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KINETICS OF DEHYDROXYLATION AND OF OH-OD EXCHANGE IN MACROCRYSTALLINE MICAS

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ABSTRACT

The quantitative interpretation of the OH and OD stretching bands of muscovite single crystals allowed measurement of the kinetics of dehydroxylation under vacuum and of deuteration under high D_2O vapor pressures in the temperature range of 580–670°C. The procedure used gives an estimation of the diffusion coefficient limiting the progress of the reactions in the c^* direction. The rates of both reactions are similar, the diffusion coefficient computed for deuteration being equal to

$$3.5 \times 10^{-3} \times \exp\left(-\frac{47\ \text{kcal/mole}}{RT}\right)$$

The diffusion coefficients for deuteration, measured in the c^* direction, are of the same order of magnitude for muscovite and phlogopite. They are the same for the two types of hydroxyls in biotite. Therefore there is no relation between the mobility of protons or hydroxyls in micas and the real thermal stability.

The observations suggest that in deuteration also, the diffusion rate limiting step involves some local movement of an oxygen ion.

In order to provide valuable information, kinetics of dehydroxylation should be conducted under controlled atmosphere (Toussaint, *et al.*, 1963; Brindley and coworkers, 1966, 1967). Therefore kinetics of muscovite dehydroxylation in air (Sabatier, 1955a; Holt, *et al.*, 1958) have only an indicative value. Moreover at the temperature of the experiments reported (738–817°C) the reaction is very fast and is accompanied by transformations modifying the experimental conditions. Indeed it has been shown that under such treatments a muscovite sheet is transformed into a mosaic of 1–50 μm crystals (Eberhart, 1963) giving rise to increased surface area (Gaines and Vedder, 1964). According to Sabatier (1955b) the fissures appear instantaneously at a temperature of the order of 700°C but only after a few days at 650°C. Around 600°C, dehydroxylation can proceed rather far without provoking the appearance of this mosaic. A muscovite partially dehydroxylated at 600°C has been rehydroxylated by Gaines and Vedder (1964) by exposure to a high water vapor pressure at the same temperature; the restored OH stretching band has the same characteristics as in the untreated mineral.

The kinetics of dehydroxylation of a <20 μm muscovite powder has been studied under vacuum in the temperature range of 540–570°C by Kodama and Brydon (1968). The authors propose that the reaction is controlled by a two-dimensional diffusion process having an activation energy of 54 kcal/mole; however they cannot compute any diffusion coefficient owing to the granulometry of the specimen.

In this work, the dehydroxylation kinetics of muscovite single crystals has been followed, the use of infrared spectroscopy allowing to measure the progress of the reaction in one direction. This procedure eliminated the complications involved in the interpretation of data obtained with powders (Brindley, *et al.*, 1967) as well as the possible perturbations induced by a grinding process (Rouxhet and Brindley, 1966). The isotopic exchange between heavy water and the constitutional hydroxyls of various micas (muscovite, phlogopite, biotite) has also been studied comparatively.

EXPERIMENTAL PROCEDURES

The micas studied here are a phlogopite from Tongafeno (Dr. Krantz, Bonn, Germany), a biotite from Luindi (Musée Royal de l'Afrique Centrale, Tervuren, Belgium, RG5466) and a commercial muscovite of unknown origin.

Measurements. The progress of the reactions was followed by recording the OH or OD stretching bands after various periods of time. The spectra were recorded in polarized light with a Beckman IR-12 spectrograph. An area of about 0.5 cm^2 at the center of the mica sheets was submitted to the measurements.

From infrared spectra it is possible to calculate the product Kd expressed in cm^{-1} (wavenumber), proportional to the OH or OD content of the sample (Rouxhet, 1970). The integrated parallel absorption coefficient K is the integrated absorption coefficient which would be measured if the hydroxyls were parallel to the electric vector of the radiation; d is the thickness of the sheet. If oscillators are harmonic or may be considered as such, the ratio K(OH)/K(OD) is equal to μ(OD)/μ(OH), μ being the reduced mass of the oscillators (Rouxhet, 1969). This ratio is taken equal to 2; in order to compare OH and OD spectra, we use then 2 Kd (OD) and Kd(OH).

