[AMERICAN JOURNAL OF SCIENCE, VOL. 254, FEBRUARY 1956, P. 65-70]

American Journal of Science

FEBRUARY 1956

THE UNIT CELLS OF CALCITE

HORACE WINCHELL

ABSTRACT. Mineralogical literature is confused regarding the axial lengths of the morphological unit cells of crystals belonging to the calcite structure-type. The smallest unit cell is a steep rhombohedron, $\{40\bar{4}1\}$ if the cleavage is $\{10\bar{1}1\}$; the axes **a** and **c** of the corresponding hexagonal cell are about 4.99 and 17.06 A., respectively. The axial lengths usually quoted for the morphological cells, both rhombohedral and hexagonal, correspond to subcells with $\mathbf{c}' = \frac{1}{2}\,\mathbf{c}$, long enough only to extend from a CO_3-group with one corner toward the front, to a CO_3-group with a corner toward the back. The axes **a** and **c** corresponding to the cleavage rhombohedron as $\{10\bar{1}1\}$ are about 19.96 A., and 17.06 A., respectively, and the corresponding rhombohedral axes are 12.85 A. long. A complete set of transformation matrices between the hexagonal and rhombohedral cells, both structural and morphological, is in tables 1 and 2.

Errors have occurred since the structure of calcite was first compared (Bragg 1914; 1915) with that of halite by observing that the pattern of the calcium and the carbon atoms (oxygen atoms being disregarded) is similar to that of the sodium and the chlorine atoms in a halite structure deformed by compression along a cube-diagonal [111] so as to make a rhombohedron with axes $\mathbf{a}'_{Rh} = 6.42$ angstroms and interaxial angles $\alpha_{Rh} = 101°55'$. Such a deformation is reasonable because of the flat shape of the CO_3 groups, which lie with their planes parallel to (0001) and their threefold symmetry axes parallel to **c**. These triangular groups have the same orientation in alternate planes; in the intervening planes they have another orientation, turned 180° (or 60°) about **c** as compared with the groups in the first-mentioned planes. Without this second orientation of the CO_3 groups there could be no center of symmetry in calcite, and either the planes or the twofold axes of symmetry would likewise be impossible.

Dana's System of Mineralogy (Palache, Berman, and Frondel, 1951, p. 141) describes the CO_3 groups in the calcite structure as follows: "These groups are arranged in parallel position in the crystal with their threefold symmetry axes oriented along [0001]. . . . " The unfortunate words "parallel position" should of course be "parallel planes."

Elsewhere, the *System* (p. 158, ref. 1) gives a transformation matrix as follows: "morphology to structure 1000/0100/0010/0004." This is correct from the morphological viewpoint, but as will become evident below, a minor change would make it correct not only morphologically but also structurally,

Bragg (1914a,b, 1915), Schiebold (1919), Olshausen (1925), and perhaps others have apparently all erred in considering the alternate possible unit cells of calcite. Wyckoff (1920) is the first I have found who clearly and explicitly states that the unit cell with $\mathbf{a}'_{Rh} = 6.42$ and $\alpha_{Rh} = 101°55'$, *useful in comparing* with the halite structure, is not a unit cell of calcite, though the idea is implicit in the work of Bragg (1915, esp. fig. 15) and of all others who found the correct primitive rhombohedral cell containing $2CaCO_3$, with $\mathbf{a}_{rh} = 6.37$ and $\alpha_{rh} = 46°05'$. Wyckoff (1948-1951, table VIIA, 2) may give the impression that there is a cleavage-rhombohedral cell with $\alpha_{Rh} = 101°55'$ and $\mathbf{a}'_{Rh} = 6.42$, but this is corrected in his text (Par. VII, a1) with the statement that it is a subcell. Maugin (1923) states explicitly that a rhombohedral unit cell exists with $\alpha_{Rh} = 101°55'$, but that its edge $\mathbf{a}_{Rh}$ must be twice as long as the generally adopted value of $\mathbf{a}'_{Rh}$. Ewald and Hermann (1931, p. 292, 313, 316, etc.) recognize the necessity of doubling the axes $\mathbf{a}'_{Rh}$ to obtain a unit cell of the calcite structure; their description is clear, but evidently not widely enough known. The size and shape of the structural unit cell with $\alpha_{rh} = 46°05'$ has been given by several authors, as Andrews (1950) who also summarizes previous work, without discussing its relation to, or the size of, the morphological unit cell.

