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BENSTONITE, $Ca_7Ba_6(CO_3)_{13}$, A NEW MINERAL FROM THE BARITE DEPOSIT IN HOT SPRING COUNTY, ARKANSAS

FRIEDRICH LIPPMANN,[1] *Mineralogische Anstalten der Universität, Göttingen, Germany.*

ABSTRACT

Benstonite, $(Ca,Mg,Mn)_7(Ba,Sr)_6(CO_3)_{13}$, was found at the barite mine in Hot Spring County, Arkansas, where it occurs in veins within the barite body associated with milky quartz, barite and calcite. It forms white cleavable masses which show cleavage faces up to 1 cm across. H=3–4; G 3.596 (meas.), 3.648 (calc.); good rhombohedral cleavage with about the same angles as calcite. Uniaxial negative with $\omega = 1.690_5$ and $\epsilon = 1.527$. Single crystal *x*-ray studies revealed a rhombohedral lattice with the following characteristics: possible space groups $R\bar{3}$ or $R3$, the most probable being $R3$ because of the symmetry of the CO_3-group and the available equipoints; hexagonal, $a = 18.28 \pm 0.01$ Å, $c = 8.67 \pm 0.02$; rhombohedral, $a_{rh} = 10.94$ Å, $\alpha = 113.3°$; volume 2509 Å^3 (hex.), cell contents: 3 $[Ca_7Ba_6(CO_3)_{13}]$ in the hexagonal unit. The index of the cleavage face is $\{31\bar{4}2\}$ or $\{4\bar{1}\bar{3}2\}$.

The hexagonal indices of the strongest *x*-ray reflections satisfy the relation $h^2+k^2+hk = 13n$, and they may be transformed to the indices of calcite reflections. The resulting "calcite-cell" of benstonite has: $a' = a/\sqrt{13} = 5.07$ Å, $C' = 2c = 17.34$ Å; volume 386.0 Å^3; calcite: $a = 4.990$ Å; $c = 17.06$ Å; volume 367.80 Å^3. Benstonite therefore has a structure which may be described as a superstructure derived from the calcite configuration. Approximate parameters for the cation sites in benstonite are derived from the calcite arrangement, and four different models are proposed for the arrangement of the cations.

The chemical analysis was carried out on selected material from which a small admixture of calcite could not be separated. The formula $Ca_{6.118}Mg_{0.788}Mn_{0.094}Ba_{5273}Sr_{0.727}(CO_3)_{13}$ calculated after deduction of 2.23 weight per cent calcite may be generalized to $Ca_7Ba_6(CO_3)_{13}$ or possibly $MgCa_6Ba_6(CO_3)_{13}$.

Benstonite is named in honor of O. J. Benston, Malvern, Arkansas, who drew attention to the mineral.

INTRODUCTION

In Hot Spring County, Arkansas, about 2½ miles ENE of the igneous complex of Magnet Cove, a large barite deposit is mined in an open pit operation. The beds of the deposit lie between the Arkansas novaculite (Devonian-Mississippian) and the Stanley shale (Pennsylvanian) at the eastern end of a syncline that follows the strike of the Ouachita mountains. The deposit was described by Parks and Branner (1933), and the geology of the region is summarized by Fryklund and Holbrook (1950).

The barite rock is fine-grained and has a gray color owing to varying amounts of interspersed shaly matter. In certain places it contains irregular white veins, from an inch to a few inches in thickness, in which the new barium calcium carbonate, benstonite, is found. It is associated with milky quartz, barite and calcite.

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[1] Present address: Grabbeplatz 12, Dortmund, Germany.

Benstonite is named in honor of O. J. Benston, born 1901, ore dressing metallurgist, Baroid Division, National Lead Company, Malvern, Arkansas. Mr. Benston had guessed from qualitative chemical tests and from the specific gravity of about 3.60 that the mineral might be either alstonite or barytocalcite. During a visit to the mine on New Year's Eve, 1954, he kindly furnished the specimens on which the present study is based.

Physical Properties

Benstonite occurs as cleavable masses with cleavage faces up to one centimeter across. Cleavage fragments are more or less perfect rhombohedra of the same shape as calcite and the other rhombohedral carbonates. The cleavage is not quite as perfect as that of calcite. The cleavage faces are slightly curved, and, especially on the larger pieces, they are composite, with mosaic structure as in some dolomite and siderite. On the reflecting goniometer extremely diffuse signals were observed. Values of 44.7° and 44.3° were obtained for the polar distances (ρ angles) of the faces on two different cleavage rhombohedra (averages of a large number of readings). For these measured ρ angles the calculated cleavage angles (λ angles) are 75.1° and 74.4°, respectively. (The corresponding literature values of ρ and λ for calcite are: 44.6° and 74.9°.)

