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THE CRYSTAL STRUCTURE OF DELHAYELITE

Riassunto. — La delhayelite è un silicato per il quale sono state proposte dagli autori dei due ritrovamenti le seguenti due formule: $(Na, K)_4 Ca_5Al_6Si_{32}O_{80} \cdot 18H_2O \cdot 3(Na_2, K_2)(Cl_2, F_2, SO_4)$ (Sahama e Hytönen); $(Na, K)_9 Ca_4Al_2Si_{12}(O, OH, F, Cl)_{38}$ (Dorfman, Belova, Neronova).

La delhayelite appartiene al gruppo spaziale Pmmn; le costanti reticolari sono le seguenti: $a = 24.86$, $b = 7.07$, $c = 6.53$ Å.

La struttura è stata determinata attraverso l'esame della sintesi di Patterson tridimensionale e l'assunzione di una analogia fra la struttura della delhayelite e quella della macdonaldite, recentemente studiata dagli autori di questo lavoro. I rapporti fra le costanti reticolari della macdonaldite ($c = 23.56$, $a = 14.08$, $b = 13.11$ Å) e quelle della delhayelite sono evidenti. Invece la formula chimica della macdonaldite, $BaCa_4H_2Si_{16}O_{38} \cdot 10.4\ H_2O$, non sembra, a prima vista, aver molto a che fare con quelle scritte sopra per la delhayelite. Bisogna però ricordare che nella struttura della macdonaldite, fatta salva l'impalcatura costituita dai tetraedri del Si e dagli ottaedri del Ca, c'è ampio spazio per sostituzioni e aggiunte di altri cationi.

L'ipotesi assunta è stata confermata dall'esame di sintesi di Fourier tridimensionali e i parametri sono stati raffinati fino a un fattore di discordanza dell'8,8%, attribuendo via via una appropriata natura chimica ai diversi massimi di densità elettronica, sulla base delle loro intensità e delle distanze formate con quelli adiacenti.

La formula chimica della delhayelite viene così modificata dai risultati dell'analisi strutturale: $Ca_4(Na_3Ca)K_7(Si_{14}Al_2)O_{38}Cl_2F_4$. La composizione percentuale in ossidi, ricalcolata da questa formula è molto vicina a quella pubblicata da Dorfman e coll., mentre quella di Sahama e Hytönen, che trovano molto più silicio e molti meno alcali, è probabilmente viziata dall'attacco acido, resosi necessario per purificare il loro campione.

Come ipotizzato, l'impalcatura della macdonaldite si mantiene nella delhayelite. La sostituzione del Si con Al avviene ordinatamente in una delle tre posizioni indipendenti occupate dai cationi tetraedrici. Le catene di ottaedri del Ca, collegate fra loro da legami d'idrogeno nella macdonaldite, qui sono collegate da catene di prismi del Na. L'impalcatura della macdonaldite è attraversata da un doppio sistema di canali, in cui trovano posto gli atomi di bario e le molecole d'acqua non legate ai cationi. Nella delhayelite in questi spazi vuoti trovano posto atomi di K e di Cl, che occupano in parte posizioni nuove e in parte posizioni già occupate nella macdonaldite dal bario o dall'acqua.

Introduction.

Delhayelite is a silicate found by Sahama and Hytönen [1] in a complex kalsilite-bearing melilite-nephelinite lava from M. Saheru, Nyiragongo Area, North Kivu (Congo). These chemical and crystallographic data are quoted from the paper [1]: chemical formula:

$$(Na, K)_4\, Ca_5Al_6Si_{32}O_{80} \,.\, 18H_2O \,.\, 3(Na_2\,, K_2)(Cl_2\,, F_2\,, SO_4);$$

unit cell parameters:

$$a = 6.53 \pm 0.03\ \text{Å}$$
$$b = 24.65 \pm 0.2\ \ \text{Å}$$
$$c = 7.04 \pm 0.03\ \text{Å}.$$

The a side should be doubled owing to « extremely weak layer-lines » showed by the a-axis rotation photographs. The unit cell with the doubled a-axis contains one formula unit. The possible space groups are $Pmn2_1$ and Pmmn. Sahama and Hytönen write that the chemical formula (derived from chemical analyses carried out by Pennti Ojanperä of the Geological Survey of Finland) is only a provisional approximation because of the low purity of the analysed material.

In a paper on the crystal structure of macdonaldite $BaCa_4H_2$ $Si_{16}O_{38} \,.\, 10.4H_2O$ [2], the possibility of a close structural relationship of that silicate with delhayelite and the related mineral rhodesite was discussed on the basis of the similarity of the crystallographic, physical and (at least for rhodesite) chemical properties. Also the observed structural connection between macdonaldite and the fibrous zeolites as well as the resemblance of these ones with delhayelite and rhodesite [1], [3] supported the hypothesis that the three mentioned silicates could belong to the same structural family.

The aim of this work is the determination of the crystal structure of delhayelite in order to verify that hypothesis.

Experimental.

Prof. Th. G. Sahama kindly supplied a sample of delhayelite consisting of very small crystal fragments. One of those having a roughly prismatic shape (about two tenths of millimeter long with a cross section of few hundredths of millimeter) was chosen for the collection of the X-rays experimental data.

From rotation and Weissenberg photographs the cell parameters were remeasured:

$$a = 24.86 \pm 0.01 \text{ Å}$$
$$b = 7.07 \pm 0.02 \text{ Å}$$
$$c = 6.53 \pm 0.01 \text{ Å}.$$

The possible space groups are those given by Sahama and Hytönen: $Pmn2_1$ and Pmmn. The orientation of the cell axes was changed with respect to that used by the cited Authors in order to get the standard setting of the International Tables of X-rays Crystallography.

Integrated Weissenberg photographs (rotation axis b) were taken using the multiple films technique and the nickel-filtered copper radiation. No doubling of the c axis was observed with the used exposure times (10 days at 50 KV, 30 mA).

A total of 1100 independent reflexions was inspected (about 80% of the CuKα limiting sphere); 527 of them were measured photometrically; 573 were too faint to be conveniently measured or did not give any blackening on the films.

Owing to the very small dimensions of the crystal fragment employed no absorption correction was applied. The intensities were corrected for the Lorentz-polarization factor and for incomplete α_1-α_2 spot doubling. The latter correction was computed taking into account the integration technique which complicates the splitting effect for its diagonal direction with respect to the sides of the film.

Crystal Structure Analysis.

