KINETICS AND MECHANISMS OF DEHYDRATION AND RECRYSTALLIZATION OF SERPENTINE*—I

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ABSTRACT

Dehydration and recrystallization reactions of fine and coarse powders and also of massive samples of serpentine under isothermal heating conditions in air are followed by thermobalance measurements and by X-ray diffraction intensities. The rate of recrystallization to forsterite is shown to have an inverse relationship to the rate of dehydration. This result is interpreted in terms of the damage inflicted on the crystal structure of serpentine by the dehydration reaction; the more slowly this reaction occurs, the more readily is forsterite formed as a result of the topotactic relationship between forsterite and serpentine. The surface layers of particles and massive samples of serpentine which dehydrate readily appear to be highly disordered and consequently recrystallize to forsterite very slowly. The corresponding phenomena exhibited by kaolinite are discussed and compared with those by serpentine.

INTRODUCTION

THE mechanisms of dehydration and recrystallization reactions in hydrous minerals, mainly hydroxides and hydrated silicates, have been discussed in several recent papers by H. F. W. Taylor and his colleagues (1960–1963) and by one of us (Brindley, 1961, 1963). An outstanding feature of these reactions is that they take place in a crystallographically ordered manner so that the main product is oriented in a significant way with respect to the parent phase. This so-called "topotactic" relationship was interpreted for many years in terms of homogeneous processes occurring throughout the reacting crystals, but in the studies mentioned above it is argued that the experimental observations can be interpreted more satisfactorily in terms of heterogenous processes in which reacting solids develop "donor" and "acceptor" regions, terms first used by Freeman and Taylor (1960) in discussing the dehydration of tremolite, and by Ball and Taylor (1961) in relation to the dehydration of brucite.

The present paper is concerned with exploring these ideas in relation to the reactions taking place when serpentine ($3MgO.2SiO_2.2H_2O$ or

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$Mg_3Si_2O_5(OH)_4$) is heated to temperatures such that dehydration and recrystallization occur.

PREVIOUS STUDIES

The reaction of serpentine to form forsterite with a high degree of crystalline orientation was studied by Aruja (1943) and by Hey and Bannister (1948), using the fibrous variety chrysotile, and in more detail by Brindley and Zussman (1957) using individual crystals of the platy form of serpentine, lizardite. It was shown that the oxygen arrangements in the serpentine and in the resulting forsterite are very similar, and an interpretation was advanced which involved reorganization of the Mg and Si cations accompanying the loss of water. The suggested mechanism was homogeneous throughout the reacting crystals.

The orientation relationships described by Brindley and Zussman can be expressed as follows, using subscripts S and F to denote serpentine and forsterite respectively:

$$2a_S \ (10.62 \ \text{Å}) \simeq b_F \ (10.20 \ \text{Å})$$
$$2b_S \ (18.40 \ \text{Å}) \simeq 3c_F \ (17.94 \ \text{Å})$$
$$2d(001)_S \ (14.64 \ \text{Å}) \simeq 3a_F \ (14.27 \ \text{Å})$$

It was shown earlier (Brindley, 1961) that these relations can be combined into a single relation in terms of unit cell volumes,

$$8V_S \simeq 9V_F$$

and that the compositions of these volumes are respectively:

$$8V_S - 48 \text{ Mg, } 32 \text{ Si, } 144 \text{ O, } 64 \text{ H}$$
$$9V_F - 72 \text{ Mg, } 36 \text{ Si, } 144 \text{ O}$$

Within the common volume, the reaction can be considered as a loss of 64 H compensated by (24 Mg+4 Si). It is postulated that a loss of water (dehydration) takes place from reaction zones where outwardly migrating protons combine with OH ions to form H_2O molecules, and Mg and some Si ions liberated in the reaction zones migrate in a counter direction to maintain electrical neutrality. If the final products are forsterite and silica, the overall chemical equation can be written:

$$2Mg_3Si_2O_5(OH)_4 \rightarrow 3Mg_2SiO_4 + SiO_2 + 4H_2O$$
$$\text{serpentine} \qquad \text{forsterite}$$
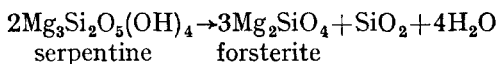
Therefore not all the Si ions liberated in the reaction zones (donor regions) are required to form forsterite (in acceptor regions). This view of the reaction treats dehydration and recrystallization as a combined operation.

