Atti Accademia Nazionale dei Lincei

Classe Scienze Fisiche Matematiche Naturali

Rendiconti

Silvio Menchetti

The crystal structure of gaylussite

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **44** (1968), n.5, p. 680–694.

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1968_8_44_5_680_0>

Mineralogia. — *The crystal structure of gaylussite.* Nota di SILVIO MENCHETTI (*), presentata (**) dal Socio G. CAROBBI.

RIASSUNTO. — La gaylussite, $Na_2Ca(CO_3)_2 \cdot 5\,H_2O$, cristallizza nel gruppo spaziale I $2/a$, con 4 unità stechiometriche nella cella elementare. Le costanti reticolari sono $a = 11{,}579$, $b = 7{,}780$, $c = 11{,}207$ $\beta = 101^\circ\,58'$.

La struttura cristallina è stata determinata (nel gruppo spaziale C $2/c$) con l'analisi della sintesi tridimensionale di Patterson. I dati sperimentali sono stati raccolti con una camera di Weissenberg.

Il raffinamento delle coordinate atomiche e dei parametri termici anisotropi è stato condotto con il metodo dei minimi quadrati. Il valore finale di R relativo a 505 riflessi osservati è di 0,053. Dal calcolo di R sono stati esclusi 10 riflessi affetti da estinzione.

Nella struttura sono presenti catene di poliedri di coordinazione del Na (ottaedri) legati l'uno all'altro alternativamente per un vertice o per uno spigolo. I poliedri di coordinazione del Ca sono costituiti da antiprismi quadrati un po' distorti; ciascun antiprisma è collegato a quattro ottaedri adiacenti tramite quattro spigoli a comune.

Le catene costituite da ottaedri e antiprismi (parallele a c) sono legate fra di loro dai gruppi CO_3 che hanno una regolare configurazione triangolare e planare. Si determina in tal modo un andamento a strati paralleli al piano (110).

Le distanze di legame rientrano pienamente nella norma.

INTRODUCTION.

In a previous paper [10] the preliminary results of a crystallographical study on gaylussite have been exposed. In the present work, the conclusive data on the structure of this mineral are given.

The mineral, with formula $Na_2Ca(CO_3)_2 \cdot 5\,H_2O$ was originally described by Boussingault [5].

The results of subsequent morphological, optical and chemical investigations are summarized in " Dana's system of Mineralogy " [13].

Infrared studies on gaylussite among several carbonate minerals were carried out by Huang and Kerr [9] and later by Adler and Kerr [1].

The first consistent data on the X–ray crystallography of gaylussite were published by Mrose [12]. The unit cell edges and angular values have been subsequently confirmed by other AA. [8] [11], as well as the space group I $2/a$.

EXPERIMENTAL.

In the present work, a specimen from Searles Lake, San Bernardino Co., California, was used. A well formed transparent crystal was chosen. It was ground to a nearly perfect sphere of 0.24 mm in diameter, by means of the apparatus described by Bond [4].

(*) Istituto di Mineralogia e Petrografia dell'Università di Bari.

(**) Nella seduta dell'11 maggio 1968.

The lattice parameters were refined by a least-squares calculation on powder-diffractometric data, and from Weissenberg photographs calibrated with an equally small quartz crystal.

The space group chosen for the structure determination was C 2/*c*.

Crystal data:

$$(\lambda\,(\mathrm{CuK}\alpha) = 1.5418\ \text{Å})$$

Chemical formula = $Na_2Ca(CO_3)_2 \cdot 5\,H_2O$

Monoclinic, space group C 2/*c*,

$$a = 14.349 \pm 0.005\ ;\quad b = 7.780 \pm 0.004\ ;\quad c = 11.207 \pm 0.002\ \text{Å}$$

$$\beta = 127^\circ\,51' \pm 02'\ ;\quad V = 987.6\ \text{Å}^3$$

$$D_m = 1.991\ \text{g cm}^{-3}\ ;\quad D_x = 1.991\ \text{g cm}^{-3}\ ;\quad Z = 4$$

$$\mu = 69.76\ \text{cm}^{-1}\ ;\quad \mu R = 0.84.$$

Experimental density of 1.991 g cm^{-3} is given in Dana's System of Mineralogy [13] as the average of several determinations.

The X-ray diffraction data were collected, by equi-inclination Weissenberg photographs taken around the *b* axis (*k* from 0 to 4) using the multiple film technique. A total of 652 reflexions were inspected; 137 of them were too weak to be observed. The integrated intensities were evaluated by means of a microdensitometer and Weissenberg different levels were put on the same scale taking account of exposure time; after each structure factor calculation the scale factor was improved by the criterion $\Sigma F_o = \Sigma F_c$, applied separately to each level.

The corrections applied to the intensities were concerned with absorption (spherical crystal) and Lorentz-polarisation factor. Empirical correction was also applied for $\alpha_1 - \alpha_2$ spot doubling.

STRUCTURE DETERMINATION.

A three-dimensional Patterson synthesis was computed from all actually observed reflections. Since the general position in C 2/*c* is eightfold, Ca atom and the oxygen of one water molecule must lie in a special position. O can lie only on twofold axes because the symmetry of H—O—H molecule; Ca atom either on symmetry centres or twofold axes.

Patterson's strongest peaks show that also Ca atoms lie on twofold axes in position 0 , *y* , 1/4; difference on *y* coordinates of Ca and O atoms must be nearly 1/2 *b*.

Several calcium-oxigen and calcium-sodium vectors were recognized on Patterson's map; they gave full information on the coordinates of Na , O_1, O_2 , O_3 , O_5 atoms. At this stage a structure factor calculation gave a R index of 0.35.

Scattering factors used for structure factor calculation were the ones given by Cromer and Waber [7].

By means of a three-dimensional Fourier synthesis the remaining O and C atoms were located. C atom was confirmed in position already postulated on the basis of geometric considerations. R index dropped to 0.17.

The refinement was carried out by two more Fourier syntheses and pursuived by least-squares method.

