

THE CRYSTAL CHEMISTRY OF THE AMPHIBOLES: V. THE STRUCTURE AND CHEMISTRY OF ARFVEDSONITE

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ABSTRACT

The crystal structure of an arfvedsonite of composition $(K_{0.71}Na_{0.29})(Na_{1.84}Ca_{0.16})(Fe^{2+}_{3.80}Mg_{0.11}Mn_{0.13}Fe^{3+}_{0.92}Ti_{0.09}Al_{0.15})(Si_{7.83}Al_{0.17})O_{22}(OH,F,O)_2$ from the Red Wine alkaline complex, Labrador has been determined by least-squares refinement of three-dimensional counter-diffractometer X-ray data (R -factor 4.7% for 1193 observed reflections). The space group is $C2/m$, a 10.007(2), b 18.077(2), c 5.332(1)Å, β 104.101(7)°, $V=935.48\text{Å}^3$, $Z=2$.

Constrained refinement of the octahedral site-populations indicates that the small amount of Mg present is ordered into $M(1)$. A consideration of mean bond lengths shows that the small trivalent cations are ordered into the $M(2)$ site as found for other monoclinic amphiboles. The atoms occupying the A -site show positional disorder in the mirror plane, suggesting that in the absence of tetrahedral Al, the occupancy of $M(4)$ by Na is not related to the occurrence of A -site atom disorder along the two-fold axis.

Examination of the cell contents of amphiboles of the eckermannite-arfvedsonite and magnesioctaphorite-cataphorite groups shows that the sum of the conventionally accepted Y -type cations is generally less than 5.0, and of the amphibole analyses examined, only 10% are satisfactory according to generally accepted criteria (Papike *et al.* 1974). The deviations from the ideal Y -group sum of 5.0 are inversely correlated with the X -group sum, suggesting occupancy of the Y -sites- $M(1)$, $M(2)$ and $M(3)$ -by the X -type cations. If Ca is included as a Y -type cation, 70% of the analyses may be considered as satisfactory. Therefore, either the majority of sodic amphibole analyses are subject to a systematic error of little significance in calcic and subcalcic amphiboles, or Ca can substitute into the octahedral sites in sodic amphiboles.

SOMMAIRE

La structure cristalline d'un arfvedsonite ayant une composition $(K_{0.71}Na_{0.29})(Na_{1.84}Ca_{0.16})(Fe^{2+}_{3.80}Mg_{0.11}Mn_{0.13}Fe^{3+}_{0.92}Ti_{0.09}Al_{0.15})(Si_{7.83}Al_{0.17})O_{22}(OH,F,O)_2$ et provenant du complexe alcalin Red Wine, au Labrador a été déterminée par affinement moindres carrés des données tridimensionnelles obtenues par diffraction des rayons-X sur diffractomètre à compteur (l'indice $R = 4.7\%$ pour 1193 réflexions observées). Le groupe spatial est $C2/m$, a 10.007(2), b 18.077(2), c 5.332(1)Å, β 104.101(7)°, $V=935.48\text{Å}^3$, $Z=2$. L'affinement avec contrainte des populations-sites octaédriques indique que la petite

quantité de Mg présente est ordonnée dans $M(1)$. Les longueurs moyennes de liaison démontrent que les trois petits cations trivalents sont ordonnés dans le site ($M2$) de la même façon que pour les autres amphiboles monocliniques. Les atomes du site- A démontrent un désordre de position dans le plan à miroir; ceci suggère qu'en l'absence du Al tétraédrique, il n'y a aucun rapport entre l'occupation de $M(4)$ par Na et l'occurrence d'un désordre atomique du site- A le long de l'axe de l'ordre 2. L'examen des compositions d'amphiboles des groupes eckermannite-arfvedsonite et magnesioctaphorite-cataphorite démontre que la somme des cations de type- Y est habituellement moins que 5.0; seulement 10% des analyses d'amphiboles examinées sont satisfaisantes selon la norme habituellement acceptée (Papike *et al.* 1974). Les déviations de la somme 5.0 en cations Y sont inversement reliées à la somme du groupe- X , ce qui laisse supposer l'occupation des sites- Y , $M(1)$, $M(2)$ et $M(3)$, par les cations de type- X . Si le Ca est inclus comme cation de type- Y , alors 70% des analyses peuvent être considérées satisfaisantes. Donc, soit que la majorité des analyses d'amphiboles sodiques est en erreur sur ce point, ce qui a aucune conséquence pour les amphiboles calciques et sub-calciques, ou le Ca peut peupler les sites octaédriques dans les amphiboles sodiques.

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INTRODUCTION

Arfvedsonite is a sodic iron amphibole typically found in alkaline plutonic rocks. It is particularly common in aegaitic associations as a product of late-stage crystallization, and as a major ferromagnesian phase in alkali granites (e.g. Borley 1963). The ideal formula, $Na_2(Fe^{2+},Mg)_4(Fe^{3+},Al)Si_8O_{22}(OH,F)_2$ proposed by Sundius (1945) corresponds more closely to most analyses than the formula $Na_2Ca_{0.5}(Fe^{2+},Mg)_{3.5}Fe^{3+}_{1.5}(Si_{7.5}Al_{0.5})O_{22}(OH,F)_2$ proposed by Miyashiro (1957). The A -site is generally fully occupied by (Na+K) and although substitution of some Ca into the $M(4)$ site together with additional octahedral (Fe^{3+},Al) and tetrahedral Al is common, the formula of Sundius must be considered as more appropriate. It is also more advantageous from a crystal-chemical viewpoint as it does correspond to an in-

tegral point (012) in the charge distribution space of Whittaker (1968).

A two-dimensional refinement of an arfvedsonite from Tunngdliarfik, Greenland (Kawahara 1963) confirmed its general similarity with crocidolite (Whittaker 1949) despite the apparent *c*-glide extinctions in the diffraction pattern. However, this result contradicts the conclusions of Singh & Bonardi (1972), based on their interpretation of the Mössbauer spectrum of an arfvedsonite from Joan Lake, Labrador. They suggest that the *M*(2) atoms may have local *O_h* symmetry, whereas in the crocidolite structure, the *M*(2) octahedron is the most distorted of the octahedra.

In this regard, the occurrence of local *O_h* symmetry around the *M*(2) site is completely incompatible with local bond strength requirements. The structure of arfvedsonite is refined here to present a precise characterization of the structure.

EXPERIMENTAL

The arfvedsonite used in this study is from an amphibole-aenigmatite-nepheline agpaitite in the Red Wine Complex, Labrador (Curtis *et al.* 1974a,b,c.). Electron microprobe analyses (L. W. Curtis, pers. comm.) indicate very little chemical variation; the mean analysis and the results of a wet-chemical analysis of a hand-picked separate are given in Table 1. The Fe³⁺/Fe⁺² ratios for the two independent determinations are virtually identical and agree with that determined by Mössbauer spectroscopy (unpublished work). The cell contents were calculated on the basis of 24(O,OH,F) from the mean of the two analyses; for the refinement, the occupancies of the octahedral and *A*-sites were normalized to integral values.