The hardness is between 3 and 4. The specific gravity as determined by the pycnometer method is 3.596.

The color is snow white to ivory. When irradiated with long or short wave ultraviolet radiation benstonite fluoresces red, which is almost identical with that of a glowing cigaret. The same fluorescence occurs when the mineral is exposed to x-rays. Phosphorescence is perceptible at 20 kilovolts. At 50 kilovolts the afterglow lasts a couple of minutes.

Optical Properties

In thin section benstonite shows numerous bubbles of about a micron to a few microns diameter and other more irregularly shaped cavities of similar dimensions. These are responsible for the white overall appearance of the mineral which otherwise would be translucent. Extinction of individual grains is not uniform. Domains varying in size from 0.1mm to over 1mm are displaced a few degrees. In some cases the boundaries are sharp, but usually the domains merge almost imperceptibly with each other. This phenomenon, which occurs commonly in siderite and dolomite correlates with the composite nature of the cleavage faces. It is similar to the undulatory extinction of deformed quartz grains in metamorphic rocks.

Benstonite yields a uniaxial negative interference figure. Even in thick sections there is no indication that the mineral is biaxial with a small 2V. This is important for the distinction from alstonite and barytocalcite, for which axial angles of 6° and 15°, respectively, are reported.

The refractive indices were determined for sodium light by the immersion method: $\omega = 1.690_5 \pm 0.0005$; $\epsilon = 1.527 \pm 0.001$. Cleavage fractures 10–100 microns across may be filled by another carbonate mineral, probably calcite because of its lower ω.

X-RAY CRYSTALLOGRAPHY

A well terminated cleavage rhombohedron about 0.2 mm in size was mounted parallel to its trigonal axis. After orientation by the oscillation method, a rotation photograph and equi-inclination Weissenberg photographs of zero, first, and second levels were taken with Ni-filtered Cu-K_α radiation. All reflections observed satisfy the condition of rhombohedral centering $-h+k+l=3\text{n}$ for $hk \cdot l$. The lattice level symmetries C_6 of the zero layer and C_3 of the first and second layers yield the diffraction symbol $\bar{3}\ R-$ which includes the space groups $R\bar{3}$ and $R3$. The lattice constants were determined to be $a = 18.4$ Å, from the zero-layer Weissenberg photograph, and $c = 8.75$ Å, from the layer-line spacings on the rotation photograph.

In indexing the powder data obtained with NaCl as an internal standard $a = 18.28 \pm 0.01$ Å and $c = 8.67 \pm 0.02$ Å gave the closest fit of calculated and measured d-spacings (Table 1). For these hexagonal lattice constants the axial ratio is: $a:c = 1:0.4743$. The calculated dimensions of the rhombohedral cell are: $a_{\text{rh}} = 10.94$ Å and $\alpha = 113.3°$. The cleavage rhombohedron must have the index $\{3\ 1\ \bar{4}\ 2\}$ or $\{4\ \bar{1}\ \bar{3}\ 2\}$[1]. For these indices the calculated ρ angle of 44.6° ($\lambda = 75.0°$) is within the range of the two measured ones. The indices of the cleavage face are substantiated by the fact that the corresponding powder diffraction line, which is the strongest of the whole pattern, is of greatly variable intensity with more or less preferred orientation.

The cleavage and the x-ray diffraction properties suggested that the structure of benstonite might be related to calcite. It was found that the strongest reflections in the powder pattern have hexagonal indices which satisfy the condition $h^2+k^2+hk = 13\text{n}$. These may be subdivided into two groups with $4h+k = 13\text{n}$ and $3h-k = 13\text{n}$. If the first group is converted by the transformation $^4/_{13}\ ^1/_{13} \cdot 0/^{-1}/_{13}\ ^3/_{13} \cdot 0/0\ 0 \cdot 2$ the set of indices of x-ray reflections of calcite is obtained. The same result is arrived at when the indices of the second group undergo the transformation

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[1] Right- or left-handed, respectively.

TABLE 1. *X*-RAY POWDER DATA FOR CALCITE (SWANSON AND FUYAT, 1953) AND FOR BENSTONITE,[1] $Ca_7Ba_6(CO_3)_{13}$, HEXAGONAL, $a=18.28\pm0.01$ Å, $c=8.67\pm0.02$ Å, PROBABLE SPACE GROUP *R*3 (PRESENT STUDY)
Strong reflections are underlined.

