The Relation between the Structures Proposed for Parawollastonite, β-CaO.SiO₂*

By M. G. Vincent† and J. W. Jeffery

Department of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX, England

Abstract

The two structures proposed for monoclinic parawollastonite [Tolliday (1958). *Nature (London)*, **182**, 1012–1013; Trojer (1968). *Z. Kristallogr.* **80**, 291–308] are in fact identical within the limits of experimental error. The nature of the relationship is discussed and it is shown that the equivalence is due to the specialized values of the *y* coordinates of all atoms in the structure. A review of the data sets used in the structure determinations, which allows a decision to be made on the true space group, is also given.

Introduction

A structure for the monoclinic form of wollastonite (β-CaO.SiO₂), generally known as parawollastonite, was first proposed by Barnick (1936) based on a ring system of SiO₄ tetrahedra. His proposal was strongly criticized at the time since it did not account for the fibrous character of the material. Later, Dornberger-Schiff, Liebau & Thilo (1955) reported on the similarities of the lattice constants and disorder phenomena observed in parawollastonite and Madrell's salt NaPO₃, as well as the similarities of certain of their Patterson projections. They concluded that the two compounds were isomorphous and, from an analogy with the related compound NaAsO₃, proposed that their structures were based on infinite chains of PO₄ or SiO₄ tetrahedra. Tolliday (1958, 1959), in confirming these proposals for parawollastonite, assigned the structure to space group $P2_1$ but further symmetry due to absences in *hkl* reflexions for $2h+k = 4n+2$ led her to conclude that there must be a non-lattice point at $(\frac{1}{2},\frac{1}{4},0)$ equivalent within the cell to $(0,0,0)$. Tests on the presence of a centre of symmetry were inconclusive. Refinement of the structure assuming a space group

$P2_1/a$ plus the second lattice point at $(\frac{1}{2},\frac{1}{4},0)$ [which requires certain atoms to lie on the special positions of the limited mirror planes at $y = \frac{1}{8}$ ($0 \leq x < \frac{1}{2}$) and $y = \frac{5}{8}$ ($\frac{1}{2} \leq x < 1$); Dornberger-Schiff, 1956] was not satisfactory and she subsequently refined the structure in the non-centrosymmetric space group to $R = 26\%$.

Trojer (1968) reviewed the structure of parawollastonite from a new set of data with the atomic coordinates of Mamedov & Belov (1956) for triclinic wollastonite referred to a double (twinned) monoclinic cell as starting values in the refinement. His investigations showed that the structure amplitudes of the reflexions corresponding to the extinction rule $2h+k = 4n+2$, although small, were not zero. Refinement of the structure in space group $P2_1$ was not successful and it was subsequently refined in $P2_1/a$ to $R = 6\cdot6\%$.

By shifting the origin of Trojer's cell by $(\frac{1}{4},0,0)$ so that it is the same as Tolliday's (1959), a comparison between the fractional coordinates of the atoms in both structures can be made (Table 1). The table shows remarkable similarity between the two sets, the largest deviation of any coordinate from its equivalent being 0·045, and in most cases no greater than 0·01. This striking similarity suggests, therefore, an equivalency of the two space groups (neglecting enantiomorphic relationships), the nature of which is discussed in this paper along with a review of the data used in the structure determinations.

The relationship

The positions derived from the centring point at $(\frac{1}{2},\frac{1}{4},0)$ are not space-group equivalent positions. This is shown by Table 2 which attempts to use the four positions produced by the 2_1 axis and the centring point (hereinafter referred to as $C'2_1$) as an equivalent set, with inconsistent results. The selection of fractional coordinates of atoms in the cell defining the asymmetric unit in terms of $C'2_1$ must therefore be chosen with care. This point is emphasized for reasons that will be clear in the ensuing analysis of Trojer's and Tolliday's structures.

The general equivalent positions for space group $P2_1/a$ with the origin shifted by $(\frac{1}{4},0,0)$ are: x,y,z; $\bar{x},\frac{1}{2}+y,\bar{z}$; $\frac{1}{2}-x,\bar{y},\bar{z}$; $\frac{1}{2}+x,\frac{1}{2}-y,z$. Comparing these with the positions in $C'2_1$ (first column of Table 2) it will be seen

Table 1. *Comparison of the fractional coordinates of atoms in the* $P2_1/a$ *and* $C'2_1$ *structures of parawollastonite*

y' is the nearest value of $(2n + 1)/8$ to y for $C'2_1$. Arrows indicate equivalent atomic positions.