Long-exposure single-crystal precession photographs displayed diffraction symmetry 2/*mC*-/-, consistent with the space group *C2/m* exhibited by all other sodic clino-amphiboles; no streaking or subsidiary maxima occurred. Cell dimensions determined by least-squares refinement of 15 reflections aligned automatically on a 4-circle diffractometer are presented in Table 1, together with other information pertinent to the refinement.

A regular cleavage fragment of dimensions 0.041 × 0.062 × 0.157 mm was used to collect the intensity data. The crystal was mounted on a Syntex PI automatic diffractometer operating in the θ -2 θ scan mode with variable rates from 2.0–24.0°/min., depending on the peak count through an angle of 2° and the α_1 - α_2 separation. Graphite-monochromatized MoK α radiation ($\lambda=0.71069\text{\AA}$) was used, and background

TABLE 1. CRYSTAL DATA FOR ARFVEDSONITE

	Micro-probe*	Wet Chem.	Mean Anal.	Unit cell contents, based on 24(O,OH,F)	Unit Cell Contents used in refinement	
SiO ₂	48.78	49.20	48.99	Si	7.830	7.830
Al ₂ O ₃	1.61	1.70	1.66	Al ^{IV}	0.170	0.170
TiO ₂	0.58	0.96	0.77	Tetrahedral Σ	8.000	8.000
FeO	26.47	26.64	26.56	Al ^{VI}	0.143	0.145
Fe ₂ O ₃	7.53	7.50	7.52	Ti	0.093	0.094
MnO	0.89	0.98	0.94	Fe ²⁺	3.550	3.604
MgO	0.49	0.40	0.45	Fe ³⁺	0.905	0.919
CaO	0.95	0.90	0.93	Mn	0.127	0.129
Na ₂ O	6.66	7.22	6.94	Mg	0.107	0.109
K ₂ O	3.95	3.39	3.67	Octahedral Σ	4.925	5.000
H ₂ O	-	1.64	1.64	Ca	0.159	0.159
F	0.21	-	0.21	Na ^{M(4)}	1.861	1.841
Σ , wt %	97.21	100.53	100.29	<i>M</i> (4) Σ	2.000	2.000
			-0.11	Na ^A	0.310	0.293
			100.18	K	0.748	0.707
				<i>A</i> site Σ	1.058	1.000

$$a = 10.007(2)\text{\AA}$$

$$b = 18.077(2)\text{\AA}$$

$$c = 5.332(1)\text{\AA}$$

$$\beta = 104.101(7)^\circ$$

$$V(\text{\AA}^3) = 935.48\text{\AA}^3$$

Space Group *C2/m*

$$Z = 2$$

$$\text{Temperature factor form used: } \exp \left[-\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij} \right]$$

$$R^w = \left(\frac{\sum (|F_{\text{obs}}| - |F_{\text{calc}}|)}{\sum |F_{\text{obs}}|} \right) / \Sigma |F_{\text{obs}}|$$

$$R_w = \left[\frac{\sum w (|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{\sum w F_{\text{obs}}^2} \right]^{1/2}, w=1$$

* Electron microprobe analysis by L.W. Curtis, University of Toronto

counts were made at the beginning and end of each scan. Two standard reflections were monitored every 50 reflections; no significant change in their intensities was observed during the data collection. A total of 1567 reflections was measured in one asymmetric unit out to a 2 θ of 65°. The data were corrected for absorption (for polyhedral crystal shape), Lorentz, polarization and background effects. A reflection was considered as observed if its magnitude was greater than four standard deviations based on counting statistics. Application of this criterion resulted in 1193 observed reflections.

REFINEMENT

Scattering curves for neutral atoms were taken from Cromer & Mann (1968) together with anomalous dispersion coefficients from Cromer & Lieberman (1970). The final atomic coordinates and equivalent isotropic temperature factors of ferrotschermakite (Hawthorne & Grundy 1973a) were used as initial input to the least-squares program RFINE (Finger 1969); initial site-populations of the octahedral sites were assumed to be completely disordered. Several cycles of full-matrix least-squares refinement gradually increasing the number of variables resulted in convergence at an *R*-factor

of 7.3%. As with previous refinements of clin amphiboles (Papike *et al.* 1969; Hawthorne & Grundy 1972, 1973a,b; Robinson *et al.* 1973), the A-site temperature factor was anomalously large (5.7\AA^2) at this stage. The A-site atoms were positionally disordered in the mirror plane and along the twofold axis, using the refined parameters for aluminohastingsite (Hawthorne & Grundy 1975). One cycle of least-squares varying the positional parameters and site-populations of the A(2) and A(m) sites together with all other variables reduced the R-factor from 7.3% to 5.8% and the R_w -factor from 7.6% to 5.9%; this improvement is significant at the 0.005 level (Hamilton 1965). The site-occupancy of the A(2) site was zero within two standard deviations, and this site was removed from the refinement. Except for the A(m) atoms, temperature factors were converted to anisotropic and a correction for isotropic extinction (Zachariassen 1968) was introduced into the refinement. Full-matrix refinement of all variables resulted in convergence at R-factors of 4.7% (observed) and 7.0% (all data) and R_w -factors of 4.8% (observed) and 6.9% (all data). Observed and

TABLE 3. FINAL ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR ARFVEDSONITE

Site	x	y	z	B _{equiv.}
0(1)	0.1096(3)	0.0914(2)	0.2082(7)	0.72(5)
0(2)	0.1201(4)	0.1731(2)	0.7332(7)	0.89(5)
0(3)	0.1074(5)	0	0.7067(9)	0.74(7)
0(4)	0.3643(4)	0.2473(2)	0.7984(7)	0.91(5)
0(5)	0.3440(4)	0.1273(2)	0.0827(7)	0.74(5)
0(6)	0.3363(4)	0.1172(2)	0.5841(7)	0.82(5)
0(7)	0.3262(6)	0	0.2988(10)	0.95(7)
T(1)	0.2738(1)	0.08618(7)	0.2917(3)	0.46(2)
T(2)	0.2864(1)	0.17104(7)	0.8018(2)	0.48(2)
M(1)	0	0.09205(5)	½	0.66(2)
M(2)	0	0.18443(5)	0	0.60(2)
M(3)	0	0	0	0.65(3)
M(4)	0	0.2779(2)	½	1.23(5)*
A(m)	0.0172(5)	½	0.0402(9)	1.28(8)*

* anisotropic temperature factors were not refined for the A-site atoms.

