

# STUDIES IN POSITION AND MOBILITY OF THE H ATOMS IN HYDROUS MICAS

*by*

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## ABSTRACT

The hydrogen content of dioctahedral and trioctahedral micas has been investigated by means of infrared spectroscopy and radioactive measurements. Dioctahedral and trioctahedral micas have been treated with deuterium oxide and tritium-bearing water. The introduced isotopes of hydrogen have been determined after various thermal treatments.

It is concluded that dioctahedral hydrous micas may represent mixed crystals between  $\text{K}(\text{Si}_3\text{Al})\text{Al}_2\text{O}_{10}(\text{OH})_2$  and  $\text{H}_2\text{O}(\text{Si}_3\text{Al})\text{Al}_2\text{O}_9(\text{OH})_3$ , whereas trioctahedral micas seem to represent mixed layer minerals between phlogopite and vermiculite.

## INTRODUCTION

The present paper represents the first report on a series of investigations carried out at the Geological Institute, Oslo University, mainly by Per Jørgensen and the present author. We have tried, by means of radioactive technique and other procedures, to follow up the mobility and exchange properties of the various components in micas, mainly in the hydrous varieties. We hope to present a collective paper on the results obtained in the not too far future.

The work has been sponsored by the Norwegian Research Council for Science and the Humanities, to whom we are indebted for economic aid. We are further thankful for help and measurements carried out at the Institute for Nuclear Energy, Kjeller, and would like to thank Mr. Gunnar Eia, The Central Institute for Industrial Research, and Mr. Just Grundnes, Chemical Institute, Oslo University.

## MATERIALS AND STRUCTURAL CONCEPTS

The structure of the mica minerals has been known in general for many years. The refined studies by E. W. Radoslovich (1960 and 1962) confirm the general picture, but prove conclusively that the tetrahedral layer is di-triagonally arranged, so that the interlayer alkali ions are not twelve-coordinated to oxygen, but six + six coordinated in a double oxygen shell. Various hydrous micas have been described in literature. None of them have

been examined in the same refined way as was done for the muscovite mica by Radoslovich.

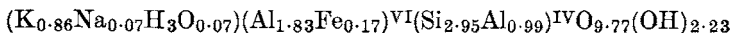
In very many cases it seems that the hydrous micas represent interstratified minerals with montmorillonite, chlorite or vermiculite sandwiched between layers with the structure of true micas, or mica with alkali deficiencies. Especially in the case of soil-forming minerals admixture of alien material makes investigations and analyses complicated. As a rule there seems to be a correlation between the potassium deficit and the discrepancy from the mica structure, probably because of interstratification.

In order to investigate the bonding conditions in dioctahedral and trioctahedral micas having deficit in alkali content, we selected a muscovite and a phlogopite, both of them with fairly well developed crystals, but with marked deficit in the alkali content and surplus in the hydrogen content. The reason for selecting micas with large crystal size instead of investigating the mica minerals of the clay fraction in actual soils was partly due to our interest in examining the influence of surface-adsorbed vapour. This could only be done if a material of identical composition, but various grain size was available. In the infrared technique used, flakes from single crystals were necessary. As the macro crystals did not have the same high alkali deficit as found in the soil minerals, we concentrated on material not very remote from the composition of the ideal alkali micas. This will, however, be an advantage, as interstratification is not as likely in these micas as in those with a greater discrepancy from the ideal formula.

The dioctahedral mica used was a hydro-muscovite from Bjortjenn, Aust-Agder, South-Eastern Norway. The trioctahedral mica was a phlogopite from Skåtøy, South-Eastern Norway. Both micas were examined for purity by X-ray diffraction inspection. The hydro-muscovite gave a perfect 2 M muscovite X-ray pattern. We prepared samples of controlled grain size by means of sedimentation and microscopic control. The flake thickness was 0.8 micron  $\pm$  0.2 micron, the edge length 10–20 microns.

Chemical analysis of the hydro-muscovite was carried out by Mr. Finn Langmyhr at the University's Chemical Institute, and the phlogopite was analysed by Mr. C. U. Wetlesen at the Central Institute for Industrial Research.

