The Thermal Decomposition of Hydrous Layer Silicates and their Related Hydroxides

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1 Introduction

Several years ago, two excellent reviews[1,2] concerned primarily with crystallographic aspects of the thermal decomposition of hydroxides and hydrous silicates were published. There have been many subsequent investigations of these reactions using *X*-ray and other techniques, and these are the subject of this Review.

The structures of the mineral silicates are usually classified according to Bragg's system, which is based on the observation that silicon is almost always found in tetrahedral co-ordination with respect to oxygen (except in rare instances, *e.g.* stishovite). This classification over-emphasises the importance of the SiO_4 tetrahedron as a structural unit, whereas the cation polyhedra are neglected. Yet chemically related elements, such as Mg and Ca, form silicates of formulae $MSiO_3$ and M_2SiO_4, which have different structures.

Furthermore, similarities between the sheet structures of the layer silicates and the closely related hydroxides of Mg, Ca, Al, *etc.*, which are based on the cadmium iodide structure (Figure 1A), and between the layer and chain silicates (Figure 1B), can easily be overlooked in terms of Bragg's classification. This Review is concerned with the decomposition of these structurally related compounds. The principal cation in the silicates is usually Mg, Al, or Fe; those silicates in which Ca is the major cation have different structures and their decompositions have been reviewed by Brindley[2] and Taylor.[3]

2 Hydroxides and Oxyhydroxides

The layer hydroxides are probably the simplest class of compounds in which the thermal decomposition process has been thoroughly investigated using a wide variety of techniques. When orientation relationships develop during thermal decomposition, between the crystal structure of the starting material and that of its product, the reaction is described as topotactic and the phenomenon observed as topotaxy. A three-dimensional correspondence between the crystal structure of the starting material and product is implied in a topotactic reaction, in contrast to epitaxy where the correspondence is two-dimensional.

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[1] L. S. Dent, F. P. Glasser, and H. F. W. Taylor, *Quart. Rev.*, 1962, **16**, 343.
[2] G. W. Brindley, 'Progress in Ceramic Science', Pergamon, 1963, vol. 3, p. 1.
[3] H. F. W. Taylor, 'Progress in Ceramic Science', Pergamon, 1961, vol. 1, p. 89.

A

—— 6 (OH)	—— 4 O + 2 (OH)	—— 6 O	—— 6 O	—— 6 (OH)
Vacant	4 Si	Vacant	2 K	Vacant
—— 6 (OH)	—— 6 O	—— 6 O	—— 6 O	—— 6 O
6 Mg	Vacant	4 Si	3 Si + 1 Al	4 Si
—— 6 (OH)	—— 6 (OH)	—— 4 O + 2 (OH)	—— 4 O + 2 (OH)	—— 4 O + 2 (OH)
Vacant	6 Mg	6 Mg	6 Mg	6 Mg
—— 6 (OH)	—— 4 O + 2 (OH)	—— 4 O + 2 (OH)	—— 4 O + 2 (OH)	—— 4 O + 2 (OH)
6 Mg	4 Si	4 Si	3 Si + 1 Al	4 Si
—— 6 (OH)	—— 6 O	—— 6 O	—— 6 O	—— 6 O
				Vacant
Brucite	Serpentine	Talc	Phlogopite	—— 6 (OH)
				6 Mg
$Mg(OH)_2$	$Mg_6Si_4O_{10}(OH)_8$	$Mg_6Si_8O_{20}(OH)_4$	$K_2Mg_6(Si_6Al_2)O_{20}(OH)_4$	—— 6 (OH)
				Ideal Chlorite
(Cd I_2 Structure)	(1:1 Layer Silicate)	(2:1 Layer Silicate)	(Mica)	
				$Mg_6Si_4O_{10}(OH)_8$

Figure 1A *Schematic representation of the structural relationship between hydroxides and hydrous layer silicates*

B

——— 12 O	——— 11 O + 1 (OH)	——— 12 O
8 Mg	7 Mg	Vacant
——— 12 O	——— 11 O + 1 (OH)	——— 12 O
8 Si	8 Si	8 Si
——— 12 O	——— 11 O + 1 (OH)	——— 8 O + 4 (OH)
8 Mg	7 Mg	12 Mg
——— 12 O	——— 11 O + 1 (OH)	——— 8 O + 4 (OH)
8 Si	8 Si	8 Si
——— 12 O	——— 11 O + 1 (OH)	——— 12 O
Enstatite	Anthophyllite	Talc
$Mg_8Si_8O_{24}$	$Mg_7Si_8O_{22}(OH)_2$	$Mg_6Si_8O_{20}(OH)_4$
(Pyroxene)	(Amphibole)	(2:1 Layer Silicate)

Figure 1B *Schematic representation of the structural relationships between pyroxenes amphiboles and* 2:1 *layer silicates*

Shannon and Rossi[4] suggest that one may describe a continuum of degrees to topotaxy since the degree of related orientation found in practice varies tremendously.

A. Brucite, $Mg(OH)_2$.—In the conversion of brucite to periclase, MgO, the reaction takes place in an ordered manner as the hexagonal close-packed structure of oxygen ions rearranges to a cubic close-packed structure. A high degree of topotaxy is preserved and the orientation relationships have been confirmed by several workers.[5,6,7] These relations are not limited to the crystallographic structure of the starting material and its product, but extend to the macroscopic structure of the materials. Thus, magnesium oxide prepared by the thermal decomposition of nesquehonite ($MgCO_3$,- $3H_2O$), retains the needle-like structure of the carbonate, whilst that prepared from brucite has the form of hexagonal platelets which the hydroxide itself exhibits.[8]

From a knowledge of the structure of the parent and product of a decomposition reaction and their orientation relationships, it is an obvious step to postulate the reaction mechanism. Investigations of the dehydroxylation of brucite have resulted in two differing models for the decomposition process. In the first,[6] it is assumed that water is lost, in a similar manner, from all regions of the crystal. Hydroxy-groups from adjacent layers combine to form water which can then diffuse away; the main shrinkage occurs in the *c*-direction with a smaller shrinkage in the basal plane. Kinetic and optical microscope studies[9] suggest that reaction commences at an internal surface and advances towards the centre of the crystal. This is known as the homogeneous mechanism. The second model, the inhomogeneous mechanism, was proposed independently by Ball and Taylor,[7] and by Brindley,[2] who assumed that the reaction takes place simultaneously throughout the bulk of the crystal, which develops 'donor' and 'acceptor' regions[7] during the decomposition process. Mg^{2+} ions migrate from the former to the latter with a counter-migration of protons. The 'acceptor' regions thus become MgO crystals, whilst protons combine with hydroxyl ions to form water molecules, which escape from the 'donor' regions leaving intercrystalline pores.

The strengths of the inhomogeneous mechanism are twofold. Firstly, a good explanation of topotaxy is provided since less disturbance of the structure would be expected if cations and protons, rather than water molecules, were the migrating species. Secondly, the formation of a porous decomposition product is explained by the creation of donor and acceptor regions in the brucite lattice. Its weakness lies in the *ad hoc* nature of the postulate of donor and acceptor regions, and the corollary of counter-migration of two positively charged ions.

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[4] R. D. Shannon and R. C. Rossi, *Nature*, 1964, **202**, 1000.
[5] J. Garrido, *Ion, Rev. Espan. Quim. Apli.*, 1951, **11**, 206, 220, 453.
[6] J. F. Goodman, *Proc. Roy. Soc.*, 1958, *A*, **247**, 346.
[7] M. C. Ball and H. F. W. Taylor, *Mineralog. Mag.*, 1961, **32**, 754.
[8] R. M. Dell and S. W. Weller, *Trans. Faraday Soc.*, 1959, **55**, 2203.
[9] P. J. Anderson and R. F. Horlock, *Trans. Faraday Soc.*, 1962, **58**, 1993.

The original evidence for the inhomogeneous mechanism for the decomposition of brucite was based not only on the observed topotaxy and porous product but also on a reported intermediate phase.[7] *X*-Ray powder and single crystal photographs of brucite crystals which had been decomposed at about 800° exhibited 'spinel-like' reflections, indicating the presence of tetrahedral magnesium ions which must, therefore, be migrating. More recently, this observation of spinel reflections during the decomposition of natural brucite has been shown to be an artefact arising from the presence of impurities.[10] Pure samples of $Mg(OH)_2$ powder gave no extra reflections on decomposition and it was concluded that the experimental basis for the inhomogeneous mechanism is invalid.

