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COMPARISON OF THE CRYSTAL STRUCTURES OF BUSTAMITE AND WOLLASTONITE

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ABSTRACT

The structures of bustamite and wollastonite differ principally only in the relative arrangement of chains of tetrahedra. Both structures have a pseudomonoclinic cell, this unit having space group $P2_1/m$ in wollastonite and $A2/m$ in bustamite.

INTRODUCTION

On the basis of a comparison of optical properties, Sundius (1931) postulated that bustamite ($CaMnSi_2O_6$) is Mn-rich wollastonite ($CaSiO_3$). Schaller (1938, 1955) also concluded that bustamite had the wollastonite structure because of a close relationship between the optical properties of the two minerals. Berman and Gonyer (1937), using rotating-crystal photographs, found that their unit cells were similar, and concluded that they were related only by solid solution. Buerger, however, (1956) found that the unit cell of bustamite (Table 1) is closely related to, but different from, the cell of wollastonite. He noted that there is a sort of superstructure relation between the two minerals. Liebau *et al.* (1958) confirmed Buerger's unit cell and guessed that the difference in structures is based only on a different ordering of chains and cations.

TABLE 1. SYMMETRY AND UNIT-CELL DATA FOR BUSTAMITE AND WOLLASTONITE

	Wollastonite Buerger	Bustamite Peacor and Buerger	Bustamite Peacor and Prewitt
a	7.94 Å	15.412 Å	7.736 Å
b	7.32	7.157	7.157
c	7.07	13.824	13.824
α	90°02′	89°29′	90°31′
β	95°22′	94°51′	94°35′
γ	103°26′	102°56′	103°52′
Space group	$P\bar{1}$	$F\bar{1}$	$A\bar{1}$

The structure of bustamite has recently been determined and refined (D. R. Peacor and M. J. Buerger, in press). The structure of wollastonite was determined by Mamedov and Belov (1956) and refined by Buerger

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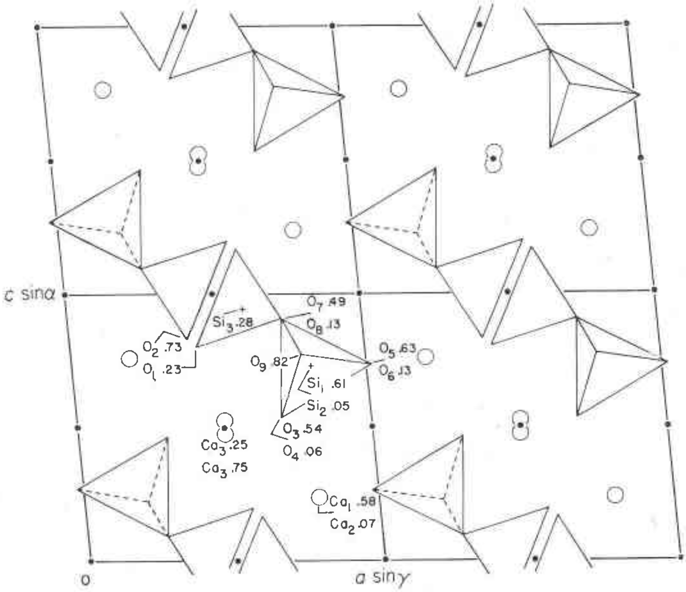

FIG. 1. Projection along *b* of the structure of wollastonite (space group $P\bar{1}$).

and Prewitt (1961). These structures are different but bear a very close relationship to one another.

DESCRIPTION OF STRUCTURES

The face-centered unit cell of bustamite may be transformed to an *A*-centered cell with the following transformation matrix:

$$\begin{pmatrix} -\frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

The *A*-centered cell bears a close relationship to the wollastonite cell, as does the face-centered cell (Table 1). Since the relation between the structures of wollastonite and bustamite is clearer if bustamite is described in terms of the *A*-centered cell, all description of bustamite in this paper is referred to this cell.

