HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids.* New York: Benjamin.

HOARD, J. L. (1975). *Stereochemistry of Porphyrins and Metalloporphyrins,* edited by K. M. SMITH, pp. 317–380. Amsterdam: Elsevier.

International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2a and 2.3.1, p. 3. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*: Oak Ridge National Laboratory Report ORNL-3794.

KASS, K. & SØRENSEN, A. M. (1973). *Acta Cryst.* B29, 113–120.

KOENIG, D. F. (1965). *Acta Cryst.* 18, 663–673.

LIMINGA, R. (1967). *Acta Chem. Scand.* 21, 1206–1216.

MEYER, E. F. JR (1972). *Acta Cryst.* B28, 2162–2167.

PATTON, R. L. & RAYMOND, K. N. (1969). *Inorg. Chem.* 8, 2426–2431.

PETTERSEN, R. C. (1969). *Acta Cryst.* B25, 2527–2539.

SAYER, P., GOUTERMAN, M. & CONNELL, C. R. (1977). *J. Amer. Chem. Soc.* In the press.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The X-RAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

TEMPLETON, L. K. & TEMPLETON, D. H. (1973). Amer. Cryst. Assoc., Abs. Papers (Summer Meeting), 143.

WRIGHT, D. A. & QUINN, J. D. (1974). *Acta Cryst.* B30, 2132–2138.

Redetermination of the Structure of β-Dicalcium Silicate

BY K. H. JOST, B. ZIEMER AND R. SEYDEL

Zentralinstitut für Anorganische Chemie der Akademie der Wissenschaften der DDR, Rudower Chaussee 5, 1199 Berlin, Germany (DDR)

The structure of β-Ca$_2$SiO$_4$ [first determined by Midgley, *Acta Cryst.* (1952), 5, 307–312] has been redetermined on the basis of three-dimensional diffractometer data. In spite of a systematic error in indexing in the original work, the new result confirms the principles of the previous determination. In the second part of the paper a hypothesis on the structural background of hydraulic activity of calcium silicates is discussed. High coordination of Ca by Ca, low mean Ca–Ca distances within these polyhedra and the sharing of faces of neighbouring CaO$_x$ polyhedra seem to be characteristic features of hydraulically active compounds.

Introduction

The structure of β-Ca$_2$SiO$_4$ was determined more than 20 years ago by Midgley (1952) from $hk0$, $h0l$ and $0kl$ data within the limits of the Cu sphere. The structure was later refined by Cruickshank (1964) with the same set of intensity data. In the results the strong distortion of the SiO$_4$ tetrahedron is particularly striking. Therefore, and because β-Ca$_2$SiO$_4$ is now the only Portland cement mineral whose structure is not known accurately,* we have examined it with new experimental data. An error in indexing – all hkl and $hk\bar{l}$ were interchanged – was found to be the reason why Midgley could not obtain a reliable result. That the main features of the former structure are correct, in spite of this error, is due to the relatively small deviation of the monoclinic angle in β-Ca$_2$SiO$_4$ from 90°.

---

* The structure of an alite remains unknown but Golovastikov, Matveyeva & Belov (1975) have determined the structure of pure tricalcium silicate, $Ca_3O(SiO_4) = Ca_3SiO_5$.

Crystallographic data and intensity measurement

Crystallographic and intensity measurement data are in Tables 1 and 2.

In the measurement of the intensities it had to be taken into account that the $hk0$ reflexions of both twin orientations obscure one another and, because of the lattice dimensions, the reflexions $hk,10$ and 11 are in the immediate neighbourhood of $h + 1,k,10$ and 11 re-

Table 1. *Crystallographic data*

Substance:	β-Dicalcium silicate, grown at 1300°C from a CaCl$_2$ melt without addition of stabilizing reagents
Symmetry:	Monoclinic, space group $P2_1/n(C_{2h}^5)$
Cell parameters:	$a = 5.502 \pm 0.001$; $b = 6.745 \pm 0.001$; $c = 9.297 \pm 0.001$ Å; $\beta = 94.59 \pm 0.02°$ $V = 343.9$ Å^3; $Z = 4$; $D_x = 3.326$ g cm^{-3} at 20°C
Remarks:	All crystals twinned on (100)

Table 2. *Intensity measurement*

Crystal investigated:	Cube-like with edge length 0·1 mm, twin on (100)
Instrument:	Hilger four-circle diffractometer
Radiation:	Mo $K\alpha$, graphite-monochromated
Measurement:	$\omega/2\theta$ scan; for reflexions with $\theta \le 5°$: ω scan
Range:	$\theta \le 30°$, corresponding to 995 reflexions, 859 of which were observed
Intensity correction:	Lorentz–polarization, no absorption

spectively of the twin orientation. Trials showed that the resolution was good enough for these reflexions to be approximately resolved. For scaling the $hk0$ intensities in such a case it is necessary to know the volume ratio of the twin orientations in the crystal. Hence the intensities of some equally indexed reflexions in the two orientations were measured, the ratios of these pairs of intensities were calculated and the mean value of these was assumed to be the volume ratio.

