CRYSTAL STRUCTURES OF ARAGONITE, STRONTIANITE, AND WITHERITE

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Abstract

The crystal structures of the three isostructural carbonates aragonite, $CaCO_3$, strontianite, $SrCO_3$, and witherite, $BaCO_3$, were re-examined and refined by least squares methods using three-dimensional X-ray data obtained by a counter-diffractometer. All three carbonates belong to the orthorhombic space group *Pmcn* with $Z=4$. The cell constants are a 4.9614(3), b 7.9671(4), c 5.7404(4) Å for aragonite, a 5.090(2), b 8.358(2), c 5.997(4) Å for strontianite, and a 5.3126(5), b 8.8958(5), c 6.4284(5) Å for witherite. The final conventional R-factors are 0.031, 0.031 and 0.033 respectively. The average cation to oxygen bond lengths are 2.528 Å in aragonite, 2.636 Å in strontianite, and 2.807 Å in witherite. The average C–O bond lengths are 1.282 Å in aragonite, 1.285 Å in strontianite, and 1.287 Å in witherite.

The CO_3 group in aragonite is slightly but probably significantly non-planar; the carbon atom lies 0.020 Å ($\sigma=0.006$ Å) out of the plane of the oxygen atoms. The three structures are very similar, with the witherite structure being the closest to the ideal close-packed structure.

Introduction

The crystal structure of aragonite was determined by Bragg (1924) and by Wyckoff (1925). The structure of witherite was investigated by Colby and La Coste (1935) and the cerussite structure by Colby and La Coste (1933). The structure as proposed by Bragg is still the most nearly correct one up till now. No previous investigation of the structure of strontianite is available.

To explain the splitting of some of the normal vibrational modes of the CO_3 group, as observed in the infrared spectra of the orthorhombic carbonates, deformation of the CO_3 group from D_{3h} symmetry was suggested by Schaeffer, Matossi, and Dane (1927) and Adler and Kerr (1963). Davydov (1962) has shown, however, that it is not necessary for the CO_3 group to be non-planar in order to explain the splitting.

The present investigation was carried out to determine the distortions in the structures, to obtain more accurate bond lengths and inter-atomic angles, and to resolve the question of the non-planarity of the CO_3 group.

Experimental

The samples used were kindly supplied by John S. White Jr., Division of Mineralogy, Smithsonian Institution, U.S. National Museum, Washington D. C. They are aragonite (U.S.N.M. No 95534) from Grapevine Mountains, Beatty, Nevada; strontianite (U.S.N.M.

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No 97256) Suiza Mine, Sierra Mojada, Mexico; and witherite (U.S.N.M. No 103262), Anglesarke, Lancashire, England.

The samples were chemically analyzed as follows: Gravimetric determinations of the major element concentrations were made. The minor element concentrations were determined by atomic absorption spectroscopy, except for Ba in aragonite, which could not be determined because of excessive interference by Ca. The Ba content of aragonite was checked by X-ray fluorescence and was found to be insignificant. The carbon determinations were not reliable enough so that the theoretical CO_3 content was used in all cases. The formulas $Ca_{0.997}Sr_{0.0021}Mg_{0.0004}Pb_{0.0005}CO_3$ for aragonite, $Sr_{0.8882}Ca_{0.0734}Ba_{0.0371}Mg_{0.0003}$ $Pb_{0.0010}CO_3$ for strontianite, and $Ba_{0.9862}Ca_{0.0024}Sr_{0.0106}Mg_{0.0002}Pb_{0.0006}CO_3$ for witherite were used in the structure analysis.

The X-ray data were collected at the crystallographic laboratory of the Geophysical Laboratory, Carnegie Institution, Washington D.C.

The axial setting used by Bragg is also used in this paper. The diffraction symmetry in all three structures was observed as *mmm P-cn* with cell contents $Z = 4$. The two space group possibilities are No. 62, *Pmcn* or No. 33, $P2_1cn$. Space group *Pmcn* was assumed to be the correct one in all three cases.

Nearly all the aragonite crystals investigated show twinning and the only untwinned crystal which was encountered was used. The only type of twinning observed is the common twinning about the (110) plane (Bragg, 1924).

