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Crystal structure of a silica- and alkali-rich trioctahedral mica

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Abstract

The crystal structure of a trioctahedral mica of unusual composition from melilite-bearing eruptive rocks has been determined ($R = 3.0\%$). This mica, which has excess silica ($Si > 3$) and alkalis ($\sum Na + K > 1$), is the first known layer silicate with octahedral sodium. In spite of the complexity of the octahedral layer, which includes Mg, Fe, Li, Ca, Mn, Na, Ti, and vacancies, there is no evidence for cation ordering between the two distinct octahedral sites. Both sites have the same mean M–O distance (2.077Å) and the same electron density. The structural formula of the mica, based on chemical analysis and the structure refinement, is:

$$(K_{0.969}Ba_{0.018}Na_{0.013})^{XII}(Mg_{2.457}Fe_{0.031}Mn_{0.006}Ca_{0.005}Ti_{0.088}Li_{0.225}Na_{0.110}\square_{0.078})^{VI}$$
$$(Si_{3.312}Al_{0.042}Fe^{3+}_{0.646})^{IV}O_{10}F_2.$$

Introduction

Velde (1979) described a suite of trioctahedral micas of various compositions from melilite-bearing eruptive rocks. Of special interest is a group of silica-rich micas, characterized by high alkalis and ferric iron and low aluminum, in addition to significant amounts of Li, Ba, and Ti. These micas are unusual because $\sum(K + Na + Ba) \gg 1.0$, $Si \gg 3.0$, and $\sum(Si + Al) \ll 4.0$. Substantial deviations from the ideal biotite, $(K,Na)(Mg,Fe)_3AlSi_3O_{10}(OH)_2$, therefore obtain. The principal objective of this study is to document the site distributions of cations in this mica.

Experimental

Euhedral single crystals of a silica-rich mica (sample Y253, Gragnani, 1972) from the type coppaelite, at Cupaello, Italy, were selected for X-ray investigation. These crystals are unzoned and display a slight reverse pleochroism, characteristic of micas with tetrahedral Fe^{3+} (Hazen and Wones, 1972).

The composition of the crystals was determined by ion and electron microprobe analysis (Table 1). Fluorine was detected in significant amounts (>3 wt.%) by both ion and electron microprobe, but exact quantitative determination could not be made. No OH^- was detected by infrared analysis and the mica thus has $F/(F + OH) \approx 1$. It is not known if there is a significant oxy-biotite component. Ion microprobe analysis indicated 0.75±0.25 wt.% Li_2O (tourmaline standard), and boron in only trace amounts.

X-ray diffraction photographs of a crystal plate $140 \times 130 \times 50$ μm revealed sharp diffraction maxima with none of the smearing or streaking of spots characteristic of deformed crystals or disordered stacking arrangements. Unit-cell parameters of this silica-rich mica (Table 2) are typical for a one-layer trioctahedral mica with potassium in the interlayer position (Hazen and Wones, 1972).

All X-ray reflections in one octant of reciprocal space ($\sin\theta/\lambda < 0.9$) were collected on an automated four-circle diffractometer with Nb-filtered Mo$K\alpha$ radiation (Finger *et al.*, 1973). All reflections were corrected for specimen absorption ($\mu_l = 21.0$ cm^{-1}) as well as Lorentz and polarization effects. A total of 625 nonequivalent data were observed ($I > 2\sigma_I$). Trial refinements in space group $C2$, in which adjacent tetrahedra are symmetrically independent, and $C2/m$, in which all tetrahedra are equivalent, yielded similar results. The $C2/m$ refinement yielded the residual of

0003–004X/81/0506–0586$0.200

Table 1. Composition and calculated structural formula of silica-rich trioctahedral mica

