American Mineralogist, Volume 72, pages 959–964, 1987

Characterization of cation ordering in synthetic scandium-fluor-eckermannite, indium-fluor-eckermannite, and scandium-fluor-nyböite by Rietveld structure refinement

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ABSTRACT

Characterization of cation order-disorder relationships in synthetic amphiboles is essential for the proper interpretation of physical and thermodynamic properties. In this study, scandium-fluor-eckermannite, indium-fluor-eckermannite, and scandium-fluor-nyböite were synthesized and characterized by Rietveld structure refinement, scanning-electron microscopy, and X-ray diffraction. High amphibole yields were obtained for the three species. Fluor-indium-eckermannite yields were virtually 100%; scandium-fluor-eckermannite and scandium-fluor-nyböite yields were 95 to 98%. Rietveld structure refinement showed Sc and In to be completely ordered at the M(2) site in fluor-eckermannite and fluor-nyböite. Furthermore, the total composition of the octahedral cations was determined with apparent accuracy; fluor-indium-eckermannite was essentially of the nominal composition, whereas scandium-fluor-eckermannite and scandium-fluor-nyböite were slightly off-composition. These results agree with amphibole yields in the run products. Mean T–O bond lengths were consistent with the Al-site ordering T(1) ≫ T(2); ⟨T(1)–O⟩ and ⟨T(2)–O⟩ distances in scandium- and indium-fluor-eckermannite were consistent with the tetrahedral sites being solely occupied by Si. Rietveld structure refinement is particularly useful for characterization of octahedral-cation ordering in fluor-amphiboles, as infrared spectroscopy cannot be used in non-hydroxl-bearing amphiboles.

INTRODUCTION

Eckermannite and nyböite are alkali amphiboles with the *C*2/*m* structure (Hawthorne, 1983) and ideal end-member formulae $NaNa_2Mg_4M^{3+}Si_8O_{22}(OH,F)_2$ and $NaNa_2Mg_3M_2^{3+}Si_7AlO_{22}(OH,F)_2$, respectively. In a previous paper (Raudsepp et al., 1987), we reported on the synthesis and characterization of cation order-disorder in octahedral M^{3+} (Al, Cr, Ga, Sc, In) analogues of pargasite and fluor-pargasite. Here, we discuss the synthesis and characterization of M^{3+} (Sc, In) analogues of fluor-eckermannite and of scandium-fluor-nyböite; in particular, we use Rietveld structure refinement to derive structural and compositional information from complex, fine-grained synthesis products. This work is part of a systematic study of cation ordering in synthetic amphiboles (Raudsepp, 1984; Raudsepp et al., 1982, 1984, 1987; Hawthorne et al., 1984).

Previous syntheses of eckermannites and nyböites are rare, and no one has synthesized fluor-eckermannite with high yields. From gels of eckermannite composition crystallized at 770 to 1000°C and 1 to 5 kbar, Phillips and Rowbotham (1968) grew an amphibole presumed to be eckermannite that coexisted with a talc-like mineral. Because of the presence of the talc-like mineral, the exact composition is uncertain. Our cell-dimension refinement from their powder X-ray data gave very different results from those reported in the original paper (Table 1); the source of this discrepancy is not clear. Carman and Gilbert (1983) synthesized amphiboles apparently near nyböite composition, with yields of about 90%. Attempts to synthesize fluor-eckermannite in the solid state at 1000 to 1100°C, by Eitel (1952) and Shell et al. (1958), resulted in low amphibole yields, and no physical properties were reported.

EXPERIMENTAL METHODS

Experimental methods are fully described in Raudsepp et al. (1987). A brief summary follows. Dry mixtures of fluor-amphibole stoichiometry were prepared from commercial reagent-grade chemicals. About 20 to 40 mg of mix were reacted isothermally in a sealed Pt capsule suspended in a vertical furnace. Runs were quenched by dropping the capsule into distilled water. All products were examined by X-ray powder diffraction and scanning-electron microscope to identify any extraneous phases.

Powder diffractograms were obtained on a Philips Automated Powder Diffractometer System PW1710 using monochromatized Cu*K*α radiation. BaF_2 (*a* = 6.19860 (5) Å) calibrated against Si (NBS Standard Reference Material 640a, *a* = 5.43083 (4) Å), was used as an internal standard. Peak positions were calculated by a five-point parabolic fit to each peak, followed by correction against the internal calibration pattern and allowance for $K\alpha_1$-$K\alpha_2$ splitting as a function of 2θ. Cell dimensions were refined using the least-squares program of Appleman and Evans (1973).

