium-rich and intermediate Mg-Fe^{2+} clinoamphiboles are common but, excepting grunerites, ferrous iron-rich members are rare; however, some calcic and sodic amphiboles closely approach ferrous-ferric end members. Substitution of sodium and aluminum^{iv} for one silicon appears to be complete in calcic amphiboles.

Few natural amphiboles approach pure end member compositions but evaluation of cell dimensions for synthetic amphibole end members, some produced for the first time in this investigation (edenite, ferroedenite, magnesiohastingsite and hastingsite), shows that replacement of Mg by Fe^{2+} results in systematic unambiguous lattice parameter increases: (1) b increases because the larger atom in M_2 pushes adjacent double chains farther apart; (2) $a \sin \beta$ increases as a result of the increased mean size of the octahedrally coordinated atoms; and (3) c increases slightly through unkinking of the double chains. Replacements of silicon by aluminum^{iv} and magnesium by ferric iron do not affect the unit cell dimensions significantly. Furthermore, study of refined amphibole structures shows that the basic structural unit, the double chain, changes only slightly in size with substitutions; the emplacement of larger ions is reflected in unkinking of chains and increasing distances between adjacent chains. Among iron-bearing amphiboles, both Fe^{2+} and Fe^{3+} commonly are present, hence these amphiboles have both expanded lattice parameters and higher indices of refraction than their magnesium counterparts.

INTRODUCTION

The structural formula for amphiboles is often abbreviated $A_{0-1}X_2Y_5Z_8O_{22}(OH,O,F,Cl)_2$. Cation coordination numbers are as follows: $A = 10$; $X = 6-8$; $Y = 6$; $Z = 4$. For amphiboles in which the A site is unoccupied, the formulas will be written $\circ X_2Y_5Z_8O_{22}(OH,O,F,Cl)_2$. The calcic amphiboles edenite, tremolite, tschermakite and the hornblendes magnesiohastingsite, pargasite and iron-bearing equivalents are members of complicated solid solution series. This is reflected in their variable chemical compositions: $(Na, K)_{0-1}$ $(Na, Ca, Mn^{2+}, Mg, Fe^{2+})_2$ $(Mg, Fe^{2+}, Fe^{3+}, Mn^{2+}, Ti, Al)_5$ $(Si, Al, Fe^{3+})_8O_{22}(OH, O, F, Cl)_2$. Because of their chemical complexity, these amphiboles cannot be expressed graphically in the familiar two or three component composition diagrams. Not only do the number of components exceed three, but the substitution of some

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ions can take place in dissimilar structural sites giving rise to different properties. For example, iron can be found in tetrahedral, octahedral and eight-fold sites; the site Fe occupies as well as its valence state can affect the physical properties of the amphibole and even the occupancy of other sites.

Sodic amphiboles are somewhat more simple. With the exception of arfvedsonites and kataphorites which contain tetrahedral aluminum (and rarely ferric iron), and alkali metal ions in the A site, most sodic amphiboles can be referred to the glaucophane and magnesioriebeckite series with the formula $\circ(Na, K, Ca)_2(Mg, Fe^{2+}, Fe^{3+}, Al)_5Si_8O_{22}(OH, O, F, Cl)_2$.

Members of the cummingtonite-grunerite series are chemically the simplest amphiboles. These are adequately represented by the formula $\circ(Mg, Fe^{2+})_2(Mg, Fe^{2+})_5Si_8O_{22}(OH, F, Cl)_2$; however, Mn-bearing and aluminous varieties also exist.

Mean sizes of the ions in the various structural positions significantly affect lattice dimensions of the clinoamphiboles. Whittaker (1960) showed that increases in the mean size of the cations[1] in the M_4 site were related to increase in β. A. A. Colville and G. V. Gibbs (pers. comm.) plotted $a \sin \beta$ (d^{100}) versus β for a large number of amphiboles and showed that the amphiboles fall into natural series according to the size of the cation[1] in the M_4 site and the average size of the metal cations in the octahedral sites. Klein (1964) working with natural cummingtonite-grunerites was able to correlate increases in unit cell size and refractive indices to corresponding increases in iron content. Similar relations have been presented recently by Viswanathan and Ghose (1965). However, most attempts to assess the effects of substitutions on lattice parameters have not been especially successful, owing to the chemical complexities and a lack of adequate knowledge concerning the structural site occupancies of the amphiboles studied.

Graphical and statistical work by Deer, *et al.* (1963) and by Winchell (1963) shows that although the substitution of sodium and aluminum for magnesium and silicon has little effect on the optical properties of amphiboles, the substitution of Fe^{2+} for Mg or Fe^{3+} for Al greatly increases the indices of refraction for every amphibole solid solution series considered.

Chemical variation of the calcic amphiboles was discussed by Hallimond (1943) and Boyd (1959) and the sodium and aluminum variation presented graphically. In the present work Hallimond's and Boyd's plots have been expanded in terms of iron, magnesium and aluminum

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[1] Ionic radii according to Goldschmidt (1954).

end members to show the extent of the Fe^{2+}-Mg and Fe^{3+}-Al variations in natural calcic amphiboles. Previous efforts to establish relationships between hornblende lattice parameters and chemical compositions have been largely unsuccessful precisely because of the chemical complexities of the natural amphiboles for which x-ray data were available.

Inasmuch as no conclusions could be drawn from consideration of the data on complex natural amphiboles, unit cell parameters were determined for the more simple synthetic analogues. The new amphiboles synthesized were edenite, ferroedenite, magnesiohastingsite and hastingsite. Samples of synthetic tremolite and pargasite were obtained through the courtesy of F. R. Boyd of The Geophysical Laboratory. The cell parameters of fluortremolite, fluoredenite, ferrotremolite, ferropargasite, riebeckite, magnesioriebeckite and glaucophane were available from earlier work. Structural studies on riebeckite (Colville and Gibbs, 1965), crocidolite (Whittaker 1949), tremolite (Warren 1929), actinolite (Zussman, 1955), cummingtonite (Ghose, 1961) and grunerite (Ghose
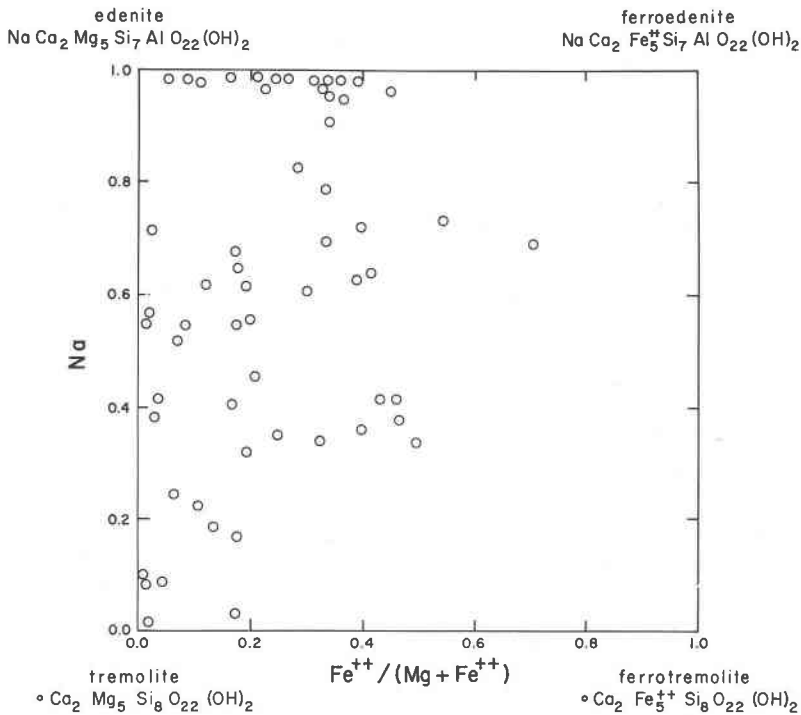

FIG. 1. Distribution of natural amphiboles in the composition range:
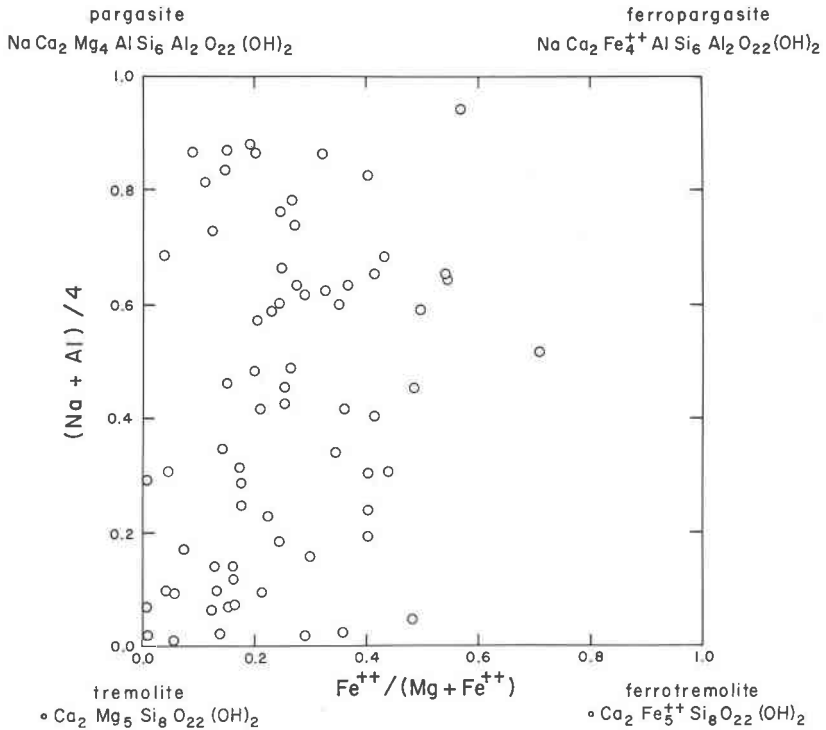tremolite-ferrotremolite-edenite-ferroedenite.