Structure determination

Refinement started with the coordinates determined by Midgley (1952) but with $(1 - z)$ instead of z because of the above mentioned error in indexing. With the 895 reflexions used in refinement [9 × 9 blocks, weight given by counting statistics, scattering factors from *International Tables for X-ray Crystallography* (1962)] a final residual of $R = 0.048$ was reached; with all 995 reflexions $R = 0.059$. Atomic parameters are given in Table 3.* A final difference map showed no maxima or minima higher than $1.3\sigma(\rho_o - \rho_c)$.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32357 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Description of the structure

The SiO$_4$ *tetrahedron*

Interatomic distances and valence angles within the SiO$_4$ group are given in Tables 4 and 5. In addition the interatomic distances found by Midgley (1952) and Cruickshank (1964) in β-Ca$_2$SiO$_4$ and by Czaya (1971) in γ-Ca$_2$SiO$_4$ are given for comparison. It can be seen that the SiO$_4$ tetrahedron is normal. The relatively short distance between Si and O(1) in comparison with those involving O(2), O(3) and O(4) is easily explained by the less frequent participation of O(1) in the CaO$_x$ poly hedra. The mean Si—O distance is 0·02 Å shorter in β-Ca$_2$SiO$_4$ than in γ-Ca$_2$SiO$_4$. This may be due to the longer Ca—O distances in β-Ca$_2$SiO$_4$ which allow a better overlap of Si and O orbitals.

Table 4. Si—O *distances*

The standard deviations for the values in the present work are 0·006 Å.

	Distances in β-Ca$_2$SiO$_4$		Distances in γ-Ca$_2$SiO$_4$
	(this work)	(Midgley/Cruickshank)	(Czaya)
Si—O(1)	1·61 Å	1·61 Å	1·63 Å
Si—O(2)	1·63	1·51	1·65
Si—O(3)	1·64	1·67	1·66
Si—O(4)	1·65	1·70	1·66
$\langle$Si—O$\rangle$	1·63	1·62	1·65

Table 5. *Edge lengths and valence angles in the* SiO$_4$ *tetrahedron*

The standard deviations are 0·007 Å and 0·3°.

Edge lengths		Valence angles	
O(1)—O(5)	2·67 Å	O(1)—Si—O(2)	111·0°
O(1)—O(3)	2·65	O(1)—Si—O(3)	109·4
O(1)—O(4)	2·69	O(1)—Si—O(4)	111·5
O(2)—O(3)	2·71	O(2)—Si—O(3)	111·8
O(2)—O(4)	2·69	O(2)—Si—O(4)	110·2
O(3)—O(4)	2·57	O(3)—Si—O(4)	102·8
$\langle$O—O$\rangle$	2·66	$\langle$O–Si–O$\rangle$	109·5

Table 3. *Atomic parameters with the standard deviations in multiples of the last decimal in parentheses*

The temperature factor is: $\exp[(-B_{11}h^2 - \cdots - B_{23}kl - \cdots) \times 10^{-4}]$.