	Wt, %	No. Atoms	Per Site No. Atoms	Per Site No. Charges	Per Site No. Electrons*
SiO_2	44.43	3.312	4.000	Tetrahedron +15.31	15.9$\bar{e}$
Al_2O_3	0.47	0.042			
B_2O_3	trace				
Fe_2O_3	11.38	0.646			
FeO†	0.49	0.031	2.922	Octahedra +5.68	11.5$\bar{e}$
MgO	22.11	2.457			
MnO	0.09	0.006			
CaO	0.07	0.005			
TiO_2	1.57	0.088			
Li_2O‡	0.75	0.225			
Na_2O	0.84	0.110			
		0.013	1.000	Alkali site +1.02	19.6$\bar{e}$
BaO	0.62	0.018			
K_2O	10.18	0.969			
F§	4.5	2.000			
H_2O‖	(<0.1)				
Totals	97.50		7.922	+22.01	

*Number of electrons per site = Σ (number of atoms per site × atomic number).
†Octahedral Fe^{2+}/Fe^{3+} is unknown.
‡Based on ion probe analysis with tourmaline standard. Value cited is ±0.25 weight percent.
§Fluorine present in significant amounts (>3%), based on ion and electron microprobe analysis. Calculations are based on end member fluoro-mica.
‖Based on infrared spectra analysis by B. Velde.

Table 2. Unit-cell dimensions

Unit-Cell Parameter*	Value
a (Å)	5.3290(9)†
b (Å)	9.2300(15)
c (Å)	10.2191(11)
α (°)	90.00(1)
β (°)	99.98(1)
γ (°)	90.01(1)
V (Å^3)	495.0(1)

*Refinement of unit-cell parameters from diffractometer data was unconstrained (i.e. triclinic).
†Parenthesized figures represent esd's.

Table 3. Refinement conditions

Parameter	Value
Weighted R (%)*	3.0
R (%)†	3.0
No. of observations	625
Extinction parameter	$0.6(\pm 1.2) \times 10^{-5}$

*Weighted $R = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$.
†$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

greatest significance, however, and the centrosymmetric space group, as observed in previous refinements of one-layer biotites, was thus selected. All observed reflections were included in the refinement of atomic positions, anisotropic thermal parameters, unconstrained occupancy factors for all metal sites and the fluorine site, and an isotropic extinction parameter. Conditions of refinement are recorded in Table 3, refined positional and thermal parameters in Table 4, and observed and calculated structure factors in Table 5. Least-squares weights were derived from standard deviations based on counting statistics to which an amount equivalent to 2% of F^2 has been added.

Results and discussion

Interatomic distances and angles (Table 6) and the orientations and magnitudes of thermal vibration ellipsoids (Table 7) are similar to those of previously reported trioctahedral micas in the phlogopite–annite series (Hazen and Burnham, 1973; Bohlen *et al.*, 1980). The 5.7° tetrahedral rotation angle, which is

Table 4. Refined atomic coordinates, anisotropic temperature factors, equivalent isotropic temperature factors, and number of electrons per metal site in silica-rich trioctahedral mica

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B Equiv.	No. of Electrons
T	0.5749(1)	0.1667(1)	0.2255(1)	0.0082(2)	0.0022(1)	0.0023(1)	-0.0000(1)	0.0007(1)	-0.0001(1)	0.87(1)	15.0(2)
M1	0	1/2	1/2	0.0063(5)	0.0012(2)	0.0026(2)	0	0.0008(2)	0	0.71(4)	11.7(2)
M2	0	0.8337(1)	1/2	0.0061(4)	0.0019(1)	0.0025(1)	0	0.0007(2)	0	0.78(3)	11.7(2)
K	0	0	0	0.0227(5)	0.0068(2)	0.0057(1)	0	0.0016(2)	0	2.40(3)	19.3(2)
O1	0.8198(3)	0.2355(2)	0.1672(2)	0.0236(8)	0.0097(3)	0.0042(2)	-0.0036(4)	0.0012(3)	-0.0003(2)	2.55(4)	
O2	0.5264(6)	0	0.1669(2)	0.0347(13)	0.0066(3)	0.0041(3)	0	0.0011(5)	0	2.61(6)	
O3	0.6298(3)	0.1670(2)	0.3901(1)	0.0096(5)	0.0026(2)	0.0027(1)	-0.0001(2)	0.0006(2)	0.0000(1)	1.03(3)	
F	0.1336(4)	0	0.3992(2)	0.0113(8)	0.0035(2)	0.0027(2)	0	0.0007(3)	0	1.19(5)	8.3(2)

*Number of electrons is refined for each cation site based on electron density. No constraints are used.