Relative intensity[2]	$d_{hk\cdot l}$ Å measured	$d_{hk\cdot l}$ Å calculated	$hk\cdot l$[3]	$\bar{h}i\cdot l$	$h'k'\cdot l'$ calcite cell	Rel. int.[4] synthetic	$d_{h'k'\cdot l'}$ Å[4] calcite
3	9.21	9.140	11.0				
3	7.63	7.605	10.1				
2	5.83	5.843	02.1				
3	5.28	5.277	03.0				
4	4.93	4.925	21.1				
3	4.57	4.570	22.0				
16	4.19	4.181	01.2				
38	3.92	3.917	13.1	$\bar{1}4.1$	01.2	12	3.86
1	3.80	3.802	20.2				
9	3.60	3.601	40.1				
		3.511	12.2				
4	3.45	3.455	14.0				
10	3.53	3.350	32.1				
95	3.08_5	3.085	31.2		10.4	100	3.035
		3.047	33.0				
1	2.98	2.974	05.1				
		2.923	04.2				
1	2.89	2.890	00.3		00.6	3	2.845
		2.828	24.1				
		2.784	23.2				
3	2.755	2.756	11.3				
		2.702	51.1				
1	2.637	2.639	06.0				
2	2.557	2.557	50.2				
28	2.536	2.535	25.0		11.0	14	2.495
		2.535	03.3				
1	2.495	2.493	43.1				
1	2.46	2.462	42.2				
9	2.445	2.443	22.3		11.3	18	2.285
2	2.380	2.378	15.2				
4	2.327	2.326	16.1				
1	2.281	2.285	44.0				

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[1] Benstonite with NaCl as internal standard, Norelco *X*-ray spectrometer, $\frac{1}{2}°$ per minute, 1° slit, receiving slit 0.2 mm; CuKα radiation, Ni-filter.

[2] Relative intensities are peak heights on spectrometer trace. They are distorted by preferred orientation.

[3] Only the indices with positive numbers are listed for every diffraction line in the $hk\cdot l$ column. The other possible (enantiomorphic) index is given under $\bar{h}i\cdot l$ only when necessary for the transformation to the "calcite-cell" of a right-handed crystal.

[4] The indices, intensities, and d-spacings of calcite reflections $hk\cdot l$ with l odd are written vertical. They have no equivalent in benstonite because its c-spacing is about half that of calcite.

TABLE 1 (*continued*)

Relative intensity[2]	$d_{hk\cdot l}$ Å measured	$d_{hk\cdot l}$ Å calculated	$hk\cdot l$[3]	$\bar{h}i\cdot l$	$h'k'\cdot l'$[4] calcite cell	Rel. Int.[4] synthetic	$d_{h'k'\cdot l'}$ Å calcite
5	2.233	2.231	34.2				
10	2.217	2.217	14.3				
4	2.189	2.188	70.1				
		2.188	35.1				
?	2.15	2.148	10.4				
23	2.127	2.128	62.1		20.2	18	2.095
4	2.113	2.109	61.2				
4	2.097	2.097	17.0				
		2.097	33.3				
		2.091	02.4				
2	2.042	2.038	21.4				
3	2.006	2.005	53.2				
3	1.994	1.995	36.0				
?	1.973	1.974	54.1				
10	1.957	1.959	26.2	$\bar{2}8.2$	02.4	5	1.927
		1.949	06.3				
11	1.945	1.944	13.4	$\bar{1}4.4$	01.8	17	1.913
		1.929	08.1				
17	1.905	1.906	25.3		11.6	17	1.875
		1.901	04.4				
5	1.886	1.888	27.1				
4	1.863	1.861	32.4				
1	1.834	1.836	45.2				
		1.828	55.0				
		1.812	81.1				
		1.800	80.2				
		1.792	44.3				
		1.789	05.4				
		1.777	46.1				
		1.766	72.2				
1	1.757	1.759	09.0				
		1.755	24.4				
1	1.746	1.745	73.1				
2	1.728	1.727	28.0				
		1.724	51.4				
		1.724	01.5				
1	1.698	1.697	17.3				
1	1.692	1.694	20.5				
1	1.670	1.675	64.2		21.1	4	1.626
1	1.664	1.666	12.5				
1	1.645	1.648	37.2				
		1.642	47.0				
		1.642	36.3				
		1.630	65.1				
7	1.630	1.630	19.1		12.2	8	1.604
2	1.616	1.613	31.5		10.10	2	1.587
6	1.549	1.550	56.2		21.4	5	1.525

