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THE CRYSTAL CHEMISTRY OF THE AMPHIBOLES. VII. THE CRYSTAL STRUCTURE AND SITE CHEMISTRY OF POTASSIAN FERRI-TARAMITE

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ABSTRACT

The crystal structure and site chemistry of a potassian ferri-taramite of composition $(Na_{0.607}K_{0.381})$ $(Ca_{1.176}Na_{0.792}Mn^{2+}_{0.032})(Fe^{2+}_{2.429}Mg_{0.866}Mn^{2+}_{0.153}Fe^{3+}_{1.307}Ti_{0.186}Al_{0.039})$ $(Si_{6.178}Al_{1.822})$ $O_{22}(OH)_{1.910}$ from the York River area, Bancroft, Ontario, have been determined by full-matrix least-squares refinement of three-dimensional counter-diffractometer X-ray data; the *R*-index for 1626 observed reflections is 3.6%. The space group is *C2/m*, *a* 9.923(1), *b* 18.134(2), *c* 5.352(1)Å, *β* 104.84(1)°, V 930.9Å³, *Z*=2.

Constrained refinement of the octahedral site-populations indicates the transition-metal site-preference $M(2) \sim M(3) > M(1)$. Consideration of the mean bond lengths shows that the small trivalent cations are ordered into the *M*(2) site as found in most other monoclinic amphiboles. Similar considerations suggest that Mn^{2+} is strongly or completely ordered into the *M*(3) site, as found in arfvedsonite (Hawthorne 1976). Using the curves of Hawthorne & Grundy (1977), the $<T\text{–}O>$ bond lengths indicate that tetrahedral Al is strongly ordered into the *T*(1) site. The atoms occupying the *A* site show positional disorder. Of the several disordered structure models tested, the best results were obtained from occupancy of the *A(m)(4i)* and *A(2)(4g)* positions, although a model involving disorder over the *A(m)* and *A(1)(8j)* positions could not be rejected.

SOMMAIRE

La structure cristalline et l'occupation des sites ont été déterminées pour une ferri-taramite potassique $(Na_{0.607}K_{0.381})(Ca_{1.176}Na_{0.792}Mn^{2+}_{0.032})(Fe^{2+}_{2.249}Mg_{0.866}Mn^{2+}_{0.153}Fe^{3+}_{1.307}Ti_{0.186}Al_{0.039})(Si_{6.178}Al_{1.822})O_{22}(OH)_{1.910}$ de la région de York River, Bancroft, Ontario. L'affinement des données par moindres carrés donne un résidu *R* de 3.6% pour les 1626 réflexions observées. Le groupe spatial est *C2/m*, *a* 9.923(1), *b* 18.134(2), *c* 5.352(1)Å, *β* 104.84(1)°, *V* 930.9Å³, *Z*=2. L'affinement contraint de la population des sites octaédriques indique pour les métaux de transition une préférence dans l'ordre $M(2) \sim M(3) > M(1)$. La longueur moyenne des liaisons demande que les petits cations trivalents soient localisés en *M*(2), tout comme dans les autres amphiboles monocliniques. De même, Mn^{2+} serait fortement ou complètement ordonné en *M*(3), comme c'est le cas dans l'arfvedsonite (Hawthorne 1976). D'après les courbes de Hawthorne & Grundy (1977), la longueur des liaisons $<T\text{–}O>$ indique que l'aluminium tétraédrique est fortement concentré en *T*(1). Les atomes qui occupent le site *A* sont en désordre de position; parmi les modèles essayés, celui qui donne les meilleurs résultats requiert l'occupation des positions *A(m)(4i)* et *A(2)(4g)*; nous n'avons pu toutefois rejeter l'hypothèse du désordre qui affecterait les positions *A(m)* et *A(1)(8j)*.

(Traduit par la Rédaction)

INTRODUCTION

Ferri-taramite is a soda-calcic amphibole with the ideal formula $NaCaNa(Fe_3^{2+}Fe_2^{3+})(Si_6Al_2)O_{22}(OH)_2$. It is typically found in metasomatized alkaline gneisses (Appleyard 1967, 1969, 1975) and nepheline syenite dykes (Brock *et al.* 1964). Interest in this rare amphibole type arises from its correspondence to an integral point (120) in charge-distribution space (Whittaker 1968); thus the polyvalent cation ordering-pattern is of interest with regard to the factors that control such ordering in amphiboles. In addition, the character of the positional disorder of the large alkali cations at the *A* site will provide further information pertinent to an examination of the factors affecting this disorder.

The amphibole used in this investigation is from the York River area, Bancroft, Ontario. Polarized optical absorption spectra and a partial chemical analysis of this amphibole were given by Faye & Nickel (1970) who named the amphibole "ferrohastingsite". The nomenclature used here follows the preliminary recommendations of the IMA Subcommittee on nomenclature of the amphibole group.

EXPERIMENTAL

Fragments of the crystals used by Faye & Nickel (1970) were supplied by Mr. H. R.

Steacy, curator of the National Mineral Collection, Geological Survey of Canada. A wet-chemical analysis and the resultant cell contents, calculated on the basis of 24(O,OH), are listed in Table 1.

Long-exposure single-crystal precession photographs displayed diffraction symmetry $2/mC\text{-}/\text{-}$ consistent with the space groups *C*2, *Cm* and *C*2/*m*; the space group *C*2/*m* was assigned and found to be satisfactory for the refinement; no streaking or subsidiary maxima were observed. Cell dimensions determined by least-squares refinement of 31 reflections manually aligned on a 4-circle diffractometer are presented in Table 1, together with other information pertinent to X-ray data collection and refinement.

