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Refinement of the Margarite Structure in Subgroup Symmetry

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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 *C*2/*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 *C*2/*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 × 0.30 × 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 Mo$K\alpha$ 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 2θ 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 2θ 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_2	31.58	Si	2.110		4.000^{IV} (Si + 1.890)
Al_2O_3	49.29	Al	3.882	1.890 1.992	
FeO	0.21	Fe^{2+}	0.012		2.036^{VI} (1.992 + Fe^{2+} + Mg)
MgO	0.32	Mg	0.032		
CaO	11.35	Ca	0.812		1.011^{XII} (Ca + Na + K)
Na_2O	1.46	Na	0.190		
K_2O	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 necessary to vary the parameters of pseudosymmetry-related atoms independently. After intitial 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^{IV} became smaller and those around the postulated Si^{IV} 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	10Fo	10Fc
h = 0			
0	2	304	185
0	4	271	345
0	6	2039	1907
0	8	230	182
0	10	2013	1971
0	12	995	991
0	14	694	719
0	16	991	1030
0	18	153	186
0	20	1133	1091
0	22	761	758
0	26	386	363
2	0	398	346
2	1	321	241
2	-1	282	247
2	2	550	453
2	-2	562	442
2	3	904	770
2	-3	882	766
2	4	1176	1072
2	-4	1183	1077
2	5	1509	1384
2	-5	1508	1386
2	6	286	262
2	-6	292	254
2	7	629	606
2	-7	628	611
2	8	178	201
2	-8	190	192
2	9	82	83
2	10	433	431
2	-10	442	428
2	12	227	242
2	-12	235	244
2	13	587	606
2	-13	589	606
2	14	195	201
2	-14	201	198
2	15	631	622
2	-15	644	624
2	16	537	541
2	-16	531	534
2	17	98	82
2	18	172	168
2	-18	163	174
2	20	210	239
2	-20	245	249
2	-21	158	145
2	22	128	203
2	-22	212	194
2	23	418	393
2	-23	428	395
2	24	252	259
2	-24	294	253
2	25	299	299
2	-25	328	303
2	26	149	135
2	-26	190	142
4	0	123	108
4	1	337	285
4	-1	338	279
4	2	527	434
4	-2	500	443
4	3	682	606
4	-3	680	598
4	4	1089	981
4	-4	1073	984
4	5	591	565
4	-5	593	563
4	6	178	139
4	-6	164	152
4	7	86	76
4	8	310	322
4	-8	322	318
4	9	169	161
4	-9	147	154
4	10	800	819
4	-10	770	816
4	11	178	161
4	-11	152	158
4	12	713	723
4	-12	718	728
4	13	745	722
4	-13	747	720
4	14	569	568
4	-14	585	567
4	15	593	590
4	-15	604	593
4	16	524	524
4	-16	566	520
4	17	116	161
4	19	208	195
4	-19	195	191
4	20	139	79
4	22	126	109
4	-22	152	98
4	23	429	372
4	-23	410	375
4	24	387	395
4	-24	431	390
4	25	372	352
4	-25	362	357
6	0	3135	3090
6	1	617	546
6	-1	615	548
6	2	186	155
6	-2	189	154
6	3	143	129
6	-3	107	128
6	5	269	256
6	-5	267	258
6	6	1108	1040
6	-6	1109	1039
6	8	620	601
6	-8	615	599
6	9	422	407
6	-9	424	405
6	10	1040	1007
6	-10	1054	1008
6	11	413	412
