

## Refinement of the Margarite Structure in Subgroup Symmetry

STEPHEN GUGGENHEIM AND S. W. BAILEY

Department of Geology and Geophysics  
University of Wisconsin-Madison, Madison, Wisconsin 53706

### Abstract

The crystal structure of margarite- $2M_1$  from Chester County, Pennsylvania, has been refined as an ordered derivative structure in subgroup  $Cc$  of the ideal space group  $C2/c$ . Because of the high pseudosymmetry involved, successful refinement by least-squares required initial movement of atomic parameters away from those of the disordered phase towards those of the possible ordered models predicted by a distance least-squares program. Ordering of tetrahedral Si and Al is nearly complete in a pattern that violates centrosymmetry between the two tetrahedral sheets within a 2:1 layer. Compositionally similar tetrahedra in adjacent sheets are related instead by a pseudo two-fold axis that extends laterally through the octahedral Al atoms and is normal to the direction of intralayer shift. The two tetrahedral sheets differ significantly in Si,Al contents. A similar ordering pattern is theoretically possible in muscovite- $2M_1$  also, but was not found to be adopted by muscovite from the Diamond mine, South Dakota.

### Introduction

Margarite, the dioctahedral brittle mica, has been recognized only as the  $2M_1$  form. Takéuchi (1965) refined the structure for a specimen from Chester, Massachusetts, using three dimensional film data. He found the tetrahedral Si,Al cations to be disordered over the two non-equivalent sites  $T(1)$  and  $T(2)$  of the ideal space group  $C2/c$ . Since then, Gatineau and Méring (1966) because of the absence of diffuse X-ray scattering and Farmer and Velde (1973) because of the sharpness of the infrared spectra and the absence of Al–O–Al vibrations have suggested that margarite should be ordered.

One way to resolve the conflicting evidence above, as pointed out by Farmer and Velde, is to assume that the tetrahedral cations are ordered in a lower subgroup symmetry. Because of systematic absences, the only possible subgroup is  $Cc$ . This paper reports a successful refinement of margarite as an ordered derivative structure in space group  $Cc$ . Because of the similarities of the margarite and muscovite structures, the  $2M_1$  form of muscovite also was reexamined in subgroup symmetry.

### Experimental

A margarite crystal  $0.32 \times 0.30 \times 0.02$  mm in size from Corundum Hill near Unionville, Chester County, Pennsylvania, was chosen for study because of its sharp reflections and lack of streaking due to

stacking faults. Table 1 presents the results of electron microprobe analysis, as averaged for two adjacent crystals. Scanning electron microscopic (SEM) analysis indicates that the crystals are homogeneous and that all elements have been accounted for that are present within the detection limits of the instrument.

Intensities of 1,071 independent, non-zero reflections were measured with a Syntex  $P\bar{1}$  autodiffractometer in the variable-scan speed mode (Table 2). Graphite-monochromatized  $MoK\alpha$  radiation was used, and only reflections for which  $I > 2\sigma(I)$  were considered observed. Two reflections were monitored after every 50 measurements in order to check electronic stability. The integrated intensity  $I$  was calculated from  $I = [S - (B_1 + B_2)/B_r]T_r$ , where  $S$  is the scan count,  $B_1$  and  $B_2$  the background counts,  $B_r$  the ratio of background time to scan time, and  $T_r$  the  $2\theta$  scan rate in degrees per minute.  $\sigma(I)$  is defined as equal to  $T_r[S + (B_1 + B_2)/B_r^2 + q(I)^2]^{1/2}$ , where  $q$  is equal to 0.003, an estimate of the standard error squared. Intensities then were corrected for Lorentz-polarization effects and for absorption. Table 3 lists the cell parameters based on least squares refinement of 15 independent high  $2\theta$  reflections.

