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# ELECTRON-MICROSCOPIC OBSERVATION OF DEHYDROXYLATED MICAS

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## ABSTRACT

Transmission electron-microscopic studies of dehydroxylated micas revealed different contrast effects between muscovite and phlogopite. In general, unidimensional line contrasts were representative of muscovite patterns while clusters of irregularly shaped light-and-dark contrasts were scattered in several places in phlogopite. The origin of these different contrast effects could be attributed to a difference in the development of strain fields between these dehydroxylated micas; and this, in turn, indicated a difference between the dehydroxylation mechanisms of muscovite and phlogopite. The present observations of internal defect structures correlate well with the previously reported observations of surface structures by a phase-microscope.

## INTRODUCTION

The transmission electron-microscopic technique has been applied to the examination of the defect structures in natural mica and talc by several investigators (Amelinckx and Delavignette 1960; Demny 1961, 1963; Sugar 1961; Silk and Burnes 1961; Amelinckx and Delavignette, 1961). The dislocations and Moiré patterns observed in their studies have revealed the development of various strain fields associated with the structural defects in these minerals.

In the present investigation an attempt was made to examine the transmission electron-microscopic patterns of dehydroxylated muscovite and phlogopite in a hope that the different dehydroxylation mechanisms of these micas might be revealed through observations of the strain fields in the specimens. The microscopic patterns obtained in the present investigation were very complicated in general and their detailed interpretations based on the theory of diffraction contrast (for a review see Whelan, 1959) seemed to be almost impossible. From the general features of these patterns, however, the development of the strain fields upon dehydroxylation could be investigated in connection with the previous observation of surface structures (Nakahira, 1965), and the present report deals with these features which indicate the difference between the dehydroxylation processes of muscovite and phlogopite.

## EXPERIMENTAL

The description of the minerals used in the present experiments has been given in the previous paper (Nakahira, 1965). Single flakes, about

$5 \times 5$ mm in size, were cut from large sheets of micas and a few flakes, 100 to 200 mg in all, were placed in a spring balance. The temperature of the furnace was raised at a rate of 5° C/min to reach a predetermined point where the specimen was held until the total weight loss attained a desired value. To assure the water molecules to leave the specimen, heating was made in a vacuum ($10^{-3}$ mmHg).

Thin films of the specimens were prepared by cleaving the flakes successively with adhesive tape (Silk and Burnes, 1959). Flakes of muscovite still retained their elasticity after the heat-treatment, but those of phlogopite became brittle which made it a little difficult to make a very thin film of the specimen. When the films were judged to be sufficiently thin to transmit electrons in an electron-microscope at 75KV,—the criterion was a reddish interference color,—they were released from the tape with a solvent and transferred to an electron-microscopic grid.

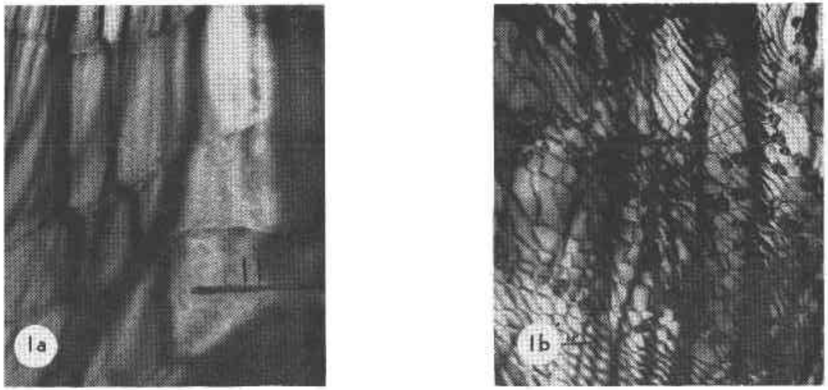
## RESULT

*Original micas:* Since the detailed studies of natural micas have been made by various investigators, only a few remarks will be needed in the present report.

(a) *Muscovite:* In muscovite very extended lines of dislocations running parallel to the cleavage planes and ending at cleavage steps were observed in most cases. Dislocation networks as observed by Silk and Burnes (1961) were developed also in the present muscovite. Figures 1(a) and (b) show the dislocation structures of these muscovites. As it can be seen in (b), small prominent spherical contours are scattered along the dislocation lines. This contrast effect arose from the water bubbles held between the layers, suggesting that dehydroxylation was started by electron bombardment. As in (b), the structure of the network varies from one place to another in the film. However, this does not necessarily reflect the actual differences between different parts of the film but reveals different aspects of the same network. Strains around dislocations cause various orientations of different parts of a film with respect to the incident electron beams, resulting in the different diffraction conditions in places. Therefore, some dislocations are visible at some places and vice versa. This was confirmed by the dark field images. Since the electron-microscope used in the present experiments did not have a specimen-tilting device, further examination could not be made.

