

DEHYDROXYLATION AND REHYDROXYLATION,
OXIDATION AND REDUCTION OF MICAS

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ABSTRACT

Infrared spectra of thin layers of muscovite were recorded during dehydroxylation, rehydroxylation and deuteration. Muscovite dehydroxylates at 600°C in the atmosphere. The resultant changes in the infrared spectrum are interpreted as due to loss of H₂O and minor rearrangement of the remaining structure. Dehydroxylated muscovite has been rehydroxylated to its original structure under relatively mild conditions: 600°C and less than 15 bars of H₂O. It is possible to deuterate a muscovite under these conditions without appreciable dehydroxylation.

There are three stages in the thermal decomposition of biotite. In biotite powders, hydrogen is lost with concomitant oxidation of Fe²⁺ at an appreciable rate at temperatures as low as 400°C. In the same material, H₂O is lost from sites near octahedral vacancies at temperatures below 500°C. Even in thick sheets these hydroxyls are lost at temperatures below 800°C. Hydroxyl close to 3 Mg or 2 Mg+trivalent ion in the octahedral layer remains to temperatures in excess of 1000°C. A correlation is established between infrared and thermogravimetric data for the decomposition of biotite.

Infrared spectra of thin sheets of very pure natural phlogopite confirm that no dehydroxylated phase occurs before final decomposition at about 1080°C in the atmosphere.

INTRODUCTION

The changes which occur in the structures of many hydroxyl bearing layer and chain silicates upon heating and the processes involved in attaining the altered states have been the subject of much recent research. Brindley (1963) summarizes work done prior to 1961, stressing particularly the role of X-ray studies which are especially powerful in delineating the broader outlines of the processes of decomposition and transformation. The second stage of this work, as Brindley observed, requires a much more detailed examination of the transitional stages. At this point, techniques other than diffraction are frequently more appropriate, especially carefully chosen spectroscopic methods.

Hydrothermal studies have shown that at a given pressure dioctahedral layer silicates dehydroxylate at lower temperatures than the corresponding trioctahedral ones. DeVries and Roy (1958) give decomposition temperatures of 1060°C for phlogopite and 650°C for muscovite, 780°C for talc and 575°C for pyrophyllite, all at about 1000 bars. Similar con-

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clusions were reported earlier by Kiefer (1949) and Yoder and Eugster (1954, 1955).

In the early stages of thermal decomposition of a hydrous silicate the focus of attention is on whether a dehydroxylated phase occurs and, if so, what is its structure. In the dioctahedral layer silicates pyrophyllite (Nakahira and Kato, 1964), and muscovite (Eberhart, 1963) it is rather certain that the first stage of decomposition is a dehydroxylated phase. A one dimensional Fourier synthesis of muscovite dehydroxylate has been reported (Eberhart, 1963).

Although there is no clear evidence that the trioctahedral hydrous silicates go through a *dehydroxylated* phase before final decomposition, a *dehydrogenated* phase may occur if a sufficient number of octahedral positions are filled by Fe^{2+} . Thus annite can be transformed to oxyannite (Rinne, 1924), and Eugster and Wones (1962) have examined the equilibrium relations in considerable detail. Barnes (1930) was able to produce oxyhornblende by heating natural hornblende and the same process is known to occur in other iron-rich amphiboles (Hodgson *et al.*, 1965a, b; Addison *et al.*, 1962; Addison and Sharp, 1963).

Fripiat and his coworkers (1965, 1966, 1967) have used careful infrared spectroscopic techniques in an effort to understand the predehydroxylation processes. In the present study we have directed our attention particularly towards understanding the processes involved in the loss and gain of hydroxyl and hydrogen in the micas muscovite, biotite and phlogopite. It is clear that for such investigations, direct study of either hydroxyl ions or protons in the structure is most likely to give meaningful results. Since the vibrational characteristics of a hydroxyl ion are quite

TABLE 1. ASSIGNMENTS IN THE HYDROXYL STRETCHING REGION OF PHLOGOPITE AND BIOTITE

Vibration frequency (cm^{-1})	Notation	Occupation of closest three octahedral sites		
3712	N _A	Mg	Mg	Mg
3696	N _B	Mg	Mg	Fe^{2+}
3680	N _C	Mg	Fe^{2+}	Fe^{2+}
3664	N _D	Fe^{2+}	Fe^{2+}	Fe^{2+}
3668	I _A	R^{3+}	Mg	Mg
3652	I _B	R^{3+}	Mg	Fe^{2+}
3636	I _C	R^{3+}	Fe^{2+}	Fe^{2+}
~3625	V _A	R^{2+}	R^{2+}	V
~3600	V _B	R^{2+}	R^{3+}	V
~3560	V _C	R^{3+}	R^{3+}	V

($\text{R}^{2+} = \text{Mg}, \text{Fe}^{2+}$; $\text{R}^{3+} = \text{Al}, \text{Fe}^{3+}$; V = vacancy).

sensitive to rearrangements in the immediate environment of the ion and all three micas have now been investigated in some detail, we also have used infrared spectroscopy as our major tool.

The assignments used in the hydroxyl stretching region are based upon detailed studies of muscovite (Vedder and McDonald, 1963) and biotite (Vedder, 1964; Wilkins, 1967) and are listed in Table 1.

Experimental data relating to the dehydroxylation, rehydroxylation and deuteration of the dioctahedral mica muscovite will be presented first. Following this, data on dehydroxylation, oxidation and deuterium reduction of the trioctahedral micas biotite and phlogopite will be discussed. On the basis of the spectroscopic data, both previously proposed and new mechanisms of thermal decomposition will be examined and evaluated.

MUSCOVITE

Dehydroxylation. When a sheet of muscovite is heated in air it begins to lose H_2O at about $600^\circ C$ due to dehydroxylation.

Yoder and Eugster (1955) have found that under equilibrium conditions muscovite will decompose into sanidine ($KAlSi_3O_8$), corundum (Al_2O_3) and water. The equilibrium decomposition temperature depends strongly on the pressure. Velde (1966) has determined the decomposition curve reversibly. It follows from his data that at $600^\circ C$ the equilibrium pressure is about 25 bars; at $700^\circ C$ about 3250 bars. The equilibrium temperature of decomposition at one atmosphere pressure is about $560^\circ C$.

This means that dehydroxylation of muscovite in the atmosphere at $600^\circ C$, or higher, is not an equilibrium process. It starts at the surface, giving rise to colored striations which are oriented parallel to the a axis. At higher temperatures gas pockets begin to form inside the sheet and these cleave the mica while growing in size until they reach the edges and the H_2O escapes. At this point *delamination* of the muscovite is the rate-controlling step in the thermal decomposition (Gaines and Vedder, 1964). The order in which the various stages of dehydroxylation appear with increasing temperature is therefore in agreement with the variation of the equilibrium decomposition pressure with temperature.

Relative to natural muscovite, the dehydroxylated mica (84 hrs at $730^\circ C$ in the atmosphere) has about the same value of a (5.20 ± 0.03 compared to $5.22 \pm 0.03 \text{ \AA}$); it is larger along b (9.17 ± 0.03 compared to $9.01 \pm 0.03 \text{ \AA}$) and has also expanded along c (20.14 ± 0.05 compared to $20.03 \pm 0.05 \text{ \AA}$).¹ Eberhart (1963) published similar data for a 900°

¹ We are indebted to J. S. Kasper and H. Brandhorst for these measurements on natural and dehydroxylated Brazilian muscovite.

dehydroxylate. Sabatier (1960) recognized that the orientation of the striations along the a axis is associated with the increase in lattice dimension along b compared to little change along a .

At 600°C it required 760 hours for a sheet of Brazilian muscovite about 1.35 μ m thick to lose 70 percent of its OH content. Throughout the process this sheet maintained the appearance of a single crystal. The interference pattern, as observed in transparent regions of the infrared spectrum also remained essentially unaltered during this dehydroxylation experiment. From this we may conclude that at 600°C the dehydroxylation proceeds via diffusion. At higher temperatures the rate of dehydroxylation increases considerably because at the same time delamination occurs and the diffusion paths are considerably shortened.

