

THE CRYSTAL STRUCTURE OF WALSTROMITE

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ABSTRACT

The crystal structure of walstromite, $\text{Ca}_2\text{BaSi}_3\text{O}_9$, has been determined by X-ray structure analysis using two-dimensional data. It contains $(\text{Si}_3\text{O}_9)^{6-}$ rings; the coordination of the divalent cations is highly irregular

INTRODUCTION

Walstromite from Fresno County, California was described by Alfors, Stinson, Matthews and Pabst (1965), who showed it to be the same phase as the synthetic $\text{Ca}_2\text{BaSi}_3\text{O}_9$ prepared by Eskola (1922). Glasser and Glasser (1961) had studied the synthetic material and defined a triclinic unit cell. In the study of walstromite, Pabst chose a different setting, and gave the appropriate transformation matrices. The structure is more readily described in terms of Pabst's setting, and this is the one used here.

EXPERIMENTAL

A small equant grain of synthetic $\text{Ca}_2\text{BaSi}_3\text{O}_9$ was used for data collection. The unit cell obtained agreed well with that for the natural mineral. It is given below; Pabst's values for the natural mineral are quoted in parentheses.

$$\begin{aligned} a &= 6.73_3 (6.743 \pm 0.005) \text{ \AA} & \alpha &= 69^\circ 37' (69^\circ 51') \\ b &= 9.61_6 (9.607 \pm 0.005) \text{ \AA} & \beta &= 102^\circ 20' (102^\circ 14') \\ c &= 6.72_3 (6.687 \pm 0.005) \text{ \AA} & \gamma &= 96^\circ 54' (97^\circ 6\frac{1}{2}') \end{aligned}$$

Previous work had shown the space group to be $P\bar{1}$ with $Z=2$. The structure was determined from about 165 hkk and 225 $hk0$ reflections ($hk0$ and $0kl$ respectively in Glasser and Glasser's original setting). Intensities were estimated visually from Weissenberg photographs taken with MoK_α radiation and multiple film packs. No corrections were made for absorption or extinction.

The Patterson function for each projection was calculated and the peaks corresponding to the Ba—Ba vector were readily identified. Minimum functions based on these peaks enabled coordinates to be assigned to the calcium and silicon atoms. Successive electron density and difference maps were used to place the oxygen atoms and to refine the structure. With an overall isotropic temperature factor $U=0.0152$, the final R -factor was 0.16; unobserved reflections were included as $\frac{1}{2}F_{\text{min}}$ (for the

appropriate value of $\sin \theta$).¹ Calculations were made on an Elliot 803 computer, mainly using programmes kindly made available by J. J. Daly, F. S. Stephens and P. J. Wheatley of Monsanto, S.A.²

RESULTS AND DISCUSSION

The final coordinates are given in Table 1, and the structure is illustrated in Figures 1 and 2. $(\text{Si}_3\text{O}_9)^{6-}$ rings are arranged in layers parallel to $(10\bar{1})$, with calcium ions about halfway between them. The barium ions are roughly coplanar with the oxygen atoms. Bond distances and bond angles in the Si_3O_9 rings are given in Table 2.

TABLE 1. FINAL COORDINATES

	<i>x</i>	<i>y</i>	<i>z</i>
Ca(1)	0.272	0.507	0.763
Ca(2)	.435	.831	.935
Ba	.049	.848	.323
Si(1)	.096	.222	.145
Si(2)	.235	.484	.284
Si(3)	.442	.196	.511
O(1)	.236	.251	-.027
O(2)	-.098	.114	.102
O(3)	.042	.366	.212
O(4)	.366	.556	.089
O(5)	.125	.580	.389
O(6)	.352	.365	.494
O(7)	.613	.238	.368
O(8)	.517	.084	.765
O(9)	.238	.130	.389

The oxygen positions are not well determined because of presence of barium, and because the structure is solved in projection only. The variation in Si-O bond lengths is thus probably not significant, although the variation in O-Si-O angles almost certainly is. The SiO_4 tetrahedra are all distorted so that the angles subtended at Si by the shared oxygen atoms (O(3), O(6), O(9)) are all less than the tetrahedral angle (Table 2a). The coordination polyhedra of the divalent cations are irregular (Table 2b).