Upon examination of the Weissenberg photographs of several strontianite crystals, diffuseness in the high-angle region was noted, occurring in the b^* and c^* directions. This is possibly a consequence of cation disorder of Ca and Ba in the structure causing a layer disorder. The diffuseness occurs as elongation of diffraction spots towards the high-angle side, obliterating the $K\alpha_1$–$K\alpha_2$ separation of the spots. No crystals free from this effect could be obtained. This effect also introduced a considerable error in measurement of the back-reflection Weissenberg data.

The witherite crystal used was free from any visible defects. The crystal dimensions are 0.150, 0.094, 0.043 mm for aragonite, 0.184, 0.10, 0.05 mm for strontianite, and 0.134, 0.12, 0.03 mm for witherite.

Cell parameters were obtained by least-squares refinement of back-reflection Weissenberg measurements, using a program by Burnham (1962). The cell values are a 4.9614 ± 0.0003, b 7.9671 ± 0.0004, c 5.7404 ± 0.0004 Å for aragonite, a 5.090 ± 0.002, b 8.358 ± 0.002, c 5.997 ± 0.004 Å for strontianite, and a 5.3126 ± 0.0005, b 8.8958 ± 0.0005, c 6.4284 ± 0.0005 Å for witherite. The measurements were made at room temperature, 21°C, with wavelengths for $CuK\alpha_1 = 1.54051$, and for $CuK\alpha_2 = 1.54433$. In the case of aragonite and witherite, the agreement with the ASTM values of Swanson and Fuyat (1954) is fair, but the values for strontianite are lower than the ASTM values. This is probably caused by the predominance of substituted Ca in the structure.

X-ray diffraction intensity data were collected using a Supper-Pace automated single crystal diffractometer with Weissenberg geometry. Nb-filtered MoKα radiation was used for all three minerals. A step-scan mode of counting was used and the integrated intensities determined with the method described by Cetlin and Abrahams (1963). The ω-scan or moving-crystal-stationary-counter method of scanning was used. In all three cases the c-axes coincided with the spindle axis.

Integrated intensity data were converted to observed structure factors by applying a Lorentz-polarization correction as well as an absorption correction, using a data reduction program by Burnham (1966a). The absorption correction was done by a numerical integration technique as described by Burnham (1966b). The linear absorption coefficients, μ, are 23.608, 210.382, and 135.69 cm^{-1} for aragonite, strontianite, and witherite respectively.

The structure determination by Bragg was confirmed by Patterson and Fourier synthesis using the program ERFR2 by W. G. Sly, D. P. Shoemaker, and J. H. van den Hende (Massachusetts Institute of Technology, Esso Research and Engineering Co., 1962).

Refinement of the three structures was carried out using the unpublished full matrix least squares program written by Prewitt and modified to use analytic expressions for the atomic scattering factor curves (Prewitt and Burnham, 1966). Initially the scattering factors for the neutral atoms were used.

Isotropic refinement of the three carbonates was initiated using the transformed Wyckoff (1964) parameters as starting values together with a weighting scheme in which the observations were weighted in an inverse proportion to their variance obtained from counting statistics. When anisotropic refinements were attempted using this weighting scheme, nonpositive definite temperature factors resulted for aragonite and strontianite. This weighting scheme was discarded in favour of the one suggested by Cruickshank *et al.*, (1960), where the variance of the observed structure factors is given as:

$$\sigma_{F_0}{}^2 = k(2F_{\min} + F_0 + 2/F_{\max} \cdot F_0{}^2)$$

The same weighting scheme was used for all three carbonates, using $F_{\min} = 2.49$, $F_{\max} = 27.06$ for aragonite, $F_{\min} = 3.83$, $F_{\max} = 40.52$ for strontianite, and $F_{\min} = 2.41$, $F_{\max} = 36.22$ for witherite.

Anisotropic refinements of aragonite and witherite proceeded satisfactorily and gave low R-values, the function

$$\Sigma \omega (F_o - F_c)^2$$

being minimized, but β_{33} of the carbon atom in strontianite consistently became negative.

Refinement using ionic M^{2+} scattering factor curves for Ca, Sr, and Ba resulted in a slight decrease in the R-factors and standard deviations, so that these curves were subsequently used.

An extinction correction was also attempted using the method described by Asbrink and Werner (1966), modifying the absorption program by Burnham (1966). This correction decreased the negative β_{33} for strontianite, but it still stayed negative. Further refinement using the corrected F-values was discontinued since no significant improvement resulted.

