

MINERALOGICAL STUDY OF AN UNNAMED BARIUM CALCIUM CARBONATE
FROM THE CAVE-IN-ROCK DISTRICT, ILLINOIS

Project 680023

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Abstract

A new mineral, nearly identical to alstonite, was discovered by X-ray powder diffraction methods in three samples which originated from the Cave-in-Rock district, Illinois, U.S.A. It occurs as colourless euhedral crystals about 1 mm long which display {221} pyramidal habit and a vitreous lustre. The hardness is between 4 and 4 1/2. It fluoresces pale to bright orange, and effervesces in dilute HCl. The symmetry is hexagonal, space group choices are P312, P321, P3m1, P31m, P31m or P3m1; refined unit cell parameters are $a=8.692(3) \text{ \AA}$, $c=6.148(4) \text{ \AA}$, $V=402.24 \text{ \AA}^3$. The strongest lines (\AA) of the X-ray powder diffraction pattern are 3.550 (100)(111), 2.510 (67)(300), 2.048 (21)(221), 6.15 (18)(001), 1.943 (18)(302), and 1.853 (15)(113). Microprobe analysis (averaged) gave BaO 45.6, CaO 18.8, SrO 5.2, CO₂ (calc.) 30.0 wt.%, corresponding to Ba_{0.8722}, Ca_{0.9832}, Sr_{0.1473} (CO₃)₂ or ideally Ba Ca (CO₃)₂. The number of formula weights per unit cell (Z) is 3 and the calculated density (D_x) is 3.62. Optically, it is uniaxial negative with $n_e=1.527(3)$ and $n_o=1.672(3)$. Pertinent data on alstonite are also reported, particularly those data useful in distinguishing between the two minerals. The crystallographic relationship suggests that they belong to a family of OD (order-disorder) structures of general composition Ba Ca (CO₃)₂.

Introduction

During an extensive study of alstonite (Roberts, 1976), a mineral was found that could not be identified by its X-ray powder diffraction pattern. The data reported here are results from a mineralogical study of the mineral and are compared to alstonite.

Locality and Specimen Description

The unnamed mineral, referred to as BA-1 in this report and in Roberts (1976), has been encountered in three samples, all labelled "Cave-in-Rock district, Illinois, U.S.A.". The specific locality is uncertain, but the specimens probably originated from the Minerva #1 Mine.

The largest specimen, measuring 11 by 10 by 5 cm, consists of centimetre-sized scalenohedra of yellow calcite protruding from a matrix of massive to globular barite. BA-1 coats the globular barite as thin layers of colourless, hexagonal pyramids. Associated phases include drusy aggregates of grey alstonite, traces of purple fluorite and dark brown sphalerite. The other two specimens consist entirely of numerous crystal fragments of BA-1 without matrix.

Morphological, Physical and Optical Properties

BA-1 occurs as euhedral crystals, not exceeding 1 mm in length, with an approximate length to width ratio of 2:1. The crystals are hexagonal and display {221} pyramidal habit. Hexagonal dipyramids have been observed but are rare. The faces are heavily striated normal to the axis of elongation (c-axis) and are divided parallel to the c-axis by a medial, irregular, slightly reentrant "suture".

The crystals are colourless to smoky white, grading to grey-white in masses, and have a vitreous lustre. The streak is white; the hardness is between 4 and 4 1/2; the fluorescence varies from pale to bright orange under long wave ultraviolet light; and the effervescence is quite vigorous in dilute HCl.

The optical characterization of BA-1 is as follows: colourless in transmitted light, uniaxial negative with $n_e=1.527(3)$ and $n_o=1.672(3)$.

Crystallography

Pyramids of BA-1 were crushed, and selected fragments checked for multiple reflections using the precession camera. Untwinned chips were subsequently run on precession and Weissenberg cameras by utilizing both Zr-filtered Mo radiation ($\lambda\text{MoK}\alpha=0.7107 \text{ \AA}$) and Ni-filtered Cu radiation ($\lambda\text{CuK}\alpha=1.5418 \text{ \AA}$).