A more detailed investigation by Ball and Taylor (1963) confirmed the earlier experimental data and brought to light many additional facts. In particular, the dehydration stage is separated from the subsequent recrystallizations. Ball and Taylor consider that the sequence of reactions can be broken down into four stages as follows:

(1) *Dehydration.*—Protons migrate to reaction zones, Mg and Si ions counter-migrate, the oxygen arrangement remains more or less unchanged, the Mg : Si ratio remains at 3 : 2, and the product is a partly disordered material.

(2) *Cation reorganization.*—Partial separation into Mg-rich and Si-rich regions commences.

(3) *Forsterite crystallization.*—An ordering of cations and a change in oxygen ion packing results in the formation of forsterite. Stages (2) and (3) may be largely concurrent.

(4) *Enstatite formation.*—The Si-rich regions change to enstatite, but this stage occurs less readily than the others and the process is easily halted at the end of stage (3). It is not clear why stage (4) is considerably more difficult.

It appears that below 1000°C, there are essentially two stages to be considered, namely (1) dehydration, and (2)+(3), recrystallization.

PRESENT STUDIES

The formation of forsterite has been measured quantitatively in relation to the time and temperature of heat treatment of powdered serpentines of different particle sizes, and in relation to the proximity to the external surface in the case of massive samples of serpentine. In the course of the work, an inverse relationship between the rates of formation of forsterite and of the preceding dehydration has been discovered and a number of confirmatory experiments have been carried out.

The material employed was mainly a massive serpentine from Quebec Province of fine grain size and pale buff color. No mineral impurities were detected by X-ray diffraction. Crystallographically the material is a layered structure with considerable stacking disorder. Two grades of powder were prepared: (a) coarse powder, <60 mesh, >100 mesh screen size. (b) fine powder, ≪200 mesh screen size.

Heat-treatments were carried out in air in temperature-controlled furnaces. Dehydration was followed quantitatively by thermo-balance measurements, and forsterite formation by quantitative X-ray diffraction using boehmite as an internal standard, calibrated with respect to a nearly pure forsterite supplied by the General Electric Company.

REACTIONS OBSERVED IN SERPENTINE POWDERS

Powder diffraction data showed that over a temperature range of about 30°C at temperatures of about 600°C, the heated serpentine powders passed through an X-ray amorphous phase prior to the formation of forsterite. The particular temperatures depend on the conditions of heating and on the particle size of the powders. The results are consistent qualitatively with a dehydration reaction and a combined reorganization-recrystallization reaction as described by Ball and Taylor (1963). The powder data differ apparently from X-ray single-crystal data in which the formation of forsterite is observed while reflections from serpentine are still obtained. The relatively large crystals used in single crystal studies could easily contain regions of serpentine and of forsterite, and also of X-ray amorphous material, so that apparent differences between powder and single crystal data should not be over-emphasized.

DEHYDRATION DATA FOR SERPENTINE POWDERS

Thermogravimetric data for the dehydration reaction obtained under (a) rising temperature conditions and (b) isothermally, are shown respectively in Figs. 1 and 2. In both cases, dehydration proceeds more rapidly in the fine than in the coarse powders.

Other measurements, made on massive pieces of serpentine of the order of 0.5–1 cm in size, showed considerable variation between the dehydration of external layers (which was very rapid) and of the interior (which was
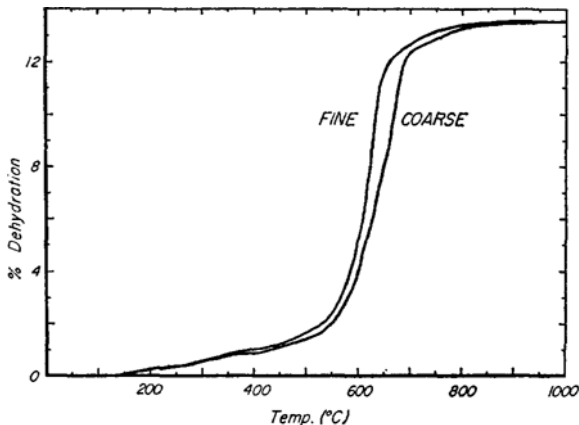

