

The Crystal Structure of $\text{BaCa}(\text{CO}_3)_2$ (barytocalcite)

B. Dickens and J. S. Bowen*

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

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The barytocalcite phase of $\text{BaCa}(\text{CO}_3)_2$ crystallizes in the monoclinic unit cell $a=8.092(1)$ Å, $b=5.2344(6)$ Å, $c=6.544(1)$ Å, $\beta=106.05(1)^\circ$ at 25°C with cell contents of $2[\text{BaCa}(\text{CO}_3)_2]$. The structure previously reported by Alm is correct in its coarse details but has been redetermined here and refined to $R_w=0.028$, $R=0.023$ in space-group $\text{P}2_1/\text{m}$ using 1652 observed reflections. Corrections were made for absorption, isotropic extinction, and anomalous dispersion.

The structure of barytocalcite has an . . . ABCABC . . . stacking of cation layers and repeat every 3 layers. The calcite phase of CaCO_3 has an ABC cation layer sequence and repeats every 6 layers. The orientations of the CO_3 groups in barytocalcite are like the CO_3 group orientation in the aragonite phase of CaCO_3 , and are rotated about 30° from the CO_3 group orientation in calcite. The cation layer sequence in aragonite is . . . ABAB . . . and the structure repeats every 2 layers.

The Ca ion in barytocalcite is coordinated to seven oxygens, including an edge of a CO_3 group, with Ca . . . O distances in the range 2.305(2) Å to 2.518(2) Å. The Ba ion is coordinated to five edges and one apex of the CO_3 groups with Ba . . . O distances ranging from 2.729(3) Å to 3.140(2) Å. The distances of the C atoms in the CO_3 groups from the planes of the O atoms are 0.025(5) Å and 0.022(4) Å for C(1) and C(2), respectively.

Key words: Aragonite; barium calcium carbonate; calcium carbonate; crystal structure; single crystal x-ray diffraction.

1. Introduction

The crystal structure of the barytocalcite phase of $\text{BaCa}(\text{CO}_3)_2$ has been redetermined in our program of structural investigations [1]¹ on calcium carbonates, calcium phosphates, associated hydrates, and related compounds. The structural features in these compounds have important applications in understanding possible epitaxy, syntaxy, and substitutional solid solution in biological minerals such as hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) and calcite, aragonite and vaterite, the three phase of anhydrous CaCO_3 .

From a consideration of the morphologies, d -spacings and possible space-groups of barytocalcite and calcite, Gossner and Mussgnug [2] gave a structure for barytocalcite which is a rearrangement of the calcite structure. They assumed the space-group to be $\text{P}2_1$. Alm [3] used a relatively large (0.3 mm) single crystal of barytocalcite and unfiltered Cu radiation to collect photographic data from the $h0l$, $h1l$, $hk0$ and hkh levels. He also assumed the space-group to be $\text{P}2_1$, rather than $\text{P}2_1/\text{m}$, on steric considerations which are invalid. The structure he gave for barytocalcite differs from that given by Gossner and Mussgnug in the orientations of the CO_3 groups. However, Alm made no corrections for what must have been considerable absorption, gave no

standard deviations on any parameters and used limited film data. The structure of barytocalcite was, therefore, poorly known by modern standards, and has been redetermined here.

2. Data Collection and Structure Refinement

The crystal used in the data collection is an approximate sphere, radius 0.094(3) mm, ground from a crystal from mineral sample R13868 (from Cumberland, England) obtained from the National Museum of Natural History, Smithsonian Institution, Washington, D.C., and supplied by J. S. White, Jr. It was mounted in our usual way [4].

formula (ideal): $\text{BaCa}(\text{CO}_3)_2$ (barytocalcite phase).
cell: monoclinic
 $a=8.092(1)$ Å at 25°C
 $b=5.2344(6)$ Å
 $c=6.544(1)$ Å
 $\beta=106.05(1)^\circ$
volume = 266.4 Å³
space-group $\text{P}2_1/\text{m}$; cell contents $2[\text{BaCa}(\text{CO}_3)_2]$
reciprocal lattice extinctions, $0k0:k=2n+1$
calculated density 3.72 g·cm⁻³; observed density 3.71 g·cm⁻³ [5].

*Research Associate of the American Dental Association at the National Bureau of Standards, Washington, D.C. 20234.

¹ Figures in brackets indicate the literature references at the end of this paper.