(b) *Phlogopite:* The development of dislocation lines in phlogopite was similar in general to that in muscovite. Figure 2 shows one of the images of the original phlogopite flakes.

Characteristic of the phlogopite patterns is an extensive development of Moiré patterns with various spacings. It is probable that some of the Moiré patterns in both muscovite and phlogopite were due to the misfit



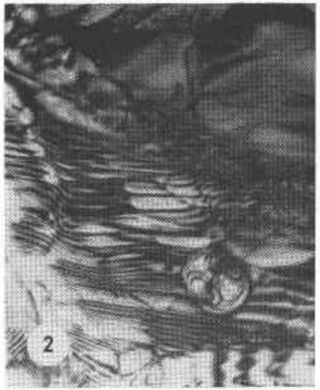


FIG. 1. Patterns of natural muscovite. (a) A type of dislocation lines. (b) A dislocation network.

FIG. 2. Dislocations and Moiré patterns in a natural phlogopite.

FIG. 3. Patterns of dehydroxylated muscovite. (a) Diffraction contrasts showing the linear contrast effects. (b) A dark field image of the same area as in (a). The operating reflection is 020. (c) Linear contrast effects associated with Moiré patterns and extinction lines.

of the layers caused by the present thinning method. In view of the strong bond between the layers, however, most of the patterns may have originated from defective crystal growth. In fact, half planes were observed occasionally in Moiré patterns, indicating the dislocations not lying on the cleavage planes. These dislocations must have been related to the crystal growth.

The dislocations at the upper half of Fig. 2 are modified by Moirés at the lower half, and the dehydroxylation nuclei are seen also in places. Eventually these nuclei obscured the entire view of the pattern. Therefore, in order to examine the dehydroxylated flakes, the water bubbles were expelled in vacuum in an electric furnace.

*Dehydroxylated micas:* A large number of dehydroxylated mica flakes were examined in both the bright and dark field images. In the following some of the patterns will be shown to illustrate the features of these flakes. General characteristics of the patterns are that the original features were partially retained in dehydroxylated muscovite whereas they were not in dehydroxylated phlogopite.

(a) *Muscovite:* Although the patterns of the dehydroxylated muscovite flakes were very complicated in detail, a unidimensional deformation—a linear distribution of strain fields—was a common feature observed in several flakes. The sequence of photographs in Fig. 3 serves to illustrate this feature. The linear contrast effects as seen at the central part of Fig. 3(a) (bright field image) and (b) (dark field image) seem to indicate a development of unidimensional deformation associated with very extended straight lines of dislocations. The strong diffraction effects at the marginal parts of the figures also show a linear arrangement of small flakes or strips of the crystals parallel to the deformation. In Fig. 3(c), dislocation lines associated partly with Moiré patterns also indicate a unidimensional deformation. The width of the linear contrast effects is partly of the order of 1000A. The extinction lines in the figure became stepped at the points of intersections with the dislocation lines. The origin of the unidimensional deformation will be discussed in the following chapter.

(b) *Phlogopite:* Contrary to the linear contrast effects in muscovite, the patterns of phlogopite are characterized by the development of irregularly shaped contrasts. Figure 4 serves to illustrate several properties of the overall pattern of phlogopite. Clusters of light-and-dark contrasts are developed along the probable grain boundaries of the original mica or scattered in places within these boundaries. (These are marked "A" on the photograph.) These contrasts appear to reflect the regions consisting of irregularly shaped dislocation loops. Some regions of the same type but with less contrast (marked "B") are observed also in places.

The Moiré surrounding the nearly spherical region of this type "B" as seen at the upper half of the photograph (two of the clusters are observed here) represent the grain boundaries produced upon dehydroxylation. A few small dark dots near this place may be some jogs, or alternatively, the nodes of two intersecting dislocations.

By following the clusters at "A" of the left side of the photograph along the direction of their extension, one can see that the complicated Moiré patterns are produced through the superposition of a triangular sheet on the other larger sheet containing "A"s. This part of the photograph also reveals a number of fundamental features of dehydroxylated phlogopite. At a part marked "C" and some other places, half planes are observed in the Moiré patterns, indicating the dislocations not lying in the plane of observation. The Moiré pattern on a nearly spherical part "D" shows a complicated dislocation structure and an abrupt change of Moiré spacing. This may represent small angle tilt boundaries as observed by Demny (1960) in his study on gold films.