Single crystal photographs indicate that the symmetry of BA-1 is hexagonal with measured cell parameters $a=8.68 \text{ \AA}$ and $c=6.14 \text{ \AA}$. The hk0 level photographs display 6 mm symmetry, whereas hk1 and hk2 level photographs show three fold symmetry with a mirror plane coincident with a*. This implies that six space group choices are possible: P312 (149), P321 (150), P3m1 (156), P31m (157), P31m (162), and P3m1 (164). Least squares refinement of the approximate cell parameters yielded $a=8.692(3) \text{ \AA}$ and $c=6.148(4) \text{ \AA}$, with a computed cell volume of 402.24 \AA^3 . A fully indexed powder diffraction pattern is presented in Table 10.1.

Twinning

Complete pyramids of BA-1 are twinned, as shown on single crystal films. The "a" cell parameter is doubled to approximately 17.40 \AA by the presence of medium to weak supercell reflections and the hexagonal 6 mm symmetry is retained throughout the zero and upper levels. These diffraction phenomena due to twinning are not unexpected since the twin condition for hexagonal crystals states that $a^2:c^2$ must approach a rational number and the calculated ratio for BA-1, 1.997:1.000 fulfills this requirement perfectly.

Chemical Composition

Colourless pyramidal aggregates of BA-1 were hand-picked under a 50X binocular microscope, mounted in a polished section and submitted for electron microprobe analysis. Because preliminary energy dispersive spectra indicated the presence of major amounts of Ba and Ca and minor amounts of Sr, quantitative determinations for these elements were carried out with a MAC electron microprobe, using benitoite (Ba), calcite (Ca) and strontianite (Sr) as standards. Sample degradation was minimized by operating

Table 10.1
Powder diffraction data for unnamed BaCa(CO₃)₂*

I/Io	2θ meas.	dÅ meas.	dÅ calc.	hkl
2	11.79	7.51	7.53	100
18	14.39	6.15	6.15	001
3	18.64	4.76	4.76	101
11	20.41	4.35	4.35	110
100	25.08	3.550	3.549	111
2	27.83	3.206	3.210	201
3	29.03	3.076	3.074	002
11	31.38	2.851	2.846	102
5	34.75	2.581	2.582	211
67	35.71	2.510	2.509	300
1	37.97	2.370	2.381	202
6	38.77	2.323	2.323	301
9	41.52	2.175	2.173	220
8	43.39	2.085	2.088	310
21	44.22	2.048	2.049	221
3	45.96	1.975	1.977	311
18	46.74	1.943	1.944	302
15	49.16	1.853	1.853	113
1	50.76	1.799	1.799	401
3	51.56	1.773	1.774	222
2	53.01	1.727	1.727	320
2	55.23	1.663	1.663	321
2	55.98	1.643	1.643	410
2	57.43	1.605	1.605	402
11	58.13	1.587	1.587	411
1	60.25	1.536	1.537	004
1	61.60	1.506	1.506	104
6	62.30	1.490	1.491	223
2	63.60	1.463	1.463	501
9	64.35	1.448	1.449	330
2	65.65	1.422	1.422	420
2	66.30	1.410	1.410	331
1	67.62	1.385	1.386	403
1	69.55	1.352	1.352	510
2	71.37	1.321	{ 1.321	323
			{ 1.320	511
8	72.04	1.311	{ 1.311	304
			{ 1.310	332
1	73.22	1.293	1.291	422
6	73.94	1.282	1.282	413
11	75.77	1.255	1.255	600
3	76.96	1.239	{ 1.238	512
			{ 1.238	430
2	77.64	1.230	1.230	005
2	78.79	1.215	{ 1.213	503
			{ 1.213	431

*—114.6 mm Debye-Scherrer camera; Ni filtered Cu Kα radiation;
—line intensities calculated from diffractometer trace;
—indexed with a=8.692 Å, c=6.148 Å;
—film No. 48934 corrected for film shrinkage.