Another sheet of Brazilian muscovite about 4 μ m thick was heated at 730°C in the atmosphere, and spectra were taken after 1, 3, 23 and 84 hours. The intensity of the OH stretching absorption band at 3628 cm^{-1} decreases and there are also small changes in its shape. Considerable delamination occurred and the sample became covered with striations, some of which persisted to the end of the experiment, resulting in a somewhat wrinkled, but still surprisingly flexible sheet, colored by interference effects. The following table gives the peak intensity of the OH stretching band after the various periods of heating.

PEAK INTENSITY OF ν_{OH} AT 3628 cm^{-1} DURING DEHYDROXYLATION AT 730°C

Time of heating in hrs	1	3	23	84
Intensity at maximum ($\log I_0/I$)	0.55	0.45	0.02	0

The intensity of a second OH fundamental vibration, at 925 cm^{-1} , decreased proportionally. (For reasons explained below it is difficult to observe the change of intensity of the third OH related frequency at 405 cm^{-1} .) At the same time other changes occurred in the spectrum as can be seen by comparison of the spectra of natural and dehydroxylated muscovite in Figure 1.

As a result of the structural changes which take place during dehydroxylation we may expect changes to take place in all optically active absorption bands. In addition, vibrational modes which are not normally infrared active may become active after dehydroxylation.

The frequencies of some of the active fundamentals, namely those at 1010, 530 and 470 cm^{-1} , appear to shift only slightly (to about 1010, 555 and 485 cm^{-1}). The shifts seem to be modest for some of the weaker infrared active bands also; for instance those at 750 and 685 cm^{-1} to

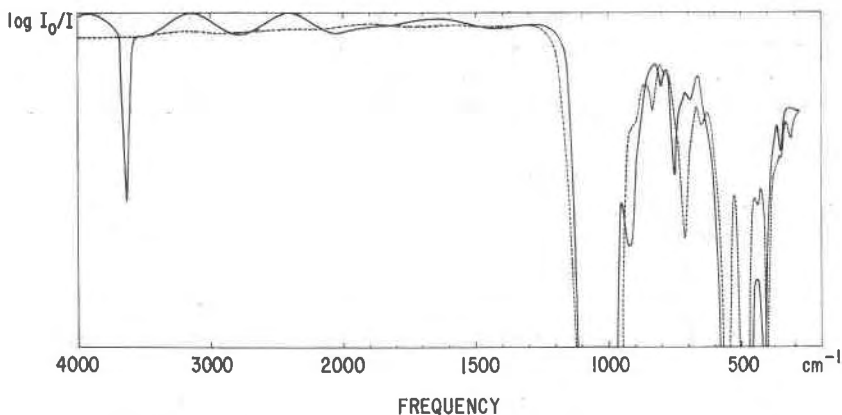


FIG. 1. Infrared spectrum of normal (—) and completely dehydroxylated (---) Brazilian muscovite. Perpendicular incidence.

715 and 655 cm^{-1} . The relative intensities of these bands did not change much either.

In three cases, however, at 835, 403 and 315 cm^{-1} , an entirely new band appeared. At first sight this may not be obvious in case of the 403 cm^{-1} band because the normal muscovite absorbs in the same area. It has been shown earlier that this band in muscovite involves one of the librational modes of the OH ions. Hence the band at 403 cm^{-1} in the dehydroxylated muscovite is new.

A clue to the interpretation of the new absorption band at 835 cm^{-1} can be found from the reflection spectrum of muscovite (Vedder, 1964). A transition occurring at this frequency in normal muscovite has its transition moment oriented perpendicular to the cleavage plane (001).

The same transition can also be observed in the absorption spectrum if the sample is rotated such that the electric vector does not lie in the (001) plane. Figure 2 shows the spectrum of a sheet of muscovite when it makes an angle of 45° with the direction of propagation of the infrared beam, compared with a spectrum of the same sample at normal incidence. The new band at about 830 cm^{-1} is just visible in the spectrum of the rotated sample.

Because the dehydroxylation has led to exfoliation of the originally single sheet of mica into many thinner sections the appearance of the new band could, in principle, be due to randomization of the orientation of these sections. However, it is found by X-ray diffraction that the misorientation is on the order of only 10°. Comparison with Figure 2 shows that such small rotations could never lead to an intensity of absorption of the 830 cm^{-1} band as shown in Figure 1. It appears more

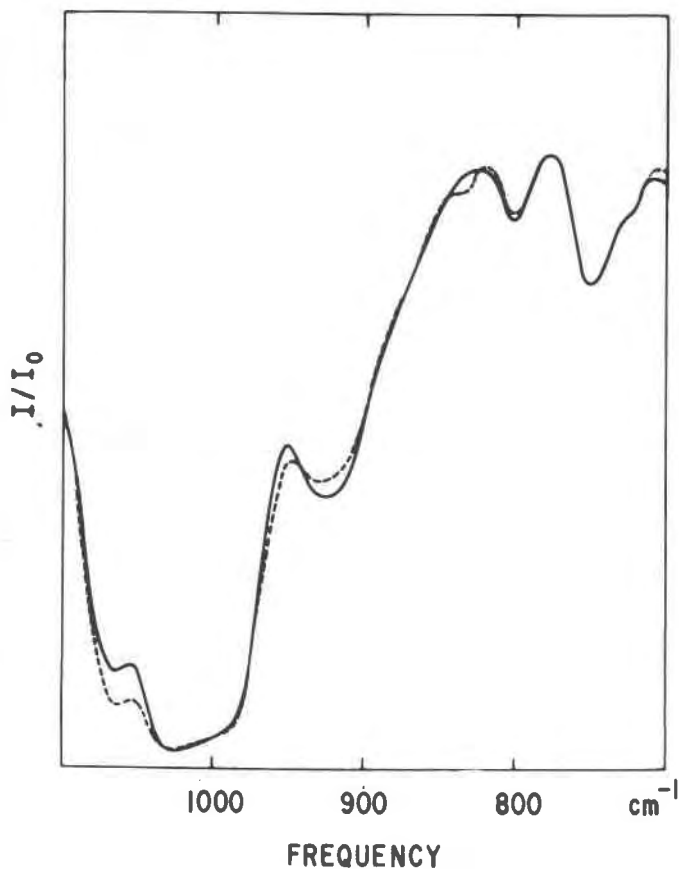


FIG. 2. Absorption spectra of Brazilian muscovite with normal incidence to the cleavage plane (—) and with an angle of 45° between normal to cleavage plane and beam direction (- - -).

likely that the transition moment of the vibration involved was perpendicular to the cleavage plane in the original mica but has been turned away from this orientation in the dehydroxylated mica.

There is no general agreement how to describe the atomic displacements for the vibration at 830 cm^{-1} . Farmer and Russell (1963) have pointed out that in layer silicates absorption in this region increases with increasing aluminum content. They, therefore, associate the band at 830 cm^{-1} with A1-O (apical) stretching vibrations. On the other hand, model calculations for a layer of coupled SiO_4 tetrahedra indicate that the motion of bridged oxygens ($[\text{O}_3]$) against the SiO (apical) group gives rise to a very broad energy band, from 554 to 818 cm^{-1} (Vedder, 1964).

All but the lowest frequency of this band would be infrared forbidden for a network of hexagonal symmetry consisting of SiO_4 tetrahedra only. However, Al substitution invalidates this selection rule. Vibrational modes may now become active in which the SiO_4 tetrahedra execute a bending type vibration as $[\text{O}_3]$ versus Si-O (apical) but the AlO_4 tetrahedra are involved in a stretching motion as $[\text{O}_3]$ -Al versus O (apical). The 830 cm^{-1} band may be such a vibration in which both SiO_4 and AlO_4 tetrahedra vibrate, with the same frequency but with different atomic displacements.

In either case, in agreement with the structure of normal muscovite in which the tetrahedra have only a few degrees of tilt (Burnham and Ranslovich, 1964), the transition moment of this mode would be essentially perpendicular to the sheet. The considerable intensity with which the mode appears in the spectra of the heated muscovite indicates that the SiO_4 and AlO_4 tetrahedra have been tilted from their original positions during dehydroxylation. This is not inconsistent with the one-dimensional Fourier analysis of dehydroxylated muscovite by Eberhart (1963) which provides evidence that the O^{2-} ion left over from hydroxyl condensation goes into the vacant site in the Al layer. An O^{2-} ion in this site substituting for two hydroxyl ions would lead to some distortion of the silicate layer.

