TOPOTACTIC REACTIONS IN INORGANIC OXY-COMPOUNDS

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In some reactions of crystalline solids, the crystal structures are partly preserved, and in this way the structure and crystallographic orientation of a starting material may control the orientation and even the nature of the products. Such reactions can therefore be adequately explained only if the relevant crystal structures are taken into account. Two differing degrees of structural control can be distinguished: epitaxy, which is a two-dimensional effect, and topotaxy, which is three-dimensional.

In epitaxy, crystals grow on the surface of another substance (the host) in certain definite orientations. The host need not be a reactant and may even be chemically unrelated to the overgrowth. Thus, certain organic compounds crystallise on the surface of mica in definite orientations controlled by a fortuitous correspondence of the lattice-repeat distances. This kind of epitaxy, perhaps better called oriented overgrowth, is not relevant to this discussion. When the host is also a reactant, the product forms partly or wholly at its expense and grows on the surface in an oriented way. Some oxides form on metals in this manner, and these will be briefly discussed, as they have some relevance to the question of topotaxy.

In topotaxy, a single crystal of a starting material is converted into a pseudomorph* containing one or more products in a definite crystallographic orientation; the conversion takes place throughout the entire volume of the crystal. For true topotaxy there must be some three-dimensional correspondence between the structures of the product and its host (in contrast to epitaxy, in which the correspondence need only be two-dimensional). We shall confine ourselves to reactions involving major first-order phase transitions. This eliminates from consideration such minor changes as the α–β quartz inversion, ferroelectric transitions, or the onset of ionic rotation in ammonium nitrate.

Pseudomorphs formed from single crystals vary greatly. When more than one phase is formed, the regions occupied by each may be macroscopically visible, or they may range in size down to intimate mixtures in which the individual phases are detectable only by *X*-rays. There may be no change in the bulk composition, as in polymorphic transformations or exsolution phenomena,† or there may be a net gain or loss of material, as in oxidations or dehydrations. When a loss occurs, the crystal does not usually shrink in external dimensions, but becomes porous. The pseudomorph sometimes has crystallinity comparable with that of the starting material but usually there is a marked deterioration. It may consist of

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* A pseudomorph is a crystal which has become converted into another substance, or mixture of substances, without change in its external form.

† Exsolution describes the process in which a single, homogeneous solid phase breaks up into two solid phases, thus becoming heterogeneous.

crystallites which are small, or poorly crystalline, or imperfectly oriented (or any combination of these). If there are two or more phases, these may differ in crystallinity; amorphous material may be formed. Differing degrees of crystallinity cause characteristic *X*-ray diffraction effects, the reflections being broadened or streaked along powder lines (Fig. 1). In general, examples of pseudomorph formation may be found which provide a continuous gradation from very well-ordered topotactic changes down to changes in which the structure is completely disrupted and crystallites in random orientation are formed.

Partly because of this continuous gradation, opinions differ as to exactly which reactions should be regarded as topotactic. Lotgering[1] proposed the term topotaxy "for all chemical solid state reactions that lead to a material with crystal orientations which are correlated with crystal orientations in the initial product" (sic). Mackay[2] defines topotaxy more narrowly to cover transformations in which "the majority of the atomic positions in the original and in the transformed material are substantially the same and there is accord in three dimensions between the initial and final lattices". He regards as epitaxy those transformations in which "crystals . . . grow on certain internal . . . crystal planes of the initial material so that there is two dimensional accord between the packings in these planes but otherwise the structures are dissimilar, the second phase appearing as an intergrowth in the first phase". Mackay's definitions lead to practical difficulties as many transformations do not fall clearly into either category; a detailed knowledge of their mechanisms would be necessary to classify them. Lotgering's definition, on the other hand, ignores what may be a valid distinction. We have adopted an intermediate position.

Experimental Methods.—Although some studies have been made with the polarising microscope, the most powerful tools are *X*-ray and electron diffraction, and only these methods will be described here. Some additional and more specialised techniques will be mentioned later.

A simple *X*-ray method, using only standard single-crystal apparatus, is to determine the orientation of a crystal of the starting material which has easily recognisable outlines. The crystal is then treated in the desired way, and the orientation of the product relative to the crystal outline afterwards determined. In this way orientation of product relative to starting material is found. This method can be applied to topotactic reactions of all kinds,[1,3,4,5] but its accuracy depends on the ease with which the outlines of the crystal can be recognised and the accuracy with which it can be set visually. If the reaction can be halted before it is complete, the pseudomorph will give reflections from both starting material and product (Fig. 1), and the accuracy is improved. In thermal transformations, it is sometimes

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[1] F. K. Lotgering, *J. Inorg. Nuclear Chem.*, 1959, **9**, 113.
[2] A. L. Mackay, Proc. 4th Internat. Symp. Reactivity of Solids, Amsterdam, 1960, 571.
[3] H. Saalfeld, Proc. 4th Internat. Symp. Reactivity of Solids, Amsterdam, 1960, 310.
[4] L. S. Dent Glasser and F. P. Glasser, *Acta Cryst.*, 1961, **14**, 818.
[5] G. M. Faulring, W. K. Zwicker, and W. D. Forgeng, *Amer. Min.*, 1960, **45**, 946.

possible to do this by heating one end only of a prismatic crystal. It is often preferable to heat the crystal without removing it from its mounting; a device for doing this using a Weissenberg goniometer has been described.[6] Various forms of high-temperature single-crystal cameras have been described[7] which enable reactions reversible on cooling to be studied too. A high-pressure single-crystal camera has also been described.[8]

Selected-area electron diffraction has only limited application in these studies, but is occasionally very useful when single crystals large enough for *X*-ray work cannot be obtained. Some materials decompose in the electron beam, and topotactic reactions occurring thus can be studied directly.[9] Others have crystals or cleavage fragments with an easily recognisable shape which persists in the product, and can therefore be reasonably assumed to be pseudomorphic; the orientation relationship can be deduced from a comparison of the electron micrographs and diffraction patterns of product and starting material.[10]

Some different classes of topotactic reactions will now be considered.

Oxides and Mixed Oxides

In some simple topotactic reactions of oxides or mixed oxides, cations migrate while the oxygen packing stays approximately unchanged. Thus FeO, Fe_3O_4 (magnetite), and γ-Fe_2O_3 can be interconverted by heating in suitable atmospheres. All have structures based on cubic close packing of oxide ions, and differing in the number and kind of interstices occupied by the cations. It has long been accepted that reaction proceeds topotaxially by addition or removal of oxygen layers, with appropriate migrations of cations,[11] though direct crystallographic evidence for this has only recently been obtained.[2,12,13] Another example is provided by the occurrence in Nature of pseudomorphs in which rutile (TiO_2) has been formed from ilmenite ($FeTiO_3$). Both of these structures are based on hexagonally close packed oxygen, and the change evidently occurs by migrations of iron and titanium.[14]

Slightly more complex cases occur where there is also a change in the type of oxygen packing. Thus Fe_3O_4 can be oxidised to α-Fe_2O_3 (haema-

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[6] L. S. Dent, *J. Sci. Instr.*, 1957, **34**, 159.

[7] J. D. Donaldson, *J. Sci. Instr.*, 1961, **38**, 286; J. V. Smith and W. L. Brown, *Z. Krist.*, 1961, **115**, 93.

[8] L. F. Vereshchagin, S. S. Kabalkina, and V. V. Evdokimova, *Pribory i tekhnika eksperimenta*, 1958, No. 3, 90.

[9] J. F. Goodman, *Proc. Roy. Soc.*, 1958, *A*, **247**, 346.

[10] J. A. Gard and H. F. W. Taylor, *Amer. Min.*, 1958, **43**, 1.

[11] A. F. Wells, "Structural Inorganic Chemistry," 3rd ed., Oxford University Press, London, 1962, 490.

[12] J. D. Bernal, D. R. Dasgupta, and A. L. Mackay, *Nature*, 1957, **180**, 645; *Clay Minerals Bull.*, 1959, **4**, 15.

[13] W. Feitknecht and H. W. Lehmann, *Helv. Chim. Acta.*, 1959, **42**, 2035.