TABLE 4. ANISOTROPIC TEMPERATURE FACTOR COEFFICIENTS FOR ARFVEDSONITE

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
0(1)	146(30)	73(9)	611(97)	2(12)	83(45)	-11(25)
0(2)	254(33)	63(9)	829(116)	8(14)	101(48)	27(26)
0(3)	202(45)	63(13)	585(160)	0	79(68)	0
0(4)	338(34)	58(9)	747(115)	-45(14)	223(49)	-16(25)
0(5)	207(32)	70(9)	610(106)	-3(12)	208(45)	77(25)
0(6)	293(34)	65(9)	467(98)	3(12)	96(46)	-78(24)
0(7)	311(49)	33(12)	1241(179)	0	227(74)	0
T(1)	145(11)	35(3)	374(38)	-3(4)	79(16)	13(9)
T(2)	162(11)	36(3)	367(37)	-10(5)	79(16)	0(9)
M(1)	210(9)	52(3)	508(31)	0	128(12)	0
M(2)	188(9)	42(3)	546(32)	0	88(13)	0
M(3)	231(16)	42(4)	501(53)	0	87(21)	0
M(4)	382(30)	86(8)	1267(98)	0	411(44)	0

* $\beta_{ij} \times 10^5$

TABLE 5. SELECTED CATION-ANION DISTANCES IN ARFVEDSONITE

Atoms	Bond Multiplicity	Distance	Atoms	Bond Multiplicity	Distance
T(1) Tetrahedron					
T(1)-0(1)	1	1.598(4)Å	T(2)-0(2)	1	1.615(4)Å
T(1)-0(5)	1	1.634(4)	T(2)-0(4)	1	1.585(4)
T(1)-0(6)	1	1.632(4)	T(2)-0(5)	1	1.667(4)
T(1)-0(7)	1	1.641(2)	T(2)-0(6)	1	1.680(4)
Mean T(1)-0		1.626	Mean T(2)-0		1.637
M(1) Octahedron					
M(1)-0(1)	2	2.110(3)	M(3)-0(1)	4	2.138(4)
M(1)-0(2)	2	2.100(4)	M(3)-0(3)	2	2.103(5)
M(1)-0(3)	2	2.136(3)	Mean M(3)-0		2.126
Mean M(1)-0		2.115	M(3) Octahedron		
M(2) Octahedron					
M(2)-0(1)	2	2.161(4)	M(4)-0(2)	2	2.419(4)
M(2)-0(2)	2	2.084(4)	M(4)-0(4)	2	2.374(4)
M(2)-0(4)	2	1.953(4)	M(4)-0(5)	2	2.937(4)
Mean M(2)-0		2.066	M(4)-0(6)	2	2.614(4)
A(m) Polyhedron					
A(m)-0(5)	2	2.846(5)	Mean M(4)-0		2.586
A(m)-0(5)	2	2.923(5)	M(4) Polyhedron		
A(m)-0(6)	2	3.037(5)	M(4)-0(2)	2	2.419(4)
A(m)-0(6)	2	3.397(5)	M(4)-0(4)	2	2.374(4)
A(m)-0(7)	1	2.616(8)	M(4)-0(5)	2	2.937(4)
A(m)-0(7)	1	2.666(8)	M(4)-0(6)	2	2.614(4)
A(m)-0(7)	1	3.491(7)	Mean M(4)-0		2.586
A(m)-0(7)	1	3.950(8)	Conventional A-Site		
Mean for 12		3.094	A-0(5)	4	2.755(3)
Mean for 8		2.862	A-0(6)	4	3.212(3)
T(1)-T(2)					
T(1)-T(2) through 0(6)		3.098(2)	A-0(7)	2	2.629(2)
T(1)-T(2) through 0(5)		3.059(2)	A-0(7)	2	3.720(2)
T(1)-T(1) across mirror		3.116(2)	Mean for 12		3.047
M-M					
Miscellaneous					
M(1)-M(1)		3.328(2)	A(m)-A(m')		3.428(5)
M(1)-M(2)		3.146(1)	A(m)-T(1)		3.650(3)
M(1)-M(3)		3.143(1)	A(m)-T(2)		
M(1)-M(4)		3.360(3)			
M(2)-M(3)		3.534(1)			
M(2)-M(4)		4.157(2)			

TABLE 6. POLYHEDRAL EDGE LENGTHS FOR ARFVEDSONITE

T(1) Tetrahedron		T(2) Tetrahedron	
0(1)-0(5)	2.672(5)Å	0(2)-0(4)	2.734(5)Å
0(1)-0(6)	2.677(5)	0(2)-0(5)	2.673(5)
0(1)-0(7)	2.675(5)	0(2)-0(6)	2.687(5)
0(5)-0(6)	2.700(5)	0(4)-0(5)	2.681(5)
0(5)-0(7)	2.600(4)	0(4)-0(6)	2.598(5)
0(6)-0(7)	2.596(5)	0(5)-0(6)	2.647(5)
Mean 0-0	2.653	Mean 0-0	2.669
M(1) Octahedron		M(3) Octahedron	
0(1 ^u)-0(2 ^d)	2.813(5)	0(1 ^u)-0(1 ^d)	2.714(7)
0(1 ^u)-0(2 ^u)	3.114(5)	0(1 ^u)-0(1 ^u)	3.305(7)
0(1 ^u)-0(3 ^d)	2.852(5)	0(1 ^u)-0(3 ^d)	2.852(5)
0(1 ^u)-0(3 ^u)	3.134(6)	0(1 ^u)-0(3 ^u)	3.139(6)
0(2)-0(2)	3.009(7)		
0(2)-0(3)	3.134(4)	Mean 0-0	3.000
0(3)-0(3)	2.678(9)	M(4) Polyhedron	
Mean 0-0	2.982	0(2)-0(2)	3.009(7)
M(2) Octahedron		0(2 ^u)-0(4 ^u)	3.217(5)
0(1 ^u)-0(1)	2.714(7)	0(2 ^u)-0(4 ^d)	3.030(5)
0(1 ^u)-0(2 ^d)	2.813(5)	0(2 ^u)-0(5 ^u)	3.733(5)
0(1 ^u)-0(2 ^u)	2.956(5)	0(4 ^u)-0(5 ^d)	3.567(5)
0(1 ^u)-0(4)	2.929(5)	0(4 ^u)-0(6 ^u)	2.598(5)
0(2 ^u)-0(4 ^d)	3.030(5)	0(5 ^u)-0(6 ^u)	2.700(5)
0(2 ^u)-0(4 ^u)	2.854(5)	0(5 ^u)-0(6 ^d)	3.264(5)
0(4)-0(4)	3.025(7)	0(6 ^u)-0(6 ^d)	3.602(7)
Mean 0-0	2.909	Mean 0-0	3.177

