

TOPOTAXY IN THE ANATASE-RUTILE TRANSFORMATION

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ABSTRACT

The anatase-rutile transformation has been shown to result in preferred orientation of the product but with no preservation of the anatase axes of symmetry. It is, therefore, classified as a case of intermediate topotaxy.

Single crystals of anatase were transformed to rutile at 900°–950° C. Oscillation patterns indicated polycrystalline specimens exhibiting preferred orientation. Interpretation of the resultant pole figures suggested a mechanism of transformation involving retention of the {112} pseudo-close-packed planes of oxygen in anatase as the {100} pseudo-close-packed planes in rutile, and rearrangement of the titanium and oxygen ions within these planes. A cooperative movement of the titanium and oxygen ions is proposed in which the majority of the titanium ions, in order to reach their new sites, break only two of their original six Ti-O bonds.

INTRODUCTION

It is frequently possible to determine the mechanism of crystallographic phase transformations by studying the orientation of the product phase with respect to that of the reactant. If the transformation occurs so that the orientation of the product phase is correlated with the orientation of the reactant phase, then a topotactical relation is said to exist² (Lotgering, 1959; Shannon and Rossi, 1964). The degree of correlation determines the degree of topotaxy. If the atoms undergo only a change in secondary coordination and no primary bonds are broken, such as in displacive phase transformations, then a high degree of topotaxy results. A crystal undergoing such a reaction results in a single-crystal diffraction pattern before and after the transformation. If, however, the atoms must undergo extensive rearrangement, little accord exists between the original and final structures and the transformation is weakly topotactical or reconstructive. The dehydroxylation of γ -FeOOH to form γ Fe₂O₃ (Mackay, 1960) and the α - β quartz transformation are two examples of strong topotaxy. Cases of intermediate and weak topotaxy occur respectively in the dehydration of Mg(OH)₂ and Ca(OH)₂ (West, 1934),

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² Bernal (1960) and Mackay (1960) use more restricted criteria of (a) the retention of at least one axis of symmetry, or (b) a three-dimensional accord between the structures and preservation of the majority of the atomic positions. Taylor *et al.* (1962) assume Lotgering's definition with the added restriction that three-dimensional accord between the initial and final structures is present.

while the quartz-cristobalite transformation is reconstructive (Chaklader, 1963) and is thus not expected to exhibit topotaxy.

A study of the brookite-rutile transformation (Barblan *et al.*, 1958) revealed a moderately topotactical transformation and allowed the investigators to postulate a mechanism involving small atomic rearrangements. The brookite [100] was found to remain coincident with the rutile [100]. In the brookite (100) plane, the rutile assumed three different orientations: (1) at 700° C., rutile [100] || brookite [001]; (2) at 800° C., rutile [001] || brookite [010]; and (3) also at 800° C., rutile [001] || brookite [027] or [023]. In a [100] projection of the brookite structure, zig-zag chains of TiO₆ octahedra running along the c-axis are evident so that formation of the chains of octahedra in rutile in case (1) is not unexpected and involves only a straightening of the chains and breaking up of every other octahedron by a shift of the Ti atom from its octahedral site to a new one. In cases (2) and (3) the movement required of the oxygen atoms is less than that in case (1), but the movement of the Ti atoms is greater. Barblan *et al.* suggested that the mobility of the oxygen atoms relative to that of the Ti atoms is greater at lower temperatures, making case (1) reasonable. As the temperature increases, the mobility of the Ti atoms becomes greater and case (2) becomes predominant. The same authors made an attempt to find similar behavior in the anatase-rutile transformation but failed to discover any preferred orientation of the rutile crystals. From Table 1 it can be seen that the volume contraction in the brookite-rutile transition is ~3%, while that in the ana-

TABLE 1. PROPERTIES OF TiO₂

Form	Symmetry	Space group	Unit cell dimensions, Å	Calculated density, gm/cm ³
Brookite	Orthorhombic	$D_{2h}^{15} Pbc_a$	$a = 9.18^1$ $b = 5.45$ $c = 5.14$	4.126
Anatase	Tetragonal	$D_{4h}^{19} I \frac{4}{a} md$	$a = 3.785^2$ $c = 9.514$	3.892
Rutile	Tetragonal	$D_{4h}^{14} P \frac{4}{m} nm$	$a = 4.593^3$ $c = 2.959$	4.249

¹ Pauling and Sturdivant, *Zeit. Krist.* **68**, 239-56, 1928.