The validity of the K coefficient calculation supposes that the orientation of hydroxyls has not changed during the treatment; this was checked with a sample dehydroxylated during 163 h at 640°C. Similarly it has been verified with a sample submitted to deuteration during 47 h at 671°C that the OD groups have approximately the same orientation as the hydroxyls.

OH-OD Exchange. The thickness of the 4 muscovite sheets used for each kinetics ranged from 5 to 100 μm, corresponding to d values of 1.5 to 30 mg/cm^2; their dimension was of the order of 1.5×2 cm. For other micas d varied from 10 to 80 mg/cm^2.

The stainless steel apparatus used for deuteration is schematized in Figure 1; it was designed in such a way that the pressure would not be influenced by small leaks. The pressure was regulated by the temperature of the hot box, which was controlled automatically. The mica sheets were placed in the lower part of the bomb where the temperature was more homogeneous. The temperature, as measured by thermocouples fixed on the outside of the bomb, was close to the inside temperature. The fluctuations of the furnace temperature were limited by the use of a stabilized power supply. The experiments were performed under 155 kg/cm^2 of D_2O vapor pressure. Once the pressure and temperature had reached the desired value, the pressure was practically constant, and the temperature did not fluctuate by more than ±10°C. One experiment lasted for about 100 hours and the same samples were used for a whole experiment. However the procedure was such that the same sample was submitted to no more than 4 or 5 exchange periods in order to limit the variations in temperature and pressure.

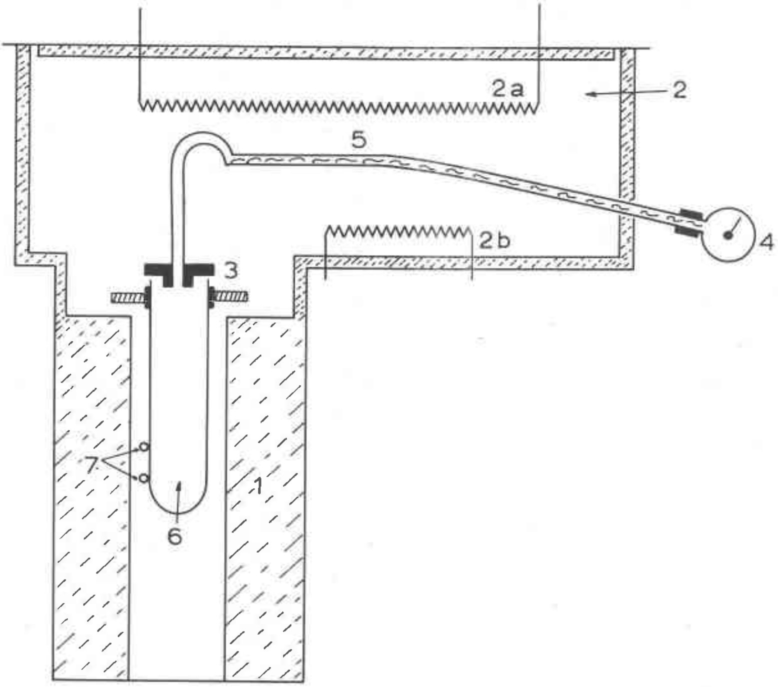

FIG. 1. Scheme of the apparatus used for the deuteration of micas: 1 furnace; 2 insulated box, 2a heating resistance, 2b control resistance; 3 tight joint; 4 manometer; 5 heavy water; 6 samples; 7 thermocouples.

Dehydroxylation. Only muscovite was investigated. As the measurements concern slight diminutions of infrared band intensities, the dispersion of experimental points was rather strong. Therefore the experiments were carried on with 6 or 7 crystals ranging from 0.8 to 3.3 mg/cm^2; their dimensions were about 1×1 cm.