Fig. 2. Distribution of natural amphiboles in the composition range:
tremolite-ferrotremolite-pargasite-ferropargasite.

and Hellner, 1959) proved most useful in evaluating lattice parameter differences and site occupancies in the synthetic amphiboles. Structural studies of common hornblendes (Heritsch *et al.*, 1957, 1960; Heritsch and Kahler, 1960; Heritsch and Riechert, 1960) were two dimensional refinements and were not sufficiently detailed to be useful in the present investigation in that they provided no information on the distributions of Mg, Fe and other metal cations in the various cation sites.

Compositional Variations of the Natural Amphiboles

The diagrams which follow were prepared from analyses of calcic and sodic amphiboles collected from the literature. Chemical formulas were calculated by a program written for the IBM 1620 computer; the formulas were computed on the basis of 46 negative charges per formula ($=23$ oxygen) assuming one H_2O ($=2OH^-$). All of the calcic amphibole analyses utilized contain less than 0.29 ions Ti per calculated chemical formula, $Mn < 0.28$, $(Na+K) < 1.5$, $Ca > 1.5$, $(F+Cl) < 0.30$ and negli-
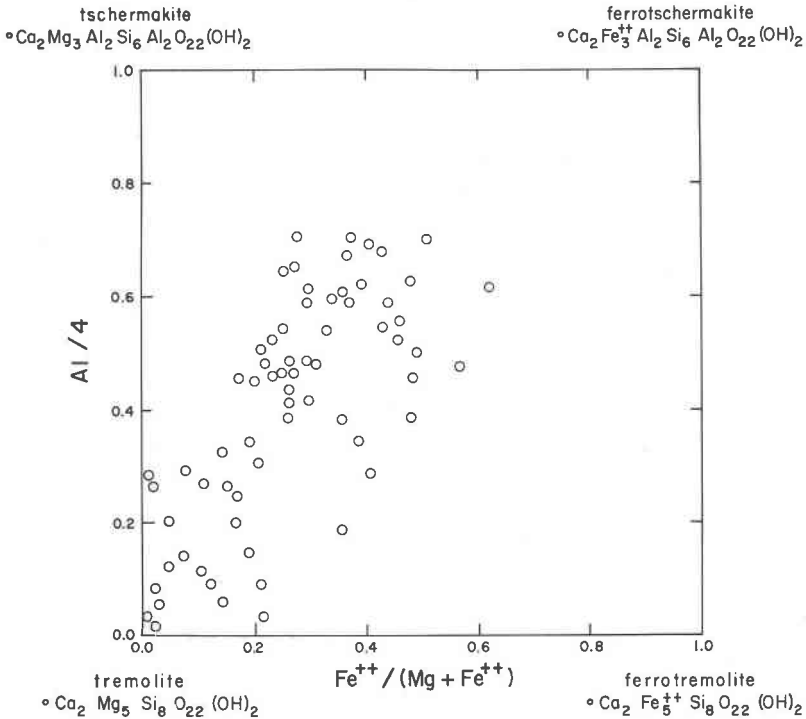
FIG. 3. Distribution of natural amphiboles in the composition range:
tremolite-ferrotremolite-tschermakite-ferrotschermakite.

gible amounts of unusual components. For sodic amphiboles, extraneous
ions per formula unit were: $Ti < 0.25$, $Mn < 0.30$, $(Ca+K) < 0.50$, Na
> 1.35 and $(F+Cl) < 0.30$. The data were plotted on eight diagrams
(Figs. 1–8) to show the ranges of composition among *relatively pure* mem-
bers of various solid solution series. The calcic amphibole plots are essen-
tially expansions of the pseudobinary side lines and the tremolite-parga-
site diagonal of the plots of Hallimond (1943) and Boyd (1959). The pur-
pose of the new diagrams is to show the significant natural variations
between iron- and magnesium-bearing end members whereas Hallimond
and Boyd lumped Fe^{2+} and Mg and showed compositional distributions
among types varying in $(Mg+Fe^{2+})$, Na and Al contents only.

As seen from Figs. 1–3, where ferric iron-bearing compositions are
excluded, natural variations are restricted to relatively Mg- rich am-
phiboles, approaching the compositions of tremolite, edenite and parga-
site, but not tschermakite (see diagrams for formulas). Figure 4 exhibits
the chemical range among the sodic hornblendes; no natural hornblendes

close to ferropargasite have been described. Figures 5–7 demonstrate that common hornblendes carry abundant pargasite+magnesiohastingsite, ferropargasite+hastingsite, edenite, and tremolite end members, but only minor amounts of the ferroedenite, ferrotremolite, tschermakite and ferrotschermakite end members. Sodic amphiboles are less common than calcic analogues, but chemical variation as shown in Fig. 8 is vir-
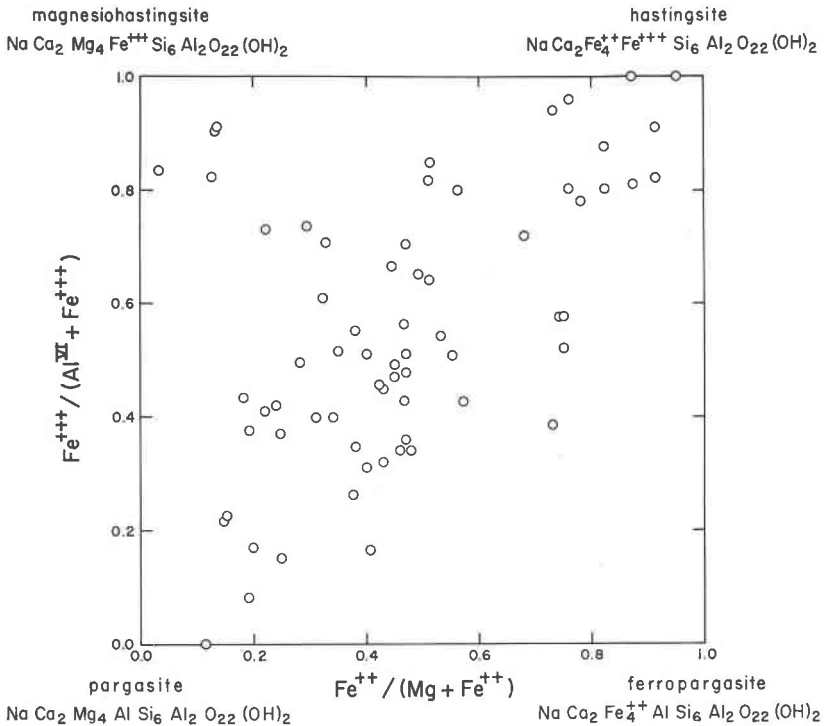

FIG. 4. Distribution of natural amphiboles in the composition range: pargasite-ferropargasite-magnesiohastingsite-hastingsite.

tually complete among the three end members glaucophane, magnesioriebeckite and riebeckite; ferroglaucophane apparently does not occur in nature.

The variation is clearly not as extensive between Fe^{2+}-Mg substitution types as between (Na+Al)-Si types. As demonstrated by Leake (1965a), the maximum amount of octahedrally coordinated aluminum is proportional to Al^{IV} in calcic amphiboles; however, this relationship seems to be inapplicable to sodic amphiboles. The Mg-rich hornblendes are much more common than Fe^{2+}-rich hornblendes, some ferrous horn-

blendes not even being represented. Synthetic studies by Boyd (1959) and Gilbert (1966) show that the Mg hornblende pargasite is stable under a wide variety of temperature and pressure conditions, whereas the Fe^{2+} hornblende ferropargasite is confined to conditions of lower temperatures and relatively low oxygen partial pressures. The riebeckites and ferro-tremolites are also of more restricted stability range than their Mg
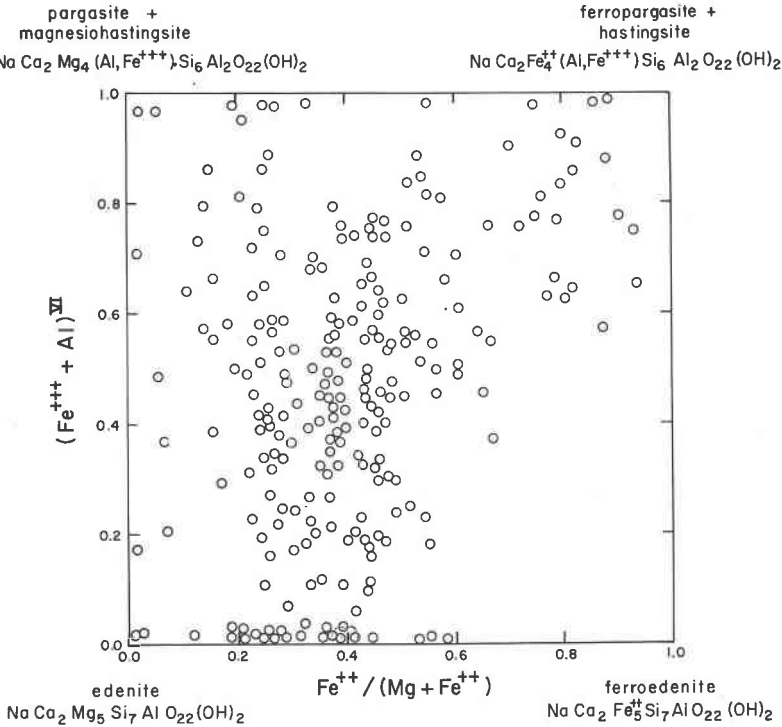

Fig. 5. Distribution of natural amphiboles in the composition range: edenite-ferroedenite-pargasite+magnesiohastingsite-ferropargasite+hastingsite.

counterparts (Boyd, 1959; Ernst, 1960, 1962, 1966). Restricted stability as well as rarity of very iron-rich bulk compositions probably accounts for the scarcity of iron-rich amphiboles in nature. However, laboratory syntheses of several iron-rich amphiboles show that there is no struc-tural or chemical barrier to complete solid solution between most Fe^{2+} and Mg end members.

Many amphiboles could not be plotted on diagrams such as Figs. 1–8 because they contain appreciable amounts of other constituents, or have

compositions intermediate to several of the end members considered. The importance of these plots lies in the fact that they show *unambiguously* the compositional range of a large number of amphiboles; combination of independent chemical variables has been largely avoided.