X-ray intensity data for Rietveld structure refinement were collected on a Philips Automated Diffraction System PW1710 equipped with graphite-crystal monochromator for Cu*K*α radia-

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TABLE 1. Cell dimensions of synthetic alkali amphiboles

Mineral composition	Run no.	Reference*	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*V* (Å³)
		A. This study					
Scandium-fluor-eckermannite $NaNa_2Mg_4ScSi_8O_{22}F_2$	FScEC-A3		9.8384 (3)	18.0634 (6)	5.2926 (2)	103.650 (2)	914.01
Indium-fluor-eckermannite $NaNa_2Mg_4InSi_8O_{22}F_2$	FInEC-A3		9.8527 (3)	18.0966 (7)	5.2928 (2)	103.521 (2)	917.55
Scandium-fluor-nyböite $NaNa_2Mg_3Sc_2Si_7AlO_{22}F_2$	FScNY-A3		9.8425 (5)	18.157 (1)	5.3381 (3)	103.979 (4)	925.72
		B. Previous studies					
Eckermannite $NaNa_2Mg_4AlSi_8O_{22}(OH)_2$		1	9.762 (6)	17.892 (11)	5.284 (6)	103.17 (5)	898.6 (8)
		2	9.675 (3)	17.889 (7)	5.270 (2)	102.73 (3)	889.6 (4)

* References: (1) Phillips and Rowbotham (1968). (2) X-ray powder data of (1), re-refined in this study.

tion. Beam divergence was controlled with an automatic divergence slit so that a constant area (approximately 1.9 cm²) of the specimen was irradiated throughout the scanning range. Intensities were measured at 0.04°2*θ* steps with counting times of either 8 or 16 s per step; scanning ranges were between 8° and 73°2*θ*. Structures were refined using a slightly modified version of the program DBW 2.9 (Wiles and Young, 1981). Best refinement results (lowest *R* factors) were obtained with the Mod2 Lorenzian profile function and by refining an overall "isotropic temperature factor" as an approximate absorption-extinction correction. Isotropic temperature factors for individual atoms were fixed at values approximately correct for amphiboles (Table 4).

EXPERIMENTAL RESULTS AND DISCUSSION

Synthesis products

Synthesis conditions and products for typical alkali amphiboles grown in this study are given in Table 2. Only

