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THE CRYSTAL CHEMISTRY OF THE AMPHIBOLES. VIII. THE CRYSTAL STRUCTURE AND SITE CHEMISTRY OF FLUOR-RIEBECKITE

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ABSTRACT

The crystal structure of a fluor-riebeckite of composition $(Na_{0.037}K_{0.290})(Ca_{0.013}Na_{1.987})(Li_{0.334}Mg_{0.011}Mn_{0.182}Fe^{2+}_{2.299}Fe^{3+}_{2.025}Ti_{0.016}Al_{0.103})(Al_{0.252}Si_{7.748})O_{22}(OH_{0.892}F_{1.253})$ has been refined by a full-matrix least-squares method using three-dimensional counter-diffractometer X-ray data; the *R* index for 1158 observed reflections is 3.6%. The space group is *C*2/*m*, *a* 9.811(3), *b* 18.013(5), *c* 5.326(2)Å, β 103.68(1)°, *V* 914.5Å³, *Z* = 2. Constrained refinement of the octahedral site populations shows Li to be confined to the *M*(3) site. Consideration of mean bond lengths shows tetrahedral Al strongly ordered in *T*(1) and octahedral trivalent cations strongly ordered in *M*(2). The curves of Hawthorne (1978) *suggest* strong ordering of octahedral Fe^{3+}, in excess of that required to fill *M*(2), in *M*(1), and of octahedral Mn in *M*(3). The atoms occupying the *A* site show positional disorder in the mirror plane, supporting the arguments (Hawthorne & Grundy 1978) that *A*-site K occupies *A*(*m*) whereas *A*-site Na occupies *A*(2) or *A*(1). Complete ordering of Li in *M*(3) minimizes deviations from Pauling's rule of local neutralization of charges.

SOMMAIRE

La structure cristalline d'une riebéckite fluorée, répondant à la formule $(Na_{0.037}K_{0.290})(Ca_{0.013}Na_{1.987})(Li_{0.334}Mg_{0.011}Mn_{0.182}Fe^{2+}_{2.299}Fe^{3+}_{2.025}Ti_{0.016}Al_{0.103})(Al_{0.252}Si_{7.748})O_{22}(OH_{0.892}F_{1.253})$ a été affinée en *C*2/*m*, par moindres carrés à matrice entière sur 1158 réflexions X observées au diffractomètre à compteur, jusqu'au résidu *R* = 3.6%. Paramètres réticulaires: *a* 9.811(3), *b* 18.013(5), *c* 5.326(2)*Å*, β 103.68(1)°, *V* 914.5 Å³, *Z* = 2. L'affinement contraint de la population des sites octaédriques confine Li aux sites *M*(3). Les longueurs moyennes de liaison indiquent une forte mise en ordre de l'Al tétraédrique en *T*(1) et des cations trivalents octaédriques en *M*(2). D'après nos courbes (Hawthorne 1978), le Fe^{3+} octaédrique, après avoir rempli *M*(2), serait fortement ordonné en *M*(1), tandis que le Mn octaédrique le serait en *M*(3). Le désordre de position, dans le plan miroir, des atomes de sites *A* étayent l'argument (Hawthorne & Grundy 1978) que, de ces atomes, le K occupe *A*(*m*), alors que le Na occupe *A*(2) ou *A*(1). La mise en ordre complète du Li en *M*(3) minimise toute déviation à la règle de Pauling de neutralisation locale des charges.

(Traduit par la Rédaction)

INTRODUCTION

Riebeckite is a sodic iron amphibole found in a wide variety of parageneses. It is a common constituent of alkalic granites and syenites (Borley 1963; Lyons 1972, 1976), and is found in low-grade greenschist-facies rocks (White 1962) and meta-ironstones (Peacock 1928; Villiers 1949) where the fibrous variety (crocidolite) is a commercial source of asbestos fibre. Authigenic riebeckite was reported by Milton & Eugster (1959) but this was later shown to be magnesio-arfvedsonite (Milton *et al.* 1974). The ideal formula of riebeckite is $Na_2Fe_3^{2+}Fe_2^{3+}Si_8O_{22}(OH)_2$; complete solid solution exists between riebeckite and magnesio-riebeckite, $Na_2Mg_3Fe_2^{3+}Si_8O_{22}(OH)_2$. Distinct compositional differences occur between riebeckites from different parageneses. Igneous riebeckites are usually characterized by high fluorine contents (Borley 1963; Lyons 1976) whereas metamorphic riebeckites contain little F (Onuki & Ernst 1969; Coleman & Papike 1968; in addition, Li can be a major component in igneous riebeckites.

