# SYNTHETIC ASBESTOS INVESTIGATIONS, II: X-RAY AND OTHER DATA ON SYNTHETIC FLUOR-RICHTERITE, -EDENITE, AND -BORON EDENITE*

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ABSTRACT

As a portion of a general research program on the synthesis of asbestiform minerals, $x$-ray and other data have been obtained on the following chemically analyzed synthetic fluor-amphiboles: richterite, $Na(CaNa)Mg_5(Si_4O_{11})_2F_2$, edenite, $NaCa_2Mg_5(Si_{3.5}Al_{0.5}O_{11})_2F_2$, boron edenite, $NaCa_2Mg_5(Si_{3.5}B_{0.5}O_{11})_2F_2$. Comparisons are made with the values previously reported for fluor-tremolite, $Ca_2Mg_5(Si_4O_{11})_2F_2$.

A detailed indexing of $x$-ray powder diffraction patterns has been made in the range up to 76° $2\theta$, and accurate unit cell dimensions have been determined. The observed cell-dimension variations are discussed with reference to ionic location and polarization. The synthesis and analysis of additional specified compositions are needed to elucidate the factors controlling fibrosity and flexibility in layered and allied silicate structures.

## INTRODUCTION

During an extensive study of the synthesis of fluor-amphiboles from melts, over 100 different batch compositions were investigated; the effect of fluoride concentration and various isomorphic substitutions in the batch on the development of asbestiform amphibole were evaluated (1). Concurrently, some of the fundamental constants of various "end-members" of the monoclinic fluor-amphiboles were determined.

In the present study, the optical and $x$-ray constants of synthetic fluor-richterite, $Na(CaNa)Mg_5(Si_4O_{11})_2F_2$, fluor-edenite, $NaCa_2Mg_5(Si_{3.5}Al_{0.5}O_{11})_2F_2$, and a boron-containing fluor-edenite, $NaCa_2Mg_5(Si_{3.5}B_{0.5}O_{11})_2F_2$, have been evaluated and are compared with the values previously measured for synthetic fluor-tremolite, $Ca_2Mg_5(Si_4O_{11})_2F_2$ (2).

## EXPERIMENTAL PROCEDURE

The method of synthesis and the techniques employed were the same as previously reported (2); that is, a batch corresponding to the composition of the desired fluor-amphibole was melted and cooled, during which time the amphibole devitrified. Graphite crucibles with screw-on covers were used to minimize the extent of volatilization and to prevent the introduction of impurities that might enter the amphibole structure or otherwise cause a deviation from the desired composition.

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The percentage of each raw material used in compounding the synthetic fluor-amphiboles is given in Table 1. To eliminate the presence of carbonates, hydroxides, or other compounds that decompose with liberation of gases, certain components were initially reacted to form stable, anhydrous, nonvolatile materials, such as $Na_2MgSi_3O_8$ (as glass), $CaSiO_3$, and $MgB_2O_4$. Others, such as the clay and silicic acid, were dehydrated before use. In every instance, the particle size of the ingredients was minus-100 mesh. After dry mixing in a glass jar with rubber balls, the batches were packed in the crucibles to hand tightness.

TABLE 1. FLUOR-AMPHIBOLE BATCH COMPOSITIONS (WEIGHT—PER CENT)

| Raw Material | Richterite | Edenite | Boron edenite |
|---|---|---|---|
| $Na_2MgSi_3O_8$* | 34.4 | 16.9 | 17.2 |
| $CaSiO_3$* | 14.1 | 27.7 | 28.2 |
| $MgF_2$ (tech. grade) | 7.6 | 7.5 | 7.6 |
| MgO† | 14.7 | 16.9 | 14.8 |
| $MgB_2O_4$* | — | — | 6.7 |
| Dehydrated Georgia clay ($Al_2Si_2O_7$) | — | 13.2 | — |
| Dehydrated silicic acid† ($SiO_2$) | 29.2 | 17.9 | 25.6 |
| | 100.0 | 100.1 | 100.1 |

* Prepared from reagent-grade chemicals.
† Reagent-grade chemicals.

The batches were fired to 1350° C., maintained at this temperature for 5 hours, and then cooled at 36° C. per hour to 1100° C., at which temperature the furnace was turned off. The resulting crystalline reaction products, consisting primarily of brittle, acicular crystals of fluor-amphibole (at least 80%), were ground to minus-200 mesh. Beneficiation was carried out by heavy-liquid separation using tetrabromoethane and methylene iodide (adjusted to 2.97 and 3.10 gm./cc., respectively) until fractions containing at least 95% fluor-amphibole (microscopically determined) were obtained. Each of these samples was divided into four aliquot portions: The first was examined petrographically, and the optical constants determined; the second was chemically analyzed; the third was used for the *x*-ray study; and the last portion was filed.