The weighting scheme used in least squares calculations was:

$$w_{(hkl)} = 1/[a + bK\,F_o + c(K\,F_o)^2]$$

where a is $\simeq$ the minimum observed F_o, b is nearly 1, c is nearly the reciprocal of the maximum observed F_o.

First a program, written by Albano *et al.* [2] for the IBM 1620 computer, was used and four isotropic cycles were accomplished. Initial isotropic temperature factors were derived from the ones published for pirssonite by Corazza and Sabelli [6].

Later two more cycles were carried out on the IBM 360/40 computer, using the Albano *et al.* program [3] originally written for the IBM 7040; anisotropic thermal parameters were taken into account during the final least-squares cycles. The reflections affected by secondary extinction and the unobservable ones were excluded from the least-squares calculations. The final R value for all observed reflections (except 10 affected by extinction) was 0.053.

The atomic and thermal parameters with their standard deviations are given in Tables I, II and Table III. The observed and calculated structure factors are listed in Table IV.

TABLE I.

Atomic coordinates and their standard deviations (in parentheses).

ATOM	*x/a*	*y/b*	*z/c*
Na	0.4122 (2)	0.8182 (5)	0.5109 (2)
Ca	0.5000	0.8065 (3)	0.2500
O_1	0.3345 (3)	0.9902 (8)	0.0894 (3)
O_2	0.3962 (3)	0.9960 (8)	0.3245 (4)
O_3	0.2149 (3)	0.0909 (8)	0.1367 (4)
O_4	0.3526 (3)	0.5965 (8)	0.1893 (4)
O_5	0.5707 (3)	0.7073 (8)	0.5034 (4)
O_6	0.5000	0.3191 (11)	0.2500
C	0.3153 (4)	0.0266 (11)	0.1844 (5)

TABLE II.

The final anisotropic temperature factors ($\times 10^4$) *and their standard deviations (in parentheses).*

Thermal parameters are in the form $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

ATOM	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Na . . .	35 (1)	— 1 (4)	56 (2)	70 (8)	— 15 (6)	48 (2)
Ca . . .	12 (1)	0 (0)	19 (1)	29 (5)	0 (0)	20 (1)
O_1 . . .	22 (2)	— 6 (7)	36 (3)	37 (10)	— 14 (9)	37 (3)
O_2 . . .	29 (2)	— 3 (7)	29 (3)	12 (9)	8 (10)	36 (3)
O_3 . . .	28 (2)	57 (7)	57 (3)	58 (10)	48 (11)	59 (3)
O_4 . . .	28 (2)	11 (8)	45 (3)	64 (10)	17 (10)	43 (3)
O_5 . . .	31 (2)	— 2 (8)	44 (3)	37 (10)	8 (11)	45 (3)
O_6 . . .	29 (3)	0 (0)	47 (4)	60 (15)	0 (0)	43 (4)
C . . .	24 (2)	15 (10)	36 (3)	6 (15)	20 (13)	36 (4)

LOCATION OF HYDROGEN ATOMS.

In the crystal structure of gaylussite five hydrogen atoms per asymmetric unit are present. In the attempt to locate them, a three-dimensional difference Fourier synthesis was calculated, after the last cycle of refinement.

The strongest peaks fitted well with the positions expected for hydrogen atoms H_1, H_3, H_4 and H_5 on the basis of the shortest O—O distances and assuming a length of 1 Å for the O—H distance. The H_2 peak was fairly evident on the map.

However, these peaks being not too well resolved, the information from the Fourier-difference synthesis was considered not so stringent as to suggest the exact location of hydrogen atoms. Thus the positions of H_1, H_2, H_3 and H_5 were chosen on the O—O alignment and at 1 Å of distance from the oxygen with which they are bound.

From the position of H_4 peak on the Fourier-difference map, some experimental evidence indicates that H_4 does not lie exactly on the O_5—O_3 direction.

This fact was taken into account in choosing the H_4 coordinates; actually the O_5—H_4 and $O_3 \cdots H_4$ distances come to 1.035 Å and 1.893 respectively; the $O_5\widehat{H_4}O_3$ angle is nearly 151°.

TABLE III.

Analysis of the anisotropic thermal parameters.

(root mean square thermal vibrations along the ellipsoid axes (Å), magnitude of the principal axes (Å^2) and angles (°) between the crystallographic axes and the principal axes of the vibration ellipsoids).

ATOM	r.m.s.	B	α	β	γ
Na	0.15	1.78	50	41	108
	0.15	1.87	61	120	73
	0.12	1.17	126	65	25
Ca	0.09	0.64			
	0.09	0.70	90	0	90
	0.09	0.62			
O_1	0.12	1.09	8	83	130
	0.13	1.29	83	116	50
	0.10	0.79	95	27	66
O_2	0.12	1.14	80	84	47
	0.15	1.96	169	84	44
	0.06	0.26	85	8	98
O_3	0.14	1.53	130	109	20
	0.18	2.55	68	50	72
	0.07	0.39	49	134	100
O_4	0.13	1.33	30	118	113
	0.15	1.75	73	40	74
	0.12	1.19	114	117	28
O_5	0.14	1.46	94	78	34
	0.15	1.69	10	98	120
	0.10	0.85	81	15	105
O_6	0.14	1.45	90	0	90
	0.14	1.53	47	90	80
	0.12	1.19	137	90	10
C	0.12	1.15	131	83	8
	0.13	1.32	41	77	87
	0.03	0.06	95	15	98

TABLE IV.

Observed and calculated structure factors.