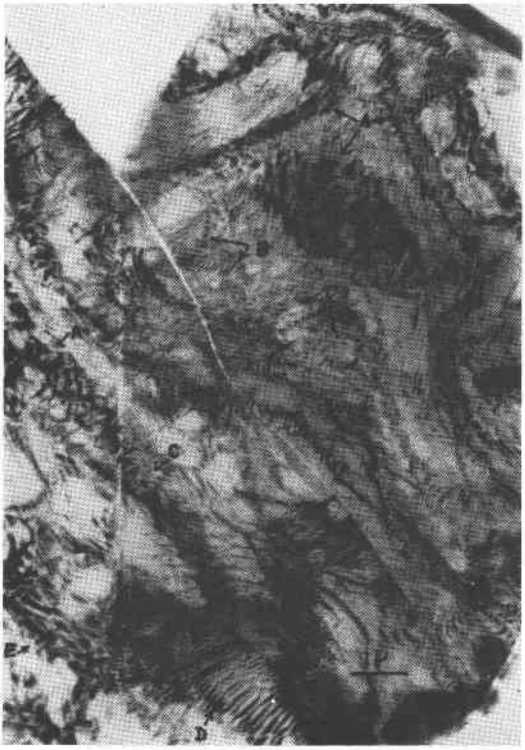


Fig. 4. A type of patterns of dehydroxylated phlogopite.

In the clusters marked "E", a half of which is outside the overlapping region, several different contrast effects are seen in several places, indicating a distribution of various different strain fields within the cluster.

*Dissociation into partials:* Whereas the textures of the diffraction contrast patterns in the dehydroxylated micas were too complicated to make detailed accounts of each visible dislocation line, dissociation into partials was observed mostly in partially dehydroxylated flakes, especially of phlogopite. Figure 5 shows one of the phlogopite patterns of this type. Dislocation ribbons observed at the lower part of the photograph resemble those found in talc by Amelinckx and Delavignette (1961). They have discussed the mechanism of dissociation in talc; but, different from talc, the structure of mica contains potassium ions between the layers and for a dislocation to be dissociated into partials a simultaneous movement of these ions is required. The mechanism may probably be similar to that of corundum discussed by Kronberg (1957). The heat input and the partial dehydroxylation may have caused the dissociation, but further study is warranted.

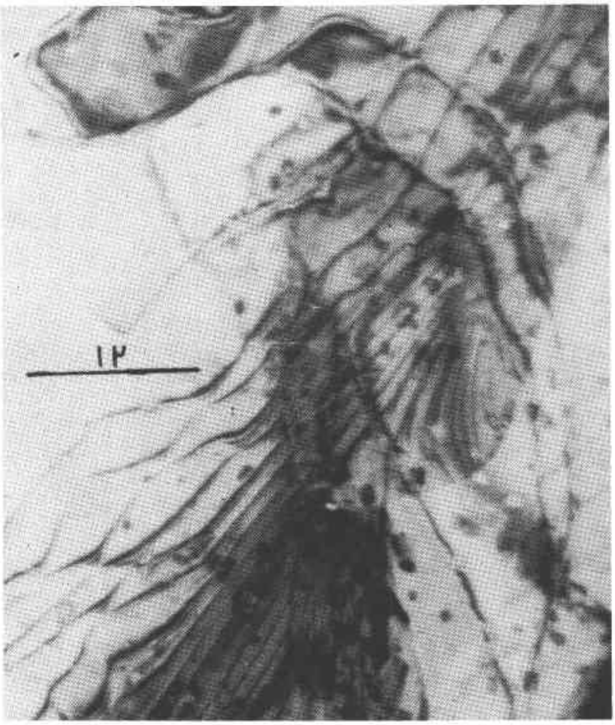


FIG. 5. Dislocation ribbons in partially dehydroxylated phlogopite.

## SOME CONSIDERATIONS OF THE DEHYDROXYLATION PROCESSES

The conclusions that can be drawn from the present experiments are that dehydroxylated muscovite exhibits patterns consisting mainly of unidimensional line contrasts whereas irregularly shaped contrasts of probable dislocation loops with a random distribution of their clusters are characteristic of the patterns of dehydroxylated phlogopite. As has been described in the previous report (Nakahira, 1965), the observation of the surface structures of these minerals by a phase-microscope also showed linear cracks running parallel to each other on muscovite and a random distribution of strained regions on phlogopite. The interpretation of the results was given in terms of a homogeneous mechanism of dehydroxylation for muscovite and an inhomogeneous mechanism for phlogopite. (Taylor's terminology (1962) of dehydroxylation mechanisms is being used here.) The contrast effects observed in the present experiments also point to the same interpretation.

*Muscovite:* The linear contrast effects suggest a homogeneous mechanism in the dehydroxylation of muscovite.

