show that it is always possible to scan a reflexion in a situation in which it is not subject to maximum broadening.

The construction of the linear diffractometer has depended on the patience and skill of Mr T. H. Faulkner, who made the entire instrument in the Royal Institution workshop and is responsible for much of the detailed design. Our thanks are also due to Mr W. A. Coates for his help in the earliest stages of the development and to Messrs F. B. Jones and A. Long for building many of the final circuits. Without the continued encouragement of Sir Lawrence Bragg and Prof. R. King none of this work would have been possible. We are indebted to the National Institutes of Health (U.S.A.) for financial assistance.

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Silicate Transformations: Rhodonite-Wollastonite

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(*Received* 26 *September* 1960 *and in revised form* 28 *November* 1960)

Details of the oriented transformation rhodonite → wollastonite have been studied. The results show conclusively that the cation–oxygen skeleton is preserved during the change, at the expense of silicon–oxygen bonds. This provides direct evidence of the migration of silicon during thermal transformations of silicates.

Introduction

In most silicate structures the Si–O bond is the strongest bond and the SiO_4 tetrahedron the most regular part of the structure. There is therefore a tendency to think of silicate structures in terms of the disposition of the tetrahedra, whether isolated or linked as endless chains, sheets, frameworks, etc., and to consider the other cations as occupying interstitial sites. This convenient simplification is not always justifiable, especially since it tends to imply that the Si–O framework is the most stable part of the structure as well as the most obvious.

Donnay, Wyart & Sabatier (1959) have pointed out that the tetrahedral units, which they refer to as building blocks, may be deformed from their idealized state by substitution of Al for Si or by variation of the cations. They emphasize that too little attention has been paid to the role of the cations in silicate structures, and also assemble convincing experimental evidence of the mobility of Si^{4+} and tetrahedral Al^{3+} under hydrothermal conditions. They postulate a mechanism to explain this, involving water as an essential catalyst.

Dent & Taylor (1956) had earlier studied the dehydration of xonotlite, ($Ca_6Si_6O_{17}(OH)_2$) to β-$CaSiO_3$, and had concluded from the orientation relationships that the most probable reaction mechanism involved a disruption of the Si–O units of the structure and a relative preservation of the Ca–O portions. They admitted that the evidence was not conclusive, as it was possible to postulate alternative mechanisms for the transformation not involving mobility of Si as atoms or ions (see discussion). Several further instances of oriented transformations were studied (Gard & Taylor, 1958; Taylor, 1957, 1959), all of which tended to support the conclusions of Dent & Taylor regarding the mobility of Si. Some of the reactions were performed hydrothermally, and in all cases water was present in the original structure, so that the theory of Donnay, Wyart & Sabatier might be applicable. Taylor (1960) has summarized these results.

In the current work, it was decided to investigate a reaction in which no water was present and in which nothing was lost or gained during the reaction, so as to eliminate some of the complications which had previously arisen when trying to postulate reaction mechanisms. Concurrent studies on a series of manganese minerals led to the selection of the rhodonite–wollastonite inversion.

The structures of both these metasilicates are known. Using the classical approach, they may be described in terms of the repeat distances along their infinite $(SiO_3)^=$ chains (Hilmer, Liebau, Thilo & Dornberger-Schiff, 1956; Liebau, 1957). In this classification, wollastonite contains 'Dreierketten' and rhodonite 'Fünferketten', that is, their chains repeat after three and five tetrahedra respectively. The German words for the chain types will be used throughout, as there are no satisfactory English translations.

Rhodonites are known to occur in nature having compositions ranging from pure $MnSiO_3$ to a calcium-containing solid solution approximating to the formula $Mn_4Ca(SiO_3)_5$. All rhodonites have similar structures. Sheets of (Mn, Ca) cations which approximate to octahedral layers are interleaved with layers of fünferketten (Liebau, Hilmer & Lindemann, 1959*). Phase-rule studies of the system $CaSiO_3$–$MnSiO_3$ (Dent Glasser & Glasser, 1960) indicate that rhodonite solid solutions containing about 10–20% $CaSiO_3$ invert to wollastonite solid solutions upon heating; the thermal instability of the rhodonite solid solutions increases with increasing Ca^{2+} content. A rhodonite of composition $Mn_4Ca(SiO_3)_5$ is thermodynamically stable only at low temperatures, experimentally shown to be less than 600 °C. At about 1100 °C. a rhodonite of this composition inverts to a wollastonite solid solution very rapidly and may be heated in air for short periods of time without serious danger of oxidation.