TABLE 1. CRYSTAL DATA

Chemical analysis		Cell contents*		Miscellaneous	
SiO_2	39.05	Si	6.178	a	9.923(1)Å
Al_2O_3	9.98	Al	1.822	b	18.134(2)
TiO_2	1.56	Σ^{IV}	8.000	c	5.352(1)
Fe_2O_3	10.98	Al	0.039	β	104.84(1)°
FeO	18.36	Ti	0.186	V	930.9Å^3
MnO	1.38	Fe^{3+}	1.307		
MgO	3.76	Fe^{2+}	2.429	Space Group	C2/m
CaO	6.94	Mn	0.185	Z	2
Na_2O	4.56	Mg	0.886	Density$_{calc}$	3.384
K_2O	1.88	Σ^{VI}	5.032	μ	41.80cm^{-1}
H_2O	1.81			Crystal Size	0.14x0.14x0.23mm
wt.%	100.26	Ca	1.176	Rad/Filter	Mo/Zr
		Na	0.792	Total no. of I	3362
		$\Sigma^{M(4)}$	1.968	No. of non-equivalent $\lvert F_o\rvert$	1626
		Na	0.607	No. of $\lvert F_o\rvert > 3\sigma$	1421
		K	0.381	Final R (obs)	3.6%
		Σ^A	0.988	Final R_w(obs)	4.1%
		OH	1.910		
Temp. factor form used	$\exp\left[-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\right]$			$R=\Sigma(\lvert F_o\rvert-\lvert F_c\rvert)/\Sigma\lvert F_o\rvert$ $R_w=(\Sigma w(\lvert F_o\rvert-\lvert F_c\rvert)^2/\Sigma wF_o^2)^{\frac{1}{2}}, w=1$	

*calculation based on 24(OH,O)

A regular cleavage fragment of dimensions 0.14×0.14×0.23mm was used to collect the intensity data. The crystal was mounted on a GE-XRD6 automatic diffractometer operating in the θ–2θ scan mode with a scan rate of 2°/min.; the scan range was calculated according to the formula $1.8 + \tan\theta$ (Alexander & Smith 1964) and 20 sec. background counts were made at the beginning and end of each scan. Six standard reflections were monitored every 50 reflections; no significant change in their intensities was observed during the data collection. A total of 3362 intensities was measured using Zr-filtered Mo*Kα* radiation (λ=0.71069Å) over two asymmetric units out to a 2θ of 65°. The data were corrected for absorption (for polyhedral crystal shape), Lorentz, polarization and background effects, subsequently averaged and reduced to structure factors. A reflection was considered as observed if its magnitude was greater than three standard deviations based on counting statistics. Application of this criterion resulted in 1421 observed reflections.

REFINEMENT

Quoted *R*-indices are of the form given in Table 1 and are expressed as percentages; anisotropic temperature factors are of the form given in Table 1. Scattering curves for neutral atoms were taken from Cromer & Mann (1968) together with anomalous dispersion coefficients from Cromer & Liberman (1970). The final atomic coordinates and equivalent isotropic temperature factors of ferrotschermakite (Hawthorne & Grundy 1973a) were used as input to

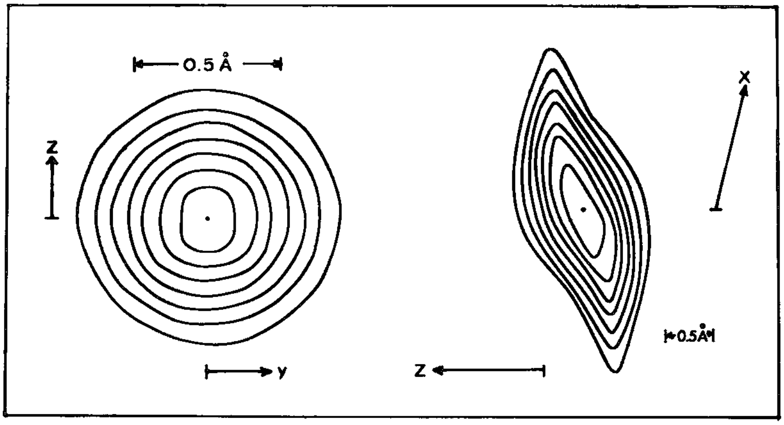

FIG. 1. Difference fourier sections through the *A* site, calculated with the *A*-site cations removed from the structure model. The contour interval is arbitrary.

the least-squares program RFINE (Finger 1969a). For the initial part of the refinement, the scattering power at the octahedral sites was represented by the species Fe° ($=Fe^{2+}+Fe^{3+}+Mn+Ti$) and Mg° ($=Mg+Al$) which were assumed to be completely disordered over the $M(1)$, $M(2)$ and $M(3)$ sites. Subsequent site-population refinement was performed using the cell contents as linear constraints in the manner outlined by Finger (1969b). Several cycles of full-matrix least-squares refinement, gradually increasing the number of variables, resulted in convergence at an R-index of 7.0% for an isotropic thermal model. As with previous refinements of clinoamphiboles (Papike *et al.* 1969; Hawthorne & Grundy 1972, 1973a,b; Robinson *et al.* 1973), the A-site temperature factor was anomalously large (6.8Å^2) at this stage. Figure 1 shows two difference fourier sections through the A site, calculated with A-site cation(s) removed from the structure model. Although the maximum density occurs at the $2a$ position, the density is strongly elongated in the (010) plane; in the (100) section, no elongation is apparent. This has been interpreted as positional disorder of the cations occupying the $2b$ position in the clinoamphiboles (Papike & Clark 1968). Three different models have been proposed for this positional disorder (Papike *et al.* 1969; Hawthorne & Grundy 1972; Cameron *et al.* 1973a). Initially, the model of Papike *et al.* (1969) was used; the A-site cations were assumed to be disordered into the $4i$ positions with starting positional parameters taken from Kakanui hornblende (Papike *et al.* 1969). Full-matrix least-squares refinement of all variables resulted in reductions in the R– and R_w–indices from 7.0% to 6.4% and 7.0% to 6.5%, respectively; this is significant at the 0.005 level (Hamilton 1965). With the exception of the disordered A-site atoms, temperature factors were converted to an anisotropic form as given in Table 1. Full-matrix refinement of all variables resulted in convergence to R– and R_w–indices of 4.7% and 4.8%, respectively.

Hawthorne & Grundy (1972) proposed that the disordered A-site atoms occupied the $4g$ and $4i$ positions in a series of calcic and sub-calcic amphiboles. Cameron *et al.* (1973a) proposed that the disordered A-site Na occupied the $8j$ position in richterite. The models tested for potassian ferri-taramite are summarized in Table 2. Inspection of Table 2 shows that the two-site models produce significantly lower R-indices than the one-site models; in addition, the isotropic temperature factors in the one-site models are larger than are generally encountered in well-refined structures. The model involving $A(m)$ and $A(2)$ produced a significantly lower R–index than that involving $A(m)$ and $A(2/m)$. Models involving constrained temperature factors are to be preferred as this damps variable correlation in the refinement procedure. However, even this constraint was not sufficient to produce convergence for the model involving $A(m)$ and $A(1)$. From the results of Table 2, it seems that the model involving $A(m)$ and $A(2)$ is to be preferred for potassian ferri-taramite. However, it should be emphasized that disorder over the $A(m)$ and $A(1)$ positions cannot be rejected.