This infrared result provides an interesting tool by means of which the alteration of the Si-O network by dehydroxylation can be detected.

From a comparison of the reflection spectra with the electric vector perpendicular or parallel to the cleavage it follows that the 403 and 315 cm^{-1} bands cannot be explained in a way similar to the one at 830 cm^{-1} . In these regions there is no indication of a transition with a moment polarized perpendicular to the cleavage plane. One or possibly both of these new bands may be associated with the vibrations of the "left over" oxygen ion relative to its environment. This oxygen atom may reasonably be expected to bond fairly strongly to the Al ions. However, although the spectra of Al_2O_3 and its hydrates show various absorption bands in this general area there appears to be no firm basis yet for any significant conclusions.

Rehydroxylation. A sheet of muscovite about $1.35\mu\text{m}$ thick was dehydroxylated at 600°C in the atmosphere until after 760 hours only 29 percent of the OH ions were left (as determined from the intensity of the 3628 cm^{-1} band). Little or no exfoliation occurred; the interference pattern that is visible in the infrared spectrum remained essentially unaltered. This sample was subsequently heated for 215 hours at 600°C under a H_2O pressure of about 16 bars. Its OH content was restored to about 65

percent of the original. It was next heated another 270 hours at 600°C under a H₂O pressure of about 13 bars and the restoration of its OH content progressed to 84 percent. During a third period of heating the OH content did not increase much further.

The data are not very accurate but indicate conclusively that during dehydroxylation and rehydroxylation the dichroic ratio (intensity $\parallel b$ /intensity $\parallel a$) of the 3628 cm⁻¹ band remains close to the value in natural muscovite. Simultaneously with the growth of the intensity of the OH stretching band, the 925 cm⁻¹ band reappears, whereas the band at 830 cm⁻¹ decreases in intensity.

It is interesting that, along with the reconstitution of the OH content of the mica, the distortion of the SiO network is repaired.

In summary, we have evidence that dehydroxylation proceeds via diffusion and gives rise to only minor structural rearrangements. From anisotropy it follows that upon rehydroxylation hydroxyl ions re-occupy the original sites in the original orientation.

Although other possibilities can be suggested, the simplest mechanism to rationalize these observations is that two OH⁻ ions located across an Al ion vacancy in the octahedral layer condense to form H₂O which subsequently diffuses from the structure.

These experiments have not yet been performed with a completely dehydroxylated mica, nor has complete rehydroxylation been achieved. There appears to be little doubt, however, that at 600°C and about 15 bars of H₂O pressure normal mica is more stable than dehydroxylated mica. This conclusion is further supported by exchange of hydrogen with deuterium.

Deuteration. A sheet of muscovite a few microns thick can be deuterated at 600°C at D₂O pressures above 5 bars. At this temperature the process is slow; with a sample 1.77 μm thick it took as much as 700 hours to reach about 80 percent deuteration. However, at higher temperatures dehydroxylation begins to interfere.

The infrared spectrum shows the progress of deuteration in the decrease of intensity of OH stretching (3628 cm⁻¹) and OH libration bands (925 and possibly 405 cm⁻¹) and the appearance and subsequent growth in intensity of the corresponding OD bands (2678 and 705 cm⁻¹; the third is below 300 cm⁻¹ and has not yet been observed).

For isolated OH ions the substitution of H by D is expected to lead to a decrease in the integrated intensity of the stretching band by a factor μ_{OD}/μ_{OH} which is equal to 1.887 (μ is the reduced mass). Within experimental error the change of frequency of the stretching mode on deuteration is equal to what is theoretically predicted for isolated ions. In

addition, there is no evidence of vibrational coupling between OH ions. As far as the stretching motion is concerned the OH ions can therefore be considered as isolated and the change of intensity with deuteration may be expected to follow closely the theoretical prediction. The variation of the quantity $A = (\log I_0/I \text{ at band maximum}) \times (\text{width in cm}^{-1} \text{ at half height})$ which is a fair measure of band area, is shown in Table 2. The sum $A_{\text{OH}} + 1.887 A_{\text{OD}}$ is also tabulated in Table 2 and is found to be practically constant throughout the deuteration process.

The data of Table 2 confirm our earlier conclusion: under the conditions defined above the rate of dehydroxylation is still small or zero. However, under these same conditions there is at least one H or D containing species, the mobility of which through the mica structure is

TABLE 2. DEUTERATION OF MUSCOVITE (BENGAL RUBY)
Intensity $A = (\log I_0/I \text{ at band maximum}) \times (\text{width in cm}^{-1} \text{ at half height})$ as
function of deuteration. Thickness $1.77\mu\text{m}$; 600°C and 30 bars D_2O

	OH(3628 cm^{-1})		OD(2768 cm^{-1})		$A_{\text{OH}} + 1.887 A_{\text{OD}}$	
	<i>E//a</i>	<i>E//b</i>	<i>E//a</i>	<i>E//b</i>	<i>E//a</i>	<i>E//b</i>
Nondeuterated	9.12	23.42	—	—	9.12	23.42
1×deuterated (~70% OD)	2.78	7.15	3.46	9.19	9.31	24.49
2×deuterated (~82% OD)	1.68	4.22	4.05	9.81	9.32	22.73

already considerable. It can exchange deuterium with an OH ion. Again the simplest assumption would be that this mobile species is a water molecule.

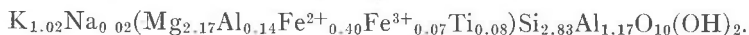
BIOTITE

Dehydroxylation. In muscovite, octahedral occupation does not exceed 2.05 per three available sites (lithium containing muscovites excluded). Biotites vary widely in octahedral occupation, the large deviations from full occupancy (down to 2.45 per three available sites) generally occurring among the more iron-rich varieties (Foster, 1956, 1960a, b). On the basis of the studies of dehydroxylation of muscovite, a correlation would be expected between the number of vacancies in the octahedral layer and the temperature of thermal decomposition for micas with intermediate octahedral occupancy. Unfortunately little or no quantitative information concerning this point is available. The thermal stability of the trioctahedral micas, in fact physical and chemical properties in general, can vary considerably. Some biotites begin to delaminate at about 600°C .

Some very light colored Canadian phlogopites remain virtually unchanged until about 900°C.

As a consequence of orientation differences between the hydroxyl ions in N or I associations and those in V associations, biotite single crystals are particularly useful for observing changes in the V bands with heating. To study changes in the N and I regions powders have been used with advantage since in all biotites N and I bands are more prominent in this mode of examination.

Two biotites were chosen for a single crystal study. The more iron-rich specimen 196513 showed almost identical features during decomposition with a dark Madagascar Amber W#4 (Vedder, 1964) and only the latter will be discussed in detail. Its structural formula calculated by the method used by Foster (1956) is



Infrared spectra in the region from 3400 to 3800 cm^{-1} have been obtained on the natural mica and on samples heated for 24 hours at various temperatures. As a result of exposure to heat some delamination occurs and reflection losses at the increased number of mica-air interfaces reduce transmission and interfere with a measurement of the absorption spectrum. Such reflection losses were minimized by suspending the samples in hexachlorobutadiene between two NaCl windows. Spectra were measured with perpendicular incidence and the light polarized parallel to the *a* and *b* axes; they are shown in Figure 3. The characteristic anisotropy of these bands is shown in Figure 4.

It follows that the OH ions responsible for the V bands disappear entirely from the structure below 800°C. In this magnesium rich specimen, most of the OH ions associated with the N and I bands are present till at least 990°C.

Stated differently, OH ions near a vacancy are expelled from the structure long before much happens to those surrounded by a completely filled octahedral layer. If the filled parts of the octahedral layer contain much Fe^{2+} , this is not true. This point is pursued in the next section. These observations add support to the mechanism of dehydroxylation of muscovite proposed: two OH ions across a vacancy condense and H_2O diffuses out. It follows that thermal stability of biotites varies widely because the number of octahedral vacancies varies considerably.