## RESULTS

### (1) *Chemical Composition*

The beneficiated samples of the synthetic fluor-amphiboles were examined petrographically, and in no case was the estimate of the total

TABLE 2. CHEMICAL ANALYSES OF SYNTHETIC FLUOR-AMPHIBOLES*

| Constituent | Fluor-richterite | | Fluor-edenite | | Fluor-boron edenite | |
|---|---|---|---|---|---|---|
| | Theo-retical | Actual | Theo-retical | Actual | Theo-retical | Actual |
| $SiO_2$ | 58.45 | 58.88 | 50.17 | 51.09 | 51.16 | 52.21 |
| $Al_2O_3$ | .00 | — | 6.08 | 6.47 | .00 | — |
| $B_2O_3$ | .00 | — | .00 | — | 4.24 | 3.91 |
| $Fe_2O_3$ | .00 | 0.17 | .00 | .21 | .00 | .24 |
| MgO | 24.51 | 24.24 | 24.05 | 23.06 | 24.52 | 24.09 |
| CaO | 6.82 | 7.00 | 13.38 | 12.30 | 13.64 | 12.69 |
| $Na_2O$ | 7.54 | 7.20 | 3.70 | 4.26 | 3.77 | 3.99 |
| $F^-$ | 4.62 | 4.74 | 4.53 | 4.89 | 4.62 | 4.85 |
| O=F | −1.94 | −2.00 | −1.91 | −2.06 | −1.95 | −2.04 |
| | 100.00 | 100.23 | 100.00 | 100.22 | 100.00 | 99.94 |

* Analysts: H. R. Shell, R. L. Craig; samples No. 3848, 3867, and 3850, respectively. Analytical data based on samples dried at 110° C.

impurities greater than 4%. The fluor-richterite sample contained less than 1% impurity, mostly $CaF_2$. In the case of fluor-edenite, the major contaminant was 1–2% pyroxene, probably diopside. The remaining impurity concentration was less than $\frac{1}{2}$%. The extraneous phases in fluor-boron edenite totaled less than 4%, of which approximately 3% was forsterite.

The chemical analyses of the beneficiated samples are given in Table

TABLE 3. COMPARISONS OF THEORETICAL AND EMPIRICAL IONIC RATIOS OF SYNTHETIC FLUOR-AMPHIBOLES

| | $(WO_{12})$ | $(XO_8)$ | $(YO_6)$ | $(ZO_4)$ | |
|---|---|---|---|---|---|
| | | | *Richterite* | | |
| Theoretical | Na | (CaNa) | $Mg_5$ | $Si_8$ | $O_{22}F_2$ |
| Calculated* | $Na_{0.93}$ | $(Ca_{1.03}Na_{0.97})$ | $Mg_{4.93}$ | $Si_{8.04}$ | $O_{22}F_{2.04}$ |
| | | | *Edenite* | | |
| Theoretical | Na | $Ca_2$ | $Mg_5$ | $(Si_7Al)$ | $O_{22}F_2$ |
| Calculated* | $Na_{0.99}$ | $(Ca_{1.84}Na_{0.16})$ | $(Mg_{4.79}Al_{0.18})$ | $(Si_{7.12}Al_{0.88})$ | $O_{22}F_{2.15}$ |
| | | | *Boron edenite* | | |
| Theoretical | Na | $Ca_2$ | $Mg_5$ | $(Si_7B)$ | $O_{22}F_2$ |
| Calculated* | $Na_{0.93}$ | $(Ca_{1.87}Na_{0.13})$ | $Mg_{4.92}$ | $(Si_{7.16}B_{0.92})$ | $O_{22}F_{2.10}$ |

* Calculated from chemical analysis on basis of 22 oxygen atoms. No attempt was made to correct for the small amounts of impurities present.

2. A comparison between the theoretical and empirical formulas of the three fluor-amphiboles appears in Table 3.

(2) *Optical Properties*

Comparisons of the optical constants reported on various naturally occurring richterites and edenites with those measured on the synthetic fluor-amphiboles are rendered difficult because the natural minerals invariably contain significant amounts of cations other than those required for theoretical compositions (3, 4). For this reason, the observed differences cannot be attributed entirely to complete replacement of hydroxyl by fluoride.

The refractive indices of the synthetic fluor-amphiboles were measured at room temperature with a petrographic microscope, using the oil-immersion technique. The results obtained are compared in Table 4 with those previously measured for synthetic fluor-tremolite.