A three-dimensional crystal structure refinement of crocidolite (magnesio-riebeckite) was reported by Whittaker (1949), who showed that the trivalent cations (Fe^{3+} and Al) occupy the *M*(2) site and the monovalent cation (Na), *M*(4). This has since been confirmed for a number of riebeckites by infrared and Mössbauer spectroscopy (Strens 1970; Burns & Prentice 1968; Bancroft & Burns 1969), and by X-ray diffraction (Colville & Gibbs 1964). In addition, a considerable amount of spectroscopic work has focused on the oxidation mechanism in riebeckites (Rouxhet *et al.* 1972; Addison & White 1968; Ernst & Wai 1970). The cell contents of Li-bearing Na-amphiboles indicates that Li occurs in the octahedral sites (Sundius 1946; Borley 1963). The site preference of Li is thus of considerable interest with regard to polyvalent cation-ordering in amphiboles. On the basis of an infrared spectrum, Addison & White (1968) suggest that Li occurs in the *M*(1) and *M*(3) sites in riebeckite. In order to determine the ordering pattern of Li in riebeckite and provide a more precise characterization of the structure, a refinement of the crystal structure of a riebeckite is presented here.

EXPERIMENTAL

The riebeckite used in this study is from a granitic pegmatite in the Pikes Peak area, Colorado, and was taken from the University of Manitoba Mineral Museum. The results of a wet-chemical analysis of a hand-picked separate are given in Table 1; the Fe^{3+}/Fe^{2+} ratio agrees with that determined by Mössbauer spectroscopy (unpublished work). The cell contents were calculated on the basis of 24 (O,OH,F).

Long-exposure single-crystal precession photographs displayed diffraction symmetry $2/mC\text{-}/\text{-}$, consistent with the space group $C2/m$ exhibited by all other sodic clinoamphiboles; 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 0.05×0.07×0.12mm was used to collect the intensity data according to the experimental procedure described by Hawthorne & Ferguson (1975). No significant change occurred in the intensities of two standard reflections monitored every 50 reflections during data collection. A total of 1628 reflections was measured in one asymmetric unit out to 2θ 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 three standard deviations, based on counting statistics. Application of this procedure resulted in 1158 observed reflections.

TABLE 1. CRYSTAL DATA

Chemical analysis(wt%)		Cell contents*		Miscellaneous	
SiO_2	50.45	Si	7.748		
TiO_2	0.14	Al	0.252	a	9.811(3)Å
Al_2O_3	1.96	Σ^{IV}	8.000	b	18.013(5)Å
Fe_2O_3	17.52	Al	0.103	c	5.326(2)Å
FeO	17.90	Ti	0.016	β	103.68(1)°
MnO	1.40	Fe^{3+}	2.025	V	914.5Å^3
MgO	0.05	Fe^{2+}	2.299		
CaO	0.08	Mn	0.182	Space group	$C2/m$
Na_2O	6.80	Mg	0.011	Z	2
K_2O	1.48	Li	0.334	D_{calc}	3.371g/cm^3
Li_2O	0.54	Σ^{VI}	4.970	μ	43.5cm^{-1}
H_2O	0.87	Ca	0.013	Crystal size (mm)	0.12×0.07 ×0.05
F	2.58	Na	1.987	Rad/Mono	Mo/C
	101.77	$\Sigma^{M(4)}$	2.000	Total # of non-equivalent $\lvert Fo\rvert$	1628
O ≡ F	-1.09	Na	0.037		
Σ	100.68	K	0.290	# of $\lvert Fo\rvert > 3\sigma$	1158
		Σ^{A}	0.327	Final R (obs)	3.6%
		OH	0.892	Final R_w (obs)	3.7%
		F	1.253		

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

$R = \Sigma(|Fo|-|Fc|)/\Sigma|Fo|$

$R_w = (\Sigma w(|Fo|-|Fc|)^2/\Sigma wFo^2)^{\frac{1}{2}}$, $w = 1$

*based on 24(O, OH, F)

TABLE 2. ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS

Site	x	y	z	B_{equiv}(Å^2)
O(1)	0.1098(3)	0.0913(2)	0.2047(6)	0.70(4)
O(2)	0.1195(3)	0.1723(2)	0.7378(6)	0.69(4)
O(3)	0.1118(4)	0	0.7095(8)	0.96(6)
O(4)	0.3656(3)	0.2491(2)	0.8013(6)	0.84(4)
O(5)	0.3491(3)	0.1282(2)	0.0814(5)	0.79(4)
O(6)	0.3399(3)	0.1206(2)	0.5778(5)	0.81(4)
O(7)	0.3325(5)	0	0.3004(8)	0.89(6)
T(1)	0.2796(1)	0.08585(6)	0.2905(2)	0.51(2)
T(2)	0.2901(1)	0.17057(6)	0.8015(2)	0.50(2)
M(1)	0	0.09069(5)	1/2	0.63(2)
M(2)	0	0.18262(5)	0	0.42(1)
M(3)	0	0	0	0.70(4)
M(4)	0	0.2782(1)	1/2	1.32(4)
A(m)	0.0387(11)	1/2	0.0833(19)	1.67(14)