TABLE 2. CATION-DISORDERED MODELS FOR THE A-SITE

Site(s)*	Occ.	B(Å^2)	Occ.	B(Å^2)	R	R_w
A(m)	0.647	3.28(7)	–	–	4.7	4.8
A(1)	0.324	3.4(1)	–	–	4.6	4.7
A(m)+A(2/m)**	0.380(7)	2.49(8)	0.534	2.49	3.9	4.3
A(m)+A(2/m)	0.42(2)	2.9(2)	0.45	2.0(2)	3.9	4.3
A(m)+A(2)**	0.344(6)	1.8(1)	0.273	1.8	3.6	4.1
A(m)+A(2)	0.44(2)	2.7(2)	0.21	0.9(3)	3.6	4.1
A(m)+A(1)**	Would not converge					

*A(2/m)=2b; A(m)=4i; A(2)=4g; A(1)=8j. **Isotropic temperature factors constrained to be equal at each site.

Final atomic positions and equivalent isotropic temperature factors are given in Table 3; final anisotropic temperature factor coefficients are presented in Table 4. Structure factor tables may be obtained at nominal cost from the De-

TABLE 3. ATOMIC PARAMETERS

Site	x	y	z	B_{equiv} (Å^2)
O(1)	0.1063(2)	0.0912(1)	0.2136(4)	0.85(3)
O(2)	0.1210(2)	0.1745(1)	0.7356(4)	0.82(3)
O(3)	0.1104(3)	0	0.7099(6)	0.94(5)
O(4)	0.3662(2)	0.2499(1)	0.7939(4)	0.93(3)
O(5)	0.3494(2)	0.1364(1)	0.1004(5)	1.06(3)
O(6)	0.3425(2)	0.1189(1)	0.6015(5)	1.04(3)
O(7)	0.3353(4)	0	0.2886(7)	1.27(5)
T(1)	0.27973(9)	0.08621(5)	0.3005(2)	0.56(1)
T(2)	0.29085(8)	0.17241(4)	0.8105(1)	0.53(1)
M(1)	0	0.08945(4)	½	0.84(2)
M(2)	0	0.17993(4)	0	0.66(2)
M(3)	0	0	0	0.74(2)
M(4)	0	0.28033(6)	½	0.89(2)
A(m)	0.0437(8)	½	0.0906(16)	1.8(1)
A(2)	0	0.4889(5)	0	1.8

pository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Interatomic distances and angles, and the magnitudes and orientations of the principal axes of the thermal ellipsoids were calculated with the program ERRORS (L. W. Finger, pers. comm.) and are presented in Tables 5-8.

TABLE 4. ANISOTROPIC TEMPERATURE FACTOR COEFFICIENTS*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
0(1)	234(19)	70(5)	695(69)	-11(8)	99(29)	-8(16)
0(2)	165(18)	75(5)	777(68)	0(8)	56(27)	1(16)
0(3)	260(29)	78(8)	809(93)	0	136(44)	0
0(4)	359(21)	52(5)	851(73)	-35(9)	272(31)	-17(16)
0(5)	225(20)	101(6)	936(74)	-2(9)	98(30)	126(17)
0(6)	259(20)	83(6)	1015(74)	1(9)	153(31)	-118(17)
0(7)	313(32)	79(9)	1451(122)	0	127(50)	0
T(1)	178(7)	40(2)	496(25)	-9(3)	93(10)	-8(6)
T(2)	161(7)	41(2)	464(24)	-8(3)	104(10)	5(5)
M(1)	261(7)	77(2)	594(25)	0	173(10)	0
M(2)	198(7)	46(2)	645(24)	0	132(9)	0
M(3)	274(10)	43(3)	608(34)	0	99(13)	0
M(4)	317(10)	54(3)	948(35)	0	352(15)	0

*β_{ij} x 10^5

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å)

Atoms	Distance	Atoms	Distance
T(1)-0(1)	1.666(2)	M(1)-0(1)	2.072(2) x2
T(1)-0(5)	1.683(2)	M(1)-0(2)	2.153(2) x2
T(1)-0(6)	1.680(2)	M(1)-0(3)	2.113(2) x2
T(1)-0(7)	1.664(1)	Mean M(1)	2.113
Mean T(1)	1.673		
		M(2)-0(1)	2.096(2) x2
T(2)-0(2)	1.630(2)	M(2)-0(2)	2.080(2) x2
T(2)-0(4)	1.604(2)	M(2)-0(4)	1.962(2) x2
T(2)-0(5)	1.646(2)	Mean M(2)	2.046
T(2)-0(6)	1.658(2)		
Mean T(2)	1.635	M(3)-0(1)	2.130(2) x4
		M(3)-0(3)	2.117(3) x2
M(4)-0(2)	2.437(2) x2	Mean M(3)	2.126
M(4)-0(4)	2.368(2) x2		
M(4)-0(5)	2.729(3) x2		
M(4)-0(6)	2.552(3) x2	A-0(5)	3.008(2) x4
Mean for 8	2.522	A-0(6)	3.152(2) x4
		A-0(7)	2.520(4) x2
Mean for 6	2.452	A-0(7)	3.739(4) x2
		Mean for 12	3.097
A(2)-0(5)	2.845(8) x2		
A(2)-0(5)	3.177(8) x2		
A(2)-0(6)	3.017(7) x2	A(m)-0(5)	2.974(5) x2
A(2)-0(6)	3.294(7) x2	A(m)-0(5)	3.145(5) x2
A(2)-0(7)	2.528(4) x2	A(m)-0(6)	2.773(6) x2
A(2)-0(7)	3.744(4) x2	A(m)-0(6)	3.580(7) x2
Mean for 12	3.101	A(m)-0(7)	2.554(8)
		A(m)-0(7)	2.609(8)
Mean for 8	2.892	A(m)-0(7)	3.231(9)
		A(m)-0(7)	4.261(9)
T(1)-T(2) through 0(6)	3.123(1)	Mean for 12	3.133
		Mean for 8	2.868
T(1)-T(2) through 0(5)	3.079(1)	M(1)-M(1)	3.244(2)
T(1)-T(1) across mirror	3.127(2)	M(1)-M(2)	3.139(1)
		M(1)-M(3)	3.129(1)
		M(1)-M(4)	3.461(1)
A-A(2)	0.202(9)	M(2)-M(3)	3.263(1)
A-A(m)	0.562(8)	M(2)-M(4)	3.237(1)