6	-11	433	414
6	12	588	551
6	-12	584	550
6	14	725	685
6	-14	743	684
6	15	165	161
6	-15	129	160
6	16	691	662
6	-16	695	664
6	-17	111	83
6	19	116	153
6	-19	147	150
6	20	901	844
6	-20	903	845
6	21	172	173
6	-21	134	175
6	22	560	539
6	-22	594	538
8	0	237	264
8	1	175	168
8	-1	161	177
8	2	426	413
8	-2	409	404
8	3	425	400
8	-3	403	396
8	4	358	329
8	-4	326	332
8	5	832	767
8	-5	798	768
8	7	371	344
8	-7	346	344
8	8	116	127
8	-8	151	121
8	9	106	72
8	10	171	187
8	-10	158	182
8	13	330	308
8	-13	341	307
8	14	145	165
8	-14	144	166
8	15	463	434
8	-15	435	434
8	16	136	166
8	-16	151	158
8	17	154	150
8	18	245	215
8	-18	246	222
8	20	174	216
8	-20	205	222
10	1	198	173
10	-1	177	171
10	2	350	330
10	-2	383	335
10	3	166	160
10	-3	164	154
10	4	604	524
10	-4	609	524
10	5	185	161
10	-5	191	160
10	6	153	160
10	-6	146	170
10	7	193	185
10	-7	175	177
10	8	234	227
10	-8	253	227
10	9	181	168
10	-9	166	163
10	10	592	525
10	-10	559	522
10	11	153	159
10	-11	153	158
10	12	655	619
10	-12	639	623
10	13	352	330
10	-13	328	326
10	14	551	480
10	-14	510	479
10	15	342	322
10	-15	365	325
10	16	281	238
12	0	921	810
12	1	422	353
12	-1	428	355
12	2	182	97
12	-2	137	95
12	5	225	187
12	-5	216	190
12	6	404	314
12	-6	405	314
12	-7	125	132
h = 1			
1	0	492	455
1	1	576	490
1	-1	927	819
1	2	385	331
1	3	239	223
1	-3	847	775
1	4	1304	1271
1	-4	1122	1055
1	5	1186	1171
1	-5	380	353
1	6	818	805
1	-6	1196	1174
1	7	266	257
1	-7	554	568
1	8	96	100
1	-8	382	376
1	9	279	262
1	-9	141	160
1	10	126	132
1	-10	157	158
1	11	198	198
1	-11	293	266
1	12	361	368
1	-12	90	86
1	13	495	517
1	-13	277	284
1	14	722	740
1	-14	628	636
1	15	106	145
1	-15	746	762
1	16	181	157
1	-16	362	332
1	17	251	297
1	-17	276	300
1	19	117	97
1	-20	112	99
1	21	437	458
1	-21	226	256
1	22	333	295
1	-22	256	256
1	23	205	204
1	-23	447	467
1	24	398	404
1	-24	427	434
1	-25	285	261
1	-26	154	132
3	0	366	366
3	1	2261	2121
3	-1	1115	1128
3	2	93	88
3	3	884	852
3	-3	1508	1344
3	-4	172	180
3	5	2071	1884
3	-5	1078	1095
3	7	685	630
3	-7	960	913
3	-8	220	235
3	9	2054	2058
3	-9	1333	1295
3	10	215	201
3	-10	303	286
3	11	412	417
3	-11	2752	2742
3	13	746	747
3	-13	1506	1448
3	-14	246	243
3	15	110	157
3	-15	235	236
3	16	108	128
3	17	1050	1107
3	-17	443	429
3	-18	139	187
3	19	744	801
3	-19	1122	1079
3	20	112	25
3	-20	206	204
3	21	539	521
3	-21	615	596
3	-22	105	75
3	23	1038	1030
3	-24	130	110
3	25	285	314
3	-25	285	274
5	0	188	186
5	1	380	351
5	-1	262	249
5	-2	347	329
5	3	489	491
5	-3	264	278
5	4	653	642
5	-4	1127	1076
5	5	645	636
5	-5	373	362
5	6	597	591
5	-6	915	903
5	7	316	335
5	-7	130	122
5	8	225	208
5	9	334	349
5	-9	267	289
5	10	211	204
5	-10	269	283
5	-11	223	214
5	12	430	417
5	13	231	232
5	-13	346	353
5	14	497	498
5	-14	720	685
5	15	141	122
5	-15	597	591
5	-16	526	494
5	-17	257	214
5	18	153	126
