

Synthesis and X-ray properties of Fe-Mg orthoamphiboles

ROBERT K. POPP, M. CHARLES GILBERT AND JAMES R. CRAIG

Department of Geological Sciences
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Abstract

Orthoamphiboles ranging in composition from $\text{Mg}_6\text{Fe}_1\text{Si}_8\text{O}_{22}(\text{OH})_2$ to $\text{Mg}_1\text{Fe}_6\text{Si}_8\text{O}_{22}(\text{OH})_2$ have been synthesized by standard hydrothermal techniques. The entire range of compositions appears optically orthorhombic. Variation of unit-cell parameters with compositions suggests that they are members of a single, continuous solid solution [$a(\text{\AA}) = 18.577(12) + 0.001284(190)X_{\text{Fe}}$; $b(\text{\AA}) = 17.942(11) + 0.004862(170)X_{\text{Fe}}$; $c(\text{\AA}) = 5.285(3) + 0.000617(50)X_{\text{Fe}}$; $V(\text{\AA}^3) = 1760.8(1.7) + 0.8226(280)X_{\text{Fe}}$; X_{Fe} = mole percent Fe end member]. Electron-diffraction patterns of composition Mg_5Fe_2 are consistent with that of an orthorhombic amphibole with an a unit-cell repeat of $\sim 18.6\text{\AA}$. A strong enhancement in intensity for reflections of the type $l = 2n$, $h = 0 \pmod{4}$ in the $h0l$ net of the synthetic amphibole indicates the presence of a $\sim 4.7\text{\AA}$ subcell repeat parallel to a^* , unlike any known amphibole structure. Even though the structure type is unknown, measured shifts in peak locations on the powder X-ray diffraction patterns allow compositions to be measured to within ± 3 mole percent Fe end-member. Combining these results with those of Forbes (1971) and Greenwood (1963), it is now clear that the entire range of amphiboles across the join can be synthesized.

Introduction

Amphiboles chemically approaching the join $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ - $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ occur naturally as anthophyllite and as cummingtonite-grunerite. Natural specimens have been studied in considerable detail because they are important in understanding metamorphism of certain chemically restrictive (low Ca and Al) geological environments (*e.g.*, Klein, 1966). Despite the considerable attention directed to natural specimens, iron-magnesium amphiboles are still poorly understood in terms of both phase equilibria and crystal chemistry. This is unfortunate since these are the chemically simplest amphiboles and should serve as end-member models for understanding the chemically more complex series.

Problems in the determination of phase relations on the join arise from the sluggishness of reactions, as shown by the difficulties in the synthesis of the Mg(anthophyllite) and Fe(grunerite) end-members (Greenwood, 1963; Forbes, 1971). Boyd (1955) reported the synthesis of some intermediate compositions on the join at 1 kbar and temperatures in the range of 800°C , but he was unable to crystallize amphibole from its high-temperature breakdown as-

semblage, hypersthene and quartz. Hinrichsen (1967) determined a T - X phase diagram for orthorhombic forms on the join at 2 kbar in the range 500° - 700°C . Both Hinrichsen and Boyd reported that the most iron-rich amphibole which could be synthesized contained approximately 60 mole percent Fe end-member. Cameron (1975) investigated the composition $\text{Mg}_{3.5}\text{Fe}_{3.5}\text{Si}_8\text{O}_{22}(\text{OH})_2$ as one end of a join into the Ca-bearing amphibole quadrilateral. Aside from these studies, detailed experimental investigations of intermediate members on the Mg-Fe join are lacking. Greenwood (1963) and Forbes (1971) give detailed summaries of previous experimental studies relevant to the Mg and Fe end-member, respectively.

Amphiboles of the anthophyllite and cummingtonite-grunerite groups are known to crystallize in 3 of the 4 amphibole structure types so far identified: orthorhombic with space group $Pnma$, monoclinic $C2/m$, and monoclinic $P2_1/m$. The protoamphibole structure type (Gibbs, 1969; space group $Pnmm$) has not been found in nature and accordingly is not represented. Papike *et al.* (1969) have shown that the structure and stacking sequence of the double chains in the $P2_1/m$ structure most closely resemble that of

the anthophyllite (*Pnma*) structure. Prewitt *et al.*, (1970) have demonstrated that $P2_1/m$ is the low-temperature polymorph of the monoclinic $C2/m$ type. The phase relationships between the anthophyllite and the cummingtonite ($C2/m$) structures are still unclear. Although some authors have evoked chemical explanations for the existence of these two structure types (*e.g.* Layton and Phillips, 1960), the two forms are known to coexist in nature with nearly the same chemical composition (Evans *et al.*, 1974). Routine optical and powder-diffraction examination would not distinguish protoamphibole from anthophyllite.

This paper presents the first portion of a study of the stability of amphiboles on the join $Mg_7Si_8O_{22}(OH)_2-Fe_7Si_8O_{22}(OH)_2$ with respect to T , P , $f(O_2)$, and $f(S_2)$. The goal was to synthesize a series of amphiboles across the join, to determine the structure type(s), and to establish the relationship between unit-cell parameters and composition. For use in further studies on these synthetic amphiboles, a simple but accurate method of relating amphibole composition to 2θ angles given by X-ray powder diffraction patterns is presented.

Experimental procedures

Starting materials

Starting materials for most of the amphibole syntheses were oxide mixes composed of fired MgO, Fe sponge, and SiO₂ glass. A few experiments on Fe end-member amphibole were made from an additional "oxygen balanced" oxide mix containing Fe₂O₃ in addition to the above materials. Reagents were dried and stored in a vacuum desiccator prior to weighing. Treatment of Fe sponge with hot H₂ gas resulted in a weight loss which was attributed to release of oxygen. Appropriate adjustments were made to produce stoichiometric amphibole starting compositions.

After weighing, all mixes were ground under acetone in an automated agate mortar and pestle for one hour to achieve homogeneity. Portions of certain mixes were ground in the same apparatus up to an additional eight hours to determine the effect of smaller grain size on synthesis rates.

Mixes equivalent to whole-number Mg-Fe formula units across the join were made (*i.e.* Mg₇Si₈, Mg₆Fe₁Si₈, . . . Mg₁Fe₆Si₈, Fe₇Si₈). For the sake of simplicity, compositions will hereafter be referred to only by their Mg-Fe formula units (Mg₅Fe₂, *etc.*) or by mole percent of the Fe end-member.

Apparatus, buffering techniques and sample containers

Most experiments were carried out in Tuttle-type pressure vessels depicted by Ernst (1968, p. 34). Two systems, one with a 5 kbar pressure capability and the other with a 7 kbar capability, were used for various steps of the syntheses. Control of oxygen fugacity was normally accomplished with the solid-buffer technique of Eugster (Huebner, 1971), using sealed Ag₇₀Pd₃₀ inner capsules, and Au outer capsules. A number of runs, also in sealed Ag₇₀Pd₃₀, were carried out in a CH₄-C buffering system with a 1 kbar pressure capability. This system is similar to the hydrothermal systems described above but utilizes methane as the pressure medium and graphite filler rods (Eugster and Skippen, 1967; Huebner, 1971).