An asterisk marks the reflections excluded in R calculation because affected by extinction.

h	*k*	*l*	Fo	Fc	*h*	*k*	*l*	Fo	Fc	*h*	*k*	*l*	Fo	Fc
0	0	2	52.5	—51.5	10	0	—10	48.4	—48.6	3	1	4	64.0	—65.3
		4	90.7	99.9			—12	56.7	55.9			—4	59.8	58.2
		6	51.4	49.0			—14		—15.0			5	43.7	—44.9
		8	51.0	48.6	12	0	0	65.3	65.5			—5	35.9	32.6
		10		11.5			2		—9.8			6		—7.5
2	0	0	56.9	56.0			—2		8.1			—6		—7.7
		2	21.7	16.7			—4	61.7	62.3			7	21.5	21.7
		—2	55.5	—56.6			—6		—12.9			—7	38.0	—35.9
		4*	134.1	157.3			—8	47.7	46.2			8		—10.1
		—4*	128.8	161.9			—10		—13.6			—8	34.5	—33.0
		6		6.5			—12	81.9	77.8			9	20.9	—23.2
		—6	64.4	—67.4			—14	27.9	—28.0			—9	17.6	18.6
		8	38.0	38.3	14	0	0	34.3	36.0			—10	41.8	40.7
		—8	87.2	90.4			—2	26.2	—27.8			—11	26.1	—26.0
		10	19.9	—22.4			—4	23.9	24.9			—12	11.4	11.1
		—10	23.4	—22.4			—6	25.6	—24.8	5	1	0	34.3	35.8
		—12	12.5	15.7			—8	76.1	75.1			1	49.5	—49.8
4	0	0	51.8	—46.0			—10	40.9	—39.1			—1	45.6	45.3
		2	112.0	—117.7			—12		2.7			2		9.3
		—2	40.2	—34.7			—14	21.3	—23.7			—2		7.5
		4	46.6	46.9	16	0	—4	54.3	52.7			3	32.9	31.5
		—4	12.0	—13.0			—6	60.3	—55.5			—3	47.4	38.0
		6	79.7	—82.3			—8		4.7			4	14.9	15.4
		—6	81.1	—92.3			—10	34.3	—32.9			—4	81.4	—82.7
		8	64.6	57.8			—12		9.8			5	31.1	—28.1
		—8	44.8	39.9	18	0	—8	18.0	17.7			—5	39.2	32.7
		—10	116.5	—127.1			—10	32.6	—34.2			6	22.0	22.8
		—12	25.2	24.0	1	1	1	62.6	—68.0			—6	73.8	76.4
6	0	0	28.2	27.1			2	52.3	—54.5			7	17.8	17.3
		2	115.0	—128.6			—2	53.9	58.4			—7		—8.8
		—2*	120.7	—144.2			3	42.5	42.0			8		—8.6
		4		—10.7			—3	53.9	—57.8			—8	42.5	41.8
		—4	25.7	—14.1			4	44.8	—43.5			—9	58.8	60.1
		6	64.8	—62.8			—4	52.3	50.2			—10		5.2
		—6*	155.1	—192.2			5		—4.7			—11		—5.4
		—8	27.3	—25.9			—5	9.4	10.7			—12		—4.0
		—10	16.8	—21.0			6	21.6	22.7			—13	33.0	31.9
8	0	0		7.3			—6	33.6	—32.2	7	1	0	11.6	—11.3
		2	21.5	—18.4			7	14.6	14.4			1		—6.0
		—2*	158.2	—199.6			—7	61.1	—58.9			—1	68.2	71.1
		4		—1.7			8		6.4			2	42.1	—44.1
		—4	84.7	88.7			—8		—7.9			—2	47.3	52.5
		6	39.2	—38.9			9		—9.4			3	43.5	42.6
		—6	63.6	—56.9			—9		—2.0			—3	12.4	—6.5
		—8	31.9	30.9			10		—6.1			4	26.4	26.1
		—10	25.9	—26.1			—10		7.8			—4	13.8	10.8
		—12	15.1	14.7			—11	20.2	—21.9			5	18.4	—17.8
10	0	0	64.1	63.7	3	1	0	25.4	22.2			—5	84.0	87.9
		2	56.8	—57.2			1		0.4			6	17.1	16.4
		—2		9.4			—1		3.8			—6	55.0	56.2
		4	28.9	31.4			2	85.5	94.3			—7	36.3	32.5
		—4	63.5	60.9			—2	48.0	—52.6			—8	54.3	—52.2
		—6		—6.5			3		—4.3			—9	42.3	38.6
		—8	77.2	82.4			—3	66.8	—81.3			—10	11.4	—13.0

Continued: TABLE IV.