FIGURE 1.—Percentage dehydration of fine and coarse powders of serpentine as a function of temperature under rising-temperature conditions. Dehydration expressed as per cent weight loss with respect to initial weight.
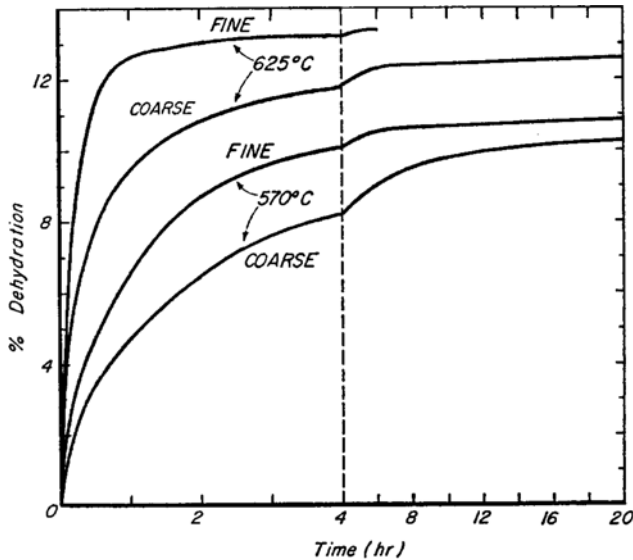
FIGURE 2.—Percentage dehydration of fine and coarse powders of serpentine as a function of time under isothermal conditions, with temperatures 570° and 625°C. Dehydration expressed as for Fig. 1.

relatively slow). The results are in general agreement with similar data obtained by Brindley and Nakahira (1957) on the dehydration kinetics of pressed discs of kaolinite. The data for massive specimens are discussed later in relation to the subsequent recrystallization reaction.

FORMATION OF FORSTERITE FROM SERPENTINE ANHYDRIDE

As noted earlier, there is a temperature interval between the dehydration reaction and the recrystallization to forsterite. To study the latter reaction independently of the former, coarse and fine powders (as previously defined) were given preliminary heat-treatments of 18 hr at 570°C which suffices to complete or very largely to complete their dehydration. Subsequent isothermal heat-treatments were made at temperatures from 650–800°C and for times up to 100 hr. At these temperatures any residual hydration is lost very rapidly.

Figures 3 and 4 show the development of forsterite, expressed as a percentage of the weight of anhydrous serpentine, for the coarse and fine powders respectively. The curves shown in Fig. 4 relating to the reactions of fine powders appear to resemble either parabolic curves, $y = k\sqrt{t}$, or
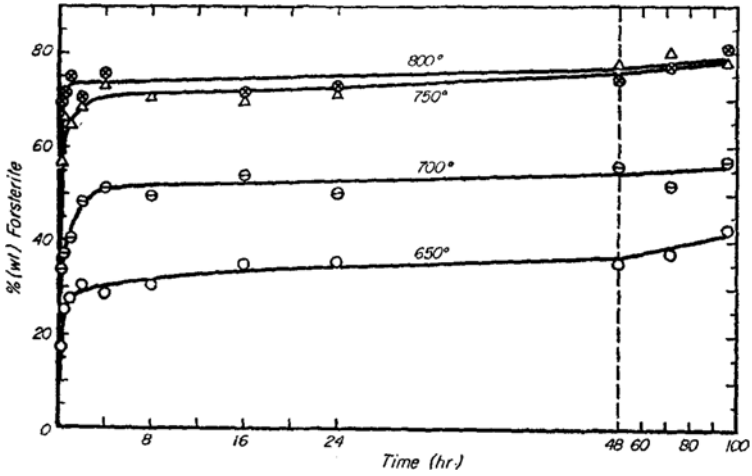
FIGURE 3.—Formation of forsterite from coarse powders of serpentine anhydride as function of time under isothermal conditions. Amount of forsterite expressed as weight percentage of the anhydride phase.
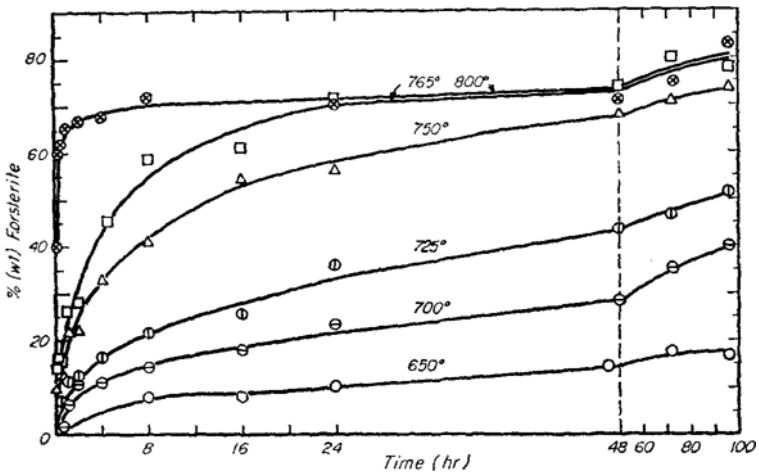