Since the V bands of the infrared spectrum are a measure of the number of OH ions near an octahedral vacancy, these bands are also a fairly sensitive measure of the amount of dehydroxylation of a biotite that will occur at temperatures below 800°C as will be shown later.

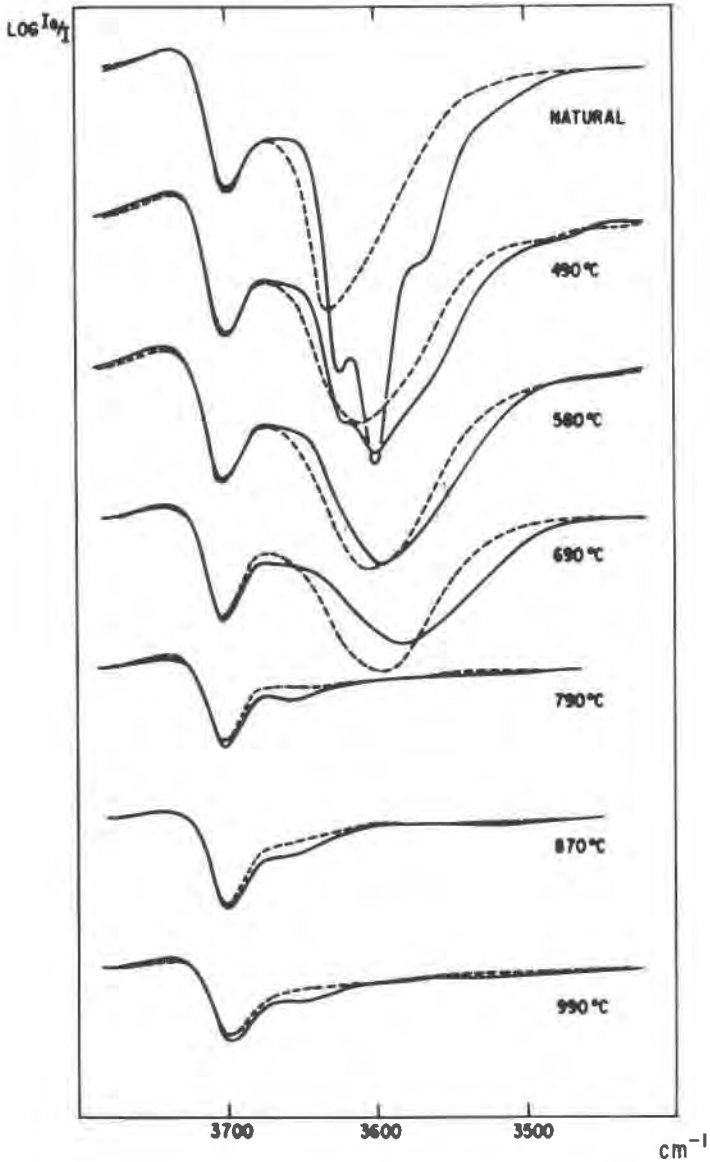


FIG. 3. Madagascar amber (W#4) heated for 24 hour periods at various temperatures; spectra at room temperature; sample in hexachlorobutadiene. ——— polarised //a. - - - - - polarised //b.

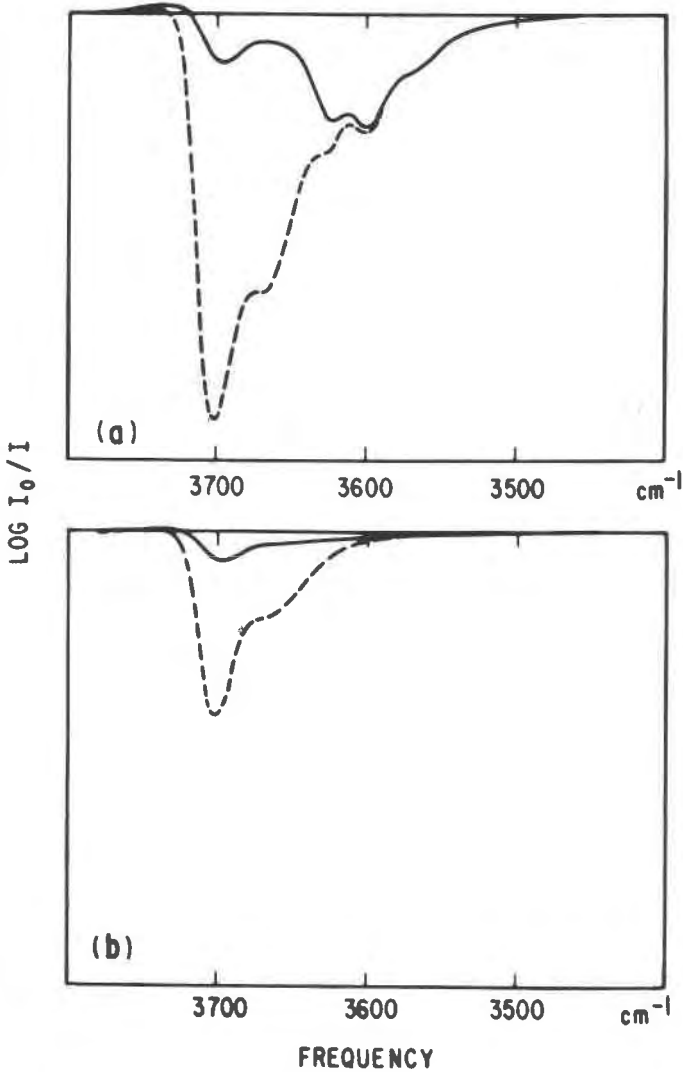


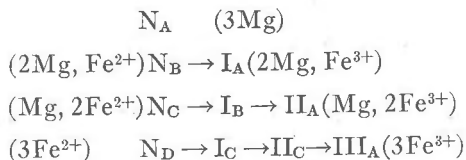
FIG. 4. (a) Madagascar amber (W#4) natural; unpolarized light; perpendicular incidence (—) and 30° tilted (---). (b) Madagascar amber (W#4) 24 hours at 990°C; unpolarized light; perpendicular incidence (—) and 30° tilted (---).

In addition to the gross features of the spectra and the general conclusions arrived at above there are some interesting details. In the natural mica the integrated intensity of the V bands is larger for light polarized parallel to the a than to the b direction. After the sample has

been heated to 690°C, in addition to other changes, the ratio of these intensities is reversed. Absorption intensities are reduced after heating, the bands become broader, they appear to shift to lower frequencies and the individual components are no longer observed after heating at the higher temperatures. Some of these features can be translated in terms of the tentative assignments proposed (Vedder, 1964). However what follows is necessarily at least as speculative as the assignment on which it is based.

There are two crystallographically non-equivalent octahedral sites corresponding to the vacant (site *b*) and occupied octahedral sites (sites *a*₁ and *a*₂) in muscovite respectively (Steinfink, 1962; Donnay *et al.*, 1964). Since the OH dipole will be in the (010) plane if the octahedral vacancy is on the unique cation site, the spectra of the initial sample indicate that the majority of vacancies occur on that site. On heating, the ratio of intensities parallel to the *a* and *b* axes is reversed. Thus the rate of dehydroxylation is larger near a vacancy on the *b* site than near a vacancy on the *a* sites. In the first case, as in muscovite, a water molecule would form from two hydroxyl ions bonded to different octahedral ions; apparently that process is easier than in the second case in which the two OH ions would have a common octahedral neighbor. Since the mean frequency of the V band decreases on heating, it might appear that dehydroxylation is easier for OH ions bonded to two divalent ions and a vacancy than for those bonded to two trivalent ions and a vacancy. Vacancies do not appear to be very mobile after they have been involved in dehydroxylation. Otherwise their mobility would provide a mechanism of dehydroxylation of all remaining OH ions.

Oxidation. In biotites the dehydroxylation process is complicated by possible loss of hydrogen as a result of oxidation of Fe²⁺. Changes in the immediate OH environment that may occur during oxidation are analyzed as follows. For simplicity it is assumed that octahedral impurity associations are isolated in brucite-type layer but similar considerations will apply when Fe²⁺ is in higher concentration so that different associations interact. The three closest octahedral ions are indicated between parentheses.