TABLE 2. COMPARISON BETWEEN DIMENSIONS OF "CALCITE-CELL" OF BENSTONITE AND STRUCTURE CELL OF CALCITE

"Calcite-cell" of benstonite	Structure cell of calcite
hexagonal $a'\frac{a}{\sqrt{13}}=5.07$ Å	$a=4.990$ Å[1]
$C'=2c=17.34$ Å	$c=17.06$ Å[1]
$V'=\frac{2V}{13}=386.0$ Å	$V=367.80$ Å^3
$a':C'=1:3.420$	$a:c=1:3.4189$
index of cleavage face: $\{10\bar{1}4\}$	$\{10\bar{1}4\}$
rhombohedral $a'_{rh}=6.47_9$ Å	$a_{rh}=6.375$ Å
$\alpha'=46.1°$	$\alpha=46.08°$

[1] Goldsmith and Graf, 1958.

$^3/_{13}\ {^{-1}}/_{13}\cdot 0/{^1}/_{13}\ {^4}/_{13}\cdot 0/0\ 0\cdot 2$. The inverse matrices are $3-1\cdot 0/1\ 4\cdot 0/0 0\cdot {^1}/_2$ and $4\ 1\cdot 0/-1\ 3\cdot 0/0\ 0\cdot {^1}/_2$, respectively. If the indices of the x-ray reflections of calcite with $l=2n$ are converted by one of the reverse transformations the indices of the strongest benstonite spacings result. This means that the structure of benstonite is based on a pseudo-cell the hexagonal dimensions a' and c' of which are related to the structure cell dimensions of benstonite, a and c, by $a'=a/\sqrt{13}$ and $c'=c$. Two adjacent pseudo-cells in the c-axis direction have total dimensions similar to the structure-cell of calcite. The numerical data of the "calcite-cell" of benstonite are compared with the structure cell data of calcite in Table 2. The axial ratios are almost identical, but the "calcite-cell" of benstonite is larger, as can be expected from the larger size of the barium ions with respect to the calcium ions. From this similarity as well as from the similarity of the x-ray powder pattern of calcite and the strongest reflections of benstonite it may be concluded that the structure of benstonite is of the same general scheme as the structure of calcite with the cations ordered to form a superstructure (and perhaps the CO_3-groups rotated with respect to the calcite configuration).

The pseudo-cell (and also the "calcite-cell") is rotated by 13.9° versus the real cell. The sense is counterclockwise, if the indices of benstonite with $4h+k=13n$ are transformed, or clockwise, if the indices with $3h-k=13n$ are involved. In the space group $R\bar{3}$ both orientations are identical if viewed from opposite directions along the c-axis. In the space group $R3$ the two arrangements are enantiomorphic. Since the cleavage face is the most prominent morphological feature it will customarily be indexed

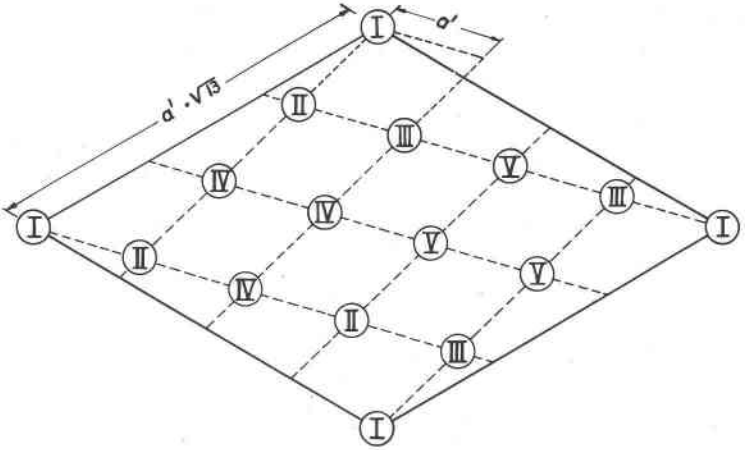

FIG. 1. Calcite-type cation layer (calcite-cells: dashed lines, lattice constant a') with right-handed benstonite-type superstructure cell (full lines, lattice constant $a' \cdot \sqrt{13}$) containing 13 cations per unit in the layer. Equipoints are numbered according to the symmetry of $R3$ as in Table 3, column 1.

$\{31\bar{4}2\}$ in right-handed crystals or $\{4\bar{1}\bar{3}2\}$ in left-handed ones. Whether this assignment is really true could only be decided by a determination of the absolute configuration. From the customary indexing and the relation to the calcite structure it follows that the strong reflections are assigned indices with $4h+k=13\text{n}$ in the right-handed enantiomorph and with $3h-k=13\text{n}$ in the left-handed one.

