

The redetermination and refinement of the crystal structure of rhodonite, $(\text{Mn,Ca})\text{SiO}_3$

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With 5 figures

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Auszug

Rhodonit hat die Raumgruppe $P\bar{1}$ und die Gitterkonstanten $a = 7,682 \text{ \AA}$, $b = 11,818 \text{ \AA}$, $c = 6,707 \text{ \AA}$, $\alpha = 92,355^\circ$, $\beta = 93,948^\circ$ und $\gamma = 105,665^\circ$ bei zehn Formeleinheiten in der Elementarzelle. Eine Modellstruktur, gewonnen durch Anwendung einer Minimum-Funktion auf eine Patterson-Funktion $P(xyz)$, wurde bestätigt und verfeinert mittels Fourier-Synthesen und der Methode der kleinsten Quadrate.

Ebenen mit oktaedrisch-koordinierten Kationen wechseln ab mit Ebenen aus tetraedrisch-koordinierten Si-Ionen, die von Ebenen aus O-Ionen in nahezu dichtester Kugelpackung umgeben sind. Die Tetraeder sind zu Ketten mit einer Periode von fünf Tetraedern verbunden. Die Kationen besetzen fünf Komplexe allgemeiner Lage, von denen einer vorzugsweise von Ca-Atomen, ein zweiter von Mg- und Fe-Atomen eingenommen wird. Durch gemeinsame Kanten bilden die Oktaeder Bänder, die parallel zu den SiO_4 -Ketten verlaufen und durch Klüfte aus oktaedrischen Lücken getrennt sind.

Abstract

Rhodonite has space group $P\bar{1}$ and unit-cell parameters $a = 7.682 \text{ \AA}$, $b = 11.818 \text{ \AA}$, $c = 6.707 \text{ \AA}$, $\alpha = 92.355^\circ$, $\beta = 93.948^\circ$, and $\gamma = 105.665^\circ$. A trial structure determined through application of the minimum function to the Patterson function, $P(xyz)$, was improved and refined with Fourier syntheses and least squares.

Planes containing octahedrally coordinated cations alternate with planes of tetrahedrally coordinated Si ions between planes of approximately close-packed oxygen ions. Tetrahedra are linked to form chains with a repeat unit

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of five tetrahedra. Octahedrally coordinated cations occupy five general equi-points, with Ca preferentially distributed in one position, and Mg and Fe in another. Octahedra share edges to form bands extending parallel to the silica chains and separated by a rift of unoccupied octahedrally coordinated sites.

Introduction

Two different structures have been proposed for rhodonite, $(\text{Mn,Ca})\text{SiO}_3$, by the LIEBAU school^{1,2} and by MAMEDOV³. These structures contain the same basic features in that Mn and Ca ions are octahedrally coordinated, with octahedra occurring in discontinuous sheets. Silica tetrahedra are arranged in chains with a repeat unit of five tetrahedra. Both the relative arrangement of octahedra and the relation of the chains to the octahedra are different in each structure, however. Since both structures were proposed using only projections and film-intensity data, and neither was refined to a reasonable *R* factor, they must both be considered provisional.

Unit cell and space group

Unit-cell parameters for rhodonite are listed in Table 1. Rhodonite from Pajsberg, Sweden, kindly provided by Dr. CLIFFORD FRONDEL of Harvard University, was used in this investigation. The unit cell

Table 1. Unit-cell parameters of rhodonite

	MAMEDOV	HILMER <i>et al.</i>	This work "Buerger cell"	This work "Hilmer cell"
<i>a</i>	7.77 Å	6.68 Å	7.6816 ± .0002 Å	6.7073 ± .0004 Å
<i>b</i>	12.20 Å	7.66 Å	11.8180 ± .0004 Å	7.6816 ± .0002 Å
<i>c</i>	6.70 Å	12.20 Å	6.7073 ± .0004 Å	12.2337 ± .0004 Å
α	85° 15'	111.1°	92.355 ± .006°	111.538 ± .002°
β	94° 00'	86.0°	93.948 ± .005°	85.247 ± .005°
γ	111° 29'	93.2°	105.665 ± .004°	93.948 ± .005°
Specimen source	Switzerland	Franklin, N.J.	Pajsberg, Sweden	Pajsberg, Sweden

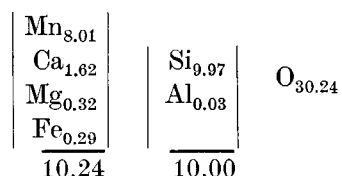
¹ W. HILMER, F. LIEBAU, E. THILO und K. DORNBERGER-SCHIFF, Ein neuer Kettentyp in der Kristallstruktur des Rhodonits $[(\text{Mn,Ca})\text{SiO}_3]_x$. Naturwissensch. **43** (1956) 177–178.