Other workers[11] have reported the existence of an intermediate hexagonal phase, but this too has been rejected in an electron and optical microscope study by Gordon and Kingery.[12] From kinetic data these authors[13] interpreted the decomposition process as a nucleation and growth process in which MgO nuclei form coherently with the brucite matrix. This interpretation is similar to that of Pampuch,[14] who considered that the formation of new phases in topotaxial decomposition reactions proceeds through an intermediate stage of hybrid crystals. These crystals contain domains of the product phase in a homogeneous matrix of the parent crystal, instead of independent nuclei separated from the matrix by phase boundaries. The latter mechanism is reserved for reactions where the structure of the starting material and the product are considerably different.

Recently, Freund[15] has proposed a hydrogen-bond model for the decomposition of ionic hydroxides. In the case of brucite, the broadening of the O—H band in the i.r. spectrum at temperatures just below 300°C, was interpreted as the commencement of OH–OH interaction at the surface of crystals. Proton transfer by a tunnelling mechanism is then supposed to occur between adjacent hydroxyl groups, followed by removal of water molecules by diffusion. Tunnelling can take place at low temperatures when the energy levels of two adjacent OH groups overlap, but at higher temperatures where widely spaced OH groups exist, proton jumping leads to the removal of OH groups with the loss of hydrogen.[15] Freund's interpretation of the dehydroxylation process is consistent with the advancing interface concept, rather than the inhomogeneous mechanism, since the reaction of OH groups in adjacent layers[6,9] is satisfactorily explained by proton tunnelling. Moreover, no counter migration of cations is required to preserve electrical neutrality.

B. Portlandite, $Ca(OH)_2$.—This has a similar structure to that of brucite (CdI_2 layer structure) with no evidence of OH bonding, although Freund considers that

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[10] N. H. Brett and P. J. Anderson, *Trans. Faraday Soc.*, 1967, **63**, 2044.

[11] R. R. Balmbra, J. S. Clunie, and J. F. Goodman, *Nature*, 1966, **209**, 1088.

[12] R. S. Gordon and W. D. Kingery, *J. Amer. Ceram. Soc.*, 1966, **49**, 654.

[13] R. S. Gordon and W. D. Kingery, *J. Amer. Ceram. Soc.*, 1967, **50**, 8.

[14] R. Pampuch, Proc. IXth Conf. Silicate Ind., Budapest, 1968, p. 143.

[15] F. Freund, *Angew Chem. Internat. Edn.*, 1965, **4**, 445; F. Freund and H. Gentsch, *Ber. deut. keram. Gesellschaft*, 1967, **44**, 51.

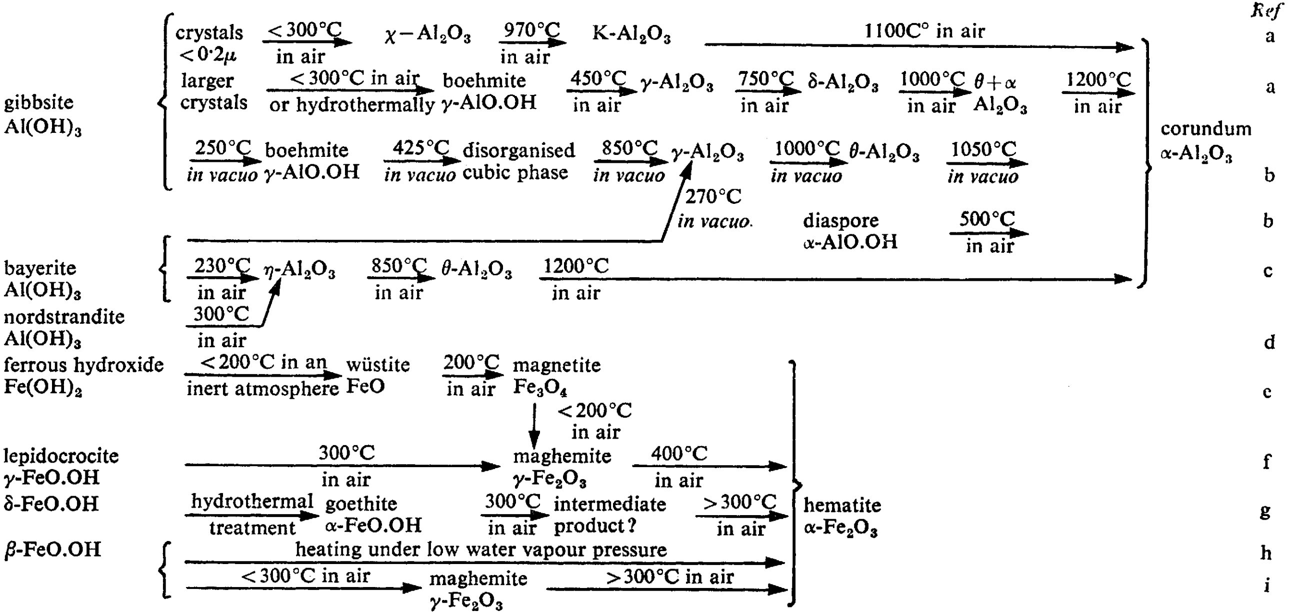
proton tunnelling occurs near the decomposition temperature.[15] In contrast to brucite the decomposition product, CaO, is poorly oriented when the reaction takes place in air.[16] The degree of topotaxy is improved if the dehydroxylation takes place *in vacuo* rather than in air;[17,18,19] the absence of an intermediate phase and the observation of a reaction interface[18,19,20] which moves in from the edges of the crystal are consistent with a homogeneous mechanism. Various explanations for the differing topotaxial behaviour of brucite and portlandite have been suggested, *viz.*, the disruptive effect of the larger Ca^{2+} ion,[1,2] the lowering of the decomposition temperature of portlandite *in vacuo* and the consequent lower thermal vibration,[19] and the high nucleation rate of CaO crystallites in air which increases the chance of mismatch with the parent crystal.[18]

C. Hydroxides and Oxyhydroxides of Aluminium and Iron.—The structure of the hydroxides and oxyhydroxides of aluminium and iron, like that of brucite, is based on the approximate close packing of anions in double layers with cations occupying intermediate octahedral sites. Important differences are, however, discernible. The hydroxyl and oxygen ions can assume either cubic or hexagonal arrangements, forming a framework which persists during dehydroxylation and results in oxide products with preferred orientation. Hydrogen bonding occurs between hydroxy-groups in adjacent layers with a consequent shortening of the OH—OH distance. In gibbsite, cubic $Al(OH)_3$, where two-thirds of the available octahedral sites are filled, this results in a different stacking arrangement of the double layers and a less tightly packed structure than in brucite.[21]

The thermal transformations which occur in these compounds are complex, particularly in the case of aluminium where several metastable oxide phases exist; the transformations are summarised in Table 1. The confusion in the earlier literature was due in part to the difficulty in recognising mixtures of the oxide products in *X*-ray powder patterns (see for example, Lippens and De Boer[22] for recent diffraction data on the γ-, η-, δ-, and θ-forms of Al_2O_3), and to the lack of well characterised hydroxide starting materials. The presence of water vapour in the ambient atmosphere or hydrothermal treatment markedly affects the phases formed and their recrystallisation rate (the tetragonal oxide, δ-Al_2O_3, is not observed in vacuum dehydration products, nor is the χ—K sequence in the dehydration of gibbsite[23]). The effect of micropore systems in partially decomposed powders, on the transformation of the disordered spinel-type η- or γ-Al_2O_3 into more crystalline phases, has also been noted;[22,24] this

[16] C. D. West, *Amer. Mineralogist*, 1934, **19**, 281.
[17] S. Chatterji and J. W. Jeffery, *Mineralog. Mag.*, 1966, **35**, 867.
[18] N. H. Brett, *Mineralog. Mag.*, 1969, **37**, 244.
[19] N. Datta, S. Chatterji, J. W. Jeffery, and A. L. MacKay, *Mineralog. Mag.*, 1969, **37**, 250.
[20] R. Sh. Mikhail, S. Brunauer, and L. E. Copeland, *J. Colloid Interface Sci.*, 1966, **21**, 394.
[21] A. F. Wells, 'Structural Inorganic Chemistry', 3rd edn., Oxford University Press, London, 1962, p. 552.
[22] B. C. Lippens and J. H. De Boer, *Acta Cryst.*, 1964, **17**, 1312.
[23] J. Beretka and M. J. Ridge, *J. Chem. Soc.* (*A*), 1967, 2106.
[24] D. Aldcroft, G. C. Bye, J. G. Robinson, and K. S. W. Sing, *J. Appl. Chem.*, 1968, **18**, 301.