The cleavage-like subcell, with $\mathbf{a}'_{Rh} = 6.42$, $\alpha_{Rh} = 101°55'$, has only one-eighth the volume and one-half the edge-length of a true lattice cell of calcite, for if the origin of coordinates is placed at a carbon atom, then each rhombohedral "axis" $\mathbf{a}'_{Rh}$ extends from the origin to a carbon atom at the center of a CO_3-group of the opposite orientation; $\mathbf{a}_{Rh}$ must be doubled to extend to a group with the same orientation as that at the origin. The doubled length, $\mathbf{a}_{Rh} = 2\mathbf{a}'_{Rh}$, is the axial length for this cell. The statement that the carbon and calcium atoms form a halite-like structure with the smaller subcell is still perfectly true, but this is not a unit cell of the whole calcite structure.

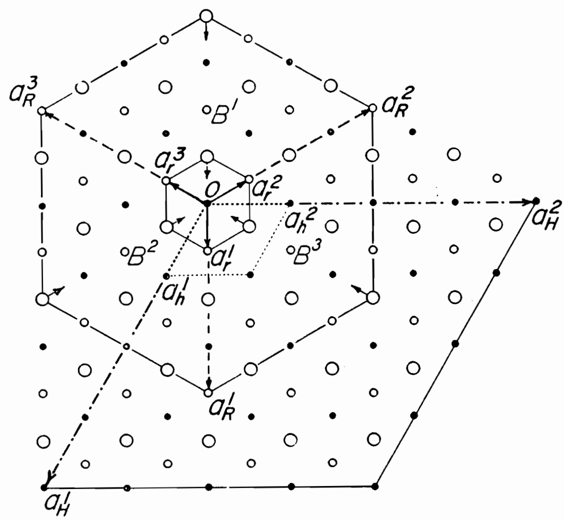

Fig. 1. Part of a rhombohedral lattice. Solid circles represent points in the lowest, or origin plane; small and large open circles represent points in the first and second lattice planes above the origin; the third plane has points directly over the solid circles, but is omitted for clarity. Axes a_r define the smallest, or structural rhombohedral unit cell; a_h (and c, not shown, normal to the page at O) define the corresponding hexagonal unit cell. Similarly, a_R and a_H (and c, not shown) define the rhombohedral and the hexagonal unit cells corresponding to the cleavage rhombohedron, as $\{10\bar{1}1\}$, of crystals with the calcite structure.

Figure 1 is a diagram of a rhombohedral lattice. By their sizes the circles represent lattice points at three different levels including, and above, the plane containing the origin O. The fourth level would have points coinciding in this figure with those of the first. The threefold symmetry axis is normal to the plane of the diagram. A primitive (structural) rhombohedral cell with axes $\mathbf{a}_{rh}$ is outlined in solid lines about O, except that its uppermost third is represented only by three arrows pointing toward the lattice point above O in the fourth level. A cell of calcite with this shape and size has parallel CO_3 groups at every corner, and an oppositely oriented CO_3 group at the center (above O, at a level of $\mathbf{c}/2$, not shown): the calcium centers are also above O, at levels (not shown) $\mathbf{c}/4$ and $3\mathbf{c}/4$. The nearest oxygen neighbors to each calcium belong to CO_3 groups associated with adjacent unit cells, so that it is hard to visualize the relations from just a single structural cell.

The hexagonal unit cell corresponding to the primitive rhombohedral cell is obtained by the transformation (1): it is said to be rhombohedrally centered; its axes $\mathbf{a}_h$ are shown by dotted lines in the figure: its axis $\mathbf{c}_h$ is normal to the page at O. The vector equations defining this cell (Henry and Lonsdale, 1952, p. 15) are as follows:

$$\begin{aligned} \mathbf{a}_1(h) &= \mathbf{a}_1(rh) - \mathbf{a}_2(rh) \\ \mathbf{a}_2(h) &= \qquad\qquad \mathbf{a}_2(rh) - \mathbf{a}_3(rh) \\ \mathbf{c}(h) &= \mathbf{a}_1(rh) + \mathbf{a}_2(rh) + \mathbf{a}_3(rh) \end{aligned}$$

Transformation matrix, rh(struc.) to hex (struc.):

$$\left\| \begin{matrix} 1 & \bar{1} & 0 \\ 0 & 1 & \bar{1} \\ 1 & 1 & 1 \end{matrix} \right\| \quad \text{Modulus 3.} \qquad (1)$$

The lengths of the resulting axes are $\mathbf{a}_{hex} = 4.9898$, $\mathbf{c}_{hex} = 17.060$ A. This matrix and others are collected in table 1. For a discussion of many uses of these matrices, see Henry and Lonsdale (1952, p. 15).