² FRIEDRICH LIEBAU, WALTRAUD HILMER und GERHARD LINDEMANN. Über die Kristallstruktur des Rhodonits $(\text{Mn,Ca})\text{SiO}_3$. Acta Crystallogr. **12** (1959) 182–187.

³ KH. S. MAMEDOV, The crystal structure of rhodonite. Doklady Akad. Nauk Azerb. S.S.R. **16** (1958) 445–450.

chosen for this material is different than that of MAMEDOV and LIEBAU *et al.*, although each cell has two translations in common. The third translation was chosen by MAMEDOV and LIEBAU *et al.* parallel to the two major cleavages, while our choice is consistent with the selection of a reduced unit cell. Unit-cell parameters were refined using an IBM 709/7090 refinement program⁴ with data obtained from three zero-level, back-reflection, precision Weissenberg photographs. The space group is $P1$ or $P\bar{1}$. Since LIEBAU *et al.* reported that a test for piezoelectricity was negative, space group $P\bar{1}$ was assumed to be correct.

Five analyses of Pajsberg rhodonite are tabulated by DOELTER⁵, an average of which was used for our investigation. The following unit-cell contents were calculated using this analysis, the refined cell parameters, and a value for the specific gravity obtained by normalizing the cell contents to 10.00 Si + Al atoms per cell:



The crystal used in the measurement of intensities was a triangular cleavage prism approximately 0.10 mm long with triangular-face edges of lengths 0.12, 0.13, and 0.10 mm. The intensities of 2016 reflections were recorded using the single-crystal Geiger-counter diffractometer and measured by integrating recorded peaks with a planimeter. These data were corrected for graphically determined Lorentz and polarization factors and used to calculate the Patterson function $P(xyz)$. The intensity data were later corrected for absorption using an IBM 709/7090 program⁶. All refinement was carried out with the data in this form.

Preliminary analysis

LIEBAU⁷ has pointed out that the magnitude of the translation parallel to the two principal cleavages of pyroxenes and pyroxenoids is a function of the repeat unit of the chain of silica tetrahedra which

⁴ CHARLES W. BURNHAM, LCLSQ, crystallographic lattice-constant least-squares refinement program. Carnegie Inst. Wash. Yearbook **61** (1962) 132–135.

⁵ C. DOELTER, *Handbuch der Mineralchemie*. (Steinkopff, Dresden and Leipzig, 1912).

extends in that direction. Rhodonite, with a translation of 12.2 Å probably has a repeat unit of five tetrahedra in the proposed chain. In addition, two translations may be chosen with similar relations to the two cleavages (approximately normal to them) in these minerals. These translations are approximately equal to or multiples of a common factor. Thus the overall arrangement of atoms is probably similar in pyroxenes and pyroxenoids. In those structures which are well known this arrangement includes approximately close-packed planes of oxygen atoms and planes of octahedrally coordinated cations (e.g. Ca, Mn, Fe).

The similarity of these structures is further seen in the similar substructures of each. For example, the substructures seen in *c*-axis, zero-level photographs of wollastonite and rhodonite have approximately the same dimensions. The sublattice in projection has the following translations in rhodonite:

$$\begin{aligned} A &= \frac{1}{5} a + \frac{2}{5} b \\ B &= \frac{1}{5} a + \frac{3}{10} b. \end{aligned}$$

The magnitude of *B* is related to chains of edge-sharing octahedra arranged parallel to *B* in wollastonite. Thus rhodonite may also contain such chains oriented parallel to *B*.

Interpretation of the Patterson function

Figure 1 is a projection along *c* of some of the highest peaks of $P(xyz)$. It is clear that this resembles a diagram of a chain of octahedra in which each octahedron shares edges with adjacent octahedra, as proposed above. For simplicity, peaks corresponding to the upper and lower vertices of each octahedron are not shown. Interpeak distances and relative peak heights correspond closely to values predicted for a chain of Mn octahedra. The collection of all such peaks in the full cell defines a plane of octahedra which is parallel to $(\bar{1}11)$.