Discussion

Site populations

The results of the constrained site-population refinement are given in Table 9. These refined site populations are considered only in terms of scattering species that differ significantly. However, it is desirable to derive complete site populations in terms of the different cation species that are present in the crystal. This may be done by an examination of the mean bond lengths together with the constraints provided by the site-population refinement results. Hawthorne & Grundy (1977) have derived equations relating mean tetrahedral bond lengths in the *T*(1) and *T*(2) sites to Al content. Use of these relationships gives the tetrahedral site populations listed in Table 9; the total tetrahedral Al indicated by these equations (1.80 Al per formula unit) agrees closely with the amount indicated from the chemical analysis (1.82 Al). As in all other amphiboles examined thus far (Hawthorne & Grundy 1977), Al shows the tetrahedral site preference *T*(1) > *T*(2). For the octahedral sites, there are six cation species to be distributed over three sites. Hawthorne (1977) has provided equations relating mean bond length to constituent-cation radius for the three octahedral sites in the clinoamphiboles; these may be used to help

TABLE 6. POLYHEDRAL EDGE LENGTHS (Å)

T(1) Tetrahedron		T(2) Tetrahedron	
0(1)-0(5)	2.758(3)	0(2)-0(4)	2.738(3)
0(1)-0(6)	2.750(3)	0(2)-0(5)	2.676(3)
0(1)-0(7)	2.755(4)	0(2)-0(6)	2.677(3)
0(5)-0(6)	2.719(3)	0(4)-0(5)	2.663(3)
0(5)-0(7)	2.688(3)	0(4)-0(6)	2.575(3)
0(6)-0(7)	2.720(3)	0(5)-0(6)	2.672(3)
Mean 0-0	2.732	Mean 0-0	2.667
M(1) Octahedron		**M(3) Octahedron**	
$0(1^u)-0(2^d)$	2.786(3)	$0(1^u)-0(1^d)$	2.685(4)
$0(1^u)-0(2^u)$	3.147(3)	$0(1^u)-0(1^u)$	3.306(4)
$0(1^u)-0(3^d)$	2.824(3)	$0(1^u)-0(3^d)$	2.824(3)
$0(1^u)-0(3^u)$	3.120(4)	$0(1^u)-0(3^u)$	3.172(4)
0(2)-0(2)	3.005(4)	Mean 0-0	2.997
0(2)-0(3)	3.168(2)		
0(3)-0(3)	2.707(6)		
		M(4) Polyhedron	
Mean 0-0	2.984	0(2)-0(2)	3.005(4)
		$0(2^u)-0(4^u)$	3.180(3)
M(2) Octahedron		$0(2^u)-0(4^d)$	2.963(3)
0(1)-0(1)	2.685(4)	$0(2^u)-0(5^u)$	3.533(3)
$0(1^u)-0(2^d)$	2.786(3)	$0(4^u)-0(5^d)$	3.420(3)
$0(1^u)-0(2^u)$	3.007(3)	$0(4^u)-0(6^u)$	2.575(3)
0(1)-0(4)	2.897(3)	$0(5^u)-0(6^u)$	2.719(3)
$0(2^u)-0(4^d)$	2.963(3)	$0(5^u)-0(6^d)$	3.081(3)
$0(2^u)-0(4^u)$	2.842(3)	$0(6^u)-0(6^d)$	3.563(5)
0(4)-0(4)	2.986(5)	Mean 0-0	3.094
Mean 0-0	2.888		

assign specific cation species to specific sites, although due to the complexity of the chemistry of the amphiboles, this process is necessarily somewhat subjective. As is apparent from Table 5, <*M*(2)–O> is considerably less than <*M*(1)–O> and <*M*(3)–O>. This suggests that the smaller trivalent cations are located in the *M*(2) site, as has been found in previous studies of calcic and sodic amphiboles (Papike *et al.* 1969; Hawthorne & Grundy 1973a; Robinson *et al.* 1973; Hawthorne 1976). If all the octahedral trivalent cations are assigned to the *M*(2) site, constituent-cation radius values of 0.670 ($Ti=Ti^{3+}$) and 0.664 ($Ti=Ti^{4+}$) result. The *M*(2) site equation of Hawthorne (1977) gives calculated <*M*(2)–O> distances of 2.048 and 2.043Å, respectively. Both of these values agree with the observed value of 2.046Å and thus do not give any information as to the valence of Ti. However, they do indicate that all the trivalent (and tetravalent) octahedral cations may be assigned to the *M*(2) site with a reasonable degree of confidence. This leaves three species (Mg, Fe^{2+} and Mn^{2+}) to be distributed over the *M*(1) and *M*(3) sites. As the site-refinement results give the individual Mg site occupancies, this reduces to assigning Fe^{2+} and Mn^{2+} site populations from the equations relating <*M*(1)–O> and <*M*(3)–O> to the constituent-cation and anion radii. Using the curves of Hawthorne (1977), the following values are obtained:

$M(1) = 0.653Fe^{2+} + 0.077Mn^{2+} + 0.270Mg$
$M(3) = 0.859Fe^{2+} + 0.141Mg$
$\langle M(1){-}O\rangle_{calc} = 2.122$Å, $\langle M(1){-}O\rangle_{obs} = 2.113$Å
$\langle M(3){-}O\rangle_{calc} = 2.116$Å, $\langle M(3){-}O\rangle_{obs} = 2.126$Å
$M(1) = 0.730Fe^{2+} + 0.270Mg$
$M(3) = 0.706Fe^{2+} + 0.153Mn^{2+} + 0.141Mg$
$\langle M(1){-}O\rangle_{calc} = 2.118$Å, $\langle M(1){-}O\rangle_{obs} = 2.113$Å
$\langle M(3){-}O\rangle_{calc} = 2.122$Å, $\langle M(3){-}O\rangle_{obs} = 2.126$Å

The root-mean-square deviations for the two extreme distributions (all Mn^{2+} in *M*(1) or in *M*(3)) are 0.010 and 0.004Å respectively, suggesting that the octahedral Mn^{2+} is strongly ordered into the *M*(3) site. It should be stressed that the degree of confidence in this result is not high as the mean bond length–constituent-cation radius relationships for the *M*(1) and *M*(3) octahedra are not very well defined (Hawthorne 1977); however, this result is in accord with the octahedral