Table 1 *Thermal decomposition of the hydroxides and oxyhydroxides of aluminium and iron*



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[a] H. Saalfeld and B. Behrota, *Ber. deutsch keram. Gesellschaft*, 1965, **42**, 161; G. W. Brindley and J. O. Choe, *Amer. Mineralogist*, 1961, **46**, 771. [b] Ref. 23. [c] Ref. 22. [d] D. Aldcroft and G. C. Bye, 'Science of Ceramics', ed. G. Stewart, Academic Press, London, 1967, p. 75. [e] Ref. 33. [f] G. W. Van Oosterhout, *Acta Cryst.*, 1960, **13**, 932. [g] Ref. 35; M. H. Francombe and H. P. Rooksby, *Clay Minerals Bull.*, 1959, **4**, 1. [h] Ref. 32. [i] K. C. Chandry, *Mineralog. Mag.*, 1965, **35**, 666.

was considered to be due to inhibition of the diffusion of aluminium ions into better ordered positions by the surface of the pores.[22] In nordstrandite [a form of $Al(OH)_3$ first prepared synthetically[25] but which has since been found in nature[26]] the formation of fine cylindrical pores in a direction normal to the original hydroxide sheet during dehydration was taken to indicate an inhomogeneous mechanism.[27] This evidence alone is insufficient to establish the mechanism since the formation of porous products is a general phenomenon in decomposition reactions.

Recent work has centred on the mechanism of dehydroxylation in aluminium hydroxides and oxyhydroxides. Following their studies on micas and kaolinite (see section 3B) Fripiat and co-workers have carried out similar investigations with boehmite, γ-AlO.OH, using i.r. and dielectric measurements.[28] A continuous decrease in the intensity of the fundamental O—H vibration bands was observed, the effect being reversible on cooling when the temperature had not exceeded 400°C. To explain this, a proton delocalisation process was postulated, facilitated by the oxygen–hydroxyl zigzag chain structure of boehmite,[29] γ-AlO.OH, where proton tunnelling takes place through a potential barrier. Later work using n.m.r. techniques[30] indicated that two proton spin populations could be differentiated, in accordance with the suggestion that $\mathrm{Al{-}\overset{+}{O}H_2}$ units are formed. At the dehydroxylation temperature, a substantial proportion of protons ($\sim$10%) is associated with these defects, resulting in a strong repulsion which enhances the diffusion of water molecules from the lattice. Proton tunnelling during the initial stages of the dehydroxylation of gibbsite has also been suggested, followed by diffusion and subsequent desorption of water molecules.[15] After 90% reaction has taken place the isolated OH groups, which are more difficult to remove because the probability of proton tunnelling is decreased, are eliminated as molecular hydrogen. The persistence of adsorbed hydroxyl ions during the dehydration of γ-Al_2O_3 was also observed, although the migration of OH groups, possibly through proton transfer, occurred readily at 400—600°C.[31]

Several excellent reviews have been written on the structure, phase transformations, and topochemical relationships of iron hydroxide and oxyhydroxides,[2,32] and only a short account of more recent work will be given here. In contrast to aluminium, iron has a variable valency, exhibits fewer inter-

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[25] R. A. Van Norstrand, W. P. Hettinger, and C. D. Keith, *Nature*, 1956, **177**, 713.

[26] J. R. D. Wall, E. B. Wolfenden, E. H. Beard, and T. Deans, *Nature*, 1962, **196**, 264; J. C. Hathaway and S. O. Schlanger, *ibid.*, **196**, 265.

[27] J. D. C. McConnell, 'International Symposium on Reaction Mechanisms of Inorganic Solids (Abstracts)', Aberdeen, 1966.

[28] J. J. Fripiat, H. Bosmans, and P. G. Rouxhet, *J. Phys. Chem.*, 1967, **71**, 1097; A. Mata Arjona and J. J. Fripiat, *Trans. Faraday Soc.*, 1967, **63**, 2936.

[29] K. A. Wickersheim and G. K. Korpi, *J. Chem. Phys.*, 1965, **42**, 579.

[30] J. J. Fripiat and R. Touillaux, *Trans. Faraday Soc.*, 1969, **65**, 1236.

[31] J. B. Peri, *J. Phys. Chem.*, 1965, **69**, 211.

[32] A. L. Mackay, *Proc. 4th Internat. Symp. Reactivity of Solids*, Amsterdam, 1960, p. 571; H. P. Rooksby, 'The *X*-Ray Identification and Crystal Structures of Clay Minerals', ed. G. Brown, 2nd edn., Mineralogical Society, 1961, p. 354.

mediate oxide structures and forms the stable oxide hematite, α-Fe_2O_3, at substantially lower temperatures (Table 1). No trihydroxide of iron analagous to gibbsite or bayerite has been reported but ferrous hydroxide, $Fe(OH)_2$, crystallises with the layer structure of CdI_2. The dehydration behaviour of ferrous hydroxide is similar to that of brucite, provided that air is excluded during the reaction,[33] and activation energies of the same magnitude have been reported.[34] Four forms of the oxyhydroxide FeO.OH are known; goethite, α-FeO.OH, and lepidocrocite, γ-FeO.OH, are the most common and are isomorphous with diaspore and boehmite respectively. Recent evidence suggests that intermediate structural states are formed during the dehydration of goethite (and diaspore) prior to the formation of hematite (and corundum),[35] although no disruption of the oxygen ion packing is involved in this transformation. β-FeO.OH (akananeite) has been found in limonite deposits[36] and shows interesting features in its fine structure in aqueous dispersions;[36,37] low temperature calcination leads to the formation of a spinel phase (probably γ-Fe_2O_3) prior to the recrystallisation of α-Fe_2O_3.[32] Hydrothermal treatment of δ-FeO.OH gives rise to goethite[32] with which it has structural similarities.[38] The end product of the heat treatment of iron oxyhydroxides is hematite and the intermediate phase changes are topotactic with the tendency to retain the existing oxygen framework.

3 Hydrous Layer Silicates

The layer silicates are usually divided into two groups, the 1:1 layer silicates in which there is one tetrahedral sheet for every octahedral sheet, and the 2:1 layer silicates containing two tetrahedral sheets per octahedral sheet (Figure 1a). An alternative classification is based on the number of available octahedral sites occupied; those minerals containing divalent cations being called trioctahedral since all the available cation sites are filled. Minerals containing trivalent cations are called dioctahedral, having only two-thirds of the octahedral sites filled. Although isomorphous replacement invariably occurs in these minerals, their thermal decomposition can conveniently be divided into two series, those containing only magnesium in the octahedral sites, and those containing aluminium.

The magnesium minerals decompose at higher temperatures than their aluminium analogues but recrystallise almost immediately, whereas the aluminium minerals tend to form stable dehydroxylates which recrystallise only after further heating. The decomposition reactions of the magnesium silicates show good topotactic relations and are usually interpreted in terms of an inhomogeneous mechanism, but the decomposition of aluminium silicates is generally more complex.

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[33] J. D. Bernal, D. R. Dasgupta, and A. L. Mackay, *Clay Minerals Bull.*, 1959, **4**, 15.
[34] I. F. Hazell and R. J. Irving, *J. Chem. Soc.* (*A*), 1966, 669.
[35] J. Lima-de-Faria and P. Gay, *Mineralog. Mag.*, 1962, **33**, 37.
[36] A. L. Mackay, *Mineralog. Mag.*, 1962, **33**, 270.
[37] J. H. L. Watson, R. R. Cornell, and W. Heller, *J. Phys. Chem.*, 1962, **66**, 1757.
[38] S. Okamoto, *J. Amer. Ceram. Soc.*, 1968, **51**, 594.