Atomic coordinates for both bustamite and wollastonite are listed in Table 2. The similarity shows that the asymmetric units of each structure are essentially the same. The structures are shown projected along *b* in Figs. 1 and 2. Four wollastonite unit cells and two bustamite unit cells are shown. Ca or Mn atoms are shown as large open circles, inversion centers at $y=\frac{1}{4}, \frac{3}{4}$ as small open circles, and inversion centers at $y=0, \frac{1}{2}$ as small solid circles. The structures are the same in projection except for minor coordinate shifts. The arrangement of the oxygen atoms of both structures approximates close packing in a crude way with an obvious layering parallel to (101). Layers consisting of Ca (wollastonite) or Ca

TABLE 2. COORDINATES AND ISOTROPIC TEMPERATURE FACTORS OF ATOMS IN WOLLASTONITE (UPPER VALUES) AND BUSTAMITE (LOWER VALUES). FOR COMPARISON, BUSTAMITE z COORDINATES ARE MULTIPLIED BY 2. COORDINATES OF ATOMS IN BUSTAMITE ARE GIVEN RELATIVE TO THE A-CENTERED UNIT CELL

Atom	x	y	z	B
Ca_1	.1985	.4228	.7608	.41
Mn_1	.2018	.4284	.7466	.56
Ca_2	.2027	.9293	.7640	.45
Ca_1	.1988	.9411	.7570	.69
Ca_3	.4966	.2495	.4720	.37
Mn_2	1/2	1/4	1/2	.56
Ca_3	.5034	.7505	.5280	.37
Ca_2	1/2	3/4	1/2	.73
Si_1	.1852	.3870	.2687	.24
	.1768	.3881	.2686	.34
Si_2	.1849	.9545	.2692	.24
	.1775	.9434	.2650	.32
Si_3	.3970	.7235	.0560	.22
	.3950	.7171	.0436	.16
O_1	.4291	.2314	.8019	.48
	.4316	.2400	.8054	.68
O_2	.4008	.7259	.8302	.37
	.4036	.7178	.8138	.57
O_3	.3037	.4635	.4641	.60
	.3126	.4725	.4586	.48
O_4	.3017	.9374	.4655	.64
	.3017	.9302	.4630	.50
O_5	.0154	.6254	.7343	.63
	.0261	.6167	.7098	.64
O_6	.0175	.1319	.7353	.71
	.0280	.1627	.7434	.66
O_7	.2732	.5118	.0919	.37
	.2574	.5047	.0786	.57
O_8	.2713	.8717	.0940	.51
	.2729	.8739	.0822	.29
O_9	.2188	.1784	.2228	.68
	.1851	.1676	.2294	1.34

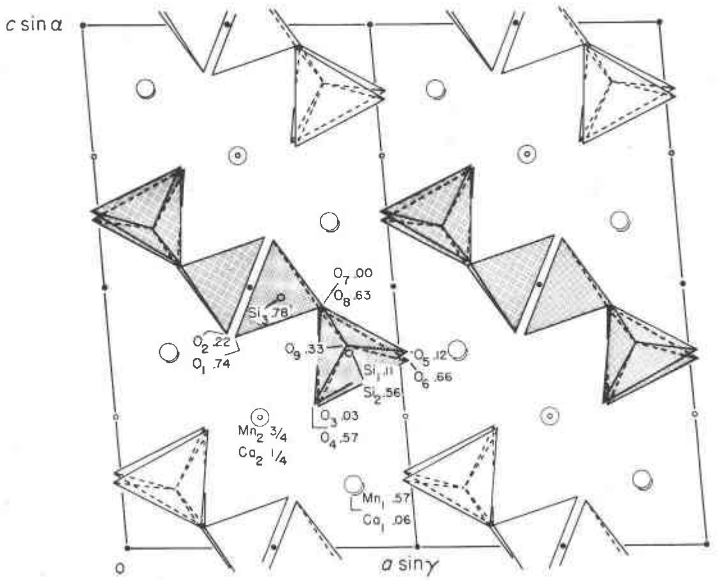

FIG. 2. Projection along *b* of the structure of bustamite (space group $A\bar{1}$). Pairs of chains shifted by $b/2$ are shaded in.