Temperatures in all of the apparatus were measured by means of chromel-alumel thermocouples. Furnace-bomb assemblies were calibrated against 1 atm NaCl (800.5°C) and CsCl (646°C) melting points. Temperature variations of $\pm 3^\circ\text{C}$ were typical for the runs. Pressures were measured on Heise bourdon-tube gauges, which were factory-calibrated, and set to read 0.0 bars at one atm. Typical pressure variations during runs were ± 20 bars.

Phase identification

Run products were routinely examined with the petrographic microscope and a Norelco X-ray powder diffractometer equipped with a graphite monochromator using Ni-filtered CuK α radiation. Qualitative identification was made by scanning at $2^\circ 2\theta/\text{min}$ between 8° and $70^\circ 2\theta$. X-ray data used to determine the unit-cell parameters were collected from four scans (two oscillations) run at $0.5^\circ 2\theta/\text{min}$ with synthetic MgAl₂O₄ spinel ($a = 8.0831 \text{ \AA}$) as an internal standard. Unit-cell parameters were then obtained by a least-squares refinement using the computer program of Appleman and Evans (1973). All peaks were weighted equally. Grain size (maximum $100\mu \times 6\mu$; average $10-15\mu \times 1-2\mu$) precluded use of single-crystal X-ray techniques.

Because of the small grain size, measurement of the three indices of refraction could not be accomplished. However, an average index of refraction of the bulk amphibole was obtained ($n = 1.620$, Mg₆Fe₁; 1.632, Mg₅Fe₂; 1.644, Mg₄Fe₃; 1.660, Mg₃Fe₄; 1.674, Mg₂Fe₅; 1.690, Mg₁Fe₆). Estimation of the percentage amphibole in the runs was based primarily on optical examination.

Optical and X-ray data are consistent with the presence of a single homogeneous amphibole phase in all runs.

TABLE 1. Amphibole synthesis conditions

Run #	Comp.	T(°C)	P(kbar)	Buffer	Dur(days)*	Run Products**
145	Mg ₆ Fe ₁	650	2	none	2	T+01
		815	2	none	1	A(20)+T+01+C+Q+P
		700	2	FMQ	61(1)	A(99)+P+Q
290	Mg ₆ Fe ₁	650	2	none	1	T+01
		820	2	none	1	A(20)+Px+Q+01
		700	2	FMQ	44(2)	A(99)+Px+Q
68	Mg ₅ Fe ₂	750	2	FMQ	23	A(100)
26	Mg ₅ Fe ₂	700	2	FMQ	7	A(50)+T+01
		750	2	FMQ	10	A(100)
125	Mg ₅ Fe ₂	750	2	FMQ	30	A(100)
82	Mg ₄ Fe ₃	700	2	FMQ	35(1)	A(98)+Q+01
149	Mg ₄ Fe ₃	700	2	FMQ	45(1)	A(98)+Q+01
80	Mg ₃ Fe ₄	700	2	FMQ	19	A(50)+Q+01
		650	2	FMQ	17	A(99)+Q+01
150	Mg ₃ Fe ₄	650	2	FMQ	51(1)	A(99)+Q+01
140	Mg ₂ Fe ₅	700	4	none	26	A(40)+Q+01
		600	1	CH ₄ -C	102(3)	A(95)+Q+01
226	Mg ₂ Fe ₅	700	4	none	6	A(5)+Q+01+K
		600	1	CH ₄ -C	101(5)	A(99)+Q+01
486	Mg ₁ Fe ₆	700	6	none	12	A(5)+Q+01+P
		600	1	CH ₄ -C	63(2)	A(30)+Q+01+P+M
		550	1	CH ₄ -C	105(3)	A(60)+Q+01+M
		500	1	CH ₄ -C	35	A(98)+Q+01

*Number in parentheses indicates number of times capsule was opened and charge examined optically and with X-ray methods.

**Starting material for first run of each series was oxide mix + H₂O. Numbers in parentheses indicate percent amphibole in charge. Abbreviations: A-amphibole, K-keatite, M-magnetite, OL-olivine, P-orthopyroxene, T-talc, C-cristobalite.

Synthesis techniques

Because of possible partitioning of Fe and Mg between amphibole and other run products, unit-cell parameters are reported only for runs which yielded greater than 95 percent amphibole. Synthesis procedures used to achieve these high yields are summarized in Table 1. Errors in X_{Fe} , resulting from the partitioning of Fe and Mg between amphibole and the minor amounts of olivine or pyroxene in run products, were calculated to have a maximum value of ~1 mole percent assuming Fe/Mg distributions for coexisting amphibole and olivine similar to those reported by Ramberg (1952).

Yields of about 50 percent amphibole have been achieved for composition Mg₇, but the amphibole is not well enough crystallized to allow unit-cell parameters to be determined. Although a number of differ-

ent techniques have been used to synthesize the Fe₇ end-member, yields of greater than 5 percent have not been realized. Maximum yields occurred using well-ground "reduced" mix at 4-6 kbar.

Amphiboles for which unit-cell parameters are reported were synthesized at the FMQ buffer [except Mg₂Fe₅ and Mg₁Fe₆ (Table 1)]. The effect of different oxygen fugacities on cell parameters is discussed below.

Determination of crystal system

The amphiboles synthesized in this study cannot be characterized as monoclinic or orthorhombic on the basis of X-ray powder patterns alone. The method discussed by Cameron (1975) for distinguishing between cummingtonite and anthophyllite on the basis of the monoclinic 131 reflection at approximately 26°

2θ $\text{CuK}\alpha$ has not been found applicable. As discussed by Cameron, the monoclinic 131 peak may be overlapped by several weaker anthophyllite peaks. A weak peak at 26° 2θ is present in the synthetic amphibole patterns of this study, but the distinction as to type of reflection cannot be made. All major peaks in the X-ray patterns can be indexed as either monoclinic or orthorhombic, and least-squares unit-cell refinement gives equivalent standard errors.

Although the grain size is too small for single-crystal X-ray studies, multi-crystal masses were mounted on a spindle stage and examined optically. Extinction angles for individual crystals within these larger masses could be determined. Parallel extinction was invariably observed, and on this basis the amphiboles are assumed to be orthorhombic. Klein (1964) reported values of $Z \wedge c$ of 13° – 20° for naturally occurring low-Ca cummingtonite–grunerites in the composition range 60–90 mole percent Fe end-member. Rice *et al.* (1974) gave $Z \wedge c$ of 14° – 15° for a natural magnesiocummingtonite of approximately 14 mole percent Fe end-member. Amphiboles synthe-

sized in this study have a composition range from 14–86 mole percent Fe end-member.