Let us first assume that O²⁻ and Fe³⁺ produced by oxidation stay close together. In the N_B case, the Fe²⁺ interacts closely with two OH

ions, one of which is lost during oxidation, the other becomes I_A . If the two Fe^{2+} are on neighboring a sites, no OH ions will be left close to II_A associations. But if one Fe^{2+} is on a and the other on a neighboring b , the two of them interact with three OH ions of which one will remain and give either a I_A or a II_A band. A III_A band is not possible. It may be concluded that the only survivors of the N-I region will be N_A , I_A and II_A , but of the last two less than at first glance might have been expected.

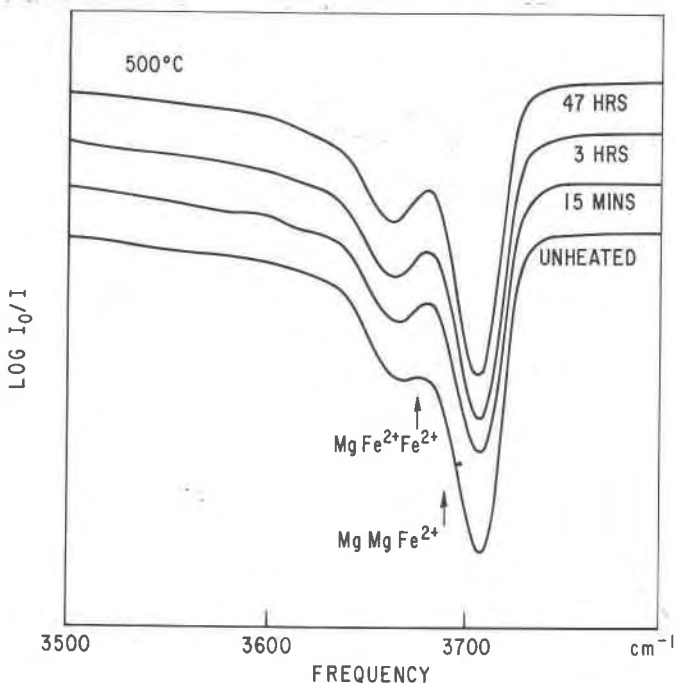


FIG. 5. Biotite 196519 heated in air at 500°C for various periods (KBr discs).

In particular it follows that the N_B , N_C , and N_D bands should disappear resulting in a marked loss of absorption between N_A and I_A bands.

If O^{2-} and Fe^{2+} separate, the ratio of the intensities of N_A , I_A , II_A and III_A is given by simple statistics *e.g.* $(1-x)^3:3x(1-x)^2:3x^2(1-x):x^3$ where x is the fraction of Fe^{3+} ions. The II_A band has not been identified but should occur in the V band region.

Powders (<4 micron) of four biotites covering a $Mg/(Mg+Fe^{2+})$ range of 0.41–0.88 were chosen for decomposition studies. Structural formulae of biotites 196519 and 196513, upon which more complete studies were made, are $K_{1.81}Na_{0.17}(Mg_{4.75}Fe^{2+}_{0.63}Fe^{3+}_{0.17}Al_{0.26}Ti_{0.22})(Si_{3.55}Al_{2.45})O_{20.45}(OH)_{3.09}F_{0.41}Cl_{0.05}$ and $K_{2.02}Na_{0.08}(Mg_{3.03}Fe^{2+}_{1.67}Fe^{3+}_{0.11})$

$\text{Al}_{0.71}\text{Ti}_{0.41}(\text{Si}_{5.73}\text{Al}_{2.27})\text{O}_{21.39}(\text{OH})_{2.15}\text{F}_{0.46}$ respectively. Spectra were obtained with KBr discs.

The results of heating biotite 196519 in air at 500°C for different periods of time are shown in Figure 5. As expected, noticeable loss in intensity occurs between the N and I band peaks. In Figure 6a the N-I region has been resolved by the method proposed by Wilkins (1967). In Figure 6b, all N and I bands resulting from associations containing ferrous ion close to OH have been graphically removed from the cal-

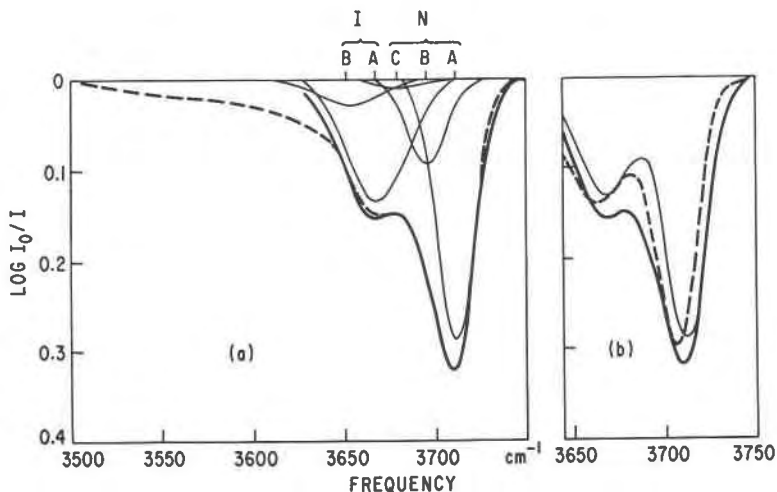


FIG. 6. Resolution of the spectrum of biotite 196519. Observed spectrum at room temperature shown by broken line in (a) compared to the sum (thick line) of the various components (thin lines). In (b) is compared the sum of the components from (a) (thick line) with the shape after removal of all but N_A and I_A (thin line) and the observed spectrum after 47 hours at 500°C from figure 5 (broken line).

culated spectrum. The spectrum of the sample after 47 hours of oxidation closely approaches this shape. This is surprising since we would have anticipated that the annihilation of N_B and N_C associations would result in additional I_A intensity. Both remaining N and I bands are displaced 6 cm^{-1} lower in frequency compared to their original positions.

The results of heating powders of biotite 196513 at 400 and 500°C are shown in Figures 7a and 7b. The N-I region of the unheated powder is shown in Figure 8a resolved into its component bands. Again in Figure 8b all N and I bands associated with hydroxyl close to Fe^{2+} have been removed and the result is compared to the spectrum of the sample after 12 hours of oxidation at 500°C . In this case it is even more surprising that the agreement in figure 8b is good because substantially increased

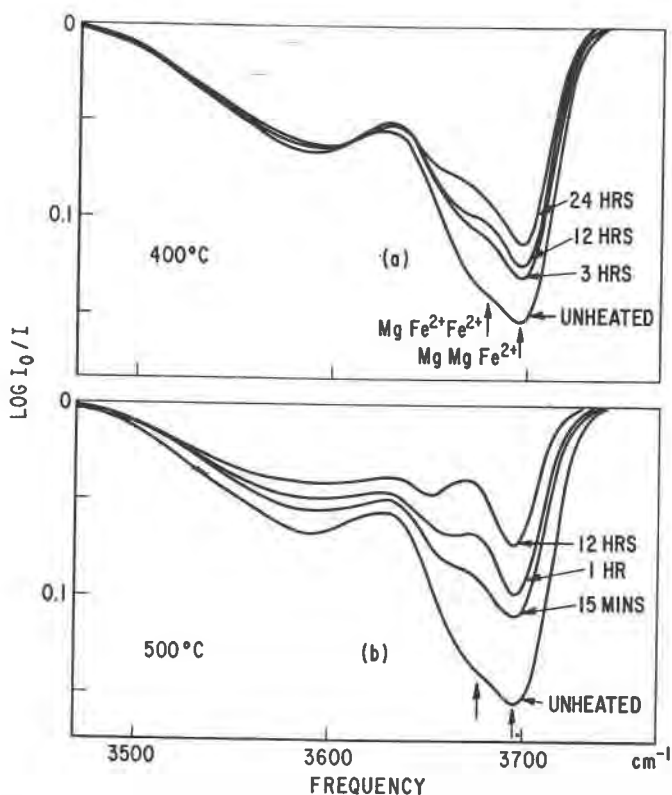


FIG. 7. Changes upon heating biotite 196513 for various periods at 400°C and 500°C.

intensity in the I_A region should have resulted from annihilation of the intense N_B and N_C bands. It is evident that either no new I_A associations are being formed or that protons are being lost from I_A associations. It will be noted that in this specimen N_A and I_A bands are displaced by as much as 16 cm^{-1} to lower frequencies and that at the higher temperature considerable loss in hydroxyl has accrued from sites close to vacancies.

