

THE CRYSTAL STRUCTURE OF CARBOCERNAITE

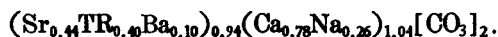
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The carbocernaite was first found in USSR by A. Г. Булах et al.^[1]. Except its space group, the formula $(\text{Ce, Na, Sr, Ca})\text{CO}_3$, the lattice parameters ($a = 5.21 \text{ \AA}$, $b = 7.28 \text{ \AA}$, $c = 6.40 \text{ \AA}$) and the orthorhombic system were all given. In China Liang Youbin et al. reported that carbocernaite was found in large scale in the rare earth deposit of Bayan Obo, Baotou, following its occurrence in Shandong Province first announced by Qian Dengfu in 1978^[2].

The specimen under study was from the deposits of the Bayan Obo, Baotou, supplied by Liang Youbin, and Gao Desheng.

Complete chemical analysis of the mineral gave Ce_2O_3 10.27, La_2O_3 8.78, Pr_6O_{11} 0.99, Nd_2O_3 2.47, Sm_2O_3 0.30, Gd_2O_3 0.39, SrO 17.77, BaO 5.24, CaO 16.68, FeO 0.53, Na_2O 3.15, CO_2 33.85, H_2O 1.22%, total 101.64%. Excluding water (1.22), it gives



Oscillation and Weissenberg photographs were adopted to confirm that it was really a single crystal with orthorhombic system. Approximate cell dimensions obtained were $a = 5.26$, $b = 6.40$, $c = 7.34 \text{ \AA}$. The extinction rule shown is

$$h0l, l = 2n; \quad 00l, l = 2n.$$

Hence the space group will be one of $Pmc2_1$, $P2cm$, $Pmcm$. By Weissenberg photographing a crystal which can be used to 4-circle single crystal automatic diffractometer was selected, its size being $0.25 \times 0.30 \times 0.10 \text{ mm}$. The collection of intensity data was finished by RASA-IIS type single crystal automatic diffractometer. The refraction intensities were measured with graphite monochromated, $\text{MoK}\alpha$ radiation, $\omega - 2\theta$ scan $3-55^\circ$, $\Delta\omega = 2.32 + 0.5\theta$ and a speed of $4^\circ/\text{min}$ for ω scan. 381 independent reflections with $|F| > 3\sigma|F|$ were collected, among which 313 were applied to intensity calculation and Lorentz and polarization corrections were made. The cell parameters refined by least squares method and other crystal data are listed in Table 1.

The correct structure model was obtained by using the Patterson method and direct method. The coordinates of $\text{Sr}(\text{TR}, \text{Ba})$ and $\text{Ca}(\text{Na})$ were got according to the coordinates given by Patterson function $P(\text{OVW})$ and the MUTAN program. The coordination of O and C were got by Fourier synthesis. By block matrix refinement with the least square the R -factor was reduced to 0.094 when using isotropic temperature factors, but to 0.062 when using anisotropic temperature factors. The coordinates

of atoms are shown in Tables 2 and 3. Interatomic distances and angles in carbocernaite are shown in Table 4.

Table 1
Crystal Data of Carbocernaite

(Sr, TR, Ba) (Ca, Na) (CO ₃) ₂	$Z = 2$
Orthorhombic, $Fmc2_1$	$Dm = 3.53$
$a = 5.214(3) \text{ \AA}$	$Dc = 3.64$
$b = 6.430(3) \text{ \AA}$	$\lambda = 0.70926 \text{ \AA}, \text{ MoK}\alpha$
$c = 7.301(12) \text{ \AA}$	$\mu = 124.8 \text{ cm}^{-1}$
$V = 244.797 \text{ \AA}^3$	

Table 2
Atom Coordinates of Carbocernaite

No.	Atom	GI	x	y	z
1	Sr	0.5	0	0.1168(4)	0.2555(11)
2	Ca	0.5	0.5	0.4844(14)	0.5495(10)
3	O ₁	1	0.2097(26)	0.4907(24)	0.2951(20)
4	O ₂	1	0.2850(33)	0.1288(27)	0.5452(23)
5	O ₃	0.5	0	0.2313(43)	0.9204(41)
6	O ₄	0.5	0.5	0.1433(41)	0.1462(36)
7	C ₁	0.5	0	0.4176(40)	0.8436(38)
8	C ₂	0.5	0.5	0.0343(49)	0.5782(45)

Table 3
Thermo-parameters of Carbocernaite.