The structures of other pyroxenes and pyroxenoids have a similar octahedral sheet, as discussed above. In each of these, the planes of cations coincide with planes of inversion centers. If an idealized sheet

⁶ CHARLES W. BURNHAM, Absorption corrections for prismatic crystals and evaluation of end effect. Abstract, 1962 Meeting of the American Crystallographic Society, 19.

⁷ FRIEDRICH LIEBAU, Bemerkungen zur Systematik der Kristallstrukturen von Silikaten mit hochkondensierten Anionen. Z. physik. Chem. **206** (1956) 73–92.

is oriented parallel to $(\bar{1}11)$ in rhodonite, it may be shown that the period between inversion centers of the sheet is the same as that between centers in the unit cell. It was therefore assumed that such an arrangement exists in rhodonite.

Examination of an octahedral sheet shows that there are only two kinds of positions in the plane containing cations where inversion

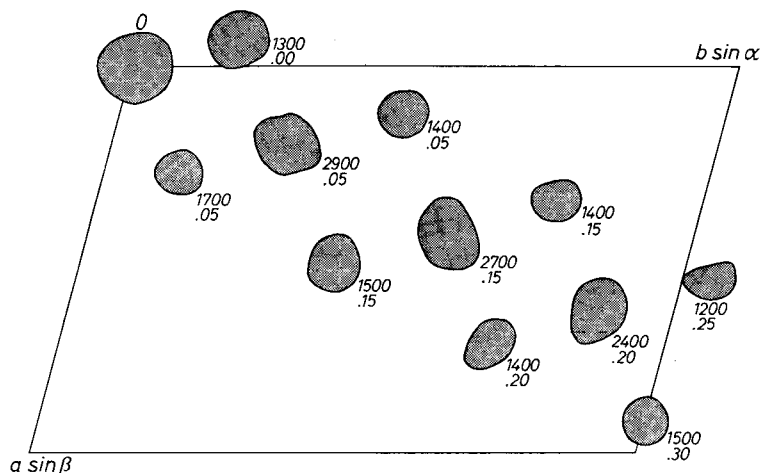


Fig.1. Projection along c of selected peaks of $P(xyz)$. Peaks are labelled with their approximate heights and the level, in 100ths, on which they occur

centers may be placed. These correspond to the center of a shared edge and to the center of an octahedron at a cation position. The Liebau and Mamedov structures differ principally in having these two arrangements respectively.

Test of the Mamedov-type structure

The arrangement of cations with two cations on inversion centers corresponds to the structure determined by MAMEDOV. Minimum-function maps were constructed following prediction of the location of cation-inversion peaks. These failed to yield peaks corresponding to all cations. Structure factors calculated assuming this arrangement, and electron-density syntheses (all syntheses were calculated using the IBM 709/7090 program ERF2⁸), failed to indicate that this atom distribution is correct.

⁸ W. G. SLY, D. P. SHOEMAKER and J. H. VAN DEN HENDE, Two- and three-dimensional crystallographic Fourier summation program for the IBM 7090 computer. (ESSO Research Laboratory, 1962).

Application of the minimum function

The arrangement of atoms where inversion centers lie on the center of shared octahedron edges was investigated in the following way. Inversion peaks corresponding to each of four cations were identified in the Patterson function, $P(xyz)$, and the minimum functions, $M_2(xyz)$, contoured. Two of these were combined to form the function $M_4(xyz)$. The peaks of the asymmetric unit of this function are shown projected along c in Fig. 2. From a consideration of peak heights and interpeak distances, peaks were correlated with atoms, as follows.

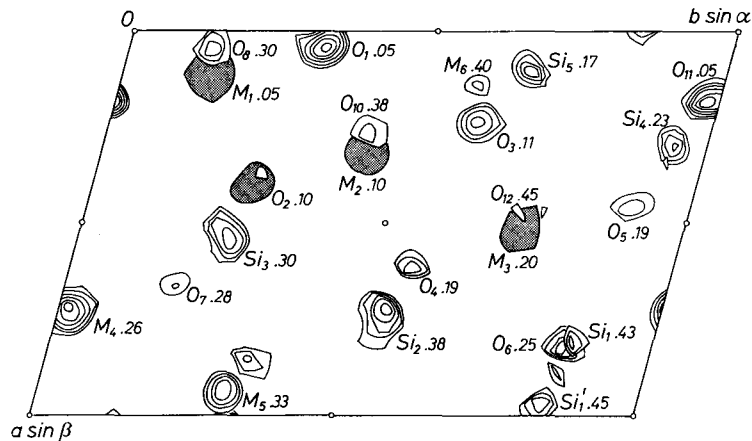


Fig. 2. Peaks of $M_4(xyz)$ projected along c , labelled with the level, in 100ths, on which they appear