h	*k*	*l*	Fo	Fc	*h*	*k*	*l*	Fo	Fc	*h*	*k*	*l*	Fo	Fc
7	1	—11		11.8	15	1	—4		1.1	4	2	—5	50.2	—47.2
		—12		9.7			—5	19.2	18.2			6	15.7	14.7
		—13	40.0	43.3			—6	8.3	—7.8			—6	81.6	84.1
9	1	0		1.4			—7	40.4	—38.6			7	22.7	19.6
		1		—6.3			—8		—0.6			—7	66.6	64.4
		—1	53.9	54.5			—9	8.2	7.9			8		2.9
		2	32.4	31.1			—10	43.9	43.6			—8		4.8
		—2		—0.1			—11	11.1	—10.0			—9	17.4	15.8
		3	19.6	17.4			—12		—2.2			—10		1.5
		—3	22.2	—19.4	17	1	—5	30.3	30.6			—11	10.3	12.3
		4	32.9	—32.8			—6	17.9	19.8	6	2	0	45.2	41.5
		—4	30.1	—29.1			—7		—3.7			1		4.3
		5		—3.4			—8	21.8	22.8			—1	54.3	—50.0
		—5	46.3	47.6			—9	34.0	37.6			2	88.7	94.1
		—6	56.9	—58.6			—10	8.8	—8.5			—2	107.6	117.1
		—7	21.9	—19.7			—11	9.8	—9.5			3		10.4
		—8		—0.9			—12	8.8	9.8			—3	64.9	59.1
		—9	45.5	43.2	0	2	1	33.8	—30.9			4	18.1	—18.3
		—10		2.6			2	69.6	—67.6			—4	25.5	20.5
		—11		—12.1			3	59.6	—58.3			5	29.0	28.2
		—12	28.5	—28.1			4*	137.1	—156.7			—5	63.5	—64.5
		—13		8.7			5	66.3	64.7			6	37.9	38.9
		—14	22.4	20.8			6	12.6	11.4			—6	36.9	37.5
11	1	0	56.7	—58.0			7	57.3	—56.5			7	24.3	—29.0
		1	22.5	—22.3			8	82.4	—84.4			—7	35.8	33.5
		—1	9.1	—8.7			9	20.3	16.8			—8	18.4	—18.1
		2	18.4	17.8			10	18.8	19.5			—9	56.7	—58.3
		—2	9.0	9.7			11	28.5	—28.6			—10	83.6	90.3
		3	19.7	21.2	2	2	0*	118.6	—172.1			—11	25.4	22.9
		—3	28.7	—27.9			1*	135.1	170.5			—12	11.6	—13.4
		—4	21.9	—20.7			—1	40.2	—41.5			—13	16.0	—19.3
		—5	8.5	8.5			2	28.0	25.7	8	2	0	26.5	—24.9
		—6	35.9	—35.0			—2	7.8	—3.5			1	18.2	16.8
		—7	62.5	—62.3			3	18.3	—13.8			—1	52.1	—48.6
		—8	22.8	20.6			—3	80.7	86.9			2	82.4	84.2
		—9		—2.2			4	34.3	—33.1			—2		5.4
		—10		2.6			—4	92.0	—94.7			3	62.3	—62.9
		—11	50.1	—49.0			5	73.1	74.6			—3	52.3	—47.9
		—12	32.2	—29.4			—5	76.5	80.2			4	10.6	—11.3
		—13		3.0			6	16.4	14.6			—4	12.3	7.6
		—14		—7.0			—6	25.8	26.2			5	12.5	12.2
13	1	0		7.1			7	15.0	—14.1			—5	61.0	—59.9
		1	30.9	—35.7			—7	52.2	50.0			6	35.2	35.8
		—1	12.3	10.9			8	61.4	—59.9			—6	69.5	71.9
		—2	14.8	—15.5			—8	11.5	—11.2			—7	18.1	17.8
		—3	49.9	—50.0			9	29.5	29.6			—8	19.3	—17.8
		—4		4.3			—9	11.6	—13.3			—9	67.0	—66.6
		—5	23.7	—26.1			—10	17.8	16.7			—10	48.8	48.2
		—6	55.0	56.4			—11	48.5	48.3			—11		4.1
		—7	40.7	—38.8	4	2	0	82.0	—84.2			—12	37.0	—36.7
		—8	54.0	—54.6			1	105.7	115.5			—13	34.8	—37.6
		—9	15.8	—15.3			2	42.1	39.3	10	2	0	26.3	—25.9
		—10		—1.2			—2*	141.7	179.3			1		3.1
		—11	56.6	—55.1			3	11.9	—12.1			—1	64.4	—65.8
		—12		9.9			—3*	121.5	140.1			2	15.0	—13.0
		—13		0.3			4		—2.5			—2	36.9	34.2
15	1	—1	7.6	9.3			—4	27.4	—27.8			3	35.6	—35.6
		—3	29.8	—30.6			5	48.1	45.2			—3	38.0	36.5

Continued: TABLE IV.

h	*k*	*l*	Fo	Fc	*h*	*k*	*l*	Fo	Fc	*h*	*k*	*l*	Fo	Fc
10	2	4	21.5	—24.4	1	3	5	32.3	31.5	7	3	—6		8.0
		—4	59.7	—59.3			—5		—5.1			—7	25.9	24.3
		—5	58.0	—56.0			6	17.6	—16.0			—8	25.7	24.7
		—6	54.0	51.0			—6	26.9	—27.3			—9	55.0	—56.9
		—7	25.9	—24.7			7	42.6	—43.0			—10	53.0	—53.2
		—8	67.4	—65.1			—7		1.8			—11	10.3	9.4
		—9	19.2	—16.8			8	64.5	65.4			—12	36.3	37.3
		—11	22.0	21.2			—8	22.1	20.3	9	3	0	43.4	41.4
		—12	21.7	—20.7			9	11.4	8.6			1	18.1	18.4
		—13	27.6	—29.3			—9	13.0	—13.1			—1	10.6	9.6
12	2	0	31.3	—31.1			10		—7.0			2		—0.2
		1	23.9	25.2			—10	32.2	—32.4			—2	17.4	18.2
		—1	29.0	—27.0			—11	26.8	26.5			3	31.2	—30.9
		—2	19.9	19.1	3	3	0	89.7	99.2			—3		—5.5
		—3	23.7	22.6			1	73.9	74.7			4	16.6	16.8
		—4	65.4	—63.9			—1	58.5	—57.9			—4	49.6	46.0
		—5	24.3	—24.6			2	19.0	—18.0			—5	13.6	—12.2
		—6		—4.0			—2	80.1	—88.4			—6	26.3	—23.4
		—7	59.7	58.4			3	45.5	—42.6			—7		9.3
		—8	53.7	—56.2			—3	34.1	—33.2			—8	55.1	53.8
		—9	24.9	—25.2			4	15.2	—15.3			—9		4.4
		—10	18.9	20.2			5		—1.0			—10	26.2	26.0
		—11	21.8	21.4			—5		—3.9			—11	20.2	20.3
		—12		—13.1			6		—3.0			—12	41.6	42.4
		—13		2.9			—6	60.5	—61.7			—13	23.1	—27.2
14	2	0	39.0	—39.7			7		—7.1	11	3	0	19.4	18.5
		—1		4.2			—7	21.9	17.8			1	23.1	21.9
		—2	14.1	12.9			8	13.2	12.9			—1	37.1	—36.8
		—3	37.4	36.9			—8	37.0	—36.2			2	16.3	16.6
		—4	46.0	—46.0			—9	15.0	—13.6			—2		—12.1
		—5	13.7	—15.7			—10		—5.8			—3	47.6	48.9
		—6	21.1	20.4	5	3	1	21.5	—22.2			—4	56.6	54.4
		—7	41.3	42.1			—1	44.6	—45.5			—5	13.9	13.6
		—8		5.1			2	30.0	—26.5			—6		0.6
		—9		—7.8			—2	105.3	—119.1			—7		8.3
		—10	14.2	15.0			3	12.3	—11.3			—8	70.8	73.6
		—11	37.2	38.7			—3	62.2	62.0			—9		7.0
		—12	34.5	—37.6			4	13.3	12.5			—11	15.4	16.1
		—13	17.7	—20.2			—4	19.0	—15.0			—12	12.4	11.0
16	2	—3	19.6	20.1			5	11.0	11.6			—13		8.8
		—4		4.3			—5	62.9	—66.5	13	3	0	19.6	20.3
		—5		2.4			6	15.6	—13.8			—1	14.8	15.2
		—6	23.3	23.5			—6	35.3	—33.2			—2	18.7	—18.5
		—7	16.3	17.2			—7	14.9	—17.1			—3	17.7	18.1
		—8	31.4	—31.7			—8		4.8			—4	38.9	39.0
		—9	25.4	—25.3			—9		—7.0			—5	25.4	—26.2
		—10	28.9	29.8			—10	32.7	—32.7			—6		—6.8
		—11	24.7	27.5	7	3	0		2.9			—7	53.3	53.4
		—12	21.6	—23.4			1		6.3			—8		—12.0
1	3	0	23.8	—19.3			—1	18.4	—16.7			—9		—4.6
		1	24.8	—23.1			—2	16.1	17.5			—10	27.7	—26.2
		—1	7.3	—5.1			3		—1.7			—11		10.0
		2	8.1	—6.9			—3	24.2	—21.4			—12	10.1	10.6
		—2	38.1	40.0			4	26.2	25.5			—13	9.4	9.9
		3	14.2	—12.5			—4		—0.4	15	3	—2	29.8	—29.6
		—3	37.3	40.7			5		1.1			—3		6.4
		4	46.9	47.1			—5	25.2	—20.1			—4	8.4	—8.4
		—4	72.5	77.9			6	18.5	—19.8			—5		5.7