The apparatus was essentially a silica tube which could be introduced in an automatically controlled furnace; the temperature fluctuations were negligible. The device supporting the sheets was hanged to the thermocouple, the junction of the latter being very close to the samples. The apparatus was maintained under a vacuum better than 10^{-3} torr with a liquid air trap placed not far from the silica tube. A whole experiment was conducted with the same samples, the reaction being interrupted for infrared measurements. The time required for cooling down or heating the samples was negligible as compared with the total reaction time.

RESULTS

Kinetics of Muscovite Deuteration. The amount of deuterium introduced into the sheets after a given time does not depend on their thickness. It is therefore concluded that the exchange rate, as measured at the center of the flakes, is limited by a process starting from the surface and pro-

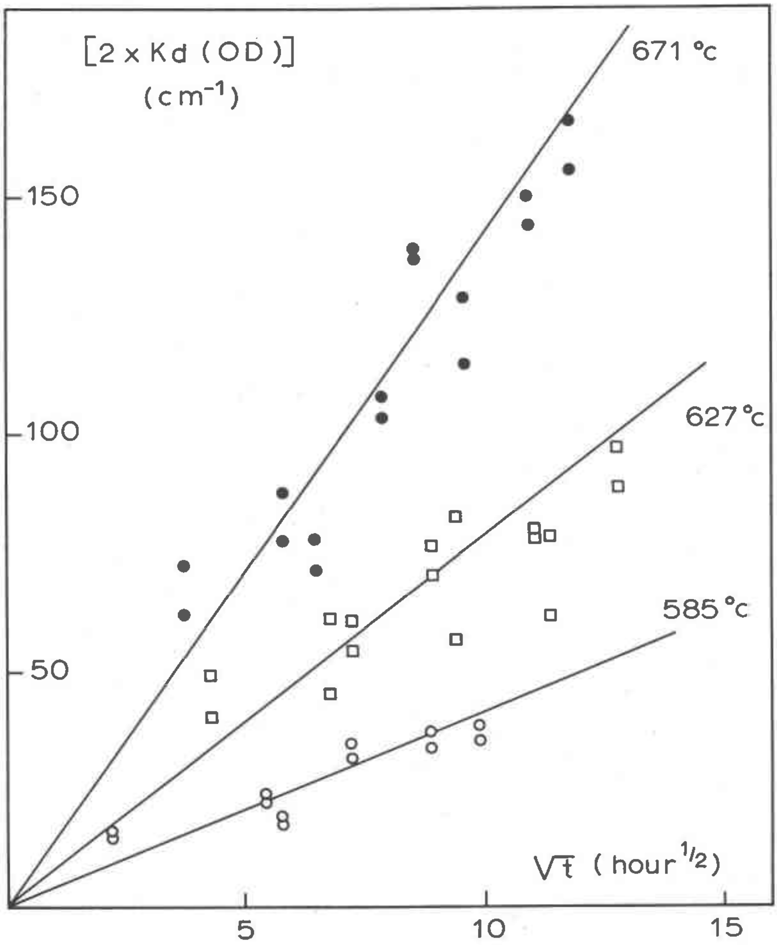

FIG. 2. Kinetics of deuteration of muscovite treated at the indicated temperatures under 155 kg/cm^2 of D_2O vapor pressure; K (wavenumber ×cm^2×mg^{-1}) is the integrated parallel absorption coefficient of the OD stretching bands and d (mg×cm^{-2}) the thickness of the sheets.

gressing along the c^* direction. This process is a diffusion as shown by the linear variation of Kd(OD) as a function of the square root of the reaction time (Fig. 2). As the extent of exchange is independent of thickness, the diffusion fronts coming from the two opposite faces of the sheets do not interfere. The sample can then be considered as homogeneous one-dimensional semi-infinite system and the amount M of diffusing species introduced per unit area of the flakes is given by:

$$M = \frac{4C_0\sqrt{D}}{\sqrt{\pi}}\sqrt{t} = \alpha\sqrt{t} \tag{1}$$

where t is the reaction time, D the diffusion coefficient, and C_0 the concentration of the diffusing species near the surface. A factor of 2 takes into account the diffusion proceeding from both sides of the sheets.

