

CARLETONITE, $\text{KNa}_4\text{Ca}_4\text{Si}_8\text{O}_{18}(\text{CO}_3)_4(\text{F}, \text{OH}) \cdot \text{H}_2\text{O}$, A NEW
MINERAL FROM MOUNT ST. HILAIRE, QUEBEC

G. Y. CHAO, *Department of Geology, Carleton University,
Ottawa, Canada*

ABSTRACT

Carletonite, $\text{KNa}_4\text{Ca}_4\text{Si}_8\text{O}_{18}(\text{CO}_3)_4(\text{F}, \text{OH}) \cdot \text{H}_2\text{O}$, occurs in thermally metamorphosed inclusions in the nepheline syenite at Mount St. Hilaire, Quebec. It is associated mainly with pectolite, albite, arfvedsonite, calcite, fluorite, and apophyllite.

The mineral is tetragonal, $P4/mbm$, with $a=13.178 \pm 0.003 \text{ \AA}$, $c=16.695 \pm 0.004 \text{ \AA}$, $c/a=1.2669$. The strongest X-ray powder diffraction lines and their relative intensities (visual), are: 8.353(100), 4.171(100), 4.053(50), 2.903(90), 2.384(60). $Z=4$

Carletonite is pink to pale blue, with vitreous to pearly luster. $H=4-4\frac{1}{2}$ on {001}. Density (meas.) = 2.45 g/cm^3 , (calc.) = 2.426 g/cm^3 . Cleavage {001} perfect, {110} good, fracture conchoidal. Optically uniaxial (-), $\omega=1.521 \pm 0.001$, $\epsilon=1.517 \pm 0.001$, in Na light, for pink and blue varieties. The blue variety is weakly pleochroic with O = very pale blue and E = very pale pinkish brown.

Analyses of pink and blue varieties gave, respectively, SiO_2 44.9, 44.7, TiO_2 tr., tr., Al_2O_3 0.5, 0.6, total Fe n.d., n.d., MgO 0.09, 0.13, CaO 19.92, 19.97, Na_2O 10.23, 10.64, K_2O 3.28, 3.31, CO_2 —, 15.2, F 0.70, 0.73, H_2O^- 0.70, 0.63, H_2O^+ —, 3.51, LOI 19.92, —, sum 100.24, 99.42, $-(\text{O}=\text{F}_2)$ 0.29, 0.30 = 99.95, 99.12%.

DTA shows endothermic peaks at 300°C (vw), 692°C (vs), and 915°C (vw), and an exothermic peak at 736°C (w). TGA shows 0.7% weight loss below 430°C and 17.3% above 430°C with major loss between 650° and 750°C. Infrared spectrum and its interpretation are given.

INTRODUCTION

In a previous paper, Chao *et al.* (1967) briefly reported the occurrence of ten unidentified minerals from the nepheline syenite at Mount St. Hilaire, Quebec. One of these minerals, UK15, was later named carletonite, after Carleton University where it was first recognized. The name was approved by the Commission of New Minerals and Mineral Names of I.M.A. in June, 1969. The type specimens are deposited at the National Museum of Canada (No. T711).

OCCURRENCE

The geological setting of the Mount St. Hilaire pluton has been given by Dresser and Denis (1944) and summarized by Chao *et al.* (1967).

Carletonite was found in the cores of wall-rock inclusions (shale interbedded with limestone) in the nepheline syenite. The inclusions are thermally metamorphosed, either to greenish gray and gray hornfels or to siliceous marble. In one occurrence carletonite was found in the quartz veins of a greenish gray hornfels, associated with lemon-yellow narsarsukite, calcite, purple fluorite, and minor amounts of ancylite, molyb-

denite, leucosphenite, ramsayite, and galena. In another occurrence, carletonite was found in the core of an inclusion two feet in diameter. The outer zone of this inclusion was mainly dark gray hornfels with large patches of pink and white massive albite. The inner zone consisted primarily of coarse fibrous pectolite, medium-grained arfvedsonite, small patches of massive pink albite, fine-grained quartz, apophyllite, purple fluorite, and carletonite. Massive pink carletonite, constituting approximately 80 percent of the core (about 8 inches in diameter), was associated with euhedral crystals of arfvedsonite, apophyllite, and acicular leifite. In a third occurrence the outer zone of the inclusion was a coarse-grained marble and the inner zone was almost pure, fibrous, radiating pectolite. Pale blue carletonite was found at the core with microcline, arfvedsonite, and minute euhedral crystals of apophyllite. No crystals of carletonite were found in any of these occurrences.

