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SURFACE STRUCTURES OF DEHYDROXYLATED MICAS, PHLOGOPITE AND MUSCOVITE, AS OBSERVED BY A PHASE-MICROSCOPE

M. NAKAHIRA, *Mineralogical Institute, Faculty of Science, University of Tokyo, Hongo, Tokyo.*

ABSTRACT

Phase-microscopic studies of the surfaces of dehydroxylated phlogopite and muscovite revealed the strain fields developed non-directionally in phlogopite and directionally in muscovite. The occurrence of these different strain fields could be attributed to the difference in the mechanism of dehydroxylation. Non-directional growth of donor regions (according to Taylor's terminology) caused by a random migration of protons in phlogopite induces the strain fields of a three-dimensional character, whereas a chain reaction of hydroxyl ions along an octahedral chain in the structure facilitates a development of strain fields in muscovite along the direction of the original chain.

It is suggested that direct observations of reaction process are needed for the interpretation of kinetic data of any solid reaction.

INTRODUCTION

The study of the mechanism of the dehydroxylation process in various hydrated silicates has been of great interest in recent years. Much of the work has been based either on the topotactic relationships between the crystal structures of the starting material and its transformation product, or on a kinetic study of the process concerned. These investigations seem to show that the dehydroxylation of magnesium silicates is an almost simultaneous process which produces recrystallization products without the formation of an intermediate dehydroxylated phase. On the other hand, aluminum silicates react to form definite anhydrous phases prior to the recrystallization of the final product. This may suggest that the mechanism is not necessarily the same for the magnesium and aluminum silicates. There is, however, little evidence for any mechanism.

The process of dehydroxylation, simple even in terms of a solid state reaction, involves various factors which affect the overall process. Crystal size, imperfection in a crystal, degree of compaction of powder, ambient gas pressure, and rate of heating; all of these factors have considerable effect on the process of dehydroxylation. Under different conditions, the mechanism may not be the same even for a same kind of mineral. The interpretation of kinetic data might lead to an inadequate (or false) conclusion, unless it is combined with some direct approaches to the problem.

In the present investigation, attempts were made to obtain some direct evidence for the mechanism. The change in both the surface and internal structures of a single crystal upon dehydroxylation were examined by the phase-microscopic and transmission electron-microscopic methods respectively. Since the reaction will start on the surface or some places where defects of various kinds are involved, the change in the surface or internal defect structure during dehydroxylation will reflect the process of the development of strain fields caused by dehydroxylation, and this, in turn, will reveal the mechanism of the reaction.

In view of the difference between the polarizing effects of magnesium and aluminum ions on adjacent oxygen ions, phlogopite and muscovite single crystals were chosen as samples to see whether any difference in the change of surface structure during dehydroxylation is observed between the minerals. As a part of the study, the present paper will deal mainly with the phase-microscopic observations.

Experimental Procedure

The minerals used are a phlogopite from Hoshi Mine, Korea, and a muscovite from Ishikawa Mine, Japan.[1] A few inclusions (zircon) were found optically in this phlogopite.

Single crystal flakes about 5×5 mm in size were cut from large sheets of these micas. The thickness of the flakes was variable due to the cleavage, ranging from about 0.1 to 0.5 mm.

About 100 to 200 mg of the flakes were placed in a spring balance and the temperature of the furnace was raised at a rate of 5° C./min. When the temperature reached a predetermined point, the specimen was held at that temperature until the total weight loss of the specimen attained a desired value. The characteristic treatments of the specimens are summarized in Table 1.

In the table, the measured weight loss concerns with the total loss of water from the system, and the degree of dehydroxylation was calculated from the measured weight loss. The completion of dehydroxylation (100± dehydroxylation) was estimated based on the ignition loss of the specimen at 1250° C. for phlogopite or at 1000° C. for muscovite. The time needed to reach a desired weight loss as given in the table also reflects a rate of reaction at a respective temperature.