TABLE 7. SELECTED INTERATOMIC ANGLES IN ARFVEDSONITE

Atoms	Angle	Atoms	Angle
T(1) Tetrahedron		T(2) Tetrahedron	
O(1)-T(1)-O(5)	111.5(2)	O(2)-T(2)-O(4)	117.4(2) ^o
O(1)-T(1)-O(6)	112.0(2)	O(2)-T(2)-O(5)	109.0(2)
O(1)-T(1)-O(7)	111.3(2)	O(2)-T(2)-O(6)	108.7(2)
O(5)-T(1)-O(6)	111.5(2)	O(4)-T(2)-O(5)	111.0(2)
O(5)-T(1)-O(7)	105.1(2)	O(4)-T(2)-O(6)	105.4(2)
O(6)-T(1)-O(7)	105.0(2)	O(5)-T(2)-O(6)	104.5(2)
Mean O-T(1)-O	109.4	Mean O-T(2)-O	109.3
M(1) Octahedron		M(3) Octahedron	
O(1 ^U)-M(1)-O(2 ^d)	83.8(1)	O(1 ^U)-M(3)-O(1 ^d)	78.8(2)
O(1 ^U)-M(1)-O(2 ^U)	96.6(1)	O(1 ^U)-M(3)-O(1 ^U)	101.2(2)
O(1 ^U)-M(1)-O(3 ^U)	84.4(2)	O(1 ^U)-M(3)-O(3 ^d)	84.5(1)
O(1 ^U)-M(1)-O(3 ^U)	95.1(2)	O(1 ^U)-M(3)-O(3 ^U)	95.5(1)
O(2)-M(1)-O(2)	91.5(2)	Mean O-M(3)-O	90.0
O(2)-M(1)-O(3)	95.4(1)	M(4) Polyhedron	
O(3)-M(1)-O(3)	77.7(2)	O(2)-M(4)-O(2)	76.9(2)
Mean O-M(1)-O	90.0	O(2 ^U)-M(4)-O(4)	78.4(1)
M(2) Octahedron		O(2 ^U)-M(4)-O(4 ^U)	84.3(1)
O(1)-M(2)-O(1)	77.8(2)	O(2 ^U)-M(4)-O(5 ^U)	87.8(1)
O(1 ^U)-M(2)-O(2 ^d)	83.0(1)	O(4 ^U)-M(4)-O(5 ^U)	83.6(1)
O(1 ^U)-M(2)-O(2 ^U)	88.3(1)	O(4 ^U)-M(4)-O(6 ^U)	62.6(1)
O(1)-M(2)-O(4)	90.7(2)	O(5 ^U)-M(4)-O(6 ^U)	71.8(1)
O(2 ^U)-M(2)-O(4 ^U)	97.2(2)	O(5 ^U)-M(4)-O(6 ^U)	57.8(1)
O(2 ^U)-M(2)-O(4 ^U)	89.9(2)	O(6)-M(4)-O(6)	87.1(2)
O(4)-M(2)-O(4)	101.5(2)	Mean O-M(4)-O	76.0
Mean O-M(2)-O	89.8	Tetrahedral Chain	
A-Site		T(1)-O(5)-T(2)	135.8(2)
O(7)-O(7)-O(7)	69.0(1)	T(1)-O(6)-T(2)	138.6(2)
Δ* = 0.233		T(1)-O(7)-T(1)	143.4(3)
		O(5)-O(6)-O(5)	171.5(2)
		O(5)-O(7)-O(6)	170.2(3)

$$*_{\Lambda} = \left[90^{\circ} - \Delta \cdot O(7)-O(7)-O(7) \right] / 90^{\circ}$$

calculated structure factors are given in Table 2*. Final atomic positions and equivalent isotropic temperature factors are presented in Table 3, and the final anisotropic temperature factors are presented in Table 4. Interatomic distances and angles were calculated with the program ERRORS (L. W. Finger, pers. comm.) and are presented in Tables 5, 6, and 7. The magnitudes and orientations of the principal axes of the thermal ellipsoids were calculated with ERRORS and are presented in Table 8.

Site populations

According to the chemical analysis, a small amount of aluminium occurs in the tetrahedra of the chains. It has been shown (Papike *et al.* 1969; Hawthorne 1973; Robinson *et al.* 1973) that the mean tetrahedral bond lengths in the amphiboles are sensitive to the aluminium occupancy of the tetrahedra. Of the three methods of estimating the tetrahedral aluminium occupancies proposed by Papike *et al.* (1969), the second method appeared to give the most consistent results for the small amount of data

TABLE 8. MAGNITUDES AND ORIENTATIONS OF THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS IN ARFVEDSONITE

Atom	R.M.S. Displacement	Angle to a-axis	Angle to b-axis	Angle to c-axis
O(1)	0.082(9) ^Å	6(40) ^o	94(13) ^o	109(45) ^o
	0.091(8)	96(45)	97(17)	159(42)
	0.111(7)	87(12)	8(16)	98(17)
O(2)	0.097(8)	82(24)	144(24)	59(26)
	0.110(7)	68(267)*	120(103)	149(26)
	0.111(7)	23(252)	71(143)	90(231)
O(3)	0.089(12)	93(54)	90	11(54)
	0.099(11)	177(54)	90	79(54)
	0.102(10)	90	0	90
O(4)	0.084(9)	123(7)	136(25)	58(31)
	0.096(8)	84(19)	123(28)	146(30)
	0.135(6)	34(6)	114(7)	81(7)
O(5)	0.058(11)	126(9)	114(7)	34(6)
	0.103(7)	132(10)	62(18)	100(13)
	0.119(7)	80(16)	39(16)	58(7)
O(6)	0.063(11)	98(6)	60(7)	30(7)
	0.112(7)	109(39)	38(24)	115(14)
	0.120(7)	21(36)	69(33)	106(18)
O(7)	0.074(13)	90	0	90
	0.114(10)	25(24)	90	129(24)
	0.133(9)	65(24)	90	39(24)
T(1)	0.066(4)	112(9)	117(13)	29(13)
	0.078(4)	88(26)	151(15)	118(13)
	0.084(3)	22(9)	98(25)	84(15)
T(2)	0.068(4)	110(9)	103(20)	15(22)
	0.075(4)	108(12)	153(14)	105(22)
	0.090(3)	27(8)	113(10)	89(7)
M(1)	0.080(3)	115(4)	90	10(4)
	0.094(2)	90	0	90
	0.102(2)	25(4)	90	80(4)
M(2)	0.083(3)	90	0	90
	0.085(3)	69(14)	90	173(14)
	0.092(2)	22(14)	90	83(14)
M(3)	0.082(4)	98(7)	90	7(7)
	0.083(4)	90	0	90
	0.105(4)	8(7)	90	97(7)
M(4)	0.098(6)	140(5)	90	36(5)
	0.120(6)	90	0	90
	0.150(5)	50(5)	90	54(5)

*The large standard deviations indicate virtual indeterminacy of the axis orientation.

available at that time. This method of assigning tetrahedral aluminium depends on the individual mean tetrahedral bond lengths, and the curves of Robinson *et al.* (1973) and Hawthorne (1973) are essentially refined versions of this scheme utilizing a larger data set. Whereas the curves of Robinson *et al.* (1973) were derived from data on 5 amphiboles and 4 pyroxenes, the curves of Hawthorne (1973) were derived from data on 10 amphiboles showing the maximum range of tetrahedral aluminium known ($Al^{IV} = 0.0-2.73$ atoms per formula unit), and for this reason the curves of Hawthorne (1973) are used here. However, none of the relationships between mean tetrahedral bond lengths and aluminium occupancy is completely satisfactory. It

*Table 2 may be obtained from: Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ontario, Canada.