TABLE 7. SELECTED INTERATOMIC ANGLES

T(1) Tetrahedron		T(2) Tetrahedron	
0(1)-T(1)-0(5)	110.9(1)°	0(2)-T(2)-0(4)	115.7(1)°
0(1)-T(1)-0(6)	110.6(1)	0(2)-T(2)-0(5)	109.5(1)
0(1)-T(1)-0(7)	111.6(1)	0(2)-T(2)-0(6)	109.0(1)
0(5)-T(1)-0(6)	107.9(1)	0(4)-T(2)-0(5)	110.0(1)
0(5)-T(1)-0(7)	106.8(1)	0(4)-T(2)-0(6)	104.2(1)
0(6)-T(1)-0(7)	108.9(2)	0(5)-T(2)-0(6)	108.0(1)
Mean 0-T(1)-0	109.5	Mean 0-T(2)-0	109.4
M(1) Octahedron		M(3) Octahedron	
0(1^u)-M(1)-0(2^d)	82.5(1)	0(1^u)-M(3)-0(1^d)	78.2(1)
0(1^u)-M(1)-0(2^u)	96.3(1)	0(1^u)-M(3)-0(1^u)	101.8(1)
0(1^u)-M(1)-0(3^d)	84.9(1)	0(1^u)-M(3)-0(3^d)	83.4(1)
0(1^u)-M(1)-0(3^u)	96.4(1)	0(1^u)-M(3)-0(3^u)	96.6(1)
0(2)-M(1)-0(2)	88.5(1)		
0(2)-M(1)-0(3)	95.9(1)	Mean 0-M(3)-0	90.0
0(3)-M(1)-0(3)	79.7(1)		
		M(4) Polyhedron	
Mean 0-M(1)-0	90.0		
		0(2)-M(4)-0(2)	76.1(1)
M(2) Octahedron		0(2^u)-M(4)-0(4^d)	76.1(1)
		0(2^u)-M(4)-0(4^u)	82.9(1)
0(1)-M(2)-0(1)	79.7(1)	0(2^u)-M(4)-0(5^u)	86.1(1)
0(1^u)-M(2)-0(2^d)	83.7(1)	0(4^u)-M(4)-0(5^d)	84.0(1)
0(1^u)-M(2)-0(2^u)	92.1(1)	0(4^u)-M(4)-0(6^u)	63.0(1)
0(1)-M(2)-0(4)	91.0(1)	0(5^u)-M(4)-0(6^d)	71.3(1)
0(2^u)-M(2)-0(4^d)	94.2(1)	0(5^u)-M(4)-0(6^u)	61.9(1)
0(2^u)-M(2)-0(4^u)	89.3(1)	0(6)-M(4)-0(6)	88.6(1)
0(4)-M(2)-0(4)	99.1(1)	Mean 0-M(4)-0	75.9
Mean 0-M(2)-0	90.0		
		Tetrahedron	
A Polyhedron			
		T(1)-0(5)-T(2)	135.3(1)
0(7)-0(7)-0(7)	65.7(1)	T(1)-0(6)-T(2)	138.7(2)
		T(1)-0(7)-T(1)	139.9(2)
Δ^*	0.270	0(5)-0(6)-0(5)	166.2(1)
		0(5)-0(7)-0(6)	164.7(2)

$^*\Delta = [90^\circ - 0(7)\text{-}0(7)\text{-}0(7)] / 90^\circ.$

TABLE 8. VIBRATION ELLIPSOIDS FOR POTASSIAN FERRI-TARAMITE

	R.M.S. Displacement (Å^2)	Angle to a-axis(°)	Angle to b-axis(°)	Angle to c-axis(°)
	0.097(5)Å	87(35)°	80(26)°	21(41)°
0(1)	0.102(5)	146(21)	122(22)	69(42)
	0.111(4)	57(20)	146(20)	92(15)
	0.087(5)	24(11)	91(8)	80(11)
0(2)	0.106(5)	66(11)	89(30)	170(12)
	0.112(4)	90(14)	1(30)	89(29)
	0.103(7)	117(41)	90	13(41)
0(3)	0.110(6)	153(41)	90	103(41)
	0.114(6)	90	0	90
	0.085(5)	118(8)	147(16)	67(19)
0(4)	0.097(5)	70(11)	117(18)	152(16)
	0.136(4)	35(4)	107(4)	74(5)
	0.091(5)	99(19)	126(4)	36(4)
0(5)	0.102(4)	166(13)	93(12)	88(16)
	0.146(4)	100(4)	36(3)	54(3)
	0.088(5)	109(10)	47(4)	44(4)
0(6)	0.110(4)	160(9)	98(8)	93(8)
	0.140(4)	97(6)	136(4)	46(4)
	0.115(6)	90	0	90
0(7)	0.121(6)	160(12)	90	96(12)
	0.143(6)	111(12)	90	6(12)
	0.079(2)	78(30)	27(38)	70(61)
T(1)	0.081(2)	63(17)	74(58)	159(59)
	0.093(2)	30(7)	111(6)	83(7)
	0.073(2)	126(5)	114(8)	34(9)
T(2)	0.083(2)	98(11)	144(11)	121(10)
	0.090(2)	37(6)	116(11)	79(8)
	0.082(2)	118(2)	90	13(2)
M(1)	0.112(2)	152(2)	90	103(2)
	0.113(2)	90	0	90
	0.087(2)	136(6)	90	31(6)
M(2)	0.088(2)	90	0	90
	0.099(2)	46(5)	90	59(5)
	0.084(3)	90	0	90
M(3)	0.091(3)	85(4)	90	170(4)
	0.114(2)	5(4)	90	100(4)
	0.081(3)	137(2)	90	33(2)
M(4)	0.095(2)	90	0	90
	0.135(2)	47(2)	90	57(2)