[14] S. W. Bailey, E. N. Cameron, H. R. Spedden, and R. J. Weege, *Econ. Geol.*, 1956, **51**, 263; K. P. Yanulov and I. V. Chulkova, *Doklady Akad. Nauk S.S.S.R.*, 1961, **140**, 215.

tite), in which the oxygens are hexagonally close packed. Optical studies on partly oxidised magnetite crystals show that the haematite forms as exsolution lamellae oriented so as to allow the best possible fit between the close packed oxygen planes of the two structures [haematite (0001) // magnetite (111)].[15] A single-crystal study of the oxidation of a manganese–zinc–iron spinel similarly showed formation of haematite as exsolution lamellae.[16]

An *X*-ray study of the γ–α Fe_2O_3 transition gave a result similar to that found when α-Fe_2O_3 is formed from magnetite; the orientation relationship was such as to give the best possible fit between close packed oxygen planes.[12] Polymorphic transitions in alumina occur in the same way and are discussed later. An anomalous result was obtained in the Fe_2O_3 transition when selected-area electron diffraction was used, a different orientation relationship being observed.[2] This was attributed to recrystallisation in the thin flakes used (probably 100—500 Å) in such a way as to cause the close packed oxygen planes to re-form parallel to the plane of the flake. This seems to be the only known case of an orientation relationship being controlled by external morphology and not by internal structure.

In the above reactions, the cations which migrate (*e.g.*, Fe, Ti) are much smaller than the oxide ions. With oxides of large, electronegative cations, topotactic processes may occur by a different mechanism. It has been suggested that, in redox processes in actinide and lead oxides,[17] oxygen migrates through a relatively unchanged cation framework, though no single-crystal studies have been made to support this. Redox changes in manganese oxides have been studied using single-crystal *X*-ray methods, starting from cryptomelane, which is approximately MnO_2. The sequence

$$\underset{\text{cryptomelane}}{MnO_2} \xrightarrow{1} Mn_2O_3 \xrightarrow{2} \underset{\text{hausmannite}}{Mn_3O_4} \xrightarrow{3} \underset{\text{spinel}}{Mn_3O_4}$$

occurs topotactically;[5] the orientation relationships were determined but no attempt was made to suggest a mechanism. In stage 3 the oxygen packing is clearly preserved, but this may not be true of stages 1 and 2; the behaviour of manganese is probably intermediate between that of "small" and "large" cations.

Topotactic changes can also occur in which both oxygen and metal ions remain approximately fixed and only hydrogen ions and electrons move. γ-Manganese dioxide can be reduced topotactically with hydrazine;[18] hydrogen ions and electrons are added, and the reaction can proceed as

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[15] J. W. Gruner, *Econ. Geol.*, 1926, **21**, 375; J. W. Greig, E. Posnjak, H. E. Merwin, and R. B. Sosman, *Amer. J. Sci.*, 1935, **30**, 239.

[16] R. E. Carter, W. L. Roth, and C. A. Julian, *J. Amer. Ceram. Soc.*, 1959, **42**, 533.

[17] L. E. J. Roberts, *Quart. Rev.*, 1961, **15**, 442; J. S. Anderson and M. Sterns, *J. Inorg. Nuclear Chem.*, 1959, **11**, 272.

[18] W. Feitknecht, H. R. Oswald, and U. Feitknecht-Steinmann, *Helv. Chim. Acta*, 1960, **43**, 1947.

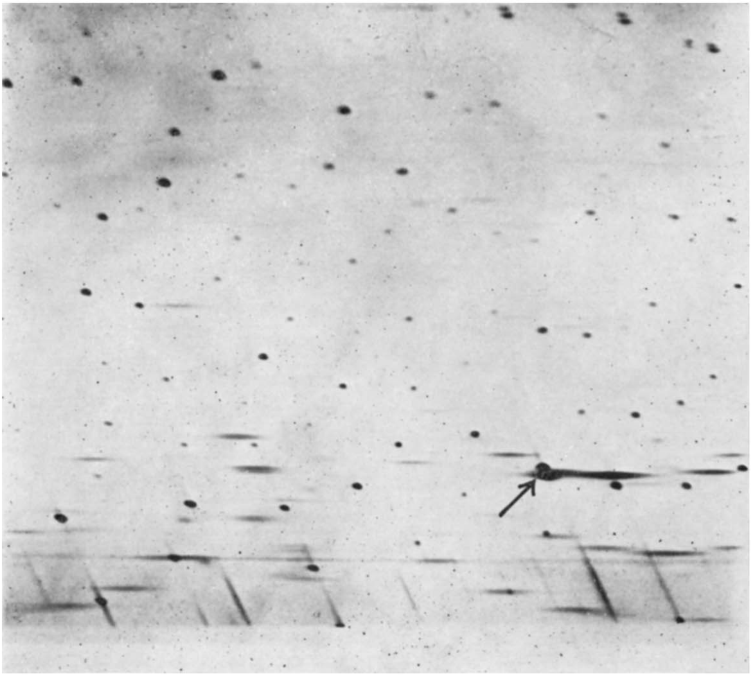

FIG. 1. *Typical experimental data obtained in the study of a topotactic reaction: an* X-*ray Weissenberg photograph from a crystal which has undergone such a reaction. The sharp spots are from traces of unchanged starting material; the reflections streaked horizontally* (i.e., *along powder lines*) *are from the major product, and a few additional, broad reflections, of which the strongest is indicated by an arrow, are from a minor product. From such photographs the relative orientations of products and starting material can be found.*

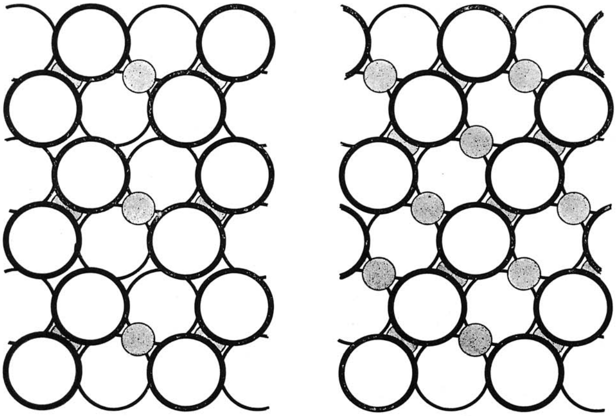

Fig. 2. *Crystal structure of* (a) *magnesium hydroxide and* (b) *magnesium oxide, showing the relative orientations observed when magnesium oxide is formed by heating magnesium hydroxide. Large open circles represent nearly close packed hydroxyl or oxide ions; small shaded circles represent magnesiums.* (001) *planes are horizontal in* (a) *and* (111) *planes are horizontal in* (b).

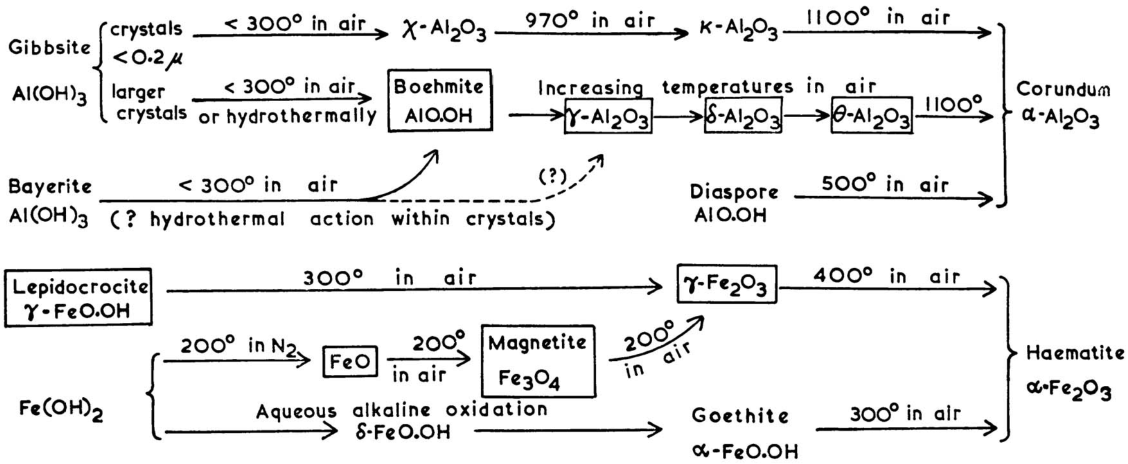

FIG. 3. *Some topotactic reactions of aluminium and iron compounds. Phases enclosed in rectangles have structures based, at least approximately, on cubic close packed oxygen layers. All other phases shown have structures based, at least approximately, on hexagonally close packed oxygen layers.*