REFINEMENT

Scattering factors for neutral atoms were taken from Cromer & Mann (1968) together with anomalous dispersion coefficients from Cromer & Liberman (1970). Atomic coordinates and equivalent isotropic temperature factors of arfvedsonite (Hawthorne 1976) were used as initial input to the program RFINE (Finger

TABLE 3. ANISOTROPIC TEMPERATURE FACTOR COEFFICIENTS*

Site	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	216(27)	61(8)	526(89)	1(11)	114(41)	1(20)
O(2)	139(26)	60(8)	718(90)	-16(11)	65(39)	-18(19)
O(3)	296(39)	67(10)	919(131)	0	186(59)	0
O(4)	290(29)	63(7)	709(86)	-35(12)	224(41)	-40(21)
O(5)	221(27)	81(8)	512(84)	-5(12)	114(39)	74(21)
O(6)	206(29)	81(8)	605(87)	-11(11)	99(40)	-97(21)
O(7)	261(41)	35(10)	987(137)	0	-68(62)	0
T(1)	172(11)	32(3)	456(32)	-10(4)	84(16)	-5(7)
T(2)	146(10)	40(3)	453(33)	-8(4)	83(15)	-5(7)
M(1)	207(8)	46(2)	525(27)	0	101(12)	0
M(2)	119(7)	32(2)	386(25)	0	72(11)	0
M(3)	252(18)	44(5)	563(58)	0	76(24)	0
M(4)	469(29)	79(7)	1500(95)	0	569(44)	0

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

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å)

Atoms	Distance	Atoms	Distance
T(1)-O(1)	1.623(3)	M(1)-O(1)	2.106(3) x2
T(1)-O(5)	1.627(3)	M(1)-O(2)	2.106(3) x2
T(1)-O(6)	1.630(3)	M(1)-O(3)	2.130(3) x2
T(1)-O(7)	1.628(2)	⟨M(1)-O⟩	2.114
⟨T(1)-O⟩	1.627		
		M(2)-O(1)	2.121(3) x2
T(2)-O(2)	1.627(3)	M(2)-O(2)	2.034(3) x2
T(2)-O(4)	1.598(3)	M(2)-O(4)	1.926(3) x2
T(2)-O(5)	1.652(3)	⟨M(2)-O⟩	2.027
T(2)-O(6)	1.656(3)		
⟨T(2)-O⟩	1.633	M(3)-O(1)	2.121(3) x4
		M(3)-O(3)	2.098(4) x2
M(4)-O(2)	2.432(4) x2	⟨M(3)-O⟩	2.113
M(4)-O(4)	2.357(3) x2		
M(4)-O(5)	2.906(3) x2	A-O(5)	2.832(3) x4
M(4)-O(6)	2.504(4) x2	A-O(6)	3.252(3) x4
⟨M(4)-O⟩$^{\mathrm{VIII}}$	2.550	A-O(7)	2.550(3) x2
⟨M(4)-O⟩$^{\mathrm{VI}}$	2.431	A-O(7)	3.700(4) x2
		⟨A-O⟩$^{\mathrm{XII}}$	3.070
A(m)-O(5)	2.788(7) x2		
A(m)-O(5)	2.964(7) x2	M(1)-M(1)	3.267(2)
A(m)-O(6)	2.894(7) x2	M(1)-M(2)	3.136(1)
A(m)-O(6)	3.646(9) x2	M(1)-M(3)	3.124(1)
A(m)-O(7)	2.556(12)	M(1)-M(4)	3.377(3)
A(m)-O(7)	2.645(11)	M(2)-M(3)	3.290(1)
A(m)-O(7)	3.225(11)	M(2)-M(4)	3.171(2)
A(m)-O(7)	4.183(12)		
⟨A(m)-O⟩$^{\mathrm{XII}}$	3.099	T(1)-T(2) through O(6)	3.100(2)
⟨A(m)-O⟩$^{\mathrm{VIII}}$	2.812	T(1)-T(2) through O(5)	3.041(2)
A-A(m)	0.51(2)	T(1)-T(1) across mirror	3.093(2)

TABLE 5. POLYHEDRAL EDGE LENGTHS (Å)

