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A FURTHER REFINEMENT OF THE CRYSTAL STRUCTURE OF CUMMINGTONITE, $(Mg,Fe)_7(Si_4O_{11})_2(OH)_2$

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ABSTRACT

By refining the atomic scattering power of each of the four cation sites, M_1 through M_4, of the crystal structure of Cummingtonite, the distribution of Mg^{2+} and Fe^{2+} over these sites were determined to be:

M_1:84% Mg and 16% Fe,
M_2:95% Mg and 5% Fe,
M_3:84% Mg and 16% Fe,
M_4:13% Mg and 87% Fe.

Ghose's original data (1961) were used for this work. The results demonstrate the usefulness of the f-refinement technique for the evaluation of mixed populations for more than one equipoint.

The crystal structure of this mineral has been refined by Ghose (1961, 1962), using three-dimensional Geiger counter intensity data. Ghose obtained the distribution of Fe and Mg atoms over the four cation sites, M_1 through M_4, by a "trial and error" procedure under the assumption that the temperature factors of these atoms are close to 1.0. At that time, Fischer (1962, 1963) developed the extension of the usual least-squares refinement technique to the refinement of atomic scattering factors. It was, therefore, of interest to apply this method to the problem of mixed populations of cation sites. For this purpose, an f-curve for each site was defined by

$$f(\sin\theta/\lambda) = m_1 \cdot f_1(\sin\theta/\lambda) + m_2 \cdot f_2(\sin\theta/\lambda), \tag{1}$$

where the coefficients m_1 and m_2 were refinable parameters together with the other parameters of the structure, and f_1 and f_2 represented the scattering factor curves of Mg^{2+} and Fe^{2+}, respectively. As a useful approximation for f-curves of any atom i, Silverman and Simonsen (1960) have suggested the expression

$$f_i(\sin\theta/\lambda) = \exp \sum_{n=0}^{6} a_n \cdot (\sin\theta/\lambda)^n \tag{2}$$

which was used to compute f_1 and f_2. The well known full-matrix least-squares refinement program ORXLS written by Busing and Levy (1959) was extended for the purpose of f-refinement.[1]

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Dr. Ghose kindly supplied his data for this work. After three cycles of conventional refinement which brought the R-factor from 0.12 down to 0.10 (based on all 1161 observed F's), six more cycles were computed with 1087 reflections (unobserved F's and a few apparently uncertain ones omitted). During three cycles, only the m_1 and m_2 of each of the four metal sites were varied; in the last three cycles, all conventional parameters plus these 8 "mix parameters" were refined. The R-factor (based on 1087 reflections) dropped from 0.104 to 0.077; a final computation of *all* (1161) F's yielded an R of 0.102.

The results were especially interesting with regard to the correlation effects between the f-curves for Mg^{2+}, Fe^{2+}, and the temperature factor. The sum of the "real" m_1 and m_2 should be 1.00 for each cation equipoint, but this condition had not been used in the refinement. Therefore, due to

TABLE 1. OCCUPANCIES AND TEMPERATURE FACTORS OF THE METAL SITES IN CUMMINGTONITE

Site	m_1 (Mg^{2+}) After Ghose (1961)	m_2 (Fe^{2+}) After Ghose (1961)	m_1' (Mg^{2+})	m_2' (Fe^{2+})	m_1 (Mg^{2+}) Computed with Equations (3, 4)	m_2 (Fe^{2+}) Computed with Equations (3, 4)	B′	B	B (Ghose, 1961)
M_1	0.67	0.33	0.817	−0.087	0.84	0.16	0.047	0.23	1.00
M_2	0.85	0.15	0.708	−0.074	0.95	0.05	0.150	0.27	0.95
M_3	0.67	0.33	0.334	−0.012	0.84	0.16	0.115	0.22	0.99
M_4	0.25	0.75	0.592	0.215	0.13	0.87	0.766	0.88	0.84

the correlation effects mentioned above, the numerical results obtained for each of the four equipoints (m_1' and m_2') appeared to be incorrect at first sight (see middle of Table 1). However, based on the two equations

$$10m_1' + 24m_2' = Z = 10m_1 + 24m_2 \tag{3}$$

$$1.00 = m_1 + m_2 \tag{4}$$

(Z = electron content of a site)

it was easy to compute a "real" m_1 and m_2 for each site. These are listed at the right hand side of Table 1. The sum of all m_1 and m_2 match fairly well with the chemical analysis quoted by Ghose (1961). Thus the "real" m_1 and m_2 are essential.

A similar treatment had to be applied to the numerical temperature factors, B′, obtained directly from the least-squares refinement:

$$(m_1' \cdot f_{Mg} + m_2' \cdot f_{Fe}) \cdot \exp\left(-B' \cdot \frac{\sin^2\theta}{\lambda^2}\right) = (m_1 \cdot f_{Mg} + m_2 \cdot f_{Fe}) \cdot \exp\left(-B\,\frac{\sin^2\theta}{\lambda^2}\right) \tag{5}$$