At this stage, a few of the very weak reflections with intensities slightly higher than two times their standard deviations were omitted, as well as the 200 reflections for aragonite and witherite. The weak reflections showed intensities generally higher than their calculated values, whereas the 200 reflections were affected by extinction. Refinement of the cation occupancy confirmed that the chemical analyses are satisfactory.

Lastly, an anomalous dispersion correction was made, using only the real components of the values given by Cromer (1965). The β_{33} temperature factor of carbon in strontianite still stayed negative, so that it could not be anisotropically refined.

Table 1 gives the positional the thermal parameters with their standard errors, Table 2, the interatomic distances and angles, and Tables 3 and 4 give the thermal ellipsoid displacements and their orientations. Table 5[1] gives the observed and calculated structure amplitudes for the *Pnma* axial setting, *i.e.*, the *b*, *c*, *a* setting for the axes *a*, *b*, *c* in *Pmcn*.

The number of independent reflections used in the final refinements was: aragonite

[1] To obtain a copy of Table 5, order NAPS Document 01380 from National Auxiliary Publications Service of the A.S.I.S. c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022; remitting $2.00 for microfiche or $5.00 for photocopies, in advance payable to CCMIC-NAPS.

TABLE 1. POSITIONAL AND THERMAL PARAMETERS

Aragonite		Strontianite		Witherite	
Atom	Parameters	Atom	Parameters	Atom	Parameters
Ca x	0.2500[a]	Sr x	0.2500[a]	Ba x	0.2500[a]
y	0.4150 (1)	y	0.4160 (1)	y	0.41631 (5)
z	0.7597 (3)	z	0.7569 (3)	z	0.7549 (2)
β_{11}	0.0062 (1)	B	0.508 (12) Å²	β_{11}	0.00483 (8)
β_{22}	0.0021 (1)			β_{22}	0.00182 (3)
β_{33}	0.0063 (4)			β_{33}	0.0046 (3)
β_{12}	0.0000[a]			β_{12}	0.0000[a]
β_{13}	0.0000[a]			β_{13}	0.0000[a]
β_{23}	0.0001 (2)			β_{23}	−0.0001 (2)
C x	0.2500[a]	C x	0.2500[a]	C x	0.2500[a]
y	0.7622 (4)	y	0.7601 (10)	y	0.7570 (12)
z	−0.0862 (10)	z	−0.0864 (20)	z	−0.0810 (26)
β_{11}	0.0065 (9)	B	0.592 (99) Å²	β_{11}	0.0051 (14)
β_{22}	0.0027 (3)			β_{22}	0.0023 (6)
β_{33}	0.0025 (25)			β_{33}	0.0124 (71)
β_{12}	0.0000[a]			β_{12}	0.0000[a]
β_{13}	0.0000[a]			β_{13}	0.0000[a]
β_{23}	−0.0006 (5)			β_{23}	0.0016 (14)
O(1)x	0.2500[a]	O(1)x	0.2500[a]	O(1)x	0.2500[a]
y	0.9225 (4)	y	0.9119 (9)	y	0.9011 (8)
z	−0.0962 (9)	z	−0.0946 (16)	z	−0.0878 (19)
β_{11}	0.0122 (9)	B	0.913 (88) Å²	β_{11}	0.0107 (18)
β_{22}	0.0028 (3)			β_{22}	0.0020 (6)
β_{33}	0.0086 (18)			β_{33}	0.0106 (49)
β_{12}	0.0000[a]			β_{12}	0.0000[a]
β_{13}	0.0000[a]			β_{13}	0.0000[a]
β_{23}	−0.0011 (5)			β_{23}	−0.0005 (9)
O(2)x	0.4736 (4)	O(2)x	0.4694 (8)	O(2)x	0.4595 (10)
y	0.6810 (3)	y	0.6821 (5)	y	0.6839 (6)
z	−0.0862 (5)	z	−0.0839 (11)	z	−0.0790 (14)
β_{11}	0.0053 (5)	B	0.797 (62) Å²	β_{11}	0.0072 (10)
β_{22}	0.0042 (2)			β_{22}	0.0027 (4)
β_{33}	0.0069 (12)			β_{33}	0.0081 (33)
β_{12}	0.0008 (3)			β_{12}	0.0007 (5)
β_{13}	−0.0001 (5)			β_{13}	−0.0010 (11)
β_{23}	−0.003 (4)			β_{23}	0.0006 (6)

[a] Fixed by symmetry.