Table 5. Observed and calculated structure factors (× 10)

L	OBS	CALC
-6 0 L		
1	198	192
2	756	772
3	300	298
4	78	61
5	155	163
6	432	442
7	253	267
8	102	98
9	397	393
10	330	319
-4 0 L		
1	727	744
2	941	961
3	793	820
4	126	127
5	341	366
6	995	1018
7	79	77
8	151	152
10	353	361
12	83	15
13	309	288
-2 0 L		
1	694	713
2	356	345
3	399	401
4	673	672
5	439	440
6	1015	1015
7	1187	1197
8	262	277
9	169	172
10	629	628
11	100	98
12	250	248
14	405	401
0 0 L		
1	443	400
2	275	294
3	1063	1074
4	483	514
5	1094	1101
6	312	310
7	575	555
8	643	663
10	396	418
11	500	498
12	244	240
13	317	328
14	117	136
2 0 L		
0	1100	1128
1	998	1005
2	867	878
3	335	340
4	1328	1335
5	397	406
6	374	374
7	108	115
8	689	681
9	130	129
11	499	498
12	489	482
13	85	89

L	OBS	CALC
-1 1 L		
1	191	184
2	703	702
3	859	841
4	176	171
5	118	110
6	59	70
7	402	395
8	187	190
9	79	90
11	187	192
12	160	160
14	79	80
1 1 L		
0	365	366
1	407	407
2	950	945
3	393	388
4	68	74
5	43	32
6	320	321
7	324	325
10	181	179
11	188	191
12	76	25
13	118	125
3 1 L		
1	502	502
2	393	397
5	170	173
6	288	294
9	128	132
10	194	193
11	101	91
5 1 L		
0	233	239
1	266	277
4	66	81
5	239	240
7	103	99
7 1 L		
0	188	182
1	87	47
2	72	58
-6 2 L		
3	80	83
4	216	213
6	110	111
8	186	180
9	202	210
10	93	33
-4 2 L		
1	175	175
2	175	176
3	247	242
4	386	393
5	94	97
7	68	68
8	217	221
9	67	57
10	102	87
11	89	73
12	156	167
13	120	120

L	OBS	CALC
4 2 L		
0	281	284
1	538	539
2	136	143
3	182	181
4	97	86
5	241	241
6	261	266
9	88	77
10	126	116
6 2 L		
0	193	196
1	66	67
2	72	88
4	180	179
5	193	205
-7 3 L		
2	239	231
3	355	346
4	366	359
5	102	87
6	87	96
-5 3 L		
1	512	517
2	348	354
4	315	328
5	267	262
6	153	155
7	460	469
8	600	608
9	185	183
10	138	125
11	330	337
-3 3 L		
1	1553	1550
2	474	484
3	67	59
4	265	264
5	672	658
6	458	454
7	120	117
8	574	571
9	579	588
10	119	96
11	388	378
12	463	462
-1 3 L		
1	1154	1132
2	1048	1011
3	907	875
4	340	338
5	1340	1336
6	393	406
7	366	373
8	106	112
9	684	678
10	132	126
11	76	25
12	507	492
13	497	479
14	86	87

L	OBS	CALC
-4 4 L		
2	70	80
3	268	261
4	164	163
5	120	127
6	75	76
7	209	208
8	372	355
10	196	187
12	147	141
-2 4 L		
1	256	246
2	166	171
3	569	562
4	245	244
5	58	45
7	263	258
8	215	213
9	75	84
11	163	169
12	179	177
0 4 L		
0	404	398
1	431	417
2	363	367
3	90	94
4	281	285
5	134	144
6	548	561
7	520	519
8	95	107
9	276	284
11	263	269
12	235	230
2 4 L		
0	69	61
1	544	530
2	578	570
4	175	176
5	61	55
6	367	364
7	177	184
8	68	82
10	151	137
11	133	137
4 4 L		
0	208	205
1	267	251
3	135	131
4	105	105
5	361	356
6	204	209
7	160	149
8	113	113
9	98	94
6 4 L		
0	280	275
1	160	158
2	101	82
3	98	97
4	90	85
5	208	188