T(1) Tetrahedron		T(2) Tetrahedron	
O(1)-O(5)	2.667(4)	O(2)-O(4)	2.734(4)
O(1)-O(6)	2.684(4)	O(2)-O(5)	2.665(4)
O(1)-O(7)	2.686(5)	O(2)-O(6)	2.672(4)
O(5)-O(6)	2.670(4)	O(4)-O(5)	2.666(4)
O(5)-O(7)	2.610(4)	O(4)-O(6)	2.588(4)
O(6)-O(7)	2.619(4)	O(5)-O(6)	2.666(4)
⟨O-O⟩	2.656	⟨O-O⟩	2.665
M(1) Octahedron		**M(3) Octahedron**	
O(1^u)-O(2^d)	2.759(4)	O(1^u)-O(1^d)	2.678(6)
O(1^u)-O(2^u)	3.173(5)	O(1^u)-O(1^u)	3.290(6)
O(1^u)-O(3^d)	2.849(4)	O(1^u)-O(3^d)	2.849(4)
O(1^u)-O(3^u)	3.148(5)	O(1^u)-O(3^u)	3.112(5)
O(2)-O(2)	3.018(6)	⟨O-O⟩	2.983
O(2)-O(3)	3.107(3)		
O(3)-O(3)	2.735(8)	**M(4) Polyhedron**	
⟨O-O⟩	2.985	O(2)-O(2)	3.018(6)
		O(2^u)-O(4^u)	3.235(4)
M(2) Octahedron		O(2^u)-O(4^d)	2.953(4)
O(1)-O(1)	2.678(6)	O(2^u)-O(5^u)	3.714(4)
O(1^u)-O(2^d)	2.759(4)	O(4^u)-O(5^d)	3.484(4)
O(1^u)-O(2^u)	2.904(4)	O(4^u)-O(6^u)	2.588(4)
O(1)-O(4)	2.884(4)	O(5^u)-O(6^u)	2.670(4)
O(2^u)-O(4^d)	2.953(4)	O(5^u)-O(6^d)	3.163(4)
O(2^u)-O(4^u)	2.807(4)	O(6^u)-O(6^d)	3.433(6)
O(4)-O(4)	2.965(6)	⟨O-O⟩	3.129
⟨O-O⟩	2.855		

1969a). Initial site-populations were assigned as follows: Al^{IV} was assigned to *T*(1), Ca and Na were assigned to *M*(4), and K and excess Na were assigned to the *A* site; for the octahedral sites, the scattering species were considered as Fe* (≡Fe^{2+}+Fe^{3+}+Ti+Mn) and Al* (≡Al+Mg+Li) and were disordered over the three *M* sites, no correction being made for the difference in scattering power between Al and Li. With the octahedral-site temperature factors constrained to be equal, several cycles of full-matrix least-squares refinement gradually increasing the number of variables resulted in convergence at an *R* index of 5.4% 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 (6.1Å^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 subsilicic hastingsite (Hawthorne & Grundy 1977). One cycle of least-squares refinement varying the positional parameters and site populations of the *A*(2) and *A(m)* sites together with all other variables reduced the *R* index from 5.3 to 4.3% and the R_w index from 5.3 to 4.3%; this improvement is significant at the 0.005 level (Hamilton 1965). The occupancy of the *A*(2) site was zero within four standard deviations (0.008); although this occupancy is significant, this model would not converge as the positional and occupancy parameters of the *A*(2) site were oscillating. As it was apparent that the *A*-site cation was almost completely ordered into the *A(m)* site, the *A*(2) site was removed from the refinement; no significant increase in the *R* and R_w indices occurred.

The site-population refinement of the *M*(1), *M*(2) and *M*(3) sites was not constrained to the bulk chemical composition, but constraining the octahedral-site temperature factors to be equal served to damp the correlations between site-occupancies and temperature factors; the total scattering power at these sites was equal to that indicated by the cell contents. At this stage, the Al* content of the *M*(2) site was equal to the total amount of Al^{VI}, and thus all Al^{VI} was assigned to the *M*(2) site, the site-populations of which were not varied subsequently. The scattering powers at *M*(1) and *M*(3) indicated that Li was very strongly ordered in the *M*(3) site.