In the determination of the unit cell and in the collection and processing of data, the general procedure

in reference [4] was followed. In the present case, 3379 reflections were collected from the $\pm h+k+l$ and $\pm h-k+l$ quadrants and merged into a unique set of 1772, of which 1652 are "observed" and 120 are "unobserved." The R factor

$$\sum_{hkl} |F_{hkl}^i - F_{hkl}^j| / \sum F_{hkl}^i$$

with $i < j$ between pairs F_{hkl}^i and F_{hkl}^j of observed equivalent reflections F_{hkl} was 0.018 calculated over 1189 pairs. i and j are the sequence numbers in the list of equivalent reflections. Absorption corrections for a sphere with $\mu = 85.6 \text{ cm}^{-1}$ were applied. The maximum and minimum transmission factors were 0.347 and 0.317, respectively.

The $\theta - 2\theta$ scans were carried out on an automated Picker² diffractometer at $2^\circ/\text{min}$ for 2θ ; backgrounds were counted for 20 s each. Because the least significant digit in all counts was dropped by the Picker hardware, standard deviations, σ_{hkl} , of the structure factors, F_{hkl} , were estimated from $\sigma_{hkl} = F_{hkl}/5.7$ for $F_{hkl} < 5.7$; $\sigma_{hkl} = 1$ for $5.7 < F_{hkl} < 30$; and $\sigma_{hkl} = F_{hkl}/30$ for $F_{hkl} > 30$ where F_{max} on this arbitrary scale is 113. The scattering factors used were those for the neutral atoms in reference 6 for the x-ray 67 refinements and those in references 7 and 8 for the extinction and anomalous dispersion refinements.

The quasi-normalized structure factor statistics on our barytocalcite data indicate that the structure is acentric, since $\langle |E| \rangle = 0.885$, $\langle E^2 \rangle = 1.00$ (fixed), $\langle |E^2 - 1| \rangle = 0.709$; the corresponding theoretical values are 0.886, 1.000, 0.736 for the acentric case and 0.798, 1.000, 0.968 for the centric case. E is the quasi-normalized structure factor [9]. The fraction of E values greater than 1.0, 2.0 and 3.0, respectively, was found to be 0.405, 0.0027 and 0.0000; the corresponding theoretical values are 0.368, 0.0183, 0.0001 for the acentric case and 0.317, 0.0455, 0.0027 for the centric case. The statistical procedure suggested an average temperature factor, B , of about 2.5 \AA^2 and an exponent of 1.00 for $\sin \theta/\lambda$. Our experience has been that the quasi-normalized structure factor statistics are normally much closer to the theoretical values and the exponent of $\sin \theta/\lambda$ is closer to 2.00 than was calculated here for barytocalcite.

Because of the presence of the strongly scattering Ba ions, this indication that the space-group is the acentric $P2_1$ was not considered to be reliable. The structure of barytocalcite was redetermined by us from a sharpened Patterson function calculated with $(E^2 - 1)$ coefficients and an F_0 Fourier electron density synthesis phased from the positions of the Ba and Ca ions. The y coordinate of Ba was set equal to zero to define the origin along b . The structure was refined isotropically in space-group $P2_1$ to $R_w = 0.65$, $R = 0.057$ and then anisotropically in $P2_1$ to $R_w = 0.036$, $R = 0.028$ using the x-ray 67 system of computing programs [10]. The least-squares refinements used the full matrix,

minimized $\sum w(|F_0| - |F_c|)^2$, and included those unobserved reflections for which F_{hkl} calculated more than $2\sigma(F_{hkl})$.

The highest peak in an electron density difference synthesis calculated after anisotropic refinement was equivalent to about 1/3 of an electron and was 0.49 \AA from Ba. When the space-group is assumed to be $P2_1$ the largest correlation coefficients are 0.90 to 0.95 between (i) x of O(1) and x of O(2), (ii) z of O(1) and z of O(2), (iii) x of O(4) and x of O(5) and (iv) z of O(4) and z of O(5); 0.80 to 0.90 between (i) B_{11} of O(1) and B_{11} of O(2), (ii) B_{13} of O(4) and B_{13} of O(5), and (iii) B_{23} of O(4) and B_{23} of O(5). There are 48 correlation coefficients greater than 0.50.