Six peaks, labeled $M_1 - M_6$, were identified as possibly corresponding to octahedrally coordinated cations. Since there are only five such cations per asymmetric unit of the unit cell, one peak does not correspond to a cation. The peak labeled M_6 was thought to be false, since it is the smallest of the six. A similar ambiguity occurs with respect to peaks correlated with Si ions. Peaks corresponding to $Si_2 - Si_5$ were easily identified, but the location of Si_1 was uncertain. There are two peaks, labeled Si_1 and Si_1' which may represent the remaining Si ion, of which the peak labeled Si_1' was initially chosen to represent Si_1 . An electron-density synthesis later showed this choice to be incorrect, however. The positions of all but four oxygen atoms were easily determined, as shown in Fig. 2. The locations of the four remaining oxygen atoms ($O_9, O_{13}, O_{14}, O_{15}$) were readily predicted by assuming that silica tetrahedra are linked in a chain.

Refinement

The IBM 709/7090 program SFLSQ2⁹ was used for all structure-factor calculations and least-squares refinement. Values of the form factors were based on an assumption of half-ionization of all atoms. Random distribution of Mn, Ca, Mg and Fe over all five M sites was assumed during the initial stages of refinement and the average cation-scattering function was corrected for the average real component of anomalous dispersion. All isotropic temperature factors were initially assigned a value of 0.5. The program SFLSQ2 contains provisions for weighting and rejecting reflections. The weighting scheme used throughout most of the refinement was a modified version of the scheme recommended by HUGHES¹⁰. The rejection test was initially arranged such that all reflections for which

$$(F_o - F_c)/F_o > 0.5, \text{ and } F_o = 0$$

were eliminated from least-squares calculations.

Several cycles of refinement were executed in which the value of the discrepancy factor, R , decreased very slowly from an initial value of 62% to 41%. This slow convergence appeared to indicate that either refinement was not being properly executed, or that some features of the structure were incorrect. Therefore several cycles were executed with the weighting scheme changed to one of equal weighting and the rejection test altered such that no reflections were rejected or both. In addition, since the scale factor was refining to a value not consistent with a calculated value, it was held constant in some cycles. None of these factors appreciably altered the speed of convergence.

Several tests were then made of the validity of the structure. These included; 1. Calculation of Bunn error syntheses. 2. Calculation of difference syntheses. 3. Refinement of isotropic temperature factors. These all indicated that the structure was basically correct. A final difference synthesis indicated corrections should be made in the positions of O_{11} , O_{12} , M_4 and M_5 . The value of R decreased to 35% with the introduction of these changes.

⁹ C. T. PREWITT, SFLSQ2, an IBM 7090 program for least-squares refinement. PhD thesis, M.I.T. (1962).

¹⁰ E. W. HUGHES, The crystal structure of melamine. *J. Amer. Chem. Soc.* **63** (1941) 1737–1752.

Refinement progressed satisfactorily in the ensuing cycles, during which the modified Hughes weighting scheme was used and a rejection test used which rejected all reflections for which

$$\frac{F_o - F_c}{F_o} > 0.6 \text{ and } F_o = 0.$$

Convergence was nearly complete when R had decreased to a value of 12% (R computed using only data for which $F_o > 0$). An attempt was therefore made to determine if Ca, Mn, Mg and Fe were ordered. Structure factors computed for 1620 reflections for which $F_o > 0$ were used in the computation of the difference synthesis, $\Delta\rho(xyz)$. The only major features of this function were peaks at the positions of M_1 , M_2 , M_3 , M_4 and M_5 , the heights of which are listed in Table 2. The peak heights of M_1 , M_2 and M_3 are all positive and approximately equal. Since Mn ions have more electrons than the average ion used in the refinement, this suggests that Mn occupies these positions. Similar considerations suggest that Mg and Fe occupy position M_4 , with Mn, and all Ca occupies position M_5 , with Mn.