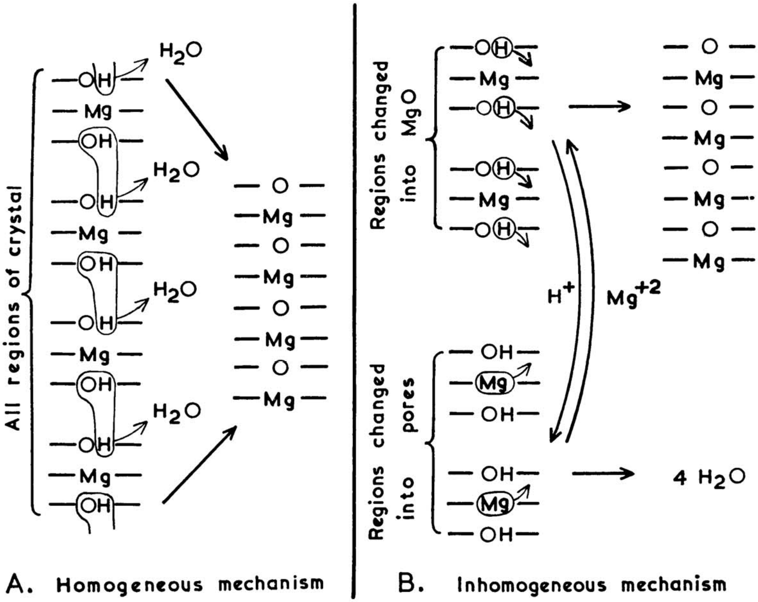

FIG. 4. *Homogeneous and inhomogeneous mechanisms for the dehydration of magnesium hydroxide. Horizontal lines represent layers of atoms or ions.*

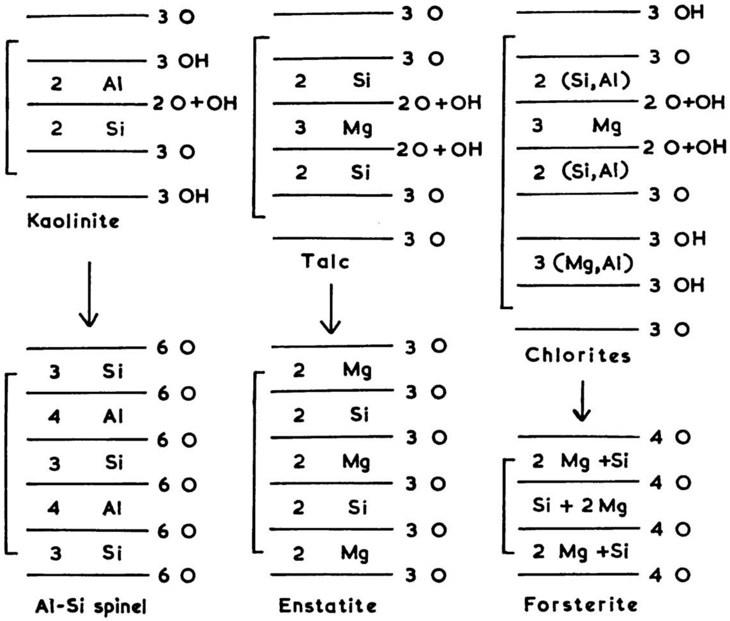

FIG. 5. *Structures of some clay minerals and of their dehydration products. Horizontal lines represent layers of oxygen or hydroxyl. Square brackets show the thickness of the elementary layer.*

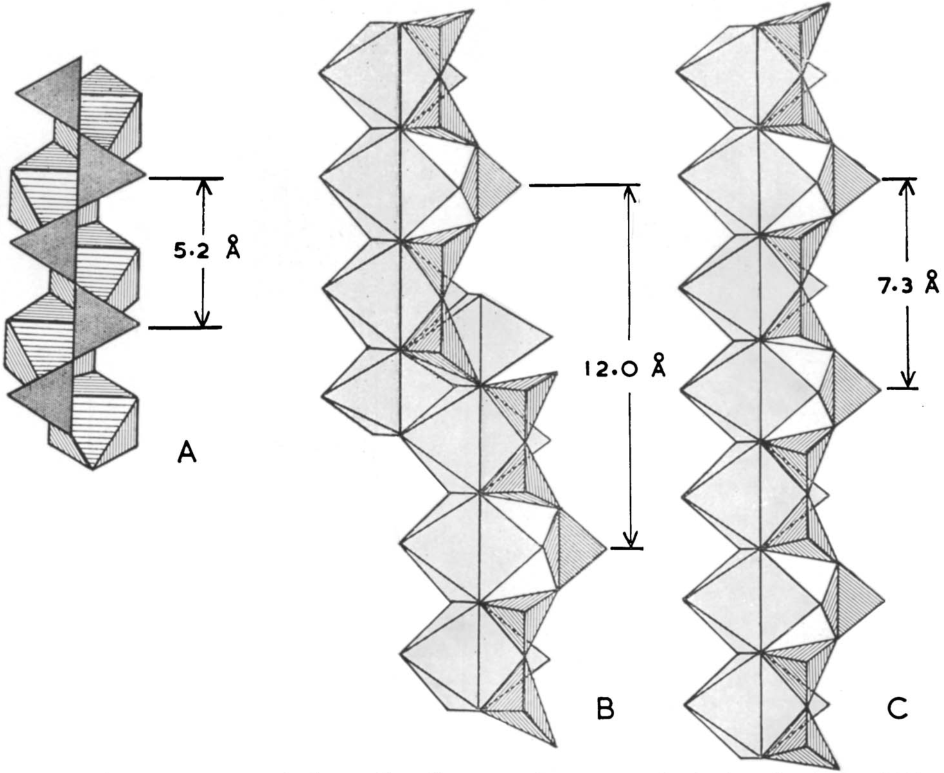

FIG. 6. *Parts of the structures of:* A, *pyroxene;* B, *rhodonite;* C, *wollastonite, showing in each case how the chains of* SiO_4 *tetrahedra are linked to the octahedral parts of the structure (after N.V. Belov).* B *and* C *are drawn in the relative orientations found experimentally when rhodonite is converted topotactically into a wollastonite solid solution.*

far as $MnO_{1\cdot46}(OH)_{0\cdot54}$. The substitution of Mn^{3+} for Mn^{4+} causes a small lattice expansion, and in the later stages of the reduction there is a change in symmetry.

Exsolution Phenomena.—$MgAl_2O_4$ (spinel) has a structure based on cubic close packed oxygen with cations in tetrahedral and octahedral interstices. At high temperatures it forms extensive solid solutions with alumina. These have the same arrangement of oxygen ions, but some of the Mg^{2+} ions are replaced by Al^{3+} and others omitted to preserve electrical neutrality. If these solid solutions are maintained at lower temperatures (850—1300°), excess of alumina exsolves. Initial distortion of the structure is followed by the appearance of a metastable phase, which exsolves topotaxially in lamellae.[19] This phase has a distorted spinel structure and contains Mg^{2+}. γ-Alumina, which has an oxygen framework similar to that of spinel, is not formed because of its instability at these temperatures. Finally, the metastable phase disappears, forming α-alumina (corundum) and nearly stoicheiometric $MgAl_2O_4$, but the lamellar texture remains. In corundum, the oxygen is hexagonally close packed, and the lamellae are oriented so that the close packed planes are parallel to those of the spinel.