The starting point of the structure analysis was the hypothesis of the close relationship of delhayelite and macdonaldite. The three-dimensional Patterson synthesis of delhayelite did not discard this supposition at least for what was concerned with the chains of Ca-octahedra and the double layers of Si-tetrahedra which are the characteristic feature of macdonaldite. So a structure factors calculation, in the centric space group Pmmn, was carried out by giving to one calcium (in a fourfold equipoint), to three Si atoms (one in a general position and two in fourfold equipoints) and to the oxygens bonded to silicon, the same atomic coordinates of macdonaldite, taking into account that in this one the b and c cell parameters are doubled.

A three-dimensional Fo's Fourier synthesis was computed on the basis of the calculated structure factors. The Fourier maps showed well resolved peaks corresponding to the atoms employed in computing the structure factors and some more maxima that were uninterpretable on the basis of the chemical analysis given by Sahama and Hytönen. In fact a chemical formula computed from the cited analysis, on the basis of a $Si_{16}O_{38}$ tetrahedral group, shows a strong deficiency of Ca, Na and K with respect to the number of maxima in the Fourier synthesis. No new chemical analysis was possible because of the scarcity and impurity of the available material. So the attribution of a 'name' to the maxima was made, step by step taking into account

TABLE I.

	1	2	3	4
SiO_2	46.34	46.53	48.19	52.60
TiO_2	traces	0.07		0.09
RE_2O_3	0.11	0.13		
Al_2O_3	6.43	6.59	5.84	9.22
Fe_2O_3	0.54	0.73		2.72
MnO	0.08	0.12		0.07
BeO	0.02	0.17		
CaO	14.39	14.55	16.07	7.99
CrO	0.12	0.17		
MgO	0.14	0.17		1.03
Na_2O	6.42	6.88	5.33	3.20
K_2O	17.92	18.37	18.90	9.27
F	2.80	2.91	4.36	0.33
Cl	3.35	3.47	4.06	3.91
S	0.06	0.27		1.31 SO_3
H_2O^+	1.23	1.48		5.93
H_2O^-	0.43	0.06		3.35
$O \equiv (F, Cl)$			—2.75	—1.01
Total			100.00	100.01

1, 2 - Analyses of Dorfman et al. [4]. These authors write the chemical formula as follows: $(K, Na)_9Ca_4Al_2Si_{12}(O, OH, F, Cl)_{38}$.

3 - Analysis computed from the chemical formula resulting from this work.

4 - Analysis of Sahama and Hytönen [1].

the elements detected in the chemical analysis, the height of the peaks, their relative distances and their distances from the oxygens of the tetrahedra. At the end of this procedure a self-consistent arrangement of atoms was obtained and submitted to the least-squares refinement. The hypothetical cell content at this stage was: $Ca_4Na_4K_8Si_{16}O_{38}Cl_2F_4$; this stoichiometric unit does not get balanced its electrostatic charges. During the refinement the multiplier of several doubtful atoms was allowed to vary in order to obtain some supplementary informations: the positions of potassium appeared incompletely occupied, the position of the supposed sodium seemed to be occupied by a heavier cation. These informations together with those obtained from the more precise values of the bond distances led to this hypothetical cell content: $Ca_4(Na_3Ca)K_7(Si_{14}Al_2)O_{38}Cl_2F_4$; it gives the best R factor: 0.088 for the observed reflexions.

TABLE II.

Final atomic parameters and their standard deviations (in parentheses).

W is the Wyckoff notation of the equipoint; N is the number of atoms per unit cell. The standard deviation of the multipliers N allowed to vary in the least-squares refinement affects the second decimal figure.

Atom	W	N	x/a	y/b	z/c	B
Na, Ca	c	4	0	0	0	1.07(15)
Ca	f	4	0.0067(1)	0.7500	0.5034 (7)	0.81 (9)
Si(1)	g	8	0.1125(1)	0.4656 (8)	0.2818 (4)	0.51 (6)
Si(2)	f	4	0.1828(2)	0.7500	0.5342 (8)	0.59 (9)
Si(3)	f	4	0.1065(2)	0.7500	0.9188 (7)	0.70 (9)
O(1)	g	8	0.0550(4)	0.4818(20)	0.3845(18)	3.76(25)
O(2)	g	8	0.1618(4)	0.5510(21)	0.4135(17)	4.01(26)
O(3)	g	8	0.1124(4)	0.5675(19)	0.0601(15)	3.28(23)
O(4)	f	4	0.0491(5)	0.7500	0.8164(20)	1.64(27)
O(5)	f	4	0.1580(6)	0.7500	0.7738(24)	2.73(31)
O(6)	f	4	0.1295(6)	0.2500	0.2433(25)	2.96(36)
O(7)	b	2	0.2500	0.7500	0.5392(32)	2.32(42)
F	f	4	0.0297(4)	0.2500	0.8146(17)	2.02(23)
Cl	a	1.8	0.2500	0.2500	0.8793(17)	3.83(32)
K(1)	f	3.7	0.1322(2)	0.2500	0.7804 (8)	1.95(14)
K(2)	a	1.8	0.2500	0.2500	0.3721(14)	2.76(25)
K(3)	b	1.7	0.2500	0.7500	0.0195(16)	4.45(31)

TABLE III.

Structure factors of Delhayelite.

Reflexions marked with an asterisk were unobservably weak. In this case Fo derives from 0.5 I_{min}.