Table 2 *Thermal decomposition of the layer silicates*

		Ref.
serpentine $Mg_3Si_2O_5(OH)_4$	$\xrightarrow{600^\circ C}$ forsterite* Mg_2SiO_4 $\xrightarrow{1100^\circ C}$ forsterite + enstatite Mg_2SiO_4 $MgSiO_3$	a, b
talc $Mg_6Si_8O_{20}(OH)_4$	$\xrightarrow{900^\circ C}$ enstatite* $MgSiO_3$	a, b
saponite $Na_{0.7}Mg_6(Si_{7.3}Al_{0.7})O_{20}(OH)_4,nH_2O$	$\xrightarrow{500^\circ C}$ anhydrous modification $Na_{0.7}Mg_6(Si_{7.3}Al_{0.7})O_{20}(OH)_4$ $\xrightarrow{900^\circ C}$ enstatite* $MgSiO_3$	c
vermiculite $Mg_{0.7}(Mg,Fe^{III},Al)_6(Si,Al)_8O_{20}(OH)_4,nH_2O$	$\xrightarrow{400-800^\circ C}$ anhydrous modifications $\xrightarrow{900^\circ C}$ enstatite* $MgSiO_3$	d
phlogopite $K_2(Mg,Fe^{II})_6(Si_6Al_2)O_{20}(OH)_4$	$\xrightarrow{1100^\circ C}$ olivine $(Mg,Fe)_2SiO_4$ + leucite $KAlSi_2O_6$ + kalsilite $KAlSiO_4$	e
kaolinite $Al_2Si_2O_5(OH)_4$	$\xrightarrow{550^\circ C}$ metakaolinite $Al_2Si_2O_7$ $\xrightarrow{980^\circ C}$ Al–Si spinel* $Al_4Si_3O_{12}$ $\xrightarrow{1100^\circ C}$ mullite* $Al_6Si_2O_{13}$	a, b
allophane Al_2SiO_5,nH_2O	$\xrightarrow{700-900^\circ C}$ mullite $Al_6Si_2O_{13}$ $\xrightarrow{1200^\circ C}$ mullite $Al_6Si_2O_{13}$ + corundum $\alpha\text{-}Al_2O_3$	f
pyrophyllite $Al_4Si_8O_{20}(OH)_4$	$\xrightarrow{750^\circ C}$ pyrophyllite dehydroxylate $Al_2Si_4O_{11}$ $\xrightarrow{1200^\circ C}$ mullite* $Al_6Si_2O_{13}$	a, b
montmorillonite $Na_{0.7}(Al_{3.3}Mg_{0.7})Si_8O_{20}(OH)_4,nH_2O$	$\xrightarrow{300^\circ C}$ anhydrous modification $\xrightarrow{700^\circ C}$ montmorillonite dehydroxylate $\xrightarrow{1000^\circ C}$ spinel* $\xrightarrow{1200^\circ C}$ mullite* $Al_6Si_2O_{13}$	g
muscovite $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$	$\xrightarrow{700^\circ C}$ muscovite dehydroxylate $\xrightarrow{1050^\circ C}$ a spinel phase + sanadine $KAlSi_3O_8$ $\xrightarrow{1300^\circ C}$ corundum* $\alpha\text{-}Al_2O_3$ + mullite $Al_6Si_2O_{13}$	h, i, j, k, l

*With separation of silica or a silica-rich phase.

[a] Ref. 1. [b] Ref. 2. [c] Ref. 48. [d] Ref. 49. [e] Ref. 51. [f] Ref. 75. [g] Ref. 81. [h] Ref. 52. [i] Ref. 84. [j] Ref. 87. [k] Ref. 88. [l] Ref. 89.

A. Layer Silicates of Magnesium.—*Serpentine*, $Mg_3Si_2O_5(OH)_4$, has the structure shown in Figure 1a, and exists in three forms, lizardite, antigorite, and a fibrous modification, chrysotile. The first decomposition product of all forms is forsterite (Table 2), which usually appears almost immediately after dehydroxylation, although chrysotiles of high surface area form an *X*-ray-amorphous phase which remains stable for at least 150°C;[39] enstatite appears only at higher temperatures. Under hydrothermal conditions serpentine transforms into talc above 500°C.[40]

In early work on the reaction[41] a homogeneous mechanism was proposed in which dehydration and recrystallisation of forsterite were viewed as a combined operation. This, however, explained neither the escape of water molecules without disordering the structure, nor the expulsion of silica. An inhomogeneous reaction sequence was later proposed for chrysotile,[42] in which a separate dehydration stage occurs by countermigration of protons and magnesium and silicon ions in a more or less unchanged oxygen framework. The disordered product, serpentine dehydroxylate, $Mg_3Si_2O_7$, then separates into magnesium-rich regions (later forsterite) and silicon-rich regions (later enstatite). This mechanism does not explain the delayed appearance of enstatite, and, from a quantitative *X*-ray analysis of the amount of forsterite formed from massive serpentine,[43] a modified inhomogeneous mechanism was suggested in which the products of the initial countermigration are disordered forsterite and silica. The forsterite recrystallises at 800°C, and above 1000°C reacts with the silica to form some enstatite.

The kinetics of dehydroxylation of serpentine[44] under constant water vapour pressures of $<10^{-3}$ to 47 mm. Hg fitted a diffusion-controlled rather than first-order model. The apparent activation energies of 68—120 kcal/mole reflected retardation by surface coverage of chemisorbed water. Kinetic studies of forsterite development from the dehydroxylate[45] have yielded, from a first-order model, an 'activation energy spectrum' from 80—100 kcal/mole. This kinetic analysis is recognised as unrealistic, although the dehydroxylate characteristically behaved as a chemically damaged solid.

The decomposition of talc, $Mg_6Si_8O_{20}(OH)_4$, (Table 2) exhibits three-dimensional orientational relations.[46] One unit cell of talc transforms into one unit cell of enstatite, both of which contain 48 O^{2-} ions. In terms of an inhomogeneous mechanism, the acceptor region loses 8 protons and is compensated by the gain of 4 magnesium ions to become enstatite.[2,46] Simultaneously, water is lost from the donor region, which becomes silica-rich.

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[39] A. W. Naumann and W. H. Dresher, *Amer. Mineralogist*, 1966, **51**, 1200.
[40] N. L. Bowen and O. F. Tuttle, *Bull. Geol. Soc. Amer.*, 1949, **60**, 439.
[41] G. W. Brindley and J. Zussman, *Amer. Mineralogist*, 1957, **42**, 461.
[42] M. C. Ball and H. F. W. Taylor, *Mineralog. Mag.*, 1963, **33**, 467.
[43] G. W. Brindley and R. Hayami, *Mineralog. Mag.*, 1965, **35**, 189.
[44] G. W. Brindley, B. N. Narahari Achar, and J. H. Sharp, *Amer. Mineralogist*, 1967, **52**, 1697.
[45] G. W. Brindley and R. Hayami, *Clays and Clay Minerals*, 1964, **12**, 35.
[46] M. Nakahira and T. Kato, *Clays and Clay Minerals*, 1964, **12**, 21.

The other 2:1 magnesium layer silicates differ from talc in the extent to which isomorphous replacement occurs in either octahedral sites, or tetrahedral sites, or both. The replacement of some of the tetrahedral silicon of talc by aluminium leads to a deficiency of positive charge which is made up in saponite by the inclusion of sodium in high co-ordination sites between the tetrahedral layers. Further substitution of aluminium for silicon leads progressively to vermiculite and phlogopite mica (Figure 1a), with more inter-layer cations providing a charge balance. Sodium is the most common inter-layer cation in saponite and related minerals (smectites), magnesium commonly occurs in vermiculite, and potassium in micas.

Although much attention has been paid to the dehydration of inter-layer water in smectites,[47] less is known about their high temperature products. In air, saponite[48] and vermiculite[49] form enstatite (Table 2), whereas under hydrothermal conditions saponite forms anthophyllite and forsterite.[50] The inter-layer cations in smectites are exchangeable and determine the composition of the resulting aluminosilicate; when sodium is present, nepheline, $NaAlSiO_4$, and albite, $NaAlSi_3O_8$, are frequent products. Phlogopite, $K_2Mg_6Al_2O_{20}(OH)_4$, forms olivine and potassium aluminosilicates[51] (Table 2) although spinel has also been reported.[52] On the basis of optical and electron microscopy, Nakahira[53] has suggested that this decomposition follows an inhomogeneous mechanism in contrast to muscovite mica.

B. Layer Silicates of Aluminium—*Kaolinite*, $Al_2Si_2O_5(OH)_4$, is the aluminium analogue of serpentine, and has three polymorphs, kaolinite, dickite, and nacrite, differing only in their stacking sequence. A hydrated form, halloysite, with tubular morphology, contains additional water accommodated between the layers. The decomposition sequence of all these minerals follows that given for kaolinite in Table 2, but the transformation temperatures vary somewhat. Under hydrothermal conditions, hydralsite and pyrophyllite are formed instead of metakaolinite.[54]

The key to the understanding of the mechanism of the reaction sequence lies in the nature of metakaolinite, which is the first product of dehydroxylation. The diffuse *X*-ray reflections of this phase have so far made a direct structure analysis impossible, but three crystal structures have been proposed.[55,56,57]

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[47] G. Brown (ed.) 'The *X*-Ray Identification and Crystal Structures of Clay Minerals', Mineralogical Society Monograph, 1961.

[48] J. D. Russell and V. C. Farmer, *Clay Minerals Bull.*, 1964, **5**, 443.

[49] B. S. Bobrov, Yu. E. Gorbatyi, and M. B. Epelbaum, Fiz.-Khim. Issled Gidroslyud, Mater. Soveshch 'Prob. Primen. Vermikulita stroit', Chelyabuisk, 1965, p. 53.

[50] J. T. Iiama and R. Roy, *Clay Minerals Bull.*, 1963, **5**, 161.