Reactions Between Oxides.—Wagner's hypothesis, put forward early in the study of solid-state reactions, states that, when two solid oxides react they do so by counterdiffusion of the cations through the layer of product. Many attempts have been made to verify this, but few have used single crystals, and orientation relationships have rarely been explicitly considered. The largest groups of studies have been diffusion or self-diffusion experiments with radioactive tracers, to determine diffusion coefficients and activation energies, and marker experiments in which an inert marker such as a molybdenum wire is placed between blocks of the reacting materials. The results have often been conflicting; for example, Wagner's hypothesis is confirmed for the formation of $ZnFe_2O_4$, but not for $ZnAl_2O_4$.[20] Recent work on the formation of $MgAl_2O_4$ and $MgFe_2O_4$, using pores within the structure as markers, supports Wagner's hypothesis for both reactions;[21] in the same paper it was suggested that earlier conflicting results from marker experiments could be attributed to splitting of the marker.

Recent work on the formation of ferrimagnetic oxides provides more direct evidence of topotaxy, together with a possible technical application of topotactic reactions.[1,22] A series of compounds exists having the general formula xBaO,yMeO,$z$$Fe_2O_3$ (where Me is a bivalent metal such as Mn, Fe, Co, or Zn). These have related hexagonal crystal structures which may be regarded as blocks of a spinel (with its cubic [111] direction parallel to the c-axis) alternating with layers of a characteristic structure containing

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[19] H. Saalfeld and H. Jagodzinski, *Z. Krist.*, 1957, **109**, 87; H. Jagodzinski, *ibid.*, **109**, 388; A. M. Lejus and M. R. Collongues, *Bull. Soc. chim. France*, 1961, **65**.

[20] R. Lindner, *Z. Elektrochem.*, 1955, **59**, 967.

[21] R. E. Carter, *J. Amer. Ceram. Soc.*, 1961, **44**, 116.

[22] F. K. Lotgering, *J. Inorg. Nuclear Chem.*, 1960, **16**, 100.

barium ions. These compounds can be formed by solid-state reactions such as

$$BaO,6Fe_2O_3 + 2Fe_3O_4 \rightarrow BaO,2FeO,8Fe_2O_3$$

$BaO,6Fe_2O_3$ is hexagonal and has strong magnetic anisotropy. When pellets of the starting materials were pressed in a strong magnetic field, its crystallites became oriented with their *c*-axes parallel, while the Fe_3O_4 remained unoriented. After firing, the product was a polycrystalline aggregate in which the *c*-axes of the individual crystallites were more or less parallel to those of the $BaO,6Fe_2O_3$ originally present. It was concluded that a topotactic reaction had occurred, but the mechanism was not elucidated.

Redox Processes involving the Metal.—A few examples of the topotactic reduction of oxides to metals are known; single crystals of copper(I) oxide may be reduced to copper topotaxially[23] and iron-containing specimens of brucite [$(Mg,Fe)(OH)_2$] can be first dehydrated and then partly reduced to give metallic iron.[24] $Ag_2Si_2O_5$ can be reduced topotaxially to silver.[25] In all these cases, the orientation relationship is such that the positions of the metal atoms roughly correspond in the two structures. This contrasts with many of the mechanisms previously described, in that oxygen atoms or ions are required to move. A more complex example is provided by the thermal decomposition of silver oxalate at 100—140°.[26] Silver is formed with good preferred orientation, but, although both structures are known, the mechanism of the reaction is not obvious.

The reverse process, namely oxidation of metals, barely falls within the scope of this Review. Oxide films or crystals are often formed epitaxially. Many diffusion and other studies have been made, especially with iron and copper; the results are complex, and no unique interpretation seems possible. More specialised reviews must be consulted.[27]

Hydroxides, Oxide Hydroxides, and Silicates of Small Cations (Mg, Al, Fe)

Dehydration and Redox Processes in Hydroxides and Oxide Hydroxides.—Many of these compounds, such as magnesium hydroxide (Fig. 2a), have layer structures based on sheets of hydroxyl and sometimes also oxide ions. The arrangement of these ions approximates in varying degrees to either cubic or hexagonal close packing; the cations occupy octahedral interstices.

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[23] A. Goswami and Y. N. Trehan, *Trans. Faraday Soc.*, 1956, **52**, 358; M. R. Piggott, *Acta Cryst.*, 1957, **10**, 364.

[24] M. C. Ball and H. F. W. Taylor, *Min. Mag.*, 1961, **32**, 754.

[25] F. Liebau, F. Wodtcke, and H. Bunge, *Acta Cryst.*, 1960, **13**, 1016.

[26] R. L. Griffith, *J. Chem. Phys.*, 1946, **14**, 408.

[27] J. Bénard, *Bull. Soc. franc. Min.*, 1954, **77**, 1061; J. A. Hedvall, *Plansee Proc.*, 1955, 1 (Publ. 1956); R. Lindner, Inst. intern. chim. Solvay 10e Conseil chim., Brussels, 1956, 459; K. Hauffe, Kinetic High-temperature Processes, Conf., Dedham, Mass., 1958, 282 (Publ. 1959); M. Wyn Roberts, *Quart. Rev.*, 1962, **16**, 71.

Dehydration to the oxides usually occurs topotaxially and below 500° on heating in air. The oxides also have structures based on approximately close packed oxide ions (*e.g.*, magnesium oxide; Fig. 2b). Because there are no hydrogen ions, more interstices are occupied by metal ions than in the hydroxides; tetrahedral as well as octahedral interstices may be occupied. The orientation relationships observed in the dehydration reactions seem always to allow the best possible fit between close packed oxygen planes of starting material and product. Fig. 2 illustrates this for the dehydration of magnesium hydroxide.

The dehydration of magnesium hydroxide was studied by *X*-rays[28] in 1919 and this was probably the first time that a topotactic reaction was investigated in this way. Many subsequent *X*-ray studies of this reaction have been made.[9,24,29] In it the type of oxygen packing changes from hexagonal to cubic. Such changes seem usually to occur quite easily when Mg^{2+} is the predominant cation.

The hydroxides and oxide hydroxides of aluminium and iron show many interesting topotactic reactions,[2,3,30,31] some of which are summarised in Fig. 3. In the case of iron these include redox processes as well as dehydrations. The behaviour of Fe^{2+} is probably closely similar to that of Mg^{2+}, but Fe^{3+} and Al^{3+} show an important difference in that changes in the type of oxygen packing occur only with difficulty, at any rate in reactions effected by heating in air. Thus, diaspore gives corundum at 500°, but with boehmite, γ-alumina is formed at this temperature and corundum (the stable phase) only appears above 1000°.[32] In diaspore and corundum the oxygen atoms are in hexagonal close packing, while in boehmite and γ-alumina they are in cubic close packing or nearly so. The tendency for the oxygen framework to persist unchanged thus determines the sequence of phase changes.

Intermediate metastable phases such as γ-alumina frequently occur in these reactions. Sometimes, as in the above example, their occurrence can at least partly be attributed to the persistence of the oxygen packing, but in the dehydration of magnesium hydroxide an intermediate phase has been detected which has the same type of packing (cubic) as that of the stable form of magnesium oxide which is afterwards formed.[24,29] Metastable arrangements of cations must therefore also be possible and probably come into existence during a process of cation migration. The intermediate phases in general have structures with simple oxygen frameworks, but with

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[28] G. Aminoff, *Geol. Fören. Forh.* (*Stockholm*), 1919, **41**, 407.

[29] J. Garrido, *Ion. Rev. Españ. Quim. Applic.*, 1951, **11**, 206, 220, 453.

[30] G. W. Brindley and J. O. Choe, *Amer. Min.*, 1961, **46**, 771.

[31] M. Deflandre, *Bull. Soc. franc. Min.*, 1932, **55**, 140; M. R. Tertian, *Compt. rend.*, 1950, **230**, 1677; M. H. Francombe and H. P. Rooksby; *Clay Minerals Bull.*, 1959, **4**, 1; H. P. Rooksby and C. J. M. Rooymans, *ibid.*, 1961, **4**, 234; G. W. Van Oosterhout, *Acta Cryst.*, 1960, **13**, 932.