The "calcite-cell" of benstonite (or two pseudo-cells) will certainly contain $6(RCO_3)$ as in the hexagonal structure cell of calcite. Since the transformation of the structure cell to the "calcite-cell" is accompanied by a change in volume by the factor 2/13, there will be 39 carbonate units, *i.e.* $39(RCO_3)$, in the hexagonal structure-cell of benstonite. In the space groups $R\,3$ and $R\,\bar{3}$ this cell content implies for a structure similar to calcite that three cations and three carbonate groups have to be located at unique threefold positions. In the space group $R\,\bar{3}$ these have the point symmetry $\bar{3}$. Since this is incompatible with the shape of the carbonate group, $R\bar{3}$ is ruled out. In the space group $R3$ the three unique cations and anions are on positions (a) 0, 0, z with $z=0$ and $z\sim 1/2$, respectively. The remaining 36 cations and 36 anions must be distributed to 4 general ninefold positions each, with $z\sim 0$ and $z\sim 1/2$ respectively. The available positions in one cation-layer as well as the pseudo-cell relation are sketched in Fig. 1. For a carbonate with two different cations the following formulae can be expected: $X_1Y_{12}(CO_3)_{13}$, $X_3Y_{10}(CO_3)_{13}$, $X_4Y_9(CO_3)_{13}$

TABLE 3. POSSIBLE PARAMETERS OF CATIONS IN A RIGHT-HANDED SUPERSTRUCTURE OF BENSTONITE TYPE

	$x'\ y'\ z'$ calcite-cell	$x \quad y \quad z^1$	Model 1	Model 2	Model 3	Model 4
		Benstonite-cell				
3 Ca_I^2	0, 0, 0	0, 0, 0	3 Ca_I^2	3Ca_I^2	3 Ca_I^2	3Ca_I^2
9R_{II}	1, 0, 0	4/13, 1/13, 0	9 Ba_I	9 Ca_{II}	9Ca_{II}	9 Ca_{II}
9R_{III}	1, 1, 0	3/13, 4/13, 0	9 Ba_{II}	9 Ba_I	9 Ca_{III}	9 Ba_I
9R_{IV}	2, 0, 0	8/13, 2/13, 0	9 Ca_{II}	9 Ba_{II}	9 Ba_I	9 Ca_{III}
9 R_V	1, 2, 0	2/13, 7/13, 0	9 Ca_{III}	9 Ca_{III}	9 Ba_{II}	9 Ba_{II}

[1] All positions have been expanded by the symmetry elements of $R3$.

[2] Or Mg for $MgCa_6Ba_6(CO_3)_{13}$.

and $X_7Y_6(CO_3)_{13}$. Of these, $Ca_7Ba_6(CO_3)_{13}$ agrees very closely with the chemical analysis (see below).

Four different arrangements (models) are possible for one enantiomorphic form. They are listed in Table 3 for a right-handed crystal. The carbonate groups will be on analogous positions with $z \sim 1/2$. No prediction can be made regarding their orientations, which must be different from those in calcite on account of the difference in the c-spacings. A detailed structure analysis will have to decide between the possible arrangements of the cations and determine the configuration of the carbonate groups.

CHEMICAL COMPOSITION

Selected cleavage fragments were tested for uniform fluorescence to insure the absence of barite and quartz. About 10 grams of powder were obtained for analysis by wet chemical methods. When this was examined by x-ray diffraction an additional line at 3.03 Å with an intensity like the medium-weak lines of benstonite appeared. Since this line is absent in the other powder diagrams prepared of benstonite it had to be assigned to the strongest reflection of calcite. This mineral accompanies benstonite and may be intimately intergrown as was seen during the optical study. In a float test with bromoform no weighable amount of calcite could be separated. Some excess of calcium carbonate is, however, to be expected in the chemical analysis.