|	x	y	z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}	B_{iso}
Ca(1)	0·2738 (2)	0·3428 (2)	0·5694 (2)	31 (4)	13 (2)	16 (1)	0 (3)	3 (3)	1 (5)	0·38
Ca(2)	0·2798 (2)	0·9976 (2)	0·2981 (2)	31 (3)	14 (2)	8 (1)	−3 (3)	−3 (3)	11 (5)	0·30
Si	0·2324 (3)	0·7814 (2)	0·5817 (2)	24 (5)	5 (3)	6 (2)	−1 (4)	3 (4)	−1 (7)	0·19
O(1)	0·2864 (10)	0·0135 (8)	0·5599 (6)	114 (17)	16 (9)	32 (6)	−22 (14)	26 (15)	−6 (22)	0·91
O(2)	0·0202 (9)	0·7492 (8)	0·6919 (6)	75 (16)	25 (9)	19 (5)	8 (12)	1 (14)	0 (20)	0·67
O(3)	0·4859 (9)	0·6682 (8)	0·6381 (5)	48 (14)	44 (10)	16 (5)	13 (12)	22 (13)	58 (21)	0·63
O(4)	0·1558 (9)	0·6710 (8)	0·4264 (5)	40 (14)	50 (10)	13 (5)	−25 (12)	−20 (13)	17 (21)	0·62
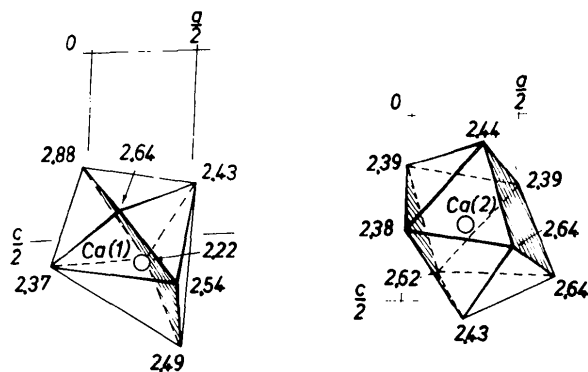
Fig. 1. Oxygen polyhedra of the cations. The Ca—O distances in Å are set near the oxygen positions. Their standard deviations are 0·006 Å, their mean values are ⟨Ca(1)—O⟩ 2·51, ⟨Ca(2)—O⟩ 2·50 Å.

The CaO$_x$ polyhedra

The two symmetrically unrelated CaO$_x$ polyhedra are shown in Fig. 1. All O atoms within a sphere of radius 2·88 Å around a Ca atom are assumed to belong to the Ca coordination sphere. O atoms outside this sphere are at distances greater than 3·14 Å from the Ca. Ca(1) is surrounded by seven O atoms which form a distorted pentagonal bipyramid. Its equatorial plane is parallel to (10$\bar{1}$). Ca(2) has eightfold coordination, its polyhedron being a distorted anticube. It is worth mentioning that the mean Ca—O distances in the two polyhedra are nearly equal in spite of the different coordination numbers.

The structure as a whole

A projection of the structure is shown in Fig. 2. As is expected for the high Ca : Si ratio, the CaO$_x$ polyhedra are three-dimensionally connected. They are most dense-
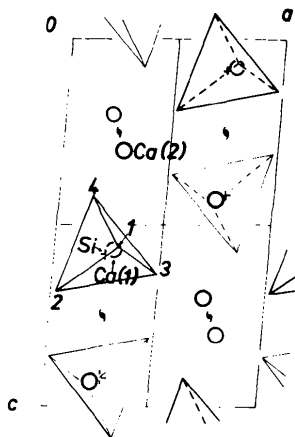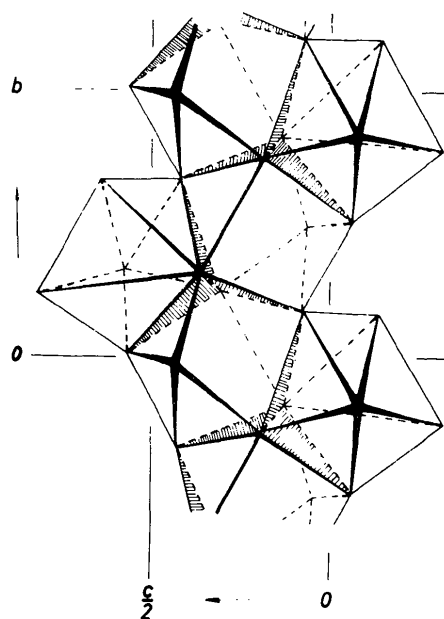

Fig. 3. Column-like structural unit made up of CaO$_x$ polyhedra. Common faces are hatched: for details see text.

ly packed in columns parallel to [010] (Fig. 3). These are built by the Ca(2) anticubes along the 2_1 axis which are connected at common triangle faces. To this nucleus are connected — also by triangle faces — the bipyramids around Ca(1). The columns are joined to each other by edges and corners only.

In the paper by Midgley (1952) special attention is drawn to the very short distance between two O(1) atoms [2·35 Å (Midgley), 2·39 Å (Cruickshank)]. This distance is now 2·68 Å, a short but not unusual value.