Table 10.2
Comparison of unnamed BaCa(CO₃)₂ and alstonite powder patterns

Unnamed BaCa(CO ₃) ₂ Cave-in-Rock, Ill. (This Study)		Alstonite (ROM-M4872) Northumberland, England (Roberts, 1976)	
I/Io	dÅ meas.	I/Io	dÅ meas.
2	7.51		
18	6.15	1	6.12
		7	5.65
		1	4.99
3	4.76		
11	4.35	4	4.35
		1	4.17
		1	3.88
100	3.550	100	3.549
		5	3.461
2	3.206		
3	3.076	6	3.057
11	2.851	8	2.835
		3	2.687
5	2.581	3	2.583
67	2.510	46	2.509
		10	2.499
1	2.370	1	2.375
6	2.323		
		3	2.290
9	2.175	7	2.178
		4	2.155
8	2.085		
21	2.048	26	2.052
		1	2.024
3	1.975	1	1.975
18	1.943	25	1.943
		1	1.900
15	1.853	19	1.846
1	1.799		
3	1.773	2	1.772
2	1.727		
2	1.663	1	1.665
2	1.643	2	1.643
2	1.605		
11	1.587	8	1.590
1	1.536	2	1.530
1	1.506		
6	1.490	3	1.489
2	1.463		
9	1.448	5	1.450
2	1.422		
2	1.410		
1	1.385		
1	1.352		
2	1.321		
8	1.311	6	1.311
1	1.293		
6	1.282	4	1.283
11	1.255	3	1.259
3	1.239		
2	1.230		
2	1.215		
		2	1.188

Table 10.3
Chemical composition of unnamed BaCa(CO₃)₂ and alstonite

Unnamed BaCa(CO ₃) ₂ Cave-in-Rock, Illinois (This Study)			Alstonite (ROM-M4872) Northumberland, England (Roberts, 1976)						
	wt. %	molecular ratio		wt. %	molecular ratio				
BaO	45.6	0.2985	}	BaO	47.0	0.3093	}		
CaO	18.8	0.3365		0.6854	CaO	20.2		0.3634	0.6902
SrO	5.2	0.0504			SrO	1.8		0.0175	
CO ₂	30.0	0.6844		CO ₂	30.1	0.6901			
Total	99.6			Total	99.1				
Specific Composition*: Ba _{0.872} Ca _{0.983} Sr _{0.147} (CO ₃) ₂ Molecular Weight: 292.14 Z: 3 Dx: 3.62 g/cc			Specific Composition*: Ba _{0.896} Ca _{1.053} Sr _{0.031} (CO ₃) ₂ Molecular Weight: 289.90 Z: 12 Dx: 3.60 g/cc						
*Calculated assuming 6 oxygen atoms per formula unit cell.									

Table 10.4
Crystallographic parameters for unnamed BaCa(CO₃)₂ and alstonite

	Unnamed BaCa(CO ₃) ₂ (This Study)	Alstonite (ROM-M4872) (Roberts, 1976)	Alstonite (Sartori, 1975)
SYMMETRY	Hexagonal	Triclinic	Triclinic
SPACE GROUP	P312, P321, P3ml, P3lm, P3̄lm or P3̄ml	P1 or PT	CI or CT
CELL PARAMETERS	a = 8.692 (3) Å c = 6.148 (4) Å V = 402.24 Å ³	a = 17.38 Å b = 17.40 Å c = 6.123 Å α ≈ 90° β ≈ 90° γ ≈ 120° V = 1603.55 Å ³	a = 30.14 Å b = 17.40 Å c = 6.12 Å α = 90° β = 90° γ = 90° V = 3209.55 Å ³
NUMBER OF FORMULA WEIGHTS PER UNIT CELL	Z = 3	Z = 12	Z = 24

at 20 KV with a sample current of 0.03 micro-amperes and using a beam of 20 microns diameter. Data were recorded at 20 spots within two areas, then averaged and corrected for matrix effects using an updated and modified version of a computer program written by Rucklidge and Gasparrini (1969).

This particular sample was apparently homogeneous and contained traces of Fe, Mn and Mg, but all were less than 0.05 per cent. A chemical analysis by the Penfield method indicated the complete absence of water, thus CO₂ was calculated to satisfy the values for stoichiometric BaCO₃, CaCO₃ and SrCO₃.

