THE AMERICAN MINERALOGIST, VOL. 45, SEPTEMBER-OCTOBER, 1960

PROTO-AMPHIBOLE, A NEW POLYTYPE

G. V. GIBBS, F. D. BLOSS, AND H. R. SHELL,* *Electrotechnical Experiment Station, Bureau of Mines, U. S. Department of the Interior, Norris, Tenn.*

ABSTRACT

An orthorhombic amphibole ($a_0=9.330$, $b_0=17.867$, $c_0=5.286$ Å, ±0.05 per cent with space group *Pnmn* or *Pn2n*) has been identified as a phase within the system Li_2O—MgO—MgF_2—SiO_2. Its unit cell is one-half that of anthophilite ($a_0=18.5$, $b_0=17.9$, $c_0=5.28$ Å; space group *Pnma*). A new structure type for amphibole, based on the space group *Pnmn*, is proposed. The term proto-amphibole is used to describe this new polytype, since it appears structurally related to the amphiboles in the same way that proto-enstatite is to the pyroxenes.

Chemical analysis reveals the proto-amphibole studied in greater detail to have the following formula: $Li_{.64}Na_{.05},Li_{.48}Mg_{1.52}.Mg_{5.00}Si_{7.93}:O_{21.91}F_{2.09}$.

Its optical constants for sodium light are: $\alpha=1.5759$, $\beta=1.5870$, $\gamma=1.5928$, $2V_{(calc.)}=71.4°$, $2V_{(meas.)}=74°$. The presence of lithium and the absence of calcium in the melts studied seems essential to the formation of proto-amphibole, a monoclinic fluor-amphibole being otherwise developed.

INTRODUCTION

The synthetic asbestos investigations of the Electrotechnical Experiment Station of the Federal Bureau of Mines at Norris, Tenn., recently led to the synthesis of some orthorhombic amphiboles which, on preliminary study, appeared to the fluoride analogs of anthophyllite. Powder diffraction data at first seemed to confirm this identification. However, precession, cone-axis, and rotation diagrams of single crystals revealed: (1) A repeat unit along the *a*-axis which was one-half that of anthophyllite and (2) a space group which was *Pnmn* or *Pn2n* rather than *Pnma* as is known for anthophyllite.

These amphiboles thus belong to a distinct new structural type which, for reasons to be developed, may be referred to as proto-amphibole. Details of the study are here presented to establish this new structure and to indicate criteria for the recognition of natural representatives. One of us (G.V.G.) is currently testing the postulated structure by Fourier synthesis at The Pennsylvania State University.

CHEMICAL SYNTHESIS

An orthorhombic fluor-amphibole was first observed as a phase in the system Li_2O—MgO—MgF_2—SiO_2. Following this observation a number

---

* Academic addresses for F.D.B. and G.V.G. are, respectively, Department of Geology, Southern Illinois University, Carbondale, Ill., and Department of Mineralogy, Pennsylvania State University, University Park, Pa.

of melts (19–43, et seq.) were studied to determine the bulk composition most favorable for the formation of this phase.

The procedure used was to melt the well-mixed raw materials in a graphite crucible, which was itself protected from oxidation by being sealed in a fire-clay crucible. After melting was effected (within the range 1350°–1450° C.), the temperature was rapidly lowered by 100°, then at a rate of 10°–15° C. per hour to 1000° C. For melt compositions subject to reduction by graphite, the procedure was varied in that only a sealed fire clay crucible was used. Consequently, it was necessary to cool these melts more rapidly in order to prevent excessive contamination. Raw materials were LiF, Li_2CO_3, MgF_2, MgO, SiO_2 (−200 mesh quartz sand), $CaCO_3$, and various oxides or carbonates.

The experiments of Table 1, as well as others, appear to indicate that Li^+ is essential for the formation of proto-amphibole. The efficacy of Li^+, however, appears affected by the nature of the other ions in the melt. For example, when Al^{+++} is present, the Li^+ combines with Al^{+++} to form β-spodumene but no fluor-amphibole; if Cl^- is present, the Li^+ containing phase is LiCl, and again no fluor-amphibole is formed.

Neither Na^+ nor K^+ yielded proto-amphibole when substituted completely for Li^+ in otherwise favorable batch compositions. With Na^+, the monoclinic fluor-amphibole, $Na \cdot NaMg \cdot Mg_5 \cdot Si_8{:}O_{22}F_2$, was obtained instead. *X*-ray and optical data on this substance will be reported separately (Miller and Gibbs, in press). K^+ always yielded a sheet structure (Shell, et al., 1958). If the lithium content was maintained (Na^+ and K^+ absent), orthorhombic fluor-amphibole was formed even when Mn^{++}, Co^{++}, Cu^{++}, Fe^{++}, or Zn^{++} were partially substituted for Mg^{++} in the batch composition. However, if Ca^{++} was substituted to the extent of $\frac{1}{2}$ or $\frac{2}{7}$ of the amount of Mg^{++} in the batch composition, monoclinic rather than orthorhombic fluor-amphiboles were formed (Table 1, 19-12). MgO—MgF_2—SiO_2 systems (Fujii, T. and Eitel, W., 1957) did not yield orthorhombic amphiboles even when Fe^{++} was partially substituted for Mg^{++}. 1 or 2 Ni^{++}, substituted for equivalent Mg^{++}, favored silicates with a sheet structure.

The fluoride content of the batch compositions strongly affected the yield of orthorhombic amphibole. Batch compositions may be compared to the theoretical fluoride content in fluor-amphiboles which is $2F^-$ per unit formula (e.g. fluor-richterite, $Na \cdot Na\ Ca \cdot Mg_5 \cdot Si_8{:}O_{22}F_2$; or to that in fluor-micas which is $4F^-$ (e.g. fluor-phlogopite, $K_2 \cdot Mg_6 \cdot Al_2Si_6{:}O_{20}F_4$). These may be written alternately as $Na \cdot Na\ Ca \cdot Mg_5 \cdot (F_2)\ (Si_4O_{11})_2$ and $K_2 \cdot Mg_6 \cdot (F_4)(Al\ Si_3O_{10})_2$, respectively.