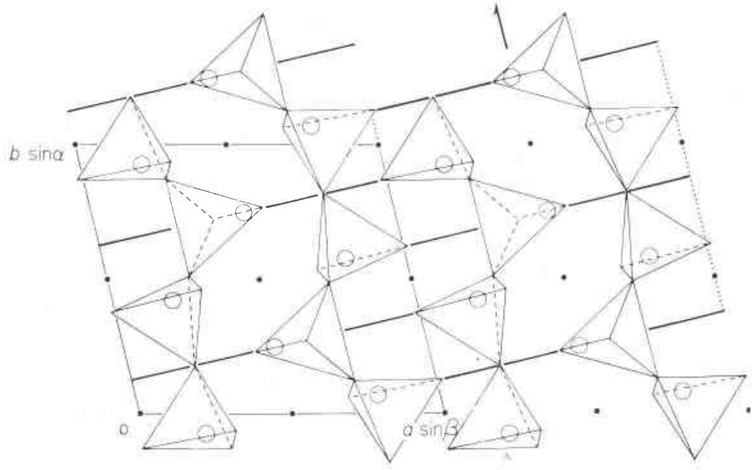

FIG. 3. Projection along *c* of the structure of wollastonite. The primitive triclinic cell is outlined with a light line. The pseudomonoclinic cell (space group $P2_1/m$) is partially outlined with a dotted line, and mirror planes are indicated with a heavy line.

and Mn (bustamite) atoms in octahedral coordination alternate with layers composed of Si atoms between the sheets of oxygen atoms. The SiO_4 tetrahedra are arranged in chains whose repeat unit is three tetrahedra and which are oriented parallel to the *b* axis (Figs. 3 and 4).

SUBSTRUCTURE RELATIONS

Both bustamite and wollastonite are characterized by a prominent substructure with period $b/2$ (Figs. 1 and 2). All atoms except Si_3 and O_9 are related to a second atom by a shift of about $b/2$. Note, for example, in Fig. 1, that Ca_1 and Ca_2 fall almost exactly over each other, and differ in y by 0.51. The relation is imperfect for some pairs of atoms, as with O_1 and O_2 of wollastonite, where the shift (Δx, Δy, Δz) is 0.03, -0.49, -0.03. Nevertheless, it is approximately true. The coordinates of the substructure atoms are very similar in the two structures. Thus, with the exception of Si_3 and O_9, the structures of wollastonite and bustamite are approximately the same. Note too, that although Si_3 and O_9 within the same chain have different x and z coordinates, they differ along b by approximately $b/2$. The difference in orientation of the chains in the two structures may be viewed roughly as an interchange in the positions of these two atoms in certain chains.

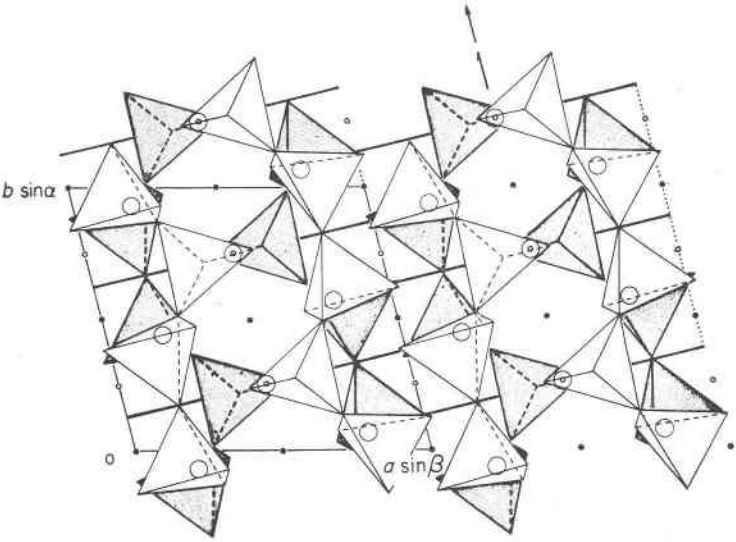

FIG. 4. Projection along *c* of the structure of bustamite. The *A*-centered triclinic cell is outlined with a light line. The pseudomonoclinic cell (space group $A2/m$) is partially outlined with a dotted line, and mirror planes are indicated with a heavy line.