[32] G. Ervin, *Acta Cryst.*, 1952, **5**, 103; K. Sasvári and A. Zalai, *Acta Geol.* (*Hungary*), 1957, **4**, 415.

complicated and sometimes disordered arrangements of cations.[24,30,33] Considerable local disturbances in cation arrangement due to stacking faults have also been postulated.[34] These intermediate phases are not always truly anhydrous; χ-alumina in particular contains much hydroxyl ion which is gradually lost as the temperature rises.[30]

Hydrothermal reactions* of these hydroxides and oxide hydroxides may also occur topotaxially, and some examples of these are included in Fig. 3. With aluminium compounds, hydrothermal conditions facilitate transformations where the type of oxygen packing must change, as for instance the conversion of gibbsite into boehmite, which occurs below 300°. Hydrothermal reactions may occur inside crystals, even on heating in air, if evolved water cannot escape easily; thus gibbsite often yields boehmite as well as χ-alumina.[35]

It has generally been taken for granted that, in the dehydrations, the water is lost more or less uniformly from all regions of the crystal. Fig. 4a illustrates this for the dehydration of magnesium hydroxide. In a recent study of this reaction, this type of "homogeneous" mechanism was rejected in favour of an "inhomogeneous" mechanism, which was considered to account better for the occurrence of the spinel-like intermediate phase.[24]† According to the new hypothesis (Fig. 4b) Mg^{2+} and H^+ ions migrate in opposite directions; oxygen atoms are not lost from those regions of the crystal where the magnesium oxide forms, but only from those regions which change into pores. Such pores might be formed initially by loss of oxygen near a dislocation or other fault in the structure. Similar mechanisms can be postulated for the other dehydration and redox reactions given in Fig. 3, but further work is needed to see whether they are more nearly correct than the previously accepted homogeneous mechanisms.

The dehydration product of calcium hydroxide, unlike that of magnesium hydroxide, is poorly oriented.[36] This may be a consequence of the larger size of the Ca^{2+} ion, which could make a process dependent on easy migration of calcium impossible. $Ca_2Al(OH)_7,3H_2O$ gives oriented calcium hydroxide when heated.[37]

Clay Minerals, Serpentine, and Micas.—These compounds are structurally derived from hydroxides by replacing most of the hydroxyl ions on one or both sides of each elementary layer by highly condensed, lamellar

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* Hydrothermal reactions are ones occurring above 100° under water pressures greater than 1 atmosphere.

† G. W. Brindley (*J. Japan. Ceramic Assoc.*, 1961, **69**, 189) has expressed a similar opinion.

[33] J. D. C. McConnell and J. Lima-de-Faria, *Min. Mag.*, 1961, **32**, 898.

[34] J. M. Cowley, *Acta Cryst.*, 1953, **6**, 53.

[35] J. H. de Boer, J. M. H. Fortuin, and J. J. Steggerda, *Proc. Acad. Sci. Amsterdam*, 1954, *B*, **57**, 170, 434.

[36] C. D. West, *Amer. Min.*, 1934, **19**, 281.

[37] F. G. Buttler, L. S. Dent Glasser, and H. F. W. Taylor, *J. Amer. Ceram. Soc.*, 1959, **42**, 121.

Topotactic reactions caused by heating some clay minerals in air (some minor products omitted)

								Reference
Kaolin-like structures	Kaolinite $Al_2Si_2O_5(OH)_4$	$\xrightarrow{600^\circ}$	Metakaolin $Al_2Si_2O_7$	$\xrightarrow{900^\circ}$	Al–Si spinel* $Al_4Si_3O_{12}$	$\xrightarrow{1100^\circ}$	Mullite* $Al_6Si_2O_{13}$	*a*
	Serpentine $Mg_3Si_2O_5(OH)_4$	$\xrightarrow{600^\circ}$	Forsterite* Mg_2SiO_4	$\xrightarrow{1100^\circ}$	Forsterite + Enstatite Mg_2SiO_4 $MgSiO_3$			*b*
	Cronstedtite $(Fe^{II}_2Fe^{III})(SiFe^{III}O_5)(OH)_4$	$\xrightarrow{275^\circ}$	Oxy-cronstedtite $Fe^{III}_3(SiFe^{III}O_5)O_2(OH)_2$	$\xrightarrow{700^\circ}$	Fe–Si spinel $Fe^{III}_4SiO_8$	$\xrightarrow{800^\circ}$	Haematite* α–Fe_2O_3	*c*
	Fe^{II}–chamosite $(Fe^{II}_{1.8}Mg_{0.2}Al_{0.8})(Si_{1.3}Al_{0.7}O_5)(OH)_4$	$\xrightarrow{350^\circ}$	Fe^{III}–chamosite $(Fe^{III}_{1.8}Mg_{0.2}Al_{0.8})(Si_{1.3}Al_{0.7}O_5)O_{2.3}(OH)$					*d*
Talc-like structures	Pyrophyllite $Al_2Si_4O_{10}(OH)_2$	$\xrightarrow{800^\circ}$	Meta-pyrophyllite $Al_2Si_4O_{11}$	$\xrightarrow{1200^\circ}$	Mullite* $Al_6Si_2O_{13}$			*e*
	Talc $Mg_3Si_4O_{10}(OH)_2$	$\xrightarrow{900^\circ}$	Enstatite* $MgSiO_3$					*f*
	Saponite (a smectite or montmorillonoid) $Mg_6(Si_7AlO_{20})(OH)_4,Mg_{0\cdot5},10\ H_2O$	$\xrightarrow{500^\circ}$	Al-talc $Mg_6(Si_7AlO_{20})(OH)_4,Mg_{0\cdot5}$	$\xrightarrow{950^\circ}$	Enstatite* $MgSiO_3$			*g*
Chlorite	Penninite $Mg_3(Si_3AlO_{10})(OH)_2(Mg_2Al)(OH)_6$	$\xrightarrow{600^\circ}$	A meta-phase $Mg_3(Si_3AlO_{10})(OH)_2(Mg_2Al)O_3$	$\xrightarrow{800^\circ}$	Forsterite* Mg_2SiO_4			*h*

* With separation of silica or silica-rich material.

[a] G. W. Brindley and M. Nakahira, *J. Amer. Ceram. Soc.*, 1959, **42**, 311, 314, 319; J. Grofcsik and F. Tamás, "Mullite, its Structure, Formation and Significance," Akademiai Kiado, Budapest, 1962. [b] G. W. Brindley and J. Zussman, *Amer. Min.*, 1957, **42**, 461. [c] R. Steadman and R. F. Youell, *Nature*, 1957, **180**, 1066. [d] G. W. Brindley and R. F. Youell, *Min. Mag.*, 1953, **30**, 57. [e] E. Thilo and H. Schunemann, *Z. anorg. Chem.*, 1937, **230**, 321; W. F. Bradley and R. E. Grim, *Amer. Min.*, 1951, **36**, 182; L. Heller, *ibid.*, 1962, **47**, 156. [f] E. Thilo and G. Rogge, *Ber.*, 1939, **72**, 341. [g] H. G. Midgley and K. A. Gross, *Clay Minerals Bull.*, 1956, **3**, 79. [h] G. W. Brindley and S. Z. Ali, *Acta Cryst.*, 1950, **3**, 25.

silicate or aluminosilicate ions (Fig. 5). They undergo dehydration reactions similar to, but more complex than those of the lamellar hydroxides. These reactions are probably all topotactic.

In some clay minerals, such as halloysite [$Al_2Si_2O_5(OH)_4,2H_2O$], the layers are separated by sheets of water molecules. The first stage of dehydration is topotactic and usually complete below 500°; the water molecules are lost with one-dimensional lattice shrinkage.[38] Above 500° more drastic, but still topotactic, changes accompany the dehydroxylation of all clay minerals; typical examples are listed in the Table. Some, such as kaolinite, pyrophyllite, and chlorites, first lose all or part of their hydroxyl without changing into basically new structures; products known as meta-phases are formed (*e.g.*, kaolinite → metakaolin). These meta-phases are similar in many respects to the intermediate phases formed during the dehydration of aluminium hydroxide and other hydroxides. Other compounds, such as talc and chrysotile, rapidly change to new structures on dehydroxylation. The compounds in the first group mostly have a high Al^{3+} content while those in the second have a high Mg^{2+} content. The difference in behaviour parallels that observed with the hydroxides and can perhaps be attributed to the greater ease with which the oxygen packing changes in the magnesium compounds.