5	19	156	160
5	-19	152	157
5	20	154	147
5	21	302	296
5	-21	159	149
5	22	415	415
5	-22	191	167
5	23	190	201
5	-23	190	213
5	-24	405	363
7	0	287	273
7	1	317	311
7	-1	899	901
7	2	325	319
7	-2	333	338
7	3	705	709
7	-3	653	633
7	4	850	835
7	-4	246	216
7	5	805	771
7	6	459	417
7	-6	509	491
7	7	351	332
7	-7	750	750
7	8	197	214
7	-8	239	253
7	9	255	200
7	10	301	277
7	-10	179	164
7	11	388	347
7	13	681	668
7	-13	471	426
7	14	487	483
7	-14	280	225
7	-15	386	372
7	16	209	209
7	-16	109	58
7	17	413	440
7	-17	269	246
7	-18	147	121
7	-19	127	101
7	-20	162	124
7	21	260	276
7	-21	220	207
7	-22	239	247
9	0	499	466
9	1	961	894
9	-1	534	504
9	2	149	114
9	-2	201	214
9	3	685	627
9	4	214	179
9	-4	192	170
9	5	352	271
9	-5	755	691
9	-6	118	100
9	7	150	140
9	-7	418	371
9	8	271	267
9	-8	308	276
9	9	1299	1183
9	-9	415	381
9	10	359	342
9	-10	441	410
9	11	121	99
9	-11	1221	1093
9	13	277	230
9	-13	680	591
9	-14	321	308
9	15	331	295
9	16	151	166
9	17	574	544
9	-17	159	133
9	-18	322	311
11	1	204	163
11	-1	185	133
11	3	281	257
11	4	390	361
11	-4	439	398
11	5	143	140
11	-5	115	67
11	6	349	322
11	-6	423	400
11	7	260	236
11	10	134	94
11	-10	120	55
h = 2			
0	0	971	1003
0	2	1504	1472
0	-2	2265	2285
0	4	919	952
0	-4	755	779
0	6	959	1010
0	-6	1908	1870
0	8	1268	1322
0	-8	702	659
0	10	2366	2604
0	-10	1879	1992
0	12	1441	1585
0	-12	334	344
0	14	134	98
0	-14	666	715
0	16	280	296
0	-16	189	213
0	17	110	0
0	18	1055	1106
0	-18	1152	1152
0	20	478	509
0	-20	870	847
0	-22	587	559
0	24	206	217
0	-24	1136	1068
0	-26	238	230
2	0	374	338
2	1	477	453
2	-1	426	405
2	2	441	440
2	3	832	831
2	-3	651	634
2	4	94	80
2	-4	107	97
2	5	419	453
2	-5	841	857
2	6	365	386
2	-6	660	688
2	7	208	220
2	-7	232	262
2	8	660	685
2	-8	464	459
2	9	143	170
2	-9	262	258
2	10	618	657
2	-10	566	593
2	11	393	451
2	-11	114	116
2	12	237	252
2	-12	363	384
2	13	831	931
2	-13	600	612
2	14	486	505
2	-14	524	550
2	15	470	513
2	-15	876	889
2	16	177	184
2	-16	136	109
2	17	162	180
2	-17	280	272
2	19	117	137
2	-19	116	125
2	22	376	405
2	-22	180	172
2	23	414	435
2	-23	238	221
2	-24	225	162
2	-25	390	390
2	-26	331	303
4	0	516	537
4	1	200	205
4	-1	165	158
4	2	732	732
4	-2	209	209
4	3	467	473
4	-3	562	536
4	-4	642	607
4	5	532	541
4	-5	1041	1048
4	6	682	698
4	-6	828	831
4	7	160	170
4	-7	457	455
4	8	241	261
4	-8	214	213
4	-9	248	264
4	10	384	394
4	-10	111	99
4	11	161	152
4	-11	362	362
4	12	492	511
4	-12	433	458
4	13	525	517
4	-13	290	285
4	14	430	410
4	-14	712	728
4	15	277	281
4	-15	691	681
4	16	230	270
4	17	124	145
4	-17	341	320
4	-18	301	309
4	20	155	179
4	21	174	152
4	-22	236	229
4	23	329	344
4	-23	178	111
4	-24	287	254
4	-25	212	229
6	0	684	666
6	1	168	159
6	-1	457	487
6	2	268	238
6	-2	1565	1549
6	3	183	205
6	-3	168	184
6	4	960	920
6	-4	769	713
6	6	528	496
6	-6	641	588
6	7	221	224
