

The Dehydration of Xonotlite

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Dehydration of xonotlite, $\text{Ca}_6(\text{Si}_6\text{O}_{17})(\text{OH})_2$, at $775\text{--}800^\circ\text{C}$. causes oriented transformation to $\beta\text{-CaSiO}_3$ with preservation of orientation parallel to b and to (100). The mechanism of the change is discussed.

Introduction

Heller (1952) showed that fibrous aggregates of xonotlite ($\text{Ca}_6(\text{Si}_6\text{O}_{17})(\text{OH})_2$, Mamedov, 1955) on heating at $700\text{--}800^\circ\text{C}$. gave $\beta\text{-CaSiO}_3$,† with preservation of orientation along the fibre axis (b). The present studies show that a single crystal of xonotlite dehydrates to give a single crystal of $\beta\text{-CaSiO}_3$, together with varying amounts of unoriented or partly oriented material. The results allow the mechanism of the change to be discussed in the light of recent structure determinations of both substances.

Experimental

Crystals of xonotlite from Army Street, San Francisco, kindly supplied by Prof. A. Pabst, were used. Rotation or oscillation photographs about the b axis gave sharp reflexions on the even layers, but the odd-layer reflexions were weak and streaked parallel to a^* . The monoclinic cell dimensions were found to be

$$a = 16.95, b = 7.33, c = 7.03 \text{ \AA}, \beta = 90^\circ,$$

in general agreement with those given by Mamedov (1955). Use of this cell admits the existence of the weak odd-layer reflexions but does not imply any attempt to index them. It is probably a pseudo-cell; because of the poor odd-layer reflexions, the true cell has not yet been determined.

To investigate the change to $\beta\text{-CaSiO}_3$, the crystal was mounted on a silica fibre cemented to a platinum wire; a mixture of high-alumina cement and water-glass was used for both joints. The orientation of the crystal relative to the X-ray beam was established by $5^\circ b$ -oscillation photographs. The crystal was then heated without removing it from the camera, using a nickel-foil furnace (Dent & Taylor, 1956). At $775\text{--}800^\circ\text{C}$. it changed to $\beta\text{-CaSiO}_3$, the orientation of which was determined by further oscillation photographs, taken at room temperature. A variable proportion of unoriented or slightly oriented material was also formed. To check these results, a 180° Weissenberg

photograph was taken of the $h0l$ layer, with half of the layer-line slit blocked out with a thin strip of brass. The cassette was then removed, and a miniature furnace of nichrome wire was placed round the crystal, which was then dehydrated as before. The other half of the layer-line slit was then blocked out and the cassette was replaced in its original position. A further 180° Weissenberg photograph was taken. Comparison of the two halves of the film showed the relative orientation of the starting material and product.

Results

It was found that the b direction was unchanged. The (100) plane of the xonotlite became the (100) plane of the $\beta\text{-CaSiO}_3$ single crystal to within $\pm 2^\circ$ as shown by the oscillation photographs, or $\pm 1^\circ$ as shown by

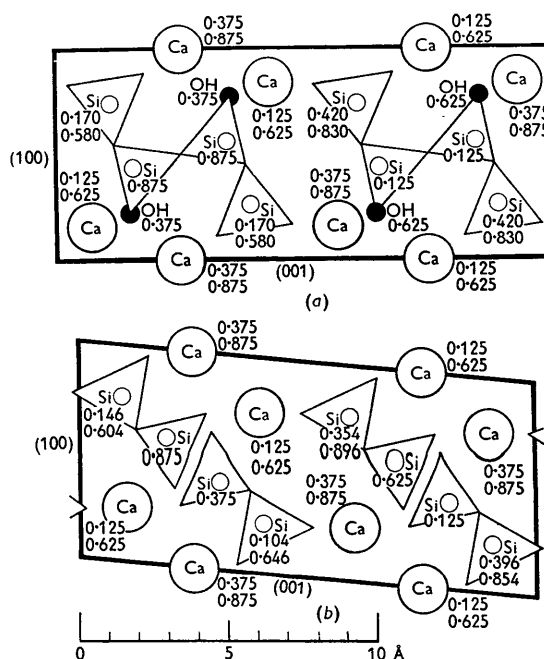


Fig. 1. Idealized structures of (a) xonotlite and (b) $\beta\text{-CaSiO}_3$ (monoclinic form); projections on (010), showing heights of atoms as fractions of b . Data from Mamedov (1955) and Tolliday (1956).