^{2,3} Cromer and Herrington, *Jour. Am. Chem. Soc.* **77**, 4708-4709, 1955.

tase-rutile transition is $\sim 8\%$; thus, in the latter case a more random distribution of the rutile crystals can be expected from the distortion alone.

Our experiments showed, however, that large octahedral single crystals of anatase could be transformed without loss of their external shape even though severe cracks had developed as would be expected from an anisotropic contraction. The fact that the crystals were still bipyramidal in shape and had not disintegrated allowed the determination of the orientation of the product phase by x -ray diffraction methods. It was hoped that a study of this orientation would provide some information concerning the mechanism of the transformation.

EXPERIMENTAL PROCEDURE AND RESULTS

Three crystals were chosen for a detailed orientation study. The first crystal, G-2,¹ from Disentis, Graubünden, Switzerland, was a bipyramid 0.5 mm \times 0.2 mm, the long dimension being along the c -axis. The other two crystals, V-2 and V-4,² from the area of Val Vals, Graubünden, Switzerland, were large bipyramidal crystals, one 4 mm \times 2 mm, and the other 1 $\frac{1}{2}$ mm \times 1 mm. Crystal G-2 was heated at 850° C. for 28 hours, 900° for 66 hours, 925° for 25 hours, and at 950° for 10 hours. Crystal V-2 was heated for 3 hours at 850° C., 3 hours at 900°, and 1 hour at 950°. Crystal V-4 was heated for 48 hours at 900° C. The transformation was found to proceed from nucleation sites on the surface of a crystal toward the center. This behavior, combined with the large shrinkage, resulted in the formation of cracks. Crystal G-2 was transparent and tan in color before the transformation and brilliant orange afterward; the other two crystals were translucent and dark green in color.

Rotation patterns resulted in discontinuous rutile powder rings, indicating polycrystalline specimens exhibiting preferred orientation. Determination of the orientation of the rutile crystallites was made in a manner similar to that used in the study of preferred orientation in metal wires and sheets (Henry, *et al.*, 1960). When a polycrystalline specimen exhibiting preferred orientation is irradiated with monochromatic x -rays, discontinuous powder rings result. If the crystallite size is large, oscillation patterns, rather than stationary patterns, must be used. Oscillation patterns provide the angle ρ which the normals to the reflecting planes make with the axis of oscillation. The intersection of the cone of angle 2ρ with the cone of angle $(180^\circ - 2\theta)$, whose axis is the incident x -ray beam,

¹ Obtained from Minerals Unlimited, Berkeley, California.

² Obtained from Scott Williams Mineral Co., Inc., Scottsdale, Arizona.

gives the position of the pole. These poles can then be plotted on a stereogram. A series of oscillation patterns made with the incident x -ray beam oriented in different positions with respect to the original anatase crystals provide the complete pole figure.

Each heat-treated crystal was mounted in an oscillation camera so that the c -axis of the original anatase crystal was perpendicular to the x -ray beam. Ten-degree oscillation patterns using filtered Cu-radiation were made at appropriate intervals around the [001] axis for crystals V-2 and V-4 and around the [001] and [100] axes for crystal G-2. The rutile (110), rather than the (100) poles, were chosen because of their relatively high intensity. The diffraction rings in a pattern of crystal G-2 were analyzed to provide the rutile (110) and (001) poles shown in Fig. 1a. Composite diagrams for both the [001] and [100] orientations of the original anatase, in which the pole figures for the three crystals were superimposed, were also constructed. Figures 1b and 1c show the composite diagrams for the anatase [100] orientation with the experimental high and low intensity reflections of rutile (110) and (001) poles, respectively. There are eight distinct directions which the rutile c -axis might assume relative to an anatase crystal. It should be emphasized, however, that all of the possible orientations expected theoretically may not occur in a single transformed crystal because of preferred directions of nucleation. Furthermore, a large degree of scatter in the positions of the poles was expected from the distortion and misorientation of the crystallites resulting from the shrinkage and cracking associated with the transformation. The expected regions of high and low intensity for the eight orientations are also indicated in the latter two pole figures (Figs. 1b, c).