The wollastonite structure also contains sheets of cations interleaved with layers of $(SiO_3)^=$ chains, but in this case the chains are dreierketten (Dornberger-Schiff, Liebau & Thilo, 1955; Buerger, 1956; Mamedov & Belov, 1956).

Experimental

A natural rhodonite crystal from Franklin, New Jersey,* of composition about $CaMn_4(SiO_3)_5$ and having recognizable cleavage outlines was selected. The directions of the principal axes relative to the crystal outline were determined from oscillation photographs about *c*; the crystal was elongated along *c* and had principal cleavage (010). It was then removed from the goniometer head, heated to about 1150 °C. for a few minutes, and remounted. The product was a pseudomorph after the original rhodonite crystal fragment. The external morphology was completely preserved. Oscillation photographs showed that a somewhat imperfect single crystal of a wollastonite solid solution had been formed; the directions of its axes relative to the crystal outline (and hence relative to the axes of the original rhodonite) were determined from them. The procedure was repeated, using different rhodonite crystals, with similar results.

Results

The relationships between the unit cells of rhodonite and wollastonite have already been pointed out (Liebau *et al.*, 1959) and are reproduced here:

Rhodonite

$$a=6{\cdot}68,\ b=7{\cdot}66,\ c=12{\cdot}20\ \text{Å};$$
$$\alpha=111{\cdot}1,\ \beta=86{\cdot}0,\ \gamma=93{\cdot}2°.$$

Wollastonite†

$$c=7{\cdot}07,\ a=7{\cdot}94,\ b=7{\cdot}32\ \text{Å};$$
$$\gamma=103{\cdot}4,\ \alpha=90{\cdot}0,\ \beta=95{\cdot}4°.$$

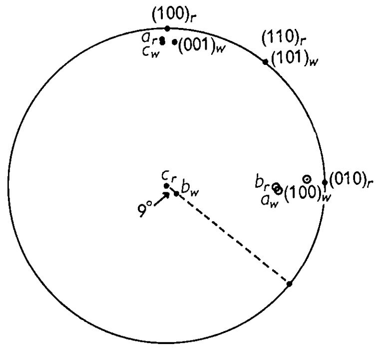

Fig. 1. Stereogram showing the relative orientations of rhodonite and wollastonite determined experimentally. a_r, b_r, c_r represent the axes of rhodonite, a_w, b_w and c_w those of wollastonite. The dashed line represents the trace of a cation layer, passing vertically through the page.

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* In private correspondence, Dr Liebau tells us that some of the coordinates given in this paper are in error, and that corrected values will be sent to *Acta Cryst.*; our diagrams are based on the corrected values.

* Specimen kindly provided by the Mineral Industries Museum, The Pennsylvania State University, University Park, Pennsylvania.

† For $CaSiO_3$; axes will be slightly smaller for $Mn_4Ca(SiO_3)_5$.

As might be expected from the above figures, *a*, *b*, and *c* of rhodonite transform approximately to *c*, *a*, and *b* of wollastonite respectively. Obviously there cannot be an exact correspondence, since the angles of the two cells differ.

Measurements on the first crystal showed that wollastonite *b* was not exactly parallel to the principal cleavages of the pseudomorph (i.e., rhodonite *c* does not become exactly wollastonite *b*). A further experiment performed with a rhodonite crystal having a perfect (010) and a good (100) cleavage gave the relative orientations shown on the stereogram (Fig. 1). The angle between c_r and b_w was measured by reading the goniometer arcs with first the crystal axis and then the cleavages parallel to the axis of rotation for both starting material and product. The first reading was made by setting the crystal in the normal way, and the second by eye, using the telescope of the goniometer; this second operation cannot be performed very accurately and repeat observations show that ± 1° is the best that can be expected, and this only under favourable conditions. No great accuracy is therefore claimed for the angle of 9° shown in Fig. 1; the rough measurement made on the previous crystal indicates that the true value may be slightly greater than 9°.