Aluminum sputtering was done vertically onto the surfaces of flakes in a vacuum and the thickness of the aluminum layer was made about

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[1] The chemical compositions of these micas are reported as follows: Phlogopite: SiO_2 39.27 Al_2O_3 17.52 Fe_2O_3 0.68 FeO 1.52 MgO 26.37 Na_2O 0.69 K_2O 8.40 F 0.63 Ign.L. 4.23 Total 99.31 (Analyst: S. Mizuma). Muscovite: SiO_2 40.92 Al_2O_3 38.81 K_2O 5.31 H_2O 4.34 TiO_2 tr. Fe_2O_3 4.49 FeO 0.63 MnO 0.02 MgO 1.55 CaO 0.20 Na_2O 2.25 Li_2O 1.13 Total 99.65 (Analyst: S. Shimizu). Honpō Kobutsu Zushi (Japanese Minerals in Pictures), v. 3, p. 466 (1940). (ed. T. Ito) (Zinmon Publ.)

TABLE 1. SPECIMEN CHARACTERIZATION

Mineral	Temperature (° C.)	Degree of dehydroxylation (%)	Time needed to reach a desired extent of weight loss	
Phlogopite	850	50	30 hr	Fig. 1b
Phlogopite	1100	50	15 min	
Phlogopite	1200	100	10 min	Fig. 1c
Muscovite	800	50	1 hr	Fig. 2b
Muscovite	900	100	20 min	Fig. 2c

500 Å. With this thickness, the surface structure of a flake could be reproduced correctly by the aluminum layer, and the reflectivity of the metal layer was good enough for the observation. As was always the case, the surfaces of dehydroxylated flakes were somewhat wavy, and the phase contrast effect can be obtained only in a small area of the surface.

RESULTS

More than ten flakes for each experiment were examined under a phase-microscope of reflection type.

Phlogopite. Figures 1 a–c show the surface structures of phlogopite at various stages of dehydroxylation. The surface of the specimen heated at a very slow rate of heating (Fig. 1b) still retains the cleavage steps as observed on the surface of the original mica (Fig. 1a). However, the phase contrast shows some uneveness of the surface as compared with the original surface. The unevenness changes rather gradually from the cleavage steps inward, and forms large bumps with a gentle slope. These bumps are confined mostly within the boundaries of the steps, suggesting a slow advance of the reaction interfaces from the reaction centers at the edges of the crystals.

In contrast with specimens heated gently, specimens reacted at rapid rates of heating as shown in Fig. 1c reveal small, spotty bumps of various shapes scattered over the entire surface. The size of the bumps in the specimen heated at 1100° C. is a little larger than that observed in Fig. 1c. The former is of a partially dehydroxylated mica (Table 1). In comparison with those of the partially dehydroxylated flake, the spotty bumps of a fully dehydroxylated mica (Fig. 1c) tend to link themselves together. The development of these bumps seems to indicate a rapid formation of the reaction nuclei scattered around over the surface. A common feature as seen in Fig. 1b and c is in that the reaction interfaces, large or small, do not advance along any particular

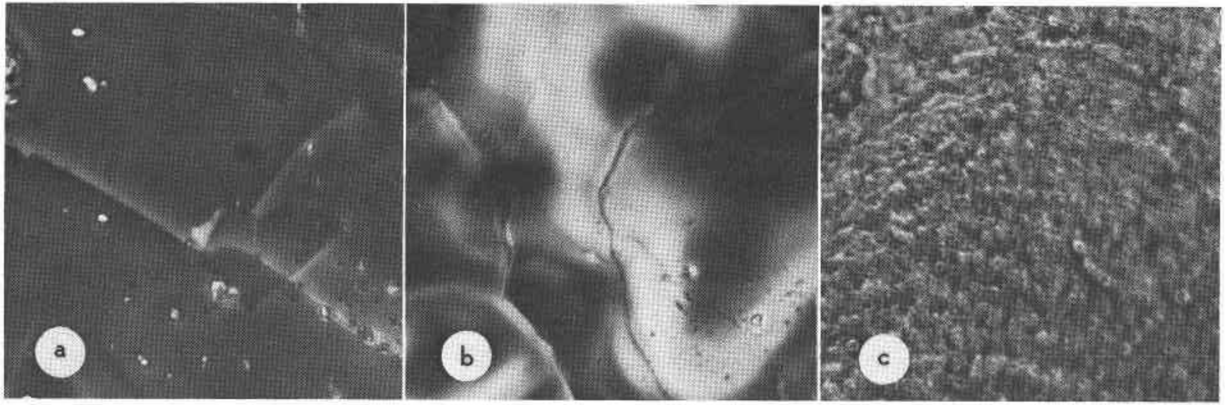

FIG. 1a. Phase contrast micrograph of the surface of original phlogopite. (×960). b. Phase contrast micrograph of the surface of partially dehydroxylated phlogopite at a very slow rate of heating. (×960). c. Phase contrast micrograph of the surface of fully dehydroxylated phlogopite at a rapid rate of heating. (×960).

