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POSSIBLE TOPOTAXY IN THE TiO_2 SYSTEM

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ABSTRACT

Possible topotactic reaction mechanisms for the brookite→TiO_2 II, anatase→TiO_2 II and rutile→TiO_2 II reactions are proposed. These mechanisms are based on maintaining the integrity of the "close packed" layers of oxygen in each phase, and are consistent with known topotaxy in the TiO_2 system. Also, observations made during a p-T study of these reactions may be explained by the proposed topotactic mechanisms.

INTRODUCTION

The synthesis of a new high pressure phase of TiO_2 (Dachille and Roy, 1962) marked a renewal of interest in phase transitions in this system over a broad p-T range. Rutile has been converted to this phase under shock conditions (McQueen *et al.*, 1967; De Carli and Lande, 1967), and the reversibility of this transition has been demonstrated in static superpressure apparatus (Bendeliany, Popova, and Vereschagin, 1966). The anatase-rutile transformation has been observed in the "Belt" apparatus (Vahldiek, 1966). Dachille, Simons and Roy, (1968) have studied the transformation of the TiO_2 polymorphs within the limits of the opposed anvil apparatus.

From observations made during p-T studies in the TiO_2 system (Dachille, Simons, and Roy, 1968) it appeared that structural factors influenced the transitions. The following examples are cited: 1) the crystallinity of the II phase obtained by conversion of anatase was quite poor. This was evident in line broadening of the X-ray diffraction pattern of II, and the anomalously low measured density of 4.10 g/cm^3 as compared to 4.33 g/cm^3 calculated from the X-ray data. This was attributed to the presence of a short range order (SRO) phase. The II crystallized from brookite yielded more numerous and well-formed X-ray diffraction maxima, and had a measured density of 4.318 g/cm^3, in good agreement with that of 4.329 g/cm^3 calculated from the lattice parameters; 2) many experiments showed that the anatase-II conversion was slow and difficult to complete, but that under the same conditions the conversion brookite-II was completed in about twenty-four hours; 3) in the attempt to determine the apparent II/p-T phase boundary, it was found that this could be done accurately only when II was used as the starting mate-

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rial. When anatase or brookite were the starting materials, the results were difficult to interpret.

The existence of structural factors for reactions in the TiO_2 system has been experimentally demonstrated in the brookite-rutile and anatase-rutile reactions (Barblan, Brandenberger and Niggli, 1958; and Shannon and Pask, 1964, respectively). Experimental difficulties with single crystals of anatase and brookite in our opposed anvil apparatus did not permit an X-ray study for evidence of topotactic transition to II or rutile. This report, therefore, is confined to an examination of *some* possible topotactical mechanisms among the reactions brookite-II, anatase-II, and II-rutile which could have a bearing on the observations listed above and others to be discussed. Using the close packed planes as a common denominator, a qualitative structural picture is presented for these proposed mechanisms. For a general review of topotaxy see Bernal (1960) and MacKay (1960).

CRYSTAL STRUCTURES OF THE TiO_2 PHASES

Table 1 lists pertinent crystallographic data of the TiO_2 phases. Detailed descriptions of the structures of anatase, brookite and rutile can be found in Bragg and Claringbull, (1966); the structure of II is described by Simons and Dachille (1967). A brief description of these phases as a function of their oxygen close packing is given below.

Anatase. The structure of anatase can be represented by a distorted pseudo-cubic close packed (*CCP*) layering of oxygen with Ti atoms occupying one half the octahedral interstices. The close packed plane is the (112) with Ti atoms forming zigzag chains along [221]. Each TiO_6 octahedron shares four edges with four other octahedra. In all, four oxygen layers are needed to produce the repeat. In adjacent layers of oxygen the zigzag chains of TiO_6 octahedra are displaced along [110] by half the distance between chains, and along [221] by 0.6 Å. The octahedral chains along [221] share two edges.

Brookite. This phase is built of oxygen layers arranged in a pseudo-doubly-hexagonal close packing scheme (*DHCP*) *i.e.*, *ABACABAC*. . . . The close packed plane is the (100) plane. One half of the octahedra are filled with Ti atoms to form zigzag chains along [001]. In this case the oxygen stacking is such that each octahedron in a chain shares three edges.