The principal high-temperature phases formed are mullite, forsterite, enstatite, and defect spinels. In all of these the cations other than Si^{4+} (*i.e.*, Al^{3+}, Mg^{2+}, Fe^{2+}) are largely or wholly in octahedral sites. The orientation relationships observed when the various clay minerals are heated in air can be summarised by the rule that the octahedra have the same orientations in the product as in the starting material. In some cases, as with talc or saponite, the arrangement of SiO_4 tetrahedra in the product also resembles that in the starting material, but sometimes (*e.g.*, with serpentine) the orientations of the tetrahedra change during the reactions. In general, the regions where topotactic change occurs become progressively poorer in silica. This silica sometimes crystallises as cristobalite (usually unoriented) above 1000°, though sometimes the existence of amorphous silica or silica-rich material must be presumed.

On heating the Fe^{2+}-containing minerals in air, oxidation of Fe^{2+} to Fe^{3+} occurs first. Electrical neutrality is maintained by loss of protons, and the lattice contracts slightly because Fe^{3+} is smaller than Fe^{2+}.

Detailed mechanisms have been suggested for most of these reactions. It has generally been assumed that the mechanisms are homogeneous, and also that the SiO_4 tetrahedra are more likely to be stable than are the cation-oxygen octahedra. There is some positive evidence for the first assumption in the case of chlorites, where the observed intensities of the $00l$ *X*-ray reflections for the meta-phase are compatible with the postulated structure.[39] There seems to be no evidence for the second; on the contrary, both

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[38] "X-Ray Identification and Crystal Structures of Clay Minerals," ed. G. Brown, 2nd edn., Mineralogical Society, London, 1961.

[39] G. W. Brindley and S. Z. Ali, *Acta Cryst.*, 1950, **3**, 25.

the greater tendency for the octahedra to be preserved, and also the tendency for SiO_2 to be expelled, suggest that the SiO_4 tetrahedra are less stable at high temperatures than the octahedra. Studies on hydrated calcium silicates, discussed later, also indicate that silicon atoms or ions are mobile at high temperatures. Inhomogeneous mechanisms might provide a better explanation of some of these reactions. The chrysotile dehydration has recently been approached in this way,[40] as was that of kaolinite in some early work,[41] though in the latter case a homogeneous mechanism was later assumed.[42]

Amesite,[43] chloritoid,[44] micas,[45] sepiolite,[46] and chrysotile under hydrothermal conditions[40] are also dehydrated topotaxially.

Interconversion and acid leaching. There is geological evidence for various reactions in which one clay mineral is changed into another, and such processes are possibly topotactic. Smectites have been changed into chlorite-like materials in the laboratory by reaction with magnesium hydroxide or other bases.[47] Attempts to reverse the process by acid leaching are successful only in certain cases.[48] With typical chlorites, acid leaching causes disintegration of the entire structure, but octahedral aluminium is attacked more readily than tetrahedral aluminium.[49]

Reactions of Pyroxenes, Amphiboles, and Olivine.—These important rock-forming minerals are silicates in which the predominant cations are Mg^{2+}, Fe^{2+}, or others of similar size (about 0·8 Å). They have structures based on fragments of octahedral layers, similar to those in the metal hydroxides and clay minerals, which are condensed with separate SiO_4 tetrahedra in olivines (*e.g.*, forsterite, Mg_2SiO_4), with infinite single chains of tetrahedra in the pyroxenes (*e.g.*, enstatite, $MgSiO_3$), and with infinite double chains in the amphiboles [*e.g.*, anthophyllite, $Mg_7(Si_8O_{22})(OH)_2$]. The chains (Fig. 6a) in each case adopt a form which is repeated at intervals of two tetrahedra (5·2 Å) and allows them to fit on to the cation-oxygen parts of the structures; such chains have been called Zweierketten*[50] to distinguish them from the different types of chain that arise when other

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* No satisfactory translation exists for this.

[40] M. C. Ball and H. F. W. Taylor, *Min. Mag.*, 1963, in the press.

[41] M. Nakahira, *Clay Minerals Bull.*, 1954, **2**, 206.

[42] G. W. Brindley and M. Nakahira, *J. Amer. Ceram. Soc.*, 1959, **42**, 311, 314, 319.

[43] G. W. Brindley, B. M. Oughton, and R. F. Youell, *Acta Cryst.*, 1951, **4**, 552; H. Steinfink and G. D. Brunton, *ibid.*, 1956, **9**, 487.

[44] H. G. Bachmann, *Z. Krist.*, 1956, **108**, 145.

[45] N. Sundius and A. M. Byström, *Trans. Brit. Ceram. Soc.*, 1953, **52**, 632; H. Wilman and T. de S. Mutucumarana, *Acta Cryst.*, 1954, **7**, 666; J. B. Holt, I. B. Cutler, and M. F. Wadsworth, *J. Amer. Ceram. Soc.*, 1958, **41**, 242.

[46] G. Kulbicki, *Amer. Min.*, 1959, **44**, 752.

[47] S. Caillère, S. Hénin, and R. Guennelon, *Compt. rend.*, 1949, **228**, 1741; R. F. Youell, *Clay Minerals Bull.*, 1950, **1**, 174; M. Slaughter and I. H. Milne, Proc. 7th Nat. Clay Conf. (U.S.A.), 1958, 114.

[48] S. Caillère, S. Hénin, and J. Esquevin, *Clay Minerals Bull.*, 1954, **2**, 166.

[49] G. W. Brindley, Proc. Int. Symp. Reactivity of Solids, Gothenburg, 1952, 349; G. W. Brindley and R. F. Youell, *Acta Cryst.*, 1951, **4**, 495.

[50] F. Liebau, *Z. phys. Chem.*, 1956, **206**, 73.

cations predominate. The sheets in clay minerals represent a higher degree of condensation of Zweierketten. Pyroxenes and amphiboles can accommodate limited proportions of larger cations, as in diopside ($CaMgSi_2O_6$) and tremolite [$Ca_2Mg_5Si_8O_{22}(OH)_2$].

Examples of topotactic processes involving these minerals have been studied in the laboratory and also found in Nature. The history of the natural specimens must be inferred from indirect evidence, and it is not always possible to distinguish between epitaxy and topotaxy.

(1) Naturally occurring pyroxene crystals have been found[51] in which inclusions occur, either of a different pyroxene mineral, or of other minerals such as magnetite (Fe_3O_4), ilmenite ($FeTiO_3$), haematite (α-Fe_2O_3), and amphiboles. In each case the included mineral bears a definite crystallographic orientation relative to the pyroxene.

(2) Iddingsites are naturally occurring alteration products of olivine in which the latter has been wholly or partly converted topotaxially into other products, especially haematite, goethite, and chlorite or other lamellar silicates; unoriented quartz may also occur.[52,53]

(3) Naturally occurring composite crystals of talc and tremolite often occur with the two minerals in a definite relative orientation; the talc seems to have been formed topotaxially from the tremolite.[54]

(4) Dehydration of amphiboles occurs topotaxially. As the main crystalline products, anthophyllite[55] gives a polymorph of the pyroxene $MgSiO_3$; tremolite gives a calcium–magnesium pyroxene, and riebeckite [$Na_2(Fe^{II},Mg)_2Fe^{III}{}_3Si_8O_{24}H_2$] gives pyroxene, iron oxides, and cristobalite, the product depending to some extent on whether an oxidising or neutral atmosphere is used.[56]

(5) Topotactic transformations in enstatite have been studied in the laboratory.[57]

(6) Oriented exsolution lamellae of willemite (α-Zn_2SiO_4) have been found in natural olivine crystals.[58]

All the phases mentioned above have structures based on nearly close-packed oxygen frameworks, and the observed orientation relationships are, broadly speaking, such as to give the best possible fit between the oxygen frameworks of starting material and product. It has been suggested[53] that the formation of iddingsites from olivine occurs by diffusion and replace-

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[51] M. G. Bown and P. Gay, *Amer. Min.*, 1959, **44**, 592.

[52] G. Brown and I. Stephen, *Amer. Min.*, 1959, **44**, 251; W. W. Smith, *Min. Mag.*, 1959, **32**, 324; *ibid.*, 1961, **32**, 823.