Atom identity	P2₁/a Fractional coordinates			Position equivalent	Atom identity	C'2₁ Fractional coordinates			
	x	y	z			x	y	z	y'
Ca(1)	0·0018	0·6242	0·0288	↔	Ca(1)	0·003	0·634	0·028	5/8
	0·9982	0·1242	0·9712	↔		0·997	0·134	0·972	1/8
	0·4982	0·3758	0·9712	↔		0·497	0·384	0·972	3/8
	0·5018	0·8758	0·0288	↔		0·503	0·884	0·028	7/8
Ca(2)	0·1511	0·8735	0·7397	↔	Ca(3)	0·150	0·875	0·737	7/8
	0·8489	0·3735	0·2603	↔		0·850	0·375	0·263	3/8
	0·3489	0·1265	0·2603	⤫		0·350	0·625	0·263	5/8
	0·6511	0·6265	0·7397	⤫		0·650	0·125	0·737	1/8
Ca(3)	0·1487	0·3791	0·7364	⤫	Ca(2)	0·150	0·375	0·737	3/8
	0·8513	0·8791	0·2636	⤫		0·850	0·875	0·263	7/8
	0·3513	0·6209	0·2636	⤫		0·350	0·125	0·263	1/8
	0·6487	0·1209	0·7364	⤫		0·650	0·625	0·737	5/8
Si(1)	0·1576	0·4093	0·2313	↔	Si(2)	0·157	0·364	0·243	3/8
	0·8424	0·9093	0·7687	↔		0·843	0·864	0·757	7/8
	0·3424	0·5907	0·7687	⤫		0·343	0·114	0·757	1/8
	0·6576	0·0907	0·2313	⤫		0·657	0·614	0·243	5/8
Si(2)	0·1575	0·8402	0·2313	⤫	Si(3)	0·152	0·827	0·248	7/8
	0·8425	0·3402	0·7687	⤫		0·848	0·327	0·752	3/8
	0·3425	0·1598	0·7687	⤫		0·348	0·577	0·752	5/8
	0·6575	0·6598	0·2313	⤫		0·652	0·077	0·248	1/8
Si(3)	0·0516	0·1239	0·4432	↔	Si(1)	0·052	0·113	0·441	1/8
	0·9484	0·6239	0·5568	↔		0·948	0·613	0·559	5/8
	0·4484	0·8761	0·5568	↔		0·448	0·863	0·559	7/8
	0·5516	0·3761	0·4432	↔		0·552	0·363	0·441	3/8
O(1)	0·0500	0·1253	0·6685	↔	O(3)	0·041	0·125	0·633	1/8
	0·9500	0·6253	0·3315	↔		0·959	0·625	0·367	5/8
	0·4500	0·8747	0·3315	↔		0·459	0·875	0·367	7/8
	0·5500	0·3747	0·6685	↔		0·541	0·375	0·633	3/8
O(2)	0·9656	0·1241	0·3031	↔	O(2)	0·969	0·125	0·297	1/8
	0·0344	0·6241	0·6969	↔		0·031	0·625	0·703	5/8
	0·5344	0·8759	0·6969	↔		0·531	0·875	0·703	7/8
	0·4656	0·3759	0·3031	↔		0·469	0·375	0·297	3/8
O(3)	0·0950	0·3603	0·0328	↔	O(8)	0·096	0·357	0·039	3/8
	0·9050	0·8603	0·9672	↔		0·904	0·857	0·961	7/8
	0·4050	0·6397	0·9672	⤫		0·404	0·107	0·961	1/8
	0·5950	0·1397	0·0328	⤫		0·594	0·607	0·039	5/8
O(4)	0·0973	0·8843	0·0348	⤫	O(9)	0·087	0·855	0·021	7/8
	0·9027	0·3843	0·9652	⤫		0·913	0·355	0·979	3/8
	0·4027	0·1157	0·9652	⤫		0·413	0·605	0·979	5/8
	0·5973	0·6157	0·0348	⤫		0·587	0·105	0·021	1/8
O(5)	0·2586	0·3774	0·2388	↔	O(4)	0·265	0·376	0·233	3/8
	0·7414	0·8774	0·7612	↔		0·735	0·876	0·767	7/8
	0·2414	0·6226	0·7612	⤫		0·235	0·126	0·767	1/8
	0·7586	0·1226	0·2388	⤫		0·765	0·626	0·233	5/8
O(6)	0·2578	0·8824	0·2347	⤫	O(5)	0·227	0·855	0·234	7/8
	0·7422	0·3824	0·7653	⤫		0·773	0·355	0·766	3/8
	0·2422	0·1176	0·7653	⤫		0·273	0·605	0·766	5/8
	0·7578	0·6176	0·2347	⤫		0·727	0·105	0·234	1/8
O(7)	0·1142	0·3038	0·4060	↔	O(6)	0·137	0·261	0·375	3/8
	0·8858	0·8038	0·5940	↔		0·862	0·761	0·625	7/8
	0·3858	0·6962	0·5940	⤫		0·362	0·011	0·625	1/8
	0·6142	0·1962	0·4060	⤫		0·637	0·511	0·375	5/8
O(8)	0·1133	0·9467	0·4067	⤫	O(7)	0·108	0·941	0·431	7/8
	0·8867	0·4467	0·5933	⤫		0·892	0·441	0·569	3/8
	0·3867	0·0533	0·5933	⤫		0·392	0·691	0·569	5/8
	0·6133	0·5533	0·4067	⤫		0·608	0·191	0·431	1/8
O(9)	0·1406	0·6245	0·2767	↔	O(1)	0·129	0·608	0·283	5/8
	0·8594	0·1245	0·7233	↔		0·871	0·108	0·717	1/8
	0·3594	0·3755	0·7233	↔		0·371	0·358	0·717	3/8
	0·6406	0·8755	0·2767	↔		0·629	0·858	0·283	7/8