TABLE 6. SELECTED INTERATOMIC ANGLES

T(1) Tetrahedron		T(2) Tetrahedron	
0(1)-T(1)-0(5)	110.3(2)°	0(2)-T(2)-0(4)	115.9(2)°
0(1)-T(1)-0(6)	111.2(2)	0(2)-T(2)-0(5)	108.7(2)
0(1)-T(1)-0(7)	111.4(2)	0(2)-T(2)-0(6)	108.9(2)
0(5)-T(1)-0(6)	110.1(2)	0(4)-T(2)-0(5)	110.2(2)
0(5)-T(1)-0(7)	106.6(2)	0(4)-T(2)-0(6)	105.4(2)
0(6)-T(1)-0(7)	107.0(2)	0(5)-T(2)-0(6)	107.4(2)
<0-T(1)-0>	109.4	<0-T(2)-0>	109.4
M(1) Octahedron		M(3) Octahedron	
0(1^u)-M(1)-0(2^d)	81.8(1)	0(1^u)-M(3)-0(1^d)	78.3(2)
0(1^u)-M(1)-0(2^u)	97.7(1)	0(1^u)-M(3)-0(1^u)	101.7(2)
0(1^u)-M(1)-0(3^d)	84.5(1)	0(1^u)-M(3)-0(3^d)	84.9(1)
0(1^u)-M(1)-0(3^u)	96.0(1)	0(1^u)-M(3)-0(3^u)	95.1(1)
0(2)-M(1)-0(2)	91.5(2)	<0-M(3)-0>	90.0
0(2)-M(1)-0(3)	94.3(1)		
0(3)-M(1)-0(3)	79.9(2)	M(4) Polyhedron	
<0-M(1)-0>	90.0	0(2)-M(4)-0(2)	76.7(2)
		0(2^u)-M(4)-0(4^d)	76.1(1)
M(2) Octahedron		0(2^u)-M(4)-0(4^u)	85.0(1)
0(1)-M(2)-0(1)	78.3(2)	0(2^u)-M(4)-0(5^u)	87.7(1)
0(1^u)-M(2)-0(2^d)	83.2(1)	0(4^u)-M(4)-0(5^d)	82.2(1)
0(1^u)-M(2)-0(2^u)	88.7(1)	0(4^u)-M(4)-0(6^u)	64.3(1)
0(1)-M(2)-0(4)	90.8(1)	0(5^u)-M(4)-0(6^d)	71.1(1)
0(2^u)-M(2)-0(4^d)	96.4(1)	0(5^u)-M(4)-0(6^u)	58.6(1)
0(2^u)-M(2)-0(4^u)	90.3(1)	0(6)-M(4)-0(6)	86.6(2)
0(4)-M(2)-0(4)	100.7(2)	<0-M(4)-0>	75.8
<0-M(2)-0>	89.8	Tetrahedron	
		T(1)-0(5)-T(2)	136.1(2)
0(7)-0(7)-0(7)	67.1	T(1)-0(6)-T(2)	141.4(2)
		T(1)-0(7)-T(1)	143.6(3)
Δ*	0.254	0(5)-0(6)-0(5)	173.0(2)
		0(5)-0(7)-0(6)	171.9(2)

*Δ = [90°-0(7)-0(7)-0(7)] /90°.

TABLE 7. VIBRATION ELLIPSOIDS

	R.M.S. Displacement	Angle to a-axis	Angle to b-axis	Angle to c-axis
0(1)	0.081(8)Å	112(17)°	90(17)°	9(17)°
	0.100(6)	125(326)	38(368)	95(48)
	0.100(6)	38(310)	59(397)	82(33)
0(2)	0.077(8)	24(15)	70(13)	89(14)
	0.097(6)	67(17)	123(43)	145(47)
	0.103(6)	83(22)	141(41)	55(47)
0(3)	0.102(5)	126(26)	90	22(26)
	0.107(6)	144(26)	90	112(26)
	0.120(8)	90	0	90
0(4)	0.085(7)	126(20)	90(34)	22(20)
	0.093(7)	113(26)	151(8)	101(37)
	0.127(5)	45(7)	119(8)	71(6)
0(5)	0.069(8)	109(10)	114(5)	25(6)
	0.101(6)	160(10)	90(12)	97(10)
	0.122(5)	98(12)	24(5)	66(6)
0(6)	0.074(8)	98(14)	60(5)	30(6)
	0.097(7)	172(14)	95(10)	82(13)
	0.127(5)	88(9)	150(5)	61(5)
0(7)	0.076(11)	90	0	90
	0.094(10)	132(8)	90	124(8)
	0.138(8)	138(8)	90	34(8)
T(1)	0.071(3)	73(9)	17(7)	91(21)
	0.077(3)	71(11)	93(21)	174(10)
	0.091(3)	26(8)	107(6)	84(10)
T(2)	0.075(3)	135(16)	109(29)	39(34)
	0.078(3)	104(28)	136(22)	125(35)
	0.086(3)	48(11)	127(15)	75(12)
M(1)	0.083(2)	110(6)	90	6(6)
	0.087(2)	90	0	90
	0.098(2)	20(6)	90	84(6)
M(2)	0.068(3)	136(13)	90	32(13)
	0.073(2)	90	0	90
	0.076(2)	46(13)	90	58(13)
M(3)	0.085(5)	90	0	90
	0.087(5)	89(8)	90	168(8)
	0.109(4)	1(8)	90	102(8)
M(4)	0.094(6)	140(3)	90	36(3)
	0.114(5)	90	0	90
	0.169(4)	50(3)	90	54(3)