Properties of β-Ca$_2$SiO$_4$

Stability

Five modifications of Ca$_2$SiO$_4$ are known. The crystals with which this paper is concerned were grown in the stability range of the α'_H modification. During cooling this transforms displacively via α'_T to β, at which point twinning occurs (Saalfeld, 1967; Worzala, 1972). During further cooling at about 400–500°C, β-Ca$_2$SiO$_4$ transforms reconstructively to γ-Ca$_2$SiO$_4$. The $\beta \rightarrow \gamma$ transformation does not occur if certain extraneous oxides are dissolved in the crystals (Schwiete, Krönert & Deckert, 1968), but an excess of dissolved CaO is also thought to act as a stabilizer. Likewise, crystals which are built of relatively small blocks should not transform to the γ modification (Yannaquis & Guinier, 1959).

The crystal investigated was synthesized without any stabilizer and in an earlier investigation of other Ca

Fig. 2. The β-Ca$_2$SiO$_4$ structure, projected along the y axis. O Ca, + Si, O atoms at the corners of the tetrahedra.

silicate crystals grown in a $CaCl_2$ melt it has been shown that neither Cl nor Pt (from the crucible) was incorporated in the crystals. Whether our β-Ca_2SiO_4 crystal contains more than the stoichiometric amount of CaO [about 1% according to Yannaquis & Guinier (1959)] cannot be decided by the investigations undertaken. But this probable excess can only be equivalent to a deficit of SiO_2 because there is no space in the structure for additional CaO. As to the question of mosaic size, we remark that the crystal investigated did not consist of small blocks because some of its reflexions are weakened by extinction ($|F_o|$ values of 200, 10$\bar{3}$, 103, 30$\bar{3}$, 400 are smaller than $|F_c|$ values by 28% on average). Therefore the structure analysis presented here gives no indication as to the origin of the stability.

Hydraulic properties

The most obvious property of β-Ca_2SiO_4 is its hydraulic activity.* Indeed this is much lower than that of Ca_3SiO_5, but in cement mortars it leads to a noticeable increase in strength in the first 1–2 years after making up the mortar.

---

* In cement chemistry substances are called 'hydraulically active' when a set paste or mortar, made of them with water, hardens during storage under water. One necessary condition for this process is that such substances react with water with sufficient velocity and it is only this condition with which we are concerned in our paper. With respect to the velocity of the reaction with water the hydraulic activity is said to be high or low. The second condition for hydraulic activity, the insolubility of the reaction products in water, is fulfilled in the case of Ca silicates, for which the hydrated compounds are mainly formed by a 'through-solution' mechanism.

The result of the present structure analysis gives no convincing reasons for the hydraulic activity, but a comparison with the structures of other calcium silicates seems worth while. For this purpose some structural parameters of both hydraulically active and inactive compounds are compared in Table 6. Other compounds well suited for comparison would be α'-Ca_2SiO_4, pseudowollastonite, $Ca_3Si_3O_9$, and rankinite, $Ca_3Si_2O_7$, but for these no precise structural data exist.

When we first compare β-Ca_2SiO_4 and γ-Ca_2SiO_4 we find, besides common features, distinct differences also. Common features are the undistorted SiO_4 tetrahedra and the strongly distorted CaO_x polyhedra. Therefore distortion of the coordination polyhedra should have no influence or only a subordinate one on hydraulic activity.

Smith, Majumdar & Ordway (1965) have drawn special attention to the differences in Ca—O distances in both structures and discussed these as a reason for the different hydraulic properties. The authors presume that during hydration Ca—O bonds must be split and that this should be easier with the longer bonds in β-Ca_2SiO_4 than in γ-Ca_2SiO_4. But this can be no general criterion, as can be seen from the few compounds included in Table 6. According to the above presumption, high-pressure pseudowollastonite and β-Ca_2SiO_4 should react faster than tricalcium silicate, and CaO should not react with water, but such conclusions are in opposition to facts.

A further, in our opinion essential, difference between β-Ca_2SiO_4 and γ-Ca_2SiO_4 consists in the kind of connexion of the CaO_x polyhedra. Whereas in γ-Ca_2SiO_4 these are connected only by common edges and corners, in β-Ca_2SiO_4 there are, in addition, common faces. In spite of the fact that in this case Paul-

Table 6. *Structural characteristics of some calcium silicates and their hydraulic activity (distances in Å)*