### Refinement

As a first step, the atomic coordinates of Takéuchi (1965) were refined by the least-squares program

TABLE 1. Electron Microprobe Analysis of Margarite from Chester County, Pennsylvania

Weight percent		Cations per 22 positive charges		
SiO <sub>2</sub>	31.58	Si	2.110	} 4.000 <sup>IV</sup>
Al <sub>2</sub> O <sub>3</sub>	49.29	Al	3.882	
FeO	0.21	Fe <sup>2+</sup>	0.012	} 2.036 <sup>VI</sup>
MgO	0.32	Mg	0.032	
CaO	11.35	Ca	0.812	} 1.011 <sup>XII</sup>
Na <sub>2</sub> O	1.46	Na	0.190	
K <sub>2</sub> O	0.10	K	0.009	
Sum of oxides	94.31			

ORFLS using the new data in the ideal space group  $C2/c$ . The residual  $R_1$  converged to 8.4 percent after the scattering factors were adjusted for the composition indicated by microprobe analysis. Bond lengths calculated at this stage confirmed Takéuchi's earlier finding of tetrahedral disorder in the ideal space group.

Because of the high pseudosymmetry when subgroup  $Cc$  is assumed, one cannot merely expand the parameter set over the inversion centers of  $C2/c$  and obtain reasonable results by least-squares refinement from the coordinates of the disordered model. Even if the parameters of pseudosymmetry-related atoms are refined independently, it was found that the  $R$  factor increased and convergence was not obtained. It proved necessary to move the atoms away from their pseudosymmetric positions by postulating their approximate positions for all feasible ordered models and then to refine each model separately to determine the correct one.

In  $Cc$  symmetry the two tetrahedral sheets within the 2:1 layer no longer are equivalent, and two different ordering models may be postulated for margarite that are consistent with disorder in the parent space group but full order in the subgroup. Approximate atomic coordinates for each ordered model were obtained by using the distance least-squares program OPTDIS of W. A. Dollase (University of California, Los Angeles). The coordinates for the disordered structure were used as input to this program along with the bond lengths and bond strengths that would be expected in the ordered models between first and second nearest neighbors.

Subsequent refinement by ORFLS showed that the procedure of producing artificially ordered models removed the previous problems of high correlations and lack of convergence. It was, however, still neces-

sary to vary the parameters of pseudosymmetry-related atoms independently. After initial increase in  $R_1$  to about 10 percent, both ordered models converged to better residuals than for the disordered model. It was evident, however, that one ordered model could be rejected because it was moving towards the disordered model. Bonds around the postulated Al<sup>IV</sup> became smaller and those around the postulated Si<sup>IV</sup> became larger. This model was implausible for crystallochemical reasons in addition, as it segregated Si and Al in separate tetrahedral sheets. The second model retained its postulated ordering pattern during refinement and converged to a residual of 7.5 percent with isotropic  $B$  values. Application of Hamilton's (1965) residual ratio test indicates that this ordered model is a significant improvement over the disordered model at better than the 1 percent significance level (Table 4).

An electron density difference map did not show the position of the hydrogen atom, but did show the presence of a density of approximately one electron in the vacant octahedral position  $M(1)$  in accord with the microprobe analysis of slightly over 2.0 octahedral atoms. Two final cycles of isotropic refinement incorporating this one electron in  $M(1)$  plus the hydrogen atom position calculated by Giese (in preparation) and using corrections for anomalous scattering did not affect the residual significantly. Table 5 lists the final atomic coordinates and isotropic temperature factors, as compared with Takéuchi's disordered structure.

### Discussion

The basic structure determined in this study is very similar to that of Takéuchi, except for the distortion to lower symmetry resulting from the ordering scheme. Pertinent data are summarized in Table 6. Table 7 presents bond length and angle calculations. No standard deviations of bond lengths are presented because only half of the atomic coordinates were varied in any one refinement cycle in order to reduce correlation effects. A correlation matrix involving all coordinates cannot be obtained, therefore, although the results from the two sets of refinements must be interrelated because the same data set was used for each. The standard deviations of the bond lengths are believed to be similar (approximately 0.003 to 0.005 Å) to those obtained in other isotropic refinements using diffractometer data with a similar ratio of number of reflections to variable parameters. Differences in isotropic  $B$  values for pseudosymmetry-related atoms (Table 5) are believed to be