Table 2. Peak heights at cation positions of $\Delta\rho(xyz)$, and M—O interatomic distances

Cation	Peak height in $\Delta\rho(xyz)$	Average M—O distance	Interpretation of ordering
M_1	175	2.27 Å	Mn
M_2	145	2.18	Mn
M_3	193	2.24	Mn
M_4	— 65	2.32	Mn+Fe+Mg
M_5	— 418	2.43	Mn+Ca

Average M—O distances for M_1 , M_2 and M_3 (Table 2) were between 2.18 and 2.27 Å, in good agreement with Mn—O distances of other structures. Average distances for M_4 and M_5 are greater than those for M_1 , M_2 and M_3 , that of M_5 being the largest (2.43 Å). Since Ca is the largest cation present, this indicates that most, if not all, of the Ca occupies site M_5 . The average M_4 —O distance is large only because one of the six distances for which the average was computed is very large. Two M_4 —O distances are among the smallest of all M—O distances. This indicates that Fe and Mg, the smallest cations present, occupy this position. The interatomic distances thus verify the conclusions concerning cation ordering reached on a basis of the peaks of $\Delta\rho(xyz)$. Mn occupies the positions M_1 , M_2 and M_3 , Mg and Fe the position M_4 , Ca the position M_5 , with the remaining Mn at M_4 and M_5 .

Table 3. Observed and final calculated structure factors of rhodnite

Table with 27 columns: h, k, l, |Fo|, |Fc|, h, k, l, |Fo|, |Fc|, h, k, l, |Fo|, |Fc|, h, k, l, |Fo|, |Fc|. It lists observed and calculated structure factors for various hkl reflections of rhodnite. The table is organized into seven groups of three columns each.

Table 4. *Refined coordinates and isotropic temperature factors (above), and coordinates of LIEBAU et al. transformed to our cell (below)*

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
M 1	.8819	.0002	.8517	.0002	.9697	.0003	.68	.05
Kat. 3	.963		.839		.998			
M 2	.6827	.0002	.5548	.0002	.8748	.0003	.75	.05
Kat. 1	.710		.567		.875			
M 3	.4916	.0002	.2700	.0002	.8109	.0003	.64	.05
Kat. 2	.505		.309		.734			
M 4	.3018	.0003	.9767	.0002	.7967	.0004	.65	.05
Kat. 4	.273		1.003		.700			
M 5	.0457	.0003	.6938	.0002	.6389	.0004	.93	.06
Kat. 5	.107		.730		.615			
Si 1	.2191	.0004	.1246	.0003	.4956	.0006	.24	.07
Si 3	.145		.105		.533			
Si 2	.2687	.0004	.4701	.0003	.6375	.0006	.29	.07
Si 1	.281		.462		.611			
Si 3	.4610	.0004	.7393	.0002	.7092	.0005	.12	.07
Si 2	.541		.778		.743			
Si 4	.7446	.0004	.0891	.0003	.7538	.0006	.32	.07
Si 4	.728		.059		.794			
Si 5	.9263	.0004	.3466	.0002	.8450	.0005	.19	.07
Si 5	.943		.338		.864			
O 1	.9544	.0011	.6772	.0007	.9628	.0014	.60	.19
O 15			.643		.971			
O 2	.6011	.0011	.7312	.0007	.8955	.0014	.49	.19
O 7			.734		.912			
O 3	.7485	.0011	.3895	.0007	.8858	.0013	.74	.20
O 3			.398		.626			
O 4	.3981	.0011	.4375	.0007	.8074	.0015	.65	.19
O 1			.453		.802			
O 5	.5485	.0011	.0975	.0007	.8053	.0015	.86	.20
O 12			.129		.828			
O 6	.1970	.0010	.1318	.0007	.7374	.0014	.36	.18
O 8			.141		.766			
O 7	.3218	.0011	.8149	.0007	.7438	.0015	.65	.19
O 6			.874		.749			
O 8	.9337	.0010	.8524	.0006	.6591	.0014	.33	.19
O 9			.882		.627			

Table 4 (Continued)

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
O 9	.2560	.0010	.9962	.0006	.4459	.0013	.17	.17
O 11			.998		.451			
O 10	.7457	.0012	.5871	.0008	.5846	.0016	1.16	.21
O 2			.576		.590			
O 11	.8430	.0011	.0414	.0007	.9433	.0015	.53	.19
O 10			.000		.942			
O 12	.5819	.0010	.7790	.0006	.5154	.0014	.25	.18
O 5			.739		.530			
O 13	.3191	.0010	.6142	.0006	.6300	.0014	.37	.18
O 4			.641		.665			
O 14	.0546	.0011	.4360	.0007	.7006	.0014	.45	.18
O 14			.364		.599			
O 15	.8607	.0010	.2221	.0007	.7024	.0014	.33	.18
O 13			.209		.790			

by transforming the origin of LIEBAU *et al.* by adding $1/2$ to all x coordinates and $1/2$ to the z coordinates of only Kat_{1-5} and Si_{1-5} , before transforming all coordinates to the Buerger-type cell used in our investigation. The former transformation is different from that reported by LIEBAU *et al.*¹¹ to give correct coordinates for their determination, but it was the only change which yielded satisfactory correspondence of coordinates.