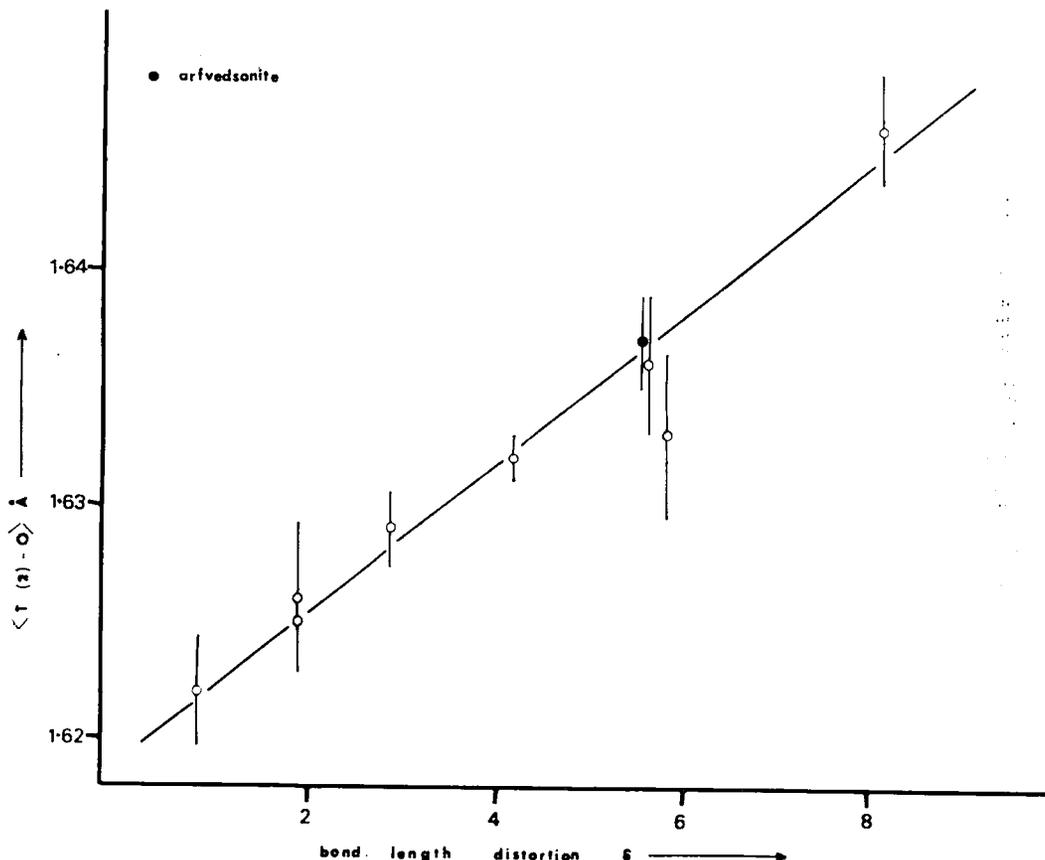


FIG. 1. The variation in mean bond length of the $T(2)$ site with tetrahedral bond length distortion for the non- Al^{IV} amphiboles. Arfvedsonite is indicated by the solid circle.

has been shown by Mitchell *et al.* (1970, 1971) and Hawthorne (1973) that the magnitudes of the deviations of the individual bond lengths from their mean value affect the mean tetrahedral bond lengths in the non-aluminous amphiboles. Although the $\langle T(2)-O \rangle$ bond length in arfvedsonite (Table 5) is larger than that expected for complete Si occupancy (1.632 Å) as derived from the curves of Hawthorne (1973), inspection of the individual bond lengths shows that this site is also more distorted than in those amphiboles from which the determinative curves were derived. Figure 1 shows the variation in $\langle T(2)-O \rangle$ with tetrahedral bond length distortion Δ^* for the non- Al^{IV} amphiboles; this suggests that the larger $\langle T(2)-O \rangle$ bond length in arfvedsonite is caused by bond length distortion, and is thus compatible with complete Si

occupancy. This would indicate that the small amount of tetrahedral aluminium present resides at the $T(1)$ site. In contrast to the $T(2)$ tetrahedron, the bond length distortion of the $T(1)$ site is similar to those distortions exhibited by the amphiboles used to derive the predictive curves of Hawthorne (1973), and hence this curve should be applicable to arfvedsonite. An occupancy of 0.04 Al at $T(1)$ is forecast from this curve, in complete agreement with the amount of tetrahedral aluminium derived from the chemical analysis and the above conclusion that $T(2)$ is completely occupied by silicon.

In the final stages of the refinement, Ti and octahedral Al were assigned to $M(2)$ and the occupancies Fe^* ($=Fe^{2+}+Fe^{3+}+Mn$) and Mg were refined over the $M(1)$, $M(2)$ and $M(3)$ sites. Slight negative occupancies of Mg were observed at the $M(1)$ and $M(2)$ sites; however, these were within one standard deviation (0.006) of zero, and consequently the Mg occupancies from $M(1)$ and $M(2)$ were set equal to zero for the final cycle of refinement. Complete occupancies were assigned from the re-

$$\Delta^* = \frac{1}{4} \sum_{i=1}^4 (l_o - l_i)^2 / l_o^2, \text{ where } l_i = \text{individual bond length and}$$

$$l_o = \frac{1}{4} \sum_{i=1}^4 l_i$$

finement results together with a consideration of mean bond length criteria. The $\langle M(2)-O \rangle$ bond length is considerably shorter than the $\langle M(1)-O \rangle$ and $\langle M(3)-O \rangle$ bond lengths, indicating that the smaller trivalent cations are ordered into this site. If all aluminium, titanium and ferric iron are considered as occupying $M(2)$, the predictive equations of Hawthorne (1973) forecast a $\langle M(2)-O \rangle$ bond length of 2.066 Å, in exact agreement with the experimental result; this is taken as an indication that the above ordering pattern is complete. With respect to the $M(1)$ and $M(3)$ sites, it is known from the refinement results that the Mg occupies the $M(3)$ site, and thus it is necessary only to derive the Fe^{2+}/Mn occupancies from bond length criteria. Using the mean bond length—ionic radii curves of Hawthorne (1973), the minimum deviation between observed and calculated mean bond lengths occurs for complete Mn ordering into $M(3)$: $\langle M(1)-O \rangle$, calc = 2.126(12) Å, obs = 2.115(3) Å; $\langle M(3)-O \rangle$, calc = 2.130(12) Å, obs = 2.126(4) Å. Although the agreement for the $M(1)$ site is not exact, the deviation is within one root mean square deviation of the forecast result. In addition, the Mn site preference $M(3) > M(1) > M(2)$ conforms to that found recently for other amphiboles (Hawthorne 1973). Complete site-populations are presented in Table 9. Because the evidence suggesting complete Mn ordering into $M(3)$ is at best scanty, these site-populations should only be considered as tentative.