[53] P. Gay and R. W. Le Maitre, *Amer. Min.*, 1961, **46**, 92.

[54] I. S. Stemple and G. W. Brindley, *J. Amer. Ceram. Soc.*, 1960, **43**, 34.

[55] E. Thilo and G. Rogge, *Ber.*, 1939, **72**, 341.

[56] A. G. Freeman and H. F. W. Taylor, *Silikattech.*, 1960, **11**, 390; and unpublished work.

[57] L. Atlas, *J. Geol.*, 1952, **60**, 125; W. L. Brown, N. Morimoto, and J. V. Smith, *J. Geol.*, 1961, **69**, 609.

[58] C. S. Hurlbut, *Amer. Min.*, 1961, **46**, 549.

ment of cations within a relatively unchanged oxygen framework, and that it is probably catalysed by protons. In natural iddingsite, the cations are not rearranged perfectly enough to give an intergrowth of distinct phases even in regions of submicroscopic extent; instead, they are arranged in a disordered, irregular way so that in small domains the structure approximates to that of one or other crystalline product.[53] The mechanism of this process is basically similar to the inhomogeneous one proposed for the dehydrations of hydroxides and clay minerals. A similar explanation has been advanced for the tremolite dehydration,[56] and many of the other processes described in the previous paragraph probably occur in the same way.

Silicates of Larger Cations

Calcium, Manganese, and Alkali Silicates.—The structures of these are usually analogous to those of the small cations only to the extent that many are based on fragments of octahedral cation-oxygen layers condensed with the silicate anion. The types of anion derived from Zweierketten, found in pyroxenes, amphiboles, and clay minerals, will not fit the larger octahedra of the calcium and manganese compounds; different anions are found, based on chains repeating at intervals of three tetrahedra (Dreierketten) or five (Fünferketten) (Fig. 6b and c).[50,59]

Xonotlite [$Ca_6(Si_6O_{17})(OH)_2$] contains double Dreierketten analogous to the double Zweierketten of amphiboles; it is dehydrated topotaxially at about 800° in air to wollastonite (β-$CaSiO_3$), which contains single Dreierketten.[60] It was concluded that the fragments of octahedral layers were preserved, and that migration of silicon and loss of some of the oxygen not attached to calcium resulted in the reconstruction of the silicate anions. Thus the Si–O skeleton, generally assumed to be the most important part of a silicate structure, was apparently less stable in a high-temperature reaction than the Ca–O part.

Rhodonite [$(Mn,Ca)SiO_3$] is transformed into a wollastonite solid solution of the same composition on heating. Rhodonite contains Fünferketten which do not run parallel to the rows of octahedra; the crystals are prisms elongated parallel to the chains (Fig. 6b). In wollastonite the Dreierketten are parallel to the rows of octahedra (Fig. 6c). *X*-Ray study of pseudomorphs formed by heating rhodonite at 1100° showed that the chains were no longer parallel to the prism axis, but that the orientation of the octahedra had been preserved.[4] This proves conclusively that the transformation proceeds by the destruction and rebuilding of the chains through migration of silicon. This probably entails a series of movements of silicon from initially filled tetrahedra to initially empty ones with which they share a face ("filled–empty tetrahedron migration").

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[59] N. V. Belov, *Zhur. Strukt. Khim.*, 1960, **1**, 39.

[60] L. Heller, Proc. 3rd. Int. Symp. Chem. Cement, London, 1952, 237; L. S. Dent and H. F. W. Taylor, *Acta Cryst.*, 1956, **9**, 1002.

Foshagite [$Ca_4(SiO_3)_3(OH)_2$] is dehydrated topotaxially at 750° to wollastonite and β-Ca_2SiO_4.[10] The structure of foshagite was unknown when this study was made, but on the assumption that the mechanism of its dehydration was similar to that of xonotite, positions could be postulated for the calcium and most of the oxygen atoms, and a probable arrangement suggested for the $(OH)^-$ groups and silicate anions (which were suspected to be single Dreierketten). This provisional structure was confirmed by Fourier methods.[61]

Other hydrated calcium silicates which undergo topotactic changes at 650—800° include okenite, nekoite, tobermorite, gyrolite, reyerite, zeophyllite, and possibly others. These reactions have not been fully interpreted but it seems likely that they occur by mechanisms essentially similar to those of the xonotlite and foshagite dehydrations.[62]

Many of the above dehydrations will proceed at a lower temperature (about 400°) under hydrothermal conditions. "Filled–empty tetrahedron migration" is thus catalysed by water at high pressures (or perhaps more accurately by protons), and this hastens the attainment of equilibrium. As already stated, workers on iddingsite reached a similar conclusion. Possibly Si–OH–Si groups exist temporarily, and this facilitates the breaking of Si–O bonds. Sometimes, as with tobermorite, hydrothermal dehydration does not give the same product as heating in air.[63]

Hydrated calcium silicates containing $\equiv$ Si–OH groups decompose in air below 500°. The dehydrations of afwillite [$Ca_3(HSiO_4)_2,2H_2O$][64] and of bultfonteinite[65] are topotactic. The hypothesis of silicon migration within a relatively stable Ca–O framework does not apply to these reactions. With afwillite the process seems to involve loss of molecular water and migration of calcium. With bultfonteinite both of these processes and also silicon migration seem to occur.

α-$Na_2Si_2O_5$ has a layer structure; the Si_2O_5 sheets are composed of fused rings of six tetrahedra, as in the clay minerals, but the rings are kinked in a way that permits condensation with the large Na–O polyhedra.[66] Treatment with fused silver nitrate at 280° causes cation exchange; $Ag_2Si_2O_5$ is formed topotaxially, the Si_2O_5 sheets being unaltered.[67] This provides a further example of the movement of large metal cations rather than of silicon and aluminium at low temperatures. Similar processes of cation-exchange occur readily in clay minerals[38] and zeolites,[68] but will not be discussed here as they probably do not fall within the present definition of topotaxy.

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[61] J. A. Gard and H. F. W. Taylor, *Acta Cryst.*, 1960, **13**, 785.
[62] H. F. W. Taylor, *J. Appl. Chem.*, 1960, **10**, 317.
[63] H. F. W. Taylor, *Min. Mag.*, 1959, **32**, 110.
[64] H. F. W. Taylor, *Acta Cryst.*, 1955, **8**, 440.
[65] E. J. McIver, Mineralogical Society, Notice of Meeting 117, 1962.
[66] F. Liebau, *Acta Cryst.*, 1961, **14**, 395.
[67] F. Liebau, *Acta Cryst.*, 1961, **14**, 537.
[68] R. M. Barrer, *Proc. Chem. Soc.*, 1958, 99.

Feldspars.—These have three-dimensional aluminosilicate frameworks of empirical formula $(Si,Al)O_2$ with relatively large cations such as sodium, potassium, or calcium. Naturally occurring feldspar crystals are often pseudomorphous after a former high-temperature solid-solution phase which has undergone a complicated series of changes on cooling. Sometimes the details of these processes are obscure. One type of change, which results in exsolution in of the homogeneous high-temperature phase is due to ordering of the large cations, *e.g.*, Na–K.[69] This process, involving Na–K migration, is topotactic. The reverse process, namely homogenisation of oriented intergrowths of $KAlSi_3O_8$ and $NaAlSi_3O_8$, occurs at 350—750°.[70]

Treatment of a feldspar, $Na_{0\cdot4}Ca_{0\cdot6}(Si,Al)_4O_8$, with aqueous potassium chloride at 500° and 600° bars resulted in replacement of sodium by potassium and exsolution of the homogeneous phase to give $KAlSi_3O_8$ and $CaAl_2Si_2O_8$. Experiments with single crystals showed that this did not result from dissolution and recrystallisation, but from a topotactic change involving migration of sodium, potassium, aluminium, and silicon. Treatment with fused potassium chloride, in contrast, caused replacement of sodium by potassium, but no change in the degree of Al–Si ordering. It was concluded that the large cations could migrate under anhydrous conditions, but that water was essential for migration of silicon and aluminium.[71] The action of water was explained by a mechanism involving diffusion into the structure of both H^+ and OH^- ions; experiments with oxygen-18 showed that considerable exchange of oxygen between crystal and solution had occurred.[72] Catalysis of silicon migration by water was also postulated in the reactions of olivine and of calcium silicates previously discussed, but a different mechanism involving only protons was assumed. From the study of rhodonite,[4] also previously discussed, it was concluded that migration of silicon can probably also occur under anhydrous conditions.