The isotropic extinction parameter, r , where $F^2 = F_{\text{unc}}^2(1 + \beta r F_{\text{unc}}^2)$ and F_{unc} is the structure factor uncorrected for extinction, was then refined together with the structural and scale parameters using the least-squares program RFINE written by L. W. Finger of the Carnegie Institution of Washington; these refinements included only the observed reflections. The resulting R values were $R_w = 0.027$, $R = 0.022$. The structure obtained had essentially the symmetry $P2_1/m$; subsequent anisotropic refinement in $P2_1/m$ gave $R_w = 0.036$, $R = 0.028$ without extinction refinement and $R_w = 0.028$, $R = 0.025$ in refinements in which r refined to $0.000100(4) \text{ cm}$. All unconstrained parameters were varied. Finally, three cycles of refinement including corrections for anomalous dispersion and extinction gave $R_w = 0.028$, $R = 0.023$; r became $0.000100(5) \text{ cm}$. The largest change in the other parameters was an increase of $\sim 0.1 \text{ \AA}^2$ in all B_{ii} parameters of Ca. In the final cycle, the average shift/error was 0.02, and the standard deviation of an observation of unit weight, $[\sum w(F_0 - F_c)^2 / (1652 - 56)]^{1/2}$, was 0.43.

The final R_w values for the centric and acentric cases are near the limit of the experimental data. The weighting scheme is arbitrary, though reasonable. Further, there are large correlation coefficients in the acentric refinement. From the first two considerations, the authors feel that the ratio test [11] on $\sum w(F_0 - F_c)^2$, the numerator of the R_w term, is not really applicable in this border-line case, even though it appears from this test that refinement in the acentric $P2_1$ is to be preferred at a confidence level greater than 99.5 percent. Because refinement in the centric space-group $P2_1/m$ gives essentially the same result as refinement in $P2_1$ but has more restraints which remove the high correlation coefficients, the space-group of barytocalcite is assumed here to be $P2_1/m$. This is consistent with the symmetry of $2/m$ in the observed crystalline forms of the mineral [12]. With refinement in $P2_1/m$, the largest correlation coefficients were removed, and only six were greater than 0.50. The four largest were about 0.60 and were between the scale factor and the extinction parameter, and between the scale factor and B_{11} , B_{22} , and B_{33} of Ba.

Because Sr has been reported [13] in the alstonite phase of $\text{BaCa}(\text{CO}_3)_2$, a refinement of barytocalcite in which the cation positions were considered to be occupied by Sr^{2+} in solid solution was carried out using Finger's least-squares program. The occupan-

² Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified is necessarily the best available for the purpose.

TABLE 1. Atomic parameters for barytocalcite BaCa(CO₃)₂

Atoms	x	y	z	B ₁₁ *	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Ba	0.14740(3)	0.25	0.28824(3)	0.883(6)	0.646(6)	0.652(6)	0.399(4)
Ca	.62320(8)	.25	.19855(9)	.64(2)	.50(2)	.58(1)21(1)
C(1)	.8972(5)	.75	.2483(5)	.83(8)	.65(8)	.55(7)17(8)
O(1)	1.0057(4)	.75	.1393(4)	1.44(9)	1.31(9)	1.03(8)77(7)
O(2)	0.8457(3)	.9620(4)	.3089(3)	1.45(6)	0.85(6)	1.25(6)	0.50(5)	.45(6)	0.03(5)
C(2)	.6149(4)	.25	.7468(5)	0.68(8)	.74(8)	0.61(7)27(6)
O(3)	.6383(4)	.25	.5644(4)	2.4(1)	1.9(1)	.80(7)97(8)
O(4)	.6066(2)	.4604(4)	.8474(3)	1.29(6)	0.61(5)	1.00(6)	.16(4)	.52(4)	-.04(4)

Figures in parentheses are standard errors in the last significant figure quoted, and were computed in the final cycle of full-matrix least-squares refinements.

*Thermal parameters have the form $\exp[-1/4(a^*B_{11}h^2 + b^*B_{22}k^2 + c^*B_{33}l^2 + 2a^*b^*B_{12}hk + 2a^*c^*B_{13}hl + 2b^*c^*B_{23}kl)]$.

cies, 1.003(13) and 1.004(4), for Ba and Ca respectively, suggest that there is no solid solution of Sr ions in this sample of barytocalcite.

The atomic parameters from the final extinction refinement in space-group P2₁/m are given in table 1. The observed structure factors are given in table 2.