Discussion

The similarity between the unit cells of rhodonite and wollastonite mentioned earlier is a consequence of the similarities of the two structures. In rhodonite the layers of chains and of cations are parallel to (110), with individual chains parallel to the *c* axis, while in wollastonite the layers are parallel to (101) and individual chains are parallel to the *b* axis. This leads to the close correspondence between *a* and *b* of rhodonite and *c* and *a* of wollastonite respectively, the difference between rhodonite *c* and wollastonite *b* being explicable in terms of the differing repeat units along the chains.

The mere fact that there are approximate directional relationships between rhodonite *a*, *b* and *c* and wollastonite *c*, *a* and *b* respectively is not sufficient to determine uniquely the mechanism of the transformation. Two separate transformation mechanisms may be imagined, both consistent with such axial relationships. In one mechanism, the fünferketten parallel to *c* of rhodonite preserve direction, twisting about their own axes to become the dreierketten parallel to *b* of wollastonite. This would necessitate rearrangement of the (Mn, Ca)O layers. In the second mechanism, the (Mn, Ca)O sheets are preserved, and the $(SiO_3)^{=}$ chains undergo reconstruction. It is in fact possible to distinguish which of these two possible mechanisms is operative, and the key to the puzzle is the fact that an angle of roughly 9° is observed between rhodonite *c* and wollastonite *b*.

Figs. 2 and 3 show the significance of this angle in determining the transformation mechanism. Fig. 2(*a*) shows the cation arrangement of the (110) layers in rhodonite, and Fig. 2(*b*) that of the similar (101) layers in wollastonite, with the trace of the unit cell outlined in each case. Fig. 2(*c*) shows how each of these cells may be defined (approximately) on a hexagonal arrangement of cations (corresponding to an ideal octahedral (Mn, Ca)O layer). $[1\bar{1}0]_r$ is parallel to $[10\bar{1}]_w$, and there is an angle of about 13° between c_r and b_w. That is, from a consideration of the cation arrangement alone, it would be concluded that a_r would transform exactly to c_w, and b_r exactly to a_w (as a consequence of the parallelism of $[1\bar{1}0]_r$ and $[10\bar{1}]_w$) but that there would be an angle of about 13° between c_r and b_w in the plane of the cation sheets. Reference to Fig. 1 shows that this is a fair description of the relationships actually observed, noting that the 13° predicted value is calculated from an idealized representation, and remembering that the 9° observed value to be compared with it has been measured only rather roughly.

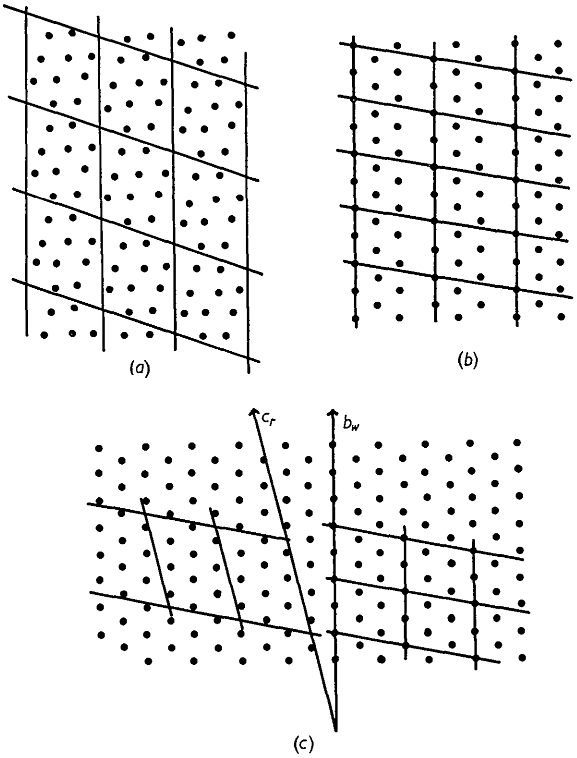
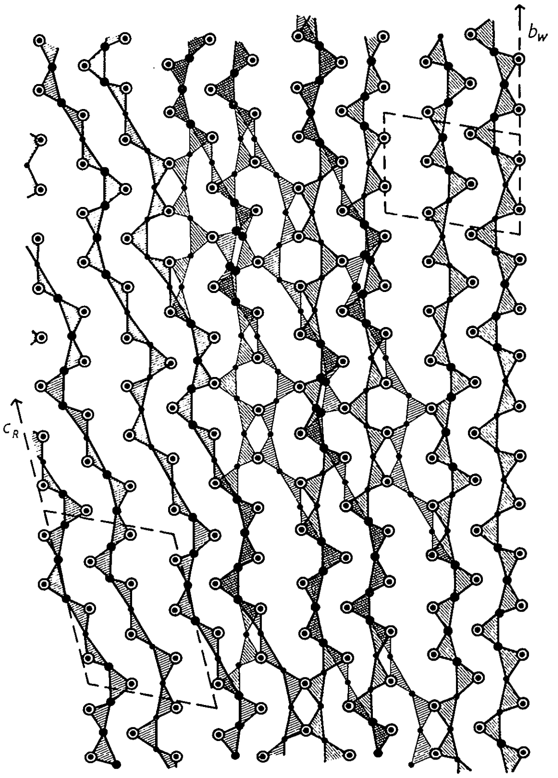