[51] H. S. Yoder and H. P. Eugster, *Geochim. Cosmochim. Acta*, 1954, **6**, 157.

[52] R. Roy, *J. Amer. Ceram. Soc.*, 1949, **32**, 202.

[53] M. Nakahira, *Amer. Mineralogist*, 1965, **50**, 1432; M. Nakahira and M. Uda, *ibid.*, 1966, **51**, 454.

[54] R. Roy and E. F. Osborn, *Amer. Mineralogist*, 1954, **39**, 853.

[55] L. Tscheischwili, W. Bussem, and W. Weyl, *Ber. deut. keram. Gesellschaft* 1939, **20**, 249.

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

[57] R. Pampuch, *Prace Mineralogiczne*, 1965, No. 6, 53.

These were deduced from the structure of kaolinite, based on the observed topotactic relations, density changes on heating, and Pauling's rules. Common features of these structures are that the Si—O network of kaolinite remains largely intact, but the aluminium changes from octahedral to tetrahedral co-ordination. Tscheischwili *et al.*,[55] proposed a structure based on chains of edge-shared AlO_4 tetrahedra. A second model with different oxygen packing and alternately corner and edge-shared AlO_4 tetrahedra was suggested by Brindley and Nakahira.[56] The third model due to Pampuch[57] contains 12% residual hydroxyls in alternate corner and edge-shared Al–O–OH tetrahedra. The suggestion that metakaolinite is not anhydrous was based on i.r. evidence, although weight-loss measurements indicate that the figure of 12% is probably high.

Taylor[58] questioned the equating of '*X*-ray density' of so poorly crystallised a substance as metakaolinite with the observed density of material prepared at 800°C. A further weakness of all these models is that such crystalline structures should give much better *X*-ray patterns than those observed for metakaolinite. This led Taylor[58] to suggest that crystalline order, such as it is, exists chiefly in the oxygen packing, whilst the cations are distributed randomly among the lattice sites. The random cation configuration is compatible with the *X*-ray pattern, and changes in oxygen packing on transforming to the next phase are quite small, preserving structural continuity. This model could accommodate areas of residual hydroxyls; in such regions the original aluminium configuration might be preserved, albeit highly distorted.[59]

The only direct experimental evidence for Al^{IV} in metakaolinite is from *X*-ray fluorescence spectroscopy,[60,68] but recent work[61] has indicated that the aluminium phosphate used as a calibration standard for Al^{IV} in earlier work[60,68] is unsatisfactory. When a zeolite is used as a standard,[61] both tetrahedral and octahedral aluminium are indicated, in agreement with i.r. studies[59] which suggest the presence of both Al^{IV} and Al^{VI} in metakaolinite, but in a very disordered state.

A metakaolinite structure containing a high concentration of defects 'frozen in' when the water is removed was proposed by Freund[62] on the basis of density measurements which revised the *c*-parameter from 6·3 Å to 7·0 Å. *X*-Ray fluorescence results were again taken to indicate Al^{IV} throughout the very open structure.

At about 980°C a cubic phase appears, considered by most earlier workers to be γ-alumina. The lattice parameter (7·886 Å) was measured by Brindley and Nakahira,[56] who deduced that it was an aluminium–silicon spinel rather than γ-alumina (measured parameter 7·906 Å). The suggested spinel was $Si_8Al_{10.7}\square_{5.3}O_{32}$, with tetrahedral silicon, octahedral aluminium, and some octahedral sites vacant. This stoicheiometry may not be invariable, but the

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[58] H. F. W. Taylor, *Clay Minerals Bull.*, 1962, **5**, 45.

[59] K. J. D. MacKenzie, *J. Amer. Ceram. Soc.*, 1969, **52**, 635.

[60] G. W. Brindley and H. A. McKinstry, *J. Amer. Ceram. Soc.*, 1961, 44, 506.

[61] J. J. Fripiat and A. Leonard, personal communication.

[62] F. Freund, *Ber. deut. keram Gesellschaft*, 1967, **44**, 5.

model gives structural continuity with the next phase, mullite. However, the variation in lattice parameter does not conclusively prove silicon inclusion in the spinel phase because of reported variations of 7·73 Å to 8·06 Å in the γ-alumina parameter, due to variations in the oxygen and aluminium content.[63] Yamada and Kimura have suggested a variable proportion of silicon in the cubic structure.[64] An alternative explanation of the 980°C reaction was given by Freund[62] in terms of the 'healing' of defects left in the metakaolinite structure, resulting in a 'metastable high pressure modification', not a spinel or even γ-alumina, although of similar parameter. Freund argues that no close-packed alumina–silica structure is known, but gives no explanation for the cubic structure of the 'metastable modification'. Pampuch[57] attributes the 980°C reaction to structural instability caused by the removal of residual hydroxy-groups. Although a sharp exotherm is observed by differential thermal analysis at 980°C, it is not accompanied by any sudden change in *X*-ray or i.r. structural properties, so its cause cannot at present be uniquely established.

It is becoming increasingly apparent that protons play an important role in the reaction mechanisms. Conductance studies of dehydroxylation[65] have yielded a temperature coefficient of 4 kcal at 100—360°C. Since this value is comparable with proton energies in ice or water, the conductance process was identified with proton rearrangement (delocalisation) in the octahedral orbitals. Below 400°C a 'predehydroxylation' state exists in kaolinite in which the i.r. hydroxyl bands reappear on cooling.[66] Above 450°C the hydroxyl bands have almost disappeared and do not reappear on cooling, although a small number of hydroxy-groups must be retained even up to 1100°C because mass spectroscopic studies have shown hydrogen evolution at these temperatures.[15] Pampuch[14] considers that proton retention influences the crystallinity of the products; those phases in which protons are retained to high temperatures being poorly crystalline. Similarly, when proton mobility in kaolinite is increased by the application of an electric field, the crystallinity of the final product, mullite, is enhanced.[67]

Mechanism of thermal decomposition of kaolinite. In the Brindley–Nakahira model[56] (Table 3), loss of water occurs more or less uniformly from all unit cells (the homogeneous mechanism), with a decrease in the number of oxygen atoms per unit cell and a change in the co-ordination of aluminium from six in kaolinite to four in metakaolinite. The n.m.r. and acid dissolution studies of Gastuche *et al.*,[68] have been taken as further evidence in support of the homogeneous mechanism. In the Al–Si spinel proposed by Brindley and Nakahira the aluminium co-ordination reverts to six, while in mullite it is both four and six.[56] This sequence of changes in the aluminium co-ordination seems implausible.

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[63] H. Konig, *Naturwiss.*, 1948, **35**, 92.

[64] H. Yamada and S. Kimura, *Yogyo Kyokai Shi*, 1962, **70**, 65.

[65] J. J. Fripiat and F. Toussaint, *J. Phys. Chem.*, 1963, **67**, 30.

[66] J. J. Fripiat and F. Toussaint, *Nature*, 1960, **186**, 627.

[67] K. J. D. MacKenzie, *J. Appl. Chem.*, 1970, **20**, 80.

[68] M. C. Gastuche, F. Toussaint, J. J. Fripiat, R. Touilleaux, and R. Van Meersche, *Clay Minerals Bull.*, 1963, **5**, 227.

Table 3 *Schematic view of the various proposed kaolinite–mullite reaction mechanisms*

MODEL	650°C	980°C		1100°C
BRINDLEY–NAKAHIRA Ref. *a*	Water lost, O population decreased, Al^{IV}. Structure ordered.	Al–Si spinel + silica formed. O framework collapse, Al^{VI}.		Spinel→mullite Al^{IV+VI} Silica→cristobalite.
TAYLOR Ref. *b*	(Si, Al) and H^+ counter-migration. Water lost from pores, O framework unchanged. Cations random.	Al and Si counter-migration. Al-rich and Si-rich areas. O framework unchanged. Cations random.	Al-rich area→spinel. Slight lattice change. Cations in Si-rich area are random.	Spinel→mullite. Si-rich areas→cristobalite.
PAMPUCH Refs. *c* and *d*	Al^{3+} and H^+ counter-diffusion. 88% OH lost. Structure ordered.	Further Al^{3+} and H^+ counter-diffusion. Alumina separates out, Si–Al spinel formed. Silica separates out.		Spinel→mullite. Silica + alumina→mullite?
FREUND Refs. *e* and *f*	Proton tunnelling; water lost. Spaces frozen in. Structure unchanged but Al^{IV}.	Defects 'heal'. Stable phase forms (not spinel). Exoelectrons + protons→hydrogen. Al^{IV}?		Mullite formed. Al^{IV}→Al^{IV+VI}.
MACKENZIE Ref. *g*	Si, Al counter-migration. Water lost; some proton retention. Al^{VI+IV}, distorted and disordered.	Residual protons lost as hydrogen (*in vacuo*). Si-doped cubic phase formed. Al^{VI+IV}. Silica separates.		Spinel→mullite. Increase in Al^{IV}. Silica→cristobalite.