No.	Atom	B_j	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
1	Sr	1.41(6)	1.25(10)	0.75(10)	2.10(10)	0	0	-0.05(15)
2	Ca	1.86(21)	1.56(26)	1.52(32)	2.73(34)	0	0	-0.22(33)
3	O ₁	2.02(33)	2.06(56)	1.48(55)	2.64(76)	0.30(53)	0.38(14)	0.08(47)
4	O ₂	2.49(34)	2.22(70)	1.35(71)	3.77(69)	-0.33(62)	-0.18(63)	0.11(64)
5	O ₃	3.15(57)	2.85(117)	1.49(118)	4.66(119)	0	0	0.04(109)
6	O ₄	2.62(53)	4.01(98)	0.66(104)	3.77(104)	0	0	0.52(96)
7	C ₁	0.95(47)	2.22(88)	0.92(86)	1.09(6)	0	0	0.35(79)
8	C ₂	1.68(62)	1.75(103)	1.23(121)	2.55(115)	0	0	0.57(97)

The anisotropic temperature factor being $\exp - \frac{1}{4} (B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}kbb^*c^*)$

The crystal structure indicates that the Sr atom and Ca atom are situated in different crystallographic positions. According to electric density calculation isomorphism replacements exist between Sr and TR, Sr and Ba, as well as between Ca and Na. This conforms basically to the rule of chemical element replacement in the periodic table. The projection along c -axis is shown Fig. 1. The Sr(TR, Ba) and Ca(Na) atom layers are arranged alternately along a -axis. They are situated at $x = 0$ and $x = 1/2$ and are perpendicular to a -axis. The (CO₃) trigonal plane is parallel to a -axis and oblique to b - and c -axis.

Table 4a
Interatom Distance and Angle in Carbocearnite

Coordination Polyhedra Sr(TR, Ba)—O	Å	Coordination Polyhedra Ca(Na)—O	Å
Sr(TR, Ba)—O ₁	2.657×2	Ca(Na)—O _{1a}	2.396×2
Sr(TR, Ba)—O _{1a}	2.587×2	Ca(Na)—O _{1b}	2.352×2
Sr(TR, Ba)—O _{1b}	2.657×2	Ca(Na)—O ₂	2.547×2
Sr(TR, Ba)—O _{2a}	2.555	Ca(Na)—O ₂	2.496
Sr(TR, Ba)—O _{2b}	2.542		

Table 4b
The (CO₃) Trigonal Plane

Distance (Å)		Angle (°)	
O ₁ —O ₁	2.187	O ₁ —C ₁ —O ₁	115.65
O ₁ —O ₂	2.287	O ₁ —C ₁ —O ₂	121.99
C ₁ —O ₁	1.292		
C ₁ —O ₂	1.323		
O ₂ —O ₂	2.242	O ₂ —C ₂ —O ₂	119.52
O ₂ —O ₃	2.205	O ₂ —C ₂ —O ₃	121.60
C ₂ —O ₂	1.298		
C ₂ —O ₃	1.245		

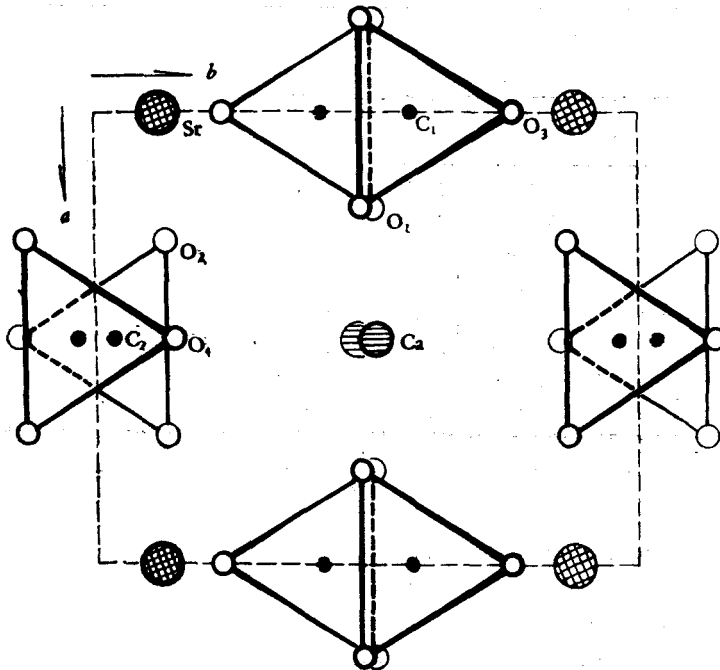


Fig. 1. Projection along c-axis of carbocearnite crystal structure.