In addition, the regions of intensity within the diffraction rings were sometimes discontinuous because of the large size of some of the crystallites. Despite all of the above difficulties, regions of concentration of the rutile (110) and (001) poles are evident in the pole figures. It can be seen that clustering of the (110) poles occurs around the equator and surrounding the anatase [001] and that the (001) poles are situated in a broad region centering on a latitude of about 45 deg. It might at first be thought that the rutile (110) poles lie parallel to the anatase [001] direction. This possibility was rejected since it would have implied that the rutile (001) poles were all situated along the equator, which is clearly not the case.

MECHANISM OF TRANSFORMATION

From a study of the kinetics of the reaction (Shannon, 1964), it was apparent that the mechanism cannot be a mere change of bond angles and/or bond lengths which result in a slight shift or retention of major

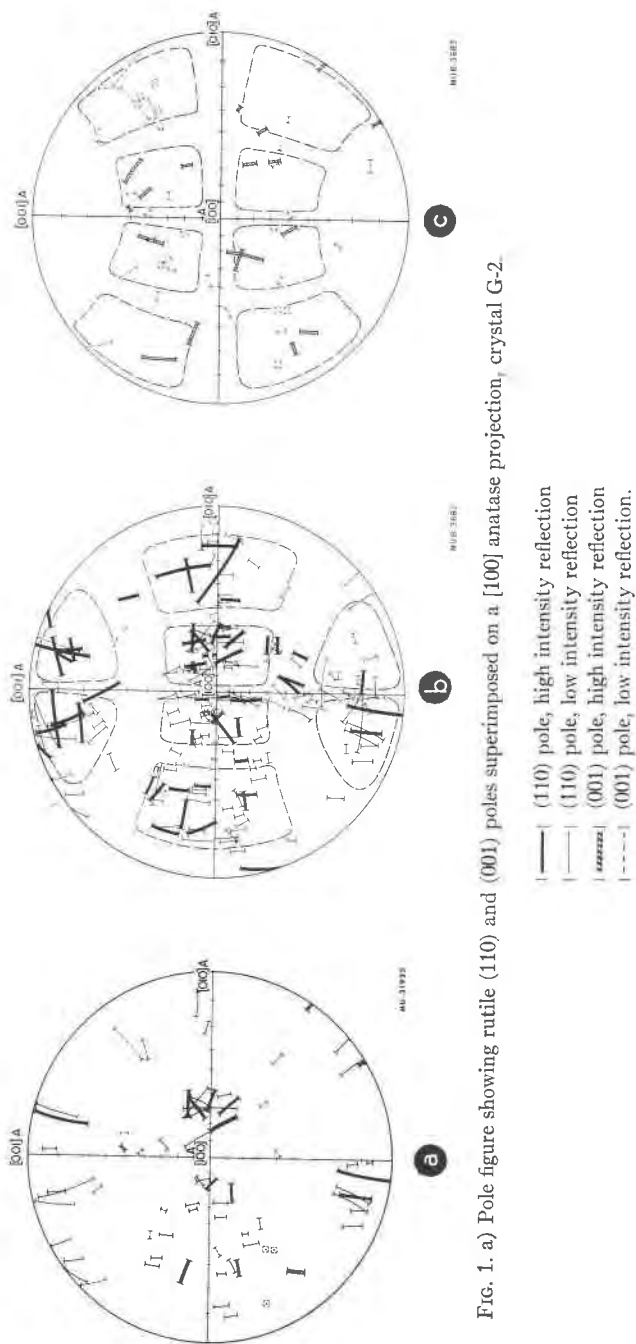


Fig. 1. a) Pole figure showing rutile (110) and (001) poles superimposed on a [100] anatase projection, crystal G-2.

b) Pole figure showing rutile (110) poles on a [100] projection of crystals V-2, V-4, and G-2.

c) Pole figure showing rutile (001) poles on a [100] projection of crystals V-2, V-4, and G-2.

crystallographic axes. The activation energy for transformation was found to vary among different samples, depending upon the impurity content, from 100 to 180 kcal/mole. These values suggest that the process involves the rupture of bonds and a major rearrangement of atoms. In addition, the lack of close similarity of the anatase and rutile structures suggests the necessity of a rearrangement of atoms.