[a] Ref. 56. [b] Ref. 58. [c] Ref. 14. [d] Ref. 57. [e] Ref. 15. [f] Ref. 62. [g] Ref. 59.

An alternative inhomogeneous mechanism proposed by Taylor[58] involves migration of aluminium and silicon to the acceptor regions, and protons to the donor regions which later become pores from which water is lost. No oxygen is lost from the acceptor regions, which segregate into aluminium-rich and silicon-rich areas, becoming spinel and cristobalite respectively. The mechanism does not require drastic changes in oxygen packing, hence topotactic and *X*-ray observations are better accounted for. Taylor does not discuss changes in aluminium co-ordination during the reaction sequence. The inhomogeneous mechanism has been modified by Pampuch[14] to take account of residual hydroxy-groups.

Freund[15] has extended the concept of proton tunnelling to explain how dehydroxylation of kaolinite occurs at temperatures much lower than those necessary to rupture the O—H bond. Fripiat's suggestion[65] of proton delocalisation provides an alternative explanation, which may, however, differ more in terminology than in substance. The overall reaction sequence proposed by Freund (Table 3) involves tetrahedrally co-ordinated aluminium in metakaolinite partially changing to octahedral co-ordination in mullite. This necessitates tetrahedral aluminium in the metastable cubic phase formed at about 980°C.

The almost identical i.r. spectra of metakaolinite and the 980°C phase have led MacKenzie to suggest that these structures are very similar, particularly with respect to aluminium co-ordination.[59] He considers (Table 3) that the cubic phase is silicon-doped γ-alumina containing octahedral and tetrahedral aluminium. Therefore, metakaolinite is also thought to contain both octahedral and tetrahedral aluminium, albeit extremely distorted. The model proposed involves a gradual increase in the amount of tetrahedral aluminium throughout the reaction sequence.

Kinetics of kaolinite decomposition. This has been studied extensively by isothermal weight-loss measurements, dynamic thermogravimetry, and differential thermal analysis methods. The dynamic techniques are less reliable since there must always be a temperature gradient within a sample when the temperature is increasing continuously. Most data obtained prior to 1962 were interpreted in terms of first order kinetics, usually attributed to a random nucleation process.[69] These experiments were almost always carried out in air, with no attempt to control the partial pressure of water vapour around the sample.

Since 1962, it has been established that *in vacuo*[70,71] and under controlled water vapour pressures[71] the kinetics are best described by a two-dimensional diffusion equation. With increase in water vapour pressure, the reaction rate decreases markedly, whereas the apparent activation energy increases. Attempts have been made to explain these observations in terms of a chemisorbed surface water layer.[71,72] Many of the earlier studies previously explained by first order kinetics can probably be re-interpreted in terms of a diffusion process, although the results of Toussaint *et al.*,[72] are an important exception.

Recent studies of the kinetics of formation of mullite from kaolinite suggest that the rate determining step is nucleation controlled.[59,73]

Other aluminium silicates. Allophane, which is composed of silica and alumina gels, is strictly not a layer silicate, although Wada[74] considers that it might possess some structural order, as does the fibrous variety, imogolite.[74] The

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[69] P. Murray and J. White, *Trans. Brit. Ceram. Soc.*, 1955, **54,** 137; G. W. Brindley, and M. Nakahira, *J. Amer. Ceram. Soc.*, 1957, **40,** 346.

[70] J. B. Holt, I. B. Cutler, and M. E. Wadsworth, *J. Amer. Ceram. Soc.*, 1962, **45,** 133.

[71] G. W. Brindley, J. H. Sharp, J. H. Patterson, and B. N. Narahari Achar, *Amer. Mineralogist*, 1967, **52,** 201.

[72] F. Toussaint, J. J. Fripiat, and M. C. Gastuche, *J. Phys. Chem.*, 1963, **67,** 26.

[73] J. F. Duncan, K. J. D. MacKenzie, and P. K. Foster, *J. Amer. Ceram. Soc.*, 1969, **52,** 74.

[74] K. Wada, *Amer. Mineralogist*, 1967, **52,** 690; J. D. Russell, W. J. McHardy, and A. R. Fraser, *Clay Minerals*, 1969, **8,** 87.

principal decomposition product of both minerals is mullite (Table 2) with minor feldspar phases formed from impurities.[75] Alumina-rich samples give corundum at higher temperatures.

Pyrophyllite, $Al_2Si_4O_{10}(OH)_2$, decomposes in air at about 800°C to form a stable dehydroxylate[76] (Table 2) which is sometimes called metapyrophyllite by analogy with metakaolinite, but the name pyrophyllite dehydroxylate is perhaps preferable. Orientational relationships exist,[46,76] although they are difficult to observe since good single crystals of pyrophyllite are rare, and pyrophyllite dehydroxylate gives a disordered *X*-ray pattern. I.r. spectroscopy suggests that aluminium in pyrophyllite dehydroxylate is in five- or six-fold co-ordination,[77] ruling out one proposed structure[78] based on a homogeneous mechanism and involving tetrahedral aluminium. At 1100°C or above, pyrophyllite dehydroxylate is transformed into mullite with a definite orientation relationship and cristobalite, which has been variously reported to be formed in random orientation[76] and oriented.[46] Opinions differ as to whether the dehydroxylation proceeds by a homogeneous[46,79] or inhomogeneous[58] mechanism. Under hydrothermal conditions at pressures between 13·5 and 27 kilobars pyrophyllite forms kyanite and coesite above 1000°C.[80]

Montmorillonite, $Na_{0\cdot7}(Al_{3\cdot3}Mg_{0\cdot7})Si_8O_{20}(OH)_4,nH_2O$, is a common clay mineral which decomposes according to the simplified scheme in Table 2, although cordierite, enstatite, and anorthite have also been reported.[78,81] Grim and Kulbicki[81] have suggested that there are two modifications of montmorillonite (Wyoming and Cheto) which differ in their high temperature reactions. The Wyoming-type decomposes essentially as in Table 2, whereas the Cheto-type forms quartz at 850°C, cristobalite at 1000°C, and cordierite at 1260°C, but no mullite. The hypothesis of two types of montmorillonite has been questioned[82] and recent work[83] indicates that completely hydrogen-exchanged montmorillonites all form mullite rather than cordierite, without the appearance of quartz.

The i.r. spectrum of montmorillonite dehydroxylate[77] is similar to that of pyrophyllite dehydroxylate, suggesting a resemblance between their layer structures, although *X*-ray evidence indicates that the layer stacking must differ. The *X*-ray pattern of montmorillonite dehydroxylate is even more diffuse than that of pyrophyllite dehydroxylate.

The dioctahedral mica muscovite, $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$, decomposes essentially as shown in Table 2. Slight differences reported in the high tempera-

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[75] K. J. D. MacKenzie, *Clay Minerals*, 1970, **8** 359.

[76] L. Heller, *Amer. Mineralogist*, 1962, **47**, 156.

[77] L. Heller, V. C. Farmer, R. C. MacKenzie, B. D. Mitchell, and H. F. W. Taylor, *Clay Minerals Bull.*, 1962, **5**, 56; V. Stubican and R. Roy, *J. Phys. Chem.*, 1962, **65**, 1348.

[78] W. F. Bradley and R. E. Grim, *Amer. Mineralogist*, 1951, **36**, 182.

[79] W. D. Johns, *Bull. Amer. Ceram. Soc.*, 1965, **44**, 682.

[80] A. A. Giardini, J. A. Kohn, D. W. Eckart, and J. E. Tydings, *Amer. Mineralogist*, 1961, **46**, 976.

[81] R. E. Grim and G. Kulbicki, *Amer. Mineralogist*, 1961, **46**, 1329.

[82] A. Varty and D. White, *Clay Minerals Bull.*, 1964, **5**, 465.