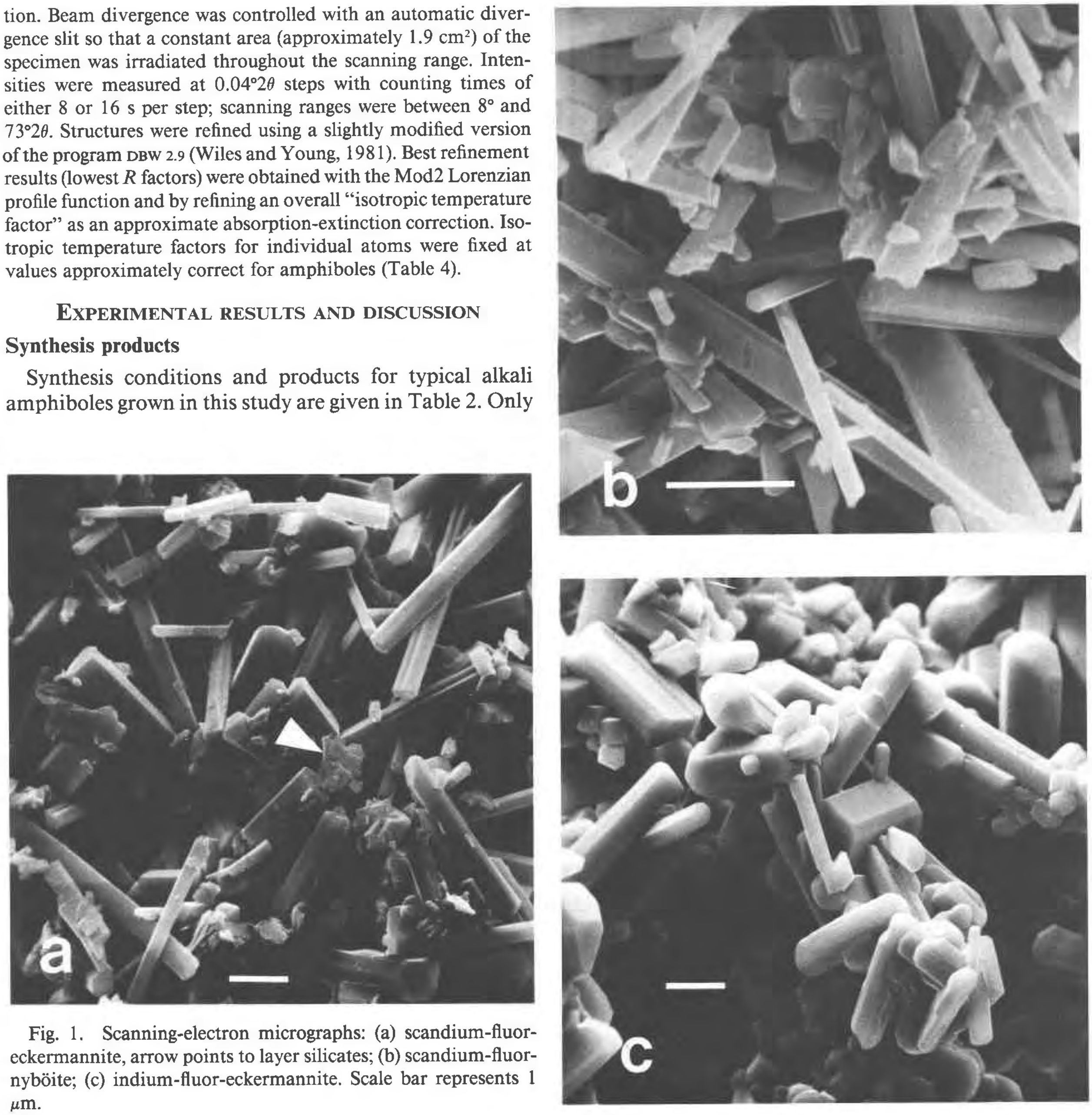

Fig. 1. Scanning-electron micrographs: (a) scandium-fluor-eckermannite, arrow points to layer silicates; (b) scandium-fluor-nyböite; (c) indium-fluor-eckermannite. Scale bar represents 1 μm.

TABLE 2. Typical synthesis conditions and products

Run no.	T (°C)	P (bar)	t (h)	Products*
		$NaNa_2Mg_4ScSi_8O_{22}F_2$		
FScEC-A3	1000	1	90	>95% cam + ly
		$NaNa_2Mg_4InSi_8O_{22}F_2$		
FInEC-A3	1000	1	90	cam
		$NaNa_2Mg_3Sc_2Si_7AlO_{22}F_2$		
FScNY-A3	1000	1	90	>95% cam + $NaScSi_2O_6$

* Abbreviations: cam—clinoamphibole; ly—layer silicate.

those phases that could be unambiguously identified from X-ray powder patterns (or, rarely, optically) are listed. Amphibole yields were 95 to 100%. Cell dimensions (Table 1) and Rietveld-derived site occupancies (Table 6) indicate that they are close to the nominal compositions. Scanning-electron micrographs showed layer silicates in scandium-fluor-eckermannite (Fig. 1a) but not in scandium-fluor-nyböite (Fig. 1b) or fluor-indium-eckermannite (Fig. 1c). Indium-fluor-eckermannite formed colorless, prismatic crystals up to 25 μm long and 4 μm wide. Both scandium-fluor-eckermannite and scandium-fluor-nyböite were acicular; typical crystals were less than 1 to 2 μm wide and up to 100 μm long. The crystals are brittle and break easily, and thus the acicular character is not obvious in the scanning-electron micrographs (Figs. 1a, 1b). Cell dimensions derived by Rietveld refinement from selected runs are given in Table 1.

Rietveld crystal-structure refinement

The Rietveld method (Rietveld, 1967, 1969) uses the whole powder-diffraction pattern to characterize the structure of the material examined. The structure parameters of the mineral (atomic coordinates, site-occupancies, and thermal parameters), together with various experimental parameters affecting the pattern, are refined by least-squares procedures to minimize the difference between the whole calculated and observed patterns. Powder structure refinements of these synthetic amphiboles are comparable with most powder refinements of other minerals (Young, 1980). Results of the structure refinements are summarized in Tables 3 to 6. A typical calculated and observed powder-diffraction pattern is given in Figure 2. In general, the cell dimensions derived from the refinements (Table 1) are significantly more precise than those derived from normal least-squares refinement of powder-diffraction data.