Polyhedral geometries and distortions

The variations in tetrahedral bond lengths are generally similar to those in other non- Al^{IV} amphiboles (Papike *et al.* 1969; Finger 1969; Papike & Clark 1968; Mitchell *et al.* 1970, 1971; Cameron 1970; Cameron & Gibbs 1971, 1973).

TABLE 9. SITE-POPULATIONS FOR ARFVEDSONITE

$T(1)$	0.96 Si + 0.04 Al
$T(2)$	1.00 Si
$M(1)^*$	1.00 Fe^{2+}
$M(2)^*$	0.460 Fe^{3+} + 0.420 Fe^{2+} + 0.073 Al + 0.047 Ti
$M(3)^*$	0.76 Fe^{2+} + 0.13 Mn + 0.11 Mg
$M(4)$	0.921 Na + 0.079 Ca
$A(m)$	0.293 Na + 0.707 K

* Site-occupancies for these sites in terms of Mg and Fe^{2+} ; Fe^{3+} ($=Fe^{2+}+Fe^{3+}+Mn$) were derived by constrained site-population refinement (final estimated standard deviation = 0.006) after assignment of octahedral Al and Ti to $M(2)$. Tetrahedral Al and octahedral Mn were assigned on the basis of observed bond lengths (see text).

It is apparent that the A -site cation has a significant effect on the bridging $T(1)-O$ bonds due to the decreased tetrahedral bond strength requirements of these anions. The $T(1)-O(7)$ bond is considerably longer in arfvedsonite than in the vacant A -site amphiboles where $T(1)-O(7) \sim 1.616$ Å, a feature that is also exhibited by richterite (Cameron 1970; Cameron & Gibbs 1971). Conversely, the $T(1)-O(5)$ and $T(1)-O(6)$ bond lengths are very similar to the corresponding bond lengths in the calcic (vacant A -site) amphiboles, and much longer than the corresponding bonds in glaucophane (where the $M(4)$ site is occupied by Na, as in arfvedsonite, but the A -site is vacant) due to the additional bond strength contributions to O(5) and O(6) from the A -site cation. The same feature is exhibited by the $T(2)$ tetrahedron, where the $T(2)-O(5)$ and $T(2)-O(6)$ are considerably longer than in glaucophane.

An empirical bond strength table was calculated for arfvedsonite (Table 10), using the curves of Brown & Shannon (1973). From an inspection of this Table, it is apparent that the bond strength requirements of the anions are the major cause of the bond length variation

TABLE 10. EMPIRICAL BOND STRENGTH* TABLE FOR ARFVEDSONITE

	M(1)	M(2)	M(3)	M(4)	A**	T(1)	T(2)	Σ
0(1)	0.374 $\frac{x^2}{4}$	0.336 $\frac{x^2}{4}$	0.347 $\frac{x^2}{4}$			1.084		2.141
0(2)	0.384 $\frac{x^2}{4}$	0.407 $\frac{x^2}{4}$		0.187 $\frac{x^2}{4}$			1.028	2.006
0(3)	0.350 $\frac{x^2}{4}$		0.380 $\frac{x^2}{4}$					1.080
0(4)		0.574 $\frac{x^2}{4}$		0.207 $\frac{x^2}{4}$			1.119	1.902
0(5)				(0.062 $\frac{x^2}{4}$)	0.107 $\frac{x^2}{4}$ 0.094 $\frac{x^2}{4}$	0.980	0.892	2.073 (2.135)
0(6)				0.120 $\frac{x^2}{4}$	0.077 $\frac{x^2}{4}$ (0.043 $\frac{x^2}{4}$)	0.985	0.861	2.043 (2.086)
0(7)					0.165 0.150	0.961 $\frac{x^2}{4}$		2.237
Σ	2.216	2.634	2.148	1.028 $\frac{[6]}{[8]}$ 1.152 $\frac{[8]}{[10]}$	0.871 $\frac{[8]}{[10]}$ 0.957 $\frac{[10]}{[10]}$	4.010	3.900	

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

** bond lengths used are for split-site model for the A -site.

TABLE 11. GENERALLY ACCEPTED SITE-OCCUPANCIES IN AMPHIBOLES

Group	Site	Occupancy
X	A	Na, K
	M(4)	Na, Ca, Mn, Fe ²⁺ , Mg
Y	M(1)	Mg, Fe ²⁺ , Mn, Al, Fe ³⁺ , Ti
	M(2)	
	M(3)	
Z	T(1)	Si, Al
	T(2)	

within individual polyhedra, with cation-cation repulsion and structural linkage requirements presumably having only a minor effect*. In this regard, the individual bond length variations are fairly similar to those exhibited by the richterites. In particular, $M(1)-O(2)$ is the shortest bond in the $M(1)$ octahedron in these amphiboles, contrasting strongly with tremolite-actinolite and glaucophane in which this bond is close to the mean $M(1)-O$ value and with the pargasites, ferrotschermakite and the ferromagnesian amphiboles where $M(1)-O(2)$ is the longest bond. It is apparent from Table 10 that this is the result of the variation in formal charge and bonding characteristics of the $M(2)$, $M(4)$ and $T(2)$ cations in these series of amphiboles. The same reasoning also accounts for the extreme variations in the $M(2)-O$ bond lengths in arfvedsonite, richterite and glaucophane. Substitution of monovalent cations into the $M(4)$ site decreases the bond strengths supplied to the $O(2)$ and $O(4)$ anions, leading to a shortening of the $M(2)-O(2)$ and $M(2)-O(4)$ bonds; this suggests that the bond length distortion, Δ , of the $M(2)$ site is strongly controlled by the monovalent cation occupancy of the $M(4)$ site. On the basis of their interpretation of the Mössbauer spectrum of an arfvedsonite, Singh & Bonardi (1972) suggest that the local symmetry around the $M(2)$ cation in arfvedsonite is O_h . This is completely incompatible with the results of the present study which shows the $M(2)$ octahedron to be very distorted. The most apparent difference between arfvedsonite and the other calcic and sodic amphiboles occurs in the $M(4)$ polyhedron. The $M(4)-O(5)$ bond is considerably longer in arfvedsonite than in the other calcic and sodic amphiboles and examination of Table 10 shows that this interaction is extremely weak. This relative lengthening of the $M(4)-O(5)$ and $M(4)-O(6)$ bonds occurs because of the additional bond strength supplied to these anions

*It should be noted that this situation contrasts with that extant in structures that are formally charge-balanced, where these factors play a major role in determining bond length variations and the anion bond strength requirements act solely as a constraint on the magnitude of their effect.

by the A-site cation, and has the effect of slightly straightening the tetrahedral double chain and promoting linkage between the octahedral and tetrahedral elements of the structure.