Li was divided between *M*(1) and *M*(3) in the ratio 1:10, and the site occupancies were subsequently considered as variable with the total amount of Li constrained to be that indicated by the chemical analysis (Finger 1969b). Temperature factors were converted to an anisotropic form as given in Table 1, and full-matrix least-squares refinement of all variables converged to *R* indices of 3.6 (5.6%) and R_w indices of 3.7 (5.4%) for observed (all) reflections. Final positional and thermal parameters are given in Tables 2 and 3. 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 4-7. Observed and calculated structure factors have been deposited and may be obtained at nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DISCUSSION

The results of the constrained site-population refinement are given in Table 8. Using the equations of Hawthorne & Grundy (1977) relating mean tetrahedral bond lengths to Al content, the tetrahedral-site populations may be derived (Table 8); the total tetrahedral Al indicated by these equations (0.24 Al per formula unit) agrees closely with that derived from the chemical analysis (0.25 Al p.f.u.). The Al site-preference exhibited by this riebeckite is *T*(1) > *T*(2), as has been found for all amphiboles for which crystal-structure data are available. For this particular riebeckite, the amount of Mg and Ti in the cell is negligible, and thus there are 5 cation species to be distributed over the three octahedral sites. During the refinement procedure, all octahedral Al was assigned to the *M*(2) site, with the remainder of the site occupied by Fe* (≡ Fe^{2+}+Fe^{3+}+Mn). The short mean-bond-length of the

TABLE 8. SITE POPULATIONS*

From site-population refinement:	
M(1)	0.996(4)Fe* + 0.004 Li
M(2)	0.057 Al + 0.943 Fe*
M(3)	0.672 Fe* + 0.328 Li
M(4)	0.007 Ca + 0.993 Na
A(m)	0.28 Na*
From examination of mean bond lengths:	
T(1)	0.05 Al + 0.95 Si
T(2)	0.01 Al + 0.99 Si
M(1)	0.066 Fe^{3+} + 0.934 Fe^{2+}
M(2)	0.057 Al + 0.943 Fe^{3+}
M(3)	0.336 Li + 0.182 Mn + 0.482 Fe^{2+}
M(4)	0.007 Ca + 0.993 Na
A(m)	0.145 K + 0.019 Na

*The relative ordering of Fe^{3+} and Mn over the M(1) and M(3) sites is somewhat speculative and should be treated with caution.

M(2) octahedron indicates that the Fe occupying *M*(2) is predominantly in the trivalent state. Using the curves of Hawthorne (1978) relating mean octahedral bond length to constituent-cation radius, an *M*(2) occupancy of $0.057Al + 0.943Fe^{3+}$ corresponds to a <*M*(2)–O> of 2.025(5)Å, which agrees well with the observed value of 2.027Å. The results of the constrained site-population refinement indicate that Li is confined to the *M*(3) site, the refined *M*(1) occupancy being equal to zero within two standard deviations. There remains three cation species (Mn, Fe^{2+}, Fe^{3+}) to be distributed over the *M*(1) and *M*(3) sites, using the curves of Hawthorne (1978) relating <*M*(1)–O> and <*M*(3)–O> to the constituent-cation and anion radii. Four extreme distributions may be recognized; these are listed in Table 9 together with the calculated and observed <*M*–O> values for each site. Scheme 3, with Fe^{3+} ordered into *M*(1) and Mn ordered into *M*(3), shows the best agreement between the observed and calculated mean bond lengths. However, considering the precision of the curves of Hawthorne (1978), scheme 4, with both Fe^{3+} and Mn ordered in *M*(1), is also acceptable. Thus the results of Table 9 provide fairly strong evidence that the small amount of Fe^{3+} available for the *M*(1) and *M*(3) sites is strongly ordered in the *M*(1) site. This is in agreement with the arguments of Hawthorne & Grundy (1973b) that any octahedral trivalent (and tetravalent) cations not occurring at the *M*(2) site should be strongly ordered in the *M*(1) site. The results of Table 9 also suggest that Mn may be partly ordered in the *M*(3) site; although the evidence for this is not conclusive, this result is compatible with the results of similar previous studies (Hawthorne 1976; Hawthorne & Grundy 1978). The *A*-site cation shows significant positional disorder only in the mirror plane; as the *A*-site cation is dominantly K (Table 1), this supports the contention of Hawthorne & Grundy (1978) that K occupies the *A(m)* site and Na occupies the *A*(2) or *A*(1) sites in clinoamphiboles.