h	l	10Fo	10Fc
h 0 l			
0	1	297	-345
0	2	527	485
0	3	329	-277
0	4	1347	1229
0	5	314	-179
0	6*	221	-53
0	7	286	-173
0	8*	164	215
1	1	346	-327
1	2	1318	1234
1	3	199	-109
1	4	826	-723
1	5*	204	98
1	6	221	-15
1	7*	207	210
1	8	569	-635
2	0	660	827
2	1	144	143
2	2	192	215
2	3	269	-207
2	4	583	555
2	5*	204	-72
2	6	445	464
2	7*	206	-131
2	8*	162	193
3	1	507	-525
3	2	852	820
3	3*	144	30
3	4	463	-437
3	5	346	-309
3	6	771	700
3	7*	206	31
3	8	378	-429
4	0	696	-820
4	1	492	-568
4	2	2058	2039
4	3	368	-424
4	4*	177	-130
4	5	483	408
4	6	1194	1223
4	7*	205	-140
4	8	480	477
5	1*	98	148
5	2	551	516
5	3*	149	-64
5	4*	180	71
5	5*	208	-35
5	6	415	-420
5	7*	203	55
5	8	321	347
6	0	280	356
6	1	1185	-1187
6	2	719	769
6	3	987	-987
6	4	933	998
6	5	301	275
6	6	632	604
6	7*	202	-190
6	8	284	292
7	1	961	986
7	2*	132	-48
7	3	840	-887
7	4*	186	180
7	5	482	398
7	6	384	-411
7	7	417	373
7	8	353	344
8	0	2315	2713
8	1	1191	1114
8	2*	138	56
8	3	397	382
8	4	1121	1118
8	5	409	-458
8	6*	220	2
8	7*	198	-49
8	8	256	333
9	1	413	388
9	2	795	761
9	3	633	-583
9	4	464	-383
9	5*	216	-176
9	6*	219	210
9	7*	195	-40
10	0*	129	157
10	1	371	363
10	2	924	954
10	3*	173	172
10	4	914	1008
10	5	1056	-1112
10	6*	217	142
10	7*	192	81
11	1	328	-325
11	2	322	-279
11	3	1041	966
11	4	525	-524
11	5*	219	-317
11	6	523	584
11	7*	189	-1
12	0	461	309
12	1	533	-600
12	2	1794	1799
12	3*	184	-81
12	4*	206	135
12	5*	220	13
12	6	517	556
12	7*	186	-89
13	1*	159	-136
13	2*	172	97
13	3	599	540
13	4*	210	-21
13	5*	221	70
13	6	404	-289
13	7*	181	73
14	0	1168	-1170
14	1	335	-268
14	2	371	286
14	3	425	-269
14	4	430	355
14	5	536	574
14	6	449	536
14	7*	173	-256
15	1	660	632
15	2	558	-441
15	3	641	-574
15	4	707	607
15	5*	220	49
15	6*	202	28
15	7*	161	-206
16	0	1630	1562
16	1	277	-316
16	2	622	592
16	3*	237	-2
16	4	761	733
16	5*	218	-155
16	6	314	338
16	7*	145	-32
17	1	452	369
17	2	381	-387
17	3	285	-177
17	4*	221	-252
17	5*	215	282
17	6	334	-335
18	0	932	1147
18	1*	199	-24
18	2	207	311
18	3	514	473
18	4	405	437
18	5	542	-570
18	6*	187	-74
19	1	522	-567
19	2*	213	-33
19	3	317	293
19	4*	219	-184
19	5*	205	-172
19	6*	180	246
20	0	883	737
20	1*	212	180
20	2	692	646
20	3	317	239
20	4*	217	-19
20	5*	199	-88
20	6	309	180
21	1	576	-591
21	2	607	521
21	3*	221	315
21	4*	212	123
21	5	268	-201
21	6*	147	111
22	0	316	-266
22	1*	220	-256
22	2	537	593
22	3	521	-577
22	4	307	340
22	5*	187	345
23	1*	221	338
23	2*	220	-193
23	3*	214	57
23	4*	200	87
23	5	303	336
24	0	396	164
24	1*	220	5
24	2*	216	122
24	3*	208	-2
24	4*	192	191
24	5	425	367
25	1	323	361
25	2*	211	-31
25	3	597	-570
25	4*	186	113
25	5*	131	154
26	0*	212	376
26	1*	210	32
26	2*	220	-151
26	3*	193	239
26	4	439	421
27	1*	202	-213
27	2*	196	-119
27	3*	185	-91
27	4*	148	-67
28	0	753	743
28	1*	194	108
28	2	402	349
28	3*	170	116
29	1	392	-390
29	2*	176	60
29	3	573	543
30	0	322	-187
30	1	346	296
h 1 l			
0	1	338	-373
0	2	674	665
0	3	355	-328
0	4*	174	-109
0	5	344	-350
0	6	427	425
0	7*	204	-94
0	8*	158	202
1	1*	77	-21
1	2	1352	1385
1	3*	142	-128
1	4	284	256
1	5	299	-251
1	6*	219	34
1	7*	204	-46
1	8*	157	-169
2	1*	80	78
2	2	589	-546
2	3*	143	-59
2	4	373	-308
2	5*	205	46
2	6*	219	-10
2	7*	204	115
2	8*	156	-91
3	1	406	448
3	2	463	468
3	3*	145	46
3	4	821	-789
3	5	399	-310
3	6*	219	-128
3	7*	203	-237
3	8*	153	-32
4	1	206	212
4	2	699	705
4	3*	147	39
4	4	484	475
4	5*	207	105
4	6*	219	-274
4	7*	202	-86
4	8*	150	95
5	0*	87	-52
5	1	338	287
5	2	339	-326
5	3*	150	-83
5	4	688	672
5	5*	208	132
5	6*	219	74
5	7*	201	-32
5	8*	145	28
6	1	274	275
6	2	274	-233
6	3*	154	51
6	4*	183	137
6	5*	210	-213
6	6*	219	279
6	7*	199	-220
6	8*	138	87
7	0	788	795
7	1	1160	-1258
7	2	603	-549
7	3	560	-520
7	4	370	355
7	5*	212	-3
7	6*	219	202
7	7*	197	65
7	8	205	228
8	1	340	287
8	2	540	529
8	3*	163	-78
8	4	560	-514
8	5*	213	139
8	6*	218	49
8	7*	195	254
8	8*	118	-161
9	0	886	-961
9	1*	128	-49
9	2	733	695
9	3	381	327
9	4*	194	121
9	5*	215	-154
9	6*	221	204
9	7*	192	139
9	8*	100	66
10	1*	136	-123
10	2	448	-386
10	3	329	-306
10	4	290	-206
10	5	308	-334
10	6*	215	248
10	7*	190	-11
11	0*	138	-45
11	1*	144	-19
11	2	753	807
11	3*	179	12
11	4	453	-447
11	5	555	-493
11	6*	213	-46
11	7	287	-314
12	1	214	-217
12	2*	231	187
12	3*	185	112
12	4	392	352
12	5*	219	-122
12	6*	210	-162
12	7*	184	-96
13	0	901	1007
13	1	252	-240
13	2	424	467
13	3	334	-343
13	4	709	715
13	5*	219	-204
13	6*	207	-111
13	7	312	-331
14	1	337	349
14	2	271	-245
14	3*	197	208
14	4*	213	5
14	6*	203	-114
14	7*	167	5
15	0*	172	-72
15	1	387	-395
15	2	504	-424
15	3*	203	104
15	4*	216	3
15	5*	218	-72
15	6*	199	66
15	7*	154	-8
16	1*	184	-36
16	2	529	514
16	3*	208	-205
16	4*	218	280
16	5*	215	-27
16	6*	194	238
16	7	240	-222
17	0	503	-501
17	1	616	-717
17	2	815	752
17	3*	212	-91
17	4	396	407
17	5	329	-335
17	6	477	456
17	7	191	199
18	1	517	-546
18	2	655	-573
18	3*	216	166
18	4*	219	-51
18	5*	207	-124
18	6*	185	-54
19	0	375	392
19	1	314	-269
19	2*	212	312
19	3	318	-303
19	4*	217	-18
19	5*	202	-176
19	6*	176	136
20	1	364	-374
20	2*	216	-164
20	3*	219	25
20	4*	214	46
20	5*	197	29