Description of the rhodonite structure

Peaks of $\rho(xyz)$, computed using data based on the refined coordinates, are shown in Fig. 3 projected along c . Only those peaks from $z = 1/2$ to $z = 1$ are shown. Several peaks of high electron density are represented by shaded rather than contoured peaks. Figure 4 is an interpretation of the corresponding projection $\rho(x, y)$, and Fig. 5 is an interpretation of the projection $\rho(x'z')$, where x' and z' are coordinates referred to the Hilmer-type cell.

The structure, at least in major features, is similar to the structure proposed by HILMER *et al.* and LIEBAU *et al.* Planes of approximately close-packed oxygen ions are arranged parallel to $(\bar{1}11)$. Planes of Mn, Ca, Mg and Fe ions in octahedral coordination alternate between

¹¹ F. LIEBAU, W. HILMER und G. LINDEMANN, Über die Kristallstruktur des Rhodonits $(\text{Mn,Ca})\text{SiO}_3$. Acta Crystallogr. 15 (1962) 622.

planes of oxygen ions with planes of Si ions in tetrahedral coordination. Tetrahedra each share two vertices with other tetrahedra to form a chain extending parallel to $[101]$. This chain has a repeat unit of five tetrahedra.

Coordination polyhedra of M_1 , M_2 , M_3 and M_4 approximate octahedra, that of M_5 is irregular with seven-fold coordination. These

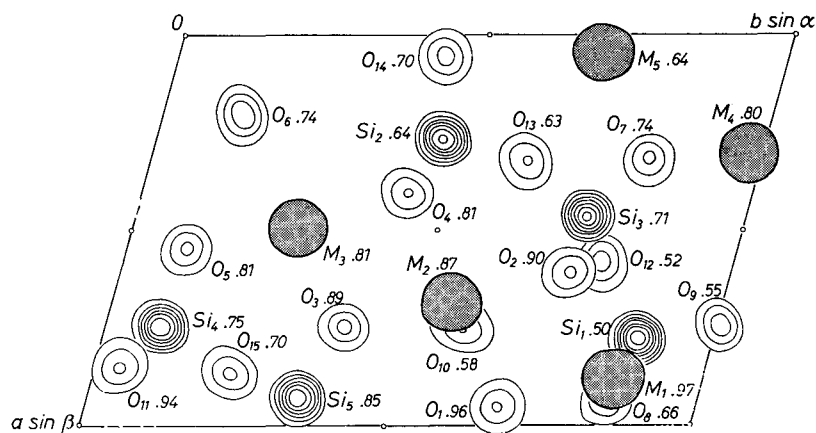


Fig. 3. Peaks of $\rho(xyz)$ projected along c . Only peaks in the asymmetric unit, from $z = 1/2$ to 1, are shown. Large M peaks are shaded in

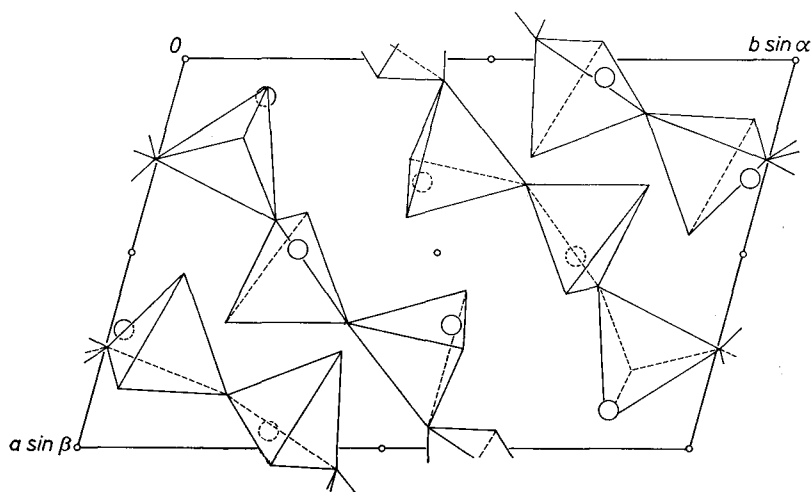


Fig. 4. Interpretation of the structure of rhodonite, projected along c . Large cations and Si-coordination tetrahedra are shown

polyhedra share edges to form chains ten polyhedra long, similar to the infinitely long chains found in wollastonite. Such chains are linked through further edge sharing in a staggered manner to form bands of linked octahedra extending parallel to $[101]$, parallel to the chains of tetrahedra. A rift of unoccupied octahedrally coordinated sites separates adjacent bands.