L	OBS	CALC
3 5 L		
1	370	369
2	312	313
5	130	136
6	209	214
9	133	127
10	169	173
5 5 L		
0	207	215
1	218	219
3	79	85
4	93	72
5	231	230
7	87	94
-6 6 L		
1	156	150
2	695	691
3	160	155
5	223	213
6	282	277
7	224	217
-4 6 L		
1	375	360
2	525	516
3	642	634
4	202	210
5	112	86
6	790	782
7	199	192
8	253	256
10	381	375
11	84	90
-2 6 L		
1	763	753
3	651	639
4	164	155
5	235	228
6	847	853
7	661	659
8	245	237
10	348	344
11	118	124
12	130	134
0 6 L		
0	1569	1567
1	478	486
2	51	61
3	274	268
4	677	665
5	463	466
6	125	118
7	574	579
8	578	598
9	107	97
10	385	387
11	464	471
12	87	64

L	OBS	CALC
-1 7 L		
11	86	101
12	115	106
1 7 L		
0	232	242
1	103	90
2	420	422
3	205	207
6	202	197
7	147	148
8	101	83
10	147	162
11	142	158
3 7 L		
0	81	67
1	362	357
2	203	197
3	88	99
4	79	77
5	151	159
6	250	257
8	80	77
9	82	51
5 7 L		
0	146	146
1	210	207
5	130	146
-4 8 L		
1	66	35
3	172	172
4	146	143
7	121	116
8	247	241
-2 8 L		
1	149	146
2	161	147
3	317	323
4	115	105
5	67	92
7	213	214
8	166	163
9	79	85
11	97	102
0 8 L		
1	131	138
2	296	296
3	67	53
4	157	149
6	301	305
7	316	318
8	72	52
9	170	174
11	179	179
2 8 L		
1	291	292
2	312	310
4	97	117
6	272	276
7	110	97
8	113	85

L	OBS	CALC
3 9 L		
0	301	301
1	64	66
2	174	173
3	452	458
4	276	291
5	112	100
6	414	415
7	348	334
5 9 L		
0	372	367
2	115	105
-4 10 L		
1	83	89
3	148	142
4	163	162
-2 10 L		
2	140	128
3	187	190
5	68	95
7	224	231
8	107	134
0 10 L		
2	270	273
3	143	144
4	78	78
6	149	152
7	197	207
9	94	80
2 10 L		
1	199	203
2	153	153
3	102	80
4	77	85
5	110	116
6	249	257
4 10 L		
0	100	110
1	215	207
2	84	42
3	93	91
-3 11 L		
1	124	107
3	182	189
4	112	105
-1 11 L		
1	75	34
2	247	234
3	253	247
5	114	124
7	197	205
1 11 L		
0	157	158
1	86	77
2	226	224
3	99	106
6	133	131

Table 5. (continued)