The angular coefficients α of Figure 2 are proportional to the square root of the diffusion coefficients. The average values of α with their standard deviations are:

at 585°C, 4.13 ± 0.54 cm^{-1} (wavenumber) × $\mathrm{hour}^{-1/2}$
at 627°C, 7.85 ± 1.42 cm^{-1} (wavenumber) × $\mathrm{hour}^{-1/2}$
at 671°C, 14.2 ± 2.0 cm^{-1} (wavenumber) × $\mathrm{hour}^{-1/2}$

When multiplied by 2, the temperature factor calculated from Figure 3 gives an activation energy of 47 ± 10 kcal/mole for the diffusion coefficient.

The evolution of $[2\,Kd(\mathrm{OD}) + Kd(\mathrm{OH})]$ has been followed for three different sheets. It confirms the conclusion that in this temperature range the sum of OH and OD populations does not vary in the course of the experiments and that reaction may be considered as a simple exchange not appreciably perturbed by any dehydroxylation (Vedder and Wilkins, 1969).

Deuteration of Phlogopite. Some sheets got cleaved during the experiments; therefore data had to be neglected somehow arbitrarily and the few results obtained have only an indicative value. The α coefficients are approximately as follows:

at 585°C, 2.9 cm^{-1} (wavenumber) × $\mathrm{hour}^{-1/2}$
at 627°C, 3.0 cm^{-1} (wavenumber) × $\mathrm{hour}^{-1/2}$
at 671°C, 7.0 cm^{-1} (wavenumber) × $\mathrm{hour}^{-1/2}$

In order to be compared with the ones of muscovite, these results should be multiplied by a factor of 3, that represents the approximate ratio of the integrated parallel absorption coefficient per hydroxyl for the two minerals (Rouxhet, 1970). However it may only be concluded that the diffusion coefficient for the isotopic exchange is of the same order of magnitude for muscovite and phlogopite.

Deuteration of Biotite. The exfoliation of the sheets submitted to deuteration ruled out any possibility of following the kinetics of the reaction. However it appeared that deuteration affects about to the same extent the hydroxyls directed towards the hexagonal cavity, responsible for the