Experimental results

Unit-cell parameters of the synthetic amphiboles are given in Table 2, and are plotted against composition in Figures 1 and 2. The peaks listed in Table 4, along with the 210 peak at approximately 10.7° 2θ , were used in the least-squares refinement. The c dimension is based only on one reflection, 053, but a minor peak indexed as 202 at approximately 35° 2θ was measurable in a number of the patterns; inclusion of this peak in the refinements did not significantly change the unit-cell parameters. The data were refined assuming the anthophyllite space group $Pnma$. As a check for reproducibility, values were obtained from three independent synthesis runs for Mg_5Fe_2 , and from two independent runs for the other compositions up to Mg_2Fe_5 . Parameters for the Mg end-member are from Greenwood (1963) and Cameron (1975). Cameron re-indexed several of the high-

TABLE 2. Orthorhombic unit-cell parameters (refined as space group $Pnma$)

Run #	Formula (and Mole % Fe)	\underline{a} (Å)	\underline{b} (Å)	\underline{c} (Å)	\underline{v} (Å ³)
Synthesized at FMQ					
145	Mg_6Fe_1 (14.3)	18.592(10)	18.045(10)	5.292(4)	1775.4(1.7)
290	Mg_6Fe_1 (14.3)	18.622(8)	17.999(14)	5.295(2)	1774.9(1.2)
26	Mg_5Fe_2 (28.6)	18.604(15)	18.088(10)	5.299(4)	1783.4(2.0)
68	Mg_5Fe_2 (28.6)	18.634(20)	18.077(11)	5.298(4)	1784.6(2.4)
125	Mg_5Fe_2 (28.6)	18.594(8)	18.078(5)	5.301(2)	1781.9(1.0)
82	Mg_4Fe_3 (42.9)	18.626(13)	18.139(9)	5.313(3)	1795.0(1.6)
149	Mg_4Fe_3 (42.9)	18.613(10)	18.136(7)	5.313(3)	1793.4(1.3)
80	Mg_3Fe_4 (57.1)	18.638(10)	18.227(7)	5.325(2)	1809.0(1.3)
150	Mg_3Fe_4 (57.1)	18.635(18)	18.223(12)	5.326(5)	1808.5(2.4)
Synthesized at CH_4 -C					
140	Mg_2Fe_5 (71.4)	18.669(11)	18.291(8)	5.329(3)	1819.8(1.5)
226	Mg_2Fe_5 (71.4)	18.672(3)	18.290(2)	5.329(1)	1819.8(0.4)
453	Mg_1Fe_6 (85.7)	18.686(7)	18.358(20)	5.336(2)	1830.3(1.3)

Numbers in parentheses represent 1 standard error as given by the least-squares refinement.

angle 2θ peaks reported by Greenwood and re-refined the data using Greenwood's 2θ values.

Curves relating individual unit-cell parameters to composition were obtained by regression analysis, using the computer program designed by Barr and Goodnight (1972), which weights observations as $1/(\text{standard error})$. Equations of first through fourth order were fit to the data assuming one, and then two, standard errors as given in Table 2. The significance of the fits was determined by a t -test assuming $|t| = 2.0$ to be significant. Using one-standard-error weighting, fits of second or third order were obtained for all unit-cell parameters. However, only first-order (straight line) equations were significant when weighting of two standard errors was employed. Gibbs and Louisnathan (1971) estimated that in order for the standard error reported in least-squares refinement to be a good estimate of that of the true population, the number of observations (m) should be at least ten times as large as the degrees of freedom (n). In the case where $m < 10n$, they recommend doubling the least-squares standard error before applying statistical tests. Since $n = 3$ for the orthorhombic system and only 8–10 peaks could be unambiguously indexed, the fits obtained using two standard errors are preferred. Equations relating unit-cell parameters to mole percent of the Fe end-member (X_{Fe}), with the intercept and slope errors indicated in parentheses, are:

$$a(\text{\AA}) = 18.577(12) + 0.001284(190) X_{\text{Fe}}$$

$$b(\text{\AA}) = 17.942(11) + 0.004862(170) X_{\text{Fe}}$$

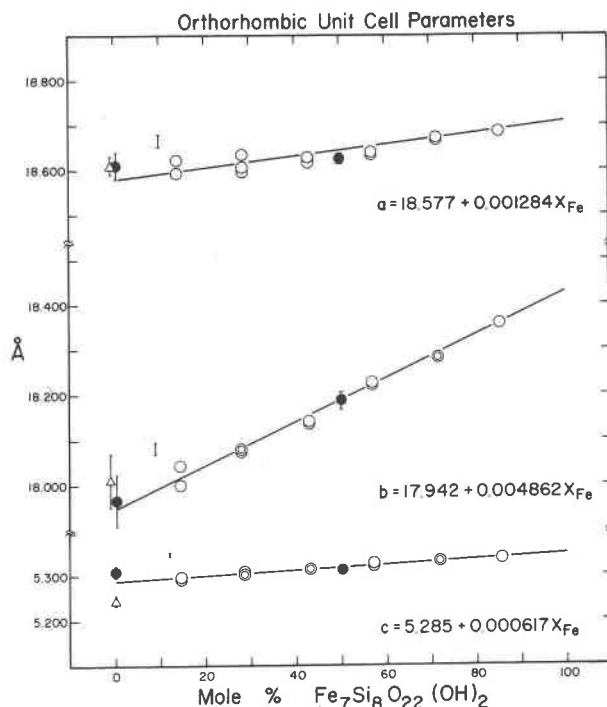


FIG. 1. Unit-cell parameters of synthetic orthorhombic amphiboles. Open circles: This study. Double circles indicate nearly identical values. Triangles: Greenwood (1963). Solid circles: Cameron (1975). Error bars at upper left indicate typical one standard error values in cell dimension. X_{Fe} = mole % Fe end-member; error less than 1% as discussed in text.

$$c(\text{\AA}) = 5.285(3) + 0.000617(50) X_{\text{Fe}}$$

$$V = (\text{\AA}^3) = 1760.8(1.7) + 0.8226(280) X_{\text{Fe}}$$

The straight-line plot of unit-cell volume *vs.* com-

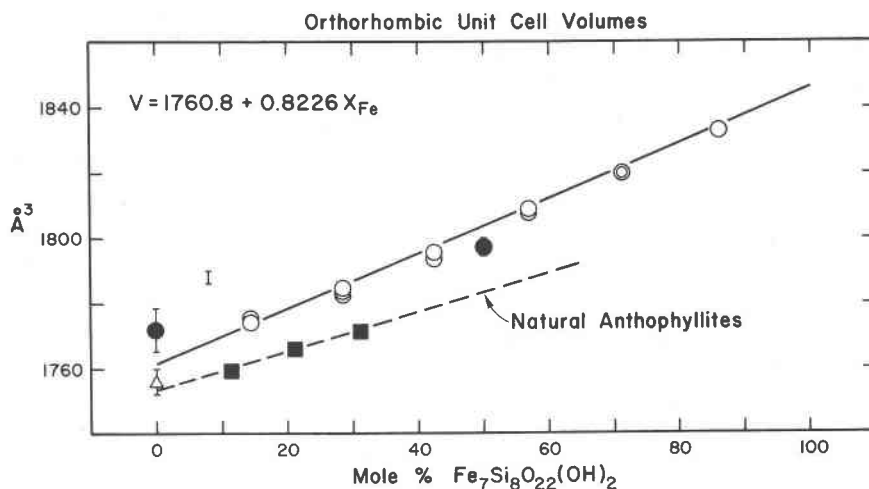


FIG. 2. Unit-cell volumes of orthorhombic amphiboles. Synthetics, solid line; natural anthophyllites, dashed line. Symbols as in Fig. 1. Solid squares: natural aluminum-poor anthophyllites from Johansson, 1930; Lindemann, 1964; Finger, 1970.