L	OBS	CALC
4 0 L		
1	629	631
2	154	147
3	228	222
4	834	855
5	648	653
6	234	237
8	341	344
9	103	117
10	139	134
6 0 L		
1	168	169
2	345	352
3	206	196
4	101	94
5	323	330
6	398	390
-7 1 L		
2	93	94
4	157	165
5	157	160
-5 1 L		
1	83	78
2	120	110
3	185	182
4	346	350
5	85	75
6	119	126
8	223	222
9	167	182
-3 1 L		
1	255	256
2	136	136
3	622	636
4	384	394
5	115	113
6	121	131
7	182	177
8	352	362
10	68	67
11	87	82
12	150	150
-2 2 L		
1	404	397
2	422	426
3	241	248
4	186*	238
5	176	177
6	328	301
7	614	622
8	336	330
9	250	255
10	190	195
11	139	131
12	290	295
13	152	139
14	92	100
0 2 L		
0	418	435
1	93	95
2	895	897
3	639	638
4	55	9
5	97	95
6	194	194
7	411	409
8	70	48
10	150	140
11	200	198
12	99	105
13	110	113
2 2 L		
0	407	400
1	420	424
2	83	86
3	311	306
5	434	443
6	616	620
7	106	112
8	318	315
10	201	208
11	292	291
1 3 L		
0	744	720
1	376	346
2	417	404
3	690	674
4	458	449
5	1034	1031
6	1199	1209
7	268	276
8	171	173
9	645	639
10	100	92
11	260	252
13	416	405
3 3 L		
0	481	478
1	54	62
2	275	271
3	677	656
4	467	467
5	107	111
6	597	575
7	597	593
8	74	93
9	401	389
10	461	467
11	92	65
5 3 L		
0	622	627
1	212	207
2	95	94
3	784	786
4	172	184
5	248	257
7	370	374
8	122	97
7 3 L		
0	269	262
1	134	129
-6 4 L		
2	137	147
4	194	199
5	157	155
8	97	86
9	125	125
-5 5 L		
2	89	94
3	130	138
4	255	257
6	101	100
8	178	196
9	130	142
10	77	74
-3 5 L		
1	225	236
2	110	115
3	548	533
4	310	308
5	127	126
6	165	160
7	125	143
8	309	314
9	76	63
10	74	57
12	93	111
-1 5 L		
1	166	163
2	372	363
3	533	522
4	118	109
5	69	53
6	96	84
7	311	306
8	104	101
9	104	99
10	75	75
11	188	188
12	158	148
13	79	65
1 5 L		
0	200	198
1	360	350
2	663	658
3	202	200
4	173	173
5	62	54
6	299	297
7	294	305
10	100	114
11	163	160
2 6 L		
0	986	982
1	831	827
2	123	129
3	363	378
4	1035	1042
5	76	72
6	144	156
8	361	371
10	72	17
11	302	301
4 6 L		
1	340	331
2	273	264
3	169	160
4	484	488
5	625	625
6	201	186
7	143	130
8	354	352
6 6 L		
0	81	60
1	228	218
2	281	275
3	231	228
-5 7 L		
1	90	100
2	100	109
3	126	149
4	281	277
5	90	62
6	117	121
8	154	152
-3 7 L		
1	143	148
3	317	310
4	203	198
7	160	156
8	213	217
10	88	74
11	91	75
-1 7 L		
2	447	444
3	459	461
5	188	193
7	309	312
8	172	167
4 8 L		
0	147	155
1	181	201
3	102	116
5	247	237
6	152	158
-5 9 L		
1	356	364
2	227	238
4	268	269
5	131	137
-3 9 L		
1	801	803
2	206	199
4	164	173
5	363	364
6	200	199
7	111	98
8	333	334
9	400	396
-1 9 L		
1	527	530
2	648	647
3	210	211
4	93	88
5	799	803
6	189	192
7	266	265
9	377	384
10	76	97
1 9 L		
0	371	372
1	69	23
2	341	339
3	269	266
4	159	164
5	488	495
6	629	630
7	190	189
8	139	131
9	342	353
3 11 L		
1	226	219
2	98	104
-2 12 L		
1	244	247
2	71	29
3	275	276
4	129	140
0 12 L		
0	720	724
1	163	158
3	236	223
4	279	290
5	244	235
2 12 L		
0	359	370
1	376	378
2	94	90
3	94	102

related to the relative sizes of octahedral and tetrahedral layers, is also typical of other trioctahedral micas.

It is important to resolve the distribution of cations among the four different metal sites (the interlayer site, the tetrahedral site, and two symmetrically distinct octahedral sites). The structure refinement with unconstrained metal occupancy factors, combined with chemical analysis (Table 1), are sufficient to derive a reasonable, if not unique, structural formula for this unusual mica. A crystal–chemical constraint common to all micas is that there must be exactly four tetrahedral cations per 11 oxygens. Of the cations present (Table 1), only Si, Al, and Fe^{3+} commonly enter tetrahedral coordination in micas. Magnesium has been observed in four coordination in iron-free synthetic mica (Tateyama, 1974), but tetrahedral magnesium has not been reported from natural micas, nor has it been observed in any mica with $\sum(Si + Al + Fe^{3+}) \geq 4$. Furthermore, the refined elec-