Samples of one half to one gram were used for every determination or separation. After decomposition with hydrochloric acid, carbon dioxide was absorbed by soda lime and weighed. Barium was separated and weighed as barium chromate, precipitated from the acidic, acetate buffered solution. Calcium and strontium were determined together as

Table 4. Chemical Analysis of Benstonite Material
Analyst: F. Lippmann

	Wt. %	$\frac{\text{Wt. \% } 10^4}{\text{Mol. wt.}}$		Wt. %[1]
BaO	43.05	2807	$BaCO_3$	55.40
SrO	4.02	388	$SrCO_3$	5.73
CaO	19.52	3481	$CaCO_3$	34.84
MgO	1.69	419	$MgCO_3$	3.53
MnO	0.35	49	$MnCO_3$	0.57
Sum of cations		7144		100.07
CO_2	31.35	7123		
Total	99.98			

[1] Calculated from cation oxides.

oxalates. In one instance both were precipitated as carbonates. These were dissolved in nitric acid, and from the dried nitrates calcium nitrate was extracted with a mixture of ether and alcohol. A value of 4.02% SrO was obtained in this way. This value agrees satisfactorily with the 3.80% SrO determined by *x*-ray fluorescence on the whole mineral with bromine (KBr) as an internal standard.

Magnesium and manganese were each determined on separate samples. In the magnesium determination, manganese was first removed with ammonia and bromine. Then barium, strontium and part of the calcium were precipitated as sulfates. The remaining calcium was removed as oxalate. From the final filtrate magnesium was precipitated as magnesium ammonium phosphate. Before the manganese could be oxidized to permanganate by persulfate for the colorimetric determination, barium, strontium and most of the calcium had to be removed as sulfates from the nitric acid solution.

There was no weighable insoluble residue. No lead and no iron were found with the usual wet chemical tests.

The results of the chemical analysis are given in Table 4. The values are averages of closely agreeing duplicates, except for SrO. Here the wet chemical value is tabulated because it was deemed more consistent with the other wet chemical data. There is only a slight excess of the cations over carbon dioxide as is evident from the quotients of weight percentages over molecular weights. Consequently, carbonate weight percentages calculated from the cation oxides and adjusted to 100% were used for the computation of the chemical formula presented in Table 5.

TABLE 5. CALCULATION OF THE FORMULA FOR BENSTONITE

	Wt. %[1]		$\frac{\text{Wt. \% } 10^4}{\text{Mol. wt.}}$		$\frac{\text{Wt. \% } 10^4}{\text{Mol. wt. } 532}$		Mol. %
$BaCO_3$	55.37		2805	3192 : 6=532	5.273	:6=0.879	40.56
$SrCO_3$	5.72		387		0.727	:6=0.121	5.59
					6,000		
$MgCO_3$	3.53		419	3947 : 7=564	0.788	:7=0.113	6.06
$MnCO_3$	0.57		50		0.094	:7=0.013	0.72
combined	$CaCO_3$	32.58	3255	3724=7 · 532	6.118	:7=0.874	47.07
free	$CaCO_3$	2.23[2]	223	223	7,000		
$CaCO_3$	34.81	34.81	3478				
Sum	100.00		7139−233=6919				

[1] From last column of Table 4 adjusted to 100%.

[2] The figures in the box were entered at a later stage of calculation.

Formula:

$$Ca_{6.118}Mg_{0.788}Mn_{0.094}Ba_{5.273}Sr_{0.727}(CO_3)_{13}$$

or

$$(Ca_{0.874}Mg_{0.113}Mn_{0.013})_7(Ba_{0.879}Sr_{0.121})_6(CO_3)_{13}$$

Average molecular weight of RCO_3: 141.35; 39(RCO_3) per hexagonal unit cell V = 2509 Å^3; G(calc.) = 3.648.

38.44 (RCO_3) per unit cell (5.91 (RCO_3) per "calcite-cell") for experimental density 3.596.

In all attempts to calculate a formula for benstonite from the chemical analysis, the large cations Ba and Sr and the smaller ones Ca, Mg, and Mn were combined in two groups. The discovery that the analyzed powder contained a few per cent of calcite as a discrete phase had to be taken into account. No quantitative *x*-ray determination of the amount of calcite was attempted because of the complications to be expected from preferred orientation. Before the relation to the calcite structure was recognized, a formula of the type $XY(CO_3)_2$ was attempted in several variations. First, 5% of free calcite was subtracted for an approximate ratio 1:1 of the two groups of cations. This procedure, however, either yielded strongly deviating calculated densities or else improbably high (about 15%) or negative amounts of free calcite had to be presumed for 36 or for