In the Li_2O—MgO—MgF_2—SiO_2 system, an 7:O ratio of 1:5 yielded fluor-micas or fluor-montmorillonites as the major phase; whereas F:O ratios approaching 1:11 gave fluor-amphibole as the major phase. This tendency was not necessarily true for all cationic substitutions, some of which (e.g. Zn^{++}) never yielded a fluor-mica.

TABLE 1.—BATCH COMPOSITIONS AND RESULTING PHASES

Exp. No.	Batch Composition	Phases formed; remarks
19-41	$Li \cdot LiMg \cdot Mg_5 \cdot Si_8 : O_{21}F_4$	97% water-swelling fluor-montmorillonoid; 3% acicular proto-amphibole
19-43	$Li \cdot Ca_2 \cdot Mg_5 \cdot BSi_7 : O_{21}F_4$	Monoclinic fluor-amphibole major phase
19-45	$Li \cdot Mg_2 \cdot Mg_5 \cdot AlSi_7 : O_{21}F_4$	Humites are major phases; some beta spodumene; mica and amphibole absent
19-47	$Li \cdot MnMg \cdot Mg_5 \cdot BSi_7 : O_{21}F_4$	10% water-swelling platy mineral; 90% orthorhombic fluor-amphibole
19-48	$Li \cdot LiMg \cdot Mg_5 \cdot B_2Si_6 : O_{20}F_4$	95% fluor-montmorillonoid; 5% norbergite, fluor-amphibole
19-49	$Li \cdot LiCo^{++} \cdot Mg_5 \cdot Si_8 : O_{21}F_4$	20% fluor-montmorillonoid; remainder orthorhombic fluor-amphibole
19-50	$Li \cdot LiCu^{++} \cdot Mg_5 \cdot Si_8 : O_{21}F_4$	Similar to 19–49, but 50% or more of Cu^{++} was as oxide
19-52	$Li \cdot LiNi^{++} \cdot Mg_5 \cdot Si_8 : O_{21}F_4$	Very fine, fluor-montmorillonoid; no fluor-amphibole
19-53	$Li \cdot LiZn^{++} \cdot Mg_5 \cdot Si_8 : O_{21}F_4$	Fluor-montmorillonoid absent; orthorhombic fluor-amphibole present
19-64	$Li \cdot LiMg \cdot Mg_5 \cdot B_2Si_6 : O_{20.5}F_3$	75% fluor-montmorillonoid; 25% proto-amphibole (see 19-47)
19-65	$Li \cdot LiMg \cdot Mg_5 \cdot B_2Si_6 : O_{22}F_2$	Fluor-montmorillonoid minor; largely orthorhombic fluor-amphibole (see 19-47, 19-64)
19-69	$Li_{.5} \cdot Mg_2 \cdot Mg_5 \cdot Si_8 : O_{21.25}F_4$	95% fluor-montmorillonoid; 5% tridymite; no fluoramphibole
19-71	$Mg_{.5} \cdot Mg_2 \cdot Mg_5 \cdot Si_8 : O_{21.5}F_4$	No fluor-amphibole or fluor-montmorillonoid
19-73	$Li \cdot LiMg \cdot Mg_5 \cdot Si_8 : O_{21.95}F_{2.1}$	20% fluor-montmorillonoid; 80% proto-amphibole
25-160	$Li \cdot LiCa \cdot Mg_5 \cdot Si_8 : O_{21.5}F_3$	Major phase formed was monoclinic fluor-amphibole
19-12	$Li \cdot LiCa \cdot Mg_5 \cdot Si_8 : O_{21.5}F_3$	Monoclinic fluor-amphibole was a major phase (75%); fluor-montmorillonoid phase minor (25%); fluor-amphibole phase contained 8. wt. % CaO
19-86	$Li \cdot LiMg \cdot Mg_5 \cdot Si_8 : O_{22.5}F_1$	Fluor-montmorillonoid, 10%; orthorhombic fluoramphibole, 55%, enstatite, 35%
19-87	$Li \cdot LiMg \cdot Mg_5 \cdot Si_8 : O_{23}F_0$	Note that fluoride was *absent* from batch; products were: clinoenstatite, 50–60%; cristobalite, 20%; "Mg equivalent of petalite," 30%; differential thermal curves showed a phase (Li_2MgSiO_4?) with reversible inversion at 880° C.

CHEMICAL FORMULA

The proto-amphibole synthesized from batch composition 19-41 (Table 1) was chemically analyzed and its ionic composition was calculated by two different methods. In the first method the total mass units (ZM) of the unit cell were determined from the standard formula:

$$ZM = \frac{\rho V \times 10^{-24}}{1.66 \times 10^{-24}}$$

where ρ and V represent the crystal's measured density and unit cell volume. For this particular proto-amphibole, as is discussed later, these were determined to be 2.928 g. cm.$^{-3}$ (at 21° C.) and 881.22 Å^3, respectively. Inserting these values in the foregoing equation, ZM can be calculated to be 1554.258 mass units. The chemical analysis (col. 1, Table 2) permits calculation of the amount of the mass units of each chemical component in the unit cell (col. 2, Table 2). Consequently, the relative numbers of different cations and fluoride ions in the unit cell (col. 4) were calculated by dividing the value in col. (2) by the equivalent weight in col. (3). Assuming Z=2, the chemical formula for proto-amphibole is determined, except for oxygen, by halving the values in col. (4). Thus $Na_{.04}\,Li_{1.12}\,Mg_{6.50}\,Si_{7.89}\,O_xF_{2.09}$. Assuming sufficient oxygen to neutralize