EXPERIMENTAL PROCEDURE

Synthetic edenite, ferroedenite, magnesiohastingsite and hastingsite were produced in this study by conventional hydrothermal techniques (e.g. Ernst, 1960, p. 11–12). The experimental conditions of the syntheses are given in Table 1.

X-RAY DATA

To obtain precise lattice parameters, samples of synthetic amphiboles were oscillated five cycles on a Norelco diffractometer using Cu K_α radiation for edenite and FeK_α radiation for the other amphiboles. Re-
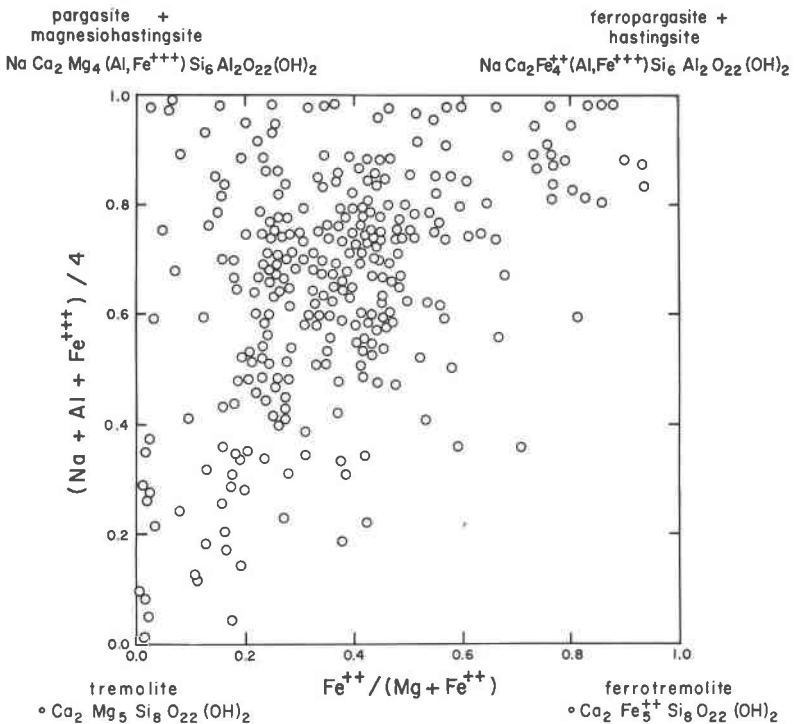

FIG. 6. Distribution of natural amphiboles in the composition range: tremolite-ferrotremolite-pargasite+magnesiohastingsite-ferropargasite+hastingsite.

pargasite + magnesiohastingsite
$Na\,Ca_2\,Mg_4\,(Al,Fe^{+++})\,Si_6\,Al_2\,O_{22}(OH)_2$

ferropargasite + hastingsite
$Na\,Ca_2\,Fe_4^{++}\,(Al,Fe^{+++})\,Si_6\,Al_2\,O_{22}(OH)_2$

tschermakite
$\circ Ca_2\,Mg_3\,Al_2\,Si_6\,Al_2\,O_{22}(OH)_2$

ferrotschermakite
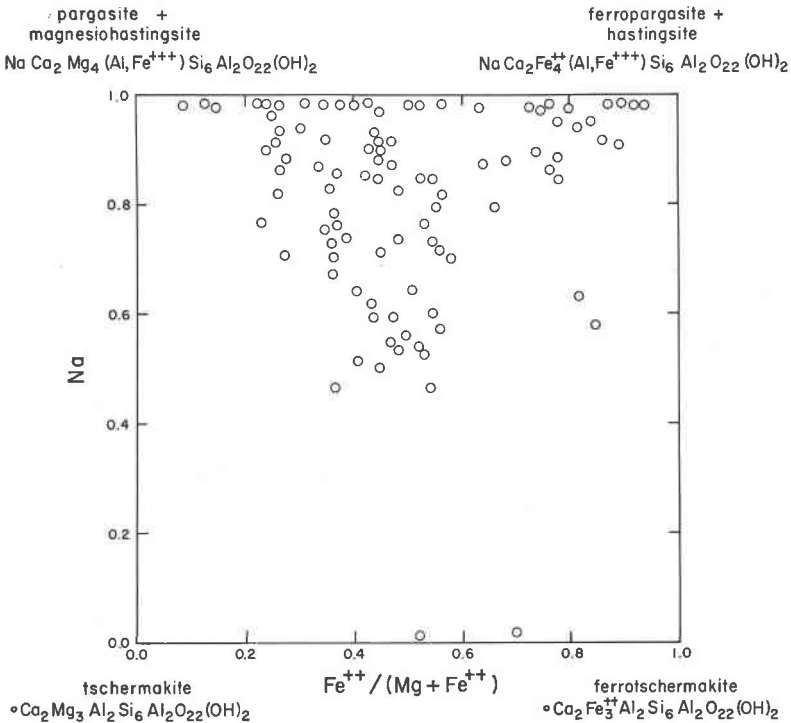$\circ Ca_2\,Fe_3^{++}Al_2\,Si_6\,Al_2\,O_{22}(OH)_2$

$Fe^{++}/(Mg+Fe^{++})$

Na

Fig. 7. Distribution of natural amphiboles in the composition range: tschermakite-ferrotschermakite-pargasite+magnesiohastingsite-ferropargasite+hastingsite.

finement techniques were described by Ernst (1962). Lattice parameters and standard errors of newly synthesized amphiboles and those synthesized by Boyd are presented in Table 2, along with published parameters of other synthetic amphiboles.

Except for the work of Kohn and Comeforo on fluortremolite and fluoredenite, all unit cell dimensions were determined in this laboratory by the techniques described above.

REFRACTIVE INDICES OF SYNTHETIC AMPHIBOLES

Optical properties of synthetic amphiboles were obtained on a flat stage microscope employing white light and refractive index oils of 0.002 refringence interval. They are estimated to be accurate to within 0.003. Winchell (1963, Table 4, first set of values) obtained corresponding end member refringence values by regression analysis of the refractive indices and chemical analyses of a large number of chemically complex natural
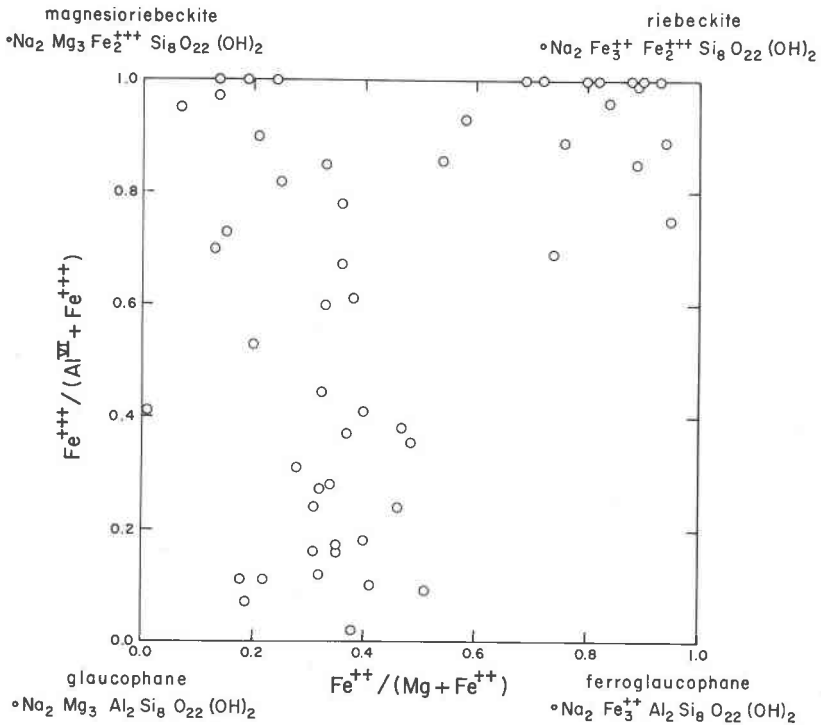
FIG. 8. Distribution of natural amphiboles in the composition range: glaucophane-ferroglaucophane-magnesioriebeckite-riebeckite.

amphiboles. Refractive index values for some of these same end member amphiboles have been presented by Deer, *et al.* (1963). These values were extrapolated directly from plots of the refractive indices of natural amphiboles of intermediate compositions.

The three above mentioned sets of refractive index data are compared in Table 3. In general, a slightly better correlation exists between the indices of our synthetics and refringence data of Deer, *et al.* (1963), than

TABLE 1. RUN CONDITIONS

	Temperature (degrees C)	Pressure (kilobars)	Time (days)	Oxygen Buffer
Edenite	850	2.0	3	—
Ferroedenite	600	3.0	31	iron-wüstite
Magnesiohastingsite	850	2.0	3	hematite-magnetite
Hastingsite	600	3.0	31	fayalite-magnetite-quartz