TABLE 4. SYNTHETIC FLUOR-AMPHIBOLE OPTICAL CONSTANTS*

| | Tremolite | Richterite† | Edenite‡ | Boron-edenite |
|---|---|---|---|---|
| X | 1.581 | 1.603 | 1.605 | 1.588 |
| Y | 1.593 | 1.614 | 1.617 | 1.598 |
| Z | 1.602 | 1.622 | 1.624 | 1.605 |
| $Z \wedge c$ | 21° | 22° | 18° | 12° |
| 2V | $86\frac{1}{2}°$ | 72° | 69° | 75° |
| Sign | (−) | (−) | (−) | (−) |

* Determinations by M. V. Denny; maximum error for X, Y, and Z is ±0.002; 2V determined by means of a 5-axis universal stage, using sodium (*D*) light.

† A natural richterite ("soda-tremolite") described by Larsen (3) was not used for comparison of optical properties owing to the presence of 3.91% $Fe_2O_3$ and 2.44% FeO.

‡ A natural, biaxial positive edenite described by Palache (4) was not used for comparison of optical properties owing to the presence of 1.02% $Fe_2O_3$ and 3.38% FeO.

(3) *X-ray Data*

No *x*-ray data are available in the literature on relatively pure synthetic or natural amphiboles of the types herein concerned. In the present study, accurate unit cell dimensions have been obtained, and complete diffraction data are given in the range up to 76° $2\theta$. The three synthetic fluor-amphiboles studied are monoclinic, with a bimolecular unit cell.

All *x*-ray diffraction data were recorded using a chart operation in conjunction with a Philips high-angle goniometer (diffractometer). The synthetic fluor-amphibole samples were packed in the usual rectangular aluminum holders. The instrumental setting used was as follows: scale factor, 16 (unless rescanning a very strong maximum); multiplier, 1.0

(giving a counting rate of 800 counts per second, full scale); time constant, 4 seconds; Geiger overvoltage, 300 volts; divergence slit, 1°; scanning speed, $\frac{1}{4}$° per minute; chart scale, $\frac{1}{2}$ inch per degree.

Both before and after each chart operation involving a fluor-amphibole pattern, appropriate silicon maxima were recorded using the silicon standard compact furnished with the instrument. Corrections ranged from 0.005° to 0.055° and were read from a curve plotting instrumental correction against $2\theta$.

A low-power microscope fitted with a movable-hair ocular, used in conjunction with a photographically processed slide of 200 lines per inch, permitted very accurate $2\theta$ readings of the diffraction maxima. For those peaks directly concerned with the calculation of the unit-cell dimensions, $2\theta$ readings to the third decimal place were obtained. For all other maxima, measurements were taken to 0.005°. Following the procedure established by Donnay and Donnay (5), the peaks were bisected at approximately two-thirds of the peak height to obtain the readings.

In the case of fluor-tremolite, the positions of the maxima directly involved in the calculation of the cell dimensions were determined by a counting operation in conjunction with the Philips unit. For the present study, a chart operation was found to be of approximately the same accuracy (see Table 8) and substantially less time-consuming. After the complete pattern of the fluor-amphibole under investigation was obtained by scanning down-scale from 76° $2\theta$, four sharp, unambiguously-indexed maxima in the higher $2\theta$ range were selected. Each chosen peak was then scanned four additional times. $2\theta$ values averaged from the 5 separate measurements were used for a solution of the quadratic form (6). The unit-cell dimensions thus derived were refined until close agreement was obtained between the calculated and observed $2\theta$ values of various selected maxima. The final cell dimensions are given in Table 9 and compared with those previously obtained for synthetic fluor-tremolite.

Following the last cell-dimension refinement, the positions of all reflections permissible by the space group symmetry ($C\ 2/m$) were calculated in the range up to 76° $2\theta$ (approximately 250 potential maxima in each case). The diffraction data for all resolved maxima (and a few significant doublets) in this range are tabulated in Tables 5, 6, and 7 for synthetic fluor-richterite, -edenite, and -boron edenite, respectively. Results bearing on the accuracy of the diffraction data, and ultimately upon the unit-cell dimensions adopted, are collected in Table 8, and compared with the values for synthetic fluor-tremolite. In the present study, no diffraction maximum showed a deviation in $2\theta$ of more than 0.02° from the calculated value, and the average deviation was in the order of $10^{-4}$ degrees.