Table 2. *The effect of substituting each of the general equivalent positions into the set of general equivalent positions for* $C'2_1$

x, y, z	$\bar{x}, \frac{1}{2}+y, \bar{z}$	$\frac{1}{2}+x, \frac{1}{4}+y, z$	$\frac{1}{2}-x, \frac{3}{4}+y, \bar{z}$
$\bar{x}, \frac{1}{2}+y, \bar{z}$	x, y, z	$\frac{1}{2}-x, \frac{3}{4}+y, \bar{z}$	$\frac{1}{2}+x, \frac{1}{4}+y, z$
$\frac{1}{2}-x, \frac{3}{4}+y, \bar{z}$	$\frac{1}{2}+x, \frac{1}{4}+y, z$	$x, \frac{1}{2}+y, z$	$\bar{x}, y, \bar{z}$
$\frac{1}{2}+x, \frac{1}{4}+y, z$	$\frac{1}{2}-x, \frac{3}{4}+y, \bar{z}$	$\bar{x}, y, \bar{z}$	$x, \frac{1}{2}+y, z$

that, besides the positions x,y,z and $\bar{x}, \frac{1}{2}+y, \bar{z}$ being common to both, the x and z coordinates of the other positions are also the same. For the general equivalent positions of the two groups to be identical then

$$(a)\ \tfrac{3}{4}+y = -y \quad \text{and} \quad (b)\ \tfrac{1}{4}+y = \tfrac{1}{2}-y,$$

which give values for y of $\frac{3}{8}$ from (a) and $\frac{1}{8}$ from (b). After substituting these values into the general equivalent positions of both sets, the sequence of y values is:

$$y = \tfrac{1}{8}\ \ P2_1/a: \tfrac{1}{8}, \tfrac{5}{8}, \tfrac{7}{8}, \tfrac{3}{8};\ \ C'2_1: \tfrac{1}{8}, \tfrac{5}{8}, \tfrac{7}{8}, \tfrac{3}{8};$$

$$y = \tfrac{5}{8}\ \ P2_1/a: \tfrac{5}{8}, \tfrac{1}{8}, \tfrac{3}{8}, \tfrac{7}{8};\ \ C'2_1: \tfrac{5}{8}, \tfrac{1}{8}, \tfrac{3}{8}, \tfrac{7}{8};$$

i.e. the two space groups are equivalent for these values. The y coordinates take the general form $(2n + 1)/8$ and require absences of hkl reflexions with $2h+k = 4n+2$, *i.e.* exactly the same conditions for a lattice point to be at $(\frac{1}{2},\frac{1}{4},0)$. If, on the other hand, the y coordinate used to define the asymmetric unit has a value of either $\frac{3}{8}$ or $\frac{7}{8}$ then the sequence of y values for the two space groups is:

$$y = \tfrac{3}{8}\ \ P2_1/a: \tfrac{3}{8}, \tfrac{7}{8}, \tfrac{5}{8}, \tfrac{1}{8};\ \ C'2_1: \tfrac{3}{8}, \tfrac{7}{8}, \tfrac{1}{8}, \tfrac{5}{8};$$

$$y = \tfrac{7}{8}\ \ P2_1/a: \tfrac{7}{8}, \tfrac{3}{8}, \tfrac{1}{8}, \tfrac{5}{8};\ \ C'2_1: \tfrac{7}{8}, \tfrac{3}{8}, \tfrac{5}{8}, \tfrac{1}{8}.$$