3. Description of the Structure

The structure of barytocalcite (fig. 1) consists of Ba . . . CO₃ chains and Ca . . . CO₃ chains, both parallel to [001], in which the cations are coordinated to an edge of one neighboring CO₃ group in the chain, and to an apex of the other CO₃ group. The C(2)O₃ group is in the CaCO₃ chain with its plane parallel to (100). The C(1)O₃ group is in the BaCO₃ chain, with its plane nearly parallel to (101), and is pushed out of the line of the chain because of the large ionic radius of the Ba ion. The chains lie in layers parallel to (210), a perfect cleavage in BaCa(CO₃)₂. The structure may also be considered to consist of layers of CO₃ groups coordinated to layers of cations, and is related in this way to the calcite [14] phase of CaCO₃, with (201) of barytocalcite corresponding to (001) of calcite.

3.1. The Barium Ion Environment

The Ba ion is coordinated (fig. 1, table 3) to 11 oxygen atoms with Ba . . . O distances less than 3.2 Å, i.e.,

in the normal range. These oxygens consist of 5 edges of CO₃ groups, O(2, 2¹), O(1¹, 2¹¹), O(1¹¹, 2¹¹¹), O(3, 4), O(3¹, 4¹) and one apex, O(1). The Ba ion is more extensively coordinated than it is in the witherite phase of BaCO₃, where it has a coordination of 9 oxygens. The structure of witherite resembles that of the aragonite phase of CaCO₃.

TABLE 3. Ba environment in barytocalcite, BaCa(CO₃)₂

Atoms	Distance, Å
Ba, O(1)	2.729(3)
Ba, O(4, 4 ¹)	2.833(2)
Ba, O(2, 2 ¹)	2.847(2)
Ba, O(2 ¹¹ , 2 ¹¹¹)	2.904(2)
Ba, O(1 ¹ , 1 ¹¹)	2.914(1)
Ba, O(3, 3 ¹)	3.140(2)
Ba, C(1)	3.152(3)
Ba, C(2)	3.294(2)

In all tables of interatomic distances and angles, the quantities in parentheses are standard errors in the last significant figure and were computed from the standard errors in the atomic positional parameters and in the cell parameters. They include contributions from the variance covariance matrix. The atom labels refer to atoms in figure 1.

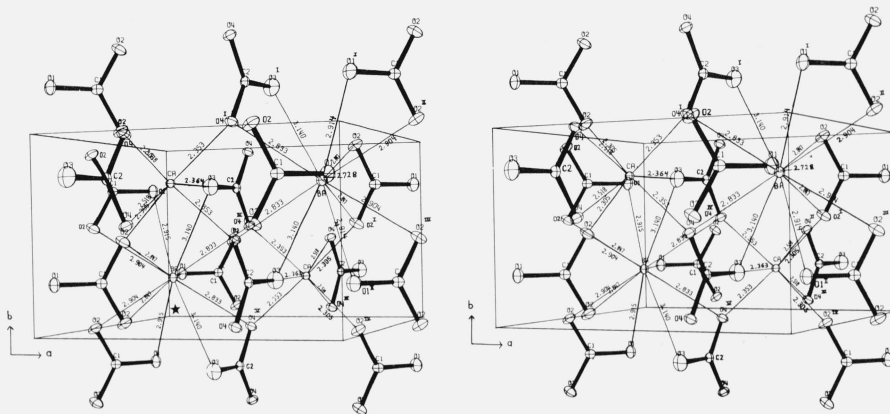


FIGURE 1. The crystal structure of barytocalcite, BaCa(CO₃)₂, and the environments of the Ba and Ca ions.

The origin of the crystallographic coordinate system is marked by *. The labels refer to atoms in tables 3 and 4.

3.2. The Calcium Ion Environment

The Ca ion is coordinated (fig. 1, table 4) to seven oxygen atoms, including one edge, O(4^{II}, 4^{III}), of a CO₃ group, with Ca . . . O distances in the normal range. The five apex oxygen atoms lie in a square pyramid. The center of the coordinated edge of the CO₃ group is near the remaining octahedral position. The coordination of Ca in barytocalcite is thus intermediate between the octahedral coordination of six CO₃ apexes with no shared edges in the calcite phase of CaCO₃ and the nine-fold coordination of three shared CO₃ edges and three apexes in the aragonite phase of CaCO₃.