Considering figure 1 and the requirement that each rhombohedral axis should extend from the origin to a point in the adjacent level, we find that the solid-line axes $\mathbf{a}_{rh}$ are the shortest possible. The axes OB (not drawn in figure 1) define a face-centered rhombohedral cell, and indeed they were derived by Wyckoff (1920), Olshausen (1925), and others, in the process of finding the 6.37-angstrom axes $\mathbf{a}_{rh}$, at 46°05′, that define the structural cell. The axes OB are derived from the axes $\mathbf{a}_{rh}$ by matrix (2).

$$\left\| \begin{matrix} \bar{1} & 1 & 1 \\ 1 & \bar{1} & 1 \\ 1 & 1 & \bar{1} \end{matrix} \right\| \quad \text{Modulus 4.} \qquad (2)$$

Olshausen (1925) gave the length of OB as 8.08 A., and the interaxial angle as 76°03′, essentially the same as may be calculated from the best modern data. Curiously, Olshausen seems to have overlooked the fact that simply

TABLE 1

Unit Cells and Axial Transformations in Calcite
Using 3-Axis Rhombohedral and Hexagonal Coordinates

	From rh (struc.)	From hex (struc.)	From Rh (morph.)	From Hex (morph.)
To rh (struc.)	$a_{rh} = 6.3748$ $\alpha_{rh} = 46°05'$ cell contains 2 $CaCO_3$	$\begin{Vmatrix} \frac{2}{3} & \frac{1}{3} & \frac{1}{3} \\ -\frac{1}{3} & \frac{1}{3} & \frac{1}{3} \\ -\frac{1}{3} & -\frac{2}{3} & \frac{1}{3} \end{Vmatrix}$ mod. $\frac{1}{3}$	$\begin{Vmatrix} \frac{1}{2} & \frac{1}{4} & \frac{1}{4} \\ \frac{1}{4} & \frac{1}{2} & \frac{1}{4} \\ \frac{1}{4} & \frac{1}{4} & \frac{1}{2} \end{Vmatrix}$ mod. $\frac{1}{16}$	$\begin{Vmatrix} \frac{1}{6} & \frac{1}{12} & \frac{1}{3} \\ -\frac{1}{12} & \frac{1}{12} & \frac{1}{3} \\ -\frac{1}{12} & -\frac{1}{6} & \frac{1}{3} \end{Vmatrix}$ mod. $\frac{1}{48}$
To hex (struc.)	$\begin{Vmatrix} 1 & \bar{1} & 0 \\ 0 & 1 & \bar{1} \\ 1 & 1 & 1 \end{Vmatrix}$ mod. 3	$a_{hex} = 4.9898$ $c_{hex} = 17.060$ cell contains 6 $CaCO_3$	$\begin{Vmatrix} \frac{1}{4} & -\frac{1}{4} & 0 \\ 0 & \frac{1}{4} & -\frac{1}{4} \\ 1 & 1 & 1 \end{Vmatrix}$ mod. $\frac{3}{16}$	$\begin{Vmatrix} \frac{1}{4} & 0 & 0 \\ 0 & \frac{1}{4} & 0 \\ 0 & 0 & 1 \end{Vmatrix}$ mod. $\frac{1}{16}$
To Rh (morph.)	$\begin{Vmatrix} 3 & \bar{1} & \bar{1} \\ \bar{1} & 3 & \bar{1} \\ \bar{1} & \bar{1} & 3 \end{Vmatrix}$ mod. 16	$\begin{Vmatrix} \frac{8}{3} & \frac{4}{3} & \frac{1}{3} \\ -\frac{4}{3} & \frac{4}{3} & \frac{1}{3} \\ -\frac{4}{3} & -\frac{8}{3} & \frac{1}{3} \end{Vmatrix}$ mod. $\frac{16}{3}$	$a_{Rh} = 12.850$ $\alpha_{Rh} = 101°55'$ cell contains 32 $CaCO_3$	$\begin{Vmatrix} \frac{2}{3} & \frac{1}{3} & \frac{1}{3} \\ -\frac{1}{3} & \frac{1}{3} & \frac{1}{3} \\ -\frac{1}{3} & -\frac{2}{3} & \frac{1}{3} \end{Vmatrix}$ mod. $\frac{1}{3}$
To Hex (morph.)	$\begin{Vmatrix} 4 & \bar{4} & 0 \\ 0 & 4 & \bar{4} \\ 1 & 1 & 1 \end{Vmatrix}$ mod. 48	$\begin{Vmatrix} 4 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & 1 \end{Vmatrix}$ mod. 16	$\begin{Vmatrix} 1 & 1 & 0 \\ 0 & 1 & \bar{1} \\ 1 & 1 & 1 \end{Vmatrix}$ mod. 3	$a_{Hex} = 19.959_2$ $c_{Hex} = 17.060$ cell contains 96 $CaCO_3$