6	8	749	749
6	-8	405	389
6	9	307	335
6	-9	130	143
6	10	1682	1579
6	-10	1473	1423
6	-11	228	256
6	12	969	932
6	-12	108	69
6	13	239	253
6	14	105	23
6	-14	364	360
6	-15	113	55
6	16	239	210
6	-16	282	285
6	17	286	293
6	-17	221	222
6	18	867	815
6	-18	895	808
6	19	226	213
6	-19	216	215
6	20	273	265
6	-20	562	522
6	-22	488	444
6	-23	136	137
8	0	156	148
8	1	312	287
8	-1	156	153
8	2	114	145
8	-2	95	37
8	3	492	471
8	-3	268	257
8	4	103	110
8	-4	158	164
8	5	312	297
8	-5	515	488
8	6	188	186
8	-6	282	278
8	7	149	147
8	-7	202	180
8	8	439	424
8	-8	411	412
8	-9	111	155
8	10	312	314
8	-10	346	332
8	11	392	368
8	12	255	274
8	-12	280	270
8	13	666	602
8	-13	400	371
8	14	205	214
8	-14	183	215
8	15	395	369
8	-15	569	536
8	-17	191	181
10	0	582	565
10	1	277	248
10	-1	163	153
10	2	516	497
10	-2	151	128
10	3	127	107
10	-3	121	140
10	-4	533	512
10	5	330	281
10	-5	534	487
10	6	554	526
10	-6	586	533
10	7	162	129
10	-7	271	249
10	-8	300	277
10	-9	155	141
10	-10	174	165
10	-11	210	184
10	12	426	378
10	-12	345	316
10	-13	137	138
10	-14	562	535
h = 3			
1	0	100	73
1	1	327	314
1	-1	190	216
1	2	796	820
1	-2	219	209
1	3	736	767
1	-3	609	616
1	4	992	1079
1	-4	231	237
1	5	318	343
1	-5	904	931
1	6	210	228
1	-6	511	527
1	7	87	105
1	8	195	231
1	-8	311	323
1	9	495	553
1	-9	450	511
1	10	199	193
1	-10	124	79
1	11	541	607
1	-11	234	273
1	12	424	444
1	-12	250	257
1	13	153	192
1	-13	100	120
1	14	483	569
1	-14	585	625
1	15	504	592
1	-15	280	322
1	-16	394	417
1	17	179	170
1	-17	351	363
1	-18	114	178
1	-19	137	124
1	20	154	134
1	-20	201	167
1	21	185	131
1	-21	157	213
1	22	277	247
1	-23	141	190
1	-24	518	481
1	-25	411	376
3	0	293	261
3	1	336	319
3	-1	3189	3166
3	2	88	73
3	-2	280	278
3	3	121	136
3	5	903	944
3	6	104	69
3	-6	146	166
3	7	689	755
3	-7	1109	1138
3	8	189	200
3	9	1009	1073
3	-9	527	540
3	10	145	175
3	-10	214	209
3	11	445	426
3	-11	1076	1083
3	-12	233	250
3	13	702	740
3	-13	733	737
3	15	618	692
3	-15	668	680
3	16	111	77
3	-16	129	64
3	-17	561	563
3	19	843	897
3	21	552	563
3	-21	904	857
3	-23	505	467
5	1	103	113
5	-1	291	325
5	2	772	765
5	-2	424	430
5	3	331	350
5	-3	805	819
5	4	1104	1111
5	-4	127	97
5	5	305	275
5	-5	596	610
5	6	355	339
5	-6	612	606
5	7	162	138
5	-7	110	136
5	8	300	298
5	-8	451	484
5	9	252	259
5	-9	322	325
5	10	248	238
5	-10	227	212
5	11	287	285
5	-11	174	153
5	12	282	295
5	-12	187	186
5	13	210	228
5	-13	135	169
5	14	506	537
5	-14	394	368
5	15	408	440
5	-15	169	106
5	16	294	281
5	-16	347	310
5	17	207	199
5	-17	180	171
5	-18	108	87
5	19	184	189
5	-19	208	217
5	20	147	144
5	-21	310	307
5	-22	191	189
7	0	105	121
7	1	340	324
7	2	234	235
7	3	647	615
7	4	362	356
7	-4	302	278
7	5	126	108
7	-5	669	632
7	-6	267	256
7	7	147	180
7	8	120	111
7	9	497	496
7	-9	315	319
7	-10	162	163
7	11	642	640
7	-11	477	469
7	12	364	347