FIGURE 4.—Formation of forsterite from fine powders of serpentine anhydride as function of time under isothermal conditions.

exponential curves, $(1-y)=\exp(-kt)$, where y is the amount of forsterite expressed as a fraction of the maximum amount. Neither of these relations is obeyed exactly and in fact no simple analytical expression can be expected to hold because the powders contain a range of particle sizes. Nevertheless, certain general conclusions can be drawn.

Comparison of Figs. 3 and 4 shows that, for any given temperature, forsterite develops much more rapidly in the coarse than in the fine powder. This is the reverse of their behavior as regards the dehydration reaction, and also is the reverse of what would be expected for any kind of surface-initiated reaction.

Secondly, the character of the curves in Fig. 3 is both striking and unusual in that, for any given temperature, the reactions proceed very rapidly to a certain development of forsterite in a period of about 2–4 hr and thereafter proceed extremely slowly with very little further reaction even after 100 hr. A similar statement can probably be made for the fine powders, but since the reactions take place much more slowly, the time scale would have to be extended by a factor of 10 (or thereabouts) to obtain similar results.

Curves of this type suggest that the material from which the forsterite develops (i.e., the X-ray amorphous phase) is markedly inhomogeneous, with the activation energies involved in the recrystallization reaction extending over a considerable range. The idea of a spectrum of activation energies is not new and was examined much earlier by Vand (1943) in relation to irreversible changes of electrical resistance of metallic films. The same concept has been employed in the interpretation of the thermal behavior of radiation-damaged solids and has been discussed, for example, by Dienes (1953), Primak (1955), and Primak and Bohmann (1962). The two last named authors emphasize that "extreme caution is required in applying ordinary methods of kinetic analysis to cases in which the processes are distributed", i.e., with respect to activation energies. The subject is discussed generally by Stone (1961).

If the form of the curves in Fig. 3 is interpreted correctly as arising from marked variations in the structure of the serpentine anhydride, it seems reasonable to correlate this condition with the amorphous character indicated by the X-ray patterns. It is not possible at present to say from the X-ray data whether coarse or fine powders are the more variable. However, on general grounds it seems likely that large particles will possess greater variability since their exterior surfaces will dehydrate considerably more rapidly than the interiors, while fine powders may be regarded as consisting very largely of exterior material. As will be shown later, the observations made on reactions in massive serpentine are consistent with these statements.

Since fine powders recrystallize more slowly than do coarse powders, it may be argued that the fine powders, being more rapidly dehydrated, will be more disordered, and since the recrystallization is a topotactic reaction

it will be impeded by the disorder. The more rapid recrystallization of coarse powders must be attributed to the more slowly dehydrated and therefore the less disordered internal portions of the particles.

The behavior of single crystals is in line with this general concept, because single crystals are purposely dehydrated very slowly in order to retain crystallographic order and this condition facilitates the recrystallization; in the limit, dehydration and recrystallization may proceed almost as a single process.

Since the crystal structure of the serpentine anhydride is disordered by the dehydration process it may be described as a *chemically damaged solid* by analogy with solids disordered by radiation being called *radiation damaged solids*.