The averaged analysis was as follows: BaO 45.6, CaO 18.8, SrO 5.2, CO₂ 30.0 wt.%. Calculated on the basis of 6 oxygen atoms this yields the following formula: Ba_{0.8722}, Ca_{0.9832}, Sr_{0.1473} (CO₃)₂ or ideally BaCa(CO₃)₂. The Sr

substitutes for both Ba and Ca, and apparently is non-essential to the stability of the structure.

The computed molecular weight (292.14) and volume (402.24 Å³), coupled with the measured specific gravity (D_m = 3.75 g/cc) dictated that there be 3 formula weights per unit cell. The calculated density (D_x) with Z=3 is 3.62 g/cc.

This discrepancy between calculated and measured densities is unsatisfactory and must be attributed to barite impurities present in the hand-picked samples submitted to Berman balance density measurements. There are two reasons for this contention:

- 1) Quantitative energy dispersive analysis of the pyramidal clusters submitted for microprobe analysis clearly indicated several zones adjacent to the unnamed carbonate for which only Ba and S spectra were observed.

- 2) Debye-Scherrer powder diffraction patterns of several optically homogeneous pyramids revealed several medium to weak lines with d-spacings corresponding to the stronger reflections of barite.

Comparison with Alstonite

Alstonite is an anhydrous barium, calcium carbonate which has recently been independently re-examined by Sartori (1975) and by Roberts (1976). Both studies clearly established the true symmetry as triclinic, even though the single crystal patterns displayed special types of non-space group absences as well as several pseudo-symmetrical crystallographic cells. To account for these peculiarities, Sartori (1975) suggested that alstonite belongs to a family of OD (order-disorder) structures of which it is an ordered member. Roberts (1976) noted the crystallographic and chemical similarities that exist between alstonite and BA-1, and proposed that they be considered as polymorphs of $\text{BaCa}(\text{CO}_3)_2$.

The chemical results summarized in Table 10.3 indicate that the specific compositions, molecular weights, and calculated densities are very nearly identical. Whether the excess strontium in BA-1 is characteristic is unknown, owing to the limited number of specimens available for study. Nevertheless, the chemical identity of the two phases is clearly evident.

Because alstonite and BA-1 are morphologically and physically indistinguishable (Roberts, 1976) as well as being chemically analogous, sophisticated methods such as optical microscopy, X-ray powder diffraction and X-ray single crystal are necessary to reliably distinguish one from the other. Optically, alstonite is biaxial negative with a 2V of 7° , whereas BA-1 is uniaxial negative; hence they are distinguishable if a favourable orientation is available. Routine identification by X-ray powder diffraction may be accomplished by using two simple criteria:

- 1) intensity variation of the 001 reflection at or near 6.12 \AA (strong for BA-1, weak to absent for alstonite);
- 2) identification of a diffraction line at 5.6 \AA (medium to medium weak for alstonite, completely absent for BA-1).

A comparative listing of all front reflection d-spacings are given in Table 10.2. Note that many of the stronger reflections are common to both patterns, suggesting a structural resemblance, especially for the heavier atoms. Nevertheless, structural uniqueness is obvious when all the d-spacings are taken into account.

This structural affinity is similarly pronounced in selected single crystal photographs. The most intense diffraction nodes on hko photographs, related to the barium and calcium atoms, are identical in distribution and intensity for both phases. Only when the weaker nodes, representative of the carbonate groups, are taken into account does the structural divergence become readily apparent. The unit cell parameters, summarized in Table 10.4, may be correlated as follows:

$$\begin{aligned} a \text{ \AA BA-1} &\approx 1/2 a \text{ \AA alstonite (Roberts, 1976)} \\ b \text{ \AA BA-1} &\approx 1/2 b \text{ \AA alstonite} \\ c \text{ \AA BA-1} &\approx c \text{ \AA alstonite} \\ V \text{ \AA BA-1} &\approx 1/4 V \text{ \AA alstonite} \end{aligned}$$

Sartori (1975) proposed that alstonite, which displays triclinic symmetry, is an ordered member of a family of OD structures with general composition $\text{BaCa}(\text{CO}_3)_2$. From the foregoing discussion, it seems reasonable to include BA-1, which displays hexagonal symmetry, within the same group as a disordered member. Confirmation of this hypothesis must await detailed crystal structure determinations of both minerals.

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