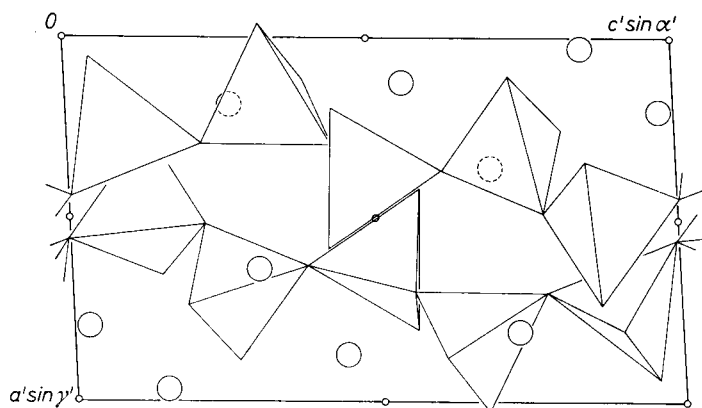


Fig. 5. Interpretation of $\rho(x'z')$ where x' and z' are coordinates related to the Hilmer-type unit cell. Large cations and Si-coordination tetrahedra are shown

Interatomic distances

Cation-oxygen interatomic distances are listed in Table 5. The M—O distances reflect the ordering of Mn, Ca, Mg, and Fe noted above, i.e. the average M—O distances for M_1 , M_2 and M_3 are similar, lying between 2.215 Å and 2.228 Å. Since these distances correspond closely to other published average Mn—O distances (e.g. 2.203 and 2.245 Å in bustamite¹²) it is probable that Mn occupies these positions. In addition, individual M_1 , M_2 and M_3 distances are all close to the average values for these polyhedra, indicating that the polyhedra are regular.

Distances for M_4 are irregular however. Three of the six distances are small (< 2.13 Å), indicating that Mg and Fe are in this position, with Mn. The M_4 — O_8 distance (2.88 Å) is exceptionally large however. This shows that the coordination of M_4 actually approaches only five oxygen atoms.

¹² D. R. PEACOR and M. J. BUERGER, Determination and refinement of the crystal structure of bustamite $\text{CaMnSi}_2\text{O}_6$. *Z. Kristallogr.* **117** (1962) 331–343.

Table 5. *Cation-oxygen interatomic distances*

Mn ₁ -O ₁	2.27 ₆ Å	Mn ₂ -O ₁	2.21 ₉ Å
O ₂	2.24 ₉	O ₂	2.33 ₅
O ₆	2.11 ₂	O ₃	2.14 ₉
O ₈	2.14 ₈	O ₄	2.25 ₃
O ₁₁	2.35 ₃	O ₄	2.26 ₆
O ₁₁	2.17 ₅	O ₁₀	2.06 ₅
Average	2.219	Average	2.215
Mn ₃ -O ₂	2.13 ₉ Å	Mn ₄ -O ₅	2.03 ₇ Å
O ₃	2.10 ₇	O ₆	2.23 ₁
O ₄	2.28 ₂	O ₇	1.97 ₈
O ₅	2.19 ₆	O ₈	2.87 ₈
O ₆	2.41 ₁	O ₉	2.38 ₆
O ₁₂	2.33 ₃	O ₁₁	2.12 ₀
Average	2.228	Average	2.272
		Average, excluding O ₈ ,	2.150
Mn ₅ -O ₁	2.32 ₉	Si ₁ -O ₆	1.64 ₄
O ₇	2.26 ₀	O ₃	1.59 ₉
O ₈	2.26 ₇	O ₉	1.64 ₁
O ₁₀	2.30 ₄	O ₁₂	1.65 ₀
O ₁₃	2.52 ₆	Average	1.634
O ₁₄	2.63 ₅	Si ₃ -O ₂	1.61 ₆
O ₁₅	2.60 ₅	O ₇	1.59 ₀
Average	2.418	O ₁₂	1.66 ₀
Si ₂ -O ₄	1.58 ₉	O ₁₃	1.62 ₄
O ₁₀	1.59 ₃	Average	1.623
O ₁₃	1.64 ₆	Si ₅ -O ₁	1.60 ₈
O ₁₄	1.67 ₃	O ₃	1.61 ₆
Average	1.625	O ₁₄	1.63 ₃
Si ₄ -O ₅	1.59 ₆	O ₁₅	1.65 ₆
O ₉	1.64 ₀	Average	1.628
O ₁₁	1.63 ₃		
O ₁₅	1.64 ₉		
Average	1.630		