TABLE 2. LATTICE PARAMETERS OF SYNTHETIC AMPHIBOLES

	a, Å	b, Å	c, Å	β	$a \sin \beta$	V, Å³
○$Ca_2Mg_5Si_8O_{22}(OH)_2$, tremolite, this study and Boyd (1959)	9.833 ±0.005	18.054 ±0.009	5.268 ±0.004	104.52 ±0.07	9.52	905.3 ±1.0
○$Ca_2Fe_5^{2+}Si_8O_{22}(OH)_2$ ferrotremolite, Ernst (1966) ave. of 10	9.87	18.34	5.30	104.5	9.59	939
$NaCa_2Mg_4AlSi_6Al_2O_{22}(OH)_2$, pargasite, this study and and Boyd (1959)	9.906 ±0.010	17.986 ±0.017	5.265 ±0.008	105.30 ±0.14	9.51	904.7 ±1.9
$NaCa_2Fe_4^{2+}AlSi_6Al_2O_{22}(OH)_2$, ferropargasite, Gilbert (1966)	9.95	18.14	5.33	105.3	9.60	928
$NaCa_2Mg_4Fe^{3+}Si_6Al_2O_{22}(OH)_2$, magnesiohastingsite, this study	9.925 ±0.015	17.982 ±0.030	5.289 ±0.011	105.61 ±0.12	9.56	909.1 %2.8
$NaCa_2Fe_4^{2+}Fe^{3+}Si_6Al_2O_{22}(OH)_2$, hastingsite, this study	9.979 ±0.027	18.152 ±0.063	5.325 ±0.027	105.20 ±0.34	9.58	930.8 ±5.97
$NaCa_2Mg_5Si_7AlO_{22}(OH)_2$, edenite, this study	9.853 ±0.015	18.005 ±0.011	5.236 ±0.015	104.40 ±0.25	9.51	899.8 ±1.0
$NaCa_2Fe_5^{2+}Si_7AlO_{22}(OH)_2$, ferroedenite, this study	9.999 ±0.010	18.217 ±0.021	5.314 ±0.014	105.50 ±0.17	9.59	932.8 ±3.0
○$Na_2Mg_3Fe_2^{3+}Si_8O_{22}(OH)_2$, magnesioriebeckite, Ernst (1963) ave. of 7	9.73	17.95	5.30	103.3	9.47	901
○$Na_2Fe_3^{2+}Fe_2^{3+}Si_8O_{22}(OH)_2$, riebeckite, Ernst (1962) ave. of 15	9.73	18.06	5.33	103.3	9.47	913
$Na_{2.4}Fe_{4.9}^{2+}Fe_{0.7}^{3+}Si_{7.7}Fe_{0.3}^{3+}O_{22}(OH)_2$ riebeckite-arfvedsonite Ernst (1962) ave. of 7	9.85	18.15	5.32	103.2	9.59	926
○$Na_2Mg_3Al_2Si_8O_{22}(OH)_2$, glaucophane I, Ernst (1963) ave. of 10	9.75	17.91	5.27	102.8	9.50	897
○$Na_2Mg_3Al_2Si_8O_{22}(OH)_2$, glaucophane II, Ernst (1963) ave. of 8	9.64	17.73	5.28	103.6	9.37	877
$NaCa_2Mg_5Si_7AlO_{22}F_2$, fluoredenite, Kohn & Comeforo (1955)	9.85	18.00	5.28	104.8	9.52	905
○$Ca_2Mg_5Si_8O_{22}F_2$, fluortremolite, Comeforo & Kohn (1954)	9.78	18.01	5.27	104.5	9.47	899

between our measurements and Winchell's (1963) machine computations. However, the three sets of data agree well only for tremolite α and γ, hastingsite α and γ, edenite γ, and magnesioriebeckite α and γ.

STRUCTURE AND SITE NOMENCLATURE OF CLINOAMPHIBOLES

Clinoamphiboles belong to the equivalent space groups $C\ 2/m$ and $I\ 2/m$. In this work $C\ 2/m$ will be used exclusively. The structure is

basically a double chain of SiO_4 (and in some cases AlO_4) tetrahedra crosslinked by cations to neighboring double chains as shown in Fig. 9. The repeat along the length of the chain is defined as the c parameter, the repeat laterally across the two overlapping double chains as b, and the separation across adjacent facing chains, normal to b and c as $a \sin \beta$, β being the obtuse angle between a and c.

There are 14 non-equivalent sites in the amphibole asymmetric unit. Six of these are occupied by oxygen; three (O_5, O_6, O_7) are shared by two Z cations each and three (O_1, O_2, O_4) are bound to one Z cation and to chain-linking X and/or Y cations. The seventh anion site (O_3) is occu-

TABLE 3. REFRACTIVE INDICES OF SYNTHETIC AMPHIBOLES COMPARED WITH END MEMBER VALUES DEDUCED FROM NATURAL AMPHIBOLES

	Synthetics[1]		Winchell (1963, Table 4)		Deer et al. (1963)	
	α	γ	α	γ	α	γ
Tremolite	1.601	1.625	1.600	1.627	1.599	1.622 (p. 249)
Ferrotremolite	1.689 (ave.)		1.672	1.693	1.688	1.705 (p. 249)
Paragasite	1.624	1.645	1.625	1.641	1.613	1.635 (p. 264)
Ferropargasite	1.700	1.718	1.682	1.694		
Magnesiohastingsite	1.652	1.665	1.646	1.668		
Hastingsite	1.702	1.728	1.703	1.721	1.702	1.730 (p. 264)
Edenite	1.621	1.634	1.613	1.631	1.61	1.63 (p. 299)
Ferroedenite	1.700	1.726	1.683	1.698	1.71	1.73 (p. 299)
Magnesioriebeckite	1.654	1.672	1.651	1.663	1.654	1.668 (p. 333)
Riebeckite	1.709	1.718	1.693	1.703	1.701	1.717 (p. 333)
Glaucophane II	1.596	1.620	1.608	1.608	1.606	1.627 (p. 333)
Ferrogluaucophane			1.651	1.649	1.69	1.71 (Fig. 86)

[1] See Table 2 for references and formulas.

pied by OH^-, O^{2-}, F^- or Cl^- and is located about in the middle of the hole in the tetrahedral chain at the level of the apical oxygens (O_1 and O_2); this anion is linked only to Y cations. Of the seven remaining sites, two are cation sites of four-fold coordination and are occupied by Z-type cations. The Z-type cations were all silicon in tremolite, the first amphibole studied (Warren 1929), and the sites were thus named Si_I and Si_{II}. Of the remaining sites, M_1, M_2, and M_3 are sites of six-fold coordination and are occupied by Y cations. M_4 is a site of six or eight-fold coordination and is occupied by X cations. The A site is a site of approximately ten-fold coordination and is occupied by A cations; this position can be vacant, partially or fully occupied.
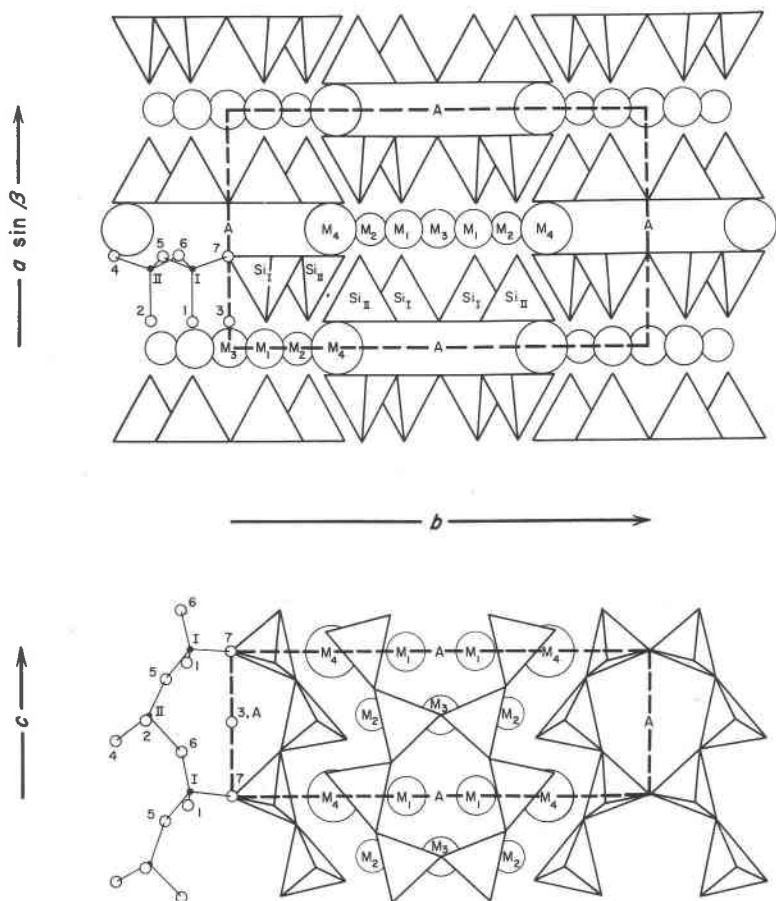
FIG. 9. Schematic diagrams showing clinoamphibole structural elements. Double chains are drawn in perspective ignoring the slight warping away from (100), with the two different tetrahedral sites designated Si_I and Si_{II}. The tetrahedral cation sites are also shown as small solid circles in the left-hand portions of the diagrams. Six-fold coordinated cations are represented by large circles M_1, M_2 and M_3, six–eight-fold coordinated cations by large circles M_4. The 10-fold cation position is represented simply by the letter A. Anion positions are shown, only on the left-hand side of the diagrams, by small open circles, 1–7; the O_3 anion is generally hydroxyl or fluorine.

THE OCCUPANCY OF STRUCTURAL SITES IN NATURAL AMPHIBOLES AND IN THE SYNTHETIC AMPHIBOLES STUDIED

General statement. In natural calcic and sodic amphiboles calculations of the formulas often show that (Ca+Na) is present in amounts in excess of that which will fill the M_4 sites. The excess sodium along with any

potassium present is assigned to the A site, the only site besides M_4 which is large enough to accommodate appreciable amounts of K, Na or Ca. In the synthetic amphiboles studied, bulk compositions were always such that the A site would always be completely full or completely empty.

The O_3 site in natural amphiboles can be occupied by OH^-, O^{2-}, F^-, or Cl^- in any combination but usually with either OH^- or F^- predominating. Since excess H_2O was present in all runs, as the only volatile constituent, the synthetics studied are assumed to contain only OH^-.

In natural amphiboles the two tetrahedral sites, Si_I and Si_{II}, corresponding to Z of the chemical formula, usually contain more than 75% Si and in many varieties like riebeckite nearly 100%. In the calcic amphiboles the substitution of Al in this site is commonly 10–15% and often reaches 25%. In the synthetic amphiboles studied three combinations are represented in these sites:

(1) All Si, e.g. tremolite, ferrotremolite, magnesioriebeckite, riebeckite, glaucophane I, glaucophane II and fluortremolite; (2) 12.5% Al, e.g. edenite, ferroedenite and fluoredenite; (3) 25% Al, e.g. pargasite, ferropargasite, magnesiohastingsite and hastingsite.