Rutile. The rutile structure may be visualized as a series of chains of TiO_6 octahedra parallel to the *c* axis, in which two opposite edges of each

TABLE 1. CRYSTALLOGRAPHIC DATA FOR TiO_2 PHASES

Phase	Symmetry	Space Group	Lattice Parameter (Å)	Density (calc)
Rutile	Tetragonal	D_{4h}^{14} $P4_2/mnm$	a 4.594[a] c 2.959 $Z=2$	4.249
TiO_2II	Orthorhombic	D_{2h}^{14} $Pbcn$	a 4.515[b] b 5.497 c 4.939 $Z=4$	4.329
Anatase	Tetragonal	D_{4h}^{19} $I\,4/amd$	a 3.785[c] c 9.514 $Z=4$	3.892
Brookite	Orthorhombic	D_{2h}^{15} $Pbca$	a 9.184[d] b 5.446 c 5.145 $Z=8$	4.126

[a] Baur (1956).
[b] Simons and Dachille (1967).
[c] Cromer and Harrington (1955).
[d] Weyl (1959).

octahedron are shared with two adjacent octahedra along the chain. A projection of this structure normal to the (100) or the (010) plane will show a gross approximation of hexagonal closest packing for the oxygen atoms, whereas a projection normal to (001) will show an approximation of a body centered array of oxygen.

TiO_2 II. This phase may also be visualized as having HCP oxygen planes with the (100) as the close packed plane. The TiO_6 octahedra are in zigzag chains along [001] with each octahedron sharing two non-opposite non-adjacent edges with its neighbor along the chain. In the [100] direction the octahedra share corners and also produce zigzag chains.

Table 2 lists the interatomic spacing between the pseudo close packed planes of these phases.

REVIEW OF TOPOTAXY IN THE TiO_2 SYSTEM

Barblan *et al.* (1958) report topotaxy in the brookite-rutile transformation. They found that the brookite [100] was coincident with the rutile [100] and that in the brookite (100) plane rutile assumed the following

TABLE 2. INTERATOMIC SPACING BETWEEN THE CLOSE PACKED LAYERS IN THE TiO_2 PHASES

Phase	Type of Packing	Spacing
Anatase	Pseudo-*CCP*	$d(112)=2.336$Å
Brookite	Pseudo-double *HCP*	$d(400)=2.296$Å
Rutile	Pseudo-*HCP*	$d(200)=2.297$Å
TiO_2II	Pseudo-*HCP*	$d(200)=2.258$Å

positions: a) at 700°C, rutile [100] is parallel to brookite [001]; b) at 800°C, rutile [001] may be parallel to brookite [010]; and c) also at 800°C, rutile [001] may also be parallel to brookite [027] or [023]. According to Barblan *et al.*, these different mechanisms are related to the oxygen and Ti mobility. They suggest that at lower temperatures the oxygen mobility is greater than that of Ti, while the opposite is true at higher temperatures. Thus, case (a), which involves the straightening of zigzag TiO_6 chains along the *c*-axis and the shift of the Ti atoms from one set of sites to another set is assumed to have greater oxygen than Ti movement. At higher temperatures, cases 2 or 3 predominate because the reverse is true.

Shannon and Pask (1964) found that in the anatase-rutile reaction between 900°–950°C the {112} pseudo *CCP* oxygen planes are retained sa the pseudo HCP planes in rutile. In Figure 1, which is a projection