Table 6. Interatomic distances and bond angles

Bond	Distance (Å)	Atoms	Angle (°)
	Tetrahedron		
T-01	1.653(2)*	01-T-01	108.16(7)
T-01	1.654(2)	01-T-02	108.08(13)
T-02	1.655(1)	01-T-02	110.74(8)
T-03	1.657(2)	01-T-03	108.06(13)
Mean T-0	1.655	01-T-03	110.75(9)
		02-T-03	110.95(10)
01-01	2.678(1)		109.46
01-02	2.677(3)		
01-02	2.677(3)		
01-03	2.723(2)		
01-03	2.725(2)		
02-03	2.729(3)		
Mean 0-0	2.701		
T-T[2]†	3.076(1)		
T-T	3.078(1)		
Mean T-T	3.077		
Interlayer Site			
K-01[4]	3.022(2)		
K-02[2]	3.020(3)		
Mean K-0 (inner)	3.021		
K-01[4]	3.282(2)		
K-02[2]	3.282(3)		
Mean K-0 (outer)	3.282		
Δ(K-0)	0.261		

Bond	Distance (Å)	Atoms	Angle (°)
	M1 Octahedron		
M1-03[4]	2.093(1)	03-M1-03[2]	94.80(8)
M1-F[2]	2.044(2)	03-M1-03[2]	85.20(8)
Mean M1-0	2.077	03-M1-F[4]	96.04(5)
		03-M1-F[4]	83.96(5)
03-03[2]	2.834(3)	Mean 0-M-0 (adjacent)	90.00
03-03[2]	3.074(3)		
03-F[4]	2.767(2)		
03-F[4]	3.075(2)	03-M1-03	180.00
Mean 0-0 (adjacent)	2.932	F-M1-F (opposite)	180.00
	M2 Octahedron		
M2-03[2]	2.092(2)	03-M2-03	85.27(9)
M2-03[2]	2.094(1)	03-M2-03[2]	85.26(6)
M2-F[2]	2.044(2)	03-M2-03[2]	94.49(6)
Mean M2-0	2.077	03-M2-F[2]	83.93(7)
		03-M2-F[2]	96.33(7)
03-03[2]	2.835(3)	03-M2-F[2]	96.06(6)
03-03	3.082(3)	F-M2-F	82.66(9)
03-03[2]	3.074(3)	Mean 0-M2-0 (adjacent)	90.00
03-F[2]	2.767(2)		
03-F[2]	3.074(3)		
03-F[2]	3.084(3)	03-M2-03	179.66(9)
F-F	2.707(4)	03-M2-F	177.83(7)
Mean 0-0 (adjacent)	2.955	Mean 0-M2-0 (opposite)	178.75

*Parenthesized figures represent esd's.
†Bracketed figures represent multiplicity.

Table 7. Magnitudes and orientations of thermal ellipsoids

Atom	Axis	rms Displacement (Å)	Angle with respect to:		
			a (°)	b (°)	c (°)
T	r_1	0.097(1)*	89(6)	6(5)	84(4)
	r_2	0.107(1)	158(12)	87(6)	102(12)
	r_3	0.110(1)	112(12)	95(4)	14(11)
M1	r_1	0.071(5)	90	0	90
	r_2	0.093(4)	178(7)	90	82(7)
	r_3	0.115(4)	92(7)	90	8(7)
M2	r_1	0.091(3)	90	0	90
	r_2	0.092(3)	175(5)	90	85(5)
	r_3	0.114(3)	95(5)	90	5(5)
K	r_1	0.171(2)	73(9)	90	27(9)
	r_2	0.172(2)	90	0	90
	r_3	0.180(2)	17(9)	90	117(9)
01	r_1	0.145(3)	83(5)	83(4)	17(6)
	r_2	0.168(3)	147(3)	121(3)	72(6)
	r_3	0.218(3)	58(3)	148(3)	93(2)
02	r_1	0.146(5)	89(2)	90	11(2)
	r_2	0.168(4)	90	0	90
	r_3	0.223(4)	1(2)	90	101(2)
03	r_1	0.107(3)	83(17)	9(21)	86(14)
	r_2	0.110(4)	139(17)	81(21)	120(17)
	r_3	0.118(3)	50(16)	90(10)	150(17)
F	r_1	0.118(4)	72(17)	90	27(17)
	r_2	0.123(4)	90	0	90
	r_3	0.128(4)	18(17)	90	117(17)