ARRANGEMENT OF CHAINS OF TETRAHEDRA

The primary difference between the structures of bustamite and wollastonite lies in the relative arrangement of the silicate chains with respect to the planes of octahedrally coordinated Ca and Mn ions. Note first that the arrangement of Ca and Mn ions in bustamite is approximately the same as the arrangement of Ca ions in wollastonite. This is easily seen in Figs. 1 and 2, and is discussed in more detail under cation ordering. Chains of tetrahedra are arranged in sheets parallel to (101) in both structures. Figures 1 and 2 show that alternating chains within a single sheet are related by inversion centers. However, the pair of inversion-related chains nearest the origin in Figs. 1 and 2 is arranged similarly in each structure and can be viewed as a common structural unit.

The end-centering translation in bustamite is partially a reflection of a shift of magnitude $b/2$ of successive pairs of chains of tetrahedra within the sheets parallel to (101), relative to the pair shown nearest the origin. In wollastonite, however, the chains are not shifted along b. Tetrahedra in silicate chains which are shifted by $b/2$ are shaded in Fig. 2.

CATION ORDERING

Schaller (1938) states that minerals in this group have been found with "MnO ranging from a few per cent . . . to a maximum of 33 per cent." During refinement of the structure of wollastonite (Buerger and Prewitt, 1961) atom scale factors were refined. The refinement showed that the composition of the material used as a source for intensity data very nearly approached the ideal composition, $CaSiO_3$. The bustamite (ideally $CaMnSi_2O_6$) whose structure was refined by Peacor and Buerger (1962) contained a slight excess of Ca relative to Mn. In wollastonite the Ca atoms are distributed over three general positions. The Ca and Mn are ordered in bustamite, with one Ca and one Mn on inversion centers and two Ca and two Mn in general positions. In addition, evidence strongly suggested that the "excess" Ca of bustamite replaced Mn at the position Mn_1 rather than the special position Mn_2.

Although all Ca or Mn atoms of each structure have approximately the same coordinates, there is not complete equivalence of positions. The Ca_2 and Mn_2 atoms of bustamite on inversion centers are equivalent to the Ca_3 atom in a general position in wollastonite. The Mn_1 and Ca_1 atoms in general positions of bustamite, however, are not equivalent to Ca_1 and Ca_2 of wollastonite. Half of the Mn_1 atoms of bustamite occupy positions in the structure similar to those of Ca_1 of wollastonite, and half occupy positions similar to Ca_2. The same is true of Ca_1 of bustamite. This is reflected in the difference in distribution of inversion centers in (101) layers containing Ca and Mn atoms, as can be seen in Figs. 1 and 2. Compounds whose compositions are intermediate between bustamite and wollastonite still must be investigated to determine the limits and mecha-

Table 3. Cation-oxygen Interatomic Distances

Bustamite		Wollastonite	
Mn_1-O_1	2.499 Å	Ca_1-O_1	2.548 Å
O_2	2.286	O_2	2.437
O_4	2.163	O_3	2.324
O_5	2.144	O_5	2.302
O_6	2.041	O_6	2.272
O_7	2.335	O_7	2.412
Av.	2.245	Av.	2.383
Ca_1-O_1	2.437	Ca_2-O_1	2.316
O_2	2.531	O_2	2.369
O_3	2.298	O_4	2.421
O_5	2.382	O_5	2.501
O_6	2.302	O_6	2.316
O_8	2.358	O_8	2.406
O_9	2.899	Av.	2.388
Av.	2.384 (excluding O_9)		
Mn_2-2O_1	2.215	Ca_3-O_1	2.439
$2O_3$	2.154	O_2	2.349
$2O_4$	2.241	O_3	2.429
Av.	2.203	O_3'	2.335
		O_4	2.441
		O_4'	2.349
		O_9	2.642
		Av.	2.390 (excluding O_9)
Ca_2-2O_2	2.344	Ca_3-O_1	2.439
$2O_3$	2.412	O_2	2.349
$2O_4$	2.421	O_3	2.429
$2O_9$	2.891	O_3'	2.335
Av.	2.392 (excluding O_9)	O_4	2.441
		O_4'	2.349
		O_9	2.642
		Av.	2.390
Si_1-O_3	1.628	Si_1-O_3	1.618
O_5	1.587	O_5	1.572
O_7	1.645	O_7	1.659
O_9	1.616	O_9	1.647
Av.	1.619	Av.	1.624
Si_2-O_4	1.626	Si_2-O_4	1.617
O_6	1.585	O_6	1.581
O_8	1.647	O_8	1.650
O_9	1.613	O_9	1.637
Av.	1.618	Av.	1.621
Si_3-O_1	1.600	Si_3-O_1	1.599
O_2	1.595	O_2	1.599
O_7	1.660	O_7	1.665
O_8	1.671	O_8	1.673
Av.	1.632	Av.	1.634