Acid Leaching.—Apophyllite $[KCa_4(Si_8O_{20})F]$ and gillespite $[BaFe(Si_4O_{10})]$ have related structures containing rings of four and eight tetrahedra, arranged in layers of Si_2O_5 composition. Leaching with dilute acid leaves the Si_2O_5 sheets unchanged and still crystalline; the residue from gillespite has the composition $H_4Si_4O_{10}$.[73] Most silicates which are attacked by acids yield either gelatinised or amorphous silica residues, depending mainly on the degree of condensation of the silicate anion,[74] and the behaviour of apophyllite and gillespite is thus unusual.

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[69] O. F. Tuttle and N. L. Bowen, "Origin of Granite in the Light of Experimental Studies in the System $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O," Geological Society of America Memoir 74, New York, 1958.

[70] E. Spencer, *Min. Mag.*, 1937, **24**, 453.

[71] J. Wyart and G. Sabatier, *Bull Soc. franc. Min.*, 1958, **81**, 223.

[72] G. Donnay, J. Wyart, and G. Sabatier, *Z. Krist.*, 1959, **112**, 161.

[73] E. H. Bailey, *Amer. Min.*, 1941, **26**, 565; A. Pabst, *ibid.*, 1958, **43**, 970.

[74] K. J. Murata, U.S. Geol. Survey Bull. No. 950, 1946, 25.

Other Oxy-salts

There have been very few systematic studies of topotactic reactions in other oxy-salts, even though, judging from the examples described below, such reactions must be common.

Gypsum is dehydrated topotaxially in three steps:

$$\underset{\text{gypsum}}{CaSO_4{,}2H_2O} \rightleftharpoons \underset{\text{hemihydrate}}{CaSO_4{,}\tfrac{1}{2}H_2O} \rightleftharpoons \gamma\text{-}CaSO_4 \rightarrow \underset{\text{anhydrite}}{CaSO_4}$$

The first two reactions are reversible. Orientation is well preserved in the second and third steps, but only partly preserved in the first. The reaction has been interpreted in terms of the preservation of the chains of Ca^{2+} and SO_4^{2-} ions which occur in all four structures. The structures of hemihydrate, γ-calcium sulphate, and anhydrite can alternatively be described in terms of analogous sheets of Ca^{2+} and SO_4^{2-} ions. One structure can change into another by small relative displacements of these sheets, together with loss of water.[75] The occurrence of γ-calcium sulphate, metastable under all conditions, is an example of structural control over the phase formed.

Potassium chlorate crystals, grown on an electron-microscope grid, were decomposed in the electron beam.[76] Potassium chloride was formed as a well-oriented pseudomorph with its (100) planes parallel to (001) of the potassium chlorate, but no interpretation was given. The chlorate ion is only slightly larger than the chloride ion, and potassium chlorate can be regarded as having a distorted potassium chloride- or sodium chloride-like structure. A homogeneous mechanism involving loss of oxygen and repacking of the large residual K^+ and Cl^- ions might be possible.

Several calcite-type carbonates decompose topotaxially when heated. The calcite structure is a rhombohedral variant of the sodium chloride structure with Cl^- replaced by coplanar CO_3^{2-} groups and Na^+ by the appropriate cation. Ferrous carbonate decomposes topotaxially to FeO and Fe_3O_4.[12] The orientation of the FeO suggests that carbon dioxide is expelled from each CO_3^{2-} group (cf. potassium chlorate). The decomposition of calcium carbonate appears to be unoriented, although the existence of an intermediate metastable phase, designated CaO*, with structure and orientation derived from the calcium carbonate, has been postulated from kinetic evidence.[77] Dolomite, $CaMg(CO_3)_2$, decomposes in two stages, the first giving oriented calcite and unoriented magnesium oxide; in the second, unoriented calcium oxide is formed from the calcite.[78] Little is known about the decomposition mechanisms of carbonates having the aragonite structure. Strontium carbonate–barium carbonate solid solu-

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[75] O. W. Flörke, *Neues Jahrb. Mineral.*, 1952, **84**, 189.

[76] M. Ross and C. L. Christ, *Amer. Min.*, 1958, **43**, 1157.

[77] E. P. Hyatt, I. B. Cutler, and M. E. Wadsworth, *J. Amer. Ceram. Soc.*, 1958, **41**, 70.

[78] R. A. W. Haul and H. Wilsdorf, *Acta Cryst.*, 1952, **5**, 250.

tions, on being heated, are said to exsolve into the pure phases before decomposing;[79] this is unusual behaviour, since solid solubility normally increases with rising temperature. Zinc carbonate also decomposes topotaxially to zinc oxide; the orientation relationships have not been given explicitly.[80]

No single mechanism can be suggested to explain both the topotactic decomposition of ferrous carbonate and $CaMg(CO_3)_2$ and also the apparently non-topotactic decomposition of calcium carbonate. Temperature may be an important factor;[12] calcium carbonate has the highest decomposition temperature of any member of the group. The topotactic decompositions may proceed, not by the homogeneous mechanism suggested for ferrous carbonate, but by an inhomogeneous one similar to that suggested for hydroxides.[24] The calcite structure can be regarded as approximately close packed oxygen atoms with cations in octahedral and carbon in triangular interstices; decomposition might then occur by migration of cations and carbon. It is tempting to correlate the non-topotactic decomposition of calcium carbonate with the relative difficulty with which calcium diffuses (as with the hydroxides), but calcium must diffuse during the first stage of the dolomite decomposition; more studies are needed before generalisations can be made.

Summary

Although the study of topotactic reactions in inorganic oxy-compounds is still in its infancy, a few tentative generalisations may be suggested.

(1) Topotactic processes are probably quite commonplace. For a transformation to proceed topotaxially, there must be a three-dimensional similarity between the structures of starting material and product. This similarity need not be very great, and even the compositions may differ radically. The mere similarity between structures is, however, not in itself sufficient to guarantee that a transformation will occur topotactically. Experimental evidence is always needed. Some reactions are topotactic under all conditions, some only under certain conditions, and others not at all. Factors which may influence the degree of orientation in any particular reaction include temperature, pressure, physical state (*e.g.*, grain size), and specific experimental conditions such as the time and rate of heating used to induce thermal changes.

(2) The sizes and electronegativities of the cations partly decide which ions move and which do not. With small cations (*e.g.*, Mg^{2+}, Al^{3+}, Fe^{3+}, Si^{4+}), the oxygen framework tends to stay relatively unchanged while cations migrate. The number of oxygen atoms in a given volume tends to remain constant in the regions where topotactic change actually occurs. However, the type of oxygen packing may change; this happens readily with

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[79] R. Faivre and G. Chaudron, *Compt. rend.*, 1948, **226**, 249.

[80] A. Rose, *Compt. rend.*, 1939, **208**, 1914.

Mg^{2+} but less readily with Al^{3+} or Fe^{3+}. At the other extreme, large electronegative cations (*e.g.*, U^{4+}, Pb^{4+}) probably remain fixed while oxygen atoms move. Large electropositive cations (*e.g.*, Ca^{2+}) represent an intermediate case. In low-temperature reactions of hydrated calcium silicates, calcium migration is important, but reactions occurring above about 500° take place mainly by migration of silicon, the Ca–O framework staying nearly unaltered.

(3) Thus, in high-temperature reactions, SiO_4 tetrahedra rarely behave as units; Si–O bonds are often less stable than the other cation–oxygen bonds. The concept of the silicate anion as the most important element of the structure is not a good starting point for an understanding of these reactions. The packing of oxygen atoms, and of any large cations present, is more important than that of silicon.

(4) Caution should be used in applying the above generalisations to redox processes involving the metal (*e.g.*, $FeO \rightleftharpoons Fe$) because it may be incorrect to use ionic radii.

(5) The effects of catalysts have been little studied. Water seems to catalyse silicon migration.

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