Recalculating these analyses (*see Table 1 opposite*) on the basis of the dioctahedral mica structure using Brown and Norrish (1952) concept of hydronium ion in the interlayer position, combined with the Hendricks and Jefferson (1938) concept, i.e. replacement of  $O^{-2}$  by  $(OH)^-$  in the vermiculite structure, we arrive at the following formula for hydro-muscovite:



or, if calculated on the assumption that part of the +110°C water is adsorbed and not entering into the structure, the following formula is obtained for the hydro muscovite:

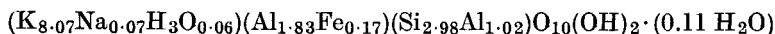
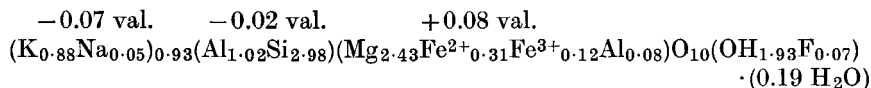


TABLE 1.

Muscovite:		Phlogopite:	
SiO <sub>2</sub>	44.30%	SiO <sub>2</sub>	40.32%
Al <sub>2</sub> O <sub>3</sub>	35.95%	TiO <sub>2</sub>	3.54%
Fe <sub>2</sub> O <sub>3</sub>	3.26%	Al <sub>2</sub> O <sub>3</sub>	12.63%
MnO	0.09%	Fe <sub>2</sub> O <sub>3</sub>	2.30%
K <sub>2</sub> O	10.20%	FeO	5.03%
Na <sub>2</sub> O	0.55%	MgO	22.02%
H <sub>2</sub> O (< 110°C)	0.03%	Na <sub>2</sub> O	0.36%
H <sub>2</sub> O (> 110°C)	5.47%	K <sub>2</sub> O	9.32%
	<hr/>	H <sub>2</sub> O (+)	4.0 %
	Σ 99.85%	F	0.3 %
	<hr/> <hr/>		<hr/> <hr/>
			Σ 99.82%
			<hr/> <hr/>
	In addition:		
V	1/10%	} spectrographically	
Ni and Cu	1/100%		
Mn and Co	1/1000%		
Ca not found	(< 1/10%)		

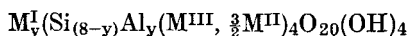
The analysis of the phlogopite does not permit a recalculation to an ideal trioctahedral formula. If the analysis is recalculated on the basis of trioctahedral structure omitting the titanium oxide which seems to be present as rutile needles, we arrive at the following formula:



The deficit in the interlayer position of 7 per cent can hardly be occupied by H<sub>3</sub>O<sup>+</sup> for valency reasons. The vacancies may be filled with water molecules. As, however, our investigations seem to indicate that this material represents some mixed layer mineral, although this is not revealed from the X-ray data, no such recalculation has been done.

The positions and exchangeabilities of the hydrogen atoms in mica structures have been discussed ever since Grim, Bray and Bradley (1937) demonstrated that soil-forming mica minerals occur with a marked deficit in potassium content compared to the potassium content of the ideal structural formula. At the same time these clay-forming micas, as published by E. Maegdefrau (1941), had hydrogen contents above that of rock-forming minerals, the hydrogen surplus seemingly increasing by decreasing potassium content. When G. Brown and K. Norrish (1952) suggested that the hydrous mica could be derived from the ideal mica structure by substituting H<sub>3</sub>O<sup>+</sup> for K<sup>+</sup>, their formula introduced a new concept, and it was adopted by very many clay scientists. The main advantage in Brown and Norrish's formula as compared to Maegdefrau's was that according to Maegdefrau, rock-forming mica could only lose potassium if silicon at the same time substituted Al in

the tetrahedral position. A metasomatic double replacement is necessary in order to fulfil transformations within the Maegdefrau formula



In many cases it seems as if muscovite can transform into hydrous micas (illites or hydro-muscovites) by leaching in water at low temperatures, without simultaneous metasomatic exchange of Al by Si.

The Brown and Norrish formula fits with the chemical analysis, whereas the Grim, Bray and Bradley or Maegdefrau formula does not fit with several of the published analyses of such minerals. Only rarely are hydrous micas or illites found with less than 50 per cent of the corresponding ideal mica formula.