42 carbonate molecules, respectively, per hexagonal unit cell. The cell content of 39 derived from the pseudo-cell relation necessitates unequal amounts of small and large cations. Their ratio is 7.42:6, without deduction of free calcite. For the ratio 7:6 demanded by the formula compatible with the unit cell and its symmetry, 2.23 weight % of $CaCO_3$ has to be subtracted from the analysis. The calculated amount of free calcite agrees with the relative intensity of 3.03 Å reflection. The resulting formula for benstonite is given under Table 5. The calculated density of 3.648 aggrees with the experimental one of 3.596, if the presence of the microscopical cavities and the possible contamination with calcite are taken into account. The sum (Mg+Mn) is high enough to permit conjecture about the concentration of these cations at the unique threefold positions of the unit cell. A structure analysis will reveal whether it is justified to write the formula

$$MgCa_6Ba_6(CO_3)_{13}$$

or in detail

$$(Mg_{0.788}Mn_{0.094}Ca_{0.118})Ca_6(Ba_{0.879}Sr_{0.121})_6(CO_3)_{13}.$$

MISCELLANEOUS OBSERVATIONS

When benstonite is crushed the odor of hydrogen sulfide is perceived. This compound must form part of the filling of the microscopic cavities. The presence of hydrogen sulfide in the voids of benstonite means that the mineral formed in a reducing environment, which was probably caused by the overlying bituminous Stanley shale. It is likely that the barium of the benstonite came from the bedded barite, a small part of which was dissolved in the reducing environment, whereas calcium and magnesium were introduced by percolating waters.

The red fluorescence of benstonite is probably due to its manganese content. This conclusion is suggested by the following experiments: Benstonite is dissolved in hydrochloric acid. If the cations are precipitated from the hot solution as a carbonate by addition of ammonia and ammonium carbonate, the carbonate obtained when exposed to *X*-rays fluoresces with the same color as benstonite. The intensity however is weaker. If the manganese is first removed by precipitation with ammonia and bromine and filtration, the carbonate precipitated from the filtrate does not fluoresce. No attempt was made to identify the nature of the precipitate. According to the experiments of Terada (1953) a rhombohedral mixed crystal of barium calcium carbonate should have formed. Therefore the above described experiments are not a direct proof that manganese causes red fluorescence in benstonite. They only show that manganese can make complex barium-calcium carbonates fluorescent.

Schulman *et al.* (1947)[1] have shown that red fluorescence in calcite requires the presence of manganese plus a second activator element such as lead, which might be present in benstonite, as a trace element. Otherwise barium could be the second activator. (See note, p. 598.)

Discussion

Two compounds of the formula $BaCa(CO_3)_2$ are known as minerals: barytocalcite, monoclinic, and alstonite, orthorhombic. The structure of barytocalcite was determined by Alm (1958). It is ordered with respect to Ba and Ca, these cations occupying discrete positions in the structure. Alstonite is very similar to aragonite and witherite both in morphology and lattice constants. It is not yet known whether alstonite is ordered with respect to Ba and Ca, but the weak additional layer lines observed by Gossner and Mussgnug (1930) on their rotation photographs may be taken as evidence in favor of a superstructure.

Rhombohedral mixed crystal carbonates of barium and calcium were synthesized by Terada (1952, 1953) with up to 55 mol % $BaCO_3$. They yielded *x*-ray powder patterns very much like those of calcite. Reflections $(hk \cdot l)$ with l odd were missing, if there were 20 or more mol % $BaCO_3$. This means that the lattice constant in the *c*-direction is about half that of calcite, just as in benstonite. Apparently the presence of enough Ba changes the articulation of the CO_3-groups in calcite-type carbonates. For the composition of 40 mol % $BaCO_3$ and 60 mol % $CaCO_3$, which compares most closely to benstonite, $a = 5.06$ Å and $2c = 17.69$ Å are calculated from the rhombohedral data of Terada. The *a*-value is slightly smaller and the 2*c*-value is higher than for the "calcite-cell" of benstonite ($a' = 5.07$ Å, $2c = 17.34$ Å). The cell volume $V = 390$ Å^3 is identical with that of the "calcite-cell" of benstonite $V' = 386$ Å^3 within the limit of error.

If compared with the barium-calcium carbonates of Terada, benstonite has a superstructure. One cause for the ordering of the cations in benstonite may be its slow rate of formation. If, however, it turns out that the Mg-ions in benstonite occupy the special equipoints 0, 0, 0 of the hexagonal cell, so that the formula is $MgCa_6Ba_6(CO_3)_{13}$, it is more likely that the presence of magnesium is responsible for the formation of the superstructure. The intervention of magnesium could be the reason why benstonite occurs at all, if one considers the existence of the other barium calcium carbonates which do not seem to contain appreciable amounts of magnesium according to the analyses reported in the literature.

Whereas dolomite, $CaMg(CO_3)_2$, and perhaps norsethite $BaMg(CO_3)_2$

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[1] Dr. Michael Fleischer kindly directed the author's attention to this article.