The anatase and rutile structures generally represented as pseudo-close-packed oxygen layers with half the octahedral sites vacant; in anatase the oxygens are in a distorted face-centered cubic arrangement and in rutile, in a distorted hexagonal arrangement. In anatase the close-packed plane is the (112) plane with the Ti atoms arranged in zig-zag chains running along [221] as indicated in Fig. 2a, and each TiO_6 octahedron shares four of its edges with four other octahedra. For the sake of clarity only one oxygen plane with its associated titanium ions is shown. Actually, four of these planes are necessary to cover the repeat distance. In the next layer of oxygen atoms the zig-zag chains of titanium ions are displaced along [110] by half the distance between chains, and along [221] by 0.6 Å. Figure 2b includes part of the second oxygen layer. In rutile the close-packed plane is (100) and the Ti atoms lie in rows along [001] as indicated in Fig. 2c. The rutile structure may also be pictured as a series of chains of TiO_6 octahedra parallel to the *c*-axis, where each octahedron shares two of its opposite edges with two other octahedra. The Ti atoms in the [001] rows form the centers of these octahedra, some of which are shown in Fig. 2c.

The anion framework is expected to undergo a minimum of rearrangement if the least spatial disturbance of the structure is to take place (Brindley, 1963). Since the interplanar spacings of the close-packed planes in anatase and rutile are nearly identical ($d_{112}^{\text{anat}} = 2.336$; $d_{200}^{\text{rut}} = 2.297$), it was assumed that most of the atomic movement occurred within the planes themselves. Because the Ti atoms lie in rows in the rutile structure, one looks for similar rows in the anatase (112) plane. The possible directions for the resultant rutile *c*-axis are indicated in Fig. 2a. Directions "a," "b," and "c" do not correspond to the experimentally observed distribution of (110) and (001) planes. The line of atoms along "d," however, is clearly the direction in which most of the [001] poles were found. Figure 3a is a stereogram showing the trace of one of the anatase (112) planes containing two directions which the *c*-axes of rutile may assume after the transformation. Figure 3b shows the orientation of four of the eight possible equivalent rutile unit cells and the complete pole figure if the rutile crystals grew in all possible orientations. Although the positions of the calculated poles (Fig. 3b) do not lie exactly at the center of the experimental intensity distribution (Figs. 1b, c), the