DEHYDRATION AND RECRYSTALLIZATION OF MASSIVE SERPENTINE

Massive material dehydrates at different rates depending on proximity to the external surface. The rate of recrystallization to forsterite would be expected also to vary in a related way. Accordingly, experiments were carried out using disc- and block-shaped specimens 0.5–1.0 cm in size heated slowly to avoid fracture and then maintained at a constant temperature on the thermobalance to achieve a desired overall percentage dehydration. After cooling, the surface of the sample was removed pro-
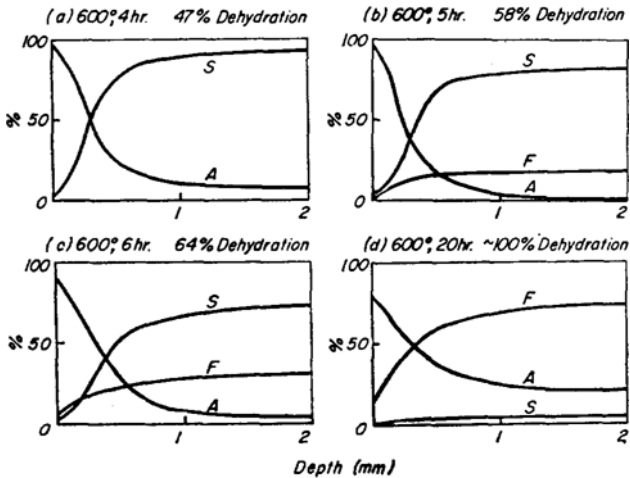

FIGURE 5.—Recrystallization as a function of depth in blocks of serpentine heated for various times and temperatures.   S = unreacted serpentine, A = amorphous phase, F = forsterite.

gressively and analysed for serpentine and forsterite and any difference from 100 per cent was attributed to the X-ray amorphous phase.

Typical results are summarized in Fig. 5.   (a) corresponds to about 47 per cent overall dehydration* obtained after 4 hr at 600°C. No forsterite is formed but the serpentine is fully dehydrated in the surface; the proportion of unreacted material increases with depth and at a depth of about 0.5–1 mm the serpentine is almost wholly unreacted.   (b), obtained from a sample heated for 5 hr. at 600°C with an overall dehydration of 58 per cent,* shows a small development of forsterite which increases with depth in the specimen more or less in proportion to the unreacted serpentine. It is particularly significant that the forsterite is not proportional to the amount of X-ray amorphous material.   With longer heat-treatments, (c) and (d), the forsterite continues to increase but still remains more or less in proportion to the residual serpentine.   After the longest heat-treatment, 20 hr, when the original serpentine has almost disappeared, the inverse relation between the X-ray amorphous material and the forsterite still remains.   It seems to be extremely difficult for the surface layer, with the highest rate of dehydration, to recrystallize to forsterite.

The relation of these results to those obtained for powders seems quite clear. The very fine powers, which dehydrate readily, behave like the exterior surface of the massive serpentine; they dehydrate rapidly and recrystallize with difficulty. Coarser powders behave similarly on the surface, but in depth they dehydrate more slowly and recrystallize more easily.
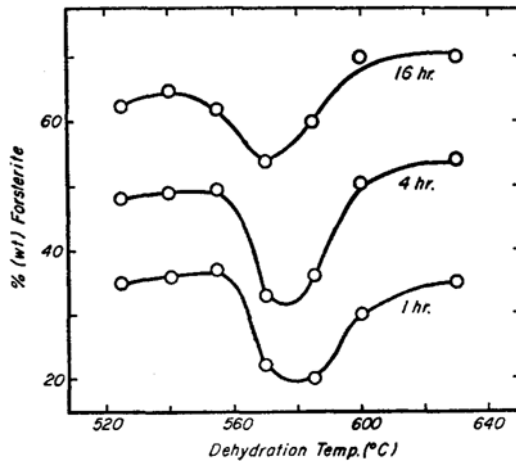

FIGURE 6.—Recrystallization of serpentine to forsterite at 750°C as a function of preceding temperature of dehydration, for various times at 750°C.

* i.e., of the total dehydration.

A DIRECT TEST OF THE INVERSE RELATIONSHIP BETWEEN RATE OF DEHYDRATION AND RATE OF RECRYSTALLIZATION

This relationship has been inferred from the behavior of coarse and fine powders, and from the reactions of massive material. It seemed important to obtain a direct confirmation. Fine powders (particle size <200 mesh size) were dehydrated for 18 hr at various temperatures from $525°$ to $630°C$. They were subsequently fired at $750°C$ for 1 hr, 4 hr, and 16 hr and the amount of forsterite developed was measured quantitatively. The results are shown in Fig. 6. With slow rates of dehydration (up to $550°C$), the amount of forsterite developed is greater than with more rapid dehydration ($500°$–$580°C$). With still higher temperatures of dehydration ($600°$ and higher) the rate of formation of forsterite again increases, but this is only a consequence of working wholly within the temperature range where forsterite is formed.