TABLE 3. Comparison of known amphibole structure types

	Monoclinic C^2/m		Monoclinic P^2_1/m		Protoamphibole $Pnmm$		Anthophyllite $Pnma$			
stacking sequence in a^* direction	(c/3)(c/3)		(c/3)(c/3)		(c/3)(-c/3)		(c/3)(c/3)(-c/3)(-c/3)			
chain types	A	A	A	B	A	A	A	B	A	B
$a(\text{\AA})$	~9.5		~9.5		~9.5		~18.6			

position indicates the absence of a volume-of-mixing term as far as can be determined by X-ray powder diffraction.

Figure 2 shows unit-cell volumes of synthetic amphiboles refined on the anthophyllite space group (solid line). The three natural amphiboles are fitted by the dashed straight line. Finger (1970) noted the difference in molar volumes between these natural anthophyllites and naturally-occurring clin amphiboles of the cummingtonite-grunerite series (Klein and Waldbaum, 1967). The synthetic, optically-orthorhombic forms studied here have molar volumes (Fig. 3) similar to those of the naturally-occurring monoclinic rather than the orthorhombic forms. Seifert (personal communication, 1974) reports that the molar volume of a Mg_5Fe_2 form which he synthesized is consistent with the curve of Klein and Waldbaum (1967). In addition, the unit cell volume of $Mg_{3.5}Fe_{3.5}$ (Cameron, 1975), refined as $Pnma$, lies on the curve for synthetic forms reported here within two standard errors reported by Cameron (see Fig. 1, 2 of this

study). Both of these amphiboles were synthesized at the FMQ buffer.

Discrepancies in the molar volume could be attributed to (1) relative amount of ordering Mg and Fe within the M sites; (2) the small amounts of Al, Na, and Ca in the three natural anthophyllites plotted in Fig. 2 and 3; (3) the synthetic amphiboles are orthorhombic but have not crystallized in the anthophyllite structure type.

Order-disorder apparently cannot account for the volume discrepancy. Seifert and Virgo (1974) have determined by Mössbauer spectra that equilibrium Fe-Mg distributions in the natural anthophyllite specimen of Finger (1970) are achieved in several days at 600°C and above, the temperature range utilized here. Seifert (personal communication, 1974) also reports that the increase in unit-cell volume accompanying disordering is too small to account for the observed difference. In support of this conclusion, an amphibole of composition Mg_5Fe_2 synthesized at 750°C, 2 kbar, and the FMQ buffer was annealed at 500°C, 2 kbar, and the FMQ buffer for 2 weeks. Unit cell parameters of the 500° sample $a = 18.594(5)$, $b = 18.078(4)$, $c = 5.299(2)$, $V = 1781.1(7)$ are not different from the 750°C data (Table 2).

Whereas natural anthophyllites can contain significant amounts of Al, Na, and Ca (Rabbitt, 1948), those plotted in Figures 2 and 3 closely approach the pure Mg-Fe join. Seifert and Virgo (1974) give the structural formula: $Na_{0.05}Ca_{0.09}Mg_{5.79}Fe_{1.17}Si_{7.81}Al_{0.18}O_{22}(OH)_2$ for the Finger (1970) sample, based on electron-microprobe analysis. From the wet-chemical analysis given by Johansson the formula $[Na_{0.08}Mg_{4.85}Fe_{1.82}^{2+}Fe_{0.15}^{3+}Ca_{0.06}Mn_{0.06}Al_{0.01}][Al_{0.09}Si_{7.91}]O_{22}(OH)_2$ was calculated, assuming 23 oxygens. Lindeman (1964) gives the structural formula $Mg_{6.2}Fe_{0.8}Si_8O_{22}(OH)_2$. Seifert (personal communication, 1974) reports that on the basis of his studies on the join between Mg_5Fe_2 and Na-gedrite of composition $Na_{0.6}Fe_2^{2+}Mg_{3.5}Al_{1.5}[Si_6Al_2 \dots]$, such small

TABLE 4. Equations relating location of major peaks (2θ CuK α) to amphibole composition*

040:	$2\theta = 19.784 - 0.0052 X_{Fe}$	$r = 0.9935$
420:	$2\theta = 21.559 - 0.0028 X_{Fe}$	$r = 0.9815$
440:	$2\theta = 27.648 - 0.0047 X_{Fe}$	$r = 0.9891$
610:	$2\theta = 29.261 - 0.0022 X_{Fe}$	$r = 0.9338$
630:	$2\theta = 32.628 - 0.0040 X_{Fe}$	$r = 0.9611$
2.11.0:	$2\theta = 57.300 - 0.0154 X_{Fe}$	$r = 0.9909$
053:	$2\theta = 58.379 - 0.0100 X_{Fe}$	$r = 0.9899$

* X_{Fe} = mole percent Fe end-member, r = correlation coefficient

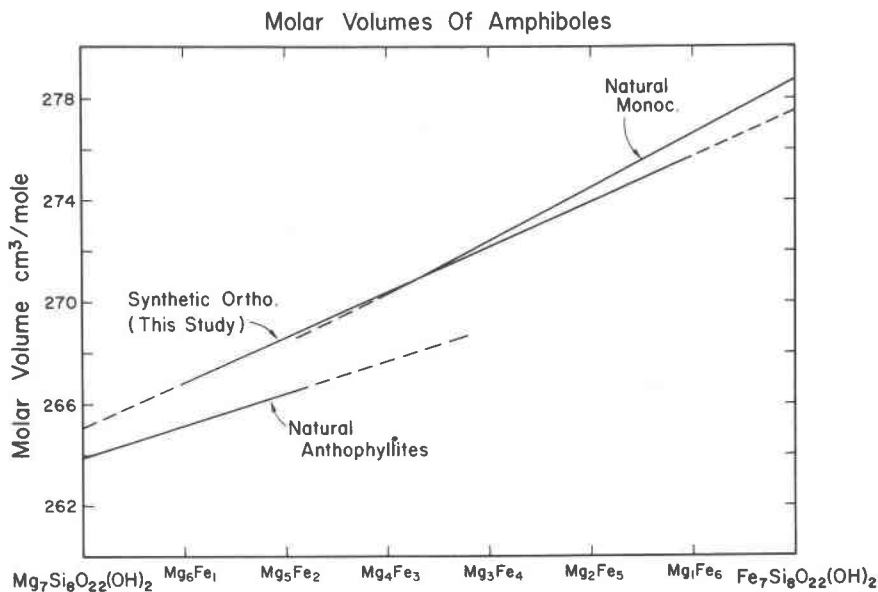


FIG. 3. Molar volumes of amphiboles. Curves represent synthetic orthorhombic forms (this study), natural monoclinic cummingtonites-grunerites (Klein and Waldbaum, 1967), and natural anthophyllites (Finger, 1970). Range of composition is shown by solid lines.

amounts of Al cannot account for the observed volume difference.

In consideration of the third possibility, a brief discussion of the basic amphibole structure is helpful. Only those details relevant to the determination of the structure type are discussed. For background, the reader is referred to references cited in the introduction and to diagrams such as that of Ernst (1968, Fig. 1, p. 5).