† $\beta\text{-CaSiO}_3$ is here used to include wollastonite (triclinic), parawollastonite (monoclinic), and intergrowths of the two, where it is not possible to be more specific than this.

the Weissenberg photograph. The angle could not be determined more accurately because of disorder in the product. Because β in xonotlite is indistinguishable from 90° , consideration of relative intensities is needed to determine whether a and c of β -CaSiO₃† are formed approximately from a and c of xonotlite, or from a and \bar{c} . The relative intensities of the 401 and $40\bar{1}$ reflexions of xonotlite were calculated from the atomic co-ordinates given by Mamedov, and it was found that $40\bar{1}$ was much stronger than 401 . Comparison with the experimental data established that a and c , as defined by Mamedov, become approximately a and c of β -CaSiO₃. The relative orientations are shown in Fig. 1.

The product gave reflexions with k odd which were weak, diffuse streaks with indefinite maxima. Comparisons of rotation photographs about the b axis with those of wollastonite and parawollastonite were inconclusive; the product could have been either, or an intergrowth of the two. Oscillation photographs about the b axis were symmetrical about the equator, showing that if the crystal were triclinic it was multiply twinned.

The specific gravity of the original xonotlite was measured by the suspension method, with preliminary boiling of the liquid under reduced pressure to remove trapped air from the crystals; the value was 2.71. The refractive indices were $\alpha = \beta = 1.583 \pm 0.002$, $\gamma(\text{elongation}) = 1.592 \pm 0.002$. After dehydration the specific gravity was 2.75. The crystals were almost opaque, and only a mean value of 1.57 ± 0.01 could be found for their refractive index; they showed very low birefringence, and positive elongation in all orientations. To establish whether dehydration caused any change in external size in the direction perpendicular to (100), crystals about $3 \times 0.3 \times 0.2$ mm. were mounted on silica fibres and then heated, using a very small flame. While this was done the crystals were observed using a microscope with a medium-power objective and a micrometer eyepiece. Their thickness perpendicular to (100) remained constant to within $\pm 2\%$.

Discussion

The preservation of (100) rather than any other plane in the prism zone probably occurs because, as shown by Mamedov, it is the best cleavage in xonotlite. Since the outline of the specimen does not change, it is supposed that the crystal of β -CaSiO₃ is formed by the conversion of crystallites, as shown in Fig. 2. Most of the slip will thus occur parallel to the good cleavage. Taylor (1955) obtained a similar result for afwillite, whose perfect (10 $\bar{1}$) cleavage becomes the (001) plane of γ -Ca₂SiO₄.

† On monoclinic axes, $a = 15.33$, $b = 7.28$, $c = 7.07$ Å, $\beta = 95^\circ 24'$ (Barnick, 1936). All reflexions given by the monoclinic form are indexable on these axes, as are ones with k even given by the triclinic form.

In Fig. 2, the shrinkage of the a axis occurring on dehydration is ignored. Since no change of size perpendicular to (100) was observed, it appears likely

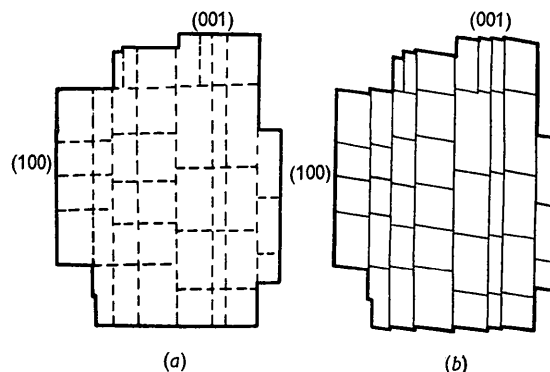


Fig. 2. Diagrammatic representation of the transformation of crystallites of (a) xonotlite into (b) β -CaSiO₃. Projection on (010).

that the principal effect of this shrinkage is the formation of minute spaces between the crystallites. In accordance with this view the specific gravity and refractive index of the product are both lower than those normally found for β -CaSiO₃ (2.915 and $\alpha = 1.620$, $\beta(\text{elongation}) = 1.632$, $\gamma = 1.634$). The product is also optically anomalous in having + and not \pm elongation. The observed specific gravity of the product (2.75) is higher than that (2.68) calculated assuming no change in volume. The specific gravity was also calculated from the mean refractive index using the Lorentz-Lorentz equation, as described by Howison & Taylor (1956); this gave a value of 2.68. These results suggest that the suspension liquid used for the specific-gravity determination was able to penetrate to some extent into the spaces between the crystallites, but that the immersion liquid used for the refractive-index determination could not. This difference is possibly due to the fact that in the latter case no precautions were taken to remove trapped air from within the crystals; the liquids used for refractive-