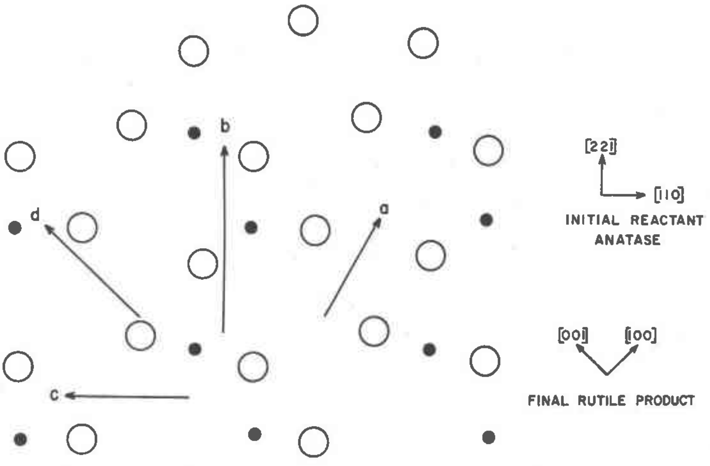

FIG. 1. Projection perpendicular to (112) the pseudo cubic closest packing plane of anatase, showing possible directions for the rutile *c* axis after the reaction. Symbols used: Large open circles represent oxygen; smaller, filled circles, Ti. (After Shannon and Pask, 1964).

perpendicular to the (112) pseudo close packed plane of anatase, the directions *a*, *b*, *c*, and *d* indicate possible *c*-axis directions of rutile. They found that direction *d* corresponds to the [001] direction in rutile. They stated that direction *b* was not followed in the reaction because "it would require a greater distortion of the oxygen configuration and an expansion along this direction which would be energetically unfavorable." Also, realignment of the Ti in the *a* or *c* directions according to Shannon and Pask "would require a diffusion type of movement of half the cations in an anion structure that remains essentially fixed, in which the cations break four Ti-O bonds and retain only two original neighbors during movement; such a rearrangement would again be energetically less favorable."

PROPOSED TOPOTAXY IN THE TiO_2 SYSTEM

The Brookite—II Reaction. A topotactic relationship would exist between brookite and II if the polymorphic transition were to proceed in this manner: Every fourth (or *C*) layer in the *DHCP* sequence of oxygen

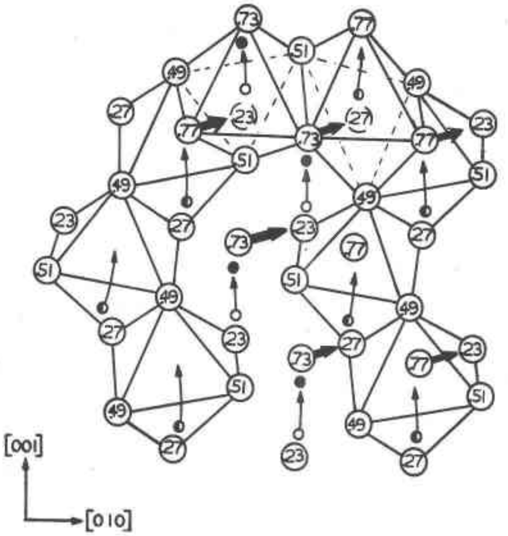

FIG. 2. Projection normal to (100) plane of brookite showing portions of two octahedral layers. Note the zigzag chains of TiO_6 octahedra in each level along [001] similar to those found in II. Symbols used: Large open circles represent oxygen and the numbers represent fractional coordinates along *a*; small circles represent Ti, with completely filled at 0.12 *a*, small open at 0.63 *a* and half filled at 0.81 *a*. Ti atoms are also located within the oxygen octahedra at 0.37 *a*. Oxygen atoms are also located above and below the oxygen at 0.49 *a* and 0.51 *a* at 0.99 *a* and 0.01 *a*, respectively. The arrows show the directions of atomic movement to complete proposed topotaxy.

in the brookite structure undergoes a translation in the [001] direction so as to convert the *ABACABAC*—layering scheme to the *ABABAB*—of the II structure. Accompanying this translation a shift of position of the Ti atoms between the third and fourth and the fourth and fifth layers of oxygen, taking an *A* layer as the first, would also have to occur. Figure 2 summarizes the necessary translation of layers and the relative displacement of Ti and oxygen atoms. The "fourth" layer of oxygen (at 0.73 *a* and 0.77 *a*) would move diagonally in the [011] direction to relocate over the 0.27 *a* and 0.23 *a* oxygen positions while the Ti atoms at 0.81 *a* and 0.63 *a* move in the *c* direction to positions above the 0.37 *a* and 0.12 *a* Ti atoms, respectively. The number of shared octahedral edges is reduced from three in brookite to two in II.