TABLE 4. Atomic positions

		FScEC-A3	FInEC-A3	FScNY-A3
O(1)	x	0.1151 (8)	0.1188 (8)	0.108 (2)
	y	0.0877 (4)	0.0844 (4)	0.0906 (8)
	z	0.214 (2)	0.222 (1)	0.210 (3)
O(2)	x	0.1159 (9)	0.1164 (9)	0.121 (2)
	y	0.1673 (4)	0.1657 (4)	0.1662 (8)
	z	0.724 (1)	0.721 (1)	0.728 (3)
O(3)	x	0.1068 (9)	0.106 (1)	0.101 (2)
	y	0	0	0
	z	0.712 (2)	0.716 (2)	0.710 (4)
O(4)	x	0.3609 (8)	0.3575 (7)	0.361 (1)
	y	0.2481 (3)	0.2453 (4)	0.2475 (6)
	z	0.795 (1)	0.789 (2)	0.788 (3)
O(5)	x	0.3490 (8)	0.3548 (9)	0.347 (2)
	y	0.1269 (3)	0.1261 (3)	0.1326 (8)
	z	0.080 (1)	0.083 (2)	0.085 (3)
O(6)	x	0.3475 (8)	0.3439 (9)	0.343 (2)
	y	0.1172 (3)	0.1173 (4)	0.1194 (7)
	z	0.590 (1)	0.586 (2)	0.593 (3)
O(7)	x	0.345 (1)	0.347 (1)	0.342 (2)
	y	0	0	0
	z	0.300 (2)	0.292 (2)	0.300 (4)
T(1)	x	0.2828 (4)	0.2848 (4)	0.2842 (8)
	y	0.0839 (2)	0.0840 (2)	0.0838 (3)
	z	0.2915 (8)	0.2905 (8)	0.290 (1)
T(2)	x	0.2884 (5)	0.2880 (4)	0.2926 (8)
	y	0.1688 (2)	0.1678 (2)	0.1679 (4)
	z	0.7945 (8)	0.7957 (9)	0.800 (2)
M(1)	x	0	0	0
	y	0.0865 (3)	0.0846 (4)	0.0876 (6)
	z	½	½	½
M(2)	x	0	0	0
	y	0.1817 (2)	0.1822 (2)	0.1801 (4)
	z	0	0	0
M(3)	x	0	0	0
	y	0	0	0
	z	0	0	0
M(4)	x	0	0	0
	y	0.2756 (4)	0.2759 (4)	0.2776 (8)
	z	½	½	½
A	x	0.032 (1)	0.029 (2)	0.043 (2)
	y	½	½	½
	z	0.080 (3)	0.077 (3)	0.102 (6)

Note: Isotropic temperature factors (*B*): O(1) = O(2) = O(3) = O(4) = 0.8; O(5) = O(6) = 1.1; O(7) = 1.2; T(1) = T(2) = 0.4; M(1) = M(2) = M(3) = 0.6; M(4) = 0.9; A = 2.3.

Raudsepp et al. (1987) have discussed in detail the current deficiencies in the Rietveld analysis of complex silicates such as synthetic amphiboles. A major problem in refining amphibole structures are the pseudo–glide planes ‖(010) at $y \approx \pm 1/4$; in particular, these result in the T(1)

TABLE 3. Refinement results

Run no.	Scale	B	P.O.	Asym	Zero	R_{exp}	R_p	R_{wp}	R_B
FScEC-A3	0.00770 (8)	1.74 (7)	0.09 (1)	1.26 (7)	0.114 (1)	2.58	10.0	11.4	2.93
FInEC-A3	0.00460 (5)	1.73 (7)	0.05 (1)	1.96 (7)	0.097 (1)	2.77	10.2	10.8	2.31
FScNY-A3	0.0008 (1)	−0.21 (8)	−0.17 (1)	0.09 (6)	0.000 (1)	3.74	7.5	10.0	3.59

Note: *B*, the overall temperature factor; P.O., preferred orientation parameter; Asym, asymmetry parameter; Zero, zeropoint correlation; R_{exp}, statistically expected value for R_{wp}; R_p, *R* pattern; R_{wp}, *R* weighted pattern; R_B, *R* Bragg.