Continued: TABLE IV.

h	*k*	*l*	Fo	Fc	*h*	*k*	*l*	Fo	Fc	*h*	*k*	*l*	Fo	Fc
15	3	—6	40.2	—40.8	4	4	—3	90.7	—96.7	8	4	—12	14.4	—13.3
		—7		—2.8			4	26.3	24.5	10	4	0	16.6	16.3
		—8	16.2	—15.4			—4	35.2	33.7			1	12.3	—12.0
		—9	13.3	—13.8			5	83.0	—86.7			—1	62.2	61.2
		—10	31.3	—32.1			—5	30.4	—29.1			2	31.1	—31.9
		—11	32.2	34.7			6		—3.0			—2		—21.9
		—12	8.3	7.9			7	17.5	19.1			3	39.7	46.6
17	3	—6	23.1	—23.5			—7	74.7	—75.9			—3		12.1
		—7		2.9			—8		4.5			—4		4.1
		—8	14.4	18.8			—9	33.8	34.0			—5	60.1	60.6
		—9	8.5	—11.6			—10	10.2	—9.8			—6	40.4	39.7
		—10	37.7	—37.7			—11	51.3	—54.7			—7	41.4	—40.8
0	4	1	88.1	—107.0	6	4	0		7.6			—8	53.2	—50.5
		2	9.4	8.3			1	72.7	—75.1			—9	63.9	65.1
		3	73.5	72.7			—1	56.3	53.4			—10	24.1	—23.8
		4		—0.9			2	44.9	42.4			—11	19.9	—20.0
		5	14.3	—15.0			—2	27.7	—29.1			—12	17.6	18.1
		6		—5.6			3	52.9	54.6			—13	29.1	31.3
		7	37.3	35.2			—3	50.3	—46.2	12	4	0	19.3	19.3
		8	15.2	—13.3			4	36.3	—34.2			1	18.0	—17.3
		9	18.9	—19.6			—4	26.5	27.5			—1	26.8	27.1
		10	9.4	10.0			5	35.5	—32.9			—2		6.9
2	4	0	20.8	19.8			—5	57.0	53.6			—3	47.2	—47.8
		1	94.4	—93.7			6	16.5	—17.2			—4		—8.5
		—1	40.8	—38.8			—6	49.1	—50.1			—5	37.5	34.8
		2	10.9	—11.4			—7	24.7	—24.4			—6	29.5	—28.9
		—2	9.6	—9.3			—8		—2.4			—7	32.8	—28.8
		3	16.2	—12.1			—9	38.1	34.9			—8	13.7	13.7
		—3*	127.4	—150.6			—10	16.0	14.9			—9	16.4	15.5
		4	44.1	41.8			—11		—11.4			—10		5.1
		—4	52.0	—50.3	8	4	0	19.9	—17.7			—11	41.2	—40.8
		5	68.8	—65.8			1		4.8			—12		—1.5
		—5	44.8	45.8			—1	82.9	85.3	14	4	—2	10.5	10.3
		6		—3.6			2		0.6			—3	35.5	—40.2
		—6	44.1	43.4			—2	22.5	—19.9			—4		3.3
		7		7.9			3	42.9	41.0			—5		8.1
		—7	91.8	—99.4			—3	31.0	—26.5			—6		—5.2
		—8	34.0	33.6			4		8.4			—7	46.7	—46.4
		9	47.5	—45.4			—4	19.0	—17.2			—8	39.2	37.4
		—9		—6.1			5	10.6	—11.3			—9	19.9	19.6
		—10	15.2	—16.2			—5	99.0	108.4			—10		—8.4
		—11	38.7	—38.7			—6	12.5	—11.0			—11	38.3	—40.6
4	4	0	35.2	—32.2			—7		0.7	16	4	—5	26.2	25.0
		1	98.8	—103.3			—8	21.6	18.8			—6	17.0	16.4
		—1		3.8			—9	63.6	62.8			—7	31.0	—38.6
		2	45.4	—45.4			—10		—2.3			—8		—4.7
		—2	55.1	51.6			—11	15.6	—15.6			—9	12.3	14.4
		3	17.2	—14.9										

The O—H—O distances in hydrogen bonds appear regular and are given in Table V together with the postulated coordinates of hydrogen atoms.