Atoms[a]	Metal-ion–oxygen polyhedra $M =$ Ca, Sr, or Ba		
	Aragonite	Strontianite	Witherite
$(M)^3–(O(1))^1$	2.419 (5)	2.552 (9)	2.737 (11)
[b]$(M)^3–(O(2))^8$	2.551 (3)	2.666 (5)	2.837 (6)
[b]$(M)^3–(O(3))^2$	2.653 (2)	2.725 (4)	2.868 (5)
[b]$(M)^3–(O(2))^7$	2.445 (3)	2.561 (6)	2.742 (7)
[b]$(M)^3–(O(2))^2$	2.519 (3)	2.634 (5)	2.816 (6)
Average M–O	2.528 Å (.132)	2.636 Å (.118)	2.807 Å (.109)
[b]$(O(1))^L–(O(2))^8$	3.238 (6)	3.353 (11)	3.537 (15)
[b]$(O(2))^8–(O(1))^2$	3.073 (5)	3.295 (9)	3.647 (11)
[b]$(O(1))^2–(O(2))^7$	3.134 (6)	3.236 (11)	3.432 (15)
[b]$(O(2))^7–(O(2))^2$	3.073 (2)	3.206 (4)	3.422 (4)
$(O(2))^2–(O(2))^5$	2.742 (4)	2.857 (9)	3.086 (10)
$(O(2))^8–(O(2))^3$	2.219 (4)	2.234 (9)	2.226 (10)

Atoms	CO$_3$ group		
	Aragonite	Strontianite	Witherite
$(C)^3–(O(1))^3$	1.279 (5)	1.269 (10)	1.282 (12)
[b]$(C)^3–(O(2))^3$	1.284 (3)	1.293 (6)	1.289 (7)
Average C–O	1.282 Å	1.285 Å	1.287 Å
[b]$(O(1))^3–(O(2))^3$	2.222 (4)	2.222 (8)	2.230 (8)
$(O(2))^3–(O(2))^8$	2.219 (4)	2.234 (9)	2.226 (10)

INTERATOMIC ANGLES IN DEGREES

Metal-ion–oxygen polyhedra

	Aragonite	Strontianite	Witherite
$(O(1))^L–(M)^3–(O(2))^8$	81.26 (12)	79.95 (22)	78.76 (26)
$(O(1))^L–(M)^3–(O(1))^2$	71.89 (10)	73.26 (18)	74.14 (18)
$(O(1))^L–(M)^3–(O(2))^7$	144.59 (6)	144.39 (12)	143.58 (14)
$(O(1))^L–(M)^3–(O(2))^2$	93.56 (12)	95.33 (22)	96.46 (25)
$(O(2))^8–(M)^3–(O(1))^2$	72.37 (10)	75.35 (20)	79.47 (22)
$(O(2))^8–(M)^3–(O(2))^7$	75.54 (9)	76.07 (17)	76.47 (17)
$(O(2))^8–(M)^3–(O(2))^2$	121.01 (3)	122.21 (7)	123.51 (8)
$(O(1))^2–(M)^3–(O(2))^7$	75.75 (12)	75.44 (23)	75.40 (28)
$(O(1))^2–(M)^3–(O(2))^2$	50.79 (9)	48.97 (19)	46.19 (19)
$(O(2))^7–(M)^3–(O(2))^2$	76.49 (6)	76.21 (11)	75.99 (12)

Atoms	CO$_3$ group		
	Aragonite	Strontianite	Witherite
$(O(1))^3–(C)^3–(O(2))^3$	120.19 (18)	120.28 (40)	120.28 (46)
$(O(2))^3–(C)^3–(O(2))^8$	119.55 (37)	119.43 (79)	119.43 (93)

[a] The equivalent positions in the space group $Pmcn$ are numbered from 1 to 8. They are respectively:

$x, y, z; -x, -y, -z; \frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z; \frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z; \frac{1}{2}+x, -y, -z; \frac{1}{2}-x, y, z; -x, \frac{1}{2}+y, \frac{1}{2}-z; x, \frac{1}{2}-y, \frac{1}{2}+z.$

[b] Only one half of the distances and angles is given. The other half is related by mirror symmetry.

The distances and angles were computed with the computer program ORFFE by W. R. Busing, K. O. Martin, and H. A. Levy (Oak Ridge National Laboratory ORNL-Tm-306).