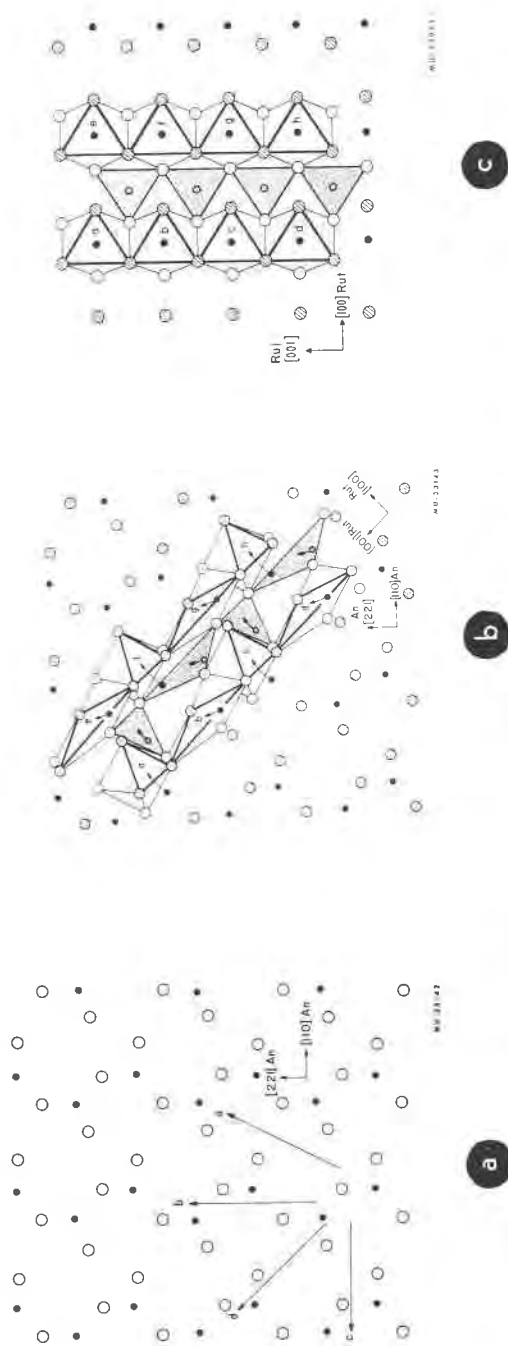


Fig. 2. a) Projection perpendicular to the (112) pseudo-close-packed plane in anatase showing possible directions of the rutile c -axes after transformation.

b) The (112) plane in anatase showing the potential rearrangement along the "d" direction necessary to form the titanium octahedral structure.

- oxygen ions
- titanium ions.
- ⊙ oxygen ions in the upper plane
- titanium ions below the upper plane of oxygen ions
- oxygen ions in the lower plane
- titanium ions below the lower plane of oxygen ions.

c) Projection perpendicular to the (100) pseudo-close-packed plane in rutile showing the titanium octahedral structure after the rearrangement indicated in Fig. 2b.

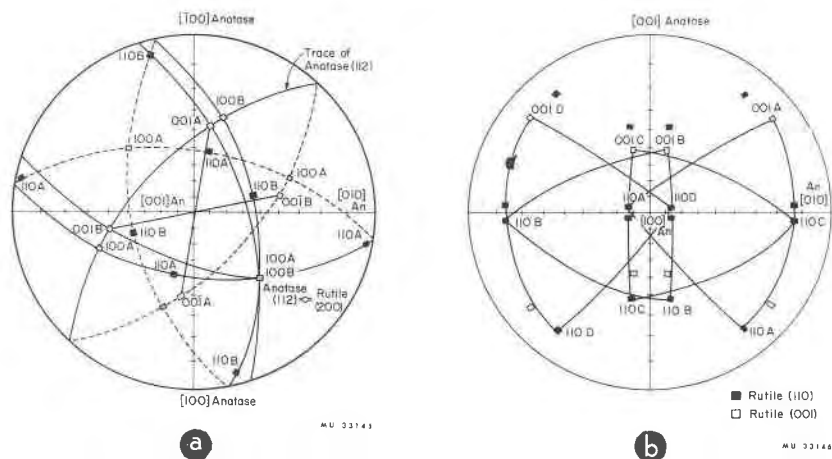


FIG. 3. a) An anatase [100] stereogram showing the orientation of two rutile crystals whose c-axes lie in an anatase (112) plane.

- rutile (110)
- rutile (001)
- ▨ rutile (100).

b) Anatase [100] stereogram showing rutile (110) and (001) poles and the orientation of four equivalent rutile crystals.

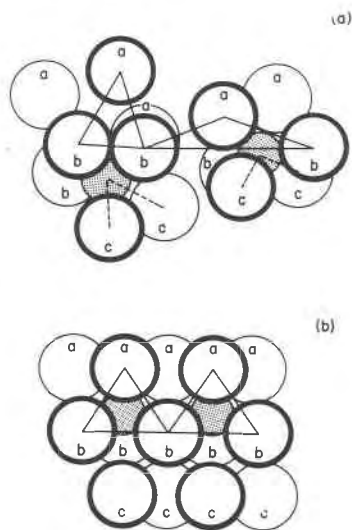
agreement is considered satisfactory in light of the larger amount of shrinkage and distortion which takes place during the transformation.