In the homogeneous mechanism a pair of neighboring hydroxyl ions at an imperfection react to form a water molecule, and leave a somewhat distorted open structure. Then, the reaction of another adjacent pair of hydroxyl ions in the same octahedral chain will be catalysed by the distortion and form a water molecule which diffuses out through the open structure. A chain reaction of this kind proceeds inward along the octahedral chain from the nucleus, leaving oxygen vacancies along the chain. Thus, parallel lines of reacting chains will develop with increasing dehydroxylation. At the same time, in order to reduce the total strain energy, these vacancies will migrate to form clusters of vacancies, eventually collapse, and result in stacking faults of the layers. This is shown schematically in the sequence of figures in Fig. 6 viewed along the chain direction in (a), (b), and (c), and normal to the layer in (d). This mechanism is similar to that predicted by Kuhlmann-Wilsdorf (1958) and observed in pure aluminum by Hirsch *et al.* (1958). In metals, this results in a formation of small dislocation loops, but in the present structure the cluster of vacancies extends from one end of a layer to the other along the original octahedral chain. Consequently, linear contrast effects will be observed as in Fig. 3. Although the vacancy migration in the structure is a little difficult as compared with that in metals because of the oxygen-cation bonds, it has been observed frequently in various ionic crystals. Demny (1963) explained a formation of cracks in natural mica by a similar mechanism involving the movement of dislocations.

Since only a small distortion of the oxygen framework is involved in this mechanism, a nearly topotactic arrangement of oxygen ions in the anhydrous phase with respect to the original structure is expected. In fact, electron diffractions of both the original and dehydroxylated flakes show the same hexagonal net-patterns. The topotactic formation of the anhydrous phase of muscovite has been confirmed also by Eberhart (1963) and Nicol (1964). The subsequent crystallization of mullite with preferred orientation involves further migration of cations but certainly indicates a structural continuity, at least of the oxygen framework, throughout the transformation process. These latter observations fit in fairly well with the present results.

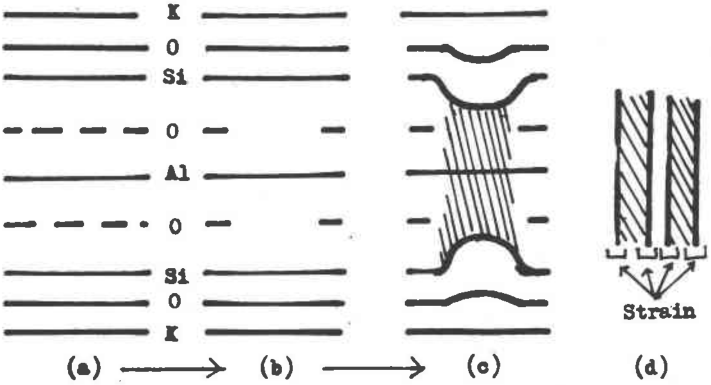


FIG. 6. Schematic representation of the process of unidimensional deformation.

*Phlogopite:* The texture of phlogopite patterns also suggests a process of nucleation and nucleus-growth. However, the fact that these nuclei did not grow over the entire region of the crystal after the completion of dehydroxylation indicates that the nucleation is a process of precipitation caused by the unmixing of the constituent ions of the crystal. If the dehydroxylation proceeds in such a way that the protons of the hydroxyl ions in the structure migrate from all of the regions of a crystal to imperfections, at which they combine with oxygen or hydroxyl ions to form water molecules, then magnesium ions must countermigrate in order to maintain the electrical neutrality of the system. This is the inhomogeneous mechanism of dehydroxylation of Taylor (1962). It is actually a process of unmixing and the precipitates at the imperfections grow with increasing dehydroxylation. Since the protons can migrate to imperfections from every part of the crystal, a directional nucleus-growth is not expected. Judging from the electron diffraction patterns of nearly dehydroxylated flakes which are not different from the original pattern, it may be safely assumed that the normal lattice parameters of these two regions do not differ much from each other. Only a small difference between the volumes of their unit cells will be evolved. (In the transformation of talc—a magnesian trioctahedral mineral like phlogopite—to enstatite and cristobalite, Nakahira and Kato (1964) have found a similar relationship.) This small difference in volume, however, may still give rise to elastic strains near the interface of the two regions and localized lattice distortion will occur in both the precipitate and the matrix. The lattice misfit between the two regions may be accommodated by dislocations which will be detected in a complicated Moiré pattern. Moreover, increasing number of vacancies in these partially coherent precipitates will result, as the dehydroxylation proceeds, in the formation of dislocation loops of irregular shape. In fact, all the features in Fig. 4 such as the Moiré patterns, complicated dislocation structures in these Moirés, and the clusters of light-and-dark contrasts can be interpreted in terms of these mechanisms. It can be concluded, therefore, that phlogopite crystals of appreciable size follow an inhomogeneous mechanism during slow dehydroxylation.

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