X-RAY CRYSTALLOGRAPHY

Weissenberg and precession photographs indicate that carletonite is tetragonal, with $a = 13.12 \pm .01 \text{ \AA}$ and $c = 16.70 \pm .01 \text{ \AA}$. Systematic extinctions are consistent with the space group $P4/mbm$, except for two weak reflections, 050 and 070. These reflections may be due to Renninger effect (multiple reflection) (James, 1958, p. 26) because they were observed only on photographs taken with $\text{CuK}\alpha$ radiation, but not on photographs taken with $\text{MoK}\alpha$ radiation. The cell parameters derived from the single crystal photographs were refined by a least-squares method, using powder diffraction data obtained from photographs taken with $\text{CuK}\alpha$ radiation and a 114.6 mm camera. Metallic silicon was used as an internal standard. The refined values are $a = 13.178 \pm .003 \text{ \AA}$ and $c = 16.695 \pm .004 \text{ \AA}$, $c/a = 1.2669$. X-ray powder diffraction data of carletonite are given in Table 1. The indexing of the lines was made by comparing the observed and calculated d -values, using single crystal photographs as a guide.

CHEMICAL COMPOSITION

The pink and the blue varieties were separated by use of heavy liquids and an isodynamic magnetic separator. The separated fractions were hand-picked under a microscope. A preliminary semi-quantitative spectrographic analysis indicated the presence of Na, Ca, K, Si as major constituents; Mg and Al as minor constituents; Mn and B as traces only. These results were used as a guide for the wet-chemical analyses.

Oxides of nine elements were determined for the pink and the blue varieties according to the procedures described by Hounslow and Moore (1966). CO_2 was determined by an acid evolution-gravimetric method.

Table 1

X-Ray Powder Diffraction Data of Carletonite

(CuK α radiation, $\lambda=1.5418\text{\AA}$, 114.6 mm camera,
Si standard)

I (Visual)	d _{obs} (\AA)	d _{cal} (\AA)	hkl
40	16.705	16.695	001
30	9.319	9.3185	110
100	8.353	8.3476	002
20	6.583	6.5892	200
10	5.890	5.8935	210
25	5.563	5.5650 5.5573	003 221
10	5.173	5.1720	202
40	4.816	4.8145	212
30	4.659	4.6592	220
10	4.250	4.2516	203
100	4.171	4.1737 4.1672	004 310
50	4.053	4.0683 4.0462	222 213
5	3.573	3.5725	223
25	3.405	3.4061	214
40	3.337	3.3357	313
10	3.236	3.2322	401
5	3.202	3.1962	410
5	3.139	3.1433 3.1391	115 411
10	3.109	3.1088	224
40	3.057	3.0550	323
25	2.945	2.9468	420
90	2.903	2.9051 2.9018	215 421
15	2.835	2.8350	403
40	2.777	2.7787	422
15	2.750	2.7497	324
20	2.713	2.7140 2.7122	225 333
5	2.667	2.6662	116
40	2.604	2.6042 2.6034	423 431
5	2.584	2.5860 2.5844	404 510
15	2.540	2.5376	414
10	2.466	2.4688 2.4652	512 325
5	2.421	2.4212	521
60	2.384	2.3850	007

Table 1 (continued)

10	2.329	2.3296	440
5B	2.265	2.2742	335
		2.2600	530
10	2.239	2.2396	531
15	2.209	2.2094	425
10	2.165	2.1665	610
10	2.149	2.1485	611
15B	2.121	2.1240	602
		2.1230	227
20	2.086	2.0869	008
		2.0836	620
5	2.065	2.0676	621
10	2.037	2.0364	118
5	2.022	2.0231	426
		2.0216	622
10	1.996	1.9974	327
10	1.971	1.9738	525
30	1.912	1.9135	436
		1.9115	417
15	1.890	1.8917	337
10B	1.860	1.8636	550
		1.8636	710
5	1.836	1.8340	605
40	1.813	1.8122	328
5	1.786	1.7852	642
<5	1.766	1.7672	553
10	1.748	1.7474	418
10B	1.731	1.7322	338
		1.7304	730
10	1.710	1.7094	616
5	1.679	1.6788	651
5	1.653	1.6538	652
		1.6523	733
10B	1.636	1.6405	740
		1.6361	537
		1.6345	438
30	1.603	1.6044	419
		1.6036	617
		1.6031	645
15	1.568	1.5692	627
15B	1.553	1.5544	448
		1.5530	660
5	1.533	1.5332	538
15	1.517	1.5177	00.11