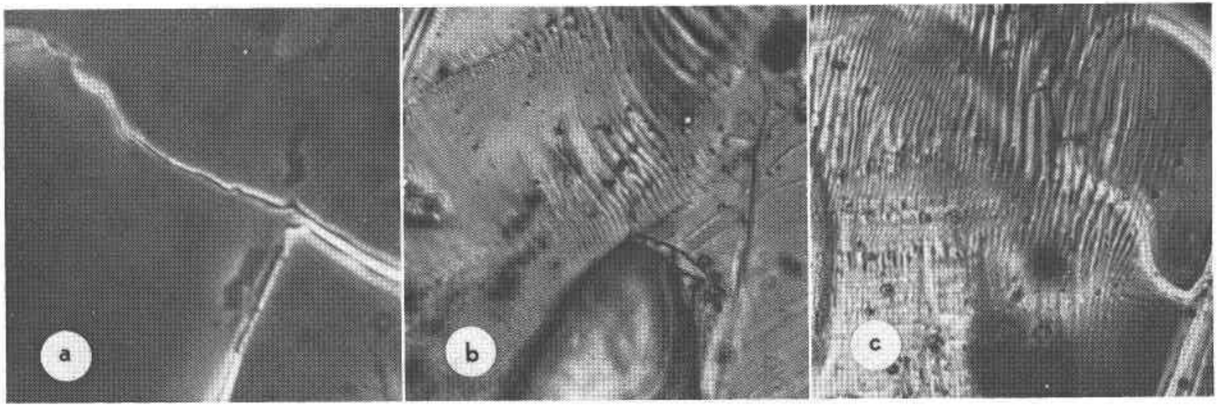

FIG. 2 a. Phase contrast micrograph of the surface of original muscovite. (×960). b. Phase contrast micrograph of the surface of partially dehydroxylated muscovite. (×960). c. Phase contrast micrograph of the surface of fully dehydroxylated muscovite. (×960).

direction. This suggests that the development of the strain fields induced by dehydroxylation is non-directional.

Muscovite. Figures 2 a–c represent three different stages of the reaction. The surface of the original flake (Fig. 2a) shows cleavage steps as in the original phlogopite. On the other hand, contrary to the behavior of phlogopite, when the dehydroxylation starts many directional cracks begin to develop from the cleavage steps inward and probably also from dislocations. They run nearly parallel to each other with spacings of about 0.5–2.0 μ. The development of these cracks on the partially dehydroxylated flake (Fig. 2b) is not completed as compared with that of fully dehydroxylated mica (Fig. 2c). In spite of the difference in the rate of heating, however, the formation of directional cracks during dehydroxylation is a general characteristic common to all of the flakes except the original ones examined in the present study. This suggests that the development of the strain fields which results in the formation of these cracks is directional. The crystallographic direction of the cracks could not be determined optically because of the coating of aluminum on the surface of the crystal.

Discussion

The observations clearly show that the strain fields induced by dehydroxylation develop non-directionally in phlogopite, and directionally in muscovite. For a large single crystal, as in the present experiments, the difference in the rate of heating does not affect the directionality. The following considerations, therefore, will be directed mainly towards the development of strain fields during dehydroxylation.

A reaction will start at some place where imperfections of some kind are involved. Even when a water molecule is formed by accident at a perfect region inside a crystal, a back reaction will take place. Jacobs and Tompkins (1955) have pointed out that the first-formed fragment of the reaction product embedded in a matrix of the original lattice causes a local deformation (strain) of the lattice, and, as a consequence of this strain, this small fragment of new phase tends to revert back to the original structure, unless the size of the fragment reaches a certain value. It is not probable that a dehydroxylation nucleus, when formed inside of crystal, can grow freely to a considerable size. A back reaction will inhibit the growth.