TABLE 2. Observed and Calculated Structure Amplitudes

$k$	$l$	$10P_o$	$10P_c$	$k$	$l$	$10P_o$	$10P_c$	$k$	$l$	$10P_o$	$10P_c$	$k$	$l$	$10P_o$	$10P_c$	$k$	$l$	$10P_o$	$10P_c$	$k$	$l$	$10P_o$	$10P_c$	$k$	$l$	$10P_o$	$10P_c$	$k$	$l$	$10P_o$	$10P_c$	$k$	$l$	$10P_o$	$10P_c$																												
$h = 0$																																																															
0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232	0	4	271	345	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
0	4	2039	1907	6	-12	588	551	1	-15	746	762	7	-16	109	50	2	-25	390	300	10	-6	586	533	5	-18	108	87	4	0	392	385	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
0	8	230	182	6	-14	743	684	1	-16	181	157	7	-17	413	440	2	-26	331	300	10	-7	162	129	5	-19	184	189	4	0	171	160	0	4	271	345	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
0	10	2943	1971	6	-15	165	161	1	-17	276	300	7	-18	147	121	4	0	516	537	10	-8	300	277	5	-21	310	307	4	-1	363	308	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
0	14	694	719	6	-15	129	160	1	-19	117	97	7	-20	162	124	4	0	200	205	10	-9	155	144	5	-22	191	189	4	-1	363	308	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
0	16	991	1030	6	-16	695	662	1	-20	117	97	7	-21	260	276	4	-2	209	209	10	-10	146	165	5	-22	191	189	4	-1	363	308	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
0	18	153	186	6	-17	111	83	1	-21	226	256	7	-22	239	247	4	-3	467	473	10	-12	345	316	7	-23	238	221	4	-1	363	308	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
0	20	1133	1091	6	-19	147	150	1	-22	437	458	7	-23	220	207	4	-3	562	536	10	-14	562	535	7	-24	302	278	7	-4	302	278	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
0	22	761	758	6	-19	116	153	1	-22	333	295	7	-24	209	246	4	-4	642	607	10	-16	642	607	7	-25	234	233	7	-3	234	233	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
0	26	386	363	6	-20	901	844	1	-22	256	256	7	-25	285	261	4	-5	532	541	10	-18	562	535	7	-26	302	278	7	-4	302	278	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
2	0	398	346	6	-20	903	845	1	-23	447	467	7	-26	201	214	4	-6	682	698	10	-20	682	698	7	-27	312	288	7	-5	312	288	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
2	1	221	241	6	-21	172	173	1	-24	398	404	7	-27	149	114	4	-6	828	831	1	0	100	73	7	-28	312	288	7	-6	312	288	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
2	-1	282	247	6	-21	134	175	1	-24	427	434	7	-28	201	214	4	-7	160	170	1	0	100	73	7	-29	312	288	7	-7	312	288	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
2	2	550	453	6	-22	560	538	1	-25	285	261	7	-29	170	179	4	-8	244	246	1	-1	190	216	7	-30	312	288	7	-8	312	288	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
2	-3	562	442	6	-22	594	538	1	-26	154	132	7	-30	179	179	4	-9	214	213	1	-1	190	216	7	-31	312	288	7	-9	312	288	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
2	3	904	770	6	-23	264	3	0	366	366	6	-2	191	184	4	-10	214	213	1	-1	190	216	7	-32	312	288	7	-10	312	288	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232	
2	-4	882	766	6	-1	175	168	3	-1	2261	2121	9	-3	755	691	4	-9	248	264	1	0	100	73	7	-33	312	288	7	-11	312	288	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
2	4	1176	1072	6	-1	161	177	3	-1	1115	1128	9	-4	118	100	4	-10	384	394	1	-3	609	616	7	-34	312	288	7	-12	312	288	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
2	-5	1509	1384	6	-2	403	396	3	-4	172	180	9	-5	308	276	4	-12	492	511	1	-5	904	931	7	-35	312	288	7	-13	312	288	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
2	5	1509	1384	6	-2	403	396	3	-4	172	180	9	-5	308	276	4	-12	492	511	1	-5	904	931	7	-35	312	288	7	-13	312	288	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
2	-6	286	262	6	-3	403	396	3	-4	172	180	9	-5	308	276	4	-12	492	511	1	-5	904	931	7	-35	312	288	7	-13	312	288	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
2	6	292	266	6	-3	403	396	3	-4	172	180	9	-5	308	276	4	-12	492	511	1	-5	904	931	7	-35	312	288	7	-13	312	288	0	2	304	185	6	-11	413	414	1	-14	628	636	7	-15	386	372	2	-23	238	221	10	-5	534	487	5	17	207	199	2	-20	222	232
2	-7	628	611	6	-5	832</																																																									