If this mechanism is followed the topotactic scheme would result in the crystallographic axes remaining coincident in orientation with the

brookite [001] parallel to II [001]
brookite [010] parallel to II [010]
brookite [100] parallel to II [100]

In terms of lattice constants the relationship would be

$$1/2\,a \text{ brookite } (4.592\ \text{Å}) \approx a \text{ II } (4.515\ \text{Å})$$
$$b \text{ brookite } (5.495\ \text{Å}) \approx b \text{ II } (5.497\ \text{Å})$$
$$c \text{ brookite } (5.145\ \text{Å}) \approx c \text{ II } (4.939\ \text{Å})$$

The Anatase—II Reaction. A topotactic relationship between anatase and II could be realized from the mechanism proposed below. As will be seen, the steps are more complicated and do not result in the coincidence of any symmetry axes. It is proposed that the {112} pseudo *CCP* oxygen in anatase can become the (100) pseudo *HCP* of II. The [221] direction in the anatase structure contains zigzag chains of TiO_6 octahedra which have edge-sharing similar to that in the [001] direction of II. Therefore, the [110] of anatase would be equivalent to the [010] of II.

A transformation of *CCP* to *HCP* involves the coordinated shifting of six layers in the stacking sequence. A simple shear displacement will transform a *CCP* layering scheme to *HCP* if every two atomic planes are considered locked together, *i.e.*, as the layers between the dashed lines in Figure 3. The planes which are "locked" together contain zigzag TiO_6 octahedral chains with the same pattern of edge sharing found in II. All the Ti atoms between the pairs of planes shift position to new octahedral sites (previously tetrahedral sites) so that the zigzag Ti octahedral network in the [100] direction of II is completed.

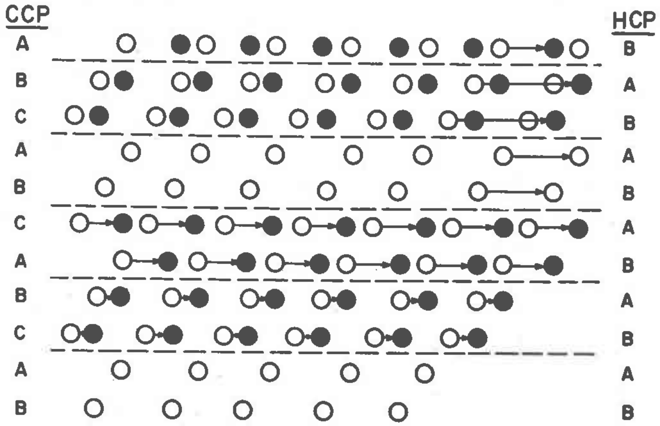

FIG. 3. Shear motion necessary to form hexagonal close packing from cubic close packing. The open circles mark the initial oxygen positions and the filled circles the positions after a shift by the amounts indicated by the arrows. In the proposed anatase→II transition mechanism all titanium atoms nestled between oxygen layers *B–C*, *A–B*, *C–A*, etc., would remain in their original sites whereas all those on the shear planes between layers have to change sites.

The relative atomic rearrangement is shown in Figure 4. There would have to be more relocation of atoms in this transition than in the others. All Ti atoms on the shear plane above the *bdfh* (and below the *aceg*)