Li is the only monovalent cation known to occupy in considerable amounts the octahedral sites in the clinoamphibole structure. Thus the site distribution of Li is of considerable interest with regard to those factors that affect polyvalent-cation ordering in amphiboles. The effect of the relative electrostatic potential at different sites on polyvalent-cation ordering in amphiboles has been considered by Whittaker (1971). He calculated the Madelung energies and electrostatic site-potentials for a variety of cation

TABLE 9. POSSIBLE SITE-POPULATIONS FOR THE M(1) AND M(3) SITES INVOLVING MAXIMUM CATION ORDERING

		Cation distributions	⟨M-O⟩obs	⟨M-O⟩calc	R.M.S. deviation
1	M(1)	1.0 Fe^{2+}	2.119Å	2.114Å	0.013Å^2
	M(3)	0.336 Li+0.182Mn+0.131Fe^{3+}+0.351Fe^{2+}	2.096	2.113	
2	M(1)	0.091 Mn+0.909Fe^{2+}	2.123	2.114	0.019
	M(3)	0.336 Li+0.131Fe^{3+}+0.533Fe^{2+}	2.087	2.113	
3	M(1)	0.066 Fe^{3+}+0.934Fe^{2+}	2.111	2.114	0.002
	M(3)	0.336 Li+0.182Mn+0.482Fe^{2+}	2.112	2.113	
4	M(1)	0.066 Fe^{3+}+0.091Mn+0.843Fe^{2+}	2.116	2.114	0.007
	M(3)	0.336 Li+0.664Fe^{2+}	2.103	2.113	

arrangements and showed that the results were compatible with the cation arrangements in glaucophane, riebeckite and pargasite; however, the ordering patterns forecast for tschermakite and hornblende do not agree with those subsequently observed in crystal-structure studies (Hawthorne & Grundy 1973a; Litvin *et al.* 1972). The site potentials calculated by Whittaker (1971) for the arrangement $M(4)^{+}M(1)^{2+}M(2)^{3+}M(3)^{2+}T(1)^{4+}T(2)^{4+}$ suggest that octahedral Li should exhibit a site preference $M(3) > M(1) > M(2)$ as was found in this study; however, Whittaker emphasizes the importance of using the total Madelung energy rather than the potential distribution in assessing relative site-preferences, and hence the significance of the agreement is not clear.

In recent years, the importance of local charge neutrality and its effect on bond-length variations in inorganic structures has become clear (Baur 1961, 1970, 1971, 1972; Donnay & Allmann 1970; Brown & Shannon 1973; Pyatenko 1973; Ferguson 1974). Because of the drastic change in formal bond strengths (= formal charge/cation coordination number: Pauling 1960) encountered in polyvalent-cation ordering in crystals, the local charge-neutrality or bond-strength requirements should exert stringent controls on cation-ordering patterns. Whittaker (1971) pointed out some difficulties encountered with this approach; specifically, it is difficult to apply to the amphibole structure because the uncertainty in the coordination of the $M(4)$ site makes an unambiguous assignment of bond strengths rather difficult. The same argument also applies to the A site. Although this factor complicates the bond-strength approach to ordering, it does not constitute an insuperable difficulty, as the method may be applied for a variety of coordination numbers; the results turn out to be rather insensitive to the assigned coordination numbers.

The occurrence of one specific charge-distribution around a particular anion together with the known stoichiometry of the overall atomic arrangement imposes restrictions on ordering at other cation sites and produces bond-strength changes around other anions. Thus the charge distribution must be examined in its entirety rather than in restricted parts of the structure; this may be done by calculating the root-mean-square (R.M.S.) deviation from Pauling's second rule (Pauling 1960). The possible ordering schemes may be examined by carrying out this procedure for all possible cation arrangements for a specific stoichiometry; in order to reduce the possible number of cation configurations, it was assumed that Si would only occur in tetrahedral coordination.

This particular study is concerned with the ordering of Li in riebeckite, and thus it is pertinent to examine the possible cation substitutions involving Li substitution for a divalent cation in the riebeckite stoichiometry. The following substitutions are *possible*: (i) $(\mathrm{Na,K}) + \mathrm{Li} \rightleftharpoons \square + \mathrm{Fe}^{2+}$: $(\mathrm{Na,K})\mathrm{Na_2LiFe_2^{2+}Fe_3^{2+}Si_8O_{22}(OH)_2}$; (ii) Ca+Li

TABLE 10. CATION ORDERING PATTERNS SHOWING BEST AGREEMENT WITH PAULING'S SECOND RULE FOR THREE LI AMPHIBOLE STOICHIOMETRIES