¹ The table of F_{obs} and F_{calc} is deposited as Document No. 9737 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. Copies may be secured by citing the document number, and remitting in advance \$1.25 for photoprints or \$1.25 for 35 mm microfilm.

² *Crystallographic programs for the Elliot 803 computer* (1963). Monsanto Res. S.A., Final Report No. 52.

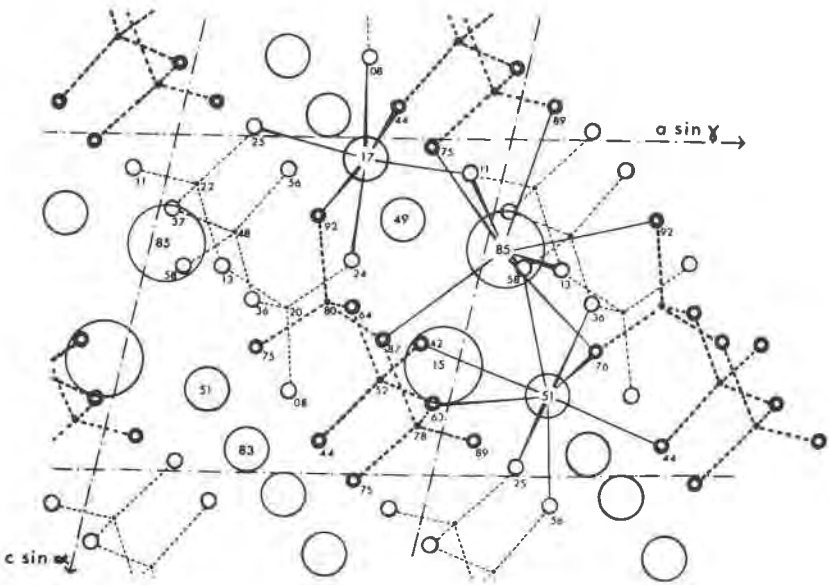


FIG. 1. The structure of walstromite viewed along b . Heights are in hundredths. Small solid circles represent silicon atoms; large, medium and small open circles represent barium, calcium and oxygen atoms respectively. Si-O bonds are represented by broken lines, and the cation—oxygen bonds by full lines.

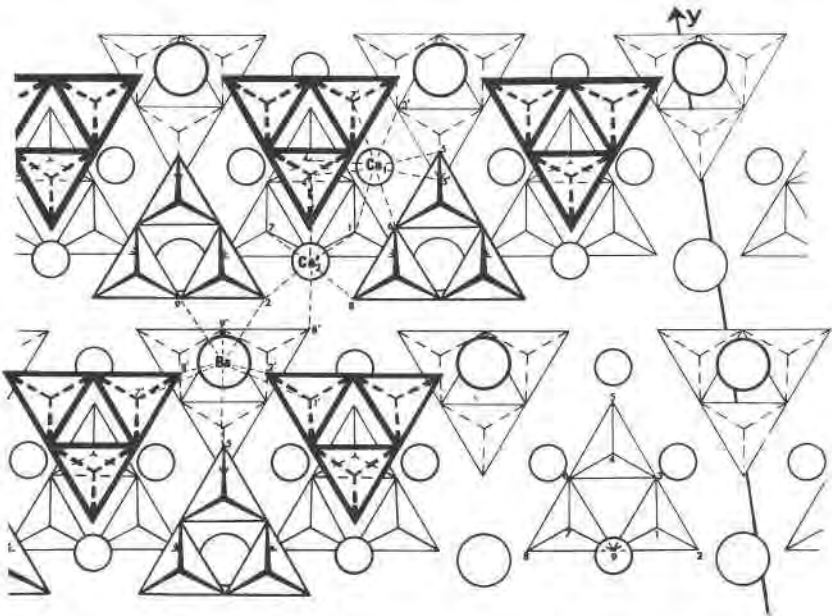


FIG. 2. An idealised representation of the structure of walstromite projected onto $(10\bar{1})$ showing how the layers of three-membered rings fit together. The direction of y is indicated.