Fig. 2. Arrangements of cations in (*a*) (110) plane of rhodonite, (*b*) (101) plane of wollastonite, (*c*) an idealized octahedral layer.

Fig. 3 shows the positions of the oxygen atoms associated with ideal octahedral layers and the way in which the different chain types fit between such layers. Some of the tetrahedra are necessarily distorted because of the idealization of the oxygen positions. The rhodonite cell and chain type are shown on the left, the wollastonite on the right. Consideration of this diagram shows which of the mechanisms



◁ Tetrahedra belonging to Fünferketten

▷ Tetrahedra belonging to Dreierketten

⊙ Oxygen atoms associated with the octahedral layers. The symbol represents two such atoms in the same tetrahedron, one being part of the octahedral layer below the chains illustrated, one being part of that above.

● Linking oxygens (i. e. oxygens attached to two silicons) which move only slightly in the transformation.

• Linking oxygens which move considerably in the transformation.

Fig. 3. The conversion of fünferketten to dreierketten.

postulated earlier must be correct. If the preservation of the infinite chains is the important factor—the transformation taking place by twisting of the chains about their axes, preserving Si–O bonds while (Mn, Ca)–O bonds are broken—*then c_r would transform exactly to b_w*. If, however, the (Mn, Ca)O part of the structure is preserved at the expense of the $(SiO_3)^=$ chains, *the axial relationships will be those actually observed experimentally.* This constitutes conclusive proof that the second mechanism is the correct one.

Details of the change may be seen in the centre of Fig. 3, where both types of chain are shown, being differentiated by the direction of the cross hatching. The mechanism of the change involves drastic movement only of silicon atoms and of oxygen atoms which are *not* part of the octahedral layers. On this hypothesis surprisingly little movement of oxygen atoms is required. The movements (deduced from a study of Fig. 3) may be summarized as follows:

$$\begin{array}{lcl} & 3 \text{ repeat units} \rightarrow & 5 \text{ repeat units} \\ & \text{fünferkette} & \text{dreierkette} \\ \text{or} & & \\ & 3\times 5 = 15[SiO_3]^= & 5\times 3 = 15[SiO_3]^= \end{array}$$

Of the 45 oxygens involved, 30 belong to the octahedral layers and need move only slightly.

Of the remaining 15 'linking' oxygens, 8 need move only slightly, 3 need move short distances, each maintaining one of its bonds to silicon, while the remaining 4 must move considerably with considerable change in coordination.

Of the 15 silicons, 8 may remain bonded to the same oxygens, while 7 must break at least one oxygen bond and move to new positions.

In fact, these figures probably represent only the net result of the transformation, during which it is visualized that there is considerable movement of oxygens and silicons between the octahedral layers, chains being broken and reformed until the structure eventually settles down to its new, stable, form.