THE CHEMISTRY OF THE ECKERMANNITE-ARFVEDSONITE SERIES

In recent years, there has been much interest in the compositional variations in the minerals of the amphibole group. However, most of the work has centred on the calcic and sub-calcic amphiboles (Leake 1965a,b, 1968, 1971; Robinson *et al.* 1971; Kostyuk & Sobolev 1969; Saxena & Ekström 1970) and the only general work on the sodic amphiboles in recent years is that of Kovalenko (1968). During the course of this study, a casual inspection of arfvedsonite analyses in the literature indicated several features that did not agree with current ideas on the crystal chemistry of the amphiboles, and this prompted a more detailed investigation of the chemistry of this series. As this was hindered by a paucity of analyses, no criteria of acceptance were applied and all analyses were used; this point is of particular importance as it is the deviations from what is generally accepted to be a superior amphibole analysis (Phillips 1963; Papike *et al.* 1974) that are of interest in this series.

The general formula of the minerals of the amphibole group is conventionally written as $W_{0-1}X_2Y_3Z_6O_{22}(OH)_2$ (Deer *et al.* 1963). Table 11 shows the corresponding site-nomenclature and generally accepted scheme of cation site-occupancies (Papike *et al.* 1974). Of the three major groups of monoclinic amphiboles, the sodic amphiboles are the only ones to contain major amounts of Li. The cell contents of Li-bearing arfvedsonites (Borley 1963; Sundius 1946) suggest that Li occupies the octahedral sites and this is supported by spectroscopic (Addison & White 1968) and X-ray (Colville & Gibbs 1965) measurements; thus Li is considered as a Y-group cation in this study*. One condition inherent in the cation distribution scheme of Table 11 is that the sum of the Y-type cations is equal to or exceeds 5.0, and this has been used as a condition of a satisfactory amphibole analysis (Phillips 1963; Papike *et al.* 1974). Examination of sodic amphibole analyses from the literature shows that this condition is not satisfied in a large number of cases. Figure 2

*This contrasts with the situation in the orthorhombic amphiboles, where Li occupies the $M(4)$ site (Whittaker 1969; Gibbs 1969) and is thus an X-group cation.

is a frequency diagram for the formal *Y*-cation sums of the amphiboles examined in this study. Approximately 60% of the analyses have sums significantly less than 5.0, and the mean value for all analyses is 4.88. This situation was noted by Phillips (1963) with respect to individual analyses; he suggested that low *Y*-group totals were caused by compensating errors in the chemical analysis together with the occurrence of vacancies in the octahedral sites. On the basis of a bond strength criterion, the occurrence of vacancies on the octahedral sites is extremely improbable. With respect to the possibility of compensating errors, this always must be considered as a possibility; however, recalculation of an analysis assuming compensating-error corrections necessary to produce the ideal cation sums is merely an algebraic exercise, based only on the premise that the cation sums be equal to a specified value. Examination of the calcic and subcalcic amphiboles (Leake 1968) shows that the sum of the *Y*-group cations do tend to be ≥ 5.0 , in contrast to the situation extant in the sodic amphiboles as illustrated by Figure 2. If it is assumed that the result in Figure 2 is due to compensating errors in chem-

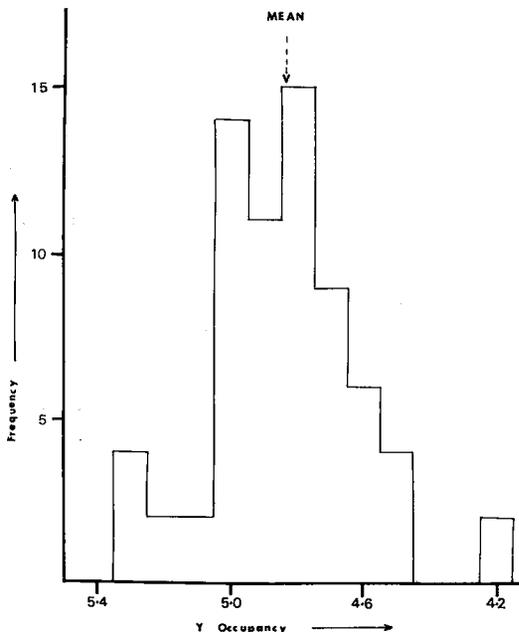


FIG. 2. Frequency diagram for the formal *Y*-cation sums in amphiboles of the eckermannite-arfvedsonite and magnesiocataphorite-cataphorite series.

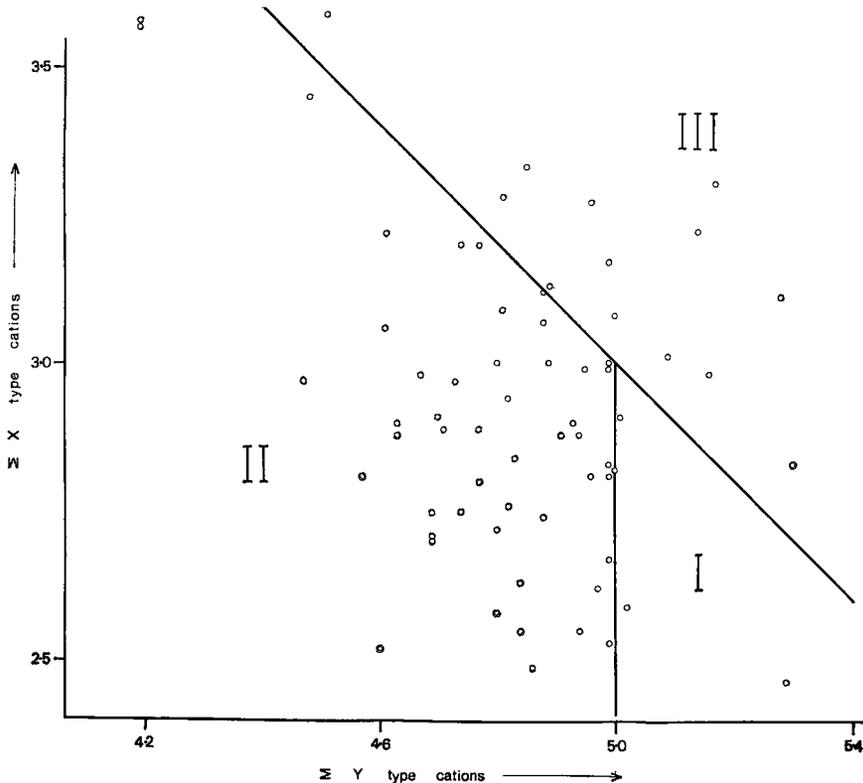


FIG. 3. The variation in conventional *X*-type cation sums with conventional *Y*-type cation sums in the alkali amphiboles with *X* 2.5. The various fields in the diagram are explained in the text.

ical analysis, we are forced to the additional observation that the quality of sodic amphibole analyses is systematically poorer than that of calcic, subcalcic and vacant *A*-site sodic amphiboles.