The M_4 sites correspond to X of the chemical formula and in natural calcic and sodic amphiboles are filled almost exclusively with Na and Ca. Minor amounts of Fe^{2+} and Mg may be present in a few cases: this must represent a small amount of solid solution between the calcic and sodic amphiboles on the one hand and members of the cummingtonite-grunerite series on the other. In cummingtonites and grunerites, M_4 is at least 75% Fe^{2+} (Ghose 1961; Ghose and Hellner 1959). In the hornblendes X is at least 75% calcium with sodium making up the balance. For sodic amphiboles X is almost entirely Na with only minor Ca or other cations. In the synthetics studied X is either entirely sodium or entirely calcium.

The M_1, M_2 and M_3 sites of natural amphiboles can contain a large variety of cations; among those reported are Mg, Mn^{2+}, Fe^{2+}, Fe^{3+}, Zn, Ti, Ni, Al, Cr, Sn and Co. A few amphiboles rich in manganese and titanium have been reported, but the most common occupants of these sites are Mg, Al, Fe^{2+} and Fe^{3+}. The work of Whittaker (1949) on the sodic amphibole crocidolite (= magnesioriebeckite) suggests that ferrous iron and magnesium are rather equally distributed in the slightly larger M_1 and M_3 sites with the smaller Fe^{3+} and Al ions concentrated in M_2. Hence the octahedrally-bound metal atoms apparently comprise two distinct types, (1) smaller M_2-preferring ions and (2) those which will be randomly distributed in M_1 and M_3. These observations may not be valid for amphiboles with compositions approaching $\circ Fe_7^{2+}Si_8O_{22}(OH)_2$. In the magnesium-rich cummingtonite, Mg is the M_2-preferring atom and as the iron content becomes larger M_1, M_2 and M_3 become more

nearly equal in Fe^{2+}, so that in iron-rich grunerite there is no distinct preference of sites (Ghose and Hellner, 1959; Ghose, 1961). In the synthetic amphiboles considered here, substitutions of iron, magnesium and aluminum in M_1, M_2 and M_3 are the important variables affecting cell parameters, and will be considered in the following section; occupancy of M_4 and Si_I and S_{II} will also be discussed.

For a scheme of cation distribution in intermediate members of amphibole solid solutions, the reader is referred to a recent paper by Ghose (1965).

The b axis. The perpendicular distance from Si_{II} to the mirror plane (the a–c plane) is a good measure of the individual double chain width in the b axis direction (Fig. 9). These distances are shown in Figs. 10–12 for sodic and calcic amphiboles of known structures. Compared values are: tremolite 3.07 Å (Warren, 1929), actinolite 3.08 Å (Zussman, 1955), crocidolite 3.05 Å (Whittaker, 1949), riebeckite 3.06 Å (Colville and Gibbs, 1965), cummingtonite 3.068 Å (Ghose, 1961), and grunerite 3.074 Å (Ghose and Hellner, 1959). Obviously the basic chain width changes very little with Fe^{2+}-Mg (or any other) substitutions in these calcic and sodic amphiboles. The b repeat must be a function of the mean sizes of, not of cations occupying M_1 and M_3, but of the lateral linking cations occupying sites M_2 and M_4. For synthetic amphiboles considered, the M_4 content is fixed as either all Ca or all Na, assuming no disorder among X and Y cations; because of the near identity of Ca and Na ionic radii,[1] the species of the X cations should scarcely affect the length of the b axis anyway. Hence, the observed changes in synthetic amphibole b axes should be a function principally of the size of the cation occupying M_2. As discussed further on, b axis repeats among members of the cummingtonite-grunerite series depend on Fe^{2+}-Mg occupancy of M_4 as well as M_2.

In tremolite $\circ Ca_2Mg_5Si_8O_{22}(OH)_2$, $b = 18.05$ Å. When all the Mg is replaced by Fe^{2+} the M_2 site will then be filled with an ion whose diameter is 0.16 Å larger. Because there are two M_2 sites in a repeat of b, the increase in b should be 0.32 Å; the observed increase in b in ferrotremolite is 0.29 Å in good agreement with the calculated value.[2]

In edenite $NaCa_2Mg_5Si_7AlO_{22}(OH)_2$, $b = 18.00$ Å. The predicted increase of b for ferroedenite is the same as for ferrotremolite. However, the observed increase is puzzling, being only 0.21 Å; this value is about

[1] All our calculations in this paper are based on ionic radii as given by Ahrens (1952) and Green (1959).

[2] It is of course true that the b axis of the amphibole structure spans two chain widths, but it does not follow that four M_2 sites are included in the repeat along b. This seeming paradox results from the staggering of adjacent double chains in the structure: as shown in Fig. 9, any line parallel b encounters no more than two M_2 sites per unit repeat.

$\frac{2}{3}$ of the predicted increase, and is well outside the analytical error. Perhaps some of the iron in the ferroedenite is actually in the ferric state.

In pargasite $NaCa_2Mg_4AlSi_6Al_2O_{22}(OH)_2$, $b = 17.99$ Å. In this case, replacement of all the Mg by Fe^{2+} does not necessarily fill M_2 with Fe^{2+} since both pargasite and ferropargasite have one octahedral aluminum per formula unit. If Al is restricted to M_2 in both cases as in crocidolite, then the predicted increase in b for ferropargasite is 0.16 Å, because M_2 occupancy would be 50% Al, 50% Fe^{2+}. The observed increase is 0.15 Å. A random distribution of Al in the M_1, M_2 and M_3 sites would give a

crocidolite (Whittaker 1949)

	b	c
Si_I	1.58	.43
Si_{II}	3.05	3.11
O_5	2.51	4.27
O_6	1.98	1.87
O_7	0.	.13
M_3	0.	0.

riebeckite (A. Colville and Gibbs 1964)

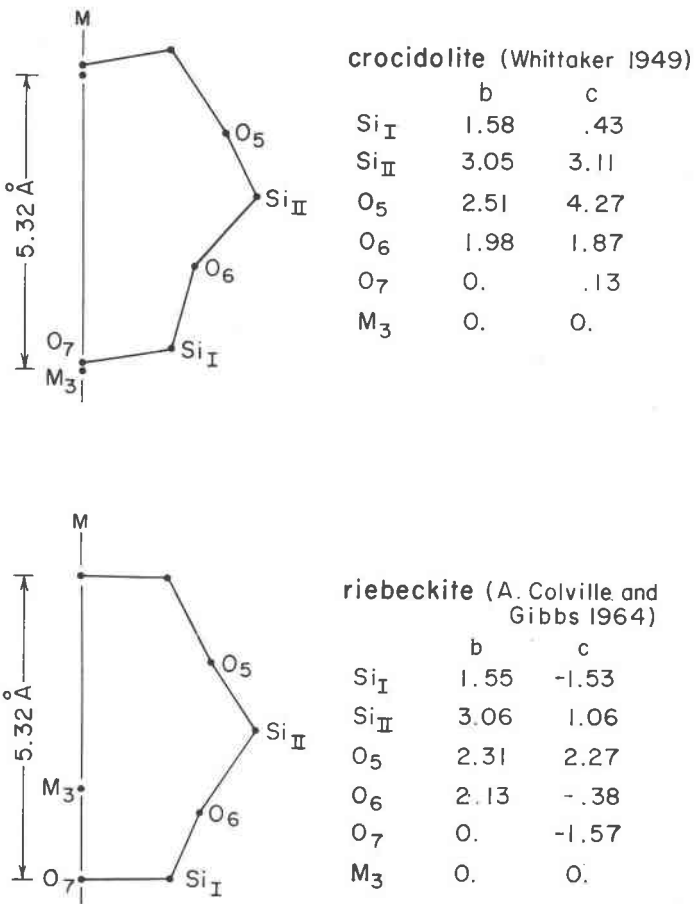|	b	c
Si_I	1.55	-1.53
Si_{II}	3.06	1.06
O_5	2.31	2.27
O_6	2.13	-.38
O_7	0.	-1.57
M_3	0.	0.

FIG. 10. (100) projection of crocidolite and riebeckite chains. The (010) symmetry plane is normal to the plane of the projection and passes through successive O_7 and M_3 sites. Coordinates given are relative to M_3 (0,0) in Å.

tremolite (Warren 1929)

	b	c
Si_I	1.51	0.05
Si_{II}	3.07	2.58
O_5	2.42	3.95
O_6	2.13	1.32
O_7	0.	-.53
M_3	0.	0.

actinolite (Zussman 1955)

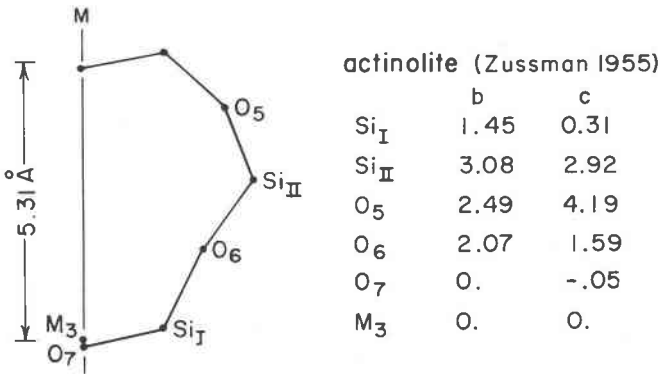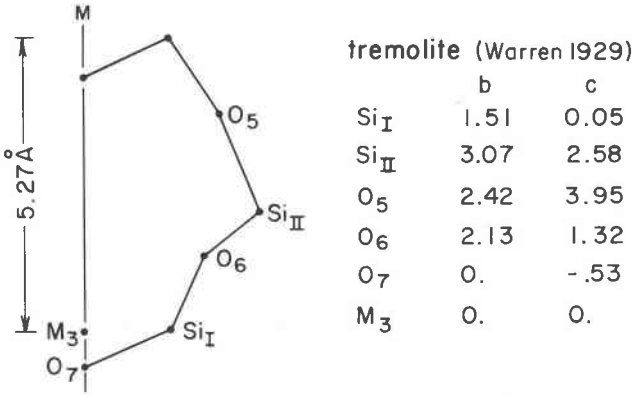|	b	c
Si_I	1.45	0.31
Si_{II}	3.08	2.92
O_5	2.49	4.19
O_6	2.07	1.59
O_7	0.	-.05
M_3	0.	0.