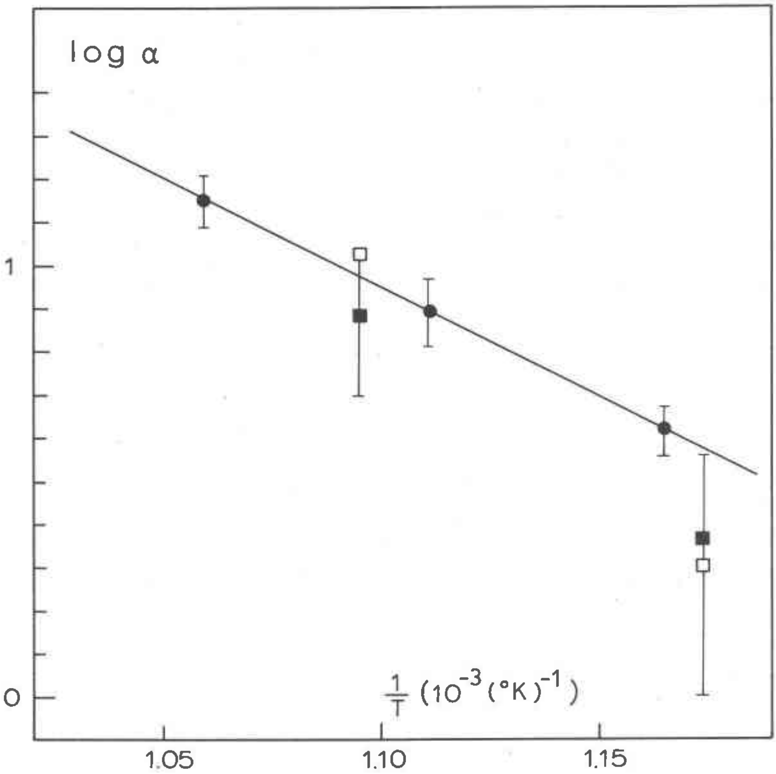

FIG. 3. Arrhenius plot for the kinetics of deuteration and dehydroxylation of muscovite; α is the angular coefficient of the straight lines of figures 2 and 5. ● Isotopic exchange (Fig. 2); average values of α ■ Dehydroxylation (Fig. 5); average values of α □ Dehydroxylation (Fig. 5); values of α given by a least square roots analysis.

high frequency (HF) band, and the hydroxyls close to an octahedral vacancy, absorbing at low frequency (BF). This is shown by Figure 4 which illustrates the linear relationship between the integrated intensity of the high frequency OD band (HF) for an incidence angle of 30° and the integrated intensity of the low frequency band (BF). The angular coefficient is 1.28 while the ratio of intensities for an untreated sample is of the order of 0.9.

Dehydroxylation of Muscovite. The maximum extent of dehydroxylation has been about $\frac{2}{3}$ of the total water content for the thinnest crystals. The diminution of Kd(OH), and therefore of the OH content of a flake, is independent of the flake thickness and is proportional to the square root

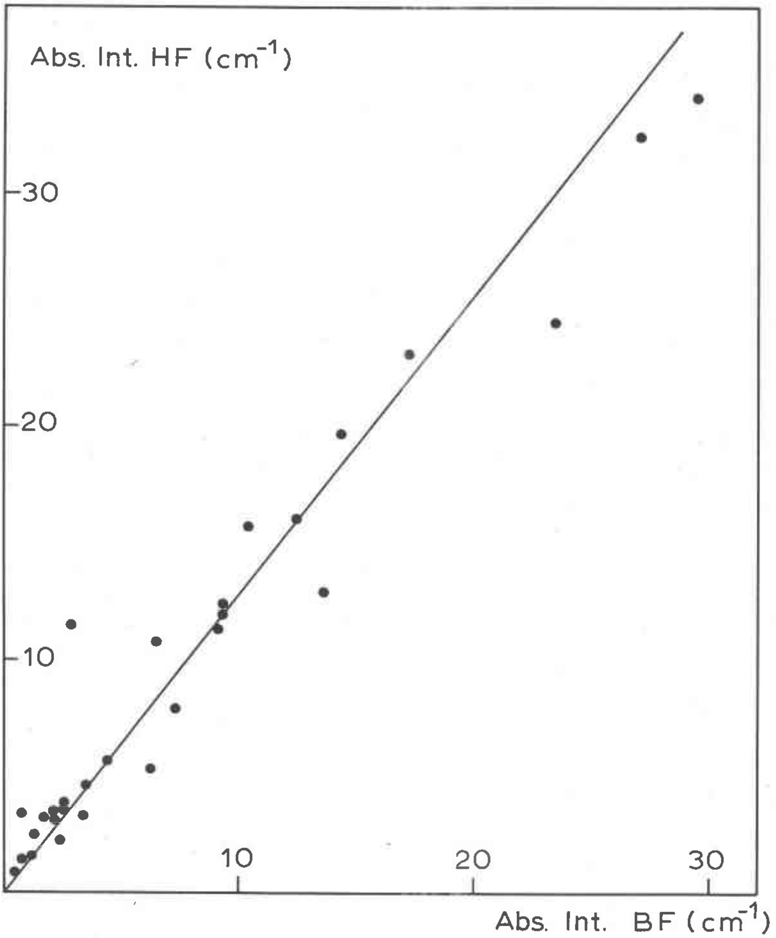

FIG. 4. Deuteration of Luindi biotite at various temperatures; correlation between, in ordinate, the integrated intensity of the high frequency OD stretching band (Abs. Int. HF) recorded at a 30° incidence angle with the light polarized along the incident plane and, in abscissa, the integrated intensity of the low frequency OD stretching band (Abs. Int. BF).

of the reaction time (Fig. 5). The reaction rate is limited by a diffusion parallel to the c^* axis and relation (1) may again be used.