TABLE 2, Continued

k	F	10Pb	10Pc	k	Z	10Pb	10Pc	k	Z	10Pb	10Pc	k	Z	10Pb	10Pc
3	-2	162	178	5	10	369	382	0	-2	1130	1311	4	1	235	230
3	3	603	651	5	-10	227	220	0	-3	115	0	4	2	411	423
1	-3	1035	1096	5	-11	391	392	0	4	295	314	4	-2	109	80
3	-4	125	92	5	12	540	582	0	6	707	783	4	3	453	448
3	5	505	524	5	13	136	163	0	-6	153	166	4	4	134	128
3	-5	509	518	5	-13	310	327	0	8	459	554	4	-4	284	287
3	7	406	493	5	14	301	353	0	10	215	219	4	-5	195	186
3	-7	200	206	5	-14	412	417	0	-10	409	530	4	-6	448	444
3	9	856	1001	5	-15	275	270	0	-12	450	500	4	-7	292	273
3	-9	231	251	5	-16	592	601	0	-14	258	382	4	8	158	184
3	11	660	751	5	-17	220	193	0	-16	410	423	4	-8	178	142
3	-11	1117	1199	7	1	474	456	2	0	106	128	4	-10	285	296
3	12	108	90	7	-1	235	217	2	1	408	468	6	0	211	160
3	-13	131	152	7	2	243	258	2	2	267	281	6	-1	195	164
3	16	132	137	7	-2	125	109	2	-2	157	219	6	-2	1026	914
3	-17	314	343	7	4	303	277	2	3	639	695	6	-3	223	184
3	-19	622	591	7	-4	130	133	2	-3	242	255	6	4	315	248
5	0	276	284	7	5	334	318	2	4	207	227	6	5	128	129
5	1	161	149	7	-5	167	181	2	-4	528	594	6	-5	130	81
5	-1	334	317	7	-6	429	401	2	5	152	184	6	-7	134	110
5	2	342	365	7	7	168	175	2	6	185	179	6	-8	458	422
5	-2	236	237	7	-7	464	456	2	-6	381	427	6	-8	458	422
5	-3	154	124	7	-8	198	193	2	7	118	155	6	-9	128	89
5	-4	290	304	7	9	181	178	2	9	138	173	1	0	256	303
5	5	176	174	7	-9	177	137	2	-9	265	305	1	-1	212	258
5	6	209	203	7	-12	171	143	2	10	285	331	1	2	187	169
5	-6	398	405	7	-13	222	190	2	-10	302	306	1	-3	277	373
5	7	478	503	7	11	157	185	2	11	157	185	1	-3	186	215
5	-7	278	302	7	-11	157	185	2	-11	157	185	1	-5	149	147
5	8	110	97	7	-13	150	180	2	-13	150	180	1	-6	346	373
5	9	489	490	7	14	164	182	2	14	164	182	1	-7	270	300
5	-9	395	387	7	-14	164	182	2	-15	241	274	1	-8	434	405
5	9	489	490	7	15	241	274	2	15	241	274	1	-8	434	405

artifacts resulting from separating the atoms into two sets during refinement.

The resultant mean  $T$ -O bond lengths of 1.640 and 1.747 Å in one tetrahedral sheet and 1.624 and 1.730 Å in the other sheet indicate (1) nearly complete ordering for the composition  $\text{Si}_{2.11}\text{Al}_{1.89}$  given by microprobe analysis, and (2) a slightly asymmetric distribution of Si,Al between the two sheets. The ordering pattern is of special interest, and is illustrated in Figure 1. Tetrahedra in the lower tetrahedral sheet (dashed) that would be related by inversion centers (small open circles) to tetrahedra in the upper sheet (full line) of the same 2:1 layer in the ideal space group  $C2/c$  prove to be compositionally different when refined in subgroup  $Cc$ . A pseudo two-fold axis normal to the direction of intralayer shift and passing laterally through the two octahedral Al atoms can be seen to relate compositionally similar tetrahedra in the two sheets instead. Güven (1971a) has pointed out for muscovite- $2M_1$  that ordering may be inhibited in the ideal space group  $C2/c$  because ordering would cause two apical oxygens (of Al-rich tetrahedra) along the same octahedral shared edge to be electrostatically unbalanced. This unstable situation is avoided in muscovite- $3T$ , where the two tetrahedral sheets are related by a true two-fold axis instead of by inversion centers and where ordering of