FIG. 11. (100) projection of tremolite and actinolite chains similar to Fig. 10. Actinolite has 40% octahedral Fe^{2+}.

calculated b increase of 0.25 Å. The Al^{vi} is apparently concentrated in M_2 and the b increment is strictly a function of the mean size of the cation in this site.

In magnesiohastingsite $NaCa_2Mg_4Fe^{3+}Si_6Al_2O_{22}(OH)_2$, $b = 17.98$ Å. The situation is analogous to that of pargasite. If the small Fe^{3+} (which has an ionic radius close to that of Mg) is assumed to be located in M_2 the predicted increase in b for hastingsite is again 0.16 Å. The observed increase is 0.17 Å. The slightly higher value may be due to minor disordering in hastingsite resulting in slightly greater amounts of Fe^{2+} in M_2, inasmuch as random distribution gives a greater increase of b than

the assumption of all Fe^{3+} in M_2. Alternatively, the ferric-ferrous ratio of the synthetic hastingsite may be slightly less than anticipated, which would yield the same observed effect.

In the sodic amphiboles, the change from magnesioriebeckite, $\circ Na_2Mg_3Fe_2^{3+}Si_8O_{22}(OH)_2$ ($b = 17.95$ Å), to riebeckite would be accompanied by no change in b if the Fe^{3+} were all ordered in the M_2 site in both end members. With disordering of Fe^{3+} and Fe^{2+}, b would increase in riebeckite; an increase in b with disorder might not be observed in magnesioriebeckite because Fe^{3+} is so close to Mg in ionic radius (0.64
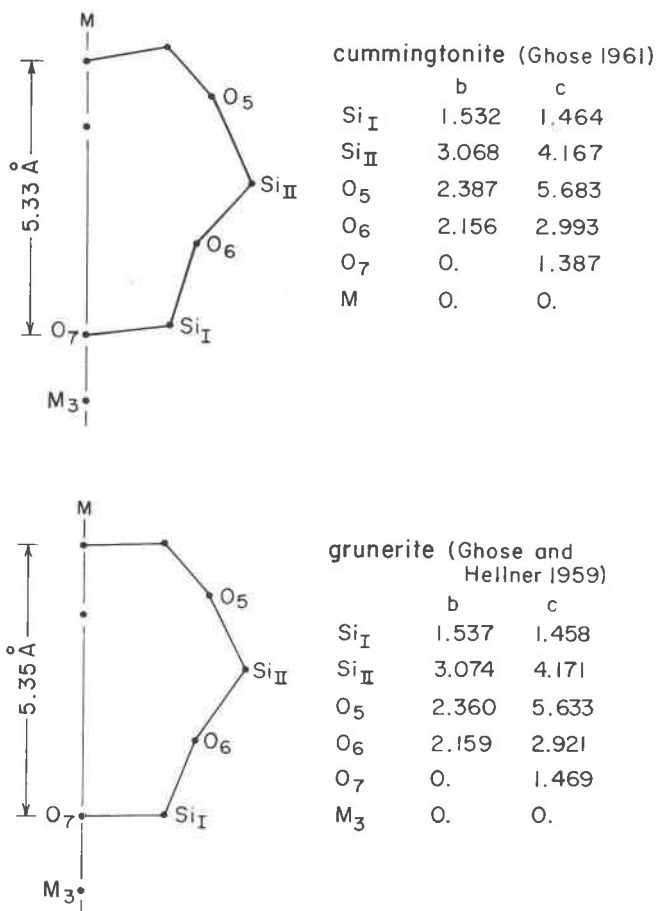
cummingtonite (Ghose 1961)

	b	c
Si_I	1.532	1.464
Si_{II}	3.068	4.167
O_5	2.387	5.683
O_6	2.156	2.993
O_7	0.	1.387
M	0.	0.

grunerite (Ghose and Hellner 1959)

	b	c
Si_I	1.537	1.458
Si_{II}	3.074	4.171
O_5	2.360	5.633
O_6	2.159	2.921
O_7	0.	1.469
M_3	0.	0.

FIG. 12. (100) projection of cummingtonite and grunerite chains similar to Fig. 10. In cummingtonite 2.50 of the 7 metal atoms in M_1, M_2, M_3 and M_4 sites are Fe^{2+}; in grunerite 4.67 of the 7 metals are Fe^{2+}.

and 0.66 Å respectively). The observed change is an increase of 0.11 Å in riebeckite. This corresponds to about 27% Fe^{2+} in the M_2 site of riebeckite. A random distribution would place 60% Fe^{2+} in the M_2 site so there appears to be a preference for Fe^{3+} to concentrate in M_2. Synthetic riebeckite-arfvedsonite solid solution appears to have 65% ferrous iron in M_2, the remainder being ferric iron, as deduced from micrometric analysis (Ernst, 1962). Mean ionic radius of this cation is thus 0.705 Å, so the computed increase in b going from magnesioriebeckite to riebeckite-arfvedsonite solid solution would be 0.26 Å; the observed value is 0.20 Å,

Although data are not available on the change between glaucophane. $oNa_2Mg_3Al_2Si_8O_{22}(OH)_2$, and ferroglaucophane, glaucophane itself undergoes a significant change of lattice parameters, apparently from a high temperature-low pressure polymorph, Gl I ($b=17.91$ Å) to a low temperature-high pressure polymorph, Gl II ($b=17.73$ Å). The change in b is most significant and has been ascribed to more complete disordering of M_2 occupancy at high temperature and more complete ordering at high pressures (Ernst, 1963). The calculated change from perfect Al order in M_2 to perfect disorder for b is approximately 0.36 Å. The observed change is 0.18 Å. This can mean that Gl I is not perfectly disordered or that Gl II is not perfectly ordered or that both are less than perfect. In any case the magnitude of the change suggests that the M_2 site of Gl I is about 50% ordered than that of Gl II.

Klein (1964), in a study of natural amphiboles of the Mn-bearing cummingtonite-grunerite series, $^0Mg_7Si_8O_{22}(OH)_2$-$^0Fe_7Si_8O_{22}(OH)_2$, found the b dimension to change by 0.23 Å in the range from 55–100% grunerite. This change is not to be compared directly with the calcic and sodic amphibole increases because in this case the occupancy of the M_4 site is related to the iron-magnesium ratio, hence M_4 should also affect the b dimension. The studies of Ghose and Hellner (1959) and Ghose (1961) show that in cummingtonite M_4 is 75% Fe^{2+}, M_2 25% and M_1 and M_3 33% Fe^{2+}, whereas in grunerite M_4 as 100% Fe^{2+} and M_1, M_2 and M_3 all 60% Fe^{2+}. The b increase in these natural amphiboles is 0.11 Å. The calculated increase considering only M_4 is 0.08 Å and considering only M_2 is 0.11 Å. It is not known how these increases combine to give the observed increase; the change could be accounted for by M_2 occupancy alone. However, recent work of Viswanathan and Ghose (1965) shows that (projected) natural end member cummingtonite and grunerite would have b axis lengths of 17.935 Å and 18.452 Å respectively. The maximum possible calculated increase in b cell dimension, assuming sizes of ions occupying both M_2 and M_4 produce the change, is 0.64 Å, somewhat greater than the (projected) observed difference, 0.517 Å.

In addition to changes in b caused by replacement of Mg by Fe^{2+}, small differences can be observed in the b axes of pure Mg end members. This can be attributed to a combination of two effects: (1) the chains are not perfectly rigid units, as demonstrated by the crystal structure analyses previously cited, and (2) the M_2 occupants are not the same for all pure Mg end members. Tremolite has only Mg in M_2 while pargasite has half Mg, half Al and glaucophane II probably has almost all Al. Therefore we expect b in pargasite to be less than tremolite and b in glaucophane II to be less than both. Taking into account only the differences in M_2 occupancy and ignoring the minor variations in chain width, the calculated decreases are 0.30 Å between tremolite and pargasite and 0.60 Å between tremolite and glaucophane II (assuming complete Al ordering in glaucophane). The observed decreases are 0.07 Å and 0.32 Å respectively. Apparently the change in b axis length in both cases results from partial ordering of aluminum in M_2.

The question as to why the b axis length of magnesiohastingsite, with M_2 occupancy of 50% Mg, 50% Fe^{3+}, is identical to that of pargasite, with M_2 occupancy of 50% Mg, 50% Al, remains unanswered. The ferrous iron analogues exhibit the same problem too. The calculated difference in b of either of these pairs on substitution of Fe^{3+} for Al if both are assumed to occupy M_2 is 0.26 Å. The only difference noted is an insignificant 0.01 Å in the iron-rich end members. By following the changes in b through the two substitutions (Fe^{3+} for Al and Fe^{2+} for Mg) required to give the four end members pargasite, ferropargasite, magnesiohastingsite, and hastingsite, it becomes evident that not only is no "unique" solution available for occupancy of M_2 but contradictory results appear no matter what the assumptions concerning M_2. Thus the geometrical images connected with the concept of ionic radius have very real limitations.

Finally we may inquire as to the effect of substituting Fe^{3+} for Al in M_2 by comparing glaucophane II ($b = 17.73$ Å) and magnesioriebeckite ($b = 17.95$ Å). The calculated difference in b, assuming complete restriction of Fe^{3+} and Al to M_2 is 0.52 Å; the observed difference is 0.22 Å. The discrepancy is similar to that previously discussed regarding magnesiohastingsite and pargasite.

In general, replacement of Mg or Fe^{3+} in M_2 by Al causes b to decrease by a maximum of about 0.30 Å (observed) and replacement of Mg by Fe^{2+} causes b to increase by approximately 0.32 Å (observed = calculated). Apparently the contraction along b reflecting the presence of very small Al ions in M_2 is achieved only with great difficulty, probably because other bonds hold the structure open.