If it is considered that the occurrence of vacancies on the octahedral sites is unlikely, the only alternative is the substitution of large *X*-type cations (Na, Ca) into the octahedral sites. This possibility is examined in Figure 3 which shows the variation in *X*-cation sums with that of the *Y*-cation sums. This Figure may be divided into three areas; the area to the bottom right is the allowable field of alkali amphiboles if the large *X*-type cations (Ca, Na, K) are considered as being restricted to the *M*(4) and *A* sites; the area to the left is the allowable field for alkali amphiboles if the *X*-type cations are considered as allowable substitutions into the octahedral sites; the area to the top right is that part of the diagram completely forbidden to amphiboles as the total number of cations exceeds the number of crystallographic sites available in the amphibole structure. Only 10% of the available analyses fall into the allowable field, and several of these are analyses calcu-

lated on the basis of 23 oxygens because the water analyses were unavailable; it has been shown (Borg 1967) that the calculation of amphibole formulae on the basis of 23 oxygens produces cation sums that tend to the ideal values because of self-compensating errors, and thus the possibility exists that this small percentage could be even further decreased if it were possible to recalculate these analyses on the basis of 24(O,OH,F). Twenty percent of the analyses fall into the forbidden field and thus are presumably in error. The remaining 70% of the analyses lie in the field that would be allowed for amphiboles if the *X*-type cations substituted into the octahedral sites; if this substitution does not occur, the inevitable conclusion is that 90% of all sodic amphibole analyses are significantly in error. The latter is unlikely, and the alternative conclusion is that the large *X*-type cations do substitute into the octahedral sites. This feature of the chemistry of the eckermanite-arfvedsonite amphiboles was not apparent in the earlier work of Kovalenko (1968) as all the amphibole formulae were calculated on the basis of 13(*Y*+*Z*) cations, and not on 24(O,OH,F).

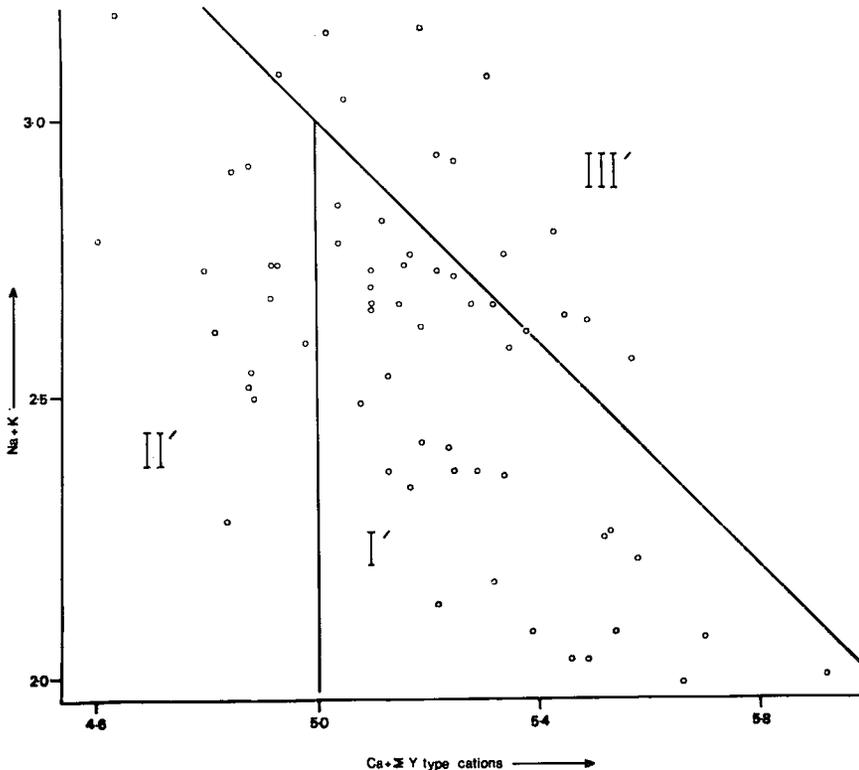


FIG. 4. The variation in (Na+K) with *Y*-type cation sums for the alkali amphiboles, where Ca is influenced as a *Y*-type cation.

The question now arises as to the chemical identity of the *X*-type cation entering the octahedral sites. On the basis of a bond strength criterion, Ca would be expected to fill this role. This premise is examined in Figure 4 which shows the variation in the *X*-cation sums with that of the *Y*-cation sums where Ca has been included in the *Y*-cation sum. The lower right field is allowable for alkali amphiboles with Ca substitution into the octahedral sites whereas the left field is allowable only if Na substitutes into the octahedral sites. The majority of the analyses (70%) lie in the Ca substitution field, suggesting that this substitution does occur. Of the remainder, 20% lie in the forbidden field and 10% lie in the Na^{VI} substitution field. The fact that the number of analyses lying in the forbidden field exceeds the number lying in the Na^{VI} field suggests that the latter may be due to bad analyses. Thus Figure 4 suggests that Ca may substitute into the octahedral sites in the sodic amphiboles, but Na is restricted to the *M*(4) and *A* sites.

With regard to the substitution of Li into the octahedral sites, there are two possible coupled substitutions

- (i) $\text{Li} \rightleftharpoons \text{Mg}, \text{Ca} \rightleftharpoons \text{Na}$
 (ii) $\text{Li} \rightleftharpoons \text{Mg}, \text{Al, Fe}^{3+} \rightleftharpoons \text{Mg}(2\text{Li} \rightleftharpoons 2\text{Mg}, \text{Ti}^{4+} \rightleftharpoons \text{Mg})$

Examination of a large number of analyses indicates complete lack of correlation between Ca^{M(4)} and Li, and thus the first possibility may be discounted. Thus the second substitution must occur; it should be noted that two substitutions denoted (ii) above are not distinguished separately as they are identical in the charge distribution space of Whittaker (1968). In addition, the ideal formula produced by this substitution (Na₃LiMg₂Al₂Si₃O₂₂(OH)₂) has coordinates identical to those of eckermanite (012). However, any direct correlation between the amounts of mono- and trivalent cations in the octahedral sites is obscured by additional coupled substitutions (Al \rightleftharpoons Mg, Al \rightleftharpoons Si; Ca \rightleftharpoons Na, Al \rightleftharpoons Si) that also affect the amounts of octahedral trivalent cations, and the chemical evidence for this substitution awaits a more detailed examination of chemical variations in the alkali amphiboles (work in progress).

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