Table VI shows the balance of the electrostatic valences.

The hydrogen atom contribution was taken into account in the final structure factor calculation.

TABLE V.

Hydrogen atom parameters postulated for the calculation of the final structure factors.

	x/a	*y/b*	*z/c*	B (Å^2)
H_1 . . .	0.1728	0.0944	0.2452	5.00
H_2 . . .	0.2174	0.0640	0.4151	5.00
H_3 . . .	0.4473	0.4182	0.2283	5.00
H_4 . . .	0.38	0.40	0.48	5.00
H_5 . . .	0.4177	0.1888	0.4363	5.00

Distances related to the probable hydrogen bonds and their standard deviations (in parentheses).

O—H···O	Distance (Å)	O—H···O	Distance (Å)
$O_{4''}$—$O_{1''}$	2.669 (4)	$O_{4''}$—O_3	2.657 (4)
O_6—O_4	2.797 (8)		
$O_{5''}$—O_2	2.854 (7)	$O_{5''}$—$O_{3'}$	2.846 (7)

TABLE VI.

Balance of electrostatic valences.

ANION	Balancing cations	Charges of cations	Total charges surrounding anion
O_1	Ca , Na , C , H_2	1/4 + 1/6 + 4/3 + 6/24	2.000
O_2	Ca , 2 Na , C , H_5	1/4 + 1/3 + 4/3 + 2/24	2.000
O_3	Na , C , H_1 , H_4	1/6 + 4/3 + 4/24 + 8/24	2.000
$O_4(H_2O)$	Ca , H_3 , H_2 , H_1	1/4 + 4/24 + 18/24 + 20/24	2.000
$O_5(H_2O)$	Ca , Na , H_4 , H_5	1/4 + 1/6 + 16/24 + 22/24	2.000
$O_6(H_2O)$	2 Na , H_3 , $H_{3'}$	1/3 + 20/24 + 20/24	2.000

Description of the structure.

Fig. 1 shows the general arrangement of the atoms in gaylussite. The bond distances and bond angles are given in Table VII and Table VIII.

The CO_3 group has the usual triangular and planar coordination; the mean distance C—O is 1.284 Å. Bond angles $\widehat{OCO}$ are nearly 120°.

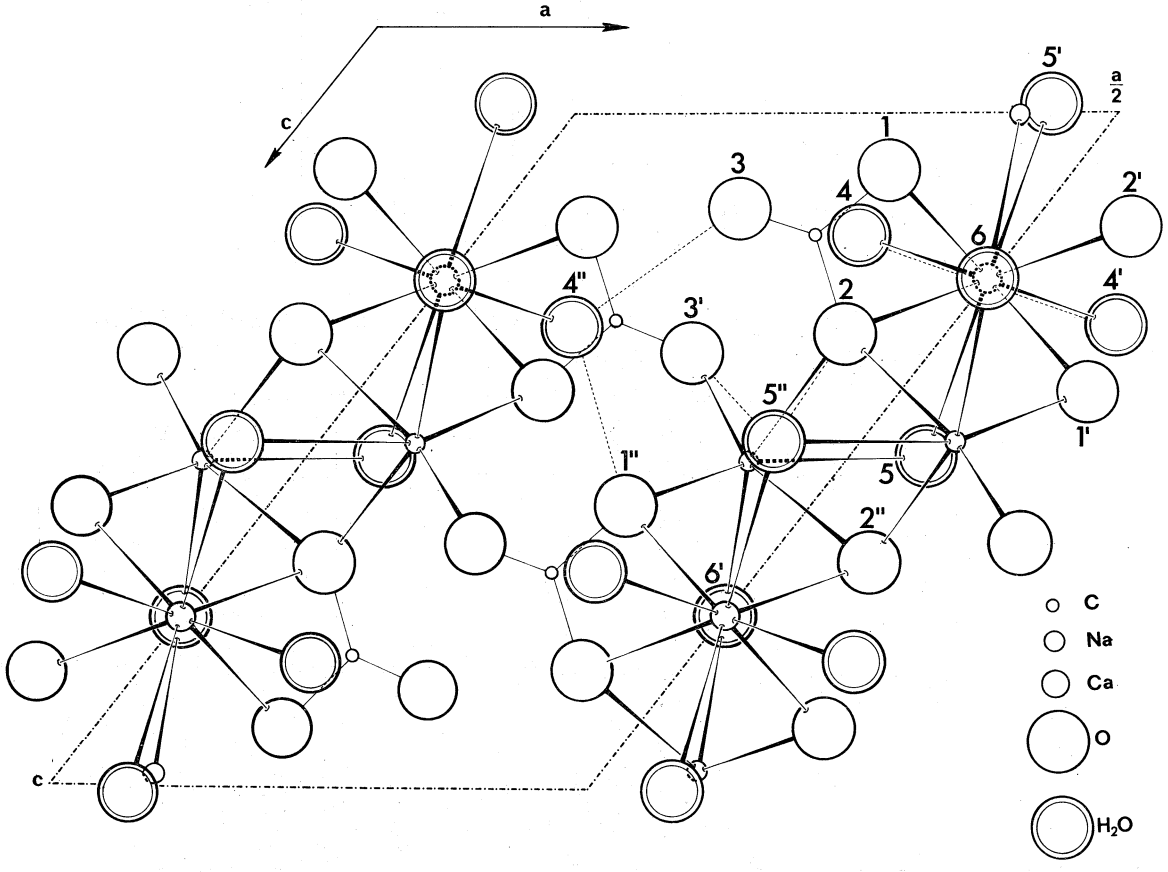

Fig. 1. – Projection of the structure along the *b* axis. Dotted lines represent postulated hydrogen bonds (one for each kind).