TABLE 2. BOND LENGTHS AND ANGLES

(a) In Si ₃ O ₉ ring.					
<i>Bond Lengths</i>	(Å)	(± .05 Å)	<i>Angles at Si</i>	(°)	± (2°)
Si(1)-O(9)	1.71		O(9)-Si(1)-O(3)	97	
-O(1)	1.58		-O(1)	106	
-O(2)	1.61		-O(2)	107	
-O(3)	1.69		O(3)-Si(1)-O(1)	120	
			-O(2)	115	
			O(1)-Si(1)-O(2)	110	
Si(2)-O(3)	1.72		O(3)-Si(2)-O(6)	98	
-O(4)	1.65		-O(4)	109	
-O(5)	1.66		-O(5)	104	
-O(6)	1.59		O(6)-Si(2)-O(4)	114	
			-O(5)	102	
			O(4)-Si(2)-O(5)	125	
Si(3)-O(6)	1.76		O(6)-Si(3)-O(9)	99	
-O(7)	1.59		-O(7)	107	
-O(8)	1.68		-O(8)	114	
-O(9)	1.62		O(9)-Si(3)-O(7)	110	
			-O(8)	112	
			O(7)-Si(3)-O(8)	114	
<i>Angles at shared oxygen atoms</i> (°):					
Si(1)-O(3)-Si(2)	120				
Si(2)-O(6)-Si(3)	127				
Si(3)-O(9)-Si(1)	126				
(b) In cation-oxygen polyhedra					
	(Å)			(Å)	
Ba-O(1)'	2.79	Ca(1)-O(1)	2.39		
O(2)	2.67	*O(3)'	2.63		
O(2)'	2.84	O(4)	2.33		
O(5)	2.56	O(4)'	2.49		
O(7)'	2.72	O(5)	2.38		
O(8)'	3.06	O(5)'	2.79		
*O(9)	2.99	*O(6)	2.78		
*O(9)'	3.07	O(7)'	2.39		
				(Å)	
Ca(2)-O(1)'				2.33	
O(2)'				2.34	
O(4)				2.50	
O(7)'				2.30	
O(8)				2.36	
O(8)'				2.37	

* indicates an oxygen atom already bonded to two silicon atoms.

Ca₁ is coordinated by six charged and two uncharged oxygen atoms forming an irregular square antiprism; Ca₂ by six charged oxygen atoms in a slightly irregular octahedron. Six charged and two uncharged oxygen atoms lie within 3.10 Å of the barium atom. Of these, O(1)', O(2), O(5), O(7)' and O(9) form a fairly regular pentagon almost coplanar with Ba; O(9)' lies to one side of this pentagon and O(2)' and O(8)' to the other. The next nearest atom to Ba is O(3)' at 3.23 Å; all other oxygen atoms are more than 3.3 Å distant.

It is interesting to note that in our original paper we predicted the presence of (Si₃O₉)⁶⁻ rings on the basis of the vague similarity of our original unit cell to those of such compounds as α-CaSiO₃, benitoite and wadeite. The predicted three-membered rings were in fact present, but their orientations were quite unlike those in the other compounds. The folly of trying to predict structures from vague resemblances between unit cell dimensions was fully paid for by the authors in time wasted attempting to interpret the Patterson function in terms of Si₃O₉ rings in the wrong orientation!

Nevertheless, our further prediction (Glasser and Glasser, 1964) that the structure of margarosanite, (Ca,Mn)₂PbSi₃O₉, is probably very similar to that of Ca₂BaSi₃O₉ seems still to be valid. Careful comparison of single crystal rotation and Weissenberg photographs of the two materials shows not only that the unit cells are virtually identical, but also that the fourier transforms are very similar. It seems reasonable to suppose, therefore, that margarosanite and walstromite are indeed isostructural.

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