

MISCELLANEOUS PAPERS

THE ROLE OF ORIENTED TRANSFORMATIONS IN MINERALOGY

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ABSTRACT

Topotactic reactions are discussed with special reference to those of proved or possible mineralogical significance. It is suggested that some mineralogical phenomena might be reinterpreted in terms of such mechanisms, which are probably more common than has generally been supposed.

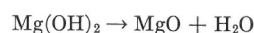
There has recently been an increasing interest in oriented transformations; that is, reactions in which a single crystal of the starting material is transformed directly into something approaching a single crystal of the product (or products). Such reactions have been termed topotactic (Lotgering, 1959; Mackay, 1960). For their occurrence, there must in general be some measure of three-dimensional correspondence between the two structures, implying that at least some chemical elements are common to both. This is in contrast to epitaxy, which demands only two dimensional correspondence; indeed one substance may grow epitaxially on another without being chemically related to it (*e.g.* the growth of hydrocarbons on mica).

Studies of such topotactic reactions can give information about their mechanisms. For example, study of the transformation of rhodonite, (Mn, Ca) SiO₃, to a wollastonite solid solution showed conclusively that the reaction proceeded by the migration of silicon and of some of the associated oxygen atoms; the remainder of the structure was relatively unchanged (Dent Glasser and Glasser, 1961). Furthermore, study of a topotactic reaction may give clues to a previously unknown structure; for example, knowledge of the orientation of the dehydration products of foshagite helped in the determination of its structure (Gard and Taylor, 1958). Because the details of such studies are complex, they will not be discussed here. We shall limit ourselves to a general survey of topotactic reactions, emphasizing their possible mineralogical importance.

Table I lists some types of reaction, all of geologic interest, which can occur topotactically; the examples given are all drawn from substances which occur as minerals. All the examples quoted involve major structural changes; processes which involve only minor changes, such as the α - β quartz inversion, have been omitted.

Topotactic reactions vary widely in the extent to

which the composition of the crystal changes. At one extreme are polymorphic transitions which involve no change in composition. At the other are reactions such as the dehydration of brucite to periclase, in which, according to the chemical equation



half the oxygen atoms are lost from the crystal. It was originally assumed that the elements of water were lost uniformly from all parts of the crystal by condensation of adjacent hydroxyl groups. A "homogeneous" mechanism of this type would result in such a disturbance of the crystal framework that it is difficult to see how it could account for a topotactic reaction. An alternative "inhomogeneous" mechanism, of the kind postulated by Taylor and co-workers (Freeman and Taylor, 1960; Ball and Taylor, 1961), and by Brindley (1961), resolves this difficulty. The oxygen for the expelled water comes entirely from certain parts of the structure which are destroyed, leaving pores. H⁺ ions diffuse into these regions (which probably begin to form around defects in the crystal) while Mg²⁺ ions diffuse into the parts of the crystal where MgO is formed topotactically. These regions thus lose no oxygen, but gain Mg²⁺ to replace the lost H⁺ ions. It has been suggested that the dehydroxylation of clay minerals should also be approached in this way (Taylor, 1962).

In most topotactic reactions, the arrangement of the bulkiest atoms or ions in the structure appears to control the orientation relationship. In oxides and silicates it is therefore the oxygen packing which is important, together with any large cations which may be present (*e.g.* Ca²⁺, Na⁺). Smaller cations, including silicon, diffuse through the oxide framework, which remains relatively unchanged. Gay and LeMaitre (1961) present a detailed picture of this process in the formation of iddingsite from olivine. They visualize a continuous series of highly disordered states, from which regions of comparative

TABLE I. SOME TOPOTACTIC REACTIONS

Type of reaction	Examples	References
Redox reactions	magnetite → hematite cryptomelane → bixbyite → hausmannite	Gruner, 1926 Faulring <i>et al.</i> , 1960
Hydrations	olivine → iddingsites	Gay and LeMaitre, 1961
Thermal dehydrations	brucite → periclase amphiboles → pyroxenes xonotlite → wollastonite gypsum → anhydrite kaolinite → metalaolin → spinel → mullite talc → enstatite seppentine → forsterite	Ball and Taylor, 1961 Thilo and Rogge, 1939; Freeman and Taylor, 1960 Dent and Taylor, 1956 Flörke, 1952 Brindley and Nakahira, 1959 Thilo and Rogge, 1939 Brindley and Zussman, 1957
Other thermal decompositions	dolomite → calcite smithsonite → zincite	Haul and Wilsdorf, 1952 Rose, 1939
Hydrothermal reactions	tobermorite → xonotlite chrysotile → forsterite	Taylor, 1959 Ball and Taylor, 1962
Exsolution	<i>e.g.</i> lamellae in pyroxenes feldspars olivines	— ¹ — ¹ Hurlbut, 1961
Anion exchange	calcite → fluorite wurtzite → zincite	Glasser, 1962 Prewitt-Hopkins and Frondel, 1956
Polymorphic transitions	rhodonite → wollastonite wurtzite → sphalerite rhombic enstatite ⇌ proto enstatite ↙ ? ↘ clino enstatite	Dent Glasser and Glasser, 1961 Kröger, 1940. Brown <i>et al.</i> , 1961
Alteration	ilmenite → rutile	Bailey <i>et al.</i> , 1956; Yanulov and Chulkova, 1961.