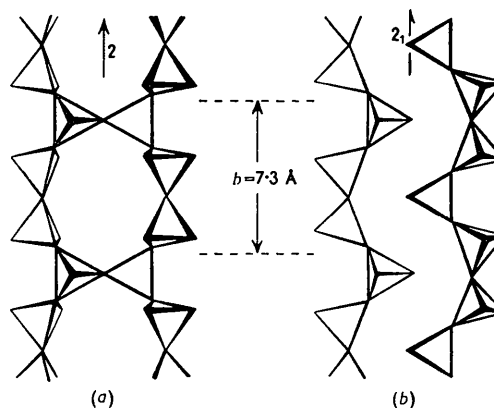


Fig. 3. Si-O chains in (a) xonotlite and (b) β -CaSiO₃.

index determination were also more viscous than those used for measurement of the specific gravity.

Idealized structures of xonotlite (Mamedov, 1955) and β -CaSiO₃ (Dornberger-Schiff, Liebau & Thilo, 1954, 1955; Buerger, 1956; Tolliday, 1956) are shown in Fig. 1. They are drawn in the relative orientation found in our determinations. In xonotlite (Fig. 1(a)) the tetrahedra form double chains (Fig. 3(a)) whose two halves are related by a diad axis, parallel to b . These are interleaved with distorted sheets of calcium ions parallel to (001). Our own studies indicate that the true structure is more complicated, but that the difference lies only in shifts of $\frac{1}{2}b$ in the position of the silicate chains, and can be ignored in the present discussion.

The idealized structure for β -CaSiO₃ (Fig. 1(b)) is that of parawollastonite (monoclinic) drawn from data provided by Tolliday (1956). The silicate chains (Fig. 3(b)) are single and closely resemble a halved xonotlite chain; they occur in pairs which are related by a screw diad. The arrangement of the calcium ions is very similar to that of xonotlite, as is the relationship of the chains to the calcium ions in the (010) projection. Because of the screw diad, only half the chains in β -CaSiO₃ have their tetrahedra in approximately the same positions as tetrahedra of the xonotlite chain. Available data do not indicate whether the centre of symmetry shown is actually present, but, as with xonotlite, any discrepancies between the idealized and the true structures probably consist only in shifts of $\frac{1}{2}b$ of the silicate chains. Wollastonite and parawollastonite differ in the arrangement of these chains; the diffuseness of the odd-layer reflexions from the product obtained by heating xonotlite indicates that it does not correspond exactly to either of these forms.

Comparison of the two structures indicates that the calcium ions do not move greatly in the transformation. For the silicon and oxygen atoms three possible mechanisms are suggested:

(1) Expulsion of H₂O from each pair of OH groups, and bodily translation of one half of each xonotlite chain through $\frac{1}{2}b$. The remaining OH oxygen satisfies the extra valency produced by the breaking of the cross-links in the double chain.

(2) As (1), except that one half of each xonotlite chain, instead of undergoing translation parallel to b , is altered by twisting two-thirds of its tetrahedra around its axis.

(3) Expulsion of hydrogen from the hydroxyl groups

together with the oxygen atoms cross-linking the two halves of the xonotlite chains, with little other movement of oxygen atoms. Some of the silicons move; the chains are broken and reformed.

Possibilities (1) and (2), while not breaking any Si-O bonds except those cross-linking the two halves of the chain, involve great disturbance of the Ca-O sheets, and the breaking of many Ca-O bonds. The third possibility appears to be the most likely. Very few or no Ca-O bonds are broken, and the Ca-O framework is almost undisturbed. The process can be visualized as movement of certain Si atoms between the oxygens. The new type of chain is formed which, like the one destroyed, is able to fit in with the Ca-O skeleton. On an idealized picture, one Si-O bond in six must be broken, and an equal number of new ones formed. This is a minimum figure. In fact, the diffuse odd-layer reflexions from the product show that there is much disorder in the stacking of the chains. This suggests that a greater proportion of bonds is broken and that the movement of Si atoms is subject to random variations.

Evidence was found of an intermediate structure formed at about 725° C. It reverted on standing at room temperature to a modified form of xonotlite, which differed from the starting material in its odd-layer reflexions, and thus in the stacking of the chains. It is hoped that investigation of this compound may provide further evidence about the transformation.

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