TABLE 3. R.M.S. COMPONENT OF THERMAL DISPLACEMENT ALONG
PRINCIPAL AXES R OF THE THERMAL ELLIPSOIDS

| | Aragonite | | | Witherite | |
Atom	R	Displacement Å	Atom	R	Displacement Å
Ca	1	0.083 (1)	Ba	1	0.083 (1)
	2	0.088 (1)		2	0.085 (1)
	3	0.103 (3)		3	0.099 (3)
C	1	0.062 (32)	C	1	0.085 (12)
	2	0.090 (6)		2	0.089 (15)
	3	0.095 (6)		3	0.165 (45)
O(1)	1	0.089 (6)	O(1)	1	0.089 (13)
	2	0.125 (5)		2	0.124 (10)
	3	0.124 (12)		3	0.150 (35)
O(2)	1	0.079 (4)	O(2)	1	0.090 (9)
	2	0.106 (9)		2	0.111 (8)
	3	0.119 (3)		3	0.133 (25)

(297), strontianite (283) and witherite (421). The final discrepancy factors

$$R = \frac{\Sigma F_o - F_c}{\Sigma F_o}$$

for reflections used are 0.031 for aragonite, 0.031 for strontianite, and 0.033 for witherite.

TABLE 4. ANGLE BETWEEN PRINCIPAL AXES R OF THERMAL ELLIPSOIDS AND
VECTOR DEFINED BY C AND O(1) ATOMS.

| | Aragonite | | | Witherite | |
Atom	R		Atom	R	
Ca	1	0.1 (8.0)	Ba	1	90.0 (—)
	2	90.0 (—)		2	170.5 (13.3)
	3	89.9 (8.0)		3	99.5 (13.3)
C	1	77.7 (16.5)	C	1	90.0 (—)
	2	90.0 (—)		2	167.2 (12.9)
	3	12.3 (16.5)		3	77.2 (12.9)
O(1)	1	24.0 (11.1)	O(1)	1	7.6 (11.3)
	2	90.0 (—)		2	90.0 (—)
	3	114.0 (11.1)		3	97.6 (11.3)
O(2)	1	102.6 (4.4)	O(2)	1	50.5 (16.7)
	2	102.3 (18.6)		2	138.8 (18.4)
	3	17.7 (13.4)		3	80.1 (19.3)

DISCUSSION

The idealized aragonite structure can be described as having the geometry of approximate hexagonal close packing, with the carbon atoms of the CO_3 groups projecting on top of each other. Figure 1 shows a projection of the aragonite structure as found from this investigation. This was drawn by the computer program ORTEP by C. K. Johnson (Oak Ridge National Laboratory ORNL-3794).

In comparing the three structures of aragonite, strontianite, and witherite, we find that they are very similar in most respects. The following comparisons are made:

The average metal-ion to oxygen bond lengths compare well with the values obtained from ionic radii (Pauling, 1960), applying the correction for the ligancy of 9. The values of aragonite and witherite are also compared with the values derived from effective ionic radii as given by Shannon and Prewitt (1969), assuming four-coordinated oxygen. The lower observed values could conceivably be explained by the highly symmetric nature of the structures.

	aragonite	strontianite	witherite
M–O dist. (observed)	2.528 Å	2.636 Å	2.807 Å
M–O dist. (corrected)	2.51 Å	2.65 Å	2.85 Å
M–O dist. (eff. ionic radii)	2.56 Å	—	2.85 Å

In all three structures it is found that the shortest M-O bond is the bond to the O(1) atom lying on the same mirror plane as the M-atom. A comparison of the differences between M-O bond lengths shows that they become more uniform going from aragonite to witherite. The standard deviations of the mean M-O bond lengths also decrease from aragonite to witherite. This implies that the polyhedron becomes less distorted with the increase in ionic size.

The carbon atoms do not project on top of each other along the c-axis as can be seen from Figure 1. They are displaced relative to each other along the b-direction. These displacements show a correlation with the cation and are as follows:

	aragonite	strontianite	witherite
$\Delta Y =$	0.194 Å	0.169 Å	0.125 Å

Again this implies that the witherite structure is closest to the ideal close-packed structure.