In some rare cases, for instance as described by Bengt Lindqvist (1959), micas which seem to have 73 per cent deficit in potassium are found. The chemical analysis in this case corresponds to a mixed crystal between the  $K(Si_3Al)Al_2O_{10}(OH)_2$  and  $H_3O(Si_3Al)Al_2O_{10}(OH)_2$ . If Lindqvist's material represents a true crystalline structure and no mixed layer mineral, his and various other analyses give a strong support to the Brown and Norrish suggestion. This formula has consequently been adopted by a great number of research workers. However, it has also been disputed, among others by J. Erdelyi and co-workers (1958-1959a and 1959b). Based on chemical and differential-thermal analyses combined with X-ray investigations they disagree with the structural type suggested by Brown and Norrish, but agree in the general chemical formula which can be derived from this structure. They assume that a part of the oxygen atoms in the backbone elements are substituted by OH in amounts equivalent to the alkali deficit in the dodecahedral positions. According to their formula these minerals should have vacancies in the dodecahedral layer of an amount corresponding to the deficit in negative charges of the backbone elements. In hydrous micas it is assumed that the number of ions in the dodecahedral positions depends solely upon the number of trivalent ions in the tetrahedral positions. The methods applied by them do not seem to make it possible to ascertain whether the vacancies in the dodecahedral positions are empty or filled by a neutral water molecule. According to the papers cited it seems as if the first alternative is the one chosen by the authors.

In a previous paper by Moum and Rosenqvist (1958), "Hydrogen (protium) deuterium exchange in clays", exchange reactions have been carried out on clay material from Åsrum, Southern Norway. At this time we used the Brown and Norrish formula. We found that hydrogen was present in at least three different states, even in material dried at 110°C. For that specific clay it was found that 13 per cent of the hydrogen content at 110°C was to be considered as adsorbed water. This water undergoes very quick exchange reactions with the surrounding water. 17 per cent of the hydrogen content at 110°C was considered to be present as  $H_3O^+$ . This hydrogen undergoes slow exchange reactions with the surrounding water. Equilibrium is obtained after a few weeks. The rest of the hydrogen, 70 per cent, undergoes a very slow exchange

reaction. Even for fine clay material equilibrium is far from reached after two years at 110°C. This hydrogen is considered as being present in OH<sup>-</sup> positions.

By the type of exchange reactions used in the paper quoted, it was not possible to ascertain whether H<sub>3</sub>O<sup>+</sup> or any other type of bonded hydrogen existed in the dodecahedral position. We could state only that hydrogen in illites had three modes of occurrence. The OH groups of micas are known to be differently bonded in trioctahedral and dioctahedral micas. White and co-workers (1961) showed this from the bending frequencies of the OH bonds at about 935 cm<sup>-1</sup>.

By infrared investigations of the stretching frequencies of the OH bonds in dioctahedral and trioctahedral micas, J. M. Serratos and W. F. Bradley (1958) found marked differences, viz. 3620 and 3710 cm<sup>-1</sup> respectively. Furthermore, the intensity of the adsorption depended upon the direction of the vibration plane of the infrared light which passed trioctahedral flakes. The fact that the stretching frequency of the OH bond in the dioctahedral micas was lower than in the trioctahedral equivalents most probably is due to the weak hydrogen bond from OH groups to the neighbouring oxygens, whereas by the trioctahedral mica the OH axis is probably oriented normal to the cleavage plane, without any secondary hydrogen bond to any other oxygen. In lepidolite they found a combination of the two types of bonds.

Based on the assumption that the hydrogen in the two micas presented above represents the same type, although not in the same relative amount as in clayforming micas, we investigated the material by aid of the two isotopes of H, viz. D and T.

## INFRARED INVESTIGATIONS

For various reasons we concentrated the infrared investigations on the hydro-muscovite whose data are given above, whereas the phlogopite was not investigated by I.R. As the hydro-muscovite clearly deviated from the ideal formula, either H<sub>3</sub>O<sup>+</sup> groups or H<sub>2</sub>O molecules must be present. For the examinations we have used the following equipment:

Perkin-Elmer Mod. 21 Infrared Spectrophotometer, and  
 Unicam Infrared spectrophotometer S.P. 100 NaCl prism and grating.

The following type of samples have been investigated: single flakes and pellets of mica powder embedded in KBr. This was done in order to elucidate the influence of surface-adsorbed water, which will be present in much higher amounts in a powder sample than in a single flake.

In order to follow up the exchange and mobility of the hydrogen atoms in the structure, the mica powder was kept in quartz tubes at 125°C for half a year in D<sub>2</sub>O. From the previous experiments by Moum and Rosenqvist (1958) we knew that such a treatment will replace most of the hydrogen supposed to be present in the interlayer position (the H<sub>3</sub>O hydrogen according to Brown and Norrish concept), whereas very little of the OH hydrogen is

substituted. For the I.R. investigation the  $D_2O$  treated powder was divided into four samples, one dried at room temperature, one heated for 5 hr to  $100^\circ C$ , one heated for 5 hr to  $300^\circ C$ , and one heated for 5 hr to  $500^\circ C$ . Figures 1 and 2 give the result of the I.R. investigation.