TABLE 2. CHEMICAL ANALYSIS OF PROTO-AMPHIBOLE AND IONIC FREQUENCIES

	(1) Analysis (wt. %)	(2) Mass units in unit cell*	(3) Equivalent weight of oxides, etc.	(4) Number of ions per unit cell
SiO_2	60.68	948.43	60.06	Si 15.79
MgO	33.51	523.76	40.32	Mg 12.99
Li_2O	2.14	33.45	14.94	Li 2.24
CaO	0.0	—	—	
Na_2O	0.17	2.66	30.99	Na 0.08
F	5.07	79.25	19.00	F 4.17
Ignition loss 350°	0.40	—		
	101.97	1587.55		
Less O=F	2.13	33.30		
Total	99.84	1554.25		

* Results in col. (1) multiplied by 1554.258/99.44. It will be noted that in this method the total of 1554.25 is obtained first, then the portions comprising the total are calculated from the chemical analysis in weight %.

all unsatisfied cations, as well as grouping the ions according to their presumed structural positions, the formula becomes

$$Na_{.04}Li_{.62}\cdot Li_{.50}Mg_{1.50}\cdot Mg_{5.00}\cdot Si_{7.89}:O_{21.82}\cdot F_{2.09}.$$

Calculating the formula on the basis of 24 anions using the method of Shell and Craig (1956), the result is

$$Na_{.05}Li_{.64}\cdot Li_{.48}Mg_{1.52}\cdot Mg_{5.00}\cdot Si_{7.93}:O_{21.91}\cdot F_{2.09}.$$

The two formulae, each calculated on a different basis, thus show excellent agreement.

OPTICAL DATA

The optical properties of the proto-amphiboles studied were obtained using a 5-axis universal stage, a monochromator, and the standard single variation technique. All crystals were biaxial negative and exhibited parallel extinction. The optical data for typical proto-amphiboles are summarized in Table 3 (A, B, and C); the α and β indices cited are believed accurate to ±0.0005. Each measured value for $2V_D$ (presented as footnotes to the table) represents an average of eighteen measurements on nine different crystals; 95 per cent of these individual measurements varied by less than one degree from the average value.

The close physical and chemical resemblance of the synthetic proto-amphibole to anthophyllite invites comparison between their optical properties. Accordingly, the data for two natural anthophyllites (Rabbitt, 1948, p. 291) were tabulated (D and E, Table 3), these two particular anthophyllites being chosen for their chemical similarity to the proto-amphibole synthesized. Compared to these anthophyllites, the synthetic proto-amphibole possessed significantly lower dispersion ($N_f - N_c$) and a smaller 2V. In addition proto-amphibole 19-41A, as well as two others examined microscopically, was optically negative for all wavelengths of light used whereas Rabbitt indicates the optic sign of anthophyllite to be often positive. The generally lower indices of the proto-amphibole compared with the natural anthophyllites may be the result of the complete substitution of fluorine for hydroxyl. Such substitution has been shown to lower the indices of refraction in the case of both fluor-phlogopite (Kohn and Hatch, 1955, p. 15) and fluor-tremolite (Comeforo and Kohn, 1954, p. 543).

MORPHOLOGY

Synthetic proto-amphibole crystallized in an acicular habit, the needles consisting of several parallel-to-sub-parallel individuals, each elongated parallel to the *c*-axis. Individual crystals with well developed faces were rare. The best developed faces were of the {110} form. The {100} form occasionally occurred as narrow, poorly developed faces. An

TABLE 3. COMPARISON OF OPTICAL CONSTANTS OF SYNTHETIC PROTO-AMPHIBOLE WITH NATURAL ANTHOPHYLLITES

λ(Å)	γ	β	α	$\gamma-\alpha$	$\gamma-\beta$	Optic sign; 2V
A. Synthetic proto-amphibole No. 19-41A						
F (4861)	1.5989	1.5930	1.5816	0.0173	0.0061	(−); 71° (calc)
D(5893)	1.5928	1.5870	1.5759	0.0169	0.0058	(−); 71.4° (calc)[a]
C (6563)	1.5903	1.5845	1.5736	0.0167	0.0057	(−); 71.8° (calc)
N_f-N_c	.0086	.0085	.0080			
B. Synthetic proto-amphibole No. 18-64B						
F (4861)	1.5987	1.5923	1.5808	0.0181	0.0064	(−); 71.3° (calc)
D(5893)	1.5938	1.5869	1.5742	0.0196	0.0069	(−); 72.3° (calc)[b]
C (6563)	1.5918	1.5847	1.5714	0.0204	0.0071	(−); 71.8° (calc)
N_f-N_c	.0069	.0076	.0094			
C. Synthetic proto-amphibole No. 19-73C						
F (4861)	1.6049	1.5996	1.5920	0.0129	0.0053	(−); 79.4° (calc)
D(5893)	1.5979	1.5926	1.5812	0.0167	0.0053	(−); 68.2° (calc)[c]
C ((6563)	1.5950	1.5897	1.5766	0.0184	0.0053	(−); 64.5° (calc)
N_f-N_c	.0099	.0099	.0154			
D. Natural Anthophyllite (Rabbitt, 1948, p. 291, No. 29)						
F (4861)	1.6451	1.6365	1.6365	0.0146	0.0086	(+); 80°
D(5893)	1.6354	1.6270[d]	1.6180	0.0174	0.0084	(−); 88°
C (6563)	1.6315	1.6230	1.6127	0.0188	0.0085	(−); 84°
N_f-N_c	0.0136	0.0135	0.0178			
E. Natural Anthophyllite (Rabbitt, 1948, p. 291, No. 30)						
F (4861)	1.6505	1.6430	1.6340	0.0165	0.0075	(−); 85°
D(5893)	1.6410	1.6280	1.6162	0.0248	0.0130	(+); 88°
C (6563)	1.6372	1.6205	1.6092	0.0280	0.0167	(+); 79°
N_f-N_c	0.0133	0.0225	0.0248			

[a] By direct measurement $2V_D=74°$

[b] By direct measurement $2V_D=75.2°$

[c] By direct measurement $2V_D=73°$

[d] Rabbitt's original paper has 1.6370, but this is presumed to be 1.6270.

excellent cleavage occurred parallel to {110}. The angle between the (110) and $(\bar{1}10)$ faces was determined with an Eichner two circle goniometer to be 55°02′; individual measurements varied as much as 10′ from these averages (although usually they were within 5′).