The amphibole structure consists of double chains of tetrahedra extending parallel to the c axis and interlocking to form sheets parallel to (100). These sheets are bound together by cations coordinated by apical oxygen and hydroxyl anions of adjacent sheets in a manner which requires a stagger of $\sim \pm c/3$ between adjacent tetrahedral chains. Two different types of tetrahedral chains have been identified in the amphibole structures studied to date. The tetrahedra in the A chain form nearly hexagonal rings, while those of the more distorted B chain form ditrigonal rings. The B chain can be roughly approximated by a close-packing of oxygens and thus would theoretically be expected to occupy a smaller volume than the A chains.

The known amphibole structure types can be distinguished by the chain type and the sequence of stacking vectors ($\pm c/3$) in the a^* direction. Table 3 summarizes the known structure types and gives the approximate a dimension.

In an attempt to determine the likelihood of hypothesis (3), electron diffraction patterns of a synthetic amphibole (Mg_5Fe_2) and a natural anthophyllite from the Minnesota River valley (L.W. Finger #M14104) were obtained by G. L. Nord using the transmission electron microscope facilities at the U.S. Geological Survey, Reston, Virginia.

Figures 4 and 5 are $h0l$ electron diffraction patterns of synthetic amphibole Mg_5Fe_2 and the natural anthophyllite, respectively, with the a^* and c^* directions and reciprocal unit-repeat distances indicated. Figures 6 and 7 are graphic $h0l$ plots of the observed X-ray structure factors of another natural anthophyllite (Finger, 1970) and protoamphibole respectively.

A repeat of approximately 18.6 Å in the a^* direction, as well as an alternating l -even = strong, l -odd = weak distribution of intensities is observed in Figures 4, 5, and 6. The electron diffraction pattern of the synthetic amphibole (Fig. 4) shows a strong enhancement of every fourth reflection in the a^* direction and suggests the presence of a $\sim 4.7\text{Å}$ subcell within the synthetic structure which is not present in either the natural anthophyllites (Figs. 5 and 6) or protoamphibole (Fig. 7). Streaking in the a^* direction may indicate large numbers of stacking faults in the a^* direction.

From Figures 4, 5, 6, 7, and Table 3, certain structure types can be rejected as inapplicable to these synthetic amphiboles. The electron diffraction pat-

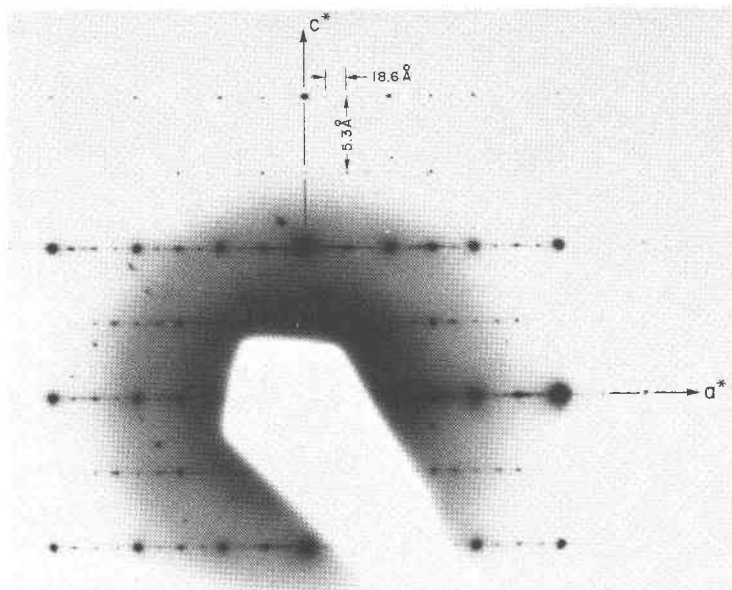


FIG. 4. $h0l$ electron diffraction photograph of synthetic amphibole $\text{Mg}_5\text{Fe}_2\text{Si}_4\text{O}_{22}(\text{OH})_2$. a^* and c^* directions and reciprocal distances representing 18.6 Å and 5.3 Å unit repeats are indicated.

terns indicate that the synthetic amphiboles have not crystallized with the anthophyllite structure. Protoamphibole (Fig. 7), which was originally considered a likely candidate because it has orthorhombic symmetry but contains only the larger A -type chains,

is rejected because of its $\sim 9.5\text{Å}$ a repeat. Superposition of Figures 6 and 7 also does not produce a distribution of intensities like that of Figure 4, and thus an interlayered mixture of protoamphibole and anthophyllite must also be ruled out. The $C2/m$ and

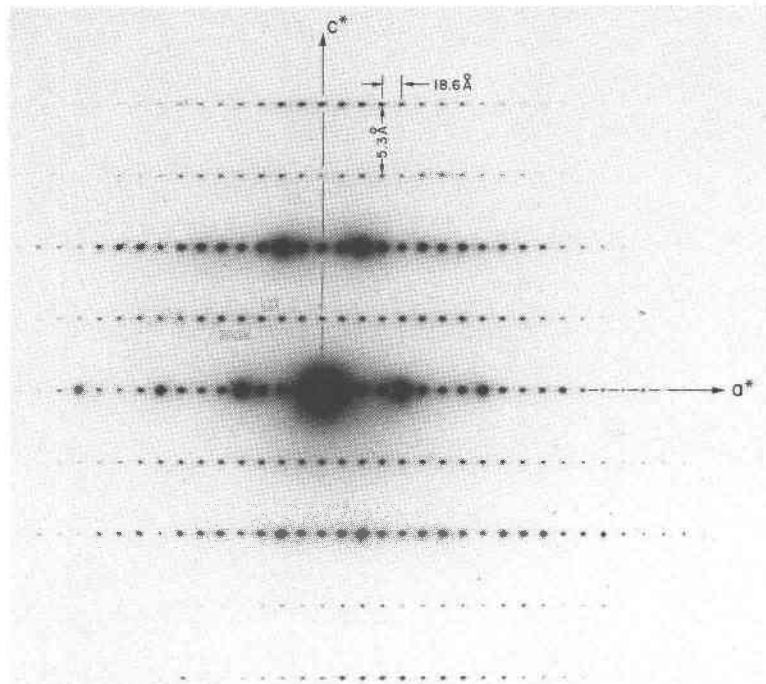


FIG. 5. $h0l$ electron diffraction photograph of natural anthophyllite (Finger sample M14104).