TABLE 3. Unit Cell Parameters

	Takéuchi (1965)	This study
a	5.123 Å	5.1038(4) Å
b	8.886	8.8287(7)
c	19.221	19.148(1)
$\beta$	95.5°	95.46(3)

TABLE 4. Results of Refinement

	In $C2/c$	In $Cc$
R (%)	8.4	7.5
wR	10.7	9.5
variable parameters	40	76
data set	1,071	1,071

tetrahedral cations has been confirmed within the ideal space group  $P3_12$ . The  $Cc$  ordered pattern in margarite- $2M_1$  also avoids two unbalanced oxygens on the same octahedral shared edge, but the two-fold axis relating compositionally similar tetrahedra in the two tetrahedral sheets does not hold for the structure as a whole.

Tetrahedral cation occupancies as calculated from the mean  $T$ -O values with the regression equation given by Hazen and Burnham (1973) for micas are listed in Table 7. The total tetrahedral Al calculated in this manner (1.895 Al) is in excellent agreement with that indicated by microprobe analysis (1.890 Al). There is a significant difference in calculated tetrahedral compositions for the two tetrahedral sheets within the 2:1 layer (1.049 and 0.846) due to the fact that ordering is more complete in the  $T(1)$  and  $T(11)$  sites than in the  $T(2)$  and  $T(22)$  sites. The sheets are internally consistent structurally in that the more Al-rich sheet also has a greater thickness and a slightly larger rotation angle  $\alpha_{tet}$  (Table 6). The Al-rich tetrahedra are slightly flattened (larger  $\tau$ ) relative to their Si-rich counterparts, due to apical  $T$ -O bonds shorter than mean basal  $T$ -O bonds (Tables 6, 7). The bonds from the octahedral Al to the under-saturated apical oxygens attached to Al-rich tetrahedra are shorter than those to apical oxygens of Si-rich tetrahedra. The oxygen configurations about the octahedral Al are distorted in nearly the same way as in muscovite- $2M_1$ , as described by Takeda and Ross (1975). Octahedral edges O(2)-O(22) and O(1)-OH(11) are nearly parallel to the  $x$ -axis, but OH(1)-O(11) is slightly more oblique than reported for muscovite.

### Possible Ordering in Muscovite

The most detailed refinements of the  $2M_1$  form of muscovite in its ideal space group  $C2/c$  all have shown similar mean  $T$ -O bond lengths as a consequence of disorder of the tetrahedral cations (e.g., Burnham and Radoslovich, 1964; Güven, 1971b). Because of the similarity of muscovite- $2M_1$  to margarite- $2M_1$ , the question immediately arises whether muscovite also is ordered in subgroup symmetry  $Cc$ . Muscovite differs from margarite in its

TABLE 5. Atomic Coordinates for Margarite

	Takéuchi (1965) C2/c				This study Cc				
	x	y	z	B	x	y	z	B	
Ca(1)	0.00	0.0942	0.25	1.14	0.00	0.0932(2)	0.25	1.02(3)	
<sup>a</sup> M(1)					0.2479	0.2507	0.4996	---	
M(2)					0.7469(7)	0.9187(4)	0.9997(2)	0.73(6)	
M(3)	0.2518	0.0815	0.00	0.29	0.2510(7)	0.0863(4)	0.9998(2)	0.55(6)	
<sup>b</sup> T(1)	0.4628	0.9283	0.1432	0.53	0.4647(7)	0.9285(4)	0.1416(2)	0.99(7)	
T(11)					0.5364(6)	0.0752(3)	0.8549(2)	0.58(5)	
T(2)	0.4543	0.2575	0.1438	0.71	0.4567(6)	0.2572(3)	0.1444(2)	0.61(5)	
T(22)					0.5500(7)	0.7437(4)	0.8573(2)	0.97(6)	
O(1)	0.9547	0.4430	0.0553	1.25	0.960(2)	0.4436(9)	0.0512(4)	1.0(1)	
O(11)					0.046(2)	0.5585(8)	0.9390(4)	0.5(1)	
O(2)	0.3874	0.2524	0.0569	1.12	0.395(2)	0.2540(9)	0.0568(4)	0.9(1)	
O(22)					0.619(2)	0.7489(9)	0.9447(4)	0.7(1)	
O(3)	0.3597	0.0884	0.1788	0.40	0.367(2)	0.0974(9)	0.1775(5)	1.1(1)	
O(33)					0.641(2)	0.9167(9)	0.8226(4)	0.6(1)	
O(4)	0.2786	0.7839	0.1695	1.46	0.266(2)	0.7784(9)	0.1665(4)	0.5(1)	
O(44)					0.711(2)	0.214(1)	0.8304(4)	1.1(1)	
O(5)	0.2700	0.3903	0.1797	0.45	0.287(2)	0.3926(8)	0.1785(4)	0.4(1)	
O(55)					0.737(2)	0.608(1)	0.8211(5)	1.4(2)	
OH(1)	0.4492	0.5624	0.0505	0.87	0.448(2)	0.5693(8)	0.0488(4)	0.4(1)	
OH(11)					0.543(2)	0.4417(9)	0.9468(4)	1.0(1)	
<sup>c</sup> H(1)					0.397	0.637	0.083	0.78	
H(11)					0.603	0.363	0.917	0.78	