This theory is essentially similar to that put forward in 1956 by Dent & Taylor in their discussion of the dehydration of xonotlite to wollastonite. The structures of xonotlite and wollastonite are very similar, except that wollastonite contains single dreierketten occurring in pairs related by a twofold screw axis, while xonotlite contains double dreierketten formed by relating similar chains by a twofold axis, every third pair of tetrahedra sharing an oxygen so as to link the two chains together. The chain thus formed bears the same relationship to the wollastonite chain as does the amphibole to the pyroxene chain. The problem in xonotlite–wollastonite is therefore to explain how, during the transformation, one half of the chain becomes displaced relative to the other, converting the twofold axis into a twofold screw axis. Movement of silicon from an initially filled tetrahedron into an initially empty one, in the manner shown in Fig. 4, was suggested as a possible mechanism for the migration of silicon (Dent & Taylor, 1956; Taylor, 1960). This hypothesis affords a very elegant explanation, and was felt by Dent & Taylor to be the most likely one. Alternative mechanisms might, however, be postulated; for example the half-chains might be visualized as remaining intact and either swinging around their axes to their new positions or being pulled bodily through the structure 'like a wick through a candle'. Both these alternative mechanisms involve considerable disruption of the structure, and were tentatively rejected, but the oriented transformation in xonotlite–wollastonite offered no grounds for deciding between the possible mechanisms.

Lacking the clear proof afforded by the rhodonite–wollastonite transformation, there has been some reluctance to accept mechanisms which postulate the

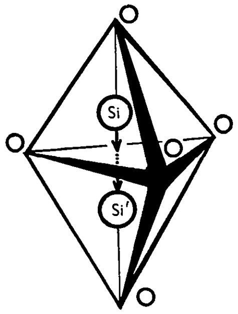


Fig. 4. Migration of silicon from an initially filled to an initially empty tetrahedron. (Reproduced from Taylor, 1960).

preservation of the cation–oxygen framework at the expense of breaking silicon–oxygen bonds. This reluctance is doubtless due in part to the habit mentioned in the introduction, of considering the disposition of the tetrahedra as the most important part of the structure. On the other hand, if it is accepted that the most likely mechanism for an oriented transformation to follow is that which involves the least spatial disturbance of ions, silicon, as the smallest ion present, will be the most likely to move.

The present study establishes one mechanism whereby this can occur, at least in transformations between silicates with similar structures based on an oxygen packing which provides some empty tetrahedra adjacent to filled tetrahedra. This may be termed filled–empty tetrahedron migration, and the mechanism differs from that suggested by Donnay *et al.* to explain silicon (and aluminium) migration in framework structures such as feldspars. Donnay *et al.* visualize an addition of H_2O at the bridging oxygen, thereby prying open two tetrahedra and enabling silicon or aluminium atoms to change place. The water is subsequently eliminated. They cite evidence of studies using H_2O^{18} to support this theory.

The present study shows that water is not essential for filled–empty tetrahedron migration. The transformation was performed under conditions which would normally be accepted as anhydrous, and although no special precautions were taken to exclude water from the specimen, it is unlikely that the amounts present could have had any significant effect. On the other hand both the rhodonite–wollastonite and xonotlite–wollastonite transformations proceed at lower temperatures under hydrothermal conditions than under dry conditions. That is, either:

(*a*) the reaction proceeds by a different, more rapid mechanism under hydrothermal conditions; or
(*b*) water, though not *essential* to filled–empty tetrahedron migration, does in fact catalyze it.

More experimental evidence is needed to distinguish between these two possibilities. In (*b*) however, it is possible to see how a variant of the mechanism suggested by Donnay *et al.* might operate. The initial attachment of a proton to a bridging oxygen (the first step in their mechanism) would weaken the bonds of the oxygen to silicon, and facilitate the migration of the silicon away from the proton, through the opposite face of the tetrahedron, as required for filled–empty tetrahedron migration.

It is concluded therefore that:

(1) The transformation studied here (and probably many others) proceeds by migration of silicon, the cation–oxygen framework being preserved.
(2) Although many, if not all, transformations involving silicon migration are catalyzed by water, there is at least one mechanism (filled–empty tetrahedron migration) which will proceed in the absence of water.

The authors are grateful to Dr H. F. W. Taylor for many helpful discussions during the course of this work.

This research forms part of a study on the structural chemistry of silicates and related substances sponsored by the Air Force Office of Scientific Research of the United States Air Force, through its European Office.

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