It will be seen that the two sets are no longer equivalent since the latter two values are reversed in one set compared with the other. How then can sets defined with y values of either $\frac{3}{8}$ or $\frac{7}{8}$ be equivalent, *i.e.* their positions in both space groups be identical? This point arises out of the restrictions placed on the manner in which the coordinates of each atom in the asymmetric unit in Tolliday's space group are defined. Since with these restrictions the y coordinates defining the asymmetric units in her structure involve all values of the general form $(2n + 1)/8$, it is not possible to select a set of positions representing the asymmetric units of all atoms with y values of $\frac{1}{8}$ or $\frac{5}{8}$ only. In $P2_1/a$ however, any one of the set of four general equivalent positions will generate the others and therefore any one of them can be chosen to define the asymmetric unit.

The solution to this problem requires two sets of independent atoms of the same species to lie at x,y,z and $x,\frac{1}{2}+y,z$ in both space groups. Those atoms with y as either $\frac{3}{8}$ or $\frac{7}{8}$ in one group will find their equivalents in the other group partly in the opposite set (for the first two positions) and in the alternate set for the other two. Those atoms with y values of $\frac{1}{8}$ or $\frac{5}{8}$ will find their equivalents in opposite sets. The $P2_1/a$ set defined by x,y,z, for example, has its equivalents in the $C'2_1$ set

also defined by x,y,z if $y = \frac{1}{8}$ or $\frac{5}{8}$. Those atoms, however, with y values of $\frac{3}{8}$ or $\frac{7}{8}$ in $P2_1/a$ x,y,z set will find two of their equivalents in $C'2_1$ $x,\frac{1}{2}+y,z$ set and *vice versa*.

A study of the atomic coordinates for both Tolliday's and Trojer's structures (Table 1) shows that, whatever the value of y used to define the asymmetric unit (in Table 1, the first position of each set) in space group $C'2_1$, the conditions under which the positions of these atoms are to be the same as those in $P2_1/a$ are followed exactly although there are slight deviations from the ideal values of $(2n + 1)/8$ in all cases. Apart from Trojer's O(7) and O(8) and Tolliday's O(6) and O(7) (Table 1), these deviations are, however, very small but, in the case of Trojer's results, apparently above the limit of error which would account for the observable reflexions of the type $2h+k = 4n+2$ in Trojer's data. The specialized locations are responsible for additional symmetry in the cell which has already been discussed by Trojer in his paper.

A review of the data sets

It is evident from the R factors quoted above that the quality of Trojer's data is superior to that of Tolliday, the difference being partly accounted for by the greater accuracy of counter measuring techniques compared with eye estimation of photographs, the two methods which they respectively employed, and partly by large absorption errors in Tolliday's data. Similarities of the two structures apart, this difference in R may be taken as sufficient proof for accepting $P2_1/a$ as the true space group, more so in view of the fact that the crystals used in both investigations were from the same location (Crestmore, California). However, there is one further decisive argument in favour of $P2_1/a$ which, in effect, eliminates $C'2_1$ as a possibility altogether. This may be explained as follows.

The reason why Tolliday eventually proposed $C'2_1$ as the space group for parawollastonite was based solely on the extra conditions $2h+k = 4n+2$ that she found limiting reflexions in her data. As previously mentioned, Trojer found that this condition did not exist in his data, pointing out that although the reflexions satisfying this rule were very weak, they were nonetheless in the majority of cases observable. Now, if the condition $2h+k = 4n+2$ really does exist, the only possible explanation for the observable intensities in Trojer's data is that they are a result of multiple reflexion effects. Briefly, if the reciprocal lattice points $h_1k_1l_1$, $h_2k_2l_2$ defined by the vectors $\mathbf{d}_1^*$ and $\mathbf{d}_2^*$ from the origin of the reciprocal lattice are in the reflecting position at the same time then the vector $\mathbf{d}_3^* = \mathbf{d}_2^* - \mathbf{d}_1^*$ will also exist. $\mathbf{d}_3^*$ corresponds to a reciprocal lattice point $h_3k_3l_3$ defined by the new origin at $h_1k_1l_1$. If $h_1k_1l_1$ and $h_3k_3l_3$ are both strong reflexions and $h_2k_2l_2$ is, for

example, a systematically extinct reflexion, then it may be possible to observe a net intensity at $h_2k_2l_2$. From this criterion, the above rule may be written as $2(h_1 + h_3) + (k_1 + k_3) = 4n + 2$, on noting that $k_1 + k_3$ must always be even. With a list of the ten strongest reflexions (some of which were not recorded by Trojer) and their symmetry equivalents to define $\mathbf{d}_1^*$ and $\mathbf{d}_3^*$, computation has shown that no combinations of $\mathbf{d}_1^* + \mathbf{d}_3^* = \mathbf{d}_2^*$ satisfy the above rule for any orientation of the crystal or any number of reciprocal lattice points on the sphere at the same time. Therefore multiple reflexion effects can be eliminated as a cause of the observable intensities and hence the true space group may be taken as $P2_1/a$.