7	-12	170	149
7	13	421	378
7	-13	419	421
7	14	346	348
7	-14	478	445
7	15	306	307
7	-15	449	421
7	-16	365	363
7	-17	346	325
7	-18	128	124
7	-20	194	173
9	0	377	353
9	1	136	126
9	-1	1389	1228
9	-2	389	362
9	4	149	139
9	5	507	445
9	-5	136	120
9	6	118	155
9	-6	252	230
9	7	615	595
9	-7	528	487
9	8	357	333
9	9	414	353
9	-9	600	550
9	10	218	218
9	-10	370	354
9	11	128	124
9	-11	531	489
9	12	170	150
9	-12	390	368
9	13	482	409
9	-13	478	420
9	-15	591	541
11	-1	234	190
11	2	384	340
11	-2	131	158
11	-3	400	378
11	4	532	486
11	-4	131	102
11	-5	195	188
11	-6	361	318
h = 4			
0	0	1271	1429
0	2	726	874
0	-2	740	883
0	4	541	625
0	6	233	300
0	-6	778	992
0	8	1283	1534
0	-8	380	391
0	10	120	154
0	-10	573	742
0	12	268	372
0	-12	1410	1760
0	-14	755	808
0	-16	141	184
0	18	376	478
0	-18	302	330
0	20	271	337
0	-20	793	906
0	-22	415	424
2	0	454	477
2	1	104	138
2	-1	388	443
2	2	384	444
2	-2	465	503
2	3	489	523
2	-3	131	132
2	4	637	703
2	-4	264	263
2	5	494	581
2	-5	848	895
2	-6	514	538
2	7	216	266
2	-7	889	937
2	8	150	203
2	-8	136	178
2	9	172	216
2	-9	150	180
2	10	183	194
2	-10	98	129
2	11	194	258
2	-11	238	288
2	13	323	348
2	-14	271	312
2	-15	372	413
2	-16	642	700
2	17	111	117
2	-17	298	349
2	18	181	166
2	-19	162	162
2	20	383	478
2	-20	222	232
2	-23	182	193
4	0	392	385
4	1	171	160
4	-1	303	309
4	2	230	243
4	-2	560	588
4	3	561	590
4	-3	110	135
4	4	626	668
4	-4	437	454
4	5	359	382
4	-5	467	452
4	-6	336	311
4	-7	566	585
4	8	142	140
4	-8	462	475
4	-9	154	174
4	-10	113	116
4	11	164	162
4	-11	163	146
4	12	375	413
4	13	409	455
4	-15	314	295
4	16	190	247
4	-16	564	595
4	17	112	98
4	-17	136	108
4	-21	134	131
4	-22	209	196
6	0	940	879
6	1	114	128
6	-1	303	295
6	2	710	683
6	-2	604	600
6	3	158	151
6	-3	149	153
6	4	331	294
6	-4	183	202
6	-5	101	121
6	6	112	87
6	-6	740	708
6	7	210	245
6	8	1260	1235
6	-8	383	343
6	9	245	255
6	-9	216	206
6	10	155	125
6	-10	428	410
6	-11	305	313
6	12	200	230
6	-12	1212	1166
6	13	123	115
6	14	217	229
6	-14	621	566
6	-15	236	246
6	16	588	568
6	-16	170	115
6	-18	165	156
6	-19	139	183
8	0	361	322
8	1	132	95
8	-1	230	217
8	2	389	396
8	-2	290	264
8	3	300	310
8	4	329	322
8	5	449	430
8	-5	651	613
8	6	214	194
8	-6	230	228
8	-7	637	624
8	9	189	200
8	10	213	170
8	11	200	190
8	-11	183	168
8	-14	396	396
8	-15	316	304
10	0	245	209
10	1	141	140
10	-1	118	64
10	2	420	381
10	-2	441	398
10	3	343	312
10	-3	162	186
10	4	432	364
10	-4	346	320
10	-7	206	168
h = 5			
1	1	300	396
1	2	367	451
1	4	214	255
1	-4	306	344
1	5	225	283
1	-5	99	76
1	-6	441	527
1	7	333	469
1	-7	408	468
1	-8	162	145
1	9	395	485
1	-9	177	236
1	10	175	221
1	-10	189	227
1	11	174	214
1	-11	300	339
1	12	426	563
1	-12	123	167
1	13	213	280
1	-13	250	289
1	14	293	374
1	-14	304	387
1	15	120	97
1	-15	370	471
1	17	153	133
1	-17	141	176
1	-18	224	237