*Parenthesized figures represent esd's.

tron density of the T site is significantly greater than that of Si, Al or Mg. It is assumed, therefore, that all silicon plus aluminum, as well as 0.646 atoms of Fe^{3+}, occupy this site. The total number of electrons on the tetrahedral site ($15.1e^-$ based on refined electron density) and the mean T–O bond distance (1.655Å) from the structure refinement, conform well with this assumed tetrahedral site occupancy.

A second crystal–chemical constraint of all micas is that there can be no more than 1.0 interlayer cation per 11 oxygens. In this mica the sum of (K + Na + Ba) is 1.11, indicating that a significant fraction of these cations are not in the interlayer position. All K + Ba, as well as 0.013 atoms of Na, are assigned to a fully-occupied interlayer site. The total number of electrons ($19.3e^-$) and the mean inner and outer K–O distances (3.021 and 3.282Å, respectively) from the structure refinement are consistent with this assignment.

All remaining cations must occupy the two octahedral sites. This necessary conclusion leads to one of the most complex site compositions in any known silicate. The resulting average octahedral layer composition, based on three octahedral cations per 11 oxygens, is:

$$Mg_{2.457}Fe_{0.031}Mn_{0.006}Ca_{0.005}Ti_{0.088}Li_{0.225}Na_{0.110}\square_{0.078}$$

The remarkable M1 and M2 sites thus have cations of valence 4+, 2+, and 1+, as well as vacancies, with cation radii ranging from 0.61 to 1.02Å (Shannon, 1976). The total refined number of electrons on the two sites, M1 and M2, are both 11.7e$^-$, and the mean M1–O and M2–O distances are both 2.077Å. Although the complexity of the octahedral site chemistry precludes a unique solution to M1–M2 cation distribution, there is no evidence for cation ordering, consistent with previous refinements of both igneous (Hazen and Burnham, 1973) and metamorphic (Bohlen *et al.*, 1980) biotites, as well as synthetic $BaLiMg_2AlSi_3O_{10}F_2$ (McCauley and Newnham, 1973).

The resulting mica, though complex, may be represented as composed primarily (65%) of the ferriphlogopite end member, $KMg_3Fe^{3+}Si_3O_{10}F_2$. Additional components include 23% of the magnesium lithium mica taeniolite, $K(LiMg_2)Si_4O_{10}F_2$, plus minor amounts of the phlogopite–annite series and a Ti-mica. Note that the calculated number of titanium atoms approximately equals the number of octahedral vacancies, as observed in many other biotites (Hazen and Burnham, 1973). The only previously unknown component of this mica is approximately 4% of an end member with Na in the octahedral layer.

Analytical uncertainties for fluorine, lithium, and octahedral Fe^{2+}/Fe^{3+} result in small but significant uncertainties in the structural formula. For example, 10% oxy-biotite substituting for fluoro-biotite could increase the total number of cations from 7.92 to the ideal value of 8.00. Refined electron density of the fluorine site (8.3 e$^-$) is smaller than the 9.0 e$^-$ value expected for a pure fluoro-mica. This electron deficiency may imply the presence of an oxy-biotite component or undetected $(OH)^-$. Uncertainties in lithium content may also affect the structural formula. If total lithium is 0.50 instead of 0.75 wt.%, then the number of octahedral cations will decrease from 2.92 to 2.85.

This unusual mica serves a special role in the crystallization history of the melilite-bearing eruptive rocks in which it is found. It appears to concentrate alkali metals, including potassium, sodium, and lithium, in an environment that is deficient in aluminum and thus underscores the adaptability of the mica structure to a wide range of compositional limits.

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