TABLE 5. X-RAY DIFFRACTION DATA (POWDER) FOR SYNTHETIC FLUOR-RICHTERITE
(*Space Group C 2/m*)

| *hkl* | 2θ obs. | 2θ calc.* | Δ2θ | Meas. Int. | *d* calc. |
|---|---|---|---|---|---|
| 020 | 9.865° | 9.855° | −0.01° | 3 | 8.979 Å |
| 110 | 10.51 | 10.515 | + .005 | >100 | 8.409 |
| 130 | 17.49 | 17.50 | + .01 | 2 | 5.067 |
| 11$\bar{1}$ | 18.25 | 18.255 | + .005 | 3 | 4.860 |
| 200 | 18.635 | 18.645 | + .01 | 11 | 4.759 |
| 040 | 19.76 | 19.775 | + .015 | 10 | 4.489 |
| 220 | 21.115 | 21.13 | + .015 | 4 | 4.205 |
| 111 | 22.275 | 22.265 | − .01 | 2 | 3.993 |
| 13$\bar{1}$ | 23.03 | 23.045 | + .015 | 4 | 3.859 |
| 131 | 26.34 | 26.345 | + .005 | 10 | 3.380 |
| 150 | 26.505 | 26.505 | 0 | 3 | 3.360 |
| 240 | 27.285 | 27.285 | 0 | 60 | 3.265 |
| 310 | 28.54 | 28.55 | + .01 | ≫100 | 3.124 |
| 221 | 30.325 | 30.33 | + .005 | 11 | 2.944 |
| 15$\bar{1}$ | 30.505 | 30.52 | + .015 | 3 | 2.926 |
| 330 | 31.91 | 31.91 | 0 | 76 | 2.803 |
| 33$\bar{1}$ | 32.91 | 32.89 | − .02 | 9 | 2.721 |
| 151 | 33.15 | 33.15 | 0 | 20 | 2.700 |
| 061 | 34.73 | 34.715 | − .015 | 7 | 2.582 |
| 20$\bar{2}$ | 35.555 | 35.535 | − .02 | 6 | 2.524 |
| 350 | 37.805 | 37.805 | 0 | 11 | 2.378 |
| 35$\bar{1}$ | 38.68 | 38.665 | − .015 | 7 | 2.327 |
| 42$\bar{1}$ | 38.885 | 38.875 | − .01 | 5 | 2.315 |
| 17$\bar{1}$ | 39.385 | 39.365 | − .02 | 7 | 2.287 |
| 171 | 41.515 | 41.50 | − .015 | 3 | 2.174 |
| 132 | 41.63 | 41.64 | + .01 | 3 | 2.167 |
| 261 | 41.81 | 41.81 | 0 | 8 | 2.159 |
| 202 | 44.20 | 44.195 | − .005 | 3 | 2.048 |
| 351 | 44.905 | 44.91 | + .005 | 5 | 2.017 |
| 370 | 45.435 | 45.43 | − .005 | 5 | 1.9947 |
| 190 | 46.465 | 46.46 | − .005 | 3 | 1.9528 |
| 510 | 48.03 | 48.025 | − .005 | 29 | 1.8928 |
| 19$\bar{1}$ | 49.06 | 49.05 | − .01 | 3 | 1.8556 |
| 530 | 50.275 | 50.255 | − .02 | 8 | 1.8139 |
| 0·10·0 | 50.815 | 50.80 | − .015 | 2 | 1.7957 |
| 51$\bar{2}$ | 52.575 | 52.585 | + .01 | 2 | 1.7389 |
| 461 | 55.67 | 55.67 | 0 | 16 | 1.6496 |
| 480 | 56.295 | 56.295 | 0 | 6 | 1.6327 |
| 1·11·0 | 57.20 | 57.205 | + .005 | 10 | 1.6090 |
| 600 | 58.10 | 58.105 | + .005 | 9 | 1.5862 |
| 55$\bar{2}$ | 58.695 | 58.715 | + .02 | 3 | 1.5711 |
| 620 | 59.105 | 59.09 | − .015 | 2 | 1.5620 |
| 551 | 61.68 | 61.675 | − .005 | 6 | 1.5026 |
| 0·12·0 | 61.96 | 61.955 | − .005 | 7 | 1.4964 |
| 442 | 63.10 | 63.10 | 0 | 1 | 1.4721 |
| 3·11·0 | 64.08 | 64.095 | + .015 | 5 | 1.4516 |
| 66$\bar{1}$ | 64.975 | 64.98 | + .005 | 11 | 1.4340 |
| 512 | 68.545 | 68.555 | + .01 | 6 | 1.3676 |
| 60$\bar{3}$<br>532 | 70.355 | 70.355<br>70.355 | — | 1 | 1.3370<br>1.3369 |
| 263 | 70.575 | 70.575 | 0 | 1 | 1.3333 |
| 75$\bar{1}$ | 72.23 | 72.23 | 0 | 3 | 1.3068 |
| 2·12·$\bar{2}$ | 73.495 | 73.505 | + .01 | 4 | 1.2872 |

* Using λ CuK$\alpha_1$ (1.54050 A) above 25° 2θ and λ CuK$_\alpha$ (1.5418 A) below 25° 2θ.