DIFFRACTION DATA

The *x*-ray diffraction data for synthetic proto-amphibole were obtained by means of a Norelco diffractometer from a glass slide smear of a mixture of powdered proto-amphibole and a synthetic spinel ($MgAl_2O_4$) internal standard. The smear was prepared by the standard technique of mixing a small portion of powder with a lacquer of 10 parts cellulose acetate dissolved in acetone and carefully spreading the resultant slurry over the slide as a uniformly thin, translucent layer.

The instrumental settings of the diffractometer were: Time constant, 4 seconds; multiplier, 1.0; scale factor, 8 and 16; divergence and scatter slits, 1°; receiving slits, 0.006″; scanning speed, $\frac{1}{4}$ degree 2θ per minute; chart scale, $\frac{1}{2}$ degree per inch; filtered Cu Kα radiation.

Three diffraction records were made within the range 5 to 70 degrees 2θ. Following each scan of this range, the smear mount was moved slightly in the clip-holder to alter the portion of the smear being *x*-rayed. The 2θ Bragg reflections recorded on the diffraction charts were located by measuring the centers of the peaks at two-thirds height as proposed by Donnay and Donnay (1952). This method of peak location was, however, only considered suitable when the α_1 and α_2 spectral components were completely resolved. For unresolved or partially resolved maxima, the peak locations were obtained by measuring their centers at half height (Smith and Sahama, 1954). The Bragg reflections were corrected by means of an internal standard and comparable 2θ values from the three separate charts were averaged and converted into Q-values from the Donnay and Donnay (1951) tables. The resultant diffraction data (Table 4) were indexed on the basis of the following orthorhombic cell dimensions:

$$a_0 = 9.330, \quad b_0 = 17.867, \quad c_0 = 5.286\ \text{Å}(\pm 0.05\%).$$

On the basis of powder diffraction data only, proto-amphibole may be mistaken for anthophyllite. For example, the values in Table 4 could also have been indexed on an orthorhombic cell comparable in size to that of anthophyllite (i.e. in our case $a_0 = 18.661$, $b_0 = 17.867$, and $c_0 = 5.286$ Å). The resultant indexing is very similar to that for anthophyllite (Table 5). However, even when thus indexed, proto-amphibole can be differentiated from anthophyllite since for it there is an absence of all reflections for which *h* is odd—indication that the value of *a* used in indexing is double the true value.

To confirm the dimensions of the unit cell, as well as to determine the space group, single crystal data from proto-amphibole were obtained. Cone-axis and rotation diagrams about [100], [010], and [001], confirmed the cell edges *a* 9.330, *b* 17.867, *c* 5.286 Å. Particular attention was given

TABLE 4. *X*-RAY POWDER DIFFRACTION DATA FOR SYNTHETIC PROTO-AMPHIBOLE
Cu Kα = 1.54178 Å, Cu Kα_1 = 1.54050 Å

hkl	I/I_1	Observed values			Calculated values*			$Q\times 10^5$
		d	2θ**	Q	*d*	2θ	Q	
020	5	8.962	9.85(α)	.01245	8.934	9.90(α)	.01253	−8
110	67	8.276	10.69(α)	.01460	8.270	10.70(α)	.01462	−2
130	4	5.019	17.67(α)	.03970	5.020	17.67(α)	.03968	2
200	14	4.666	19.02(α)	.04593	4.665	19.02(α)	.04595	−2
040	28	4.469	19.868(α)	.05008	4.467	19.876(α)	.05012	−4
220	1	4.137	21.48(α)	.05844	4.136	21.49(α)	.05847	−3
131	16	3.645	24.428(α)	.07532	3.640	24.45(α)	.07546	−14
150	6	3.339	26.697(α)	.08969	3.337	26.71(α)	.08978	−9
221	13	3.260	27.358(α)	.09411	3.258	27.38(α)	.09425	−14
240	33	3.226	27.631	.09612	3.228	27.62	.09603	9
310	100	3.063	29.134	.10663	3.064	29.12	.10651	12
231	7	3.017	29.581(α)	.10967	3.017	29.61(α)	.10990	−23
151	22	2.822	31.709(α)	.12559	2.822	31.71(α)	.12557	2
330	25	2.759	32.424	.13138	2.757	32.45	.13156	−18
102	13	2.543	35.253	.15455	2.543	35.26	.15460	−5
161 251	21	2.499	35.90	.16009	2.500	35.89	.16002	7
350	4	2.346	38.33(α)	.18166	2.346	38.33	.18167	−1
400	4	2.334	38.577(α)	.18361	2.333	38.59(α)	.18377	−16
261	7	2.268	39.708	.19442	2.268	39.71	.19448	−6
171 080	8	2.233	40.360	.20059	2.233	40.35	.20047	12
421	4	2.077	43.54	.23185	2.076	43.56	.23209	−24
361	7	1.993	45.48	.25185	1.992	45.49	.25191	−6
510	8	1.856	49.038	.29028	1.856	49.038	.29028	0
530	4	1.781	51.26	.31537	1.781	51.26	.31535	2
461	8	1.735	52.726	.33236	1.735	52.723	.33232	4
480	3	1.613	57.05	.38438	1.613	57.04	.38424	14
1.11.0	5	1.600	57.56	.39069	1.600	57.54	.39049	20
372	2	1.581	58.31	.40004	1.581	58.30	.39993	11
561	14	1.515	61.098	.43544	1.515	61.117	.43569	−25
0.12.0	10	1.489	62.303	.45105	1.489	62.303	.45105	0
661	11	1.334	70.55	.56214	1.334	70.53	.56204	10