(Mrose *et al.* 1961), are superstructures derived from the calcite configuration by the distribution of the different cations into alternating cation layers, the superstructure of benstonite is formed by the ordering of the cations within the layers. This is accompanied by a different articulation of the CO_3-groups as is evident from the *c*-value which is about half that of calcite. Another example of a rhombohedral carbonate structure with about half the *c*-value (7.82 Å) of calcite and with ordering of the cations within the cation layers is huntite $Mg_3Ca(CO_3)_4$ (Graf and Bradley, 1962).

It is interesting to note that complex calcite-type carbonates, such as the mix-crystals of Terada, norsethite, and benstonite, exist with a cation as large as barium. This does not agree with the current explanation that the crystallization of $CaCO_3$ in the form of aragonite is favored or even stabilized by the presence of small amounts of large cations, *e.g.* strontium. A different mechanism must be active in most cases where $CaCO_3$ crystallizes as aragonite in nature (see *e.g.* Lippmann, 1960 and Heinrich and Levinson, 1961, p. 1442).

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REFERENCES

ALM, KNUT F. (1958), The crystal structure of barytocalcite $BaCa(CO_3)_2$. *Arkiv Mineral. Geol.*, **2**, 399–410.

FRYKLUND, VERNE C., JR. AND DREW F. HOLBROOK (1950), Titanium ore deposits of Hot Springs County, Arkansas. *Ark. Res. Devel. Comm. Divis. Geol., Bull.* **16.**

GOLDSMITH, J. R. AND D. L. GRAF (1958), Relation between lattice constants and composition of the Ca-Mg carbonates. *Am. Mineral.*, **43,** 84–101.

GOSSNER, B. AND F. MUSSGNUG (1930), Über Alstonit und Milarit. Ein Beitrag zur Kenntnis komplex gebauter Kristalle. *Cent. Mineral.*, A 1930, 220–238.

GRAF, D. L. AND W. F. BRADLEY (1962), The crystal structure of huntite $Mg_3Ca(CO_3)_4$. *Acta Cryst.*, **15,** 238–242.

HEINRICH, E. WM. AND A. A. LEVINSON (1961), Carbonatic niobium—rare earth deposits, Ravalli County, Montana. *Am. Mineral.*, **46,** 1424–1447.

LIPPMANN, F. (1960), Versuche zur Aufklärung der Bildungsbedingungen von Calcit und Aragonit. *Fort. Mineral.*, **38,** 156–161.

——— (1961A), Über ein Barium-Calciumkarbonat aus Hot Springs County, Arkansas (abs.). *Fort. Mineral.*, **39,** 81.

——— (1961B), Benstonit, $Ca_7Ba_6(CO_3)_3$, ein neues Mineral. *Die Naturwissenschaften*, **48,** 550–551.

MROSE, M. E., E. C. T. CHAO, J. J. FAHEY AND C. MILTON (1961), Norsethite, BaMg $(CO_3)_2$, a new mineral from the Green River Formation, Wyoming. *Am. Mineral.*, **46,** 420–429.

PALACHE, C., H. BERMAN, AND C. FRONDEL (1951), Dana's System of Mineralogy Vol. II(7th): New York, John Wiley & Sons, New York.

PARKS, BRYAN AND G. C. BRANNER (1933), A barite deposit in Hot Springs County, Arkansas. *Ark. Geol. Survey, Inf. Circ.* **1.**

SCHULMAN, J. H., L. W. EVANS, R. J. GINTHER, AND K. J. MURATA (1947), The sensitized luminescence of manganese-activated calcite. *Jour. Applied Physics*, **18,** 732–739.

SWANSON, H. E. AND R. K. FUYAT (1953), Standard *x*-ray powder patterns. *U. S. Nat. Bur. Stand., Circ.* **539,** 51–54.

TERADA, JITSUO (1952), Rhombohedral crystals of Ba-Ca and Sr-Ca double carbonates. *Jour. Phys. Soc. Japan*, **7,** 432–434.

——— (1953), Crystal structure of the Ba, Sr and Ca triple carbonate. *Jour. Phys. Soc. Japan*, **8,** 158–164.

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Note added in proof: Prof. K. H. Wedepohl, Göttingen, kindly ran a spectrographic analysis for lead on the same material which was used for the chemical analysis of benstonite. The line of Pb at 2833 Å, which should still be visible at a concentration of as low as 5 ppm of Pb could not be detected. The benstonite therefore contains less than 5 ppm of lead. This renders more likely the explanation that barium is the second activator (besides manganese), as is perhaps also the case in bariumcyanoplatinate, where obviously barium and platinum act together.