The (CO₃) trigonal plane is divided into two equal parts by either the Sr(TR, Ba) or Ca(Na) atom layer because these layers are symmetrical planes. Consequently, be-

tween the Sr(TR, Ba) and Ca(Na) atom layers, there is an oxygen layer of the general position O_1 and O_2 . The special positions C , O_3 , O_4 are situated in Sr(TR, Ba) or Ca(Na) atom layers. In the crystal structure of carbocearnite the coordinate number of Sr(TR, Ba) is eight, its coordination polyhedron is made up of one trigonal prism and two tetragonal pyramids. The coordinate number of Ca(Na) is seven, its coordinate polyhedron is made up of one trigonal prism and one tetragonal pyramid. The ORTEP map of coordinate relationship of the above-mentioned atoms is shown in Figs. 2 and 3.

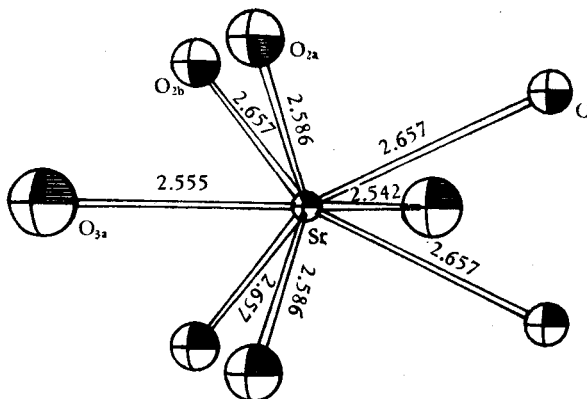


Fig. 2. The ORTEP map of coordination relationship of Sr(Tr, Ba) in carbocearnite.

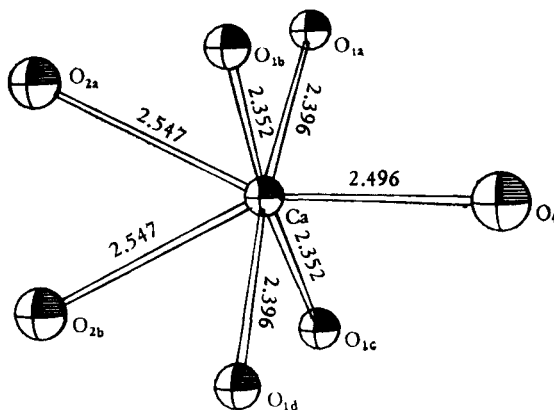


Fig. 3. The ORTEP map of coordination relationship of Ca(Na) in carbocearnite.

The determination of crystal structure of carbocearnite can be used to explain its optical properties. In the crystal structure the c -axis is approximately perpendicular to (CO_3) plane, so that Np is parallel to c -axis. The intersection of two (CO_3) planes have the same directions as a -axis, consequently Ng is parallel to a -axis so that the orientation of optical is $Ng//a$, $Nm//b$ and $Np//c$. The intersected angle between a -axis and (CO_3) plane is approximately equal to the intersected angle between b -axis and (CO_3) plane, therefore the refractive indices of Ng and Nm which are parallel to a - and b -axis respectively, are approximately equal. Since $Ng - Nm < Nm - Np$, the

optical character is negative. It is possible that the angle of $2V$ (52°) is related to the intersection between both (CO_3) planes. The close packing layer, such as of calcite or aragonite, is not existing; as a result, the cleavage of carbocernaite is not frequent.

According to crystal structure, the chemical formula of carbocernaite should be written:



The determination of crystal structure of carbocernaite is of significance to carbonate crystal chemistry. According to crystal-chemistry classification there are three types of well-known carbonates without water and additional anions. They are the calcite, aragonite and vaterite types. The crystal structure of carbocernaite, being different from any of these three types, is a new type of crystal structure.

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- [2] 钱定福, *地质论评*, 25(1979), 2: 29—35.