The angular coefficients α of the two straight lines in Figure 5, are 2.3 ± 1.2 cm^{-1} (wavenumber)$\times$hour$^{-1/2}$ at 579°C and 7.7 ± 2.7 cm^{-1} (wavenumber)$\times$hour$^{-1/2}$ at 640°C. A least square roots analysis would give respectively 2.0 and 10.7 $\mathrm{cm}^{-1}\times$hour$^{-1/2}$ as values for α. The higher value for α given by the least square roots analysis for the 640°C experiment corresponds to a positive intercept with the abscissa axis

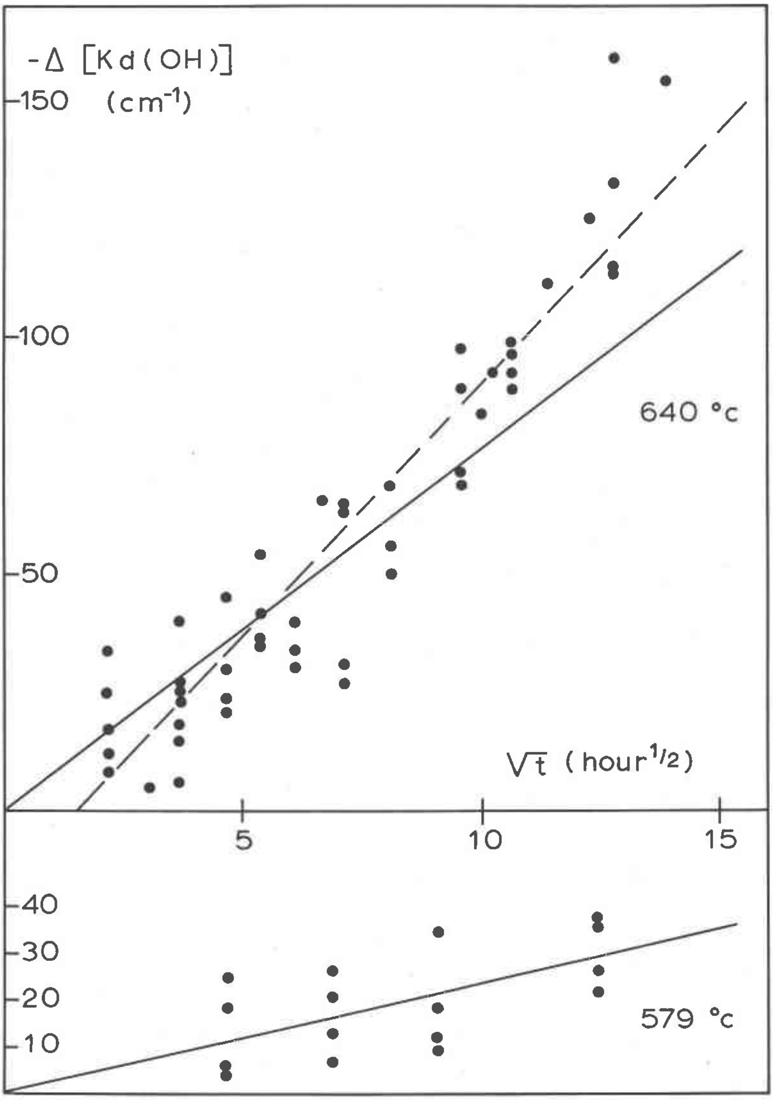

FIG. 5. Kinetics of dehydroxylation of commercial muscovite treated under vacuum ($<10^{-3}$ torr) at the indicated temperatures; K (wavenumber $\times \mathrm{cm}^2 \times \mathrm{mg}^{-1}$) is the integrated parallel absorption coefficient of the OH stretching band and d (mg cm^{-2}) is the thickness of the sheets. Full lines: drawn from the average slopes. Interrupted line: obtained by least square roots analysis.