Plus 17 lines

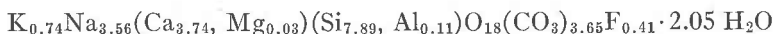
B = Broad line

H₂O was analysed by direct determination of H (on two 25 mg samples) by Dr. A. D. Campbell, University of Otago, New Zealand. Results of the analyses are tabulated in Table 2.

Crystal structure analysis (to be published elsewhere) showed that in carletonite, the SiO₄ tetrahedra share three of their four oxygen atoms to form sheets consisting of four-membered and eight-membered rings, resembling the sheets in apophyllite (Taylor and Náray-Szabó, 1931; Chao, 1971). Two apophyllite-like sheets are cross-linked in carletonite, by half of the oxygen atoms not shared in the single sheets, to form "double sheets" of the composition Si₈O₁₈. Potassium, sodium and calcium atoms occupy distinct positions. These lead to the ideal structural formula:



The formula of carletonite was calculated from the average of the two analyses, on the basis of 8 (Si, Al) atoms per formula, resulting in:



Carletonite, thus, is non-stoichiometric, with deficiencies in K, Na, Ca, CO₃, and F. The water contents given in the analyses are much higher than the structural formula requires, even if one assumes that some of the water is present in the form of OH in substitution for F. The excess water may be trapped in the vacated sites of the CO₃ group; it may have the function of stabilizing the defect structure.

Carletonite is decomposed by HCl, giving a silica residue; it is attacked by HNO₃ with gelatinization; it is only slightly attacked by H₂SO₄(1:1).

PHYSICAL AND OPTICAL PROPERTIES

Carletonite is pink to pale blue; small flakes are colorless. The streak is white. Carletonite has a vitreous to pearly luster, on long exposures to air it becomes slightly waxy. Hardness is 4–4½ on {001}. Four determinations of density on two grains, using a Berman balance and toluene, gave density 2.45 ± 0.01 g/cm³, at 24°C, in comparison to the calculated density 2.426 g/cm³. Carletonite has perfect {001} cleavage and good {110} cleavage. The fracture is conchoidal.

Carletonite is optically uniaxial (-). The refractive indices measured in sodium light at 24°C were ω = 1.521 ± 0.001 and ε = 1.517 ± 0.001. There is no measurable difference in refractive indices for the pink and the blue varieties. Only the blue variety shows a weak pleochroism, however, with O = very pale blue, E = very pale pinkish brown.

Table 2
Chemical Analyses of Carletonite

	Wt % (Pink Variety)	Wt % (Blue Variety)
SiO ₂	44.9	44.7
TiO ₂	tr.	tr.
Al ₂ O ₃	0.5	0.6
FeO	n.d.	n.d.
MgO	0.09	0.13
MnO	n.d.	n.d.
CaO	19.92	19.97
Na ₂ O	10.23	10.64
K ₂ O	3.28	3.31
CO ₂	---	15.2
H ₂ O ⁻	0.70	0.63
H ₂ O ⁺	---	3.51
F	0.70	0.73
LOI	19.92	---
	-----	-----
	100.24	99.42
less O ≡ F ₂	- 0.29	-0.30
	-----	-----
Sum	99.95	99.12

Analyst: D. Mah; CO₂ and F by C. Murray, Department of Geology,
Carleton University.

THERMAL STUDY

The DTA curve of carletonite (Fig. 1) is characterized by the presence of a very weak endothermic peak at 300°C, a very strong endothermic peak at 692°C, a weak exothermic peak at 736°C, and a very weak endothermic peak at 915°C. Up to 430°C the weight loss, according to TGA (Fig. 1), was 0.7 percent which may correspond to the weak endothermic reaction at 300°C on the DTA curve. The major weight loss of 17.3 percent took place between 650°C and 750°C, corresponding to the strong endothermic reaction at 692°C on the DTA curve. The lower-temperature weight loss may be interpreted as the loss of F and the major weight loss as escaping of CO₂ and H₂O.