As a corollary to the above analysis, it was of interest to see whether or not Tolliday's data could equally well have been described by $P2_1/a$ symmetry, a possibility which she did not apparently consider. In order to verify this, a Patterson map was computed in sections of interval $\frac{1}{30}$ with her data (Tolliday, 1959). The peaks that she found equivalent in height to the origin peak at $\pm(\frac{1}{2},\frac{1}{4},0)^*$ were in fact just over half the height in this computation. Moreover, if the interatomic vectors between symmetry-related atoms due to a-glide symmetry, which take the form $\pm (\frac{1}{2}, \frac{1}{4}+2y,0)$, are considered, then the y coordinates would have values $\frac{1}{8}, \frac{3}{8}, \frac{5}{8}$ and $\frac{7}{8}$ if the vector peaks are exactly located at $\pm(\frac{1}{2},\frac{1}{4},0)$. Since the densest part of the peaks on the Patterson map at these positions were spread over four intervals from $\pm\frac{6}{30}$ to $\pm\frac{9}{30}$ in the V direction, the expected deviations of the y coordinates from the ideal values of $\frac{1}{8}, \frac{3}{8}, \frac{5}{8}$, and $\frac{7}{8}$ would be within $\pm0\cdot07$ which, from an analysis of Table 1 for both Tolliday's and Trojer's fractional coordinates, is the case for all atoms. A structure factor calculation based on Trojer's atomic

---

* The additional peak at $(\frac{1}{2},\frac{1}{4},0)$ is invoked by the symmetry of the Patterson synthesis.

positions and isotropic thermal parameters was made with Tolliday's data. R was 30% after adjustments were made to the scale factor. Although at the time it was not feasible to pursue this analysis to least-squares refinement, the above results do clearly indicate a fit between Tolliday's data and space group $P2_1/a$.

Conclusions

The striking resemblance between Trojer's and Tolliday's structures of parawollastonite lies in their ability to satisfy the conditions for which the two space groups $C'2_1$ and $P2_1/a$ are equivalent. It is therefore not surprising that Tolliday found the structure refined successfully in $C'2_1$ and not in $C'2_1/a$, its centrosymmetric counterpart. Furthermore, in view of the conclusions of the previous section, structural descriptions based on Tolliday's space group, such as the one given by Bragg & Claringbull (1965), would seemingly have to be revised.

References

BARNICK, M. (1936). *Mitt. Kaiser-Wilhelm-Inst. Silikatforsch.* No. 172; abstracted in *Strukturbericht*, **4**, 207.
BRAGG, W. L. & CLARINGBULL, G. F. (1965). *The Crystalline State*, Vol. IV (*Crystal Structures of Minerals*), edited by W. L. BRAGG, pp. 245–249. London: G. Bell & Sons.
DORNBERGER-SCHIFF, K. (1956). *Acta Cryst.* **9**, 593–601.
DORNBERGER-SCHIFF, K., LIEBAU, F. & THILO, E. (1955). *Acta Cryst.* **8**, 752–754.
MAMEDOV, KH. S. & BELOV, N. V. (1956). *Dokl. Akad. Nauk SSSR* **107**, 463–466.
TOLLIDAY, J. (1958). *Nature (London)*, **182**, 1012–1013.
TOLLIDAY, J. (1959). PhD thesis, London Univ.
TROJER, F. J. (1968). *Z. Kristallogr.* **80**, 291–308.

Phase Extension and Refinement

BY GER J. OLTHOF, LENIE SINT AND HENK SCHENK

Laboratory for Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam, The Netherlands

Abstract

Two procedures are described to extend and refine phases starting from a medium-sized set of known phases. From tests with 376 and 400 atom structures it was found that for extension purposes the tangent formula is suitable; for refinement purposes the tangent formula was adapted in order to maintain the enantiomorph.

Introduction

In protein crystallography, direct methods have been used to extend and refine phases by employing: (1) the