(Figure 5). This may be attributed either to some nucleation period or to progressive acceleration resulting from a slight transformation of the sheet surface into a mosaic of small crystals as discussed earlier. Figure 3 shows that the α values obtained for dehydroxylation are of the same order of magnitude as those observed for the isotopic exchange.

DISCUSSION

The experiments of phlogopite deuteration show that the diffusion of the proton or the proton carrier is comparable to that observed for muscovite whilst phlogopite dehydroxylates only at temperatures as high as 1000–1080°C (Vedder & Wilkins, 1969). It has therefore no sense trying to explain the difference in thermal stability between both minerals to be the result of a difference in the mobility of hydroxyls or protons. The case of biotite illustrates still better the relevant distinction between the mobility of the "proton carrier" and the stability of the mineral. For macrocrystalline material, the hydroxyls close to an octahedral vacancy and responsible for the low frequency stretching band (3530–3620 cm^{-1}) are lost after a heat treatment around 800°C and the other hydroxyls are not removed appreciably below 900°C (Vedder and Wilkins, 1969); however both types of hydroxyls deuterate at about the same rate.

Relation (1) permits the calculation of a diffusion coefficient for the deuteration of muscovite. For the purpose α should be expressed in gram-atomic weight H or $\text{D} \times \text{cm}^{-2} \times \text{sec}^{-1/2}$ by using the integrated parallel absorption coefficient as interpreted by Rouxhet (1970). One wavenumber unit of $Kd(\text{OH})$ corresponds to 3.10^{-8} gram-atomic weight H/cm^2. The concentration C_0 is taken as 4 H per unit cell or 4/292.3 gram-atomic weight/cm^3. By this assumption it is supposed that the external layers of a muscovite sheet are almost immediately deuterated, the concentration gradient between these layers and the center of the crystals being then directly built up. The diffusion coefficient in the c^* direction calculated in the temperature range of 580–670°C is equal to

$$D = 3.5 \times 10^{-3} \times \exp\left(-\frac{47 \text{ kcal/mole}}{RT}\right) \text{cm}^2 \text{ sec}^{-1} \qquad (2)$$

The diffusion coefficient for dehydroxylation should be about the same, with an activation energy close to the value of 54 kcal/mole obtained for dehydroxylation of muscovite powder (Kodama and Brydon, 1968). Therefore the deuteration and dehydroxylation of muscovite should be limited by the diffusion of identical or at least closely related chemical species.

The use of relation (1) for dehydroxylation is based on the model of a homogeneous diffusion system, the value chosen for C_0 implying that from the very beginning the external layers are dehydroxylated. The model supposes there is a solid solution between muscovite and the dehydroxylated material, what may be expected because of the similarity of the structures (Eberhart, 1963) and the ease of rehydroxylation (Vedder and Wilkins, 1969). If instead the reaction rate was limited by a diffusion in the reaction product, relation (1) should be replaced by

$$M = 2\sqrt{2DC_mC_0'}\sqrt{t} \qquad (3)$$

where C_m and C_0' are respectively the concentrations of diffusing species in muscovite and at the internal side of the reaction product. In that case the value of D would still be of the same order of magnitude as that obtained by the use of relation (1). Obviously the two reactions must also progress along the *ab* plane, starting from the sheet edges. The rate of this progression cannot be measured by the techniques used here; moreover if such a measurement was possible, the interpretation would be complicated by the irregular borders of the edges.