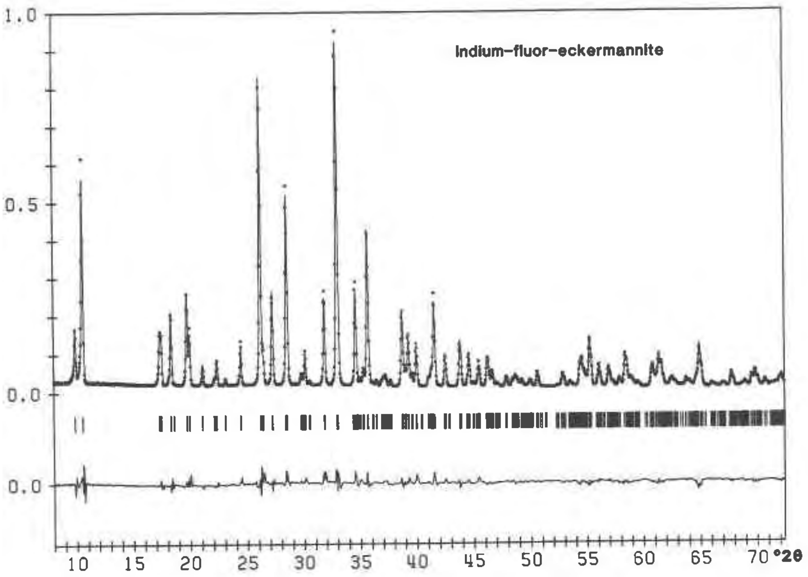

Fig. 2. Calculated and observed X-ray diffraction pattern of indium-fluor-eckermannite from Rietveld structure refinement. Open squares are the observed data, solid line is the calculated pattern, and the vertical bars below the pattern mark all possible Bragg reflections ($K\alpha_1$ and $K\alpha_2$). The residual pattern obtained by subtracting the observed and calculated patterns is shown below.

and T(2) tetrahedra being pseudosymmetrically related. The diffraction maxima containing information on the differences between the T(1) and T(2) tetrahedra are very weak, and the shifts of the atomic positions of the atoms concerned are highly correlated during least-squares refinement. As a side effect, atomic distances in the octahedral strip are also distorted to varying degrees. Furthermore, the pseudosymmetry effects seem to be exacerbated by the presence of extraneous phases in the run product. However, Raudsepp et al. (1987) also showed that the high correlations do not seem to affect site occupancies in the octahedral strip and hence they should be accurate. Thus, our previous experience shows the derivative information, such as bond lengths, to be rather inaccurate, particularly if the run products contain more than a few percent extraneous phases. Site occupancies in synthetic alkali amphiboles are given in Table 6. All neg-

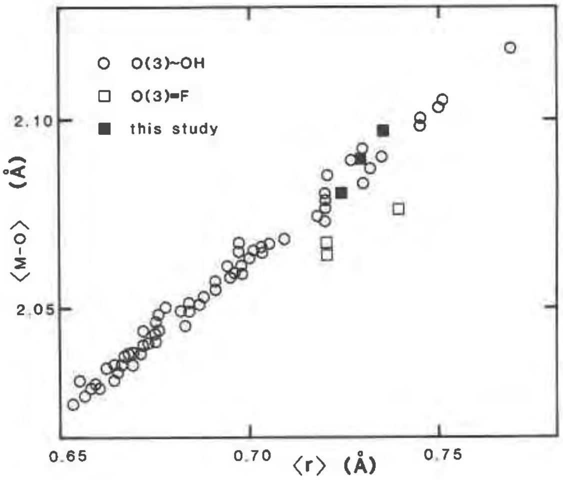

Fig. 3. Variation in grand ⟨M–O⟩ with mean ionic radius of the constituent cations in the M(1,2,3) sites for the *C*2/*m* amphiboles (Hawthorne, 1983) and alkali amphiboles synthesized in this study.

TABLE 5. Interatomic distances (Å)

	FScEC-A3	FInEC-A3	FScNY-A3
T(1)–O(1)	1.605 (6)	1.590 (8)	1.70 (1)
T(1)–O(5)	1.620 (7)	1.618 (8)	1.64 (2)
T(1)–O(6)	1.670 (8)	1.648 (9)	1.71 (2)
T(1)–O(7)	1.630 (4)	1.639 (5)	1.619 (8)
⟨T(1)–O⟩	1.631	1.624	1.67
T(2)–O(2)	1.650 (7)	1.644 (8)	1.64 (2)
T(2)–O(4)	1.600 (6)	1.565 (8)	1.60 (1)
T(2)–O(5)	1.670 (8)	1.687 (8)	1.62 (2)
T(2)–O(6)	1.635 (7)	1.631 (8)	1.58 (2)
⟨T(2)–O⟩	1.639	1.632	1.61
M(1)–O(1) × 2	2.094 (7)	2.085 (8)	2.07 (2)
M(1)–O(2) × 2	2.048 (9)	2.052 (8)	2.06 (2)
M(1)–O(3) × 2	2.060 (6)	2.045 (7)	2.06 (1)
⟨M(1)–O⟩	2.067	2.061	2.06
M(2)–O(1) × 2	2.200 (8)	2.288 (7)	2.11 (1)
M(2)–O(2) × 2	2.072 (8)	2.092 (8)	2.11 (2)
M(2)–O(4) × 2	1.989 (7)	2.050 (7)	2.03 (1)
⟨M(2)–O⟩	2.087	2.143	2.08
M(3)–O(1) × 4	2.114 (7)	2.107 (7)	2.12 (1)
M(3)–O(3) × 2	2.047 (9)	2.02 (1)	2.03 (2)
⟨M(3)–O⟩	2.092	2.079	2.09
M(4)–O(2) × 2	2.43 (1)	2.456 (9)	2.51 (2)
M(4)–O(4) × 2	2.346 (8)	2.338 (7)	2.33 (1)
M(4)–O(5) × 2	2.948 (9)	2.93 (1)	2.87 (2)
M(4)–O(6) × 2	2.562 (8)	2.575 (9)	2.55 (2)
⟨M(4)–O⟩	2.571	2.575	2.57