20	6	280	-244
21	0	561	645
21	1	322	328
21	2*	219	23
21	3*	219	-294
21	4	398	303
21	5*	190	-21
21	6*	139	-59
22	1*	219	188
22	2*	219	-5
22	3*	216	-246
22	4*	203	235
22	5*	185	-6
22	6*	104	190
23	0	616	627
23	1	408	-395
23	2*	218	310
23	3	454	-420
23	4*	197	157
23	5	350	-332
24	1*	218	141
24	2*	214	201
24	3*	205	220
24	4*	190	86
24	5	248	224
25	0*	215	-106
25	1*	213	-308
25	2*	208	145
25	3*	198	-151
25	4*	183	249
25	5*	122	-123
26	1*	122	-123
26	2*	201	-138
26	3*	190	176
26	4*	167	12
27	0	308	271
27	1*	199	-243
27	2*	193	-80
27	3	329	-289
27	4*	140	151
28	1*	191	-114
28	2*	185	75
28	3*	164	-235
28	4*	90	-73
29	0	519	561
29	1*	183	-190
29	2	366	362
29	3	383	-454
30	1	246	244
30	2*	142	-127
h 2 l			
0	2*	111	-154
0	3	2154	2170
0	4	366	387
0	5*	201	168
0	6*	212	-243
0	7	990	1128
1	1	1521	-1522
1	2	221	-194
1	3	227	-151
1	4*	174	182
1	5	683	-641
1	6	380	388
1	7*	193	-65
2	0	711	853
2	1	451	519
2	2	302	296
2	3	1177	1181
2	4*	175	-70
2	5	432	443
2	6*	212	-140
2	7	437	440
3	1	1655	-1678
3	2*	116	60
3	3*	146	13
3	4	563	-484
3	5	395	-272
3	6*	211	-206
3	7*	192	135
4	0	980	-1142
4	1	1245	1187
4	2	551	-449
4	3	237	189
4	4*	178	-92
4	5	797	814
4	6	347	-339
4	7	329	-254
5	1	310	366
5	2	366	-317
5	3*	151	-145
5	4*	180	181
5	5	585	518
5	6*	211	-9
5	7*	190	-35
6	0	375	-260
6	1	1199	1277
6	2	544	552
6	3	1013	974
6	4	821	-786
6	5	647	646
6	6*	210	-172
6	7*	188	241
7	1*	114	150
7	2	815	731
7	3	366	-366
7	4	1179	1132
7	5	425	342
7	6	440	-360
7	7	367	-330
8	0	780	-842
8	1	649	615
8	2*	139	-190
8	3	678	636
8	4	413	405
8	5*	209	-102
8	6*	208	79
8	7	742	826
9	1	566	-541
9	2	528	-516
9	3	514	467
9	4	361	325
9	5*	210	95
9	6*	207	-161
9	7*	183	61
10	0	657	724
10	1	1264	1281
10	2	1086	-1048
10	3	771	705
10	4	417	406
10	5	603	537
10	6*	205	29
10	7	552	593
11	1	635	-635
11	2	243	-270
11	3	293	231
11	4	785	-719
11	5	335	-353
11	6*	202	183
11	7*	176	-11
12	0	448	-500
12	1	881	877
12	2	459	-470
12	3*	184	62
12	4*	203	-108
12	5	863	856
12	6*	199	-105
12	7*	169	40
13	1*	160	-11
13	2	273	-243
13	3	325	-285
13	4*	206	-151
13	5*	211	-330
13	6	466	518
13	7*	159	-100
14	0	289	236
14	1	619	660
14	2	1045	912
14	3*	195	102
14	4	509	-553
14	5	454	467
14	6*	192	65
14	7*	146	-56
15	1	738	703
15	2*	186	31
15	3*	200	79
15	4	319	239
15	5	351	413
15	6	437	-501
16	0	552	-498
16	1	798	857
16	2	354	-398
16	3	667	719
16	4*	212	-195
16	5*	205	233
16	6*	184	-124
17	1	501	477
17	2*	199	-73
17	3*	208	137
17	4	578	518
17	5*	201	38
17	6*	180	51
18	0	1183	1171
18	1*	197	100
18	2	514	-485
18	3	694	653
18	4*	210	290
18	5	333	332
18	6*	171	-82
19	1	377	-370
19	2	437	339
19	3*	232	47
19	4*	227	-319
19	5	294	-221
19	6*	172	167
20	0*	226	-62
20	1*	227	76
20	2*	231	-202
20	3*	232	200
20	4*	223	207
20	5	388	418
20	6*	151	19
21	1*	231	-354
21	2*	232	-85
21	3*	229	-56
21	4	460	-560
21	5*	199	-147
21	6*	118	240
22	0	525	-570
22	1	742	717
22	2	395	378
22	3	411	362
22	4	581	-553
22	5	419	456
23	1*	231	105
23	2*	228	97
23	3	346	-332
23	4*	204	195
23	5*	168	-40
24	0*	229	-98
24	1	300	290
24	2	390	416
24	3*	212	106
24	4*	198	-87
24	5*	139	53
25	1	304	343
25	2*	216	-65
25	3*	205	-10
25	4	356	443
26	0	649	623
26	1*	215	262
26	2	333	-334
26	3	350	355
26	4	277	277
27	1*	207	-7
27	2	252	219
27	3*	183	143
27	4*	120	-16
28	0*	201	-148
28	1*	199	243
28	2	512	-472
29	1*	184	-255
29	2*	164	54
h 3 l			
0	1*	82	-43
0	2*	119	-135
0	3	1313	1225
0	4*	183	-108
0	5	361	333
0	6*	208	15
0	7*	188	173
1	1	230	157
1	2	400	-402
1	3*	152	32
1	4	424	-458
1	5	535	505
1	6*	208	-51
1	7*	188	-159
2	1	354	-299
2	2	681	719
2	3*	153	-36
2	4	337	325
2	5*	206	-58
2	6*	208	54
2	7*	187	-61
3	0	168	-225
3	1	199	218
3	2	269	306
3	3	317	-220
3	4	399	438
3	5	518	484
3	6*	208	167
3	7*	187	-91
4	1*	99	106
4	2	762	-797
4	3	934	-895
4	4	292	-240
4	5*	207	-58
4	6*	207	-163
4	7*	186	15
5	0	478	-436
5	1*	107	-17
5	2*	132	-164
5	3*	160	58
5	4	276	-268
5	5	362	-363
5	6*	206	-5
5	7*	185	143
6	1	191	168
6	2	524	-398
6	3*	164	-78
6	4	290	-246
6	5*	209	245
6	6	359	-416
6	7*	183	127
7	0	332	-319
7	1	367	381
7	2	358	-252
7	3	599	555
7	4*	193	-76
7	5*	210	-228
7	6	283	-301
7	7	299	316
8	1	474	-489
8	2*	148	-53
8	3	614	593
8	4	428	398
8	5*	210	-216
8	6*	202	304
8	7*	176	-171
9	0	809	822
9	1*	138	3
9	2	386	-428
9	3	321	-274
9	4*	199	-129
9	5*	211	178
9	6*	200	-195
9	7*	171	-138
10	1	224	-164
10	2	642	660
10	3	582	613
10	4*	200	166
10	5*	211	205
10	6*	198	68
10	7*	163	70
11	0	427	-389
11	1	488	566
11	2*	168	-121
11	3*	187	-134
11	4*	205	125
11	5	611	639
11	6*	196	152
11	7*	154	-77
12	1	543	538
12	2	540	-570
12	3*	192	-236
12	4	314	-328
12	5*	209	183
12	6*	193	-56
12	7*	142	13
13	0	664	-663
13	1*	169	120
13	2	250	-206
13	3	415	320
13	4	737	-748
13	5	285	329
13	6*	189	68
13	7	205	242
14	1*	177	-15
14	2*	188	-93
14	3	669	-675
14	4*	210	116
14	5*	205	-217
14	6*	187	-207
15	0	422	421
15	1*	184	-81
15	2*	194	-112
15	3*	205	79
15	4*	211	162
15	5*	202	-122
15	6*	183	-154
16	1*	191	-183
16	2*	199	-199
16	3*	208	201
16	4*	210	-222
16	5*	198	-9
16	6*	175	-138
17	0	449	390
17	1	614	606