TABLE 9. SITE POPULATIONS*

From site-population refinement:	
M(1)	$0.730(5)\mathrm{Fe}^* + 0.270\mathrm{Mg}$
M(2)	$0.878(5)\mathrm{Fe}^* + 0.122\mathrm{Mg}$
M(3)	$0.859(8)\mathrm{Fe}^* + 0.141\mathrm{Mg}$
M(4)	$0.589\mathrm{Ca} + 0.395\mathrm{Na} + 0.016\mathrm{Mn}$
A(m)	$0.366(6)\mathrm{Na}^*$
A(2)	$0.284(9)\mathrm{Na}^*$
From examination of mean bond lengths:	
T(1)	$0.43\mathrm{Al} + 0.57\mathrm{Si}$
T(2)	$0.02\mathrm{Al} + 0.98\mathrm{Si}$
M(1)	$0.730\mathrm{Fe}^{2+} + 0.270\mathrm{Mg}$
M(2)	$0.02\mathrm{Al} + 0.093\mathrm{Ti} + 0.102\mathrm{Mg}$ $+0.654\mathrm{Fe}^{3+} + 0.131\mathrm{Fe}^{2+}$
M(3)	$0.706\mathrm{Fe}^{2+} + 0.153\mathrm{Mn}^{2+} + 0.141\mathrm{Mg}$
M(4)	$0.589\mathrm{Ca} + 0.395\mathrm{Na} + 0.016\mathrm{Mn}^{2+}$
A(m)	$0.366\mathrm{Na}^*$
A(2)	$0.284\mathrm{Na}^*$

*$\mathrm{Fe}^* = \mathrm{Fe}^{2+}+\mathrm{Fe}^{3+}+\mathrm{Mn}+\mathrm{Ti}$; $\mathrm{Na}^* = \mathrm{Na}+1.8\mathrm{K}$

site preference of Mn^{2+} in arfvedsonite (Hawthorne 1976), where the same procedure was used to derive the site populations. In the disordered *A*-site configuration, there are three species (Na, K and vacancy) to be distributed over two sites, and thus the relative site populations may only be determined as the total electron density at the sites. In Table 9, this is expressed as Na*, where Na* = Na + 1.8K. Although there is greater electron density at the *A(m)* position, it is not possible to determine even approximately which position has the greater occupancy in terms of cation species; thus complete ordering of K into *A(m)* would result in a greater proportion of vacancies at *A(m)* even though the electron density at *A(m)* is greater than that at the *A*(2) site.

Positional disorder at the A site in clinoamphiboles

Highly anisotropic electron density observed at the *A* site in the refinements of Kakanui hornblende and potassian richterite (Papike *et al.* 1969) was interpreted as positional disorder about the 2*b* position. They considered the disorder to be primarily confined to the mirror plane (special position 4*i*), although the occurrence of residual density along the 2-fold axis (special position 4*g*) was noted. Hawthorne & Grundy (1972, 1973a,b) subsequently proposed a model wherein positional disorder of the *A*-site cations occurred both in the mirror plane and along the 2-fold axis. With this model, it is possible to obtain only the electron density at each site and not the actual site populations in terms of cation species, as there are generally three cation species (Na, K and vacancy) to be distributed over two sites. It is difficult to examine the factors controlling this disorder without a knowledge of the cation occupancies of the *A*(2) and *A(m)* sites, and hence an elucidation of these occupancies is the first problem to be considered. In general, there are two cation species sited in the *A* position, Na and K. The most obvious situation would be where K occupied one site *(A*(2) or *A(m))* and Na occupied the other (*Am)* or *A*(2)). Table 10 shows the relevant data for the clinoamphiboles for which refinements are available. Inspection of this table shows that the situation *A(m)*=Na, *A*(2)=K is not tenable. The alternative arrangement, *A(m)*=K, *A*(2)=Na is examined in more detail in Figure 2. The data scatter about the ideal relationships for this model, suggesting that this arrangement is substantially correct. However, some deviation is present and the question arises as to whether other factors may somewhat perturb this distribution. This is particularly apparent for the potassic arfvedsonite refined by Hawthorne (1976). Comparison of the electron microprobe and wet chemical analyses for this mineral shows some differences in results for $\mathrm{Na_2O}$ and $\mathrm{K_2O}$, perhaps caused by contamination of the separate by aenigmatite. Recalculation of the cell contents using the microprobe values of $\mathrm{Na_2O}$ and $\mathrm{K_2O}$ result in a much closer approach to the ideal curves in Figure 2 (K^A= 0.81, Na^A=0.16). This suggests that the scatter in the data in Figure 2 might be due to small

TABLE 10. A-SITE CATIONS AND DISORDERED A-SITE OCCUPANCIES* IN CLINOAMPHIBOLES

**	1	2	3	4	5	6
Na	0.13	0.54	0.70	0.16	0.23	0.61
K	0.14	0.43	0.30	0.12	0.75	0.38
Na A(m)	0.16	0.40	0.19	0.12	0.78	0.37
Na A(2)	0.03	0.26	0.43	0.08	-	0.28

occupancies expressed as Na = Na + 1.8K. **1: ferro-tschermakite (Hawthorne & Grundy 1973a); 2: oxy-kaersutite (Hawthorne & Grundy 1973b); 3: sub-silicic hastingsite (Hawthorne & Grundy 1977); 4: tremolite (Hawthorne & Grundy 1976); 5: potassic arfvedsonite (Hawthorne 1976); 6: potassian ferri-taramite (this study).

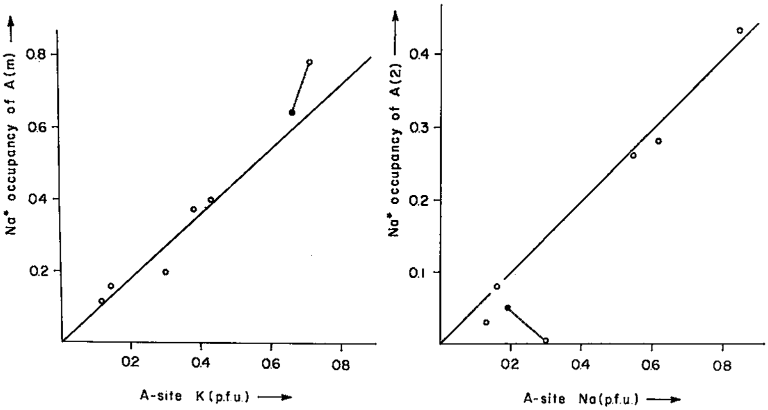

FIG. 2. The variation in *A*-site occupancies of clinoamphiboles (Table 10) as a function of the amounts of K and Na at the *A* site. The data points indicated by filled circles are redeterminations of the values for potassic arfvedsonite (Hawthorne 1976) using different total *A*-site chemistry constraints (see text).

errors in the chemical analyses, as the method of assigning cations to specific groups of sites in the amphiboles will tend to accumulate errors at the *A* site. If this is so, the model whereby K orders into the *A(m)* position and Na orders into the *A*(2) position would appear to be adequate.