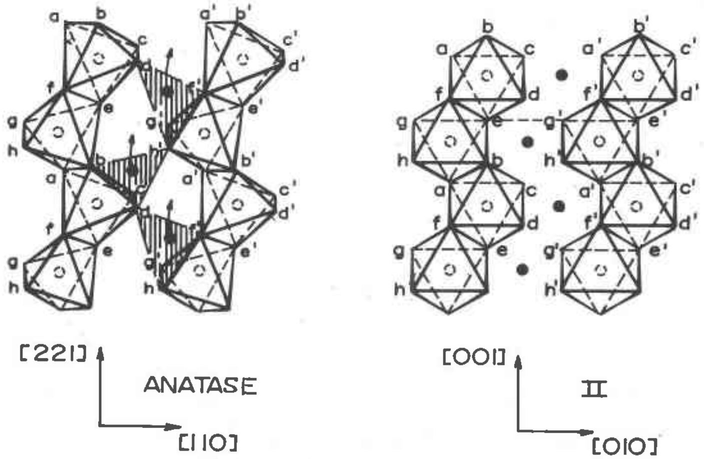

FIG. 4. Topotaxy in the anatase→II transition. Titanium atoms between oxygen layers containing *aceg* and *bdfh* remain in their respective octahedra; those sitting above *bdfh* shift sites as indicated to form the chain of octahedra lying above and between the two shown, resulting in the TiO_2-II structure.

oxygen layers in the *CCP* sequence shift position to the adjacent tetrahedral site. Actually the cations would not move into tetrahedral sites because these sites progressively become octahedral sites by the rearrangement of the oxygen atoms above. None of the Ti atoms between the complete layers would have to shift positions to new octahedral sites. The topotactic elements resulting from the proposed mechanism would be

$$2\times d(112) \text{ anatase } (4.672 \text{ Å}) \approx a \text{ II } (4.515 \text{ Å})$$
$$2\times d(110) \text{ anatase } (5.348 \text{ Å}) \approx b \text{ II } (5.497 \text{ Å})$$
$$4\times d(221) \text{ anatase } (5.305 \text{ Å}) \approx c \text{ II } (4.939 \text{ Å})$$

Actually, in the anatase structure the $\{112\}$ family of planes, *i.e.*, (112), $(1\bar{1}2)$, $(\bar{1}12)$ and the $(\bar{1}\bar{1}2)$ are the pseudo *CCP* planes of oxygen. The proposed topotaxy in reference to the (112) plane could easily be applied to the other pseudo *CCP* planes. The mechanism would remain the same; only the directions describing the atomic or planar shifts would change. It is believed that the difficulty of securing a complete transformation of anatase to II may be related to such complex topotaxy. According to this reaction mechanism, the transformation would follow the "paths" determined by all four of the $\{112\}$ family of close packed planes simultaneously and perhaps at about the same rates, placing the nuclei of the product phase under intense competition both for material and space for growth. Because of the relatively low temperatures and high pressures at which this reaction is observed, small and perhaps strained crystallites may form which would produce diffuse *X*-ray diffraction maxima. Furthermore, the conditions would appear to favor the formation of an appreciable proportion SRO phase as well. All this is consistent with what is actually observed in the II prepared from anatase.

The II-rutile Reaction. It was noted earlier that the II structure is based on layers of pseudo hexagonally close-packed oxygen and that in rutile, projections normal to the (100) and (010) show that the oxygen atoms are in approximately hexagonal close-packing in these planes. This circumstance suggests topotactic mechanisms which are definitely simpler than those proposed for the other polymorphic pairs. In the scheme deemed to be the most likely to be followed, the close-packed (100) plane of II would become the (100) or (010) plane of rutile, without involving any significant change of oxygen positions. With regard to the Ti atoms, there are two paths which may be followed but which lead to the same final configuration. In the first, one half of the Ti atoms would move in the [021] direction of II to conform with the requirements of the