The c axis. The c axis consistently shows an increase of about 0.05 Å where Fe^{2+} substitutes completely for Mg in the metal positions. In the previous discussion it was demonstrated that the relative widths of the chains remain practically constant for the known structures. However, even in these structures the lengths of the chains increase for iron-rich types. In order to visualize the relations, the chains of three structural pairs are drawn in Figs. 10–12 as projections on the *b-c* plane (100).

The iron-rich amphibole chains are less kinked than the magnesium-rich analogues. Whittaker (1960) showed that a perfectly regular chain was not reasonable since the M_2-O_4 distances would be too short to properly pack the chains. Evidently, according to Whittaker's analysis, a chain may approach regularity as the size of M_2 becomes smaller or as distance between adjacent chains becomes larger in the b direction. However, in riebeckite the mean size of the cations in M_2 does not change significantly but the chains do approach regularity, compared to magnesioriebeckite. Furthermore in the tremolite-actinolite and cummingtonite-grunerite series, the chains became more regular as the size of the M_2 cation actually increases. The approach to regularity must therefore be brought about though separation of adjacent chains. Figures 10–12 show these changes in the (100) projection.

The observed change of kinking may be correlated with a change in iron content (at a constant Si:Al ratio,) and in the length of the b and c axes. Where M_1 and M_3 sites are occupied by small cations, the double chain is shortened and by kinking crowds the M_1 and M_3 cations against the OH^-. Where the larger Fe^{2+} ions are involved, the structure must assume its more expanded form. The occupancy of the M_2 site and the amount of aluminum in tetrahedral coordination do not seem to be involved in this expansion. The change in c can then be related to the occupancy of M_1 and M_3 through the mechanism of kinking: the chain collapses around small ions and expands to accommodate larger ones. Although an increase in c through unkinking must be accompanied by an increase in b to provide room for M_2, an increase in b through an increase in the size of M_2 does not *necessarily* cause unkinking. Thus one would expect glaucophane and magnesioriebeckite to be equally kinked but to have different b axes.

G. V. Gibbs (pers. comm.) has pointed out that curvature of the tetrahedral chains away from the octahedral layer, unaccompanied by significant unkinking, may be related to cation occupancy of M_1, M_2, M_3 and M_4; he suggests that this degree of chain curvature influences b. The present authors feel that this explanation is especially appropriate for riebeckite, but most other amphibole structures do exhibit the kinking

phenomenon as seen in Figs. 10–12 in addition to slight warping away from (100).

The a axis. The clinoamphibole value $a \sin \beta$ represents the unit repeat across facing double chains; these chains are crosslinked to each other by "strips" of octahedrally coordinated cations (Fig. 9). The value of $a \sin \beta$ will be a function both of the sizes of the cations in tetrahedral coordination (which control the thickness of the individual chains) and of the sizes of the atoms in octahedral coordination between facing

TABLE 4. OBSERVED AND CALCULATED CHANGES IN $a \sin \beta$

	Obs. Å	Calc. Å
Tremolite to edenite Na+Al for Si	−0.01	0.02
Tremolite to ferrotremolite Fe_5 for Mg_5	0.07	0.16
Edenite to ferroedenite Fe_5 for Mg_5	0.08	0.16
Tremolite to pargasite $NaAl_3$ for $MgSi_2$	−0.01	0.03
Tremolite to magnesiohastingsite Na+Al_2Fe^{3+} for $MgSi_2$	0.04	0.09
Paragasite to ferropargasite Fe_4 for Mg_4	0.09	0.13
Magnesiohastingsite to hastingsite Fe_4 for Mg_4	0.02	0.13
Glaucophane$_{II}$ to magnesioriebeckite Fe_2^{3+} for Al_2	0.10	0.10
Magnesioriebeckite to riebeckite Fe_3^{2+} for Mg_3	0.00	0.09

chains. A minimum $a \sin \beta$ should be found where silicons occupy all the tetrahedral sites and Mg and Al occupy all the octahedral sites. Among the amphiboles studies, a maximum should be found where one-eighth of the Si has been replaced by aluminum and all ferrous iron is in the octahedral sites. Observed changes in $a \sin \beta$ have been tabulated in Table 4 along with calculated changes (assuming β constant) for the synthetics studies. The values obtained make it clear that the relationship is not quite so direct as was supposed, although the similar orders of magnitude show that the hypothesis might be partly correct. Calculations were made assuming that larger cations did not nestle down into the chains. However, observed chain expansions and contractions, discussed in connection with c axis changes, makes it easier for larger cations

to fit down into the chains as they unkink; hence calculated values for the $a \sin \beta$ increases are in excess of observed values.

The β angle. Whittaker (1960) plotted the mean size of the cations in M_4 against β and found a linear relationship using ionic radii after Goldschmidt (1954) Colville and Gibbs (pers. comm.) plotted $a \sin \beta$ versus β and found that these parameters place the monoclinic amphiboles in natural groups, the cummingtonite-grunerites distinguished by low values of β and $a \sin \beta$, and the sodic and calcic amphiboles with higher values. They correlate $a \sin \beta$ with the mean size of all metals in octahedral coordination and conclude that the β value of the amphibole will identify its series (occupancy of M_4) and the $a \sin \beta$ value will give an approximate iron content within the individual series. Because cummingtonite and grunerite were not synthesized it would be difficult to corroborate either of these observations using the data obtained in the present study. However the average β values of the calcic and sodic synthetic amphiboles and natural cummingtonite and grunerite (Ghose, 1961; Ghose and Hellner, 1959) are tabulated below:

M_4	*ionic radius*	*average β*
Ca	1.03 Å	104.96°
Na	1.01 Å	103.24°
100% Fe^{+2}	0.74 Å	101.50°
75% Fe^{+2}	0.72 Å	101.55°

These data do not give a simple linear relationship between the size of M_4 and β. The size of β may be controlled in part by structural elements other than the M_4 ions, perhaps the Al/Si ratio.

CONSIDERATION OF NATURAL MONOCLINIC AMPHIBOLES

This study of synthetic clinoamphibole end members has demonstrated that the b crystallographic axis is the cell dimension most sensitive to composition. Variation of this lattice parameter as a function of the calculated mean ionic radius of cations occupying M_2 is shown in Fig. 13a. Synthetic glaucophane I and II contain two octahedral Al cations per 24 anions, synthetic pargasite and ferropargasite contains one Al^{VI} and two Al^{IV}. All other synthetic amphiboles are aluminum-free, excepting edenite, ferroedenite and fluoredenite, which carry a single tetrahedrally coordinated aluminum (and it has been previously demonstrated that the Al^{IV}↔Si substitution does not affect b significantly).

The b axis discrepancy between Al-rich and non aluminous or Al-poor amphiboles is well shown. The reason for this discrepancy is unknown. Perhaps octahedral aluminum, which occurs *only* in the synthetic glaucophanes and pargasite-ferropargasites, is not concentrated in M_2 as
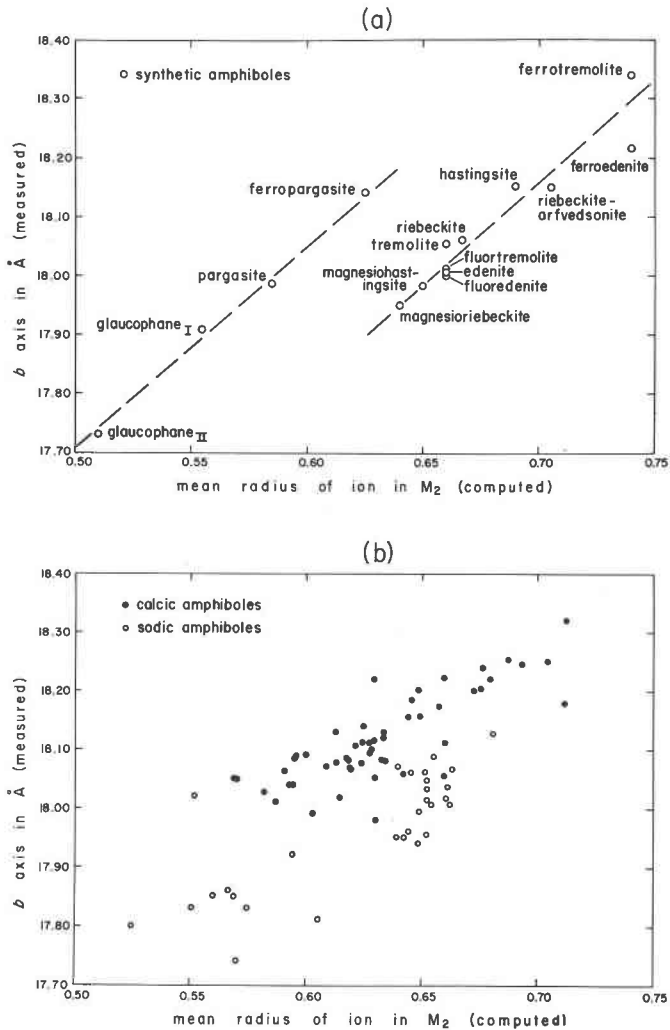
FIG. 13. (a) Variation of b crystallographic axis for synthetic clinoamphiboles as a function of the mean ionic radius of the cations occupying M_2. Glaucophane I assumed 100% disordered, glaucophane I 50% disordered, riebeckite 27% disordered, as discussed in text. (b) Variation of b crystallographic axis for natural clinoamphiboles as a function of the mean ionic radius of the cations occupying M_2. The smallest octahedrally coordinated cations were assumed to be ordered preferentially in this site.

was assumed. However, one would then be faced with the anomalous situation of apparently complete magnesium ordering in M_2 of glaucophane I, the low pressure-high temperature form, compared to a more

random Al-Mg distribution in glaucophane II; furthermore, Δb values of 0.15 Å and 0.17 Å observed for the pargasite-ferropargasite and magnesiohastingsite-hastingsite pairs would be difficult to explain.