* Based on the following direct and reciprocal lattice constants:

$$a_0=9.330;\ b_0=17.867;\ c_0=5.286\ \text{Å}\pm 0.005$$

$$a^{*2}=.0114860;\ b^{*2}=.0031323;\ c^{*2}=.035767$$

** Values for Cu Kα, radiation unless otherwise indicated.

TABLE 5. COMPARISON BETWEEN OBSERVED DIFFRACTION DATA FOR SYNTHETIC PROTO-AMPHIBOLE AND NATURAL ANTHOPHYLLITE

Synthetic proto-amphibole No. 19-41A			Natural Anthophyllites					
			Specimen from Falun, Sweden[a]			Gedrite from Inverness-Shire[b]		
hkl	d_{hkl}	I/I_1	*hkl*	d_{hkl}	I[c]	*hkl*	d_{hkl}	I/I_1
(020)	8.962	5				—	8.99	50
(210)	8.276	67	(210)	8.22	4	(210)	8.28	70
						—	7.19	50
(230)	5.019	4	(230)	5.05	2			
(400)	4.666	14						
(040)	4.469	28	(040)	4.52	3	(040)	4.45	30
(420)	4.137	1	(420)	4.13	3	(420)	4.11	30
			(131)	3.88	1	(131)	3.87	15
(231)	3.645	16						
			(321)	3.67	3	(321)	3.63	50
(250)	3.339	6	(331)	3.34	1			
(421)	3.260	13						
(440)	3.226	33	(440)	3.24	5	(440)	3.21	85
(610)	3.063	100	(610)	3.05	8	(610)	3.04	100
(431)	3.017	7						
			(521)	2.87	2	—	2.87	50
(251)	2.822	22	(251)	2.84	3	—	2.81	50
(630)	2.759	25	(630)	2.75	2	(630)	2.74	50
			(351)	2.69	3			
			(161)	2.59	3	—	2.66	50
(202)	2.543	13	(202)	2.54	4	(202)	2.56	50
						—	2.53	50
(451)	2.499	16	(451)	2.51	3	(451)	2.49	50
(261)			(261)					
(650)	2.346	4	(302)	2.43	2			
(800)	2.334	4	(551)	2.32	1	(551)	2.31	30
			(402)	2.29	1			
(461)	2.268	7						
(271)	2.233	8						
(080)								
			(502)	2.15	3	(502)	2.14	30
			(561)	2.14	4	(561)	2.12	30
(821)	2.077	4	(840)	2.065	2	(840)	2.06	15
(661)	1.993	7	(661)	1.998	2			
			(751)	1.982	1	(751)	1.98	15
			(571)	1.965	1			

---

[a] Calculated from data of Johannson (4, pp. 35–36) using 1.9373 as wavelength Fe K_{α}.

[b] As given by American Society for Testing Materials card 7-289 for gedrite.

[c] As given by Johannson (4).

TABLE 5 (*continued*)

Synthetic proto-amphibole No. 19-41A			Natural Anthophyllites					
			Specimen from Falun, Sweden[a]			Gedrite from Iverness-Shire[b]		
hkl	d_{hkl}	I/I_1	*hkl*	d_{hkl}	I[c]	*hkl*	d_{hkl}	I/I_1
			(702)	1.872	1			
			(191)	1.867				
(10.1.0)	1.856	8						
			(860)	1.837	3	(860)	1.84	15
(10.3.0)	1.781	4						
(861)	1.735	8	(861)	1.735	2	—	1.73	15
			(812)					
(880)	1.613	3	(961)	1.618	4	—	1.61	15
			(880)					
			(2.11.0)					
(2.11.0)	1.600	5						
			(053)	1.584	2			
(672)	1.581	2						
(12.0.0)	1.56	3	(12.0.0)	1.546	2	(12.0.0)	1.54	15
(10.6.1)	1.52	14	(10.6.1)	1.513	2			
			(0.12.0)	1.505	4	(0.12.0)	1.51	50
			(6.11.0)	1.451	1			
			(11.0.2)	1.421	2			
			(11.6.1)	1.418	3	(11.6.1)	1.42	15
						—	1.41	30
			(663)	1.364	2			
(12.6.1)	1.33	11	(12.6.1)	1.331	3	—	1.33	15

to determining the repeat unit along the *a*-axis (since for proto-amphibole this value was one-half that for anthophyllite, the only other orthorhombic amphibole known until now). An intentionally over-exposed (113 hour) rotation diagram about [100] (Fig. 1) confirmed the a_0 spacing of proto-amphibole as 9.330 Å.

Additional data support the accuracy of the cell parameters. The calculated specific gravity, 2.940 g. cm.$^{-3}$, is in close agreement with that measured by the sink-float method, 2.928 g. cm.$^{-3}$ at 21° C. (±0.002). The angle $(110)\wedge(1\bar{1}0)$ calculated from the values of a_0 and b_0 is 55°06′; the goniometrically measured value was 55°02′.