The difference between the powder and the flake of the same material is chiefly seen in the weak double absorption band at  $2830\text{--}2900\text{ cm}^{-1}$ , curves B–F. This effect is not present in the flake. We assume it to be due to moisture adsorbed from the atmosphere. The same bands are refound more or less clearly in the other powder samples, even though they have been preheated to temperatures up to  $500^\circ C$  before they were left to cool in air. It indicates that this adsorbed water is readily re-adsorbed from the moisture of the atmosphere, even though it may be driven off by heating. In the powder samples we have the absorption band around  $3400\text{ cm}^{-1}$  due to the KBr. In the same region there is also a slight depression in the flake which cannot be explained by the influence of the KBr. The maximal extinction was found to be situated at  $3625\text{ cm}^{-1}$ , Fig. 2, in agreement with the findings of Serratos and Bradley. By the powders which had been heated for 180 days at  $125^\circ C$  in  $D_2O$ , an additional band at  $2650\text{ cm}^{-1}$  was found. This new band must be due to the partial protium–deuterium exchange. The wave length ratio OD/OH found is 1:375 as compared to 1:35 as found by Nathan Ockman (1958). It seems that the O–D extinction remains unchanged even after 5 hr of heating at  $100^\circ C$ , but nearly completely disappeared after 5 hr at  $300^\circ C$  (Fig. 1 curve E) and remained at the same low value after 5 hr at  $500^\circ C$  (Fig. 1 curve F).

Thus we have to conclude that a distinct part of the hydrogen in the micas is replaced by deuterium after 180 days. This part does not represent the adsorbed water, nor does it represent the normal OH groups of the mica structure. The fact that the OD band nearly completely disappears by heating to  $300^\circ C$  for 5 hr makes it improbable that this hydrogen can be present as  $D_3O^+$ . The assumption of such bonding conditions for deuterium would have resulted in a loss of nearly  $2/3$  of the deuterium by heating to  $300^\circ C$ . As the deuterium–protium exchange must be statistical, the cracking of the  $D_3O^+$  group would have resulted in a loss of  $D_2O$  and one  $D^+$  left in the structure to combine with the basal oxygens of the tetrahedral layers. The fact that a small part of the OD band remains unchanged at higher temperatures is explained by us in the same way as earlier by Moun and Rosenqvist, namely that some of the OH groups of the structure are also exchanged by OD.

The conclusion as to the infrared data is that the deuterium represented by the  $2650\text{ cm}^{-1}$  band is due to two types of bonding, namely distinct water molecules in separate positions, the frequencies of the I.R. absorption overlapping the OH bonds of the octahedral layers. Consequently, the  $3625\text{ cm}^{-1}$  band also represents a combination of the stretching frequencies from the OH and the water molecules of no or very weak hydrogen bonding. The fine structure of the  $3625\text{ cm}^{-1}$  peak indicates that the bonding conditions for the H and O cannot be simple, but represent various bonds of nearly the same energy.