TABLE 2, Continued

k	l	10Fo	10Fc	k	l	10Fo	10Fc	k	l	10Fo	10Fc	k	l	10Fo	10Fc
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
3	-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	-15	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	257	7	-7	464	456	2	-6	381	427	$h = 7$			
5	-3	154	124	7	-8	198	193	2	7	118	155	1	0	128	89
5	-4	290	304	7	9	181	178	2	9	138	173	1	-1	256	303
5	5	176	174	7	-9	177	137	2	-9	265	305	1	2	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	301	306	1	3	277	373
5	7	478	503	$h = 6$				2	11	157	185	1	-3	186	215
5	-7	278	302	0	0	219	253	2	-13	150	180	1	-5	149	147
5	8	110	97	0	-1	144	0	2	-14	164	182	1	-6	346	373
5	9	489	490	0	2	168	203	2	-15	241	274	1	-7	270	300
5	-9	395	387									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 $Si_{2.11}Al_{1.89}$ 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)
β	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 $P3_112$. 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 α_{tet} (Table 6). The Al-rich tetrahedra are slightly flattened (larger τ) 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 undersaturated 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)
[a]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)
[b]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)
[c]H(1)					0.397	0.637	0.083	0.78
H(11)					0.603	0.363	0.917	0.78

[a]*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.*

[b]*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.*

[c]*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_3Al instead of Si_2Al_2. 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 *C*2/*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 $Si_{0.5}Al_{0.5}$ in adjacent tetrahedra.

This ordered model for muscovite-$2M_1$ 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 *C*2/*c*. It can be concluded that the ordered model of margarite-$2M_1$ does not extend to muscovite-$2M_1$ 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
[a]α_{tet}(°)	20.4	[b]20.76, 20.64 (20.70)
[c]τ_{tet}(°)	111.5	Si: 110.78, 110.41; Al: 110.83, 110.88 (110.73)
[d]ψ_{oct}(°)	58.9	58.8
Sheet thickness (Å)		
tetrahedral	2.330	[b]2.291, 2.234 (2.263)
octahedral	2.074	2.074
Interlayer separation (Å)	2.832	2.868
Basal oxygen Δz_{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

[a]*The amount of tetrahedral rotation α_{tet} may be calculated from $\alpha = 1/2|120° - \text{mean } O_b\text{-}O_b\text{-}O_b \text{ angle}|$*

[b]*The value referring to the more Al-rich tetrahedral sheet is given first. The average values are in parentheses.*

[c]*The tetrahedral angle τ is defined as $\tau = O_{apical}\text{--}T\text{--}O_{basal}$, ideally 109°28'.*

[d]*The mean octahedral angle ψ, ideally 54°44', is calculated from cos ψ = oct. thickness/2($\overline{M\text{--}O,OH}$), where $\overline{M\text{--}O,OH}$ 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)[a]	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)[a]	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)[a]	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)[a]	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)--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)--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	OH(1)	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 (unshared)	2.782	around O(55)	119.89
				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)--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 (unshared)	2.800		

[a] *Apical oxygen*

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.

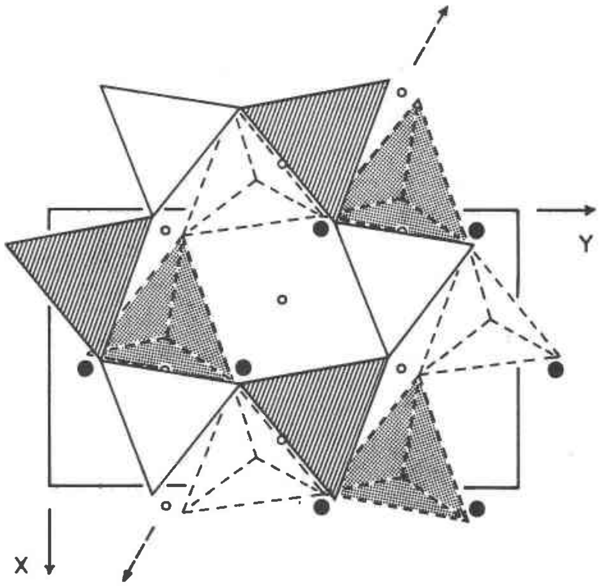

FIG. 1. Tetrahedral ordering pattern within upper 2:1 layer of margarite-$2M_1$ in subgroup *Cc*. Al-rich tetrahedra = ruled lines and dots; octahedral Al = solid circles; inversion centers of ***ideal*** space group = small open circles; pseudo 2-fold axis = dashed arrows. From Bailey (1975).

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.

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