[83] J. D. Hancock, personal communication.

ture products are probably due to variations in the composition of the mineral, especially in the Si:Al ratio.[2]

Eberhart[84] proposed a homogeneous dehydroxylation mechanism based on a one-dimensional Fourier analysis of the *X*-ray pattern of muscovite dehydroxylate. The product formed at 700°C is thought to be little changed from the parent mica, except for an increase in the cell parameters. In his model, neighbouring pairs of hydroxy-groups interact to form a molecule of water and the left-over oxygen ion occupies the vacant site in the octahedral layer, leaving the cations in five-fold co-ordination. Nicol[85] investigated the reaction under mild hydrothermal conditions when kalsilite (in epitaxial relation to muscovite) and unoriented corundum are formed. He suggests that an inhomogeneous mechanism fits his and Eberhart's observed topotactic relations better than the homogeneous mechanism. More recently, the homogeneous mechanism has again been favoured by Nakahira[53] (see phlogopite) and Vedder and Wilkins,[86] whose i.r. spectroscopy showed that when muscovite is successively dehydroxylated and re-hydroxylated, the OH ions return to their original sites, consistent with a homogeneous mechanism. However, a more refined structure determination of muscovite dehydroxylate will be needed to establish the mechanism conclusively. Under atmospheric conditions, the mica structure breaks down above 1050°C, giving products variously reported as a spinel[52,84,87,89] which is formed topotactically,[84] corundum,[52,84,87,88,89] mullite,[84,89] leucite,[84] sanadine,[87,88] and tridymite.[84] The spinel, with $a = 7{\cdot}9$—$8{\cdot}0$ Å, has been reported as γ-alumina[87,89] but may be similar to the silicon-containing spinel formed from kaolinite.

Fripiat *et al.*,[90] have reported a predehydroxylation state for the micas muscovite, phlogopite, and biotite, in which the protons become delocalised. The activation energy for the transition of protons to the excited state is 4·3 kcal/proton g. for all the micas studied. Such a low value suggests that a tunnelling mechanism is operative, similar to that of Freund.[15]

The dehydroxylation kinetics of muscovite have been investigated in air[91] and *in vacuo*.[92] Kodama and Brydon[92] report that *in vacuo* the rate is controlled by two-dimensional diffusion in the reacted product, with an activation energy of 54 kcal/mole. Both the model and the activation energy are closely similar to those reported for kaolinite,[71] serpentine,[44] and crocidolite.[93]

C. Other Related Layer Silicates—Few, if any of the silicates discussed above

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[84] J. P. Eberhart, *Bull. Soc. Franc. Mineral. Crist.*, 1963, **86**, 213.

[85] A. W. Nicol, *Clays and Clay Minerals*, 1964, **12**, 11.

[86] W. Vedder and R. W. T. Wilkins, *Amer. Mineralogist*, 1969, **54**, 482.

[87] N. A. Toropov, E. S. Sheo, and A. I. Boikova, *Izvest. Akad. Nauk, S.S.S.R. Neorg. Materialy*, 1966, **2**, 1487.

[88] H. S. Yoder and H. P. Eugster, *Geochim. Cosmochim. Acta*, 1955, **8**, 225.

[89] N. Sundius and A. M. Bystrom, *Trans. Brit. Ceram. Soc.*, 1953, **52**, 632.

[90] J. J. Fripiat, P. Rouxhet, and H. Jacobs, *Amer. Mineralogist*, 1965, **50**, 1937.

[91] J. B. Holt, I. B. Cutler, and M. E. Wadsworth, *J. Amer. Ceram. Soc.*, 1958, **41**, 242.

[92] H. Kodama and J. E. Brydon, *Trans. Faraday Soc.*, 1968, **64**, 3112.

[93] M. W. Clark and A. G. Freeman, *Trans. Faraday Soc.*, 1967, **63**, 2051.

are found in nature with the ideal compositions listed. Extensive isomorphous replacement occurs, especially in the octahedral sites, with iron(II), iron(III), nickel, lithium, and other cations substituting for part or all of the aluminium and magnesium. In addition, fluoride ions often replace hydroxide, especially in the micas.

Silicates containing divalent ions such as Fe^{2+} and Zn^{2+} of similar size to Mg^{2+} decompose analogously to magnesium silicates[58,94] whereas those containing Fe^{3+} behave like aluminium silicates.[33,58]

Since the decompositions are usually investigated in air, oxidation of iron(II) occurs before or simultaneous with dehydroxylation.[95,96,97] The reaction (equation 1) involves the conversion of OH^- to O^{2-}, while the liberated protons form water with oxygen from the atmosphere.[96]

$$4Fe^{2+} + 4OH^- + O_2 = 4Fe^{3+} + 4O^{2-} + 2H_2O \qquad (1)$$

The most important iron-rich layer silicates are the micas, *e.g.*, biotite, $K_2(Mg, Fe^{II}, Fe^{III}, Al)_6(Si_6Al_2)O_{20}(OH, F)_4$ and zinnwaldite, $K_2(Fe, Li, Al)_6(Si_6Al_2)O_{20}(OH, F)_4$. On heating in air at about 600°C, a typical biotite of composition $KMgFe^{II}_2(Si_3Al)O_{10}(OH)_2$ would form the oxybiotite $KMgFe^{III}_2(Si_3Al)O_{12}$, whereas in vacuum or inert atmosphere it would not dehydroxylate until about 1000°C, when a mixture of phases of overall composition $KMgFe^{II}_2(Si_3Al)O_{11}$ would be formed. In other respects biotite and zinnwaldite behave similarly to phlogopite, although hematite[98] and iron(III)-containing spinels are formed above 1000°C.

The vapour species evolved from biotite heated to 1100°C *in vacuo* have been identified in a mass spectrometer.[97,99] In addition to water, considerable amounts of hydrogen and traces of other gases were detected. The hydrogen may result from an internal oxidation process[97] (equation 2) which has also been reported for amphiboles[100] and chlorites.[95]

$$2Fe^{2+} + 2OH^- = 2Fe^{3+} + 2O^{2-} + H_2 \qquad (2)$$

Proton delocalisation before dehydroxylation has been discussed under muscovite.

Four other iron-containing 1:1 layer silicates, chamosite, $(Fe^{II}_2Al)(SiAl)O_5(OH)_4$, greenalite, $Fe^{II}_3Si_2O_5(OH)_4$, amesite, $(Mg, Fe^{II})_2(SiAl)O_5(OH)_4$, and cronstedtite, $(Fe^{II}_2Fe^{III})(SiFe^{III})O_5(OH)_4$, should be mentioned. The thermal decomposition of chamosite and greenalite have not been studied further since the previous reviews.[1,2]

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[94] H. F. W. Taylor, *Amer. Mineralogist*, 1962, **47**, 932.

[95] S. Orcel and P. Renaud, *Compt. rend.*, 1941, **212**, 918; G. W. Brindley and R. F. Youell, *Mineralog. Mag.*, 1953, **30**, 57.

[96] C. C. Addison, W. E. Addison, G. H. Neal, and J. H. Sharp, *J. Chem. Soc.*, 1962, 1468.

[97] A. D. White and J. H. Sharp, unpublished data.

[98] A. L. Litvin, *Zap. Ukr. Otdel. Vsesoyuz. Mineralog. Obshchestva Akad. Nauk Ukr. S.S.R.* 1962, **1**, 38.

[99] C. G. Barker, *Nature*, 1965, **205**, 1001.

[100] A. A. Hodgson, A. G. Freeman, and H. F. W. Taylor, *Mineralog. Mag.*, 1965, **35**, 445.

Brindley *et al.*,[101] heated amesite to 600°C and obtained a strong *X*-ray pattern which was tentatively identified as an iron-rich olivine, but has subsequently been shown to be a diffuse reflection caused by stacking disorder.[102] Above 900°C, a spinel phase appears.[101]

A recent study of cronstedtite by Steadman and Toy[103] has confirmed the published reaction sequence,[1] but has shown that the intermediate phases depend on the layer stacking of the original polymorphs. Thus, at about 700°C, either a spinel, a hexagonal ferrite or a phase having an ill-defined structure may be formed. The spinel phase was formed in small 'zones' rather than nuclei,[103] an observation in accordance with an inhomogeneous mechanism.

Bradley and Grim[78] have reported that the lithium-containing smectite hectorite, $Na_{0.7}(Mg_{5.3}Li_{0.7})Si_8O_{20}(OH)_4$, while not forming a stable anhydride, does not dehydroxylate until above 700°C, considerably higher than for montmorillonite. Under hydrothermal conditions it is converted into talc or anthophyllite.[104]

The iron smectite nontronite, $Na_{0.7}Fe^{III}{}_4(Si_{7.3}Al_{0.7})O_{20}(OH)_4$ dehydroxylates at lower temperatures than montmorillonite and forms mullite, cristobalite and an iron-containing spinel at 1300°C.[78]

The chlorites, which are mixed-layer minerals in which talc-like units are regularly interspersed with brucite-like units (Figure 1a), have the same ideal formulae as serpentine and related minerals, although extensive isomorphous replacement occurs. On heating a well-crystallised chlorite to about 600°C an intermediate phase is produced by loss of water from the brucite units.[1,2] Structural hydroxy-groups are lost from the talc-like units above 800°C with formation of olivine (or forsterite if the mineral is almost purely magnesian) as the principal product; spinel phases and enstatite have also been reported. Hydrogen evolution probably involving internal oxidation has been observed by Orcel and Renaud.[95]

The predominantly magnesium minerals sepiolite and palygorskite (sometimes called attapulgite), which have some of the characteristics of talc and of the amphibole anthophyllite, decompose to form enstatite and cristobalite[47] while the aluminium content of palygorskite leads to the formation of some sillimanite.[47]

Amphiboles. Figure 1b shows that amphiboles and pyroxenes have structures closely related to the layer silicates, although the tetrahedral sheets are not continuous. This structural resemblance provides a convenient explanation for the frequent occurrence of a pyroxene (usually enstatite) among the reaction products of the magnesium layer silicates. The amphiboles may be considered as intermediate between micas and pyroxenes; of the four cation sites in amphiboles, two (M_1 and M_3) are equivalent to the cation sites in micas whereas the other two (M_2 and M_4) are not co-ordinated to OH groups and are similar to

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[101] G. W. Brindley, B. M. Oughton, and R. F. Youell, *Acta Cryst.*, 1951, **4**, 552.