¹ Extensive literature; see, for example, papers by M. G. Bown, P. Gay, N. Morimoto, J. V. Smith, W. S. Mackenzie, F. Laves, O. F. Tuttle and N. L. Bowen.

order become differentiated. Composition and degree of structural order may vary continuously through the "crystal". Iddingsite may be in any of these states of disorder, and is therefore always rather poorly crystallized, but it seems likely that transformations resulting in well crystallized end products may proceed via similar disordered states.

Anions are in general bulkier than cations, but in anion exchange reactions it appears to be the cations which exert structural control. The transformation calcite → fluorite is especially interesting; fluorite pseudomorphous after calcite occurs in nature. Calcite crystals can be partially replaced with fluorite in the laboratory (Ames, 1961); examination of such crystals shows that the fluorite is oriented (Glasser, 1962; Glover and Sippel, 1962).

The hydrothermal reactions of single crystals have so far been little studied. The mechanism of the re-

action sometimes, though not always, changes with increase in water vapor pressure. Thus, dehydration of chrysotile at 520° and 500 kg/cm² gives forsterite in an orientation different from that found on heating in air at this temperature; at still higher pressures (1200 kg/cm²) the forsterite is randomly oriented (Ball and Taylor, 1962). Further studies of the effects of water pressure on topotactic reactions are badly needed.

Topotactic control over the crystal size and perfection may help explain minor discordance between different sets of P-T data obtained for hydrothermal reactions such as $\text{Mg}(\text{OH})_2 \rightleftharpoons \text{MgO} + \text{H}_2\text{O}$. Thus if the reactions $A \rightarrow B$ and $B \rightarrow A$ proceed by different mechanisms, yielding products with characteristic textures, defect contents, etc., determination of the actual "equilibrium" may be a formidable task.

It should be pointed out that Table I is by no

means an exhaustive list. Nevertheless, it includes most mineralogically important types of reaction, and the minerals listed include representatives of most important groups. We do not wish to imply that all the examples of transformations which are listed actually do occur in nature, but it does seem likely that topotactic reactions may be very much more common than has sometimes been supposed. It might be profitable to examine from this standpoint the textures of minerals and mineral assemblages, particularly those believed to record a genetic history of solid-solid transition (*i.e.* replacement, etc.).

Lauder (1961) has attempted this, using mainly optical techniques.

It is hoped that this brief review of topotactic processes may be helpful to those interested in these problems.

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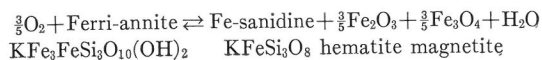
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DISCUSSION

D. R. WONES (Washington, D. C.): The growth of feldspar and magnetite lamellae during oxidation of biotite phenocrysts in volcanic rocks might provide examples of topotactic inversions.

Walter (U.S.A.) brought up the problem of metastable transi-

tions due to "inherited" structural features. It would appear that in the reaction



the Fe-sanidine "inherits" a disordered structure from the ferri-annite. In time the Fe-sanidine will convert to the more stable Fe-microcline. The structure of ferri-annite is being worked out by Morimoto and Donnay.

AUTHORS' REPLY: The evidence certainly suggests that the reaction proceeds topotactically, but this cannot be established without crystallographic evidence. Examination of the naturally occurring lamellae to establish whether or not their orientations are consistent with a topotactic reaction would provide indirect evidence. Direct evidence could be obtained by study of the oxidation of a

single crystal of ferri-annite in the laboratory, using single crystal X-ray methods to determine whether the product of the reaction is oriented. For the interpretation of such a study, a knowledge of the crystal structure of ferri-annite would be essential.

It must be emphasized that the occurrence of a metastable phase is not in itself proof of topotaxy. It is tempting to hypothesize that the appearance of a metastable phase inheriting certain structural features of the parent does indicate a topotactic mechanism. We are hoping that mineralogists will study reactions of this sort to establish the degree of structural correspondence necessary for solid-solid transformations to proceed topotactically.