The mechanism of the transformation appears to be similar to that of brookite in the sense that the close-packed planes in the reactant remain as close-packed planes in the product with almost the same spacing while the major rearrangement occurs within these planes. Figure 2b shows the atoms of the rutile TiO_6 octahedral structure as they are arranged in anatase before the transformation. In achieving the rutile configuration shown in Fig. 2c, considerable distortion occurs, as may be seen from the relative positions of the cations shown in the figures, due to rearrangement of oxygens to attain their hexagonal packing. Also, in the lower layer, half the titanium atoms undergo no change in nearest neighbors, while the other half break two Ti-O bonds and acquire two new nearest neighbors. In the upper layer all the cations must break two bonds in achieving their new position. It is clear from the positions of the cations in Figs. 2b and 2c that a shrinkage occurs in the new [001] direction and an expansion in the new [100] direction.

Figure 4 shows two adjacent cations and the surrounding oxygen configuration (a) before, and (b) after the transformation. These correspond

to octahedra a and b in Figs. 2b and 2c. The shifts of the titanium atoms to their new octahedral sites occur by breaking two bonds with "c" anions, indicated by dashed lines in Fig. 4a, and making two new bonds. During this process the cation maintains bonds with four anions; at the midpoint of the movement, thus, the cations have four nearest neighbors and two more distant neighbors. The apparent movement of the cations into adjoining tetrahedral sites does not actually occur because these sites progressively change into octahedral sites as a consequence of the indicated movements and the associated rearrangement. This mechanism is best described as a cooperative movement of the titanium and oxygen atoms in contrast to a strict diffusion mechanism in which the anion structure remains essentially fixed while the cation moves through a tetrahedral site to its new octahedral site.

The question then remains as to the reasons for the failure of the rutile *c*-axes to lie in the "a," "b," or "c" directions as indicated in Fig 2a. Alignment of the titanium atoms in the "b" direction can be achieved by a similar type of cooperative movement of the atoms, but it would require a greater distortion of the oxygen configuration and an expansion along this direction which would be energetically unfavorable. Align-



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FIG. 4. Configuration of octahedral structures associated with two corresponding cations (a) in anatase before the transformation, and (b) in rutile after the transformation. The dashed lines represent Ti-O bonds that are broken during the transformation. Structure in (a) equivalent to that shown in Fig. 2b and in (b), Fig. 2c.

ment of the titanium atoms in the "a" or "c" direction would require a diffusion type of movement of half the cations in an anion structure that remains essentially fixed, in which the cation breaks four Ti-O bonds and retains only two original neighbors during movement; such a rearrangement would again be energetically less favorable.

DISCUSSION

Oriented transformations have been assumed to occur with the least spatial disturbance (Glasser and Glasser, 1961). This concept is operable on the basis that the minimum degree of movement and rearrangement of atoms results in the path of minimum energy. However, spatial disturbance must be associated with (1) changes in position of the larger structure-determining ions, and (2) changes in distribution of the remaining ions. Thus, it is evident from this study and these principles that the anatase-rutile transformation is controlled by two factors: (1) the least spatial disturbance of oxygen ions must occur, and (2) the number of bonds broken must be at a minimum. The activation energy for the transformation should therefore be made up of two terms: (1) the strain energy which must be overcome for the oxygen atoms in the close-packed planes to reach their new configuration, and (2) the energy which is necessary to break the Ti-O bonds as the titanium atoms redistribute themselves.

Strong topotaxy implies similarity of the initial and final structures and the preservation of at least one of the axes of symmetry. The anatase-rutile transformation should not, therefore, be highly topotactical because the structures are dissimilar and none of the major axes of symmetry of the product correspond to those of the reactant. However, neither is the transformation a reconstructive or heteromorphous reaction characterized by random orientation of the product, *i.e.*, with no dimensional accord between reactant and product. Since the product exhibits preferred orientation, thus preserving some of the structural elements, the transformation could be classified as an intermediate case of topotaxy. Such a category would also include the brookite-rutile transformation as well as reactions involving substances with layer structures in which the layers are retained with reconstruction within the layers. The transformation of the brookite, however, exhibits a higher degree of topotaxy than that of the anatase because of the smaller dimensional change.

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