TABLE 2. ATOMIC PARAMETERS OF CUMMINGTONITE
(Ghose's results in brackets)

	x		y		z		B	
Si_1	0.2874	(0.2880)	0.0842	(0.0842)	0.2746	(0.2747)	0.36	(0.73)
	0.0002	(0.0002)	0.0001	(0.0001)	0.0003	(0.0005)	0.03	(0.05)
Si_2	0.2977	(0.2976)	0.1688	(0.1687)	0.7817	(0.7819)	0.43	(0.76)
	0.0002	(0.0002)	0.0001	(0.0001)	0.0003	(0.0005)	0.03	(0.05)
O_1	0.1135	(0.1129)	0.0874	(0.0878)	0.2087	(0.2056)	0.56	(0.82)
	0.0004	(0.0006)	0.0002	(0.0003)	0.0009	(0.0012)	0.06	(0.08)
O_2	0.1232	(0.1229)	0.1721	(0.1713)	0.7193	(0.7170)	.67	(0.93)
	0.0004	(0.0006)	0.0002	(0.0003)	0.0009	(0.0013)	0.06	(0.08)
O_3	0.1134	(0.1135)	0	0	0.7067	(0.7077)	0.81	(1.13)
	0.0007	(0.0009)	—	—	0.0013	(0.0018)	0.08	(0.12)
O_4	0.3798	(0.3789)	0.2460	(0.2465)	0.7716	(0.7740)	0.89	(1.35)
	0.0005	(0.0006)	0.0002	(0.0003)	0.0009	(0.0013)	0.06	(0.09)
O_5	0.3514	(0.3524)	0.1310	(0.1312)	0.0659	(0.0663)	0.89	(1.35)
	0.0004	(0.0007)	0.0002	(0.0003)	0.0009	(0.0011)	0.06	(0.10)
O_6	0.3488	(0.3484)	0.1185	(0.1185)	0.5597	(0.5616)	1.01	(1.37)
	0.0005	(0.0006)	0.0002	(0.0003)	0.0009	(0.0011)	0.07	(0.10)
O_7	0.3417	(0.3424)	0	0	0.2719	(0.2696)	0.88	(1.17)
	0.0007	(0.0009)	—	—	0.0013	(0.0017)	0.05	(0.12)
M_1	0	0	0.0872	(0.0874)	0.5	(0.5)	see Table 1	
	—	—	0.0001	(0.0001)	—	—		
M_2	0	0	0.1773	(0.1775)	0	0		
	—	—	0.0001	(0.0002)	—	—		
M_3	0	0	0	0	0	0		
	—	—	—	—	—	—		
M_4	0	0	0.2597	(0.2598)	0.5	(0.5)		
	—	—	0.0001	(0.0001)	—	—		

The first line of each equipoint gives the parameters, the second line the standard deviations.

In order to solve for the unknown B's, the F_0's were divided into groups of $\sin\theta/\lambda = 0.025 \ldots 0.075$; $\sin\theta/\lambda = 0.075 \ldots 0.125$, and so on. The number of reflections in each group was used as the weight of an observational equation (5). These were reduced to a normal equation for B and solved in the usual way. The B values obtained in this way were 0.38, 0.36, 0.30, and 0.79 for the four cation sites. They were refined in a final least-square cycle (based on all F_0's) to the values listed in Table 1.

A list of the final parameters including their standard deviations is given in Table 2 together with Ghose's results. Table 3 furnishes important bond lengths. They are not discussed here in detail as they do not differ much from Ghose's results. Furthermore, no standard deviations can be given in Table 3, because the standard errors of the cell constants are not known.

TABLE 3. IMPORTANT ATOMIC DISTANCES
(Ghoses results in brackets)

Si_1-O_1	1.61_9	(1.63_1)	Si_2-O_2	1.62_6	(1.62_6)
O_5	1.61_6	(1.61_9)	O_2	1.62_6	(1.62_6)
O_6	1.63_5	(1.64_2)	O_5	1.64_6	(1.64_6)
O_7	1.61_7	(1.61_9)	O_6	1.64_6	(1.63_8)
mean	1.62_2	(1.62_8)	mean	1.63_4	(1.63_2)
tetrahedron around Si_1:			tetrahedron around Si_2:		
O_1-O_5	2.65_2	(2.65_8)	O_2-O_4	2.75_0	(2.75_5)
O_6	2.66_4	(2.67_9)	O_5	2.65_0	(2.66_3)
O_7	2.65_5	(2.67_0)	O_6	2.65_2	(2.63_6)
O_5-O_6	2.70_3	(2.69_4)	O_4-O_5	2.66_2	(2.65_6)
O_7	2.63_3	(2.63_1)	O_6	2.56_9	(2.57_9)
O_6-O_7	2.63_9	(2.65_3)	O_5-O_6	2.64_7	(2.66_0)
mean	2.65_8		mean	2.65_5	
O_2-O_4	2.81_4		O_1-O_1	2.76_2	
M_1-O_1	2.06_6	(2.07_7) (2×)	M_2-O_1	2.14_1	(2.12_9) (2×)
O_2	2.13_4	(2.11_6) (2×)	O_2	2.08_4	(2.09_4) (2×)
O_3	2.09_9	(2.10_4) (2×)	O_4	2.03_9	(2.02_9) (2×)
M_3-O_1	2.10_6	(2.10_2) (4×)	M_4-O_2	2.17_1	(2.17_7) (2×)
O_3	2.07_5	(2.07_2) (2×)	O_3	2.02_4	(2.04_2) (2×)
			O_6	2.69_5	(2.69_9) (2×)

The emphasis of this paper is to demonstrate the usefulness of the f-refinement technique for the evaluation of mixed populations for more than one atom site, which, in these cases, cannot be computed from chemical analyses. The correlation effects encountered in this work can, at least partly, be overcome by using

$$f(\sin\theta/\lambda) = m_1 \cdot f_1(\sin\theta/\lambda) + (1 - m_1) \cdot f_2(\sin\theta/\lambda) \tag{6}$$

instead of (1), provided that m_1 and m_2 sum up to 1.00. This procedure has been successfully applied to other similar problems (Burnham, 1964; Fischer, 1965).

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The structure factor data have been deposited as Document number 8879 with the ADI Auxiliary Publications Project, Photo-duplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $3.75 for photoprints, or $2.00 for 35 mm microfilm. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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