The results from two further iron-rich biotites follow the same pattern. Not exceeding 400°C over periods of as much as 50 hours, a few hydroxyl ions near vacancies are discharged from the structure. In the same period of time, however, a substantial proportion of hydroxyls close to ferrous ions in the structure are destroyed. Given sufficient time it appears they would all be removed. At 500°C both processes occur together and the only region where there is no clear indication of intensity loss is that of the N_A band.

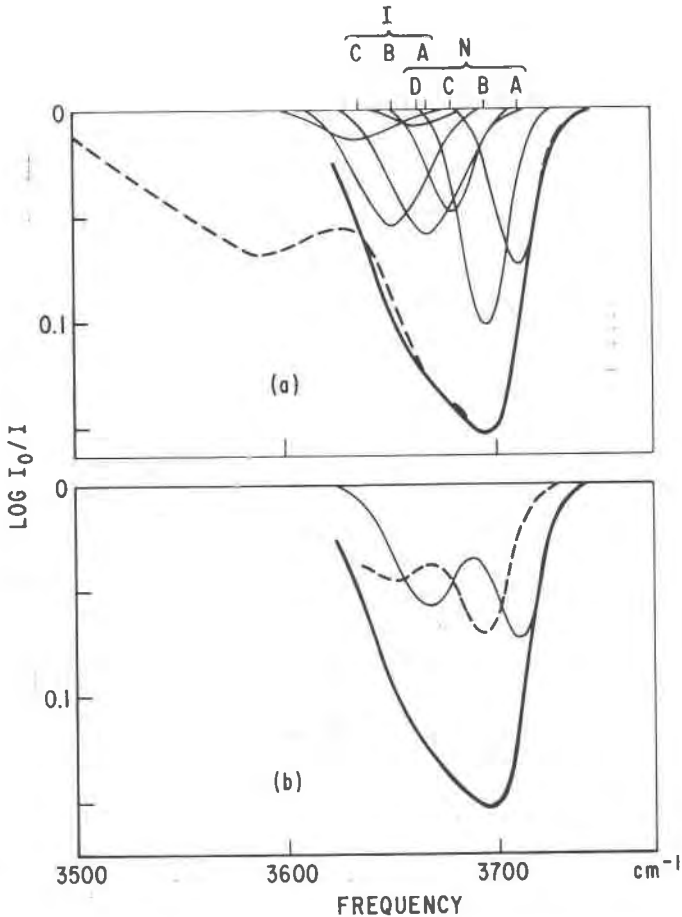


FIG. 8. (a) Spectrum of biotite 196513 before heating (broken line) compared to the sum (thick line) of all component bands (thin lines). (b) Sum of all components from (a) (thick line) compared to the sum of N_A and I_A only (thin line) and the observed spectrum after 12 hours at 500°C from figure 7 (broken line).

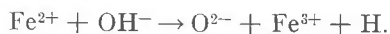
Figures 6 and 8 show that the frequencies of the N_A and I_A bands decrease during thermal decomposition. Hitherto two major controls on the vibration frequency of an isolated hydroxyl ion in a sheet silicate have been recognized. Bassett (1960) first noted the importance of the adjacent octahedral cations. Vedder (in Farmer and Russell, 1966) pointed to the significance of the interlayer cation and Farmer and Russell provided interesting experimental data relating to this effect.

The shift in the N_A and I_A bands may be evidence that changes in a

third structural element can significantly contribute to the vibration frequency. Wones (1963) on the basis of a carefully controlled set of syntheses showed that the *b* dimension of biotites near the join phlogopite-annite decreases with increasing oxybiotite content. The result of replacing larger Fe^{2+} ions with smaller Fe^{3+} ions is to shrink the octahedral layer, forcing the tetrahedral layer into greater ditrigonal distortion to retain its fit.

Although there are no ferrous ions in the first coordination sphere of N_A or I_A hydroxyls, it seems that a considerable proportion of ferrous ions converted to ferric make mere local adjustments to the structure impossible so that a general modification of the silicate net is effected. The result of this adjustment is that alternate oxygen ions are placed closer to the pseudotrigonal axis through the hydroxyl ion, shielding it from the effect of the interlayer cation and, therefore, stretching the OH bond and lowering its vibration frequency. The structural change and consequent reduction in frequency is naturally greater in the more iron-rich biotites. Evidently the method described by Wilkins (1967) and used here to resolve the biotite spectra will give spurious results if there is any substantial proportion of oxybiotite in the biotite. Where such is expected the biotite powder should be reduced in hydrogen before a resolution of the spectrum is attempted.

Biotite-oxybiotite relations in synthetic materials have been studied in some detail by Eugster and Wones (1962), Wones (1963) and Wones and Eugster (1965). The net reaction appears to be (Addison *et al.*, 1962)



This still leaves open the question whether the hydrogen diffuses to the surface atomically or separated into a proton and an electron.

Deuteration and reduction. In connection with the oxidation process it is interesting that a completely reduced talc (a complete account of the work on talc will be published separately) deuterates significantly more slowly than a partially oxidized sample. Also, upon deuteration, *all* N bands are exchanged, not only the ones associated with hydroxyl close to ferrous ions.

During deuteration, particularly in case of a reduced talc, the concentration of proton vacancies must be minimal. We therefore conclude that H-D exchange, and presumably also dehydrogenation and rehydrogenation, though accelerated by proton vacancies, are not exclusively dependent on their presence.

For comparison with talc, powders of biotites 196519 and 196513 were heated in air at 500°C for 48 hrs and 15 min, respectively. The oxidized

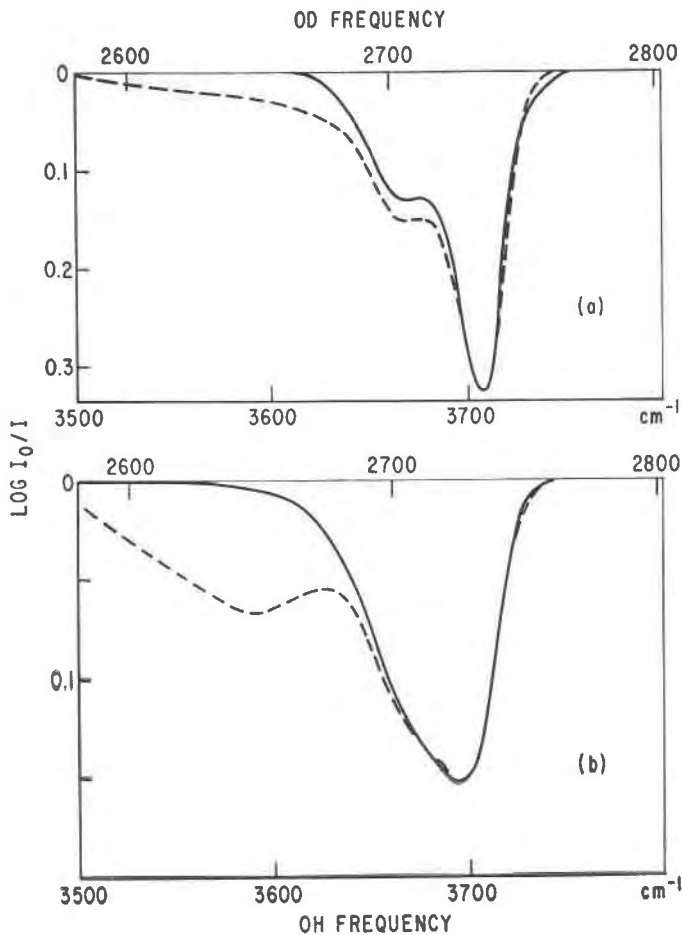


FIG. 9. (a) Biotite 196519 before (---) and after oxidation followed by reduction in D_2 (—). (b) Biotite 196513 before (---) and after oxidation followed by reduction in D_2 (—). The use of an OH frequency scale and an OD frequency scale is explained in the text.

powders were then reduced in $D_2(+He)$ for 48 hrs at the same temperature. This resulted in almost complete deuteration. In both cases there was a simple relationship between the spectrum in the OH region of the unheated material and the spectrum obtained after oxidation in D_2 , as is shown in Figure 9. Frequencies in the OH and OD region are related by a factor 1.356 (value for isolated OH ions 1.358) and using this factor the spectra have been superimposed. Also absorbances were adjusted so that peak heights are the same.