[102] H. Steinfink and G. D. Brunton, *Acta Cryst.*, 1956, **9**, 487.

[103] R. Steadman and M. Toy, *Z. Krist.*, 1965, **122**, 321.

[104] L. B. Sand and L. L. Ames, *Clays and Clay Minerals*, 1959, **2**, 392.

the cation sites in pyroxenes. Furthermore, the equivalent of the inter-layer site filled by potassium in the micas is also present as the A-site in the amphiboles, which can be vacant but is frequently occupied, as in the hornblendes.

There are, however, some unexplained differences between the micas and the amphiboles.[105] The total number of cations per 24 O atoms is always close to 7 (or 8 if the A-site is occupied) in amphiboles, but in the micas it can be 4 or 6. Thus, there are no cation vacancies in the amphiboles (*cf.* trioctahedral micas), which led Wilkins and Vedder[105] to predict that amphiboles should decompose without the formation of stable dehydroxylates. This prediction is upheld (Table 4) except for crocidolite, which forms a dehydroxylate[106,107,108] stable over a range of 200°C.

Table 4 *Decomposition products of amphiboles*

Mineral	*Products*	*Ref.*
Anthophyllite $Mg_7Si_8O_{22}(OH)_2$	$P_1 + S$	*a*
Amosite (fibrous grunerite) $Fe^{II}_{5.5}Mg_{1.5}Si_8O_{22}(OH)_2$	$P_1 + Sp_2 + H + S$	*b*
Tremolite-actinolite $Ca_2(Mg,Fe^{II})_5Si_8O_{22}(OH)_2$	$P_1 + P_2 + S$	*a, c*
Pargasite (hornblende) $NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$	$P_2 + Sp_1 + O + F_1 + F_2$	*d*
Glaucophane $Na_2Mg_3Al_2Si_8O_{22}(OH)_2$	$P_1 + O + F_3$	*e*
Crocidolite (fibrous riebeckite) $Na_2(Mg,Fe^{II})_3Fe^{III}_2Si_8O_{22}(OH)_2$	$\xrightarrow[\text{atmosphere}]{600\,°\text{C inert}} A$ $\xrightarrow{900\,°\text{C}} P_3 + Sp_2 + H + S$	*f, g*

Key

P = pyroxene. $P_1 = (Mg,Fe^{II})SiO_3$, $P_2 = CaMgSi_2O_6$, $P_3 = NaFe^{III}Si_2O_6$.
Sp = a spinel phase. $Sp_1 = MgAl_2O_4$, $Sp_2 = Fe_3O_4$.
F = feldspar. $F_1 = NaAlSiO_4$, $F_2 = CaAl_2Si_2O_8$, $F_3 = NaAlSi_3O_8$.
O = olivine $(Mg,Fe^{II})_2SiO_4$, H = hematite Fe_2O_3, S = silica SiO_2.
A = crocidolite dehydoxylate $Na_2(Mg,Fe^{II})_3Fe^{III}_2Si_8O_{23}$.

[a] Ref. 111. [b] Ref. 100. [c] Ref. 110. [d] F. R. Boyd, 'Researches in Geochemistry', Wiley, 1965. [e] W. G. Ernst, *Amer. J. Sci.*, 1961, **259**, 735., [f] Ref. 107. [g] Ref. 108.

An alternative hypothesis[107] that minerals containing trivalent ions in octahedral sites form stable dehydroxylates is not necessarily supported by the existence of crocidolite dehydroxylate, since the iron(III) ions are located chiefly in the M_2 site, which is not co-ordinated to the OH group. The temperature at which dehydroxylation occurs depends largely on the cations occupying the M_1 and M_3 sites; this temperature rises as magnesium replaces iron(II).[109]

Most studies of amphibole decompositions have been under hydrothermal

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[105] R. W. T. Wilkins and W. Vedder, 'Reactivity of Solids', Wiley, 1969, p. 227.

[106] W. E. Addison and J. H. Sharp, *J. Chem. Soc.*, 1962, 3693.

[107] A. A. Hodgson, A. G. Freeman, and H. F. W. Taylor, *Mineralog. Mag.*, 1965, **35**, 5.

[108] J. H. Patterson, *Mineralog. Mag.*, 1965, **35**, 31.

[109] A. G. Freeman, *Mineralog. Mag.*, 1966, **35**, 953.

conditions, but those shown in Table 4 are at atmospheric pressure. A pyroxene is always formed, its composition varying with that of the reactant. In the absence of a framework aluminosilicate, silica is formed as a separate phase. Good topotactic relations are frequently observed between the amphiboles and their decomposition products.[100,107,108,110] Inhomogeneous mechanisms have been postulated but not proved for some of these reactions.

When amosite,[100] actinolite,[111] or anthophyllite[111] is heated in an inert atmosphere, hydrogen evolution is so pronounced that it can be detected from differences between measurements of weight loss and water liberated. The mechanism is probably that proposed for biotite (equation 2).

Reduction of iron(III) occurs on heating crocidolite in hydrogen and it has been suggested that iron(0) is formed within the structure at 450°C.[106] This unstable arrangement leads to the destruction of the amphibole structure at 530°C, when metallic iron is one of the products.[107]

The dehydroxylation kinetics of crocidolite *in vacuo* show a change in mechanism at 550°C;[112] above this temperature a diffusion equation is obeyed[93,112] similar to that discussed for muscovite.

Attempts have been made to establish the presence of iron(0) in reduced crocidolite[113] and the co-ordination of iron in crocidolite dehydroxylate[114] by Mössbauer spectroscopy. The results are inconclusive, although the iron atoms in crocidolite dehydroxylate are probably in distorted octahedral sites. Mössbauer spectroscopy may prove more valuable in future investigations of iron-containing silicates.

4 Summary

This Review emphasises the conflicting interpretations of the decomposition mechanisms of related hydrous compounds.

The experimental basis (*viz.* the spinel intermediate) for the inhomogeneous mechanism of decomposition of brucite has been invalidated. Kinetic and microscopic evidence favours a homogeneous mechanism, although the difficulties[7] pointed out previously are still not explained. Further attempts to elucidate the reaction mechanism may rest on a less rigid approach which marries the important concepts of the previous theories. At the intermediate stage of decomposition the structure, which has already lost the bulk of its water, is amorphous to *X*-rays yet retains a memory of its previous structure. Local cation migration may then take place as magnesium ions pass through positions of tetrahedral co-ordination into their final octahedral sites.[2]

The principal evidence for an inhomogeneous mechanism in the decomposition of hydrous magnesium silicates is the observed topotaxy between the reactants

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[110] A. G. Freeman and H. F. W. Taylor, *Silikat Tech.*, 1960, **11**, 390.

[111] A. A. Hodgson, 'Fibrous Silicates', R.I.C. Lecture Series, 1965, No. 4.

[112] D. J. O'Connor and J. H. Patterson, *Conf. on Phys. and Chem. of Asbestos Minerals*, Oxford, 1967, Abst. 1—7.

[113] T. C. Gibb and N. N. Greenwood, *Trans. Faraday Soc.*, 1966, **61**, 1317.

[114] H. J. Whitfield and A. G. Freeman, *J. Inorg. Nuclear Chem.*, 1967, **29**, 903.

and products; this evidence was interpreted in terms of an inhomogeneous mechanism by analogy with brucite when the spinel intermediate was accepted. Since the latter has now been discredited, a re-examination of the mechanism postulated for magnesium silicates seems appropriate, particularly in view of possible complications presented by the presence of a second product phase. Similarly, the dehydroxylation of aluminium- and iron-containing minerals may not rigorously follow either a homogeneous or inhomogeneous mechanism.