A sample of carletonite quenched from 620°C in the DTA run gave an X-ray powder diffraction pattern identical to that of the unheated material, except that the lines were slightly diffused. A sample quenched from 708°C was amorphous, indicating a complete collapse of the structure after losing all of its H₂O and CO₂. The powder diffraction patterns of samples quenched from 775°C and 1135°C were complex but identical, except for four lines attributable to albite in the pattern of the sample quenched from 775°C. The phases identified by X-ray powder diffraction

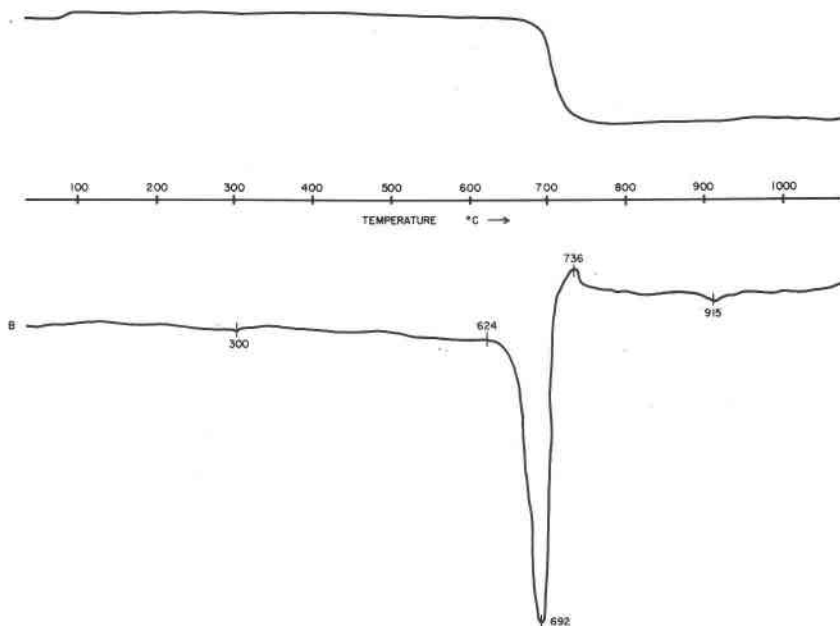


FIG. 1. DTA (A, heating rate=12°C/min, in air) and TGA (B, heating rate=6°C/min, in air) curves of carletonite.

Table 3

X-Ray Powder Diffraction Data of Carletonite Quenched at 1135°C							
(CuK α radiation, 114.6 mm camera, visual intensities)							
Carletonite Quenched at 1135°C		Na ₂ CaSi ₃ O ₈		Na ₂ Ca ₂ Si ₃ O ₉		Wollastonite	
d(Å)	I	XRPDF	12-671	XRPDF	1-1078	XRPDF	10-487
7.48	30					7.7	40
5.32	5						
4.88	15						
4.40	40			4.43	10		
3.980	5					4.05	10
3.837	10					3.83	80
3.743	50	3.75	25	3.78	30		
3.511	10					3.52	80
3.430	5					3.40	5
3.372	40	3.38	40	3.37	50		
3.320	80	3.33	50			3.31	80
						3.16	5
3.095	10					3.09	30
3.033	5	3.05	8	3.04	5		
2.979	40					2.97	100
2.790	5					2.80	10B
2.702	5					2.72	10
2.664	100	2.675	100	2.65	100		
2.623	100	2.630	85				
		2.614	10				
2.564	10					2.55	30
2.528	10			2.52	5		
2.477	15					2.47	60
2.351	20	2.360	16	2.36	10		
						2.33	40
2.303	10						
2.281	10	2.282	6			2.29	40
2.236	10	2.243	8	2.25	5		
2.188	15	2.198	6			2.18	60
2.142	20			2.15	5		
2.085	10					2.08	5
2.053	10						
2.021	10					2.01	20
1.994	10					1.98	20
1.954	10						
1.915	5					1.91	20
1.866	70	1.871	75	1.87	60	1.88	20
1.840	5						
1.830	5					1.83	60
1.799	15B			1.80	10	1.80	5
						1.79	5
1.738	10			1.74	10	1.75	40
1.717	10					1.72	60
1.695	10						
1.673	10	1.701	6	1.69	5		
1.646	15						
1.625	5	1.652	14	1.641	10		
1.596	5						
1.577	5					1.602	40
1.545	20						
				1.55	20		
1.520	30					1.531	10
1.515	5			1.52	30		
1.480	10					1.515	5
1.460	5					1.478	20
						1.455	30
						1.426	5
1.394	20			1.39	30	1.387	5
1.376	20	1.382	10				
1.361	10					1.358	30
1.331	20					1.332	10
1.310	20	1.318	6	1.33	20	1.312	5
1.293	10						
				1.30	20		