Coordination polyedra around Ca atoms are somewhat irregular square antiprisms. On the corners of the antiprism lie four oxygen atoms (of CO_3 group) and four water molecules. Ca—O distance ranges from 2.382 to 2.571 Å; the mean distance Ca—O is 2.462 Å.

The two bases of the antiprism are somewhat different: one of them is planar and parallel to the *a c* plane, whilst the other is slightly deformed, although on the whole parallel to the *a c* plane. On the first base (the planar one) lie four oxygen atoms belonging to the CO_3 group; on the other base are four water oxygens.

TABLE VII.

Interatomic distances and their standard deviations.

ATOMS	Distance	σ	ATOMS	Distance	σ
Ca—O_1	2.382 Å	0.004 Å	Na—$O_{1''}$	2.332 Å	0.004 Å
O_2	2.571	0.004	O_2	2.396	0.004
O_4	2.416	0.005	$O_{2''}$	2.612	0.005
O_5	2.480	0.002	$O_{3'}$	2.342	0.006
C—O_1	1.284	0.003	O_5	2.481	0.006
O_2	1.277	0.004	$O_{6'}$	2.401	0.004
O_3	1.290	0.006			

TABLE VIII.

Bond angles and their standard deviations.

ATOMS	Angle	σ	ATOMS	Angle	σ
O_1—Ca—$O_{1'}$ . . .	106.3°	0.2°	$O_{1''}$—Na—O_2 . .	98.5°	0.2°
O_2 . . .	52.7	0.8	$O_{2''}$ . .	85.4	0.2
$O_{2'}$ . . .	85.3	0.1	$O_{3'}$ . .	113.8	0.2
O_4 . . .	84.2	0.2	O_5 . .	153.5	0.2
$O_{4'}$ . . .	155.9	0.1	$O_{6'}$ . .	84.8	0.2
$O_{5'}$ . . .	78.7	0.1	O_2—Na—$O_{2''}$ . .	78.0	0.1
O_5 . . .	124.7	0.1	$O_{3'}$ . .	101.7	0.1
O_2—Ca—$O_{2'}$ . . .	110.1	0.2	O_5 . .	76.7	0.1
O_4 . . .	84.1	0.2	$O_{6'}$ . .	159.0	0.2
$O_{4'}$ . . .	151.3	0.1	$O_{3'}$—Na—$O_{2''}$ . .	160.4	0.2
$O_{5'}$ . . .	129.7	0.1	O_5 . .	92.6	0.2
O_5 . . .	73.6	0.1	$O_{6'}$ . .	95.7	0.2
O_4—Ca—$O_{4'}$ . . .	94.9	0.2	O_5—Na—$O_{2''}$ . .	68.1	0.1
$O_{5'}$ . . .	78.2	0.1	$O_{6'}$ . .	91.1	0.1
O_5 . . .	77.6	0.1	$O_{6'}$—Na—$O_{2''}$ . .	81.6	0.2
O_5—Ca—$O_{5'}$ . . .	143.7	0.2			
			O_1—C—O_2 . . .	118.9	0.5
			O_3 . . .	119.7	0.3
			O_2—C—O_3 . . .	121.5	0.3

The Ca polyhedra are independent of each other.

The coordination of Na is sixfold; on the corners of an irregular octahedron lie four oxygens of CO_3 group and two water oxygens. Na—O distance ranges from 2.332 to 2.612 Å; the mean distance Na—O is 2.427 Å.

These polyhedra are connected to each other alternately by the sharing of one corner (O_6) and by the sharing of one edge (O_2—$O_{2'}$) so as to form an infinite zigzag chain, on the whole running parallel to *c*.

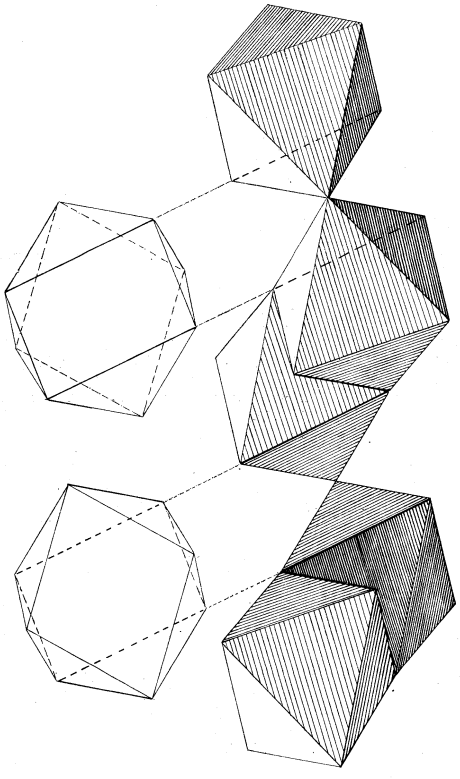

Fig. 2. – Perspective drawing of Na and Ca polyhedra chains. Ca antiprisms are placed out of their right position; the heavy lined edges of Na octahedrons are shared by Ca antiprisms.

Antiprisms are connected to octahedron chains; each Ca polyhedron is linked to four adjacent octahedrons by the sharing of four edges: O_2—$O_{1'}$; O_2—$O_{5'}$; O_2—O_1; $O_{2'}$—O_5 (fig. 2). The oxygens O_4 and $O_{4'}$ belong only to Ca antiprism.

In the structure there are two sets of equivalent chains, distant from each other by $\frac{1}{2}a + \frac{1}{2}b$ (fig. 3). The connexions between one chain and the adjacent ones are provided by the oxygens (O_1, O_2, O_3) linked to the carbon atom: in fact O_1 is shared also by one antiprism and one octahedron; O_2 by two octahedrons and one antiprism; O_3 by one octahedron.

