

Refinement of the margarite structure in subgroup symmetry: correction, further refinement, and comments

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Abstract

The theoretical absorption correction previously applied to intensity data for margarite- $2M_1$ has been found to be incorrect, and has been remedied by application of an empirical correction to new data from the same crystal. Successful convergence was obtained during refinement by using a full matrix of all atoms in a single set, instead of refining pseudosymmetry-related atoms separately. All details of the earlier ordering model in subgroup Cc are confirmed.

Introduction

As a result of refinement of another structure, it was learned that the theoretical absorption program used to correct the intensity data of margarite- $2M_1$ (Guggenheim and Bailey, 1975) was not functioning properly. Because of the importance of the results of the earlier study, a new data set has been collected on the same crystal and absorption corrections have been made by an empirical ψ -scan procedure. Additional refinement of the new data confirms the ordering details of the first study, but suggests that some modifications of the refinement procedure for subgroup symmetry are advisable.

Refinement and results

The intensities of 1,075 reflections were collected in two quadrants with a Syntex $P2_1$ autodiffractometer in the manner described by Guggenheim and Bailey (1975). Four reflections were discarded due to association with strong white radiation streaks. The data were corrected for the Lorentz-polarization factors in the usual manner, and for absorption by comparison with complete ψ -scans (10° increments in ϕ) for selected reflections spaced at 2θ intervals of 5° .

The margarite structure was refined again both in the ideal $C2/c$ symmetry and in Cc subgroup symmetry, using the previously-determined ordered model.

The results of the refinements, after correction for anomalous scattering, are given in Table 1, and the atomic coordinates for the ordered model are given in Table 2. Application of Hamilton's (1965) residual-ratio test indicates that the ordered isotropic model is a significant improvement over the anisotropic disordered model at better than the one percent significance level. The refinement in subgroup symmetry using anisotropic thermal parameters was not successful because three oxygen atoms were non-positive-definite.

It did not prove necessary to vary the parameters of pseudosymmetry-related atoms independently in alternate cycles, as done in the first study, because the refinement converged successfully using a full matrix of all atoms as one set. Because of the pseudosymmetry, some parameter correlation coefficients were high (coefficients between the x and z parameters of pseudosymmetry-related octahedral and tetrahedral cations were between 0.90 and 0.93, whereas coefficients for pseudosymmetry-related oxygen parameters were much lower). Calculated bond lengths and errors were determined using program ORFFE and the correlation matrix from ORFLS.

Mean T —O bond lengths (Table 3) indicate essentially complete ordering of tetrahedral Si and Al. Application of Hazen and Burnham's (1973) equation relating Al^{IV} content to mean T —O distances

Table 1. Results of refinement

	In $C2/c$ (Anisotropic)	In Cc (Isotropic)
R (%)	4.9	4.0
wR (%)	7.7	5.2
data set	1071	1071
variable parameters	87	75
goodness-of-fit	2.10	1.41

for micas yields a total Al^{IV} content of 1.883 for the crystal, in excellent agreement with the composition $Si_{2.11}Al_{1.89}$ given by microprobe analysis. As in the first study, a slightly asymmetric distribution of Al^{IV} between the two tetrahedral sheets of the 2:1 layer is indicated by the bond lengths, $1.006Al^{IV}$ in the upper sheet and $0.877Al^{IV}$ in the lower sheet. This asymmetry of $0.129Al^{IV}$ is less than the value of 0.203 found in the first study. The difference between the sums of the mean $T-O$ distances in the two sheets is 0.021 Å, which amounts to 3.0σ according to an analysis of the errors involved for the present study. The upper tetrahedral sheet is slightly thicker (by 0.030 Å) and has a larger rotation angle (by 0.4°) than the lower sheet. These differences also are consistent with more Al^{IV} in the upper sheet. The difference in thickness amounts to 3.8σ for the errors involved, and the difference in tetrahedral rotation amounts to 4.2σ . All three comparisons, therefore, indicate that the asymmetry is real. All conclusions in the earlier paper remain valid.¹

¹ Tables of F_o and F_c , $C2/c$ atomic parameters, and Cc bond lengths and angles for the present study may be obtained by ordering document AM-77-060 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit \$1.00 in advance for the microfiche.

Table 2. Atomic coordinates in space group Cc

	x	y	z	B
Ca	0.00	0.0933(1)	0.25	0.80(2)
M(2)	0.7449(9)	0.9177(4)	0.9996(2)	0.53(5)
M(3)	0.2488(9)	0.0858(3)	-0.0003(2)	0.44(5)
T(1)	0.4623(8)	0.9264(4)	0.1422(2)	0.46(4)
T(2)	0.4544(7)	0.2567(3)	0.1445(2)	0.22(4)
T(11)	0.5336(8)	0.0739(4)	0.8551(2)	0.59(4)
T(22)	0.5467(8)	0.7440(4)	0.8576(2)	0.89(5)
O(1)	0.962(1)	0.4445(8)	0.0527(3)	0.5(1)
O(2)	0.395(1)	0.2544(7)	0.0590(4)	0.5(1)
OH(1)	0.449(1)	0.5696(8)	0.0507(4)	0.4(1)
O(3)	0.366(1)	0.0974(7)	0.1781(4)	0.8(1)
O(4)	0.267(1)	0.7782(7)	0.1682(4)	0.6(1)
O(5)	0.289(1)	0.3924(7)	0.1788(4)	0.6(1)
O(11)	0.045(1)	0.5614(8)	0.9401(4)	0.6(1)
O(22)	0.618(1)	0.7502(7)	0.9468(4)	0.5(1)
OH(11)	0.543(1)	0.4396(9)	0.9482(4)	0.8(1)
O(33)	0.639(1)	0.9172(7)	0.8236(4)	0.5(1)
O(44)	0.712(1)	0.2149(7)	0.8323(4)	0.6(1)
O(55)	0.737(1)	0.6062(7)	0.8217(4)	0.7(1)

Table 3. Tetrahedral bond lengths (Å)

For T(1)		For T(2)		For T(11)		For T(22)	
0(1)	1.722(7)	0(2)	1.636(7)	0(11)	1.628(8)	0(22)	1.713(7)
0(3)	1.749(7)	0(3)	1.629(7)	0(33)	1.622(7)	0(33)	1.744(7)
0(4)	1.746(7)	0(4)	1.627(6)	0(44)	1.627(7)	0(44)	1.747(7)
0(5)	1.771(7)	0(5)	1.640(7)	0(55)	1.613(7)	0(55)	1.738(7)
Mean	1.747	Mean	1.633	Mean	1.623	Mean	1.736
	(0.853 Å)		(0.153 Å)		(0.092 Å)		(0.785 Å)

Discussion of procedure

Comparison of the present refinement of the margarite structure in the ideal space group $C2/c$ with the previous refinement incorporating an incorrect absorption correction shows a decrease of all temperature factors by about 0.2 \AA^2 but little effect on positional parameters. For this reason the observed differences in fractional atomic coordinates between the two refinements in subgroup symmetry Cc , an average of 0.001 along each axis or approximately one to two standard deviations (Table 2), must be attributed to the different methods of refinement. Furthermore, the success of full matrix refinement in pseudosymmetric structures after DLS modeling, as in margarite (this study), zinnwaldite (Guggenheim and Bailey, 1977), and others (e.g. Dollase and Baur, 1976), suggests that separating pseudosymmetrically-related parameters in alternate cycles of refinement is unnecessary as well as inadvisable. It is conceivable on theoretical grounds that separation of the two sets of parameters could lead to a structure that is only an approximation to the true one.

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