TABLE 4. Ca environment in barytocalcite, BaCa(CO₃)₂

Atoms	Distance, Å
Ca, O(2 ^I , 2 ^{IV})	2.305(2)
Ca, O(4 ^I , 4 ^V)	2.353(2)
Ca, O(3)	2.364(3)
Ca, O(4 ^{II} , 4 ^{III})	2.518(2)

The atomic labels refer to atoms in figure 1.

3.3. The Carbonate Groups and Their Environments

There are two crystallographically different CO₃ groups in the structure. One (table 5, fig. 2) is in the Ba . . . CO₃ chains and the other (table 5, fig. 2) is in the Ca . . . CO₃ chains. The former, the C(1) CO₃ group, coordinates with all edges to Ba ions, and coordinates one apex, O(1), to another Ba ion. The two remaining apexes O(2, 2^I) are coordinated to Ca ions.

The C(2) CO₃ group coordinates the edge containing the O(4, 4^I) atoms to Ca^{II} and the remaining two edges,

TABLE 5. The carbonate anions and their environments in barytocalcite, BaCa(CO₃)₂

CO ₃ groups	Distance or angle
C(1), O(1)	1.275(4) Å
C(1), O(2, 2 ^I)	1.286(2)
O(1), O(2)	2.221(3)
O(2), O(2 ^I)	2.220(4)
O(1), C(1), O(2)	120.3(2) ^o
O(2), C(1), O(2 ^I)	119.3(3)
C(2), O(3)	1.259(4) Å
C(2), O(4, 4 ^I)	1.294(2)
O(3), O(4)	2.229(3)
O(4), O(4 ^I)	2.203(4)
O(3), C(2), O(4)	121.6(1) ^o
O(4), C(2), O(4 ^I)	116.6(3)
O environments	Distance, Å
O(1), Ba	2.729(3)
O(1), (Ba ^I , Ba ^{II})	2.915(1)
O(2), Ca ^{III}	2.305(2)
O(2), Ba ^{III}	2.847(2)
O(2), Ba ^{II}	2.904(2)
O(3), Ca ^I	2.364(3)
O(3), (Ba ^{IV} , Ba ^V)	3.140(2)
O(4), Ca ^{III}	2.353(2)
O(4), Ca ^{II}	2.518(2)
O(4), (Ba ^V)	2.833(2)

The atomic labels refer to atoms in figure 2.

O(3, 4) and O(3, 4^I), to ions Ba^V and Ba^{IV}, respectively. The average values of the C—O bond distance in the C(1) and C(2) CO₃ groups, 1.283 Å and 1.283 Å, respectively, compare well with the C—O bond lengths ob-

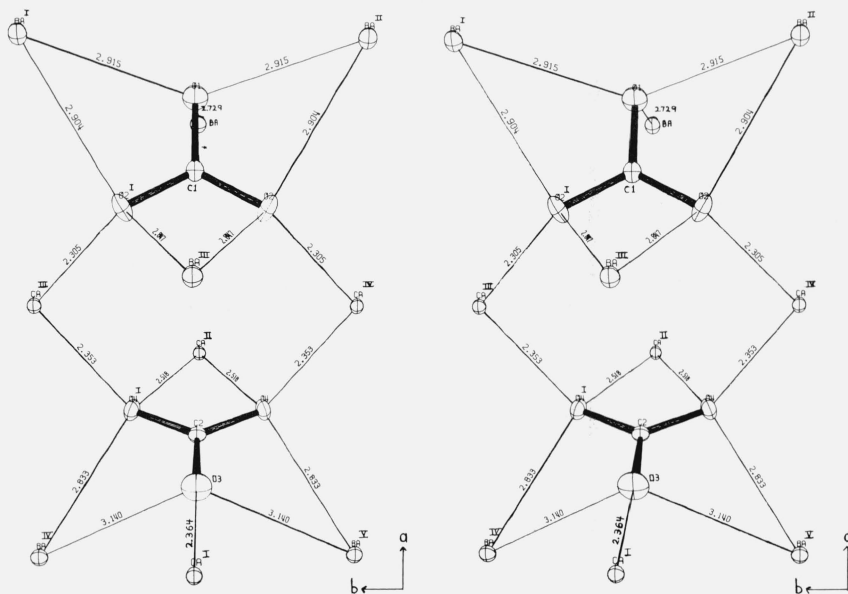


FIGURE 2. The CO₃ environments in barytocalcite, BaCa(CO₃)₂.