The M₅ polyhedron is an irregular one with seven oxygen ions, and is unusual in that distances involving O₁, O₇, and O₈ and O₁₀ (each coordinated to one Si ion and two or three M ions) are all less than 2.34 Å, while distances involving O₁₃, O₁₄ and O₁₅ (each coordinated to two Si ions and one M ion) are all greater than 2.52 Å. The high average M₅-O distance (2.42 Å) and the irregular coordination clearly support the conclusion reached above that Ca occupies

this position, with some Mn. Since the other four positions do not contain Ca, this explains why rhodonite may contain up to, but no more than, about 20% Ca relative to Mn, Mg, and Fe. LIEBAU *et al.* reached a different conclusion concerning ordering based on less conclusive evidence.

Table 6. *Oxygen-oxygen interatomic distances of silica tetrahedra*
Distances corresponding to shared edges are set in bold-faced type

Si ₁ tetrahedron			
O ₆	O ₈ 2.81 Å	O ₉ 2.61 Å	O ₁₂ 2.54 Å
O ₈		2.68	2.70
O ₉			2.61
Si ₂ tetrahedron			
O ₄	O ₁₀ 2.75 Å	O ₁₃ 2.64 Å	O ₁₄ 2.68 Å
O ₁₀		2.63	2.58
O ₁₃			2.59
Si ₃ tetrahedron			
O ₂	O ₇ 2.75 Å	O ₁₂ 2.64 Å	O ₁₃ 2.72 Å
O ₇		2.71	2.45
O ₁₂			2.59
Si ₄ tetrahedron			
O ₅	O ₉ 2.72 Å	O ₁₁ 2.65 Å	O ₁₅ 2.61 Å
O ₉		2.65	2.62
O ₁₁			2.71
Si ₅ tetrahedron			
O ₁	O ₃ 2.75 Å	O ₁₄ 2.67 Å	O ₁₅ 2.63 Å
O ₃		2.67	2.65
O ₁₄			2.57

All silica tetrahedra are regular, as can be seen from the Si—O distances listed in Table 5, and the O—O distances of Table 6. The average O—O distance is 2.65 Å, individual distances varying from this by no more than 0.20 Å. All Si—O distances are close to values found in other well refined silicate structures. The average of all Si—O

distances (1.628 Å) is close to the value predicted by SMITH and BAILEY¹³ for metasilicates (1.623 Å) and to those in bustamite (1.623 Å) and wollastonite (1.626 Å¹⁴), which have comparable structures.

Conformity of the rhodonite structure to PAULING's rules

Oxygen ions are of three types: *A*. those coordinated to two Si ions and one M ion; *B*. those coordinated to one Si ion and three M ions; *C*. those coordinated to one Si ion and two M ions. If all M ions are considered to be octahedrally coordinated, each M—O bond has strength 1/3, while each Si—O bond has strength 1. Thus all type-*A* oxygen ions receive an excess bond strength of 1/3, those of type *B* are exactly satisfied, and those of type *C* have a deficiency of 1/3. This is compensated, in general, by a lengthening of cation-oxygen bonds involving type-*A* oxygen ions and a contraction of bonds involving type-*C* oxygen ions. For example, the average Si—O distances for bonds of types *A*, *B* and *C* are 1.648, 1.615, and 1.599 Å respectively. A similar situation exists with M—O bond lengths, for which the averages are 2.48, 2.28 and 2.14 Å respectively.

There are five edges shared between tetrahedra and M polyhedra in rhodonite. The O—O distances corresponding to the shared edges are set in bold-faced type in Table 6. The sharing results in the expected contraction in such edges. For example, the average length of all tetrahedra edges is 2.65 Å, while the longest shared edge is 2.61 Å.

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¹³ J. V. SMITH and S. W. BAILEY, Second review of Al—O and Si—O tetrahedral distances. *Acta Crystallogr.* **16** (1963) 801—811.

¹⁴ D. R. PEACOR and C. T. PREWITT, Comparison of the structures of bustamite and wollastonite. *Amer. Mineral.* **48** (1963) 588—597.