Plus 16 lines

were $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$, $\text{Na}_2\text{CaSi}_3\text{O}_8$, and wollastonite (CaSiO_3). No potassium compound was identified. The absence of albite in the end product at 1135°C strongly suggests that the melting or decomposition of albite is responsible for the weak endothermic reaction at 915°C on the DTA curve.

The powder diffraction pattern of carletonite quenched from 1135°C is given in Table 3 where it is compared with the patterns of the three identified phases. The thermal study of carletonite is summarized in Table 4.

INFRARED STUDY

Infrared spectra were obtained with a Perkin Elmer Model 225 double

Table 4

Thermal behavior of Carletonite

Temp $^\circ\text{C}$	Thermal Reaction	Weight Loss %	Interpretation	Product On Quenching
300°	Endothermic (V.W)	0.7 below 430°C	Loss of F	Carletonite
620°				Carletonite
692°	Endothermic (V.S)	17.3 above 430°C	Escaping of CO_2 and H_2O	
708°				Amorphous
736°	Exothermic (W)		Recrystallization	
775°				$\text{Na}_2\text{CaSi}_3\text{O}_8$ $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$ CaSiO_3 $\text{NaAlSi}_3\text{O}_8$ (trace)
915°	Endothermic (V.W.)		Melting of albite	
1135°				$\text{Na}_2\text{CaSi}_3\text{O}_8$ $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$ CaSiO_3

beam spectrometer, using pellets containing 2 mg of sample and 300 mg of KBr.

The presence of two crystallographically distinct groups of SiO_4 and CO_3 , and their low site-symmetry, results in a very complicated spectrum, shown in Figure 2 and Table 5, where it is compared with the spectrum of apophyllite. Apophyllite was chosen as a reference because of its structural similarities to carletonite; both minerals have silicate layers composed of four-membered and eight-membered rings and not linked to octahedral cations. Thus both are not influenced by the octahedral cations which prevail in the other common layer silicates (Stubičan and Roy, 1961a, b). The similarities of the two spectra in the region from 1200 cm^{-1} to 400 cm^{-1} are striking, despite shifts of the bands and variations in band intensities. The extra bands in this region for the carletonite spectra were attributed to CO_3 vibrations. The assignment of the bands (Table 5) was based on the results on quartz and other polymorphs of silica (Lippincott *et al.*, 1958) and those of aragonite (Adler and Kerr, 1962). The splitting of ν_3 and ν_4 modes of CO_3 probably results from the removal of degeneracies of the two crystallographically distinct groups of CO_3 , both having C_s^1 symmetry (Halford, 1946).

ACKNOWLEDGMENTS

This work was partially supported by the Canadian National Advisory Committee on Research in the Geological Sciences, under Grant 10-65. The DTA and TGA analyses were provided by Dr. N. F. H. Bright of the Department of Energy, Mines and Resources, Canada. The infrared spectra were obtained through Dr. C. H. Amberg, Department of Chemistry, Carleton University. I wish to thank Dr. J. M. Moore, Jr., for his critical reading of this manuscript.

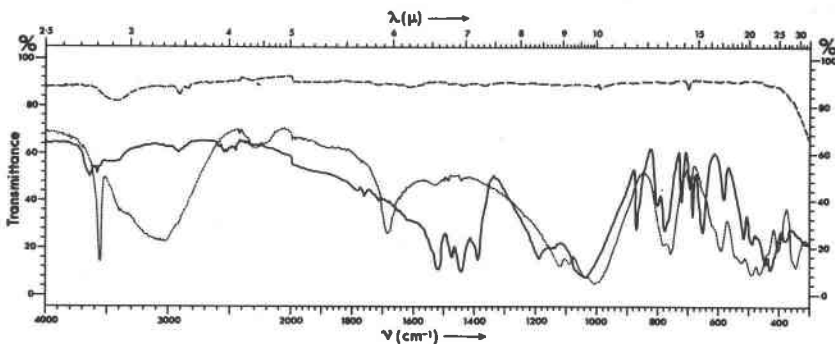


FIG. 2. Infrared spectra of carletonite (solid curve) and apophyllite (dotted curve). The spectrum of pure KBr is shown by the dashed curve. The bands in the 2900 cm^{-1} — 2800 cm^{-1} region are due to C-H vibration from the plastic container.