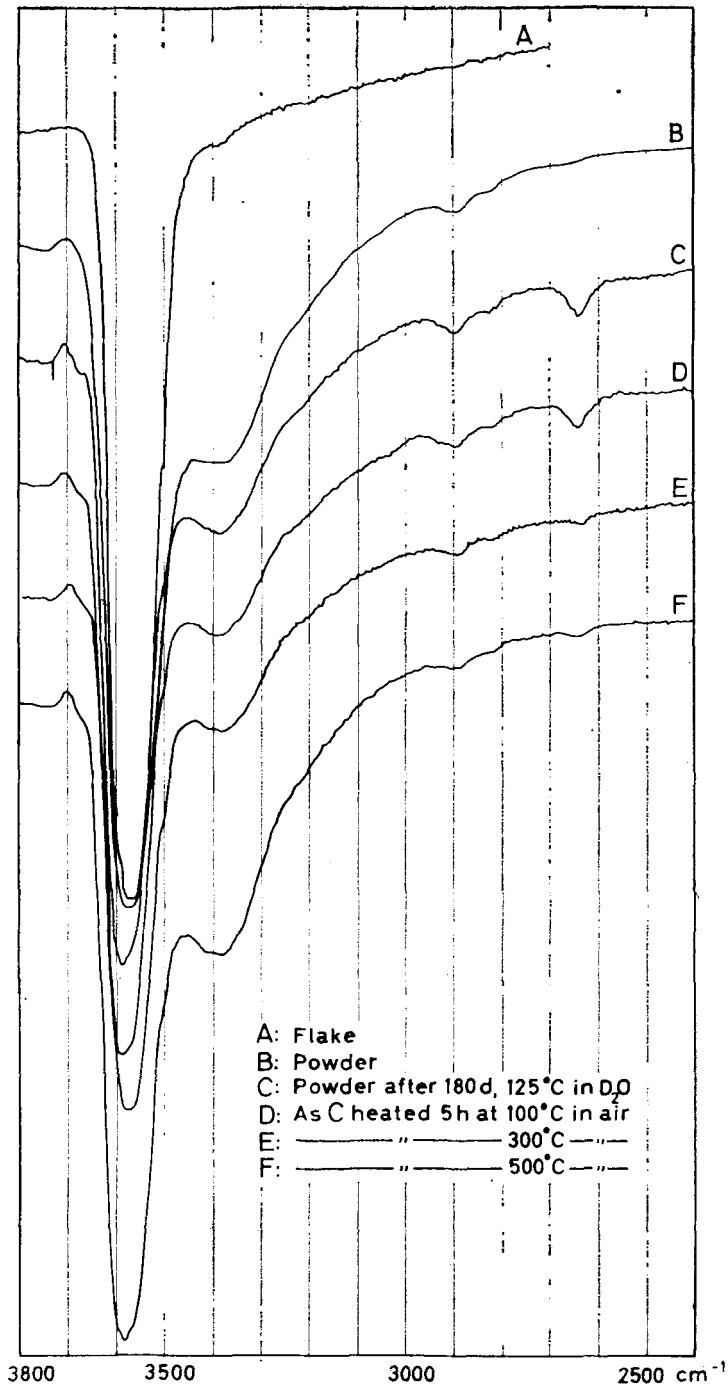


FIGURE 1.—Infrared absorption spectrogram of micas pretreated in various ways, Perkin-Elmer Mod. 21. Curves B-F tablets with KBr.

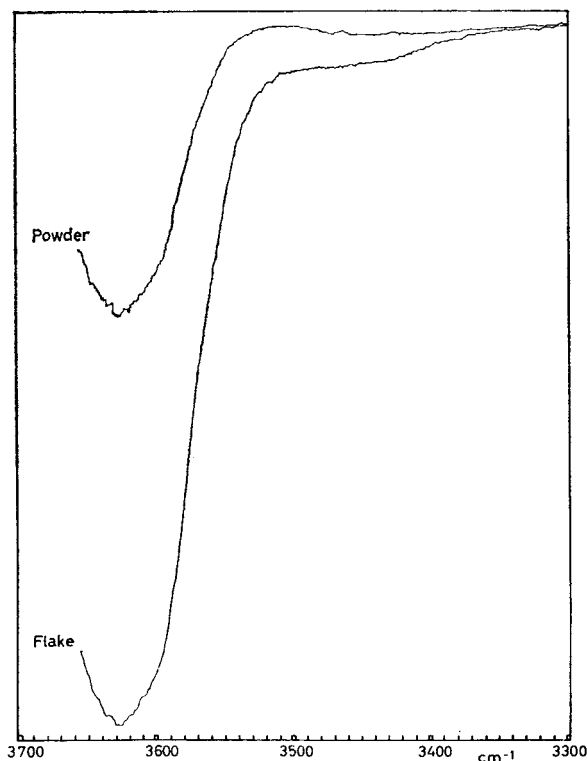


FIGURE 2.—Infrared absorption spectrogram of hydro-muscovite.  
Unicam SP 100.

### TRITIUM-PROTIUM EXCHANGE IN MICAS

In order to follow up the exchange reactions and mobilities of the various hydrogen positions by tagged atoms, tritium-bearing water was used, the tritium content being 2 mc/ml. One gram of mineral powder was heated together with  $\frac{1}{2}$  ml of this water at various temperatures and times. After this treatment one part of the mineral powder was separated from the water in excess of the adsorbed phase by keeping the powder in an exicator at 47 per cent relative humidity for four days. The vapour had the same relative radioactivity as the water used, i.e. 2 mc per gram water. In another series the mineral powder was dried in air at 110°C for 1 to 2 hr. In this case the air had a normal content of normal water, i.e. relative humidity of the order of 0.5 per cent.

After such pretreatments the samples were placed in a tube furnace, and slowly heated to a temperature of 1150°C in a stream of dried air. The rate of



heating was 100°C per hr. The air which passed the furnace was cooled in an U-shaped condensing tube using liquid nitrogen as cooling medium. For each 100°C