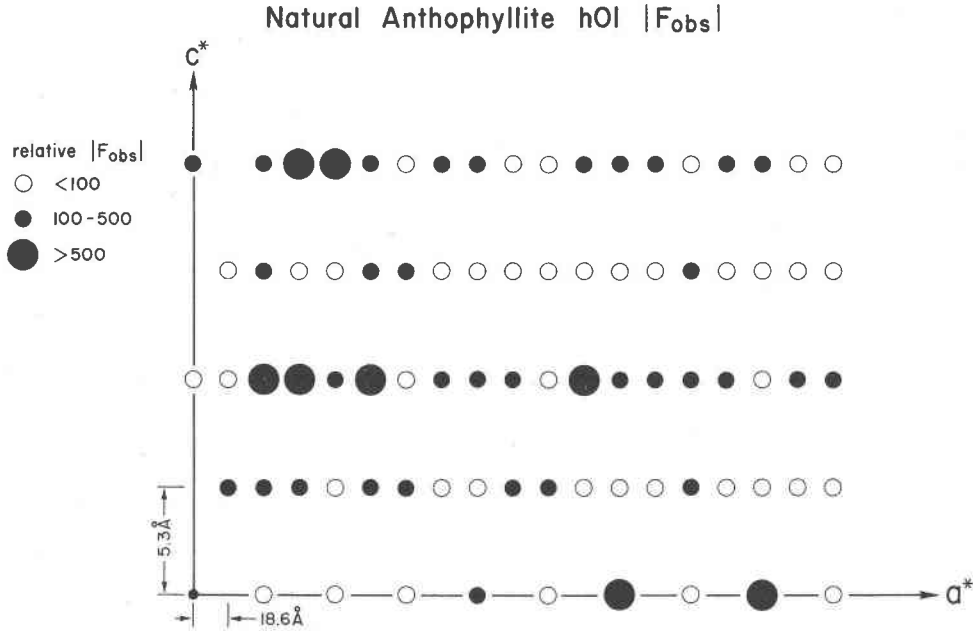


FIG. 6. Relative observed $h0l$ X-ray structure factors of the natural anthophyllite of Finger (1970).

$P2_1/m$ structures are rejected because of their $\sim 9.5 \text{ \AA}$ a unit-cell repeat and their monoclinic symmetry. Comparison with the appropriate X-ray precession photographs indicates that while twinned monoclinic amphiboles could produce additional reflections along a^* , they would not be likely to produce a regular 18.6 \AA repeat such as that observed. M. Ross

(personal communication 1975) has observed in a "fibrous talc" sample from Gouverneur, New York, an apparent epitaxial intergrowth of talc ($a \approx 5.3 \text{ \AA}$, $b \approx 9.2 \text{ \AA}$, $\gamma = 90^\circ$) with anthophyllite ($b \approx 18.0$, $c \approx 5.3$, $\alpha = 90^\circ$) so that the a - b plane of talc very closely superimposes on the b - c plane of anthophyllite with $a_{\text{talc}} || c_{\text{anth}}$ and $b_{\text{talc}} || b_{\text{anth}}$. This superposition of the

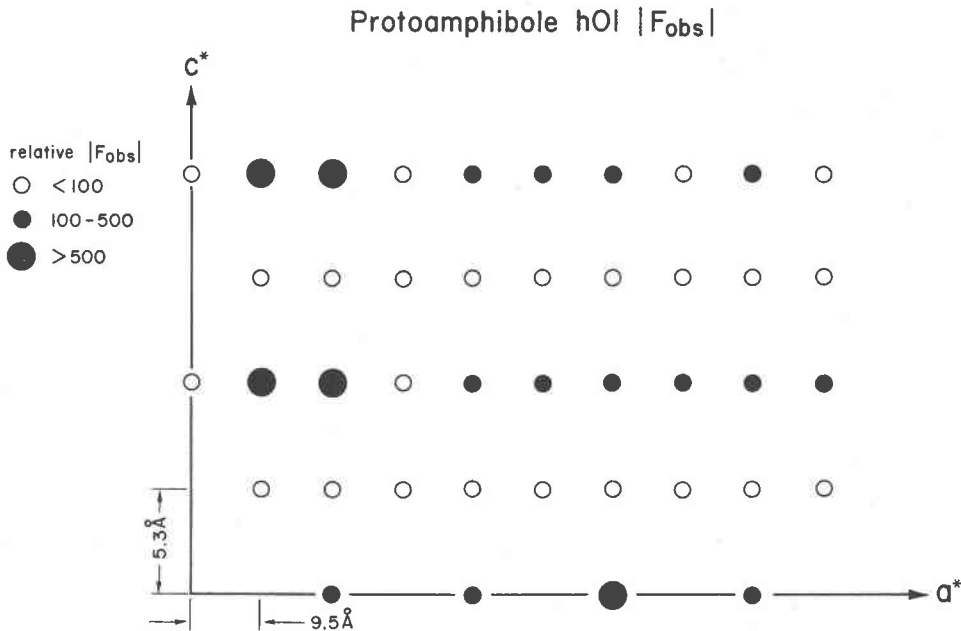


FIG. 7. Relative observed $h0l$ X-ray structure factors of protoamphibole (Gibbs, 1969).

talc and anthophyllite reciprocal lattice nets causes an enhancement of the anthophyllite $h0l$ reflections such that for $l = 2n, h = 0 \text{ mod } 4$, and for $l = 2n + 1, h = 2 \text{ mod } 4$.¹ The distribution of intensities within the $h0l$ net of synthetic amphibole (Fig. 4) bears some similarities to that described by Ross in that reflections are enhanced where $l = 2n$ and $h = 0 \text{ mod } 4$. A lesser enhancement of the reflections where $l = 2n$ and $h = 0 \text{ mod } 2$ and non-enhancement of reflections where $l = 2n + 1$ cannot be explained by the presence of talc.

By means of high-resolution electron microscopy of fibrous natural amphiboles, Hutchison *et al.* (1975) have observed what are interpreted to be triple tetrahedral silicate chains intercalated with normal amphibole chains parallel to (010). These triple chains could well be considered as finite talc-like strips, and such intergrowths might possibly be responsible for the anomalous diffraction pattern observed here. However, in light of the fact that the synthetic amphibole of Figure 4 was obtained from a run that yielded essentially all (99+%) amphibole, any such intergrowths would have to have a bulk composition equivalent to amphibole.²

We therefore conclude that the synthetic amphibole has a structure type unlike any known amphibole. The structure has orthorhombic symmetry and approximate unit-cell parameters $a = \sim 18.6\text{\AA}$, $b = \sim 18.0\text{\AA}$, $c = \sim 5.3\text{\AA}$ (composition Mg_5Fe_2). Its larger molar volume compared to anthophyllite may suggest that it contains only the larger A -type chains.

Relationship between composition and X-ray powder pattern

One of the goals of this study was to obtain a method of estimating accurate synthetic amphibole compositions from simple X-ray measurements. Linear regression analysis of peak locations ($2\theta\text{CuK}\alpha$) *vs.* composition was carried out for each reflection used in the least-squares refinement of cell parameters. The 210 peak at approximately $10.7^\circ 2\theta$ was not used because of the small shift in 2θ with interplanar spacing at low angles. From the equations in Table 4 various individual peaks and combinations of peaks were tested for their accuracy in

predicting compositions of the synthetic amphiboles of known composition. The results are shown in Table 5. In the case where a combination of peaks was used, the compositions given by the individual peaks were averaged to give the estimate of composition (*e.g.*, in Table 5, column 5, the composition given by the 040 peak, the 420 peak, and the 440 peak were averaged to give a final composition). The selection of combinations of peaks was based on their proximity on the X-ray powder pattern so as to provide the smallest 2θ range to be scanned.

In general, composition can be determined to within approximately 3–4 mole percent Fe end-member. However, the maximum error encountered using the 440, 610 combination (9.4 mole % Fe end-member) is too large to be of practical use in estimating compositions. The other methods have maximum errors ranging from 3.2–5.6 mole percent, representing the maximum error expected in estimating composition of any single unknown. There is a considerable range in the relative intensities of the peaks listed in Table 4. The 610 and 440 peaks have by far the largest relative intensities in the X-ray pattern. The 440 peak is distinguishable in X-ray patterns containing as little as 10–20 percent amphibole. Thus compositions on the join should be determinable to at worst 5–6 mole percent, even in samples containing small percentages of amphibole.