TABLE 6. X-RAY DIFFRACTION DATA (POWDER) FOR SYNTHETIC FLUOR-EDENITE (*Space Group C 2/m*)

| *hkl* | 2θ obs. | 2θ calc.* | Δ2θ | Meas. Int. | *d* calc. |
|---|---|---|---|---|---|
| 020 | 9.825° | 9.825° | 0° | 4 | 9.002 Å |
| 110 | 10.515 | 10.515 | 0 | 81 | 8.413 |
| 11$\bar{1}$ | 18.15 | 18.17 | + .02 | 2 | 4.882 |
| 200 | 18.64 | 18.645 | + .005 | 3 | 4.759 |
| 040 | 19.71 | 19.725 | + .015 | 6 | 4.501 |
| 220 | 21.095 | 21.115 | + .02 | 6 | 4.208 |
| 131 } 041 } | 26.37 | 26.37 } 26.375 } | — | 10 | 3.377 } 3.376 } |
| 240 | 27.24 | 27.245 | + .005 | 42 | 3.270 |
| 310 | 28.54 | 28.54 | 0 | 99 | 3.125 |
| 221 } 15$\bar{1}$ } | 30.395 | 30.405 } 30.415 } | — | 19 | 2.937 } 2.936 } |
| 330 | 31.87 | 31.875 | + .005 | 37 | 2.805 |
| 33$\bar{1}$ | 32.74 | 32.735 | − .005 | 7 | 2.733 |
| 151 | 33.135 | 33.14 | + .015 | 15 | 2.701 |
| 061 | 34.645 | 34.645 | 0 | 7 | 2.587 |
| 20$\bar{2}$ | 35.37 | 35.36 | − .01 | 11 | 2.536 |
| 170 | 36.145 | 36.145 | 0 | 1 | 2.483 |
| 40$\bar{1}$ | 37.35 | 37.35 | 0 | 2 | 2.406 |
| 350 | 37.76 | 37.755 | − .005 | 8 | 2.381 |
| 35$\bar{1}$ | 38.51 | 38.50 | − .01 | 7 | 2.336 |
| 42$\bar{1}$ | 38.70 | 38.71 | + .01 | 7 | 2.324 |
| 17$\bar{1}$ | 39.24 | 39.24 | 0 | 5 | 2.294 |
| 261 | 41.815 | 41.815 | 0 | 9 | 2.158 |
| 351 | 44.95 | 44.96 | + .01 | 8 | 2.014 |
| 370 | 45.36 | 45.35 | − .01 | 3 | 1.9980 |
| 190 | 46.325 | 46.34 | + .015 | 2 | 1.9577 |
| 510 | 48.02 | 48.015 | − .005 | 12 | 1.8932 |
| 46$\bar{1}$ | 48.47 | 48.46 | − .01 | 1 | 1.8769 |
| 530 | 50.25 | 50.235 | − .015 | 6 | 1.8146 |
| 0·10·0 | 50.665 | 50.66 | − .005 | 1 | 1.8004 |
| 550 | 54.485 | 54.475 | − .01 | 2 | 1.6830 |
| 461 | 55.735 | 55.72 | − .015 | 12 | 1.6481 |
| 480 | 56.205 | 56.21 | + .005 | 4 | 1.6351 |
| 1·11·0 | 57.03 | 57.045 | + .015 | 3 | 1.6130 |
| 600 | 58.095 | 58.09 | − .005 | 4 | 1.5865 |
| 402 | 59.46 | 59.445 | − .015 | 2 | 1.5535 |
| 551 } 0·12·0 } | 61.79 | 61.77 } 61.78 } | — | 12 | 1.5006 } 1.5003 } |
| 2·10·$\bar{2}$ | 63.305 | 63.29 | − .015 | 1 | 1.4681 |
| 3·11·0 | 63.95 | 63.945 | − .005 | 2 | 1.4546 |
| 66$\bar{1}$ | 64.76 | 64.77 | + .01 | 11 | 1.4381 |
| 51$\bar{2}$ | 68.80 | 68.785 | − .015 | 5 | 1.3636 |
| 710 | 69.24 | 69.23 | − .01 | 2 | 1.3560 |
| 75$\bar{1}$ | 72.01 | 72.015 | + .005 | 3 | 1.3102 |
| 2·12·$\bar{2}$ | 73.235 | 73.24 | + .005 | 2 | 1.2913 |

* Using λ $CuK\alpha_1$ (1.54050 Å) above 25° 2θ and λ $CuK_\alpha$ (1.5418 Å) below 25° 2θ.