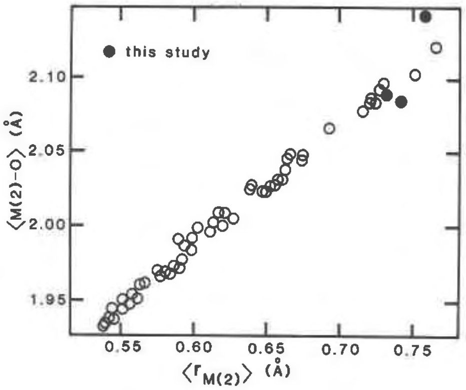

Fig. 4. Variation in ⟨M(2)–O⟩ with mean ionic radius of the constituent cations at the M(2) site for *C*2/*m* amphiboles (Hawthorne, 1983) and alkali amphiboles synthesized in this study.

ative values differ from zero by less than 3 sigma and may be regarded as zero; similarly, occupancies greater than 1.0 are not significantly different from 1.0.

Certain individual tetrahedral bond lengths (Table 5) exhibit ranges of variation that are inconsistent with single-crystal structure data for alkali amphiboles. In general, T(1)–O(5) is too short, and T(1)–O(6) is too long. T(2)–O bond lengths are more variable and do not exhibit consistent discrepancies. However, mean tetrahedral bond lengths seem more reasonable, both for the fluor-eckermannites (no ^{IV}Al) and for scandium-fluor-nyböite (1 ^{IV}Al pfu).

Many groups of isomorphous structures show a nearly linear relationship between the mean bond lengths of cation polyhedra and the mean ionic radius of cations at those sites. Figure 3 shows the variation in the grand mean bond length, ⟨M–O⟩, as a function of grand mean ionic radius for the M(1), M(2), and M(3) sites of *C*2/*m* amphiboles (Hawthorne, 1983). Amphiboles from this study are reasonably consistent with this trend; however, they are slightly displaced to larger ⟨M–O⟩ distances from the only three fluor-amphibole structures on this plot.

Although the general relationship in Figure 3 is well developed for *C*2/*m* amphiboles, the three M sites show considerable variation in local environment and ligancy; thus, it is most informative to examine such relationships separately for each site. The M(1) and M(3) sites show considerable scatter for the mean bond-length–ionic-radius relationship, but this relationship is well developed for the M(2) site (Fig. 4). Our synthetic amphiboles plot close to this general trend (Fig. 4).

The size of the relatively large M(4) site at the junction of the octahedral strip and tetrahedral chain is sensitive to cation occupancies in the M(1,2,3) sites (Hawthorne, 1983). Figure 5 shows the ⟨M(4)–O⟩ distance as a function of the mean M(1,2,3) constituent cation radius for natural alkali amphiboles (Ungaretti et al., 1978) and alkali amphiboles synthesized in this study. The synthetic alkali amphiboles fall close to the trend exhibited by the natural amphiboles. The above relationships between atomic distances and site occupancies demonstrate the utility of the Rietveld structure-refinement method in the characterization of the steric details of synthetic amphiboles. The success of this method here may be attributed to the high quality of the synthesis products, thereby minimizing the problems of interference from extraneous phases during least-squares refinement.