Because of the displacement of the O(1) atom away from the nearest M-atom, the CO_3 groups in all three structures are tilted. The tilt was
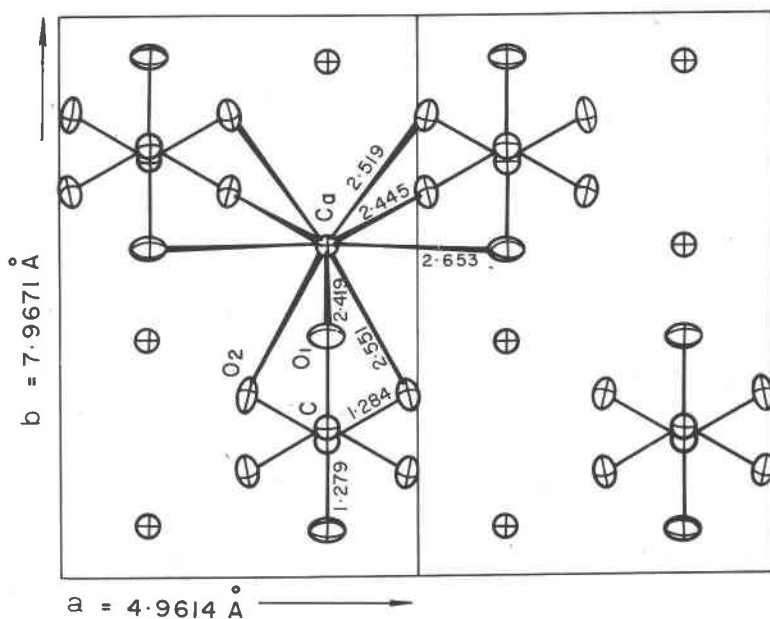
FIG. 1. Projection of the aragonite structure viewed along the c-axis.

calculated as the tilt of a plane drawn through the O-atoms from a plane parallel to the a–b unit cell plane. The angles are:

	aragonite	strontianite	witherite
$\delta=$	2°22′	2°40′	2°19′

The values for the three structures all agree within the standard deviations of the atomic positions.

The CO_3 group appears to be non-planar as can be seen from the list of coordinates. To determine whether this is significant, a least squares plane through the four atoms was determined, minimizing the distances of the atoms from this plane. A χ^2 test was applied to all three structures according to the method described in Stout and Jensen (1968).

	aragonite	strontianite	witherite
χ^2	9.497	0.300	0.124
$d_{L.S.}$	0.017 Å	0.006 Å	0.006 Å
d_0	0.020 Å	0.007 Å	0.006 Å
$\sigma(\text{ref})$	0.006 Å	0.012 Å	0.017 Å

where

$d_{L.S.}$ = distance of C-atom from least squares plane through all four atoms.
d_0 = distance of C-atom from plane through O atoms.
$\sigma(\text{ref})$ = standard deviation of atomic positions calculated from structure factor refinement

A value of $\chi^2 = 9.497$, for 1 degree of freedom, gives an approximate value of 0.1 percent for p (*International Tables for X-ray Crystallography*, Vol II). Thus, the probability that a planar CO_3 group will have $\chi^2 = 9.497$ is only $p = 0.001$. Taking into consideration only the atomic positions with their standard deviations, it can be concluded at the 0.1 percent significance level that the CO_3 group is non-planar. The magnitudes of the R.M.S. thermal displacements, however, are larger than 0.020 Å, but this does not affect the conclusion that the mean configuration is non-planar.

The average C-O bond lengths of 1.282 Å in aragonite, 1.285 Å in strontianite, and 1.287 Å in witherite, compare well with the value of 1.283 Å in the calcite structure (Chessin *et al.*, 1965).

We find that the three orthorhombic carbonate structures change gradually with witherite being the closest to the ideal structure. This can be explained by the fact that the Ba^{2+} ion has the size that fits into the 9-fold coordination polyhedron with the smallest amount of strain. We also find that the value of the minimum radius ratio for stability of a coordination polyhedron with a ligancy of 9 is given as 0.732 (Pauling, 1960, page 545). Comparing this value with the values given by Pauling, we find that the Ca^{2+} ion has a value of 0.67 and that Ba^{2+} has a value of 0.87. The value given by Pauling must, however, be taken as an approximation since examples of ten and twelve coordinated Ca^{2+} do exist (Shannon and Prewitt, 1969).

NOTE ADDED IN PROOF

After this manuscript had been accepted for publication, a structure analysis of aragonite done by A. dal Negro and L. Ungaretti, C.N.R. Centro di Studio Sulla Cristallografia Strutturale, Pavia, Italy was also submitted to the American Mineralogist [**56**, 768–772(1971).] Their results confirm the structure as described in this paper.

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