Precession diagrams (Figs. 2, 3) indexed on the basis of the following orthorhombic cell dimensions

$$a_0 = 9.330, \quad b = 17.867, \quad c = 5.286\ \text{A}(\pm .005.)$$

indicated the following conditions for Bragg reflection: *hkl*, no conditions; $0kl$, $k+l=2n$; $h0l$, no conditions; $hk0$, $h+k=2n$; $h00$ $h=2n$; $0k0$, $k=2n$; and $00l$, $l=2n$. The space groups obeying these rules are *Pnmn* and *Pn2n*. The distribution of intensities of the diffraction spots recorded on the precession diagrams indicated orthorhombic symmetry. Transmission Laue diagrams further confirmed this.

POSTULATED STRUCTURE

There is little doubt that the material under investigation is an amphibole since: (1) The observed intensities for proto-amphibole are very similar to the intensities of corresponding reflections recorded for amphibole minerals; (2) The values of the repeat units, b_0 and c_0 (i.e. 17.867 and 5.286) are typical for an amphibole chain; (3) The goniometrically measured angle for the prismatic cleavage, 55°02′, is also typical and (4). The ratio Si:O:F found in the unit cell is very close to 8:22:2, values characteristic of fluor-amphiboles. Of the two space groups possible for proto-amphibole, i.e. *Pnmn* or *Pn2n*, only *Pnmn* can be reconciled to an amphibole chain. Thus *Pnmn* is the more likely of the two space groups.

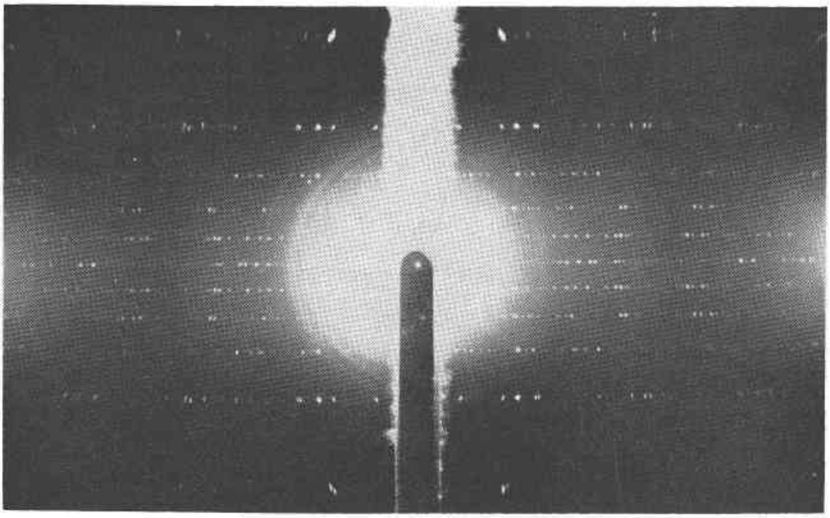

FIG. 1. X-ray rotation diagram about the a axis of proto-amphibole; Cu $K\alpha$ radiation, 113 hour exposure.

Employing atomic coordinates largely based on those found for proto-enstatite (Smith, 1959), a structure whose atoms are consistent with the space group *Pnmn* has been proposed for proto-amphibole (Figs. 4, 5). The structure is derived from that of proto-enstatite by placing a mirror plane parallel to (010) so as to produce a doubling of the pyroxene-type

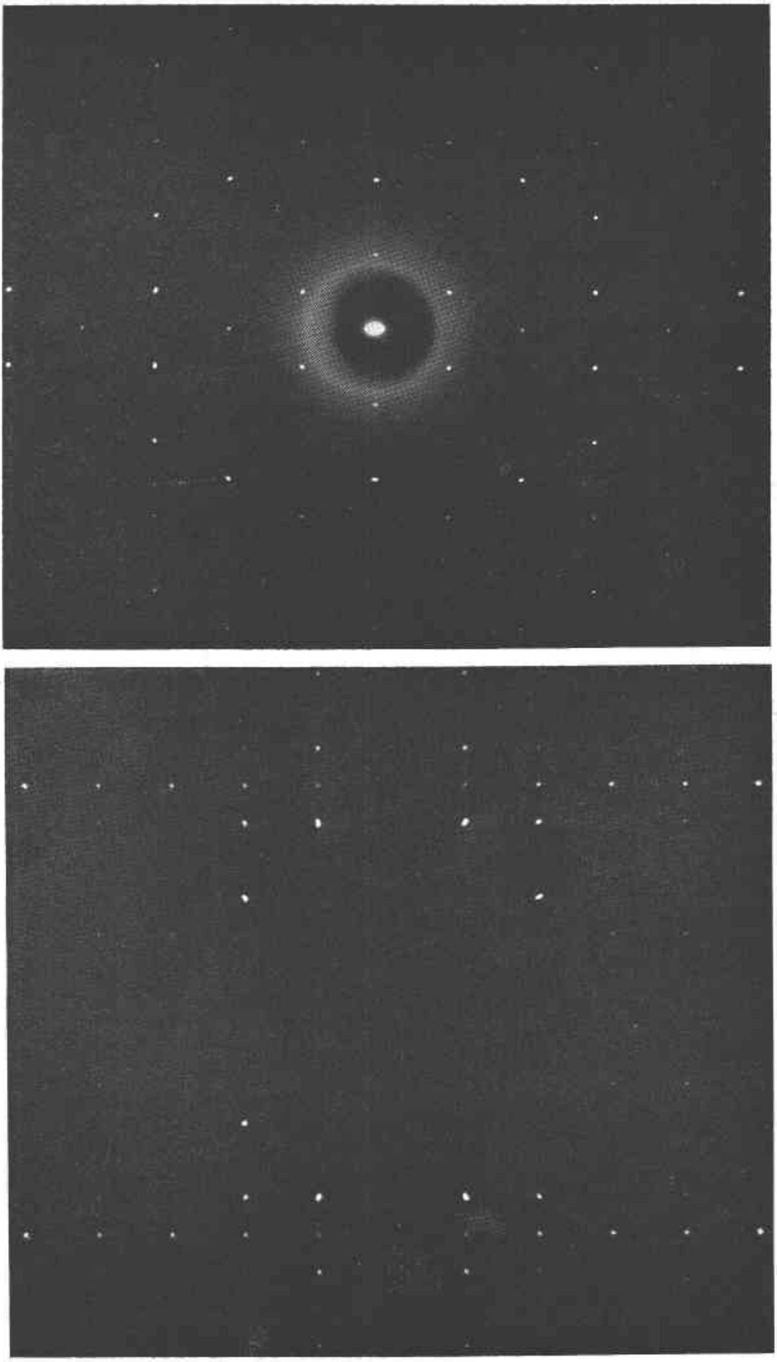

Fig. 2. (*a*) An *hk*0 precession diagram of proto-amphibole; Cu Kα radiation, 18 hour exposure; a^* horizontal, (*b*) An *hk*1 precession diagram; a^* horizontal.