17	2	868	-952
17	3*	210	186
17	4*	208	-208
17	5*	194	130
17	6	392	-409
18	1*	203	153
18	2	639	710
18	3*	211	341
18	4*	205	-129
18	5*	190	53
18	6	353	339
19	0	515	-488
19	1	360	367
19	2*	210	82
19	3*	210	151
19	4*	201	-186
19	5	349	352
20	1*	209	302
20	2*	210	182
20	3*	207	-29
20	4*	197	-27
20	5*	180	-15
21	0	707	-714
21	1*	210	-160
21	2	290	312
21	3*	204	138
21	4	424	-424
21	5*	166	210
22	1*	209	90
22	2*	206	-151
22	3*	199	-201
22	4*	187	-38
22	5*	146	87
23	0	555	-555
23	1	366	361
23	2	455	-530
23	3	387	439
23	4*	180	-8
23	5*	117	155
24	1*	201	-6
24	2*	196	-287
24	3*	188	-257
24	4*	164	-59
25	0	368	308
25	1*	195	151
25	2	481	-446
25	3	295	260
25	4*	141	-49
26	1*	189	-50
26	2	258	238
26	3*	165	128
27	0	289	-257
27	1*	183	226
27	2*	172	147
27	3	203	233
28	1*	168	-52
28	2*	149	47
29	0	738	-760
29	1	263	315
h 4 l			
0	1	351	-270
0	2	292	239
0	3	449	-423
0	4	1000	911
0	5	319	-190
0	6*	188	130
1	1*	85	136
1	2	580	630
1	3	349	243
1	4	413	-409
1	5*	194	250
1	6*	188	-16
2	0	655	541
2	1*	89	36
2	2	343	244
2	3*	154	-152
2	4	445	407
2	5*	194	-42
2	6	384	371
3	1*	95	23
3	2	707	592
3	3	313	233
3	4*	181	-69
3	5*	194	-71
3	6	478	519
4	0*	91	167
4	1	325	-230
4	2	1295	1397
4	3	226	-154
4	4*	182	24
4	5*	195	213
4	6	817	845
5	1*	109	-98
5	2	349	318
5	3	292	-205
5	4*	184	63
5	5*	195	-143
5	6*	185	-280
6	0	439	371
6	1	448	-480
6	2	738	594
6	3	673	-608
6	4	824	835
6	5*	195	73
6	6	531	518
7	1	484	439
7	2	405	-414
7	3	599	-555
7	4	268	-216
7	5*	194	148
7	6	336	-311
8	0	1184	1418
8	1	430	411
8	2*	150	8
8	3*	171	175
8	4	739	675
8	5*	194	-226
8	6*	182	67
9	1	226	261
9	2	417	442
9	3	335	-387
9	4*	191	-249
9	5*	193	-118
9	6*	180	183
10	0	454	279
10	1*	147	-69
10	2	784	722
10	3*	179	17
10	4	630	640
10	5	678	-719
10	6	266	150
11	1*	154	-94
11	2*	167	125
11	3	685	635
11	4*	194	-90
11	5*	191	-90
11	6	307	393
12	0*	157	314
12	1	316	-232
12	2	1214	1214
12	3*	186	-21
12	4*	195	207
12	5*	189	-116
12	6	394	444
13	1*	168	-46
13	2*	178	67
13	3	488	480
13	4*	194	14
13	5*	187	123
13	6*	166	-247
14	0	468	-510
14	1*	175	-40
14	2	361	241
14	3*	192	-89
14	4	361	351
14	5	346	355
14	6	373	387
15	1	334	260
15	2	399	-380
15	3	459	-461
15	4	284	275
15	5*	181	-89
15	6*	145	50
16	0	1000	1106
16	1	453	-377
16	2	457	481
16	3*	194	-92
16	4	572	558
16	5*	179	-79
16	6	246	288
17	1*	190	139
17	2	307	-250
17	3*	194	-252
17	4*	187	-259
17	5*	176	156
17	6	199	-245
18	0	648	548
18	1*	192	-10
18	2*	194	239
18	3	297	231
18	4	316	314
18	5	368	-404
19	1	307	-272
19	2*	194	-22
19	3*	190	260
19	4*	180	-56
19	5*	155	-48
20	0	508	521
20	1*	194	160
20	2	470	485
20	3*	186	162
20	4*	177	9
20	5*	137	-93
21	1	348	-312
21	2	376	384
21	3*	182	294
21	4*	171	201
21	5*	112	-86
22	0*	190	96
22	1*	189	-207
22	2	429	480
22	3	419	-385
22	4	308	345
23	1*	185	193
23	2*	181	-128
23	3*	174	39
23	4*	138	16
24	0*	181	126
24	1*	180	27
24	2*	177	65
24	3*	161	21
24	4*	109	191
25	1*	176	185
25	2*	168	-58
25	3	335	-429
26	0*	170	179
26	1*	166	-12
26	2*	151	104
26	3*	110	129
27	1*	146	-135
27	2*	124	-114
28	0	454	560
28	1*	116	30
h 5 l			
0	2	421	452
0	3*	190	41
0	4	363	-336
0	5	375	-370
0	6	585	566
1	1*	109	-13
1	2	978	1021
1	3	287	-255
1	4*	214	-33
1	5*	220	-33
1	6*	211	45
2	1*	114	-79
2	2*	157	-164
2	3*	191	-9
2	4*	215	-198
2	5*	219	22
2	6*	210	2
3	1	468	416
3	2	756	616
3	3*	193	-132
3	4	561	-624
3	5*	219	-19
3	6*	209	-23
4	1	428	386
4	2*	164	228
4	3	378	-257
4	4	527	548
4	5*	219	193
4	6	462	-440
5	0*	140	-66
5	1*	139	201
5	2	541	-415
5	3*	198	-13
5	4	482	514
5	5*	218	-53
5	6*	206	49
6	1	465	399
6	2*	175	-192
6	3*	201	-57
6	4*	218	204
6	5*	217	-69
6	6*	203	108
7	0	669	756
7	1	862	-894
7	2	546	-548
7	3*	204	-169
7	4	589	514
7	5*	217	-212
7	6*	199	95
8	1	242	-123
8	2*	186	306
8	3	314	306
8	4	541	-537
8	5*	216	-10
8	6*	193	236
9	0	529	-540
9	1*	175	-25
9	2	332	343
9	3*	211	171
9	4*	220	27
9	5*	215	-84
9	6*	187	149
10	1	383	-377
10	2*	198	-116
10	3*	213	-3
10	4*	220	-247
10	5	307	-365
10	6	304	356
11	0*	188	-255
11	1*	191	166
11	2	894	829
11	3*	216	-184
11	4	353	-446
11	5*	212	-134
11	6*	167	64
12	1*	198	111
12	2*	209	-53
12	3*	218	-54
12	4	314	313
12	5*	211	-18
12	6*	188	-226
13	0	683	651
13	1	286	-202
13	2	429	426
13	3	342	-297
13	4	336	373
13	5*	209	-99
13	6*	134	-67
14	1	557	547
14	2*	216	-220
14	3*	220	-79
14	4*	215	178
14	5	331	355
15	0	310	251
15	1	357	356
15	2	509	-542
15	3*	219	238
15	4*	213	182
15	5*	192	-210
16	1*	217	-141
16	2	370	424
16	3*	217	-114
16	4*	211	166
16	5*	179	-72
17	0*	218	-150
17	1	557	-550
17	2*	219	296
17	3*	215	-30
17	4	376	408
17	5	397	-364
18	1	566	-638
18	2*	217	-240
18	3*	213	345
18	4*	203	-230
18	5*	138	-194
19	0*	218	91
19	1*	217	-143
19	2	434	468
19	3*	211	-334
19	4*	190	-102
20	1*	215	-262
20	2*	212	-123
20	3*	208	-3
20	4*	172	7
21	0*	212	238
21	1*	212	280
21	2*	210	244
21	3	384	-324
21	4*	148	77
22	1	357	373
22	2*	206	-55
22	3	325	-405
22	4*	105	347
23	0	526	562
23	1*	205	-310
23	2*	193	133
23	3	257	-262
24	1*	191	202
24	2*	171	87
24	3*	118	120
25	0*	176	134
25	1	325	-305
25	2*	140	-100