SIGNIFICANCE OF THE EXPERIMENTAL RESULTS IN RELATION TO THE MECHANISMS OF DEHYDRATION AND RECRYSTALLIZATION

Mechanisms of two kinds have been suggested to explain the ordered nature of many of the reactions which occur when hydrated silicates are heated.

The homogeneous mechanism, which appeared to offer a reasonable explanation for the maintenance of crystallographic order, always encountered a serious difficulty in explaining how a process of the type

$$OH + OH \rightarrow H_2O \uparrow + O \tag{1}$$
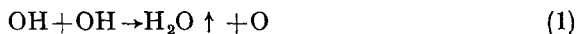
could take place throughout a volume of crystalline material and permit the water molecules to escape without disordering the structure. Similarly the apparent expulsion of SiO_2 could not be adequately explained.

The heterogeneous mechanism, by emphasizing the maintenance of an oxygen ion arrangement, accounts for the topotactic character of the reactions, and provides mechanisms for the loss of H_2O, and for the occurrence of SiO_2 (or its equivalent) as a minor product. In addition, it provides explanations for the formation of intermediate, transitional states. The formation of water takes place by a reaction which can be represented by

$$H + OH \rightarrow H_2O \tag{2}$$

and is maintained by proton migration to reaction zones such as external surfaces, grain boundaries, etc. Taylor and his colleagues consider that the

counter-migration of cations away from these zones leads to the formation of pores and these would facilitate the loss of water.

The experiments show that the anhydride phase tends to be disordered ("X-ray amorphous") and that the disorder increases with the rate of dehydration. A possible explanation is that reactions of type (2) take place increasingly throughout the volume of crystalline material. In the limit, when a proton migrates no further than the next OH ion, the process is represented by equation (1). In other words, it is now suggested that as the rate of dehydration increases, the reaction mechanism passes from what may be called "proton migration" type towards an interaction between near pairs of hydroxyl ions; the former mechanism tends to maintain order and to facilitate recrystallization and the latter to destroy order and to hinder recrystallization. While this description focuses attention on the formation of H_2O molecules and their release from the structure, it is necessary also to consider the counter-migration of Mg and Si ions, which also may be more orderly when it proceeds more slowly.

THE DEHYDRATION AND RECRYSTALLIZATION OF KAOLINITE, THE Al-ANALOG OF SERPENTINE

It is of interest to consider briefly the corresponding behavior of kaolinite, $Al_2Si_2O_5(OH)$, which has a structure almost identical with that of serpentine. Dehydration of kaolinite occurs at a somewhat lower temperature, around 500–550°C. The anhydride phase, metakaolin, is considerably disordered, appearing amorphous in X-ray powder diagrams, but retaining some two-dimensional regularity when single crystal aggregates are carefully dehydrated (Brindley and Nakahira, 1958). Recrystallization to a spinel-type phase occurs at about 950°C. The dehydration and recrystallization processes ordinarily are separated widely with respect to temperature, but Stone (1954) and Stone and Rowland (1955) have shown that in atmospheres of relatively low water vapor pressure, the two processes are brought considerably closer together, to within about 250°C in place of about 400°C.

On comparing these data for kaolinite with those for serpentine one must note first that the crystal size of kaolinite is normally considerably less than the particle size of the finely powdered serpentine used in the present study, and the disorder arising from dehydration is likely to be greater in kaolinite than in the finely powdered serpentine. The residual order in metakaolin was observed for a single crystal and aggregates dehydroxylated slowly. The retarded recrystallization of the metakaolin may be a consequence of a considerable degree of disorder in the anhydride phase. When the dehydration of kaolinite is retarded by a water-vapor atmosphere, then the subsequent recrystallization takes place more readily. This seems to parallel the behavior of coarsely powdered serpentine as

compared with that of finely powdered serpentine. Therefore the dehydration reaction of kaolinite may be nearer to the OH–OH pair interaction mechanism than to the proton-migration mechanism. In expressing the kaolinite dehydration in these terms, it is desired to avoid a sharp "either–or" distinction between the two mechanisms, since intermediate situations seem very likely to arise.

