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The term topotaxy was defined by Lotgering and Gorter[1] to include "all chemical solid state reactions that lead to a material with crystal orientations which are correlated with crystal orientations in the initial product." Mackay[2] described several reactions occurring in the hydrated iron oxides as topotactical and extended the definition to include structural transformations. He stated the necessary conditions for topotaxy to be: (1) a three-dimensional accord between the reactant and product, and (2) the majority of atomic positions remaining fixed. In a review of topotaxy, Bernal[3] defined the term so as to include transformations in which all or some of the axes of symmetry of the original crystal are retained in the product. Taylor et al.[4] recognized the problem of the definition of topotaxy and took a position intermediate between that of Lotgering and Mackay. They refer to topotaxy as the conversion of a single crystal into one or more products which have a definite crystallographic orientation with respect to the original crystal, with the added requirements that the conversion take place throughout the entire crystal and that there be three-dimensional accord between the initial and final structures.

A recent investigation of the anatase-rutile transformation[5] revealed an example which showed preferred orientation of the product relative to the reactant but did not meet the restrictions of Mackay or

Bernal. It is not clear that such cases, in which poor three-dimensional accord exists and oriented products still form, could be classified as topotaxy according to Taylor's definition. It seems preferable, therefore, to place more emphasis on experimental evidence than on an interpretation of the mechanism, thus allowing for a complete gradation of topotactical conversions based on the degree of orientation. One would then include under the broad category of topotaxy all oriented conversions except those considered to be epitactical.

From experimental data one may describe a continuum of degrees of topotaxy depending on the amount of preferred orientation. A list of criteria as in Table I might help predict or explain the degree of orientation within a continuum of topotaxy.

Displacive transformations such as the $\alpha \rightarrow \beta$ quartz transition[3] should exhibit the highest degree of topotaxy, while reconstructive changes such as the quartz $\rightarrow$ cristobalite transformation[5] should exhibit almost no orientation. The titania system illustrates two cases of intermediate topotaxy. In the brookite-rutile transition[6] completely ordered rotating crystal patterns were found in which the rutile [100] remains parallel to the brookite [100], whereas rutile [001] is parallel either to brookite [001] or to brookite [010]. The anatase-rutile transformation, involving a greater shrinkage and a higher activation energy, results in a relatively low degree of topotaxy.

Two chemical reactions showing nearly perfect topotaxy are the lepidocrocite $\rightarrow$ maghemite and the goethite $\rightarrow$ hematite dehydrations.[2] Electron diffraction patterns of single crystals resulted in good single-crystal patterns of the products. Lower degrees of topotaxy were indicated

Table I. Criteria used in interpreting topotactical reactions

| High degree | Criterion | Low degree |
|---|---|---|
| Displacive transformations | Type of reaction or transformation → | Reconstructive transformations or thermal decompositions or dehydrations of some minerals |
| Retention of symmetry axes | Symmetry → | New directions of symmetry not coinciding with the old |
| Small displacement - no primary bonds broken | Atomic displacement → | Large displacement - rupture of primary bonds |
| Small amount of shrinkage ~ less than 2% | Volume change → | Large shrinkage or expansion ~ more than 30% |
| None or very small | Activation energy → | High activation energy necessary to break bonds |
| Single-crystal diffraction pattern from product of the reaction | Diffraction patterns → | Polycrystalline diffraction pattern showing preferred orientation - the degree of preferred orientation denoting the degree of topotaxy |

in the dehydration of $Mg(OH)_2$ and $Ca(OH)_2$ in which the [111] direction of the product coincided with [0001] of the reactant.[7] In the case of $Mg(OH)_2$ the MgO [$1\bar{1}0$] was found to be parallel to the a-axis of the reactant, while in the case of $Ca(OH)_2$ the product orientation about the [111] was random indicating a lesser degree of topotaxy.

A degree of topotaxy based solely on diffraction patterns may prove to be misleading. What may appear to be perfect topotaxy by electron diffraction performed on small crystals may be shown to have a much lower degree of topotaxy by X-ray diffraction on macrocrystals. A good example of this difference is seen in Mackay's data on the lepidocrocite-maghemite reaction[2, 8] in which the electron diffraction patterns show sharp reflections, whereas the X-ray patterns show relatively diffuse reflections.

A distinction between topotaxy and epitaxy should be made. Topotaxy requires the transformation or conversion of the reactant crystal into a new oriented phase, whereas epitaxy refers to a second phase overgrowth oriented with respect to a substrate. The overgrowth may be an oriented deposition or an oriented product of a reaction with the substrate. In a reaction with the substrate, the host crystal must be converted into another phase by the gain or loss of atoms. If this new phase is also oriented with respect to the host, a topotactical reaction also results. An example of this type of reaction is the solid state reaction between sapphire and periclase.[10] An overgrowth of spinel is formed oriented with respect to the sapphire and, as a result of the reaction, the sapphire itself is converted into spinel. The spinel overgrowth formed from periclase provides an example of an epitactical product layer, and the sapphire-grown spinel represents a topotactical conversion.

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