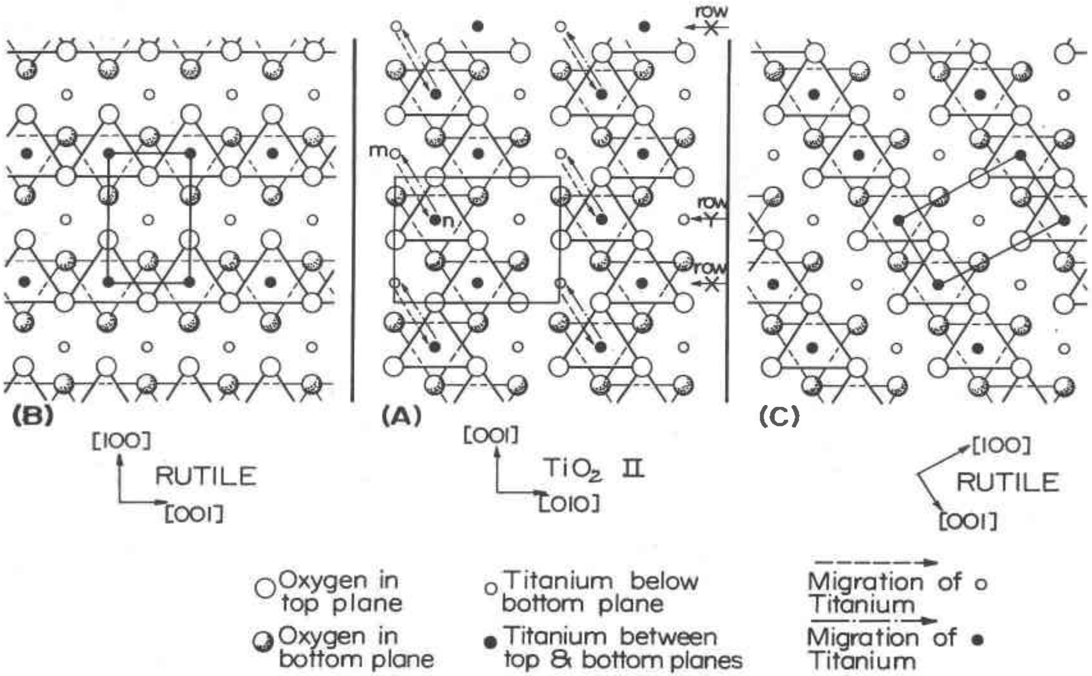

FIG. 5. Suggested topotaxy in the II-rutile transition. Two close packed oxygen layers of TiO_2-II are shown in *A*. The change of sites by Ti atoms within the layers as indicated by the dashed arrows would result in rutile with the orientation shown in B. The identical topotaxy would result if the *same* Ti atoms were to shift positions instead along [100] by one half the unit repeat distance. If the rows *X* and *Y* of Ti atoms were to shift together along [010] by one half unit repeat, rutile oriented as in *C* would result. Projections of the unit cells are outlined.

rutile structure. Figure 5 shows this site rearrangement, with the resultant rutile unit cell outlined on the II structure. In the second, the same topotaxy could be achieved by a different disposition of Ti atoms; that is, one half the Ti atoms, those labelled *n* and *m* in Figure 5 would move one half the unit repeat distance in the [100] direction of II. In either case, these mechanisms would produce the *same* topotactic elements with the three crystallographic axes coinciding as follows:

II [100] parallel to rutile [100]
II [010] parallel to rutile [001]
II [001] parallel to rutile [100]

In terms of lattice constants

a II (4.515 Å) $\approx$ a rutile)4.594 Å)
$1/2b$ II (2.749 Å) $\approx$ c rutile (2.959 Å)
c II (4.939 Å) $\approx$ a rutile (4.594 Å).

Another, perhaps less simple, reaction scheme is possible, again starting with the (100) plane of II becoming the (100) of rutile. In this case, two consecutive rows of Ti atoms parallel to *b* in II would move in the [010] direction in II one half the unit repeat distance. The next two consecutive rows of Ti parallel to *b* would remain in their original positions. This mechanism, in which the rows of atoms labelled *X* and *Y* are the ones which move to the new positions, is also shown in Figure 5.