Notes: 1. Structural elements have lower-case subscripts, morphological elements have capitalized ones.

2. The modulus of each matrix is the ratio of volumes of new to old cells.

doubling the length of the "axes" $\mathbf{a}'_{Rh}$ would give a valid unit cell. A hexagonal cell is derivable from the rhombohedral one with axes OB using the transformation matrix (1); this has axes $\mathbf{a}'_h$ twice as long as, and directed in the opposite sense to, the axes $\mathbf{a}_h$ of the structural hexagonal cell.

Another rhombohedral cell in the same series is obtained from the axes

TABLE 2

Axial Transformations in Calcite
Using 3-Axis Rhombohedral, and 4-Axis Hexagonal Coordinates

	From rh (struc.)	From hex (struc.)	From Rh (morph.)	From Hex (morph.)
To rh (struc.)	*	$\begin{Vmatrix} \frac{1}{3} & 0 & \frac{-1}{3} & \frac{1}{3} \\ \frac{-1}{3} & \frac{1}{3} & 0 & \frac{1}{3} \\ 0 & \frac{-1}{3} & \frac{1}{3} & \frac{1}{3} \end{Vmatrix}$	*	$\begin{Vmatrix} \frac{1}{12} & 0 & \frac{-1}{12} & \frac{1}{3} \\ \frac{-1}{12} & \frac{1}{12} & 0 & \frac{1}{3} \\ 0 & \frac{-1}{12} & \frac{1}{12} & \frac{1}{3} \end{Vmatrix}$
To hex (struc.)	$\begin{Vmatrix} 1 & \bar{1} & 0 \\ 0 & 1 & \bar{1} \\ \bar{1} & 0 & 1 \\ 1 & 1 & 1 \end{Vmatrix}$	*	$\begin{Vmatrix} \frac{1}{4} & \frac{-1}{4} & 0 \\ 0 & \frac{1}{4} & \frac{-1}{4} \\ \frac{-1}{4} & 0 & \frac{1}{4} \\ 1 & 1 & 1 \end{Vmatrix}$	$\begin{Vmatrix} \frac{1}{4} & 0 & 0 & 0 \\ 0 & \frac{1}{4} & 0 & 0 \\ 0 & 0 & \frac{1}{4} & 0 \\ 0 & 0 & 0 & 1 \end{Vmatrix}$
To Rh (morph.)	*	$\begin{Vmatrix} \frac{4}{3} & 0 & \frac{-4}{3} & \frac{1}{3} \\ \frac{-4}{3} & \frac{4}{3} & 0 & \frac{1}{3} \\ 0 & \frac{-4}{3} & \frac{4}{3} & \frac{1}{3} \end{Vmatrix}$	*	$\begin{Vmatrix} \frac{1}{3} & 0 & \frac{-1}{3} & \frac{1}{3} \\ \frac{-1}{3} & \frac{1}{3} & 0 & \frac{1}{3} \\ 0 & \frac{-1}{3} & \frac{1}{3} & \frac{1}{3} \end{Vmatrix}$
To Hex (morph.)	$\begin{Vmatrix} 4 & \bar{4} & 0 \\ 0 & 4 & \bar{4} \\ \bar{4} & 0 & 4 \\ 1 & 1 & 1 \end{Vmatrix}$	$\begin{Vmatrix} 4 & 0 & 0 & 0 \\ 0 & 4 & 0 & 0 \\ 0 & 0 & 4 & 0 \\ 0 & 0 & 0 & 1 \end{Vmatrix}$	$\begin{Vmatrix} 1 & \bar{1} & 0 \\ 0 & 1 & \bar{1} \\ \bar{1} & 0 & 1 \\ 1 & 1 & 1 \end{Vmatrix}$	*

* See corresponding box in table 1.