The labels refer to atoms in table 5.

served in the calcite (1.283(2) Å [14]) and aragonite (1.288(2) and 1.283(1) Å [4]) phases of CaCO₃.

The two CO₃ groups are nonplanar in barytocalcite. The displacements of C from the plane of the oxygen atoms are 0.025(5) Å for C(1) and 0.022(4) Å for C(2). Both displacements are toward the two central Ca ions Ca^{III} and Ca^{IV} in figure 2, and probably arise from polarization of the O atoms by these Ca ions. Similarly distorted CO₃ groups have been found in aragonite [15, 4] and Ca₂Na₂(CO₃)₃ [1]. (In calcite, the CO₃ group point symmetry is constrained to 32 by the choice of R3c as the space-group.)

The different C—O bond lengths in the CO₃ groups (table 5) are consistent with the observed features in the structure. O(1) is bonded to three Ba ions. O(2) is bonded to two Ba ions and one Ca ion. Thus O(2) experiences stronger interaction with its cation neighbors, which is compatible with the C(1)—O(2) distance being longer than C(1)—O(1). Similarly, O(4) is coordinated to two Ca ions and one Ba ion, whereas O(3) is coordinated to one Ca ion and two Ba ions. Thus, the C(2)—O(4) bond distance is expected to be longer than the C(2)—O(3) distance. Because the O(4, 4') edge is coordinated to Ca whereas the O(3, 4) and O(3, 4') edges are coordinated to Ba, the O(4), C(2), O(4') angle is expected to be less than 120°. Both these effects are realized.

Although O(2) and O(3) have similar environments, comparison of the lengths of the bonds C(1)—O(2) and C(2)—O(3) is not fruitful. Such a superficial comparison only applies when the oxygen atoms are competing in their bonding to the same central atom or when the other oxygens in the CO₃ groups also have similar environments.

4. Discussion

Alm [3] showed that the structure given by Gossner and Mussnug [2] is incorrect. The general features of the structure given by Alm for barytocalcite are correct to within ~0.3 Å. The details given here are, however, far more precise. Gossner and Mussnug and Alm gave the space-group of barytocalcite as P2₁ in their limited analyses of the structure. Our more extensive analysis shows, however, that barytocalcite can be refined equally well, within the limits of the data, in the centrosymmetric space-group P2₁/m.

Barytocalcite is related to the calcite and aragonite phases of CaCO₃. There are pseudo-hexagonal layers of cations parallel to (101) in the barytocalcite structure. If the difference between Ca and Ba is ignored, a pseudo-cell may be defined with $a' \sim 8.7$ Å (along [101]), $b' = 5.2$ Å (along [010]), $c' \sim 9.2$ Å (along [101]) and $\beta' \sim 95^\circ$. In this pseudo-cell, the cation layers repeat every third layer along c' as they do in calcite. The pseudo-cell of barytocalcite compares well with the orthohexagonal cell 8.641, 4.989, 17.062 Å of calcite. The orientations of the CO₃ groups in the two compounds calcite and barytocalcite differ by a rotation of ~30° (the C(2)O₃ group in barytocalcite further differs in that it makes an angle of ~20° with the (101) plane), and the cell repeat, 17.062 Å, perpendicular to the

layers in calcite encompasses six cation layers whereas barytocalcite repeats every three cation layers. As regards the . . . ABCABC . . . sequence of cation layers, barytocalcite is like calcite. However, the rotation of the CO₃ groups by ~30° relative to the CO₃ positions in calcite relates barytocalcite to the aragonite phase of CaCO₃. Thus the detailed coordinations of the CO₃ groups are like those in aragonite, which also has CO₃ groups rotated by ~30° from the CO₃ positions in calcite, because all CO₃ edges in both compounds are shared in coordination to neighboring cations and all apexes are further coordinated to cations. The coordinations of the cations in barytocalcite are however different from the coordination of Ca in aragonite, partly because in the former there are two differently sized cations.

W. E. Brown suggested the problem and gave helpful discussions; P. B. Kingsbury gave technical assistance. This investigation was supported in part by research grant DE-00572 to the American Dental Association from the National Institute of Dental Research and is part of the dental research program conducted by the National Bureau of Standards, in cooperation with the American Dental Association; the United States Army Medical Research and Development Command; the Dental Sciences Division of the School of Aerospace Medicine, USAF; the National Institute of Dental Research and the Veterans Administration.

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