In both cases the fit between N and I regions before and after reduction, though not perfect, is good. This proves that with temperatures up to 500°C at least no large amount of OH loss by condensation of hydroxyl ions in N or I sites has occurred. Most of the intensity loss in the N-I region upon heating in air is due to loss of hydrogen from sites close to Fe^{2+} .

For hydroxyl ions situated close to vacancies, however, the spectra show quite the reverse situation. The V band is almost entirely lost during oxidation and subsequent reduction. Particularly with biotite 196513, because of its high iron content, it must be assumed that many of the octahedral cations in vacancy associations are Fe^{2+} . The three associations Fe^{2+}MgV , $\text{Fe}^{2+}\text{Fe}^{2+}\text{V}$ and Fe^{2+}AlV are almost certainly present in appreciable concentration. If the intensity loss in the V band had been due to hydrogen loss from hydroxyls close to Fe^{2+} ions the band would have been restored during reduction. The results show, therefore, that here all the hydroxyl loss is by OH condensation.

The first sight it seems difficult to explain the complete loss of the V band from the spectrum since the 196513, 15 min spectrum of Figure 7 still has most of the original band intact. It is concluded that the remainder of the band is removed by OH condensation during the long period of heating in the reducing atmosphere during which the partial pressure of water vapor is very low. This then leaves open the possibility that some loss of hydrogen may still occur by reaction of OH^- with Fe^{2+} in vacancy associations during oxidation and that those hydroxyls, reformed by reduction, are subsequently lost by OH condensation under the reducing conditions used. Differences before and after reduction which do exist in the N and I region, occur especially in the I band and are too large to be explained by vacancy band overlap or inaccuracies in the method. We have also noted that during oxidation less intensity accumulates in the I_A band than we anticipated. It is possible that exchange of protons between I and V positions provides a mechanism for loss of OH by condensation. However, in that case it would be difficult to see how most of the N-I region can be restored by reduction. It seems more likely that as the Fe^{2+} concentration increases fewer I_A associations result from oxidation than is predicted for isolated N_B and N_C associations.

Weight loss. Thermogravimetric data on the decomposition of the hydrous silicates are widely recorded in the literature. In conjunction with our previous results it was particularly interesting to see whether weight loss within a specific temperature interval could be correlated with changes in intensity of some of the OH absorption bands. Spectra were recorded at

room temperature with layers of 20 to 100 micron thickness pressed between two NaCl plates again using hexachlorobutadiene to reduce interference phenomena. Perpendicular incidence and a 40° tilted orientation were used. The light was polarized in the plane of incidence. In cases of measurable optical anisotropy in the cleavage plane, the two principal directions were determined and spectra were recorded with the electric vector along each separately. Previous work had indicated that optically determined principal directions and crystallographic axes coincide.

Weight loss was recorded continuously at a rate of 10° per hour from room temperature to 1050°C on a Chevenard thermobalance. Overall accuracy was better than 0.05 percent which, however, still means that in some cases of low weight loss the measurement was not very precise. Starting material consisted of mica strips cut to a size of 1–2 by 5–10 mm. Weight loss was also determined after heating at 1200°C for 4 hours.

To obtain a measure of the integrated intensity of the V bands, a correction was applied for the overlap with the I band as follows: assuming that the intensity of the V bands does not depend on orientation at all and that the change of intensity of the N and I bands with orientation is the same for all samples, the difference between the integrated intensities of the whole OH stretching absorption band of perpendicular and 40° tilted orientations should be a true measure of the intensity of the N+I band system. This quantity could subsequently be used to subtract the N+I contribution from the integrated intensity in the perpendicular orientation leaving the intensity of the V bands. Corrected integrated intensities were reproducible to about 3 percent, but larger systematic errors are undoubtedly present.

We have shown that OH ions disappear from the structure by condensation across a vacancy followed by removal of water by diffusion. This process is accelerated when the water concentration becomes so large that the corresponding water pressure leads to delamination of the mica, thus reducing diffusion distances. The higher the water concentration, the lower will be the temperature needed to cause delamination and accelerated water loss. The larger the V band then, the lower the temperature at which important losses of H₂O occur. The thermogravimetric records of three samples showing this correlation are shown in Figure 10.

Below 500°C, weight losses were assumed to be due to adsorbed or occluded water. One of the samples lost about 0.1 percent weight below 500°C and the presence of water showed up clearly in the infrared spectrum as a very broad band with its center at about 3370 cm⁻¹. Some hydrogen could also be lost below 500°C.

Above 950°C loss of weight was observed even in samples which,

judging from the infrared spectrum, did not contain any OH ions close to octahedral vacancies. For these reasons weight reduction between 500 and 950°C were assumed to be due mainly to loss of OH ions near octahedral vacancies.

The integrated intensity of the V bands normalized by a factor chosen to numerically match the weight loss exactly for sample W#4 and the weight losses between 500° and 950°C are compared in Figure 11. The average precision of the data is also indicated in that figure. Points are scattered around the expected relationship. Many reasons for this can be suggested, such as the presence of small amounts of occluded water which

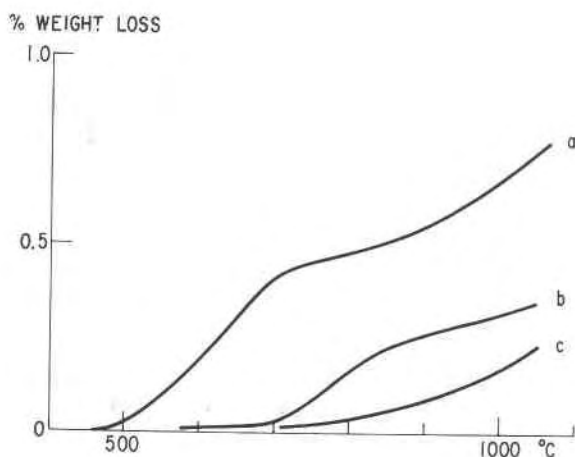


FIG. 10. Thermogravimetric record of *a*, biotite (Conklingville, N. Y.), *b*, biotite (W#10), *c*, Canadian phlogopite (W#11).

resist expulsion even at 500°C and the oxidation of ferrous content and release of hydrogen. The latter factor allows the possibility of fairly substantial errors in the more iron-rich biotites and the errors may occur in two ways.

First, hydrogen lost from N and I associations is not included in the spectroscopic measurement. Secondly, if hydrogen is lost from the vacancy associations which include Fe^{2+} , the infrared estimate which assumes hydroxyl condensation and loss of H_2O will be too high. Also some of the assumptions underlying the procedure need not hold very accurately, *e.g.*, the intensity of absorption of an OH ion will certainly depend upon its environment whereas here it is supposed to be invariant.

Even where analytical data are available it is not easy to apply corrections to the data. But some indication of the relative magnitude of the errors possible for each sample is given by the weight loss data at 1200°C.