Effect of oxygen fugacity on unit-cell parameters and X-ray determinative curves

It was important to determine the effect, if any, of $f(\text{O}_2)$ on unit-cell parameters and on the X-ray determinative curves for amphibole composition. Accordingly, amphiboles synthesized at one buffer (generally FMQ) were annealed at oxygen fugacities defined by different buffers. Cell parameters of the annealed amphiboles were then determined in the same manner as described above.

Some difficulties were encountered using the NNO solid buffer. Runs of amphibole + H_2O were carried out at 2 kbar and $600^\circ\text{--}750^\circ\text{C}$ in platinum capsules. After runs, the charges consisted of Mg-enriched amphibole and up to 20 percent quartz but no additional Fe-containing phases. Following removal of the charge, the capsules were observed to be magnetic, and thus it was apparent that loss of iron from charge to capsule had occurred. In support of this conclusion, it was noted that the amount of quartz (*i.e.*, amount of iron lost to the capsule) increased with run temperature. Therefore, an attempt to determine the effect of $f(\text{O}_2)$ at NNO buffer on unit-cell parameters

¹ $h = 0 \text{ mod } 4$ indicates the $h = 0, 4, 8, 12, \dots$ reflections, $h = 2 \text{ mod } 4$ indicates the $h = 2, 6, 10, 14, \dots$ reflections.

² After this paper was submitted, Veblen and Burnham (1975) reported similar triple-chain structures as products of the retrograde anthophyllite-talc transformation from Chester, Vermont. One such structure has a chemical formula corresponding to 1 anthophyllite + $1/2$ talc.

TABLE 5. Compositions predicted from various combinations of peaks

Run #	Composition of Mix (Mole % Fe ₇)	040					
		440	440	440	440	610	2110 053
	X _{real}	X _{observed}					
145	14.3	17.5	17.8	17.4	18.5	19.0	18.0
290	14.3	13.9	19.1	18.8	18.1	22.7	—*
26	28.6	29.8	29.0	29.3	29.8	28.8	27.9
125	28.6	24.6	23.8	24.6	23.0	19.2	27.2
68	28.6	29.1	29.9	29.8	28.3	32.8	25.5
82	42.9	42.2	43.4	43.0	42.1	41.7	41.5
149	42.9	40.5	40.5	40.0	39.4	36.1	41.1
150	57.1	56.4	59.5	58.2	57.2	58.8	59.8
80	57.1	56.7	55.6	55.5	58.0	57.0	60.0
140	71.4	71.8	73.4	73.8	68.9	68.8	70.8
226	71.4	72.7	71.2	71.3	73.8	74.4	73.6
453	85.7	--	84.9	--	87.7	85.7	--
$\Sigma X_{\text{real}} - X_{\text{obs}} $							
N		1.6	2.2	2.0	2.5	3.5	2.0
$ X_{\text{real}} - X_{\text{obs}} _{\text{max}}$		3.2	4.8	4.5	5.6	9.4	3.7

*entry left blank indicates peak not measurable in powder pattern

was carried out in Shaw apparatus (Shaw, 1967) at 1 kbar total pressure. At the low $f(\text{H}_2)$ equivalent to the NNO buffer, accurate control of $P(\text{H}_2)$ and diffusion rates across the Pt membrane posed some problems, resulting in an $f(\text{H}_2)$ of 7 ± 2 bar. For comparison, Eugster and Skippen (1967) gave a value of $f(\text{H}_2) = 4.5$ bar at 700°, 1 kbar for the assemblage Ni-NiO-H₂O, and a value of $f(\text{H}_2) = 12.8$ bar at

700°C, 1 kbar was calculated for the assemblage FMQ-H₂O from the data of Wones and Gilbert (1969), Burnham *et al.* (1969), and the JANAF Tables (1971). Thus even if $f(\text{O}_2)$ was at values lower than that of the NNO buffer, it still was considerably higher than that of the FMQ buffer.

Table 6 summarizes unit-cell parameters of runs made at various oxygen fugacities. Statistically no

TABLE 6. Unit-cell parameters for amphiboles annealed at various $f(\text{O}_2)$

T(°C)	P(kbar)	Buffer (Duration, days)	a(Å)	b(Å)	c(Å)	V(Å ³)
Mg ₆ Fe ₁						
725	2.0	H-M(16)	18.610(12)	18.007(12)	5.291(2)	1773.3(1.3)
650	2.0	H-M(14)	18.584(17)	18.017(5)	5.291(2)	1771.8(1.0)
700	2.0	FMQ*(46)	18.607(9)	18.022(12)	5.293(2)	1775.0(1.7)
Mg ₄ Fe ₃						
700	1.0	Ch ₄ -C(14)	18.612(11)	18.141(8)	5.311(3)	1793.2(1.4)
700	1.0	Shaw**(11)	18.624(12)	18.136(8)	5.311(3)	1794.0(1.5)
700	2.0	FMQ*(35)	18.620(11)	18.138(8)	5.313(3)	1794.2(1.5)
Mg ₃ Fe ₄						
650	1.0	CH ₄ -C(14)	18.643(9)	18.222(6)	5.325(2)	1808.9(1.2)
650	2.0	FMQ*(36)	18.637(12)	18.225(10)	5.326(3)	1808.8(1.9)

*FMQ value denotes average of determinations on two separate runs given in Table 1.

** $f(\text{H}_2) = 7 \pm 2$ bars; $f(\text{H}_2)$ of FMQ = 12.8 bars; $f(\text{H}_2)$ of N-NO = 4.5 bars.

differences in unit-cell parameters of these amphiboles as a function of $f(\text{O}_2)$ exist. This result is somewhat surprising since variation of unit-cell parameters with $f(\text{O}_2)$ and temperature has been reported for a number of hydroxy-silicates (e.g., biotite: Eugster and Wones, 1962; ferrotremolite: Ernst, 1966). This variation is generally attributed to the formation of oxy-silicates (e.g., oxyamphibole) by the reaction $\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \text{O}^{2-} + \text{H}$. Substitution of the smaller Fe^{3+} ions has the effect of decreasing unit-cell parameters. In Mössbauer spectral studies, Seifert and Virgo (1974) were unable to detect Fe^{3+} in the structure of an amphibole of approximate composition Mg_5Fe_2 annealed at 720°C and the FMQ buffer for four days. In light of this result, annealing at $f(\text{O}_2)$ lower than the FMQ buffer would not be expected to produce any changes in unit-cell parameters attributed to variation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. The amount of solid solution of oxy-amphibole should be greater at $f(\text{O}_2)$ defined by MH buffer. However, only very Mg-rich amphiboles are stable at these higher oxygen fugacities, and the total iron content may not be large enough for the unit-cell parameters to reflect any change. We therefore concluded that oxy-amphibole, if present, cannot be detected by changes in unit-cell parameters as measured in this study.