During the last stage of the refinement the authors of this work had the opportunity to read the summary of a paper of Dorfman *et al.* [4] about the discovery of delhayelite in the Soviet Union. This summary reported two chemical analyses which were an unexpected support to the hypothetical formula written above. In Table I the analyses of the Russian Authors are compared with that of Sahama and Hytönen and with that computed from the chemical formula resulting from this structure analysis. Of course only a microprobe analysis of congolese delhayelite could give a detailed picture of its chemical formula. In any way the formula resulting from the structural determination would not be far from the true one.

Final atomic coordinates and thermal parameters are given in Table II. The rather high values of the temperature factors of the oxygen atoms as well as the fairly high values of the standard deviations could depend from the doubling of the *c* axis observed by Sahama and Hytönen. The atomic coordinates listed in Table II should be only average values of the 'true' coordinates in the cell with the *c* axis of 13.06 Å. As it has been said in a preceding section of this paper, no extra reflexions, corresponding to the doubling of the cited cell parameter, has been observed even with the long exposure times used in taking the X-rays pictures. This fact, however, does not contradict the observation of Sahama and Hytönen because, owing to the extreme smallness of the specimen, those very long exposure times allowed the measurement of only one half of the possible reflexions. So, it is possible that, with suitable exposure times, the cell side doubling could be seen also with the crystal fragment used for this work.