TABLE 7. X-RAY DIFFRACTION DATA (POWDER) FOR SYNTHETIC FLUOR-BORON EDENITE
(*Space Group C 2/m*)

| *hkl* | 2θ obs. | 2θ calc.* | Δ2θ | Meas. Int. | *d* calc. |
|---|---|---|---|---|---|
| 020 | 9.845° | 9.85° | +0.005° | 4 | 8.979 Å |
| 110 | 10.54 | 10.54 | 0 | 95 | 8.395 |
| 130 | 17.50 | 17.515 | + .015 | 3 | 5.064 |
| 11$\bar{1}$ | 18.255 | 18.255 | 0 | 2 | 4.860 |
| 200 | 18.675 | 18.685 | + .01 | 8 | 4.748 |
| 040 | 19.755 | 19.775 | + .02 | 6 | 4.489 |
| 220 | 21.155 | 21.165 | + .01 | 5 | 4.198 |
| 111 | 22.325 | 22.305 | − .02 | 2 | 3.986 |
| 13$\bar{1}$ | 23.04 | 23.045 | + .005 | 3 | 3.859 |
| 131 | 26.39 | 26.38 | − .01 | 7 | 3.376 |
| 240 | 27.31 | 27.315 | + .005 | 35 | 3.262 |
| 310 | 28.61 | 28.61 | 0 | ≫100 | 3.118 |
| 221 | 30.405 | 30.395 | − .01 | 16 | 2.939 |
| 330 | 31.955 | 31.955 | 0 | 29 | 2.798 |
| 33$\bar{1}$ | 32.925 | 32.91 | − .015 | 9 | 2.719 |
| 151 | 33.18 | 33.175 | − .005 | 20 | 2.698 |
| 350, 400 | 37.85 | 37.85, 37.86 | — | 6 | 2.375, 2.374 |
| 35$\bar{1}$ | 38.675 | 38.68 | + .005 | 8 | 2.326 |
| 42$\bar{1}$ | 38.915 | 38.92 | + .005 | 6 | 2.312 |
| 17$\bar{1}$ | 39.375 | 39.365 | − .01 | 4 | 2.287 |
| 261 | 41.86 | 41.855 | − .005 | 7 | 2.156 |
| 351 | 45.00 | 44.985 | − .015 | 5 | 2.013 |
| 370, 222 | 45.47 | 45.47, 45.47 | — | 5 | 1.9931, 1.9929 |
| 190 | 46.48 | 46.465 | − .015 | 2 | 1.9526 |
| 510 | 48.13 | 48.13 | 0 | 19 | 1.8888 |
| 19$\bar{1}$ | 49.04 | 49.05 | + .01 | 2 | 1.8556 |
| 530 | 50.37 | 50.36 | − .01 | 9 | 1.8104 |
| 0·10·0 | 50.805 | 50.80 | − .005 | 2 | 1.7957 |
| 461 | 55.76 | 55.77 | + .01 | 8 | 1.6469 |
| 60$\bar{1}$, 480 | 56.36 | 56.355, 56.36 | — | 5 | 1.6312, 1.6311 |
| 1·11·0 | 57.185 | 57.205 | + .02 | 3 | 1.6089 |
| 600 | 58.235 | 58.24 | + .005 | 7 | 1.5828 |
| 620 | 59.235 | 59.225 | − .01 | 2 | 1.5588 |
| 402 | 59.39 | 59.39 | 0 | 2 | 1.5549 |
| 0·12·0 | 61.96 | 61.955 | − .005 | 5 | 1.4964 |
| 3·11·0 | 64.115 | 64.13 | + .015 | 2 | 1.4509 |
| 66$\bar{1}$ | 65.065 | 65.065 | 0 | 13 | 1.3423 |
| 512, 73$\bar{1}$ | 68.765 | 68.735, 68.77 | — | 3 | 1.3645, 1.3639 |
| 710 | 69.41 | 69.41 | 0 | 3 | 1.3528 |
| 730 | 71.205 | 71.205 | 0 | 2 | 1.3231 |
| 75$\bar{1}$ | 72.355 | 72.345 | − .01 | 3 | 1.3050 |
| 2·12·$\bar{2}$ | 73.50 | 73.51 | + .01 | 2 | 1.2872 |

* Using λ CuK$\alpha_1$ (1.54050 Å) above 25° 2θ and λ CuK$_\alpha$ (1.5418 Å) below 25° 2θ.