This conclusion is supported to some extent by the results given by Cameron *et al.* (1973a,b) for synthetic potassian richterite and richterite. They showed that in potassian richterite, K is restricted to the 4*i* position; in richterite, Na occupies the 8*j* position. Although our preferred model for potassian ferri-taramite involved disorder over the *A(m) and A*(2) positions, a model with disorder over the *A(m) and A*(1) positions was not rejected; examination of a more sodic amphibole may afford better resolution of these two models. However, despite the differences in the models for *A*-site occupancy of Na, the results of Cameron *et al.* (1973a,b) support the argument that the character of the *A*-site cation disorder is a function of the cation type.

The question now arises as to why the positional disorder of the *A*-site cations occurs. Table 11 lists the bond lengths and corresponding bond strengths for K and Na occupancy of the central *A* site. Irrespective of whether the cation coordination is taken as [12] or [10], K occupancy of the *A*(2/*m*) site would lead to an excess in bond strength around the cation, whereas Na occupancy of the *A*(2/*m*) site would lead to an overall deficiency in bond strength around the cation. This suggests that the observed positional disorder occurs as a result of the cation bond-strength requirements. In addition, the fact that K occupancy leads to a bond-strength excess whereas Na occupancy leads to a bond-strength deficiency suggests that K and Na will disorder differently, in agreement with

TABLE 11. A(2/m)-O DISTANCES AND BOND STRENGTHS* IN REFINED CLINOAMPHIBOLES

	Ferro-tschermakite		Oxy-kaersutite		Sub-silicic hastingsite		Tremolite		Potassic arfvedsonite		Potassian ferri-taramite	
A-O(5)x4	3.056(4)Å		3.068(9)Å		3.055(4)Å		2.973(2)Å		2.755(3)Å		3.008(2)Å	
A-O(6)x4	3.159(3)		3.079(5)		3.101(4)		3.148(2)		3.212(3)		3.152(2)	
A-O(7)x2	2.518(4)		2.456(7)		2.504(5)		2.480(3)		2.629(2)		2.520(4)	
A-O(7)x2	3.735(4)		3.700(7)		3.775(6)		3.608(4)		3.720(2)		3.739(4)	
Mean [12]	3.114		3.075		3.099		3.055		3.047		3.097	
Mean [10]	2.990		2.950		2.963		2.944		2.913		2.968	
	K	Na	K	Na	K	Na	K	Na	K	Na	K	Na
A-O(5)x4	0.093	0.066	0.091	0.065	0.093	0.066	0.105	0.075	0.148	0.103	0.100	0.071
A-O(6)x4	0.080	0.057	0.090	0.064	0.087	0.062	0.081	0.058	0.074	0.053	0.081	0.058
A-O(7)x2	0.221	0.151	0.248	0.169	0.227	0.155	0.237	0.162	0.183	0.126	0.221	0.151
A-O(7)x2	0.038	0.028	0.039	0.029	0.036	0.027	0.044	0.032	0.039	0.028	0.038	0.028
[12]	1.210	0.850	1.298	0.912	1.246	0.876	1.306	0.920	1.332	0.932	1.242	0.874
[10]	1.134	0.794	1.220	0.854	1.174	0.822	1.218	0.856	1.254	0.876	1.166	0.818

*Bond strengths (in valence units) are calculated from the universal curves of Brown & Shannon (1973)

TABLE 12. A-SITE CATION-ANION DISTANCES (Å) AND BOND STRENGTHS (v.u.)* IN SEVERAL REFINED CLINOAMPHIBOLES

	Ferro-tschermakite		Oxy-kaersutite		Sub-silicic hastingsite		Tremolite		Potassic arfvedsonite		Potassian ferri-taramite	
A(m)-0(5)x2	3.042(4)	0.095	3.026(6)	0.097	3.057(9)	0.093	2.94(1)	0.111	2.846(5)	0.128	2.974(5)	0.105
A(m)-0(5)x2	3.114(4)	0.085	3.210(7)	0.075	3.146(11)	0.082	3.10(1)	0.087	2.923(5)	0.113	3.145(5)	0.082
A(m)-0(6)x2	2.905(5)	0.116	2.705(8)	0.161	2.737(19)	0.152	2.78(1)	0.142	3.037(5)	0.096	2.773(6)	0.153
A(m)-0(6)x2	3.433(6)	0.055	3.507(11)	0.050	3.510(14)	0.050	3.56(1)	0.047	3.397(5)	0.058	3.580(7)	0.046
A(m)-0(7)	2.504(7)	0.227	2.515(11)	0.223	2.501(15)	0.228	2.49(2)	0.233	2.616(8)	0.187	2.554(8)	0.208
A(m)-0(7)	2.584(7)	0.197	2.527(11)	0.218	2.620(17)	0.185	2.58(2)	0.199	2.666(8)	0.171	2.609(8)	0.189
A(m)-0(7)	3.391(8)	0.058	3.204(12)	0.075	3.273(19)	0.068	3.19(2)	0.077	3.491(7)	0.051	3.231(9)	0.072
A(m)-0(7)	4.084(10)	0.025	4.104(12)	0.025	4.285(19)	0.020	4.10(2)	0.025	3.950(8)	0.029	4.261(9)	0.021
[12]	3.129	1.209	3.104	1.307	3.132	1.255	3.09	1.308	3.094	1.228	3.133	1.262
[8]	2.901	1.016	2.865	1.107	2.875	1.067	2.84	1.112	2.862	1.032	2.868	1.077
A(2)-0(5)x2	2.739(27)	0.106	2.945(11)	0.077	2.834(8)	0.091	2.83(3)	0.092	——		2.845(8)	0.090
A(2)-0(5)x2	3.388(30)	0.042	3.192(12)	0.055	3.285(8)	0.048	3.12(3)	0.060	——		3.177(8)	0.056
A(2)-0(6)x2	2.901(22)	0.083	2.978(11)	0.074	2.921(8)	0.080	3.03(2)	0.069	——		3.017(7)	0.070
A(2)-0(6)x2	3.441(27)	0.040	3.185(12)	0.055	3.295(8)	0.048	3.27(2)	0.049	——		3.294(7)	0.048
A(2)-0(7)x2	2.548(9)	0.144	2.460(7)	0.167	2.519(6)	0.151	2.486(4)	0.160	——		2.528(4)	0.149
A(2)-0(7)x2	3.756(9)	0.027	3.703(9)	0.029	3.785(8)	0.026	3.684(3)	0.030	——		3.744(4)	0.028
[12]	3.129	0.884	3.077	0.914	3.107	0.888	3.07	0.920			3.101	0.882
[10]	3.003	0.830	2.952	0.856	2.971	0.836	2.95	0.860			2.972	0.826