<sup>a</sup>Coordinates for the "vacant site" M(1) were obtained from an electron density difference map. These are unrefined coordinates included as fixed values in the final stages of refinement.

<sup>b</sup>Pseudosymmetry-related atoms in one tetrahedral sheet are indicated by doubling the last digit of the symbol for the corresponding atom in the other sheet.

<sup>c</sup>Coordinates for the hydrogen atom are from Giese (1975), and were treated in a fashion similar to those of M(1).

tetrahedral composition of Si<sub>3</sub>Al instead of Si<sub>2</sub>Al<sub>2</sub>. Because of this difference, only one ordered model is possible in subgroup Cc that would be disordered when averaged over the sites of the parent space group C2/c, and this is the same model that is adopted in margarite. The maximum degree of order then possible is to have alternation of Si and Si<sub>0.5</sub>Al<sub>0.5</sub> in adjacent tetrahedra.

This ordered model for muscovite-2M<sub>1</sub> has been tested using the neutron diffraction data of Rothbauer (1971) for a pegmatitic muscovite from the Diamond mine, South Dakota. The 774 reflections from Rothbauer were used to refine the ordered model in subgroup Cc by exactly the same procedure as for margarite. The coordinates refined smoothly away from those of the ordered model back to those of the disordered model, i.e., back to coordinates consistent with space group C2/c. It can be concluded that the ordered model of margarite-2M<sub>1</sub> does not extend to muscovite-2M<sub>1</sub> and that avoidance of electrostatically unbalanced oxygens along the same octahedral shared edge is not sufficient driving force

TABLE 6. Pertinent Structural Details for Margarite

	Takéuchi (1965)	This study
$\alpha_{tet}$ (°)	20.4	<sup>b</sup> 20.76, 20.64 (20.70)
$\tau_{tet}$ (°)	111.5	Si: 110.78, 110.41 (110.73) Al: 110.83, 110.88
$\psi_{oct}$ (°)	58.9	58.8
Sheet thickness (Å)		<sup>b</sup> 2.291, 2.234 (2.263)
tetrahedral	2.330	
octahedral	2.074	2.074
Interlayer separation (Å)	2.832	2.868
Basal oxygen $\Delta z_{ave}$ (Å)	0.19	0.20
Mean bond lengths (Å)		
T--O	1.692	T(1)=1.747, T(11)=1.624 (1.686)
	1.702	T(2)=1.640, T(22)=1.730 (1.685)
M(2,3)--O,OH	1.912	1.902, 1.910 (1.906)
Ca--O (inner)	2.458	2.455
(outer)	3.427	3.428

<sup>a</sup>The amount of tetrahedral rotation  $\alpha_{tet}$  may be calculated from  $\alpha = 1/2 |120^\circ - \text{mean } O_b-O_b-O_b \text{ angle}|$

<sup>b</sup>The value referring to the more Al-rich tetrahedral sheet is given first. The average values are in parentheses.

<sup>c</sup>The tetrahedral angle  $\tau$  is defined as  $\tau = \angle_{apical} \text{--} T \text{--} O_{basal}$  ideally  $109^\circ 28'$ .

<sup>d</sup>The mean octahedral angle  $\psi$ , ideally  $54^\circ 44'$ , is calculated from  $\cos \psi = \text{oct. thickness}/2(M-O,OH)$ , where  $M-O,OH$  is the mean of all octahedral cation to anion distances, including the vacant site.