The final observed and calculated structure factors are compared in Table III. Bond distances and angles as well as their standard deviations are given in Table IV.

Discussion.

Calcium. One Ca atom is present in the asymmetric unit and is located on the mirror plane (010). It has a six-fold coordination built up by five oxygens of the tetrahedra (Ca-O from 2.30 to 2.37 Å) and one fluorine (Ca-F 2.26 Å). The coordination polyhedron could be roughly described as an octahedron. These octahedra, by sharing two opposite edges, form chains parallel to *b*.

TABLE IV.

Interatomic distances (Å) *and angles* (°) *and their standard deviations* (*in parentheses*).

A sign ′ is used to distinguish equivalent atoms. The distances preceded by one asterisk occur twice; those preceded by two asterisks occur four times.

Atoms		Bond lengths	Atoms	Bond angles
Si(1)	—O(1)	1.58(1)	O(1)—Si(1)—O(2)	115.7 (7)
	—O(2)	1.62(1)	O(1)—Si(1)—O(3)	110.2 (7)
	—O(3)	1.62(1)	O(1)—Si(1)—O(6)	112.0 (8)
	—O(6)	1.60(1)	O(2)—Si(1)—O(3)	108.1 (6)
Si, Al	—O(2)	*1.70(1)	O(2)—Si(1)—O(6)	103.7 (8)
	—O(7)	1.67(1)	O(3)—Si(1)—O(6)	106.5 (7)
	—O(5)	1.68(2)	O(2)—Si(2)—O(7)	108.5 (7)
Si(3)	—O(5)	1.59(2)	O(2)—Si(2)—O(5)	108.6 (6)
	—O(4)	1.57(1)	O(2)—Si(2)—O(2)′	112.2(1.0)
	—O(3)	*1.59(1)	O(7)—Si(2)—O(5)	110.4 (8)
Na, Ca	—F	*2.27(1)	O(4)—Si(3)—O(3)	109.3 (7)
	—O(4)	*2.46(1)	O(4)—Si(3)—O(5)	118.4 (8)
	—O(1)	*2.86(1)	O(3)—Si(3)—O(5)	105.7 (6)
	—O(3)	*2.86(1)	O(3)—Si(3)—O(3)′	108.2(1.0)
Ca	—F	2.26(1)	Si(1)—O(3)—Si(1)′	145 (2)
	—O(4)	2.30(1)	Si(2)—O(7)—Si(2)′	178 (2)
	—O(1)	*2.36(1)	Si(1)—O(2)—Si(2)	142 (1)
	—O(1)′	*2.37(1)	Si(1)—O(3)—Si(3)	152 (1)
K(1)	—F	2.56(1)	Si(2)—O(5)—Si(3)	148 (1)
	—O(3)	*2.93(1)		
	—Cl	3.00(1)		
	—O(6)′	3.02(1)		
	—O(2)	*3.29(1)		
	—O(6)	3.51(1)		
	—O(5)	3.59(1)		
	—O(1)	*3.61(1)		
K(2)	—O(2)	**3.07(2)		
	—O(6)	*3.11(1)		
	—Cl	3.22(1)		
	—Cl′	3.31(1)		
K(3)	—O(5)	*2.79(2)		
	—O(7)′	3.14(2)		
	—O(7)	3.39(2)		
	—Cl	3.65(1)		
	—O(2)	**3.66(1)		
	—O(3)	**3.66(1)		

Sodium. The best scattering curve for this atom lying on a symmetry center, was that based on the assumption that the site would be occupied by 3/4 Na and 1/4 Ca. Sodium is bonded to two F atoms (Na—F 2.27 Å) and to six oxygens of the tetrahedra (two Na—O of 2.46 and four Na—O of 2.86 Å). The eight mentioned atoms occur at the vertices of a sort of orthorhombic prism. The prisms share two opposite edges thus forming chains parallel to those of octahedra.

Potassium. The potassium atoms have not a regular coordination owing to their occurrence in large cavities of the structure. One can remark the short distances between K(1) and F and K(1) and Cl; they are shorter than the sum of the ionic radii of the involved atoms. K(2) occupies the same position of Ba in macdonaldite; its coordination is more regular being formed by six oxygens at the vertices of a folded hexagon with one chlorine atom above and one below.

Some more words on the role of potassium and chlorine will be spent in the course of the description of the structure.

Silicon. Three silicon atoms are present in the asymmetric unit; one of them shares all the oxygens with other tetrahedra; the remaining two have one oxygen unshared. These ones have Si—O bond distances of about 1.60 Å while the Si—O bond lenghts of the former range from 1.67 to 1.70 Å. For this reason it was assumed that the corresponding fourfold equipoint was occupied by 50% Si and 50% Al. As one can see in Table IV the lengths of the Si—O bonds are not much influenced by the fact that the oxygens are unshared or shared with other tetrahedra: Si(1)—O(1) 1.58 Å, Si(3)—O(4) 1.57 Å; the average Si—O distance for shared oxygens is about 1.60 Å. As suggested by Cruickshank [5] this fact is due to the presence of Al in the tetrahedral framework. It seems worthy to point out that in macdonaldite, which has the same tetrahedral framework, but is free of Al, the average bond distances of Si with the unshared oxygens were about 1.57 Å and those with the shared ones were about 1.63 Å.

Description of the structure (see Fig. 1). As previously pointed out the structural features common to macdonaldite and delhayelite are the double tetrahedral layers of the apophyllite type and the chains of Ca-octahedra. The « idealized » apophyllite layer is derived from the condensation of wollastonite chains through the xonotlite ribbon. In macdonaldite the double layers are imbedded between layers of Ca-