TABLE 8. ACCURACY OF SYNTHETIC FLUOR-AMPHIBOLE DIFFRACTION DATA

| | Maximum Deviation (degrees) | Average Deviation (degrees) | Contributing Peaks (number) |
|---|---|---|---|
| Tremolite | 0.03 | $+2.5\times10^{-4}$ | 41 |
| Richterite | .02 | $-4.0\times10^{-4}$ | 51 |
| Edenite | .02 | $-2.5\times10^{-4}$ | 40 |
| Boron edenite | .02 | $+1.3\times10^{-4}$ | 38 |

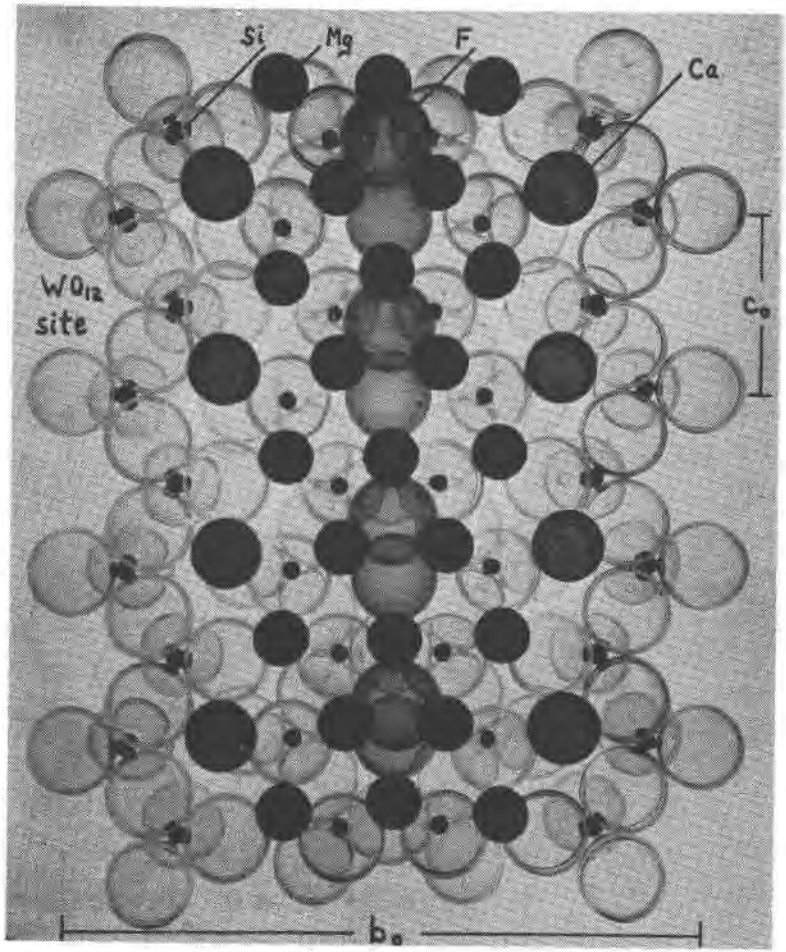


FIG. 1. Plastic-ball model (8) of a portion of the fluor-termolite structure, with $[d_{100}]$ perpendicular to the plane of the figure.

## Discussion

A model of a portion of the fluor-tremolite structure, as derived by Warren (7), is depicted in Fig. 1 to supplement the following discussion.

In richterite, $Na(CaNa)Mg_5(Si_4O_{11})_2F_2$, the substitution of 2 $Na^+$ for 1 $Ca^{++}$ presents two geometrical possibilities for the sites occupied by these cations. Specifically, 1 $Na^+$ can fill the 12-fold vacant sites known to exist in tremolite (environment similar to the 12-fold positions in mica), while the remaining $Na^+$ proxies for $Ca^{++}$ in 8-fold coordination. On the other hand, both $Na^+$ ions may replace $Ca^{++}$ in the ($XO_8$) positions, with $Ca^{++}$ occupying the ($WO_{12}$) vacant sites. In tremolite, where the $Ca^{++}$ ions are more or less free to choose between 12- and 8-fold coordination, the latter is preferred, although in calcium phlogopite, $Ca_2Mg_6(Si_3AlO_{10})_2F_4$, where no such option exists, $Ca^{++}$ does occupy the position of 12-fold coordination. Thus it would seem that in the particular structural environment presented by the tremolite arrangement, $Ca^{++}$ is more stable in the ($XO_8$) position. Since the structural environment of richterite does not differ radically from that of tremolite, it seems logical to assume that, where possible, $Ca^{++}$ will again seek positions of 8-fold coordination. Thus it is indicated that $Na^+$ occupies the ($WO_{12}$) vacant sites, and the ($XO_8$) positions are shared by both $Na^+$ and $Ca^{++}$. This double coordination of $Na^+$ is not unusual, as shown by eckermannite, $NaNa_2Mg_4Al(Si_4O_{11})_2(OH,F)_2$, where the ($WO_{12}$) and ($XO_8$) positions are filled by this cation.