CONCLUSIONS

Studies of the dehydration and recrystallization reactions of serpentine have shown a reverse relationship between the two processes, viz., the faster the dehydration, the slower is the recrystallization, and vice versa. This relationship is considered to arise because rapid dehydration tends to destroy the crystalline order which is favorable to a topotactic recrystallization.

Curves for the development of forsterite from serpentine anhydride as a function of time and temperature are shown to resemble those for the annealing of radiation damaged solids. It is considered that the anhydride phase can be described as a chemically damaged solid and that a wide range of activation energies are involved in the recrystallization reaction by which forsterite is formed.

Two mechanisms of dehydration are considered, viz. OH-pair interaction which may occur throughout a crystal and proton migration to favorable reaction sites. The former is likely to create disorder and the latter to facilitate an orderly (or topotactic) reaction.

The disorder produced when kaolinite dehydrates and the retarded recrystallization are seen as consequences of the rapid dehydration favored by small, thin crystals. The dehydration mechanism may approximate to short-range proton migration which, in the limit, becomes OH-pair interaction.

ACKNOWLEDGMENTS

REFERENCES

Aruja, E. (1943) Ph.D. Thesis, Cambridge (England).
Ball, M. C. and Taylor, H. F. W. (1961) Dehydration of brucite: *Mineral, Mag.*, v.32, pp.754–766.

Ball, M. C. and Taylor, H. F. W. (1963) Dehydration of chrysotile in air and under hydrothermal conditions: *Mineral. Mag.*, v.33, pp.467–482.

Brindley, G. W. (1961) Role of crystal structure in the dehydration reactions of some layer-type minerals: *J. Min. Soc. Japan*, v.5, pp.217–237.

Brindley, G. W. (1963) Crystallographic aspects of some decomposition and recrystallization reactions: *Prog. Ceram. Sci.*, v.3, pp.1–55.

Brindley, G. W. and Nakahira, M. (1957) Kinetics of dehydroxylation of kaolinite and halloysite: *J. Am. Ceram. Soc.*, v.40, pp.346–350. See also *Clay Min. Bull.*, v.3, pp.114–119.

Brindley, G. W. and Nakahira, M. (1958) The kaolinite-mullite reaction series: II, Metakaolin: *J. Am. Ceram. Soc.*, v.42, pp.314–318.

Brindley, G. W. and Zussman, J. (1957) Structural study of the thermal transformation of serpentine minerals to forsterite: *Amer. Miner.*, v.42, pp.461–474.

Dienes, G. J. (1953) Variable activation energy and the motion of lattice defects: *Phys. Rev.*, v.91, pp.1283–4.

Freeman, A. G. and Taylor, H. F. W. (1960) Die Entwässerung von Tremolit: *Silikattechnik*, v.11, pp.390–392.

Hey, M. H. and Bannister, F. A. (1948) Note on the thermal decomposition of chrysotile: *Mineral. Mag.* v.28, pp.333–337.

Primak, W. (1955) Kinetics of processes distributed in activation energy: *Phys. Rev.* v.100, pp.1677–1689.

Primak, W. and Bohmann, M. (1962) Radiation damage, with bibliography: *Prog. Ceram. Sci.*, v.2, pp.103–180.

Stone, F. S. (1961) Mechanism and kinetics of reactions of solids, pp.7–23, in *Reactivity of Solids*, J. H. de Boer *et al.*, editors (Elsevier).

Stone, R. L. (1954) Effects of water vapor pressure on thermograms of kaolinitic soils: *Clays and Clay Minerals*, Nat. Acad. Sci.—Nat. Res. Council Pub. 327, pp.315–323.

Stone, R. L. and Rowland, R. A. (1955) Data of kaolinite and montmorillonite under water vapor pressures up to six atmospheres. *Clays and Clay Minerals*, Nat. Acad. Sci.–Nat. Res. Council Pub. 395, pp.103–116.

Vand, V. (1943) Theory of the irreversible electrical resistance changes of metallic films evaporated in vacuum: *Proc. Phys. Soc. A.*, v.55, pp.222–246.

The following reference is also relevant to the subject:

Taylor, H. F. W. (1962) Homogeneous and inhomogeneous mechanism in the dehydroxylation of minerals: *Clay Min. Bull.*, v.5, pp.45–55.