The topotactic elements would be

II [100] parallel to rutile [100]
II [021] parallel to rutile [001]
II $[0\bar{1}2]$ parallel to rutile [010]

In terms of interatomic spacings

II $a(4.515\ \text{Å})_{\text{obs.}} \approx a_{\text{rutile}}(4.594\ \text{Å})$
II $d(021)\ (2.400\ \text{Å})_{\text{obs.}} \approx c_{\text{rutile}}(2.959\ \text{Å})$
II $2\times d(012)\ (4.508\ \text{Å})_{\text{calc.}} \approx a_{\text{rutile}}(4.594\ \text{Å})$

DISCUSSION

The topotactic mechanisms proposed for the anatase—II, brookite—II, and II—rutile polymorphic transitions do not exhaust the possibilities. They are, however, based on a principle of favoring as much as possible the maintenance of the integrity of oxygen close packing during the polymorphic transitions. This factor has been shown experimentally by others to be important in the anatase-rutile and brookite-rutile transitions noted earlier, as it also has been in the more general field of topotactic reactions (Dent Glasser, Glasser and Taylor, 1962, Brindley, 1963). It would appear then, that the reverse of the mechanisms might also be favored in the reversal direction of these polymorphic reactions, if such reactions were to occur.

Table 3 summarizes the observed and proposed topotaxy in the sys-

TABLE 3. SUMMARY OF THE ATOMIC MOVEMENT IN TOPOTAXY IN THE TiO_2 SYSTEM

Reaction	Number of Oxygen Layers Rearranged	Redistribution of the Titanium Atoms[a]	Remarks
II - rutile	None	One half in each layer *A B A B A B A B* : : : : : : : 1/2 1/2 1/2 1/2 1/2 1/2 1/2	Only reaction that has been reversed. Experimental evidence inferred from work of Bendeliany et al. (1966)
Brookite - II	1 in 4	Every Ti in two consecutive layers altering with two layers in which there is no Ti motion. *A B A C A B A C* : : : : : : : 1 1 0 0 1 1 0	Reaction without SRO phase formation. Brookite has zigzag TiO_6 octahedral chains as is found in II.
Brookite - rutile	This reaction does not involve an oxygen shearing mechanism, but there is a shifting of all oxygen.	Every other Ti in each layer in order to form straight Ti octahedral chains. *A B C A B C A B C* : : : : : : : : 1/2 1/2 1/2 1/2 1/2 1/2 1/2 1/2	Experimentally observed topotaxy.
Anatase—rutile	This reaction does not involve an oxygen shearing mechanism but all oxygen atoms shift positions.	Every other Ti in each layer in order to form straight Ti octahedral chains. *A B A C A B A C* : : : : : : : 1/2 1/2 1/2 1/2 1/2 1/2 1/2	Topotaxy experimentally observed. A large distortion occurs in the formation of straight octahedral chains from zigzag chains.
Anatase—II	4 in 6	A repeating sequence of all Ti and no Ti motion beginning with the Ti between the *A* and *C* layers. *A B C A B C A B C* : : : : : : : : 1 0 1 0 1 0 1 0	Reaction always accompanied with SRO phase formation.
Anatase—brookite	9 in 12	Very complex	Reaction reported only one time.

[a] In most cases the movement of the titanium ions is to adjacent tetrahedral sites which are in the process of becoming octahedral sites because of the accompanying oxygen motion.

The legend for the titanium motion is

1/2 every other titanium changes site

1 every titanium changes site

0 no titanium changes site

The layering scheme is that of the reactant.

tem TiO_2. A qualitative attempt has been made to list the topotactic reactions in this system in order of increasing complexity. The table was constructed on the assumption that, in general, the change of the type of close packing is initially more important than the redistribution of the cations. In all the transitions, the observed and proposed mechanisms require that the close packed planes of oxygen in the reactants remain as close packed planes in the product. It is noteworthy that for the II-rutile reaction only the Ti atoms shift sites, whereas for the other transitions both Ti and oxygen require rearrangement.

There is a high degree of consistency between the relative difficulty of the topotactic reactions as ranked in Table 3 and the nature of the polymorphic reactions observed experimentally. For example, the II-rutile reaction is the *only* one that has been made to proceed in *either* direction (in stable or metastable equilibria), and, as indicated in Table 3, the topotactic conditions for this pair are the simplest. Furthermore, in our experience, the preparation of well-crystallized II from brookite has always been easier, faster and more complete than from anatase. Lastly, the complex topotactic requirements for the anatase-brookite reaction may account in great measure for the fact that, with but one exception (Knoll, 1963), there is no evidence for this reaction.

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