On the other hand, if two or more centers of strain can be arranged so as to be adjacent, the total strain energy of the system will be reduced. Thus, surfaces or imperfections will favor the growth of nuclei. These are the places which reduce the strain energy through a combination or pairing with anhydrous fragments.

With this in mind, an interpretation of the present results can be given in the following way.

In the inhomogenous mechanism, as has been put forward by Taylor (1962), protons of hydroxyl ions in the structure migrate from all regions to imperfections, where they combine with oxygen or hydroxyl ions to form water molecules (donor region). This process involves a counter-migration of other cations to acceptor regions in order to maintain the electrical neutrality of the system. No oxygen will be lost at acceptor regions and the oxygen framework is not disturbed. Donor regions become somewhat disorganized as the protons react with the oxygen or hydroxyl ions there, and the strain fields will develop around these regions because of the differences in the volumes of donor and acceptor regions. In this case, since the protons can migrate along any direction to donor regions, lattice distortion at donor regions will be of a three-dimensional kind with a non-directional development of strain fields. The open structure of the regions will facilitate the diffusion of water molecules to escape from the system. In the present investigation, the surfaces of dehydroxylated phlogopite show the development of non-directional strains, suggesting that the dehydroxylation is probably of an inhomogeneous type.

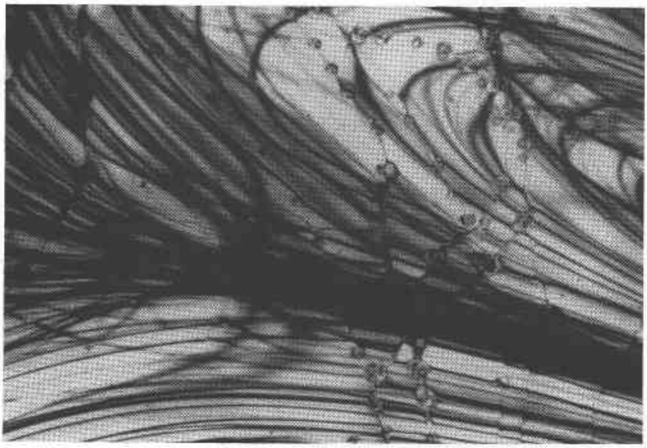

FIG. 3. Transmission electron-micrograph of a thin flake of original muscovite (×5000)

In the homogeneous mechanism, a pair of neighboring hydroxyl ions at some imperfection reacts to form a water molecule, inducing there a small local distortion due to a loss of one oxygen ion. As a consequence of this loss of an oxygen ion, an open structure will be formed. Then, the reaction of another pair of hydroxyl ions adjacent to the original pair in the same octahedral chain will be facilitated by the distortion and the water molecule thus produced will diffuse out through the open structure. A chain reaction of this kind proceeds inward along the octahedral chain from the nucleus. Water molecules will diffuse to the opposite direction and a linear strain field will be developed along this chain direction. Parallel strain fields running from various nucleation centers on the same imperfection line tend to combine with each other to reduce the total strain energy, and eventually form parallel cracks. This seems to be the case in muscovite. In the structure, three different directions of octahedral chains exist. It is not clear why only one out of three directions seems to be the line of the chain reaction. Probably a small difference in the original distortion of octahedral chains may cause a preferential reaction.

The above considerations are based on the difference in the nature of hydroxyl ions in phlogopite and muscovite. A similar concept concerning an effect of hydroxyl ions on a mica's susceptibility to alteration has been put forward by Bussett (1960). He observed that phlogopite was more susceptible to alteration than muscovite. His conclusion is that the mechanism responsible for this difference is different hydroxyl orientations in these micas.

A few remarks should be made concerning the incipient stage of dehydroxylation. Figure 3 shows a transmission electron-micrograph of an original muscovite flake. Along the dislocation lines intersecting the bent extinction contours, small, spherical, and prominent contours are scattered. These can be attributed to the occurence of water bubbles in the cleavage flake (Pashley, 1959) and suggest that the dehydroxylation has started already by electron bombardment. It implies that a kinetic study by a weight loss method may lead to a little different result from that by a DTA method. The weight loss can not be observed until the water molecules leave the specimen, whereas the latter method mainly deals with the heat of reaction. Details of the transmission electron-microscopic study will be reported in a separate paper.

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