OB by using matrix (2), but it can be obtained directly from $\mathbf{a}_{rh}$ by the transformation rh(struc.) to Rh(morph.):

$$\begin{Vmatrix} 3 & \bar{1} & \bar{1} \\ \bar{1} & 3 & \bar{1} \\ \bar{1} & \bar{1} & 3 \end{Vmatrix} \quad \text{Modulus 16.} \qquad (3)$$

This cell has axes $\mathbf{a}_{Rh} = 12.85$ A., designated in figure 1 by $\mathbf{a}_R$, drawn with dashed lines, at interaxial angles $\alpha_{Rh} = 101°55'$. Matrix (3) will be found in table 1 in the column "From rh(struc.)" and the row "To Rh(morph.)." Application of matrix (1) to this cell gives the hexagonal-morphological cell with $\mathbf{a}_{Hex} = 19.959$ A., $\mathbf{c}_{Hex} = 17.060$ A.

Table 1 contains the transformation matrices for changing either way between rhombohedral and hexagonal, and between the smallest (structural) and the morphologically preferred unit cells, except that in squares where the identity-matrix would be appropriate, the values of **a** and α or of **a** and **c** are shown.

Table 2 contains the same transformations, but with reference to four-axis Bravais coordinates for all hexagonal members.

CONCLUSION

Needless confusion regarding the axial lengths for the morphological unit cells of crystals belonging to the calcite structure-type has arisen. Axial lengths in any structure are the true repeat-distances for the whole structural pattern; the lengths of the halite-like rhombohedral subcell-edges are not axial lengths; they must be doubled when the positions of the oxygens in the CO_3-groups are considered. Likewise the lengths of the corresponding hexagonal subcell edges are not axial lengths, but must be doubled for the same reason. In all discussions involving the structure or any vector properties related to crystallographic axial lengths, authors should carefully state the reference-axes used in their work.

REFERENCES

Andrews, K. W., 1950, An X-ray examination of a sample of pure calcite and of solid-solution effects in some natural calcites: Mineralog. Mag., v. 29, p. 85-99.

Bragg, W. H., 1914a, The structure of some crystals as indicated by their diffraction of X-rays: Royal Soc. London Proc., v. (A)89, p. 248-277.

————, 1914b, The analysis of crystals by the X-ray spectrometer: Royal Soc. London Proc., v. (A)89,, p. 468-489.

————, 1915, X-rays and crystal structure: Royal Soc. London Trans., v. (A)215, p. 253-274.

Ewald, P. P., and Hermann, C., 1931, Strukturbericht, 1913-28: Leipzig, Akad. Verlag.

Henry, N. F. M., and Lonsdale, K., 1952, International tables for X-ray crystallography, v. 1: Birmingham, Kynoch Press.

Maugin, C., 1923, Reflexion des rayons de Röntgen sur certains plans réticulaires remarquables de la calcite: Acad. sci. Paris Comptes rendus, v. 176, p. 1331-1334.

Olshausen, S. von, 1925, Strukturunterschungen nach der Debye-Scherrer-Methode: Zeitschr. Kristallographie, v. 61, p. 463-514.

Palache, Charles, Berman, Harry, and Frondel, Clifford, 1951, Dana's System of Mineralogy, 7th ed., v. 2: New York, John Wiley & Sons.

Schiebold, E., 1919, Die Verwendung der Lauediagramme zur Bestimmung der Struktur des Kalkspates: Sächs. Akad. Wiss., Math.-phys. Kl., Abh., v. 36, no. 2, p. 68-213.

Wyckoff, R. W. G., 1920, Crystal structures of some carbonates of the calcite group: Am. Jour. Sci., 4th ser., v. 50, p. 317-360.

————, 1948-1951, Crystal structures, v. 1: New York, Interscience Publishers.

Department of Geology
Yale University
New Haven, Connecticut