nism of solid solution in each. It is possible, if not probable, that metastable intermediate compounds exist which have partial or complete disorder both in Ca and Mn and in silicate chain distributions.

INTERATOMIC DISTANCES

All average Ca-O distances are remarkably similar (2.388 ± .005 Å) in both structures as shown in Table 3. The comparison of Si-O distances is particularly interesting. The average of all Si-O distances is 1.623 Å in bustamite and 1.626 Å in wollastonite, the difference being well within the standard deviation. All average Si-O distances for Si_1 and Si_2 are almost exactly equal, and Si_3-O distances are uniformly larger than Si_1-O and Si_2-O distances in both structures.

There is an excellent correlation of individual Si-O distances with coordination of oxygen. For instance, all Si-O_7 and Si-O_8 distances are greater than 1.64 Å, 1.673 Å being the largest. Both O_7 and O_8 are coordinated to two Si atoms, from which they receive a total bond strength of 2, and to one Ca or Mn atom, from which they receive a bond strength of $\frac{1}{3}$. The excess of bond strength ($\frac{1}{3}$) is thus compensated by unusually large Si-O distances. All Si-O_5 and Si-O_6 distances are less than 1.59 Å, 1.572 Å being the smallest. These oxygen atoms are coordinated to one Si atom from which they receive a bond of strength 1 and to two Ca or Mn atoms from which they receive a bond of strength $\frac{2}{3}$. Thus there is a bond deficiency, $\frac{1}{3}$, which results in unusually short Si-O distances.

The only major differences in coordination between the two structures involve O_9. This is coordinated to Si_1 and Si_2 in both structures, but Si-O distances are larger in wollastonite. In addition, O_9 is coordinated to both Ca atoms in bustamite, but with very large Ca-O distances, and to only one Ca in wollastonite, at a shorter distance.

PSEUDOMONOCLINIC CELLS

Ito (1950) noted that the angle α of the wollastonite unit cell is very nearly 90° and that (140), which is normal to (100), approximates a mirror plane. From these data he suggested that the triclinic wollastonite cell is made up of "twinned or otherwise juxtaposed" monoclinic cells. Individual monoclinic units are related by the glide $b/4$ or $-b/4$. He noted that the monoclinic unit, which he called protowollastonite, must have either of the space groups $P2/m$ or $P2_1/m$.

Figures 3 and 4 are projections along c of the structures of wollastonite and bustamite respectively. Prewitt and Buerger (in press) noted that wollastonite has a pseudomonoclinic cell with space group $P2_1/m$. The cell is partially outlined on the right side of Fig. 3 with a dotted line-whereas the mirror planes are indicated by doubly heavy lines. The tri, clinic cell is outlined on the left with a lighter line. Figure 4 is an equivalent diagram of bustamite. The basic repeat unit is the same in bustamite as in wollastonite; *i.e.*, two chains related by a 2_1 axis. The bustamite pseudomonoclinic cell is *A*-centered however, with space group $A2/m$. In wollastonite 2_1 axes parallel to *b* are aligned along *c*. In bustamite there is a similar relation except that 2_1 and 2-fold axes alternate along *c*.

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