TABLE 7. Interatomic Distances and Angles

Bond lengths (Å)			Bond angles (°)		
around T(1)					
T(1)--O(1) <sup>a</sup>	1.733	O(1)--O(3)	2.853	O(1)--O(3)	110.69
O(3)	1.735	O(4)	2.898	O(4)	112.02
O(4)	1.762	O(5)	2.856	O(5)	109.79
O(5)	1.758	O(3)--O(4)	2.868	O(3)--O(4)	110.18
Mean	1.747	O(5)	2.803	O(5)	106.73
(= 0.853 Al)		O(4)--O(5)	2.833	O(4)--O(5)	107.23
		Mean	2.852	Mean	109.44
around T(11)					
T(11)--O(11) <sup>a</sup>	1.614	O(11)--O(33)	2.643	O(11)--O(33)	108.64
O(33)	1.640	O(44)	2.698	O(44)	113.40
O(44)	1.614	O(55)	2.661	O(55)	110.30
O(55)	1.629	O(33)--O(44)	2.654	O(33)--O(44)	109.35
Mean	1.624	O(55)	2.663	O(55)	109.16
(= 0.098 Al)		O(44)--O(55)	2.588	O(44)--O(55)	105.90
		Mean	2.651	Mean	109.46
around T(2)					
T(2)--O(2) <sup>a</sup>	1.677	O(2)--O(3)	2.708	O(2)--O(3)	109.98
O(3)	1.629	O(4)	2.699	O(4)	110.53
O(4)	1.606	O(5)	2.734	O(5)	110.71
O(5)	1.647	O(3)--O(4)	2.612	O(3)--O(4)	107.65
Mean	1.640	O(5)	2.639	O(5)	107.30
(= 0.196 Al)		O(4)--O(5)	2.674	O(4)--O(5)	110.57
		Mean	2.678	Mean	109.46
around T(22)					
T(22)--O(22) <sup>a</sup>	1.676	O(22)--O(33)	2.779	O(22)--O(33)	108.56
O(33)	1.747	O(44)	2.889	O(44)	113.56
O(44)	1.777	O(55)	2.790	O(55)	110.52
O(55)	1.719	O(33)--O(44)	2.845	O(33)--O(44)	107.68
Mean	1.730	O(55)	2.772	O(55)	106.17
(= 0.748 Al)		O(44)--O(55)	2.865	O(44)--O(55)	110.04
		Mean	2.823	Mean	109.42
Ca(1)					
Ca(1)--O(3)	2.436		3.391		
O(4)	2.509		3.541		
O(5)	2.430		3.375		
O(33)	2.404		3.432		
O(44)	2.470		3.514		
O(55)	2.479		3.313		
Mean (inner)	2.455	(outer)	3.428		
M(2)					
M(2)--O(1)	1.853	O(1)--O(2)	2.774	T(1) to T(2)	
O(2)	1.930	O(22)	2.844	around O(3)	119.22
OH(1)	1.877	O(11)	2.730	around O(4)	126.38
O(11)	1.927	O(2)--OH(1)	2.803	around O(5)	118.56
O(22)	1.912	OH(11)	2.839	Mean	121.39
OH(11)	1.910	O(11)--OH(1)	2.801		
Mean	1.902	O(22)	2.760	T(11) to T(22)	
		OH(11)	2.737	around O(33)	119.63
		O(22)--OH(11)	2.753	around O(44)	125.17
		Mean	2.782	around O(55)	119.89
		(unshared)		Mean	121.56
		O(1)--O(11)	2.451		
		O(2)--O(22)	2.455		
		OH(1)--OH(11)	2.346		
		Mean (shared)	2.417		
M(3)					
M(3)--O(1)	1.870	O(1)--O(2)	2.764		
O(2)	1.942	OH(1)	2.837		
OH(1)	1.890	OH(11)	2.778		
O(11)	1.999	O(2)--O(11)	2.997		
O(22)	1.870	OH(1)	2.797		
OH(11)	1.893	O(11)--O(22)	2.758		
Mean	1.911	OH(11)	2.776		
		O(22)--OH(1)	2.753		
		OH(11)	2.740		
		Mean	2.800		
		(unshared)			