Substitution	A	M(1)	M(2)	M(3)	M(4)	R.M.S. Deviation(%)	
						[6] *	[8] *
(i)	(Na,K)	Fe_2^{2+}	Fe_2^{3+}	Li	Na_2	10.05	11.24
	(Na,K)	$(Fe^{2+} + Fe^{3+})$	$(Fe^{2+} + Fe^{3+})$	Li	Na_2	10.20	11.50
	(Na,K)	$(Fe^{2+} + Li)$	Fe_2^{3+}	Fe^{2+}	Na_2	10.34	11.62
	(Na,K)	$(Fe^{3+} + Li)$	$(Fe^{2+} + Fe^{3+})$	Fe^{2+}	Na_2	10.48	11.87
(ii)	□	Fe_2^{2+}	Fe_2^{3+}	Ca	(Na + Li)	8.33	9.16
	□	Fe_2^{2+}	Fe_2^{3+}	Li	(Na + Ca)	8.84	9.66
	□	$(Fe^{2+} + Fe^{3+})$	$(Fe^{2+} + Fe^{3+})$	Li	(Na + Ca)	8.67	9.73
	□	$(Fe^{2+} + Li)$	Fe_2^{3+}	Fe^{2+}	(Na + Ca)	8.84	9.88
(iii)	□	$(Fe^{2+} + Fe^{3+})$	Fe_2^{3+}	Li	Na_2	7.98	8.67
	□	$(Li + Fe^{3+})$	Fe_2^{3+}	Fe^{2+}	Na_2	8.33	9.16
	□	$(Na + Fe^{3+})$	Fe_2^{3+}	Li	$(Na + Fe^{2+})$	8.84	9.66
	□	$(Li + Fe^{2+})$	Fe_2^{3+}	Fe^{3+}	Na_2	9.32	10.21

*indicates M(4) coordination number

$\rightleftharpoons$Na+Fe^{2+}: □NaCaLiFe$_2^{2+}$Fe$_2^{3+}$Si$_8$O$_{22}$(OH,F)$_2$; (iii) Fe^{3+}+Li$\rightleftharpoons$2Fe^{2+}: □Na$_2$LiFe^{2+}Fe$_3^{3+}$Si$_8$O$_{22}$(OH,F)$_2$.

The cell contents of this riebeckite (Table 1) suggest that substitution (i) is of primary importance, but calculations were performed for all three substitutions. The four configurations with the lowest R.M.S. deviations from Pauling's second rule for each of the three species listed above are shown in Table 10; for all stoichiometries, the coordination number used for the *A* site ([8], [10] or [12]) changed the magnitude of the R.M.S. deviation (when the *A* site was occupied) but did not affect the relative magnitudes of the R.M.S. deviations for the arrangement shown in Table 10. For substitution (i), (Na,K)+Li$\rightleftharpoons$□+Fe^{2+}, the lowest R.M.S. deviation obtained is for the arrangement found in this study, irrespective of the *M*(4) coordination number used in the calculations. As this substitution is the principal one in the riebeckite examined here, this supports the contention that local bond-strength requirements should influence cation ordering. The absence of Ca in this riebeckite (Table 1) indicates that substitution (ii), Ca+Li$\rightleftharpoons$Na+Fe^{2+}, is negligible in this crystal. However, it is of interest to compare the results with those obtained for substitutions (i) and (iii). The arrangement with the lowest R.M.S. deviation has Ca at *M*(3) and Li at *M*(4); it should be noted that the *charge* arrangement is identical to that found in ferro-glaucophane (Hawthorne in prep.), which may be derived from this species by the substitution Fe^{2+}+Na$\rightleftharpoons$Ca+Li. The second- and third-best arrangements involve Li at *M*(3) as found for substitutions (i) and (iii). Examination of an amphibole of this type would be extremely interesting in order to find out whether significant amounts of Ca can occur at the *M*(1) or *M*(3) sites or both in the clinoamphibole structure. For substitution (iii), Li+Fe^{3+} $\rightleftharpoons$2Fe^{2+}, the lowest R.M.S. deviation occurs when Fe^{3+} is at *M*(1) and Li is at *M*(3). A small amount of this substitution may occur in this riebeckite as the total trivalent cation content is in excess of 2 atoms p.f.u.; mean-bond-length considerations suggest that some Fe^{3+} does occur at the *M*(1) site (Table 9) and this is compatible with the results obtained for substitution (iii) in Table 10.

The cation-ordering pattern in this fluor-riebeckite seems to be compatible with the premise that cations will order so as to minimize the deviations from Pauling's second rule. Preliminary calculations indicate that this premise accounts for the ordering patterns observed in most clinoamphiboles. Thus, the method may be used to forecast ordering patterns in uncharacterized clinoamphiboles; it has an advantage over methods involving site potentials, Madelung energies and structure energies: it is simple and the calculations are trivial to perform.

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