*bond strengths calculated for K occupancy of A(m) and Na occupancy of A(2)

our conclusion that K occupies the *A(m)* site whereas Na occupies the *A*(2) site. Table 12 shows the bond lengths and corresponding bond strengths for the *A(m)* and *A*(2) sites assuming K and Na occupancy, respectively. For the *A(m)* site, a coordination number of [8] generally leads to a fairly satisfactory bond-strength sum around the disordered K cation. However, for the *A*(2) site the bond-strength sums are significantly lower than ideal, although they are marginally higher than those calculated for Na occupancy of the *A*(2/*m*) site. Similar calculations for synthetic richterite (Table 13) do not show this deficiency in the bond-strength sum around the Na atom, either in the ordered or disordered positions. Although these results make it difficult to account for the observed positional disorder of Na in richterite (as there is virtually no difference between the bond-strength sums around the cation *or* the anions for each model), the better bond-strength sums suggest that Na might occupy the 8*j* position in natural amphiboles.

It has been shown by both X-ray (Papike *et al.* 1969; Hawthorne & Grundy 1973a) and neutron (Hawthorne & Grundy 1976) crystal-structure refinements and by polarized single-crystal infrared spectroscopy (Burns & Strens 1966) that the O(3)–H bond is orthogonal to the octahedral strip. Thus the H atom projects out into the cavity occupied by the *A*-site alkali-metal cations. Comparison of the principal infrared stretching frequencies of vacant *A*-site amphiboles and filled *A*-site amphiboles (Table

TABLE 13. A-SITE CATION-ANION DISTANCES (Å) AND BOND STRENGTHS IN RICHTERITE (CAMERON 1970).

A(1)-0(5)	2.706(20)	0.111	A-0(5) x4	2.866(5)	0.087
A(1)-0(5)	2.781(19)	0.099	A-0(6) x4	3.114(6)	0.061
A(1)-0(5)	3.024(20)	0.069	A-0(7) x2	2.413(9)	0.182
A(1)-0(5)	3.091(19)	0.063	A-0(7) x2	3.684(10)	0.030
A(1)-0(6)	2.675(18)	0.117	[12]	3.010	1.016
A(1)-0(6)	3.332(18)	0.046	[10]	2.875	0.956
A(1)-0(6)	2.964(19)	0.075			
A(1)-0(6)	3.568(17)	0.034			
A(1)-0(7)	2.375(18)	0.195	Central A-site		
A(1)-0(7)	2.560(16)	0.141			
A(1)-0(7)	3.274(16)	0.049	Σ0(5)* = 0.348		
A(1)-0(7)	3.097(17)	0.019	Σ0(6) = 0.244		
[12]	3.307	1.018	Σ0(7) = 0.424 (0.364)**		
[11]	2.941	0.999	Split A-site		
[10]	2.878	0.965	Σ0(5) = 0.342		
			Σ0(6) = 0.272 (0.238)		
			Σ0(7) = 0.404 (0.385)		

* indicates the bond strengths contributed by the A-site cation to the bridging oxygens of the silicate chain.

**values in parentheses indicate sums calculated for coordination number of [10] .

TABLE 14. HYDROGEN-A-SITE DISTANCES IN TREMOLITE, AND PRINCIPAL OH STRETCHING FREQUENCIES FOR AN (MgMgMg)-OH- □ /A CONFIGURATION IN CLINO-AMPHIBOLES

Bond	A-site coordinates			Bond length
H-A(m)	0.4550	0	1.8973	2.35(4)Å
H-A(m)'	0.5450	0	1.1027	3.35(4)
H-A(2)	½	0.0103	1	2.833(7)
H-A(2/m)	½	0	1	2.827(6)
	Vacant A-site amphiboles			
Tremolite	3685 cm^{-1}		Hawthorne & Grundy (1976)	
Hornblende	3672		Wilkins et al. (1970)	
Crocidolite	3668		Addison & White (1968)	
Glaucophane	3665		Bancroft & Burns (1969)	
	Filled A-site amphiboles			
Na richterite	3727		Rowbotham & Farmer (1973)	
K richterite	3734			

14) indicates that there is some interaction between the hydrogen atom and the alkali-metal cation at the *A* site. Table 14 shows the interatomic distances between hydrogen and the various *A* sites, taken from the neutron refinement of tremolite (Hawthorne & Grundy 1976). Comparison of Table 5 with Table 14 shows that most of the cation–H distances are shorter than most of the cation–O distances. In this specific amphibole, the H position is only partly occupied and the close approach of the alkali-metal cation and H need not necessarily occur as occupancy of the *A* site could be associated with the occupancy of the O(3) position by F. However, in amphiboles with a fully occupied H position, some of the configurations of Table 14 must occur. Baur (1973) has considered possible interaction of H with alkali-metal cations in a series of Tutton's salts, $CuM_2^+(SO_4)_2 \cdot 6H_2O$ ($M^+ = K,NH_4,Cs$). On the basis of the sums of the *atomic* radii (Slater 1965), he concludes that similar M^+–O and M^+–H distances do not necessarily imply bonding between M^+ and H. However, it should be pointed out that the sum of the Slater radii are considerably less than the observed interatomic distances in the alkali-metal hydrides. For NaH and KH, the bond lengths are 2.44 and 2.85Å, respectively. Comparison of these distances with those listed in Table 14 suggests that only one of the configurations *A(m)* [x=0.445, y=0, z=0.897] –H=2.35(4)Å would lead to a hydride bond. If the *C*2/*m* symmetry of the bulk crystal is to be maintained, both *A(m)* positions must be occupied equally. This suggests that in a potassic hydroxy-amphibole, the H may be positionally disordered to avoid the formation of a hydride bond with half of the K atoms.

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