The similarity between the deuteration and dehydroxylation rates and the constancy of the total (OH+OD) population during deuteration confirms (Vedder and Wilkins, 1969) that, around 580–670°C, muscovite is stable under a water vapor pressure of 150 atmospheres and unstable under reduced pressure. Goldsztaub and Lang (1965) have effectively observed that the surface of a muscovite crystal is dehydroxylated at 500°C under vacuum. However the diffusion limiting the reaction rate is so slow below 600°C that the loss of constitutional water is usually observed only at higher temperatures.

The observed activation energy (47 kcal/mole) does not necessarily rule out the possibility that the reaction limiting step be a diffusion of the isolated proton. For interpreting this parameter, a precise diffusion model should be known or proposed. The comparison with activation energies obtained for hydroxides as boehmite (Wei and Bernstein, 1969; Mata and Fripiat, 1967) and goethite (Gallagher and Philips, 1968) cannot give definite informations as the crystalline structures are different from micas. However if the proton had to diffuse isolated, the diffusion paths and the potential barriers would be expected to be very different for the various micas and the diffusion coefficients would also be different.

Vedder and Wilkins (1969) showed that the hydroxyls reintroduced by rehydration of a dehydroxylated muscovite recover the same position with about the same orientation as in the untreated mineral. Therefore they are in favor of a dehydroxylated structure where an oxygen atom occupies a position intermediate between the two hydroxyl sites of muscovite, as proposed by Eberhart (1963). They reject the model implying an inhomogeneous reaction model (Nicol, 1964); the latter is also incompatible with the rates of deuteration and dehydroxylation being limited by a similar process. The anhydrous muscovite structure proposed by Eberhart (1963) requires an oxygen transport. As it is not conceivable that oxygen diffuses faster than the isolated proton, a valuable hypothesis is that the proton is associated to oxygen in the transport complex involved for dehydroxylation.

The diffusion of the proton as H_2O molecule is quite probable for the dehydroxylation of muscovite. However, as the OH stretching bands are not deeply perturbed at a well given temperature, the dehydroxylation process may not be depicted as a diffusion of stable water molecules formed by definitive condensation of two hydroxyls at a certain temperature. It is only suggested that the slowest step of the reaction is the jump of the proton included in the transport complex H_2O considered, whatever the life time of the complex. This model does not exclude for instance, that some faster steps involve jumps of the proton between oxygen atoms (Rouxhet, *et al.*, 1969). Such a mechanism may also be extended to the deuteration of all the mica species studied here.

The transport complex could be the OH group. This hypothesis does also not exclude proton jumps between oxygen atoms and does also not require any net oxygen transport in any direction. It concerns only the reaction rate limiting step and is applicable to muscovite dehydroxylation as well as to deuteration of the three types of mica studied.

CONCLUSIONS

Under elevated water vapor pressure (150 kg/cm^2) muscovite is stable in the 580–650°C range, and it may thus be deuterated in presence of D_2O vapor. The reaction rate for deuteration in the c^* direction is limited by a diffusion process with a diffusion coefficient equal approximately to

$$3.5 \times 10^{-3} \times \exp\left(-\frac{47\ \text{kcal/mole}}{RT}\right)$$

Under vàcuum muscovite is unstable at temperatures lower than 580°C but the reaction rate is too low to be detected with current techniques. In the temperature range of 580–650°C, where the morphology of the crystals is not altered by dehydroxylation, the diffusion coefficients along c^* are similar to those obtained for deuteration.

The diffusion coefficients for deuteration of muscovite and phlogopite are of the same order of magnitude. They are also the same for the two types of hydroxyls in biotite. Therefore there is no relation between the mobility of protons or hydroxyls in micas and their real thermal stability.

The observations suggest that the diffusion rate limiting step is the movement of a transport complex H_2O or OH^-. However this does not require any net oxygen transport and, between two slow steps occurring at some spots in the crystal, the proton might well jump from one oxygen to another one.

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