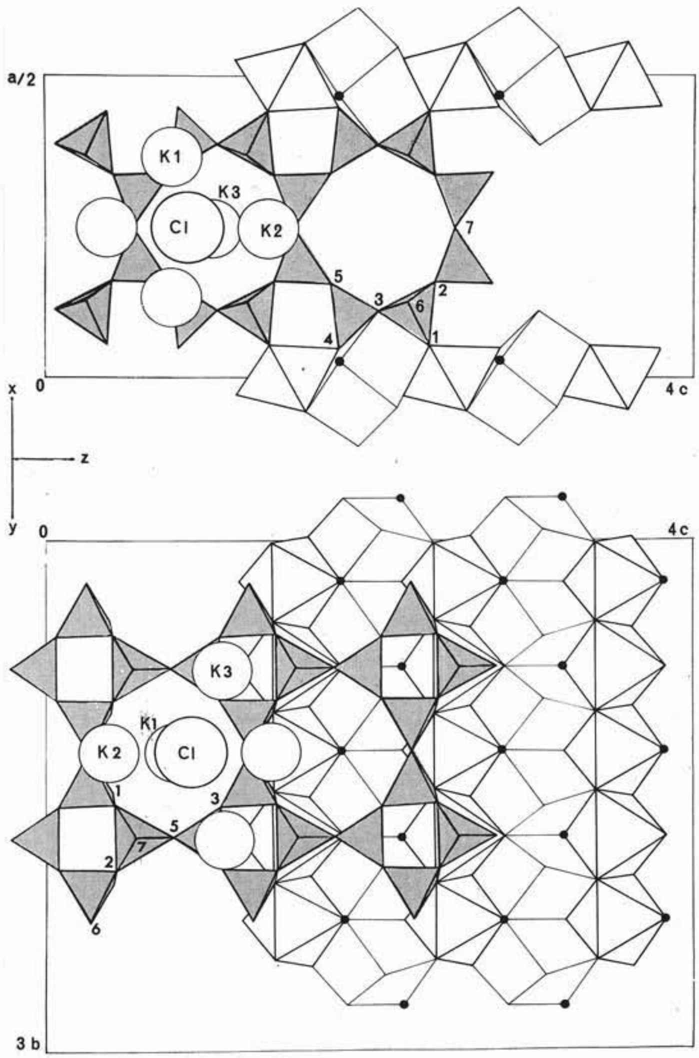

Fig. 1. — *Bottom*: schematic partial projection of the crystal structure of delhayelite along the *a* axis and key to the identification of the atoms (small black circles are fluorine atoms). The layers of Si-tetrahedra as well as of Ca-octahedra and Na-prisms are shown. *Top*: schematic partial projection along the *b* axis. A section of the channel parallel to *b* is shown. The other channel runs parallel to *c*.

octahedra. These layers are formed by chains of octahedra connected together by hydrogen bonds. In delhayelite the chains of octahedra are tied together by sodium atoms; in such a way the Ca-octahedra and the prisms of sodium form a sort of compact « wall » of polyhedra. The tetrahedral double layers occur between two of such « walls ». Taking into account the common structural features, delhayelite and macdonaldite belong without any doubt to the same structural family of Zoltai's [6] classification of silicates.

A number of structural details will be described in order to show some interesting peculiarities of delhayelite.

In macdonaldite two adjacent Ca atoms are not equivalent by symmetry: one lies on a symmetry center, the other on a mirror plane. In delhayelite both of them occur on a mirror plane. So, while in macdonaldite one octahedron is built up by six oxygens of the tetrahedra and the other by four oxygens and two water molecules, in delhayelite all the octahedra are formed by five oxygens and one fluorine. These different situations of calcium in the two minerals implies different situations of the tetrahedral layers with respect to the layers of octahedra (see Fig. 2).

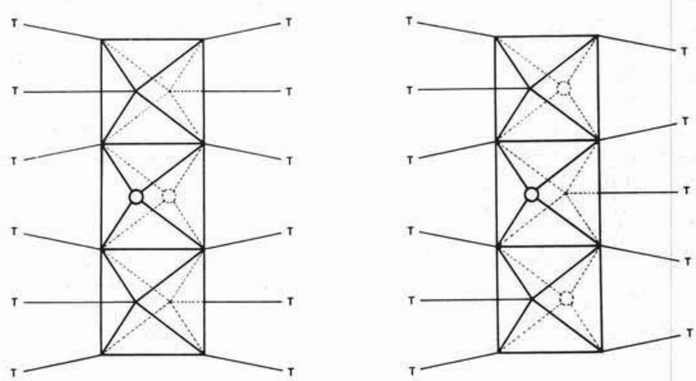

Fig. 2. — Schematic drawing showing the relationships between the chains of Ca-octahedra and the tetrahedral layers in macdonaldite (left) and in delhayelite (right). Each « T » represents a Si-tetrahedron and the segment running from one corner of the octahedron to a « T » is a Si—O bond. Small circles are water molecules in the macdonaldite chain and fluorine atoms in the delhayelite chain.

The channels that are present in macdonaldite exist also in delhayelite; they run within the tetrahedral layers parallel to b and c; their free diameter is about 3.8 Å. In macdonaldite the channels are occupied by barium and water molecules which do not fill completely the large cavities of the structure: it is a tipical feature of zeolites. In delhayelite there is no water; the channels are nearly completely filled by potassium and chlorine. In the channel parallel to c there is an infinite sequence ... K(2)—Cl—K(2)—Cl ... running at the intersection of two mirror planes. It could be of some interest to point out that the c cell parameter of delhayelite (6.53 Å) is only a little longer than the cell edge of KCl (6.26 Å). Another infinite sequence ... K(3)—Cl—K(3)—Cl ... occurs in the channel parallel to b.

Another interesting feature of delhayelite is a sort of finite chain or linear group F—K(1)—Cl—K(1)—F. This group is nearly parallel to a and runs between two adjacent walls of polyhedra in a cilindrical cavity which has the same free diameter of the channels. The chlorine atoms are located at the intersection of the two infinite sequences and the linear group; in such a way each chlorine is surrounded by six K atoms that form a distorted octahedron.

The a cell parameter of delhayelite is significatively longer than the corresponding cell edge of macdonaldite: 24.86 Å against 23.56 Å. This difference of 1.3 Å is caused by a rearrangement of the tetrahedral framework achieved through the increasing of some Si—O—Si angles.

TABLE V.

Mineral	Cell dimensions			Chemical formula
Macdonaldite	$a = 14.08$	$b = 13.11$	$c = 23.56$ Å	$4[BaCa_4H_2Si_{16}O_{38} . 10.4H_2O]$
Rhodesite	$c = 14.10$	$b = 13.08$	$a = 23.8$ Å	$4[K_2Na_2Ca_4Si_{16}O_{38} . 12H_2O]$
Delhayelite	$b = 7.07$	$c = 6.53$	$a = 24.86$ Å	$Ca_4(Na_3Ca)K_7(Si_{14}Al_2)O_{38}Cl_2F_4$

Conclusions. Table V shows a comparison of the crystallographic and chemical data of macdonaldite, rhodesite and delhayelite. The close structural relationship between macdonaldite and delhayelite has been fully confirmed by the crystal structure analysis in spite of the difficulties encountered with the chemical formula.

The absence of water and the presence of F and Cl in delhayelite as well as its occurence in a volcanic rock of unusual chemical and mineralogical composition [7] give a particular character to this mineral with respect to macdonaldite and rhodesite. These ones are more strictly comparable with fibrous zeolites for their occurence, their morphological features (rhodesite is fibrous) and their water content.

It would be very interesting to investigate the crystal structure of rhodesite also in order to know whether Na is in the channels as K and Ba or it connects together the chains of octahedra as in delhayelite. In such a way one could have a complete structural picture of this family of silicates whose members can occur in such different environments.

Acknowledgements. — We are greatly indebted to Prof. Th. G. Sahama who kindly sent us not only the sample of the mineral but also unpublished valuable informations on his preceding researches on delhayelite.

Centro Nazionale di Cristallografia del C.N.R. presso l'Istituto di Mineralogia dell'Università di Pavia. Novembre 1969.

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