Substance	Hydraulically active	CaO$_x$ polyhedra Coordination number	CaO$_x$ polyhedra Mean value (Ca—O)	Connexion of CaO$_x$ polyhedra by common faces	Ca—Ca distances Mean value (<4 Å)	Ca—Ca distances Shortest distance	Number of Ca neighbours of Ca atoms (<4 Å)	Ca density (g cm^{-3})
CaO		6	2·40	No	3·40	3·40	12	2·42
Ca$_3$SiO$_5$	Yes	48 (×6) 6 (×7)	2·43	Yes	3·47	3·16	42 (×8) 12 (×7)	1·64
β-Ca$_2$SiO$_4$	Yes	1 (×7) 1 (×8)	2·50	Yes	3·58	3·43	17	1·55
γ-Ca$_2$SiO$_4$	No	6	2·37	No	3·75	3·38	1 (×8) 1 (×6)	1·38
Kilchoanite Ca$_6$(SiO$_4$)Si$_3$O$_{10}$^{a}	No	5 (×6) 1 (×8)	2·39	No	3·71	3·60	2 (×6) 2 (×4) 1 (×3) 1 (×1)	1·25
Wollastonite (CaSiO$_3$)$_x$^{b}	No	6	2·39	No	3·62	3·59	1 (×6) 2 (×4)	0·95
High-pressure pseudowollastonite (CaSiO$_3$)$_3$^{c}	No	2 (×6) 1 (×8)	2·50	No	3·71	3·62	1 (×5) 2 (×4)	1·05

References: (a) Taylor (1971), (b) Trojer (1968), (c) Trojer (1969).

ing's third rule is not applicable without further considerations (because Ca^{2+} is not a small cation and the coordination numbers and shapes of the coordination polyhedra are different), the following observation, which is the basis of this rule, must be taken into account: Approach of cations makes a structure less stable. Therefore we checked whether there is a connexion between shortening of Ca—Ca distances and increase of reactivity with water. For this purpose, for every symmetrically independent Ca atom the distances <4 Å to the neighbouring Ca atoms and also their mean values within the unit cell were calculated. The shortest and the mean values of the Ca—Ca distances and the number of Ca neighbours of Ca atoms in one unit cell are given in Table 6.

Apart from CaO, which is a special and limiting case, the silicate with the highest hydraulic activity, Ca_3SiO_5, has not only the shortest individual Ca—Ca distance but also the lowest mean value. In our opinion the mean distance should be given more weight than the shortest in the evaluation of the reactivity with water. In accordance with this the mean Ca—Ca distance in the hydraulically active $β$-Ca_2SiO_4 is distinctly shorter than in $γ$-Ca_2SiO_4 and the other inactive compounds included in Table 6. Furthermore, in all the inactive compounds there is no connexion of CaO_x polyhedra by common faces in contrast to the active compounds Ca_3SiO_5 and $β$-Ca_2SiO_4. Finally the number of Ca neighbours of Ca atoms (at distances less than 4 Å) is higher in the active than in the inactive compounds.

In summarizing we can say that many and short Ca—Ca distances, and connexion of the CaO_x polyhedra by common faces seem to be the reasons for the hydraulic activity of a calcium silicate. On the question of the difference in hydraulic activity of Ca_3SiO_5 and Ca_2SiO_4 depending on a content of extraneous oxides in solid solution (so called alloying components), it can only be said that these components cause the formation of superstructures and modulated structures (Saalfeld, 1971; Jost, 1973). As yet, it is not possible to decide whether the extraneous ions themselves or their action on the crystal structure are the reason for the differences in the degree of hydraulic activity.

References

CRUICKSHANK, D. W. J. (1964). *Acta Cryst.* 17, 685–686.
CZAYA, R. (1971). *Acta Cryst.* B27, 848–849.
GOLOVASTIKOV, N. I., MATVEYEVA, R. G. & BELOV, N. V. (1975). *Kristallografiya*, 20, 721–729.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
JOST, K. H. (1973). XI. Siliconf., Budapest, Conf. Rep. pp. 331–334.
MIDGLEY, C. M. (1952). *Acta Cryst.* 5, 307–312.
SAALFELD, H. (1967). *Ber. dtsch. keram. Ges.* 44, 279–283.
SAALFELD, H. (1971). *Z. Kristallogr.* 133, 396–404.
SCHWIETE, H. E., KRÖNERT, W. & DECKERT, K. (1968). *Zement-Kalk-Gips*, 21, 359–366.
SMITH, D. K., MAJUMDAR, A. & ORDWAY, F. (1965). *Acta Cryst.* 18, 787–795.
TAYLOR, H. F. W. (1971). *Miner. Mag.* 38, 26–31.
TROJER, F. J. (1968). *Z. Kristallogr.* 127, 291–308.
TROJER, F. J. (1969). *Z. Kristallogr.* 130, 185–192.
WORZALA, H. (1972). II. Silichem., Brno/CSSR, Rep. pp. 185–197.
YANNAQUIS, N. & GUINIER, A. (1959). *Bull. Soc. Fr. Minér. Crist.* 82, 126–136.