Table 9. Monoclinic Cell Dimensions of Synthetic Fluor-Amphiboles*

| | Tremolite | Richterite | Edenite | Boron edenite |
|---|---|---|---|---|
| $a_0$ | 9.781 Å | 9.823 | 9.847 | 9.807 |
| $b_0$ | 18.007 | 17.957 | 18.004 | 17.957 |
| $c_0$ | 5.267 | 5.268 | 5.282 | 5.266 |
| $\beta$ | 75°29′ | 75°40′ | 75°10′ | 75°33′ |
| Calculated Density | 3.021 g/cm³ | 3.035 | 3.077 | 3.042 |

* Maximum errors are as follows: $a_0$, ±0.005; $b_0$, ±0.004; $c_0$, ±0.006; $\beta$, ±5′; calculated density ($D_x$), ±0.006.

The change in unit-cell dimensions between tremolite and richterite, as shown in Table 9, can be explained by either of the above assumptions. Both would result in an increased $a$ dimension because of filling of the vacant sites, since [$d_{100}$] parallels the principal axis of the ($WO_{12}$) coordination polyhedron. With the limited data available, the contraction along $b$ can be ascribed to substitution of a slightly smaller ion ($Na^+$ for

$Ca^{++}$) in positions between the double chains. Regardless of the actual location of the $Na^{+}$ and $Ca^{++}$ ions, no noticeable change in the *c* direction would result, as the latter parallels the elogation of the $Si_4O_{11}$ chains and is essenitally uninfluenced by the occupants of the ($WO_{12}$) and ($XO_8$) positions. Knowledge of the cell dimensions of fluor-eckermannite and various richterites, especially those in which $Mn^{++}$, $Ba^{++}$, or $Sr^{++}$ replace $Ca^{++}$, might resolve this question without recourse to a detailed structural analysis.

Edenite, $NaCa_2Mg_5(Si_{3.5}Al_{0.5}O_{11})_2F_2$, is derived from tremolite by substituting one $Al^{+3}$ for $Si^{+4}$ in tetrahedral coordination and restoring electrical neutrality by filling the ($WO_{12}$) sites with $Na^{+}$. In boron edenite, $NaCa_2Mg_5(Si_{3.5}B_{0.5}O_{11})_2F_2$, $B^{+3}$ replaces $Al^{+3}$ in the ($ZO_4$) positions. As with richterite, filling of the 12-fold sites in both edenites increases the *a* dimension relative to that observed in tremolite (cf. Table 9). This direction is also influenced by the substitution in 4-fold coordination. Thus the *a* dimension of aluminum edenite is larger than that of boron edenite, owing to the larger $(AlO_4)^{-5}$ grouping. It was expected that this difference in tetrahedron size between $(AlO_4)^{-5}$ and $(BO_4)^{-5}$ would also be reflected in the *b* direction, with aluminum edenite exhibiting the larger *b* dimension. The observed data bear out this expectation. When compared with fluor-tremolite, however, the *b* dimension of aluminum edenite remains essentially the same. This may be due either to a cushioning effect along *b* (perpendicular to the direction of the double chains) or to a distortion of the $(AlO_4)^{-5}$ grouping, which would not be unexpected with a trivalent ion in 4-fold coordination.

The *c* dimension of aluminum edenite is increased relative to that of tremolite owing to the effect of the larger $(AlO_4)^{-5}$ grouping on the direction of the double chains. In boron edenite a contraction (relative to tremolite) was expected along *c*, because of the probable smaller size of the $(BO_4)^{-5}$ grouping in comparison to $(SiO_4)^{-4}$.* This contraction, however, did not materialize, which intimates a distortion on the $(BO_4)^{-5}$ tetrahedron. Such a distortion would be in keeping with the relative ease of polarization of this group. The indicated distortions of both the $(AlO_4)^{-5}$ and $(BO_4)^{-5}$ groups are such that the tetrahedra seem attenuated (relative to *b*) along the *c* direction.

In the discussion of the fluor-richterite composition, certain isomorphic substitutions were suggested as offering promise in correlating unit-cell dimensions with ionic location. Continuing in this vein, the effect of polarization of the tetrahedra could be clarified by the synthesis and

* Analogous to the relative sizes of the $(BO_4)^{-5}$ and $(SiO_4)^{-4}$ tetrahedra in danburite, $CaB_2Si_2O_8$(9).

analysis of amphiboles and micas in which various cations, such as $Be^{++}$, $Ge^{+4}$, and $V^{+3}$, substitute for $Si^{+4}$. In a number of instances such compositions have been prepared in this laboratory, but samples pure enough for investigation have not been obtained. Likewise, additional data are needed to understand fully the effect of the replacement of $(OH)^-$ by $F^-$, (10) which is basic to the study of fluor-silicates.

When such data become available, it may be possible to comprehend the relationships existing among the many layered and allied silicate minerals. This, in turn, by clarifying the directional distribution of bond strengths, especially those perpendicular to the layers or chains, would shed light on the ultimate problems of fibrosity and flexibility and their relation to crystal structure.

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