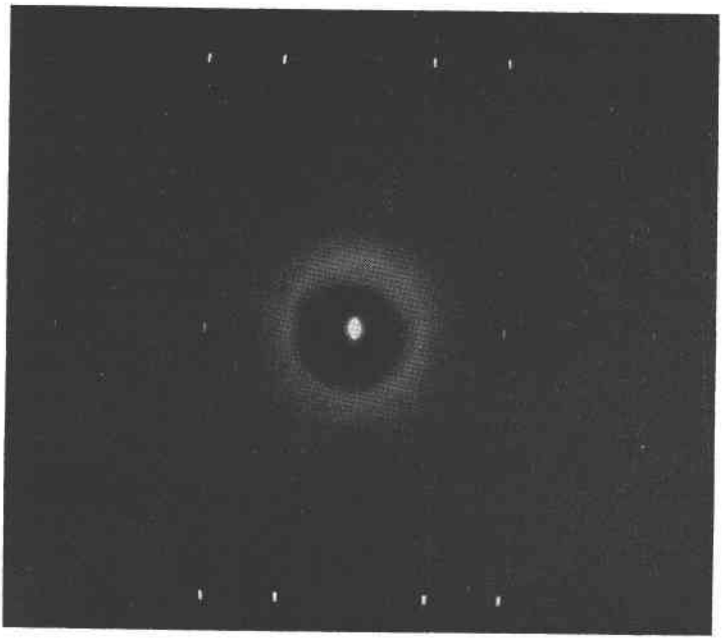

FIG. 3. An *h*01 precession diagram of proto-amphibole; Cu Kα radiation, 18 hour exposure; a^* horizontal.

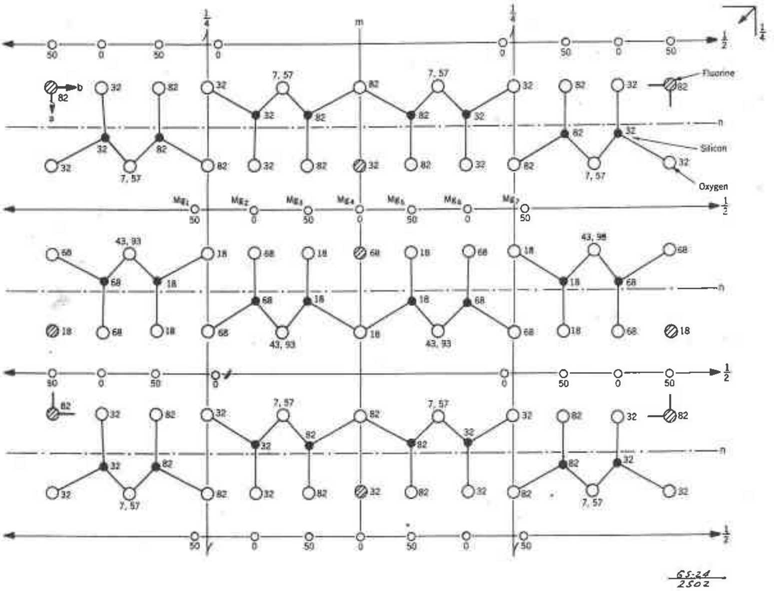

FIG. 4. Proposed structure for proto-amphibole projected on (001).