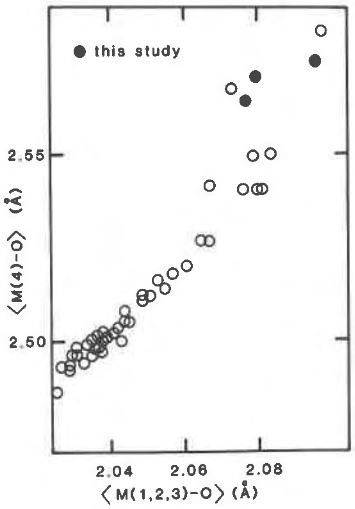

Fig. 5. Variation of ⟨M(4)–O⟩ as a function of ⟨M(1,2,3)–O⟩ in the natural alkali amphiboles (Ungaretti et al., 1978) and alkali amphiboles synthesized in this study.

Cation ordering

The tetrahedral double chain in the *C*2/*m* amphibole structure contains two unique tetrahedrally coordinated cation sites, the T(1) and T(2) sites. In nyböite end members, the relative ordering of Si and Al cannot be directly distinguished by site-occupancy refinement. However, because the ionic radii of Si (0.26 Å) and Al (0.39 Å) are considerably different, the ordering of Al in the tetrahedral chain may be determined by comparison of mean bond lengths at the T(1) and T(2) sites. In *C*2/*m* amphiboles, Al shows the ordering scheme T(1)≫T(2) (e.g., Hawthorne, 1983); thus, mean ⟨T(1)–O⟩ distances should be larger than mean ⟨T(2)–O⟩ distances. Inspection of ⟨T–O⟩ distances for scandium-fluor-nyböite in Table 5 shows that in spite of some unusual individual T–O dis-

TABLE 6. M(1), M(2), M(3) site occupancies

	(1) Scandium-fluor-eckermannite			
M(1)	Mg	0.974 (10)	Sc	0.026 (10)
M(2)	Mg	0.573 (10)	Sc	0.427 (10)
M(3)	Mg	1.063 (13)	Sc	−0.063 (13)
	(2) Indium-fluor-eckermannite			
M(1)	Mg	0.998 (3)	In	0.002 (3)
M(2)	Mg	0.519 (3)	In	0.481 (3)
M(3)	Mg	1.004 (4)	In	0.001 (4)
	(3) Scandium-fluor-nyböite			
M(1)	Mg	0.975 (30)	Sc	0.025 (30)
M(2)	Mg	0.107 (23)	Sc	0.893 (23)
M(3)	Mg	1.043 (32)	Sc	−0.011 (32)

tances, ⟨T(1)–O⟩ is considerably larger than ⟨T(2)–O⟩ and is in the range consistent for amphiboles with 1.0 Al ordered at the T(1) site (e.g., Hawthorne, 1983).

In eckermannitic amphibole end members, both the T(1) and T(2) sites are occupied solely by Si. Single-crystal studies of amphiboles with T(1) + T(2) = 8Si (Hawthorne, 1983) show that the ⟨T(1)–O⟩ and ⟨T(2)–O⟩ distances are approximately equal with ⟨T(2)–O⟩ slightly the larger. Table 5 shows this to be the case for eckermannitic amphiboles; furthermore, the ⟨T–O⟩ distances are also consistent with single-crystal structure data (Hawthorne, 1983). In summary, the Rietveld-derived ⟨T(1)–O⟩ and ⟨T(2)–O⟩ distances seem consistent with ideally ordered site occupancies in these synthetic alkali amphiboles.

Characterization of cation ordering in the octahedral strip of these amphiboles is facilitated by the large differences in scattering power between Mg and the M^{3+} species (Sc, In). The M(1,2,3) site occupancies (Table 6) demonstrate that indium-fluor-eckermannite is essentially stoichiometric with all In ordered at the M(2) site. Both scandium-fluor-eckermannite and scandium-fluor-nyböite are slightly deficient in Sc compared to their nominal compositions, but Sc ordering at the M(2) site is clearly demonstrated. These results are in accordance with our previous study of cation order-disorder in fluor-pargasitic amphiboles (Raudsepp et al., 1987), in which the octahedral trivalent cations (with the exception of Al for which we had no information) were strongly ordered at the M(2) site. Results for tetrahedrally coordinated Al were more ambiguous for the fluor-pargasites, but compared favorably with the results of this study.

CONCLUSIONS

This study has emphasized the utility of Rietveld structure refinement in determining structural information, cation ordering, and compositional data for very fine grained synthetic amphiboles not amenable to single-crystal structure analysis. The following points are of particular interest:

1. Rietveld structure refinement is a versatile technique in the extraction of structural information from very fine grained synthetic minerals, especially from high-yield run products. We are currently experimenting with the simultaneous refinement of the dominant extraneous phase in lower-yield run products; the success of this technique should improve results for the major phase of interest.