TABLE 5
Interpretation of the infrared spectrum of carletonite

Carletonite		Apophyllite		Assignment
Wave number (cm^{-1})	Intensity	Wave number (cm^{-1})	Intensity	
335	m,sh	346	s	Si-O-Si distortion
		358	s,sh	"
		370	m,sh	"
380	m	404	s	"
		435	s,sh	Si-O-Si bending
428	s	464	s	"
445	s	492	s	"
472	m			"
489	m	525	s	"
517	m	545	s,sh	"
581	w	592	s	"
650	m			O-C-O planar bending (ν_4)
685	m			"
694	w			"
697	w,sh			"
720	m	691	w	Si-Si stretching
766	m,sh			"
776	m	756	s	"
800	m	780	m	"
860	m,sh			O-C-O out-of-plane bending (ν_2)
868	m			"
1034	s	1006	s	Si-O stretching
1068	s,sh	1043	s,sh	"
1140	m,sh	1089	s	"
1188	s	1120	s	"
1388	s			C-O asymmetric stretching (ν_3)
1400	m,sh			" (?)
1408	m,sh			" (?)
1442	s			"
1472	s			"
1520	s			"
1715	w	1680	m	H-O-H bending
1760	w			"
2400-2600	vw	2200-2300	vw	Combination bands (?)
		3080	m	O-H asymmetric stretching
3580	w	3452	s	O-H symmetric stretching
3640	w			"

s = transmission <20%
m = transmission 20-40%
w = transmission 40-60%
vw = transmission >60%
sh = shoulder

REFERENCES

- ADLER, H. H., AND P. F. KERR (1962) Infrared study of aragonite and calcite. *Amer. Mineral.* **47**, 700-717.
- CHAO, G. Y. (1971) The refinement of the crystal structure of apophyllite, II. Determination of the hydrogen positions by X-ray diffraction. *Amer. Mineral.* **56**, 1234-1242.
- , D. C. HARRIS, A. W. HOUNSLOW, J. A. MANDARINO, AND G. PERRAULT (1967) Minerals from the nepheline syenite, Mont St. Hilaire, Quebec. *Can. Mineral.* **9**, 109-123.
- DRESSER, J. A., AND T. C. DENIS (1944) Geology of Quebec. *Quebec Dep. Mines, Geol. Rep.* **2**, 469-470.
- HALFORD, R. S. (1946) Motions of molecules in condensed systems: 1. Selection rules, relative intensities, and orientation effects for Raman and infrared spectra. *J. Chem. Phys.* **14**, 8-15.

- HOUNSLOW, A. W., AND J. M. MOORE, JR. (1966) Preparation and analysis of silicate rocks and minerals. *Geol. Pap.* 66-1, Carleton University, Ottawa, Canada.
- JAMES, R. W. (1958) *The Optical Principles of the Diffraction of X-rays, Vol. II, The Crystalline State*. G. Bell and Sons, London.
- LIPPINCOTT, E. R., A. VAN VALKENBURG, C. E. WEIRE, AND E. N. BUNTING (1958) Infrared studies on polymorphs of silicon dioxide and germanium dioxide. *J. Res. Nat. Bur. Stan. (U. S.)* 61, 61-70.
- STUBICAN, V., AND R. ROY (1961a) A new approach to assignment of infra-red absorption bands in layer-structure silicates. *Z. Kristallogr.* 115, 200-214.
- , AND ——— (1961b) Isomorphous substitution and infra-red spectra of the layer lattice silicates. *Amer. Mineral.* 46, 32-51.
- TAYLOR, W. H., AND ST. NÁRAY-SZABÓ (1931) The Structure of apophyllite. *Z. Kristallogr.* 77, 146-158.

Manuscript received, April 1, 1971; accepted for publication, May 10, 1971.