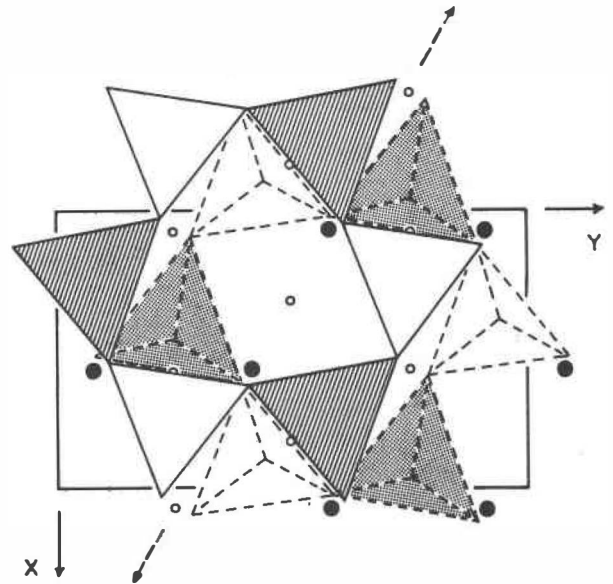
<sup>a</sup>Apical oxygen

FIG. 1. Tetrahedral ordering pattern within upper 2:1 layer of margarite-2M<sub>1</sub> in subgroup Cc. Al-rich tetrahedra = ruled lines and dots; octahedral Al = solid circles; inversion centers of ideal space group = small open circles; pseudo 2-fold axis = dashed arrows. From Bailey (1975).

It is encouraging to note here, as in the margarite refinement, that use of the ordered-model approach to avoid pseudosymmetry effects does not bias the least-squares refinement towards the ordered model so greatly that an incorrect model cannot be identified.

### Acknowledgments

We are indebted to Dr. W. A. Dollase for use of program OPTDIS, to J. T. Cheney for the microprobe analyses, to Dr. R. Rothbauer for making his neutron diffraction data available, and to Dr. L. F. Dahl for allowing use of the Syntex autodiffractometer. This research has been supported in part by the Earth Sciences Section, National Science Foundation, NSF grant GA-34918, and in part by grant AC2-4899 from the Petroleum Research Fund, administered by the American Chemical Society.

### References

- BAILEY, S. W. (1975) Cation ordering and pseudosymmetry in layer silicates. *Am. Mineral.* **60**, 175-187.
- BURNHAM, C. W., AND E. W. RADOSLOVICH (1964) Crystal structures of coexisting muscovite and paragonite. *Carnegie Inst. Wash. Year Book*, **63**, 232-236.
- FARMER, V. C., AND B. VELDE (1973) Effects of structural order and disorder on the infrared spectra of brittle micas. *Mineral. Mag.* **39**, 282-288.
- GATINEAU, L., AND J. MÉRING (1966) Relations ordre-désordre dans les substitutions isomorphiques des micas. *Bull. Groupe Franc. Argiles*, **18**, 67-74.
- GÜVEN, N. (1971a) Structural factors controlling stacking sequences in dioctahedral micas. *Clays Clay Minerals*, **19**, 159-165.

for the ordering in this case. Possible adoption by muscovite of symmetry still lower than Cc, which would require violation of systematic absences and would permit complete order, has not been investigated.

- (1971b) The crystal structures of  $2M_1$  phengite and  $2M_1$  muscovite. *Z. Kristallogr.* **134**, 196–212.
- HAMILTON, W. C. (1965) Significance tests on the crystallographic  $R$  factor. *Acta Crystallogr.* **18**, 502–510.
- HAZEN, R. M., AND C. W. BURNHAM (1973) The crystal structures of one-layer phlogopite and annite. *Am. Mineral.* **58**, 889–900.
- ROTHBAUER, R. (1971) Untersuchung eines  $2M_1$  muskovits mit neutronenstrahlen. *Neues Jahrb. Mineral. Monatsh.*, 143–154.
- TAKEDA, H., AND M. ROSS (1975) Mica polytypism: Dissimilarities in the crystal structures of coexisting  $1M$  and  $2M_1$  biotite. *Am. Mineral.* **60**, 1030–1040.
- TAKÉUCHI, Y. (1965) Structures of brittle micas. *Clays Clay Minerals*, **13**, 1–25.

*Manuscript received, February 17, 1975; accepted for publication, June 20, 1975.*