2. Rietveld analysis can be used to characterize cation order-disorder when there is a significant difference in the scattering power of the constituent cations. This approach is particularly useful for fluor-amphibole work in which infrared spectroscopy cannot be used for this purpose. We have shown that Sc and In are completely ordered at the M(2) sites in scandium- and indium-fluor-eckermannite and indium-fluor-nyböite. Furthermore, the compositions of the octahedral sites were determined; fluor-indium-eckermannite was essentially of the nominal composition, whereas scandium-fluor-eckermannite and scandium-fluor-nyböite were shown to be slightly off-composition.

ACKNOWLEDGMENTS

Financial assistance was provided by the Natural Sciences and Engineering Research Council of Canada in the form of an operating grant to A. C. Turnock.

REFERENCES

Appleman, D.E., and Evans, H.T. (1973) Job 9214: Indexing and least-squares refinement of powder diffraction data. U.S. National Technical Information Service, Document PB 216 188.

Carman, J.H., and Gilbert, M.C. (1983) Experimental studies on glaucophane stability. American Journal of Science, 238-A, 414–437.

Eitel, W. (1952) Synthesis of fluor-silicates of the mica and amphibole group. Proceedings of the International Symposium on the Reactivity of Solids, Gothenburg, Sweden, 333–345.

Hawthorne, F.C. (1983) The crystal chemistry of the amphiboles. Canadian Mineralogist, 21, 173–480.

Hawthorne, F.C., Raudsepp, Mati, Williams, B. L., and Hartman, J.S. (1984) Characterization of cation ordering in synthetic amphiboles by Rietveld structure refinement and ^{27}Al and ^{29}Si MAS NMR spectroscopy. Geological Association of Canada/Mineralogical Association of Canada Program with Abstracts, 9, 72.

Phillips, R., and Rowbotham, G. (1968) Studies on synthetic alkali amphiboles. Papers and Proceedings of the Fifth General Meeting, International Mineralogical Association, Cambridge, 249–254.

Raudsepp, Mati. (1984) Evaluation of amphibole synthesis and product characterization. Ph.D. Thesis, University of Manitoba, Winnipeg.

Raudsepp, Mati, Turnock, A.C., and Hawthorne, F.C. (1982) Synthesis and characterization of $^{VI}R^{3+}$ analogues of pargasite and eckermannite. Geological Association of Canada/Mineralogical Association of Canada Program with Abstracts, 7, 75.

Raudsepp, Mati, Hawthorne, F.C., and Turnock, A.C. (1984) Derivation of site-occupancies in synthetic pyroxenes and amphiboles by Rietveld structure refinement. Geological Society of America Abstracts with Programs, 16, 630.

Raudsepp, Mati, Turnock, A.C., Hawthorne, F.C., Sherriff, B.L., and Hartman, J.S. (1987) Characterization of synthetic pargasitic amphiboles ($NaCa_2Mg_4M^{3+}Si_6Al_2O_{22}(OH,F)_2$; M^{3+} = Al, Cr, Ga, Sc, In) by infrared spectroscopy, Rietveld structure refinement, and ^{27}Al, ^{29}Si, and ^{19}F MAS NMR spectroscopy. American Mineralogist, 72, 580–593.

Rietveld, H.M. (1967) Line profiles of neutron powder-diffraction peaks for structure refinement. Acta Crystallographica, 22, 151–152.

——— (1969) A profile refinement method for nuclear and magnetic structures. Journal of Applied Crystallography, 2, 65–71.

Shell, H.R., Comeforo, J.R., and Eitel, W. (1958) Synthetic amphibole investigations: Synthesis of fluor-amphiboles from melts. U.S. Bureau of Mines, Report of Investigations 4517, 35 p.

Ungaretti, L., Mazzi, F., Rossi, G., and Dal Negro, A. (1978) Crystal-chemical characterization of blue amphiboles. Proceedings of the XI General Meeting, International Mineralogical Association, Rock-forming Minerals, 82–110. Nauka, Moscow.

Wiles, D.B., and Young, R.A. (1981) A new computer program for Rietveld analysis of X-ray powder diffraction patterns. Journal of Applied Crystallography, 14, 149–151.

Young, R.A. (1980) Structural analysis from X-ray powder diffraction patterns with the Rietveld method. Symposium on Accuracy in Powder Diffraction, National Bureau of Standards, Gaithersburg, Maryland, 143–163.

MANUSCRIPT RECEIVED DECEMBER 15, 1986
MANUSCRIPT ACCEPTED MAY 21, 1987