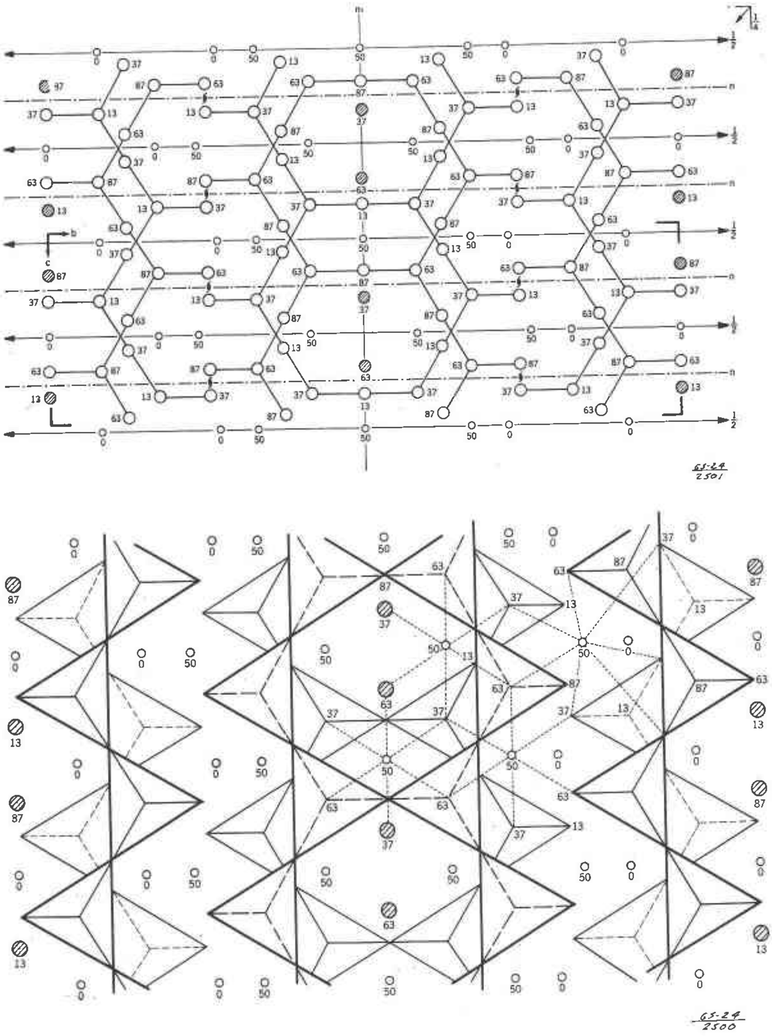

FIG. 5. (*a*) Proposed structure for proto-amphibole projected on (100). (*b*) (100) projection showing silicon-oxygen tetrahedra.

chains of proto-enstatite. This operation is similar to that used by Warren (1929) to derive the structure of tremolite from that of diopside. The resultant structure for proto-amphibole differs from that of the typical amphibole in that neighboring chains are slightly shifted relative to each other along the *c*-axis, a feature necessary to produce the orthorhombic symmetry without doubling the cell as in anthophyllite.

In Figs. 4, 5 the eight-fold-coordinated cation sites are labelled Mg_1 and Mg_7; the six-fold sites, Mg_2–Mg_6. The cation sites of twelve-fold coordination are not labelled. The details of the occupancy of these different cation sites by Mg^{++} and Li^+ are not known, the questions posed by Zussman (1955, p. 301) remaining unanswered with respect to proto-amphibole pending its structural analysis. Some conjectures may be made, however. For example, the inter-chain shift in proto-amphiboles as compared to tremolite restricts the space available for cation positions Mg_1 and Mg_7. Subject to revision following a structural analysis, the extent and significance of this restriction can be assessed by comparing the various Mg_7—O inter-atomic distances of the postulated structure with the corresponding Ca—O inter-atomic distances given by Zussman (1955, Fig. 3, p. 305) for actinolite (Table 6). Comparison of these distances with the average of the Goldschmidt, Pauling, and Zachariasen inter-atomic distances for Li^+—$O^=$, Mg^{++}—$O^=$, and Ca^{++}—O, i.e. 2.08, 2.09, and 2.39 Å, respectively, indicates that, in contrast to its role in monoclinic amphiboles, calcium ions are too large to occupy the Mg_1 and Mg_7 sites in proto-amphibole. The chemical data supports this explanation: batch compositions to which calcium was added always yielded monoclinic amphiboles rather than proto-amphiboles (Table 1).

TABLE 6. COMPARISON OF CATION-OXYGEN DISTANCES OF THE EIGHT-FOLD COORDINATED SITES IN PROTO-AMPHIBOLE AND ACTINOLITE

	Inter-atomic distances (Å)			
Mg_7-O (proto-amphibole)	2.1	1.9	2.0	3.0
Ca-O (actinolite)	2.32	2.34	2.6	2.7

ACKNOWLEDGMENTS

The writers are indebted to Mr. Irving L. Turner for the optical measurements, Mr. David Cummings for aid in drafting, Mr. M. V. Denny for the density determination, to Mr. R. L. Craig for chemical analyses, and to Drs. J. V. Smith and William L. Brown for their critical readings of the manuscript. Dr. John Koster's encouragement was appreciated.

REFERENCES

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

DONNAY, G. AND DONNAY, J. D. H. (1951), *Tables for the interpretation of X-ray diffraction data:* Baltimore, Crystallographic Laboratory, The Johns Hopkins University.

——— (1952), The symmetry change in the high-temperature alkali-feldspar series: *Am. J. Sci.*, Bowen vol., 115–132.

FUJII, TAKASHI, AND EITEL, WILHELM (1957), Solid state reaction in the system MgO-MgF_2-SiO_2: *University of Toledo, Inst. Silicate Res., Inf. Circ.* No. 11.

JOHANSSON, K. (1930), Vergleichende Untersuchungen an Anthophyllit, Grammatit und Cummingtonit, *Zeits. f. Krist.*, 31–51.

KOHN, J. A. AND HATCH, R. A., (1955), Synthetic mica investigations, VI: *X*-ray and optical data on synthetic fluor-phlogopite, *Am. Mineral*, **40**, 10–21.

RABBITT, J. C. (1948), A new study of the anthophyllite series, *Am. Mineral.*, **33**, 263–323.

SHELL, H. R. AND CRAIG, R. L., (1956), Synthetic mica investigations, VIII: Chemical analysis and calculation to unit formula of fluor-silicates, *Bureau of Mines, Report of Investigations*, No. **5158**, pp. 1–29.

———, COMEFERO, J. E., AND EITEL, W. (1958), Synthesis of fluoramphiboles from melts, *Bureau of Mines, Report of Investigations*, No. **5417.**

SMITH, J. V. AND SAHAMA, T. G., (1954), Determination of the composition of natural nephelines by an *X*-ray method, *Min. Mag.*, **30,** 439–449.

SMITH, J. V., (1959), The crystal structure of proto-enstatite, $MgSiO_3$, *Acta Cryst.*, **12,** 515–519.

WARREN, B. E., (1929), The structure of tremolite $H_2Ca_2Mg_5(SiO_3)_8$, *Zeits. f. Krist.*, **72,** 42–57.

——— AND MODELL, D. I. (1930), The structure of anthophyllite $H_2Mg_7(Si_2O_3)_8$, *Zeits. f. Krist.*, **75,** 161–178.

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

Manuscript received December 29, 1959.