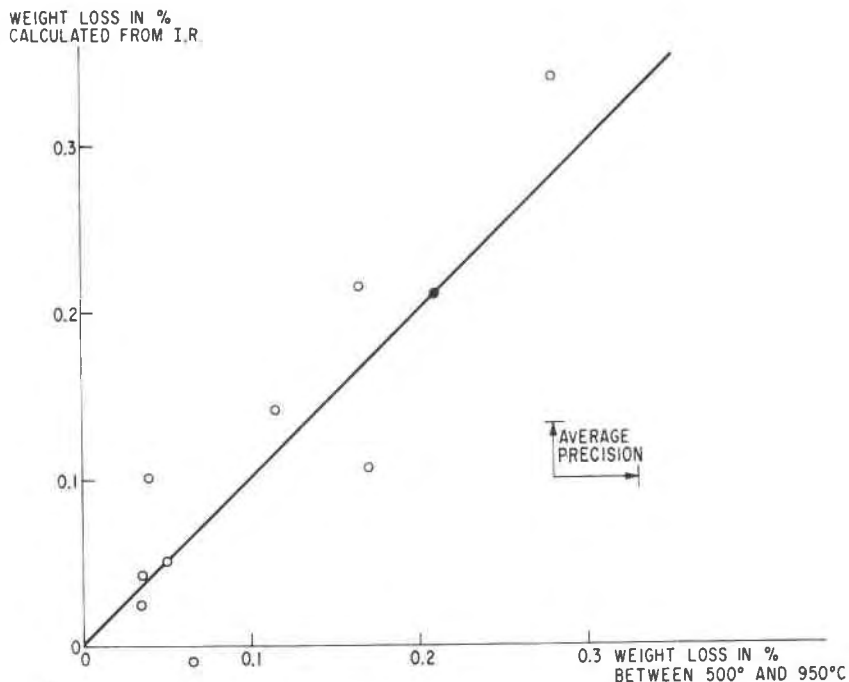


FIG. 11. Correlation between infrared intensities and weight losses measured between 500°C and 950°C. Sample W#4 was used to normalize the infrared data and is indicated by the filled circle.

It is generally assumed that under these conditions all OH and F are lost from the structure. Low weight loss is related primarily to initial high Fe^{2+} content and high loss of H_2 instead of H_2O during heating. Qualitative corrections made to the data on this basis suggest that this is one of the main reasons for the scattering of the data.

PHLOGOPITE

Pure phlogopite has no vacancies in the octahedral layer and all sites are filled with Mg. Thin sheets of an unusually pure natural phlogopite¹ (M#1; Vedder, 1964) were heated in air for one hour periods at 10° temperature intervals between 1000 and 1100°C. Spectra indicated that hydroxyl ions were not lost from the structure until about 1080° when visible recrystallization became evident. At 1100° dehydroxylation was rapid. There was no evidence of a dehydroxylated phase.

¹ Obtained through the courtesy of Mr. E. Lachance from Mica Company of Canada Ltd, Hull, Quebec.

Impurity trivalent ions in the octahedral layer of this specimen produce a small I band. During the heating process the intensity ratio between N and I bands remained constant until the recrystallization temperature showing once more that dehydroxylation near filled parts of the octahedral layer is difficult to achieve regardless of the nature of the ions filling these sites.

DISCUSSION AND CONCLUSIONS

Comparison of dehydroxylation and oxidation in muscovite, phlogopite and biotite: At 600°C and about 10 bars a thin sheet of muscovite can be virtually completely deuterated without dehydroxylation. It follows that under these conditions normal muscovite is still more stable than the dehydroxylated mica. It also appears likely that deuteration takes place via diffusion.

At 600°C in the atmosphere muscovite will dehydroxylate. The equilibrium pressure of the dehydroxylation is therefore somewhere between 10 bars and a few centimeters of H₂O pressure, as compared to the 25 bars extrapolated from data in the literature for the decomposition of muscovite to H₂O+sanidine+corundum.

Distortion of the silicate network as a result of dehydroxylation can be observed in the infrared spectrum. The spectra show that if the mica is rehydroxylated the OH ions return to their original sites and orientations and the silicate network reverts to its original structure. This shows that a heterogeneous mechanism of dehydroxylation (Nicol, 1964) is unacceptable.

In contrast to muscovite, pure phlogopite is much more resistant to thermal decomposition. No dehydroxylated phase has been detected before structural breakdown at about 1080°C. As DeVries and Roy (1958) have observed and is fully supported by this study, the essential feature of those layer silicates which lose H₂O at relatively lower temperatures is the presence of vacancies in the octahedral layer. In biotites, where the structural characteristics of both phlogopite and muscovite are to be found, hydroxyl ions near vacancies are lost at temperatures of the order of 500°C in powders and even in large sheets are entirely lost before 850°C in periods of less than 24 hours.

The similarity of the dehydroxylation of muscovite and biotite suggests that in both cases it is the same process *i.e.*, local formation of H₂O molecules across vacancies and subsequent release by diffusion and delamination. The diffraction data by Eberhart (1963) together with the spectroscopic data presented here indicate that the structural change is a removal of H₂O leaving an O²⁻ ion behind in an only slightly distorted

silicate network. Near filled parts of the octahedral layer, OH ions tend to be retained until temperatures in excess of 1000°C are reached.

Gaines and Vedder (1964) pointed out that at 730°C and higher, H₂O escape is greatly facilitated by exfoliation and the resulting reduction in diffusion distances. It is, therefore, not surprising that Holt *et al.* (1958, 1964) found that between 738 and 817°C the dehydroxylation had proceeded equally far throughout the macroscopic thickness of their sheets. Considering the complicating influence of delamination, their conclusion that the activation energy increases with the degree of dehydroxylation should be reviewed.

Fuji (1966) concluded, on the basis of X-ray data, that at any stage of dehydroxylation a partially dehydroxylated mica consists of a mixture of a normal and a dehydroxylated phase. The bearing of the infrared spectra on this point is not clear and is still under study.

The simple scheme of decomposition outlined above is complicated by the presence of Fe²⁺ in biotite where it occurs as an essential constituent. It has been established that in powders, even at temperatures lower than 400°C, ferrous ion in biotites heated in air is oxidized to ferric with concomitant release of hydrogen.

Mechanism of dehydroxylation and oxidation. Addison *et al.* (1962) have discussed a model for release of hydrogen from amphiboles. Basically there are two possibilities: either the hydrogen moves atomically, or it moves separately as proton and electron, combination occurring at the surface. These authors favor a movement of protons from oxygen atom to oxygen atom to the surface and a simultaneous migration of electrons by an electron transfer process between Fe²⁺ and Fe³⁺ in the octahedral layer. The present data on oxidation and deuterium reduction of biotite (and preliminary results on talc) have shown that the movement of protons in layer silicates can not be exclusively a random interstitial process.

The question of whether hydrogen moves by itself or dissociated into H⁺ and e, and whether H₂O moves as a molecule or dissociated as H⁺ and OH⁻, is difficult to answer. The best approach may be to consider first that the field produced by the displacement of a single electron charge over a distance of a few Å is considerable: of the order of 10⁷ volts/cm. Therefore, for H⁺ and e to move independently it would be necessary that their mobilities be different by as much as seven orders of magnitude.

In the case of H⁺ and e, it is possible to make some rough estimates. Talc platelets of a few micron thickness can be deuterated for 50 percent

in about 20 hrs. at 660°C. Assuming this process to take place by a proton diffusion mechanism the proton diffusion coefficient would be about 10^{-13} cm²/sec. This value comes quite close to the rate of proton diffusion in boehmite (2×10^{-13} cm²/sec at 660°; extrapolated from data at low temperature of Wei and Bernstein, 1959). The mobility of a proton would be 10^{-12} cm²/volt sec. We would assume that a value in the same order of magnitude applies to the micas.

Values for the resistivity of phlogopite at 660°C vary over at least seven orders of magnitude from a high of about 5×10^{10} ohm cm (Clark, 1962).¹ Assuming that in the lower range the conductivity is electronic, that an electron is available for each iron atom in the lattice and that 20 percent of the magnesium is substituted by iron it follows that the mobility of electrons varies from 5×10^{-7} to 5×10^{-14} cm²/V sec. Similarly, the resistivity of crocidolite along the chain direction is in the order of 10^8 – 10^9 ohm cm at 660°C (Littler and Williams, 1965).

It follows that even in the iron-rich micas it is probably correct to describe the mechanism of oxidation in the sense that electrons and protons travel in tandem with the field produced by an electron jump inducing a proton to follow.

We believe that during dehydroxylation similar considerations make it improbable that H⁺ and OH⁻ move independently.

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¹ Perpendicularly to the layer; unfortunately we are not aware of such data parallel to the layer.

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