Owing to these connections among adjacent chains, the general feature of the structure is a stratiform arrangement parallel to (110) and ($\bar{1}$10) planes.

From fig. 3, the lack of connection along *b* among adjacent chains (except some hydrogen bonds), and the consequent presence of gaps in the structural arrangement, are clearly evident. This feature explains the low density of gaylussite; the presence of water molecules facing the gaps is likely in connection with the low temperature (100° C) at which the dehydratation of this mineral begins.

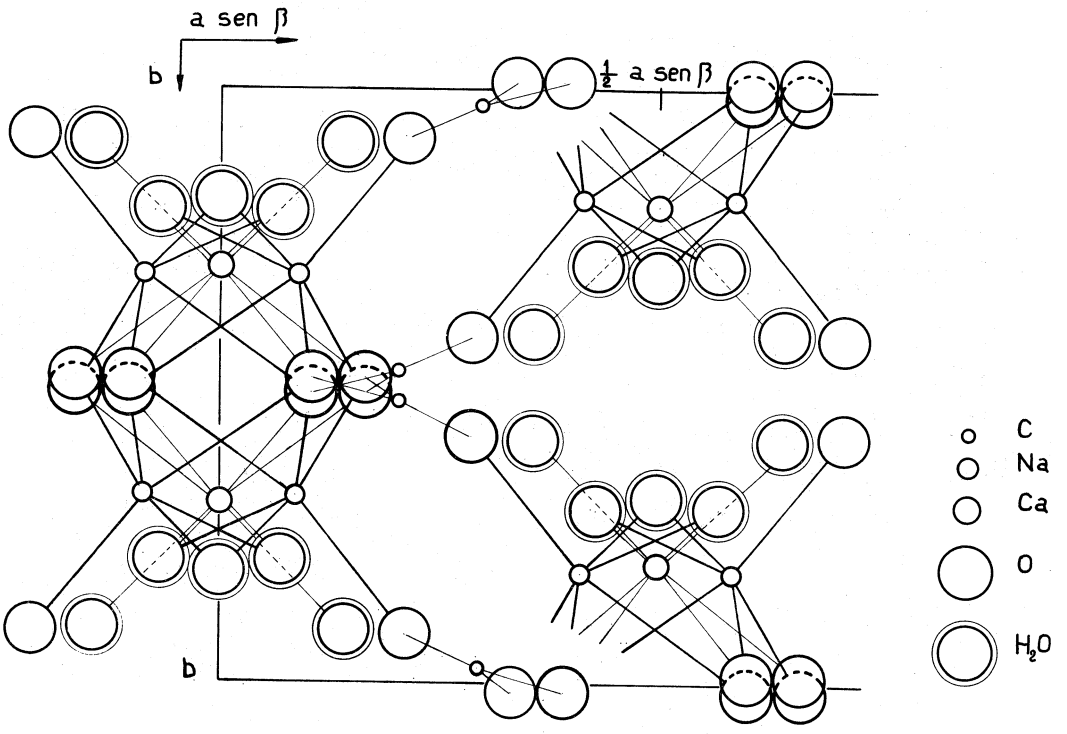

Fig. 3. – Projection of the structure along the *c* axis.

The optical properties of gaylussite are reasonably explained by the structural features. The negative optical sign depends on the stratiform arrangement; the direction of X is parallel to *b* while Z lies almost parallel to the *c* direction chains.

The perfect {110} cleavage is also explained by the structure of this substance.

I am indebted to Prof. V. Scatturin, Dr. V. Albano, Dr. P. L. Bellon, Dr. F. Pompa and to Prof. A. Vaciago, Dr. V. Albano, Dr. A. Domenicano who provided me with the programs of least-squares refinement.

REFERENCES.

[1] H. H. ADLER and P. F. KERR, *Infrared spectra, symmetry and structure relations of some carbonate minerals*, « Amer. Miner. », *48*, 839 (1963).

[2] V. ALBANO, P. L. BELLON, F. POMPA e V. SCATTURIN, *Programmi cristallografici per l'elaboratore I.B.M. 1620*, « Ric. Scient. », *3 A*, 1067 (1963).

[3] V. ALBANO, A. DOMENICANO e A. VACIAGO, *Programmi di strutturistica chimica diffrattometrica per l'elaboratore elettronico I.B.M. 7040*, « Gazzetta Chim. Ital. », *96*, 922 (1966).

[4] W. L. BOND, *Making small spheres*, « Rev. Sci. Instr. », *22*, 344 (1951).

[5] J. B. BOUSSINGAULT, « Ann. Chim. Phys. », *31*, 270 (1826).

[6] E. CORAZZA and C. SABELLI, *The crystal structure of pirssonite*, « Acta Cryst. », *23*, 763 (1967).

[7] D. T. CROMER and J. T. WABER, *Scattering factors computed from relativistic Dirac-Slater wave functions*, « Acta Cryst », *18*, 104 (1965).

[8] J. H. FANG, P. D. ROBINSON, J. F. CERVEN and L. A. WOLF, *Computer program for refining cell parameters from Weissenberg photographs and its application to indexing the powder pattern of gaylussite*, « Amer. Miner. », *52*, 1570 (1967).

[9] C. K. HUANG and P. F. KERR, *Infrared study of the carbonate minerals*, « Amer. Miner. », *45*, 311 (1960).

[10] S. MENCHETTI, *Dati cristallografico-strutturali sulla gaylussite. (Nota preliminare)*, in press on « Rend. Soc. Min. It. » (1968).

[11] E. A. MONROE, *Unit cell and space group of gaylussite*, « Zeits. Krist. », *124*, 459 (1967).

[12] M. E. MROSE, *X-ray powder data for saline minerals of the Green River Formation*, « U.S. Geol. Surv. Prof. Pap. », *405* (1962).

[13] C. PALACHE, H. BERMAN and C. FRONDEL, *The system of mineralogy*, *2*, 234, J. Wiley & Sons, New York, 1951.