Based on the above discussion, the X-ray determinative curves are assumed to be applicable, without correction, over the range of temperature and $f(\text{O}_2)$ of this study.

Acknowledgments

The authors are indebted to G. V. Gibbs, M. Ross, F. D. Bloss, and D. A. Hewitt for valuable discussion and criticism. L. W. Finger and G. V. Gibbs provided observed X-ray structure factors for anthophyllite and protoamphibole respectively, and L. W. Finger kindly provided a natural anthophyllite specimen for use. E. Dwornik, G. Nord, and M. Ross assisted in obtaining and interpreting the electron diffraction patterns. This research was supported by NSF grant DES72-01587 A01.

References

- APPLEMAN, D. E. AND H. T. EVANS, JR. (1973) Job 9214: Indexing and least-squares refinement of powder diffraction data. Natl. Tech. Inf. Serv., U.S. Dept. Commer., Springfield, Virginia, Document PB 216 188.
- BARR, A. M AND J. H. GOODNIGHT (1972) *Statistical Analysis System*. Student Supply Store, North Carolina State University, Raleigh, North Carolina.
- BOYD, F. R. (1955) The anthophyllite-cummingtonite group. *Carnegie Inst. Wash. Year Book*, **54**, 117-118.
- BURNHAM, C. W., J. R. HOLLOWAY AND N. F. DAVIS (1969) Thermodynamic properties of water to 1000°C and 10000 bars. *G.S.A. Spec. Pap.* **132**, 96p.
- 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.
- ERNST, W. G. (1966) Synthesis and stability relations of ferrotremolite. *Am. J. Sci.* **264**, 37-65.
- (1968) *Amphiboles: Crystal Chemistry, Phase Relations and Occurrence*, Springer-Verlag, New York, 125p.
- EUGSTER, H. P., AND G. SKIPPEN (1967) Igneous and metamorphic reactions involving gas equilibria. In, P. H. Abelson, Ed., *Researches in Geochemistry*, Vol. 2, John Wiley and Sons, New York, p. 492-520.
- AND D. R. WONES (1962) Stability relations of the ferruginous biotite, annite. *J. Petrol.* **7**, 82-125.
- EVANS, B. W., S. GHOSE, J. M. RICE AND V. TROMMSDORF (1974) Cummingtonite-anthophyllite phase transition in metamorphosed ultramafic rocks, Ticino, Switzerland. (abstr.) *EOS, Trans. Am. Geophys. Union*, **55**, no. 4, p. 469.
- FINGER, L. W. (1970) Refinement of the crystal structure of an anthophyllite. *Carnegie Inst. Wash. Year Book*, **68**, 283-288.
- FORBES, W. C. (1971) Synthesis of grunerite, $\text{Fe}_7\text{Si}_6\text{O}_{22}(\text{OH})_2$. *Nature, Phys. Sci.* **232**, p. 109.
- GIBBS, G. V. (1969), Crystal structure of protoamphibole. *Mineral. Soc. Am. Spec. Pap.* **2**, 101-109.
- AND S. J. LOUISNATHAN (1971) *Powder Diffraction in Geology*. Short Course Lecture Notes, 5th Annu. Meet. S.E. Sec. G.S.A., 190 p.
- GREENWOOD, H. J. (1963) The synthesis and stability of anthophyllite. *J. Petrol.* **4**, part 3, p. 317-351.
- HINRICHSSEN, T. (1967) Über den Stabilitätsbereich der Mg-Fe^{2+} -Al-Mischkristallreihe rhombischer Hornblenden, Teil I: Hydrothermale Untersuchungen der Anthophyllit-Ferroanthophyllit-Mischkristallreihe. *Neues Jahrb. f. Mineral. Monatsh.* p. 257-270.
- HUEBNER, J. S. (1971) Buffering techniques for hydrostatic systems at elevated pressures. In, G. C. Ulmer, Ed., *Research Techniques for High Pressure and High Temperature*, Springer-Verlag, New York, 367 p.
- HUTCHINSON, J. L., M. C. IRUSTETA AND E. J. W. WHITTAKER (1975) Defect structures in fibrous amphiboles. Int. Crystallogr. Conf., Amsterdam, Aug. 7-15; *Acta Crystallogr. A* **31**, S 263.
- JANAF Thermochemical Tables (1971) Natl. Stand. Data Serv., Natl. Bur. Stand. **37**, 1141 p.
- JOHANNSON, K. (1930) Vergleichende Untersuchungen an Anthophyllit, Grammatit, and Cummingtonit. *Z. Kristallogr.* **73**, 31-51.
- KLEIN, C., JR. (1964) Cummingtonite-grunerite series: a chemical, optical, and X-ray study. *Am. Mineral.* **49**, 963-982.
- (1966) Mineralogy and petrology of the metamorphosed Wabush iron formation, southwestern Labrador. *J. Petrol.* **7**, 218-330.
- AND D. R. WALDBAUM (1967) X-ray crystallographic properties of the cummingtonite-grunerite series. *J. Geol.* **75**, 379-392.
- LAYTON, W. AND R. PHILLIPS (1960) The cummingtonite problem. *Mineral Mag.* **32**, 659-663.
- LINDEMANN, W. (1964) Beitrag zur Struktur des Anthophyllits (abstr). *Fortschr. Mineral.* **42**, 205.
- PAPIKE, J. J., M. ROSS AND J. R. CLARK (1969) Crystal-chemical characterization of clinoamphiboles based on five new structure refinements. *Mineral. Soc. Am. Spec. Pap.* **2**, 117-136.
- PREWITT, C. T., J. J. PAPIKE AND M. ROSS (1970) Cummingtonite: A reversible, nonquenchable transition from $P2_1/m$ to $C2/m$. *Earth Planet. Sci. Lett.* **8**, 448-450.

- RABBITT, J. C. (1948) A new study of the anthophyllite series. *Am. Mineral.* **33**, 263-323.
- RAMBERG, H. (1952) Chemical bonds and distribution of cations in silicates. *J. Geol.* **60**, 331-355.
- RICE, J. M., B. W. EVANS AND V. TROMMSDORFF (1974) Widespread occurrence of magnesocummingtonite in ultramafic schists, Cime di Gagnore, Ticino, Switzerland. *Contrib. Mineral. and Petrol.* **43**, 245-251.
- SEIFERT, F. AND D. VIRGO (1974) Temperature dependence of intracrystalline Fe²⁺-Mg distribution in a natural anthophyllite. *Carnegie Inst. Wash. Year Book*, **73**, 405-411.
- SHAW, H. R. (1967) Hydrogen osmosis in hydrothermal experiments. In, P. H. Abelson, Ed., *Researches in Geochemistry*, Vol. 2, John Wiley and Sons, New York, 521-541.
- VEBLEN, D. R. AND C. W. BURNHAM (1975) Triple-chain biopyriboles: Newly discovered intermediate products of the retrograde anthophyllite-talc transformation, Chester, Vt., *EOS, Trans. Am. Geophys. Union*, **56**, 1076.
- WONES, D. R., AND M. C. GILBERT (1969) The fayalite-magnetite-quartz assemblage between 600° and 800°C. *Am. J. Sci.* **267A**, 480-488.

Manuscript received, August 8, 1975; accepted for publication, July 2, 1976.