The corresponding b axis variation of 50 chemically analyzed calcic, and 29 sodic amphiboles is shown in Fig. 13b. The data are taken from Heritsch, Paulitsch and Walitzi (1957), Heritsch *et al.* (1960), Heritsch and Kahler (1960), Heritsch and Reichert (1960), Zussman (1955, 1959), Borley (1963), Frost (1963), Borley and Frost (1963), Howie (1963), Ernst (1963, 1964), Raychaudhuri (1964), Binns (1965) and Leake (1965b). Mean ionic radius of the cations in M_2 was computed by summing to 2 cations per 24 anions, in sequence, octahedral Al, Ti, Fe^{3+}, Li Mg and Fe^{2+} as necessary, assuming complete preference for this site of the smallest cations.

The correlation of b axis repeat and M_2 occupancy among natural monoclinic amphiboles is direct, and compares with variation of synthetic end members presented in Fig. 13a. The distinct separation of calcic and sodic amphiboles shown in Fig. 13b depends, of course, on the calculated mean ionic radius of the cations residing in M_2. Calcic amphiboles plotted are, with four exceptions, aluminous hornblendes; in contrast, the sodic amphiboles vary principally from crossites to riebeckites and arfvedsonites, and contain only minor amounts of Al. It is possible that the behavior of aluminum in amphiboles is more complex than supposed. In any case, these ambiguities among multicomponent natural amphiboles must await three dimensional crystal structure analyses for solution.

Summary

The relationships between cell parameters and chemical compositions of monoclinic amphiboles have been studied by synthesizing important end members. This approach has had the great advantage of eliminating many compositional variables. Iron, magnesium, aluminum and silicon proportions were fixed as desired. By observing the differences in properties of substitution pairs differing chemically by one only component, it is possible to say unambiguously what the effect of a chemical substitution is. With knowledge of the crystal structure and the presumed distribution of atoms in the different structural sites, it becomes feasible to relate the variations of physical properties to structural variations. Furthermore, the quantitative differences between pairs should prove helpful in predicting the properties of intermediates. The most useful results are as follows:

The b parameter is controlled by the sizes of the cations in M_4 and M_2. Because the occupancy of M_4 is nearly constant in any one series, the control on b shifts to the occupants of M_2. The variation involves an in-

crease of 0.32 Å as the occupancy shifts from all Mg to all Fe^{2+}. If M_2 is all Al, b is observed to decrease about 0.30 Å from its Mg value. All Fe^{3+} would give approximately the same value as Mg. Obviously many combinations are possible and we may only say with certainty that where $b = 18.30$ Å, M_2 must be occupied by Fe^{2+} and where $b = 17.70$ Å, M_2 must be occupied almost entirely by Al.

As the size of the cations in octahedral coordination increases, $a \sin \beta$ increases. An $a \sin \beta$ of 9.4 Å corresponds to exclusively small cations in these sites and a value of 9.6 Å corresponds to all large cations. Tetrahedral occupancy also influences $a \sin \beta$ but to a minor extent. The increase in the size of M_1 and M_3 is reflected in an increase of c, the chain length. The chains are kinked for small cations (Mg) in these sites and unkink to accommodate larger ones (Fe^{2+}). The increase in c as all of the magnesium is replaced by iron is about 0.05 Å.

In all cases where larger ions are placed in the structure the cell volume increases, as shown by Table 3.

Strictly speaking, the conclusions stated above apply only to the synthetic amphibole end members. Properties of various intermediate solid solutions can be very similar for many different combinations of chemical substitutions because the parameters are a function of the average sizes of ions in specific sites in the structure. The series (calcic, Fe-Mg sodic) can be determined by β. Iron and aluminum contents may be indicated by the b repeat if these elements are present in large amounts but ambiguities exist as demonstrated by Fig. 13. Optical properties can also give approximate iron contents. It is still hard to distinguish hornblendes of complex chemical compositions from one another, not because the effect of various substitutions are unknown but because they are known to combine in so many ways that the effect is not indicative of any one particular substitution.

References

Ahrens, L. H. (1952) The use of ionization potentials. Part I. Ionic radii of the elements. *Geochim. Cosmochim. Acta* **2**, 155–169.

BINNS, R. A. (1965) The mineralogy of metamorphosed basic rocks from the Willyama Complex, Broken Hill district, New South Wales, Part I. Hornblendes. *Mineral. Mag.* **35**, 306–326.

BORLEY, G. D. (1963) Amphiboles from the Younger Granites of Nigeria. Part I. Chemical classification. *Mineral. Mag.* **33**, 358–376.

BORLEY, G. AND M. T. FROST (1963) Some observations on igneous ferrohastingsites. *Mineral. Mag.* **33**, 646–662.

BOYD, F. R. (1959) Hydrothermal investigations of amphiboles. In, *Researches in Geochemistry*, P. H. Abelson, ed., John Wiley & Sons, New York, pp. 377–396.

COLVILLE, A. A. AND G. V. GIBBS (1965) Refinement of the crystal structure of riebeckite (abs.). *Geol. Soc. Am. Spec. Paper* **82**, 31.

COMEFORO, J. E. AND J. A. KOHN (1954) Synthetic asbestos investigations, I: study of synthetic fluor-tremolite. *Am. Mineral.* **39**, 537–548.

DEER, W. A., R. A. HOWIE AND J. ZUSSMAN (1963) *Rock-forming Minerals.* v. 2, *Chain Silicates:* John Wiley and Sons, Inc., New York.

ERNST, W. G. (1960) Stability relations of magnesioriebeckite. *Geochim. Cosmochim. Acta* **19**, 10–40.

———— (1961) Stability relations of glaucophane. *Am. Jour. Sci.* **259**, 735–765.

———— (1962) Synthesis, stability relations, and occurrence of riebeckite and riebeckite-arfvedsonite solid solutions. *Jour. Geol.* **70**, 689–736.

———— (1963) Polymorphism in alkali amphiboles. *Am. Mineral.* **48**, 241–260.

———— (1964) Petrochemical study of coexisting minerals from low-grade schists, Eastern Shikoku, Japan. *Geochim. Cosmochim. Acta* **28**, 1631–1668.

———— (1966) Synthesis and stability relations of ferrotremolite. *Am. Jour. Sci.* **264**, 37–65.

FROST, M. T. (1963) Amphiboles from the Younger Granites of Nigeria. Part II. X-ray data. *Mineral. Mag.* **33**, 377–384.

GREEN, J. (1959) Geochemical table of the elements for 1959. *Bull. Geol. Soc. Am.* **70**, 1127–1184.

GHOSE, S. (1961) The crystal structure of cummingtonite. *Acta Cryst.* **14**, 622–627.

———— (1965) A scheme of cation distribution in the amphiboles. *Mineral Mag.* **35**, 46–54.

———— AND E. HELLER (1959) The structure of grunerite and some observations on the Mg-Fe distribution. *Jour. Geol.* **67**, 697–701.

GILBERT, M. C. (1966) Synthesis and stability relationships of ferropargasite *Am. Jour. Sci.* **264**, 698–742.

GOLDSCHMIDT, V. M. (1954) *Geochemistry.* Clarendon Press.

HALLIMOND, A. F. (1943) On the graphical representation of the calciferous amphiboles. *Am. Mineral.* **28**, 65–89.

HERITSCH, H., P. PAULITSCH AND E. M. WALITZI (1957) Die Struktur von Karinthin und einer barroisitschen Hornblende. *Tschermaks Mineral. Petrog. Mitt.* **6**, 215–225.

———— G. BERTOLDI AND E. M. WALITZI (1960) Strukturuntersuchung an einer basaltischen Hornblende vom Kuruzzenkogel, südlich Fehring, Steiermark. *Tschermaks Mineral. Petrog. Mitt.* **7**, 210–217.

———— AND E. KAHLER (1960) Strukturuntersuchung an zwei Kluftkarinthinen, ein Beitrag zur Karinthinfrage. *Tschermaks Mineral. Petrog. Mitt.* **7**, 218–234.

———— AND L. RIECHERT (1960) Strukturuntersuchung an einer basaltischen Hornblende von Černosin, ČSR. *Tschermaks Mineral. Petrog. Mitt.* **7**, 235–245.

KLEIN, C. (1964) Cummingtonite-grunerite series: a chemical, optical and x-ray study. *Am. Mineral.* **49**, 963–982.

KOHN, J. A. AND J. E. COMEFORO (1955) Synthetic asbestos investigations II. X-ray and other data on synthetic fluor-richterite, -edenite and boron edenite. *Am. Mineral.* **40**, 410–421.

LEAKE, B. E. (1965a) The relationship between tetrahedral aluminum and the maximum possible octahedral aluminum in natural calciferous and subcalciferous amphiboles. *Am. Mineral.* **50,** 843–851.

—— (1965b) The relationship between composition of calciferous amphibole and grade of metamorphism. In, *Controls of Metamorphism.* W. S. Pitcher and G. W. Flinn, eds., John Wiley & Sons, New York, pp. 299–318.

RAYCHAUDHURI, B. (1964) Relation of atomic constitution to lattice parameters in some hornblendes from the Black Hills, South Dakota. *Am. Mineral.* **49,** 198–206.

VISWANATHAN, K. AND S. GHOSE (1965) The effect of Mg^{2+}-Fe^{2+} substitution on the cell dimensions of cummingtonites. *Am. Mineral.* **50,** 1106–1112.

WARREN, B. E. (1929) The structure of tremolite. *Zeit. Krist.* **72,** 42–57.

WHITTAKER, E. J. W. (1949) The structure of Bolivian crocidolite. *Acta Cryst.* **2,** 312–317.

—— (1960) The crystal chemistry of the amphiboles. *Acta Cryst.* **13,** 291–298.

WINCHELL, H. (1963) Clinoamphibole regression studies. I. Regressions of optical properties and density on composition. *Mineral. Soc. Am. Spec. Paper* **1,** 267–277.

ZUSSMAN, J. (1955) The crystal structure of an actinolite. *Acta Cryst.* **8,** 301–308.

—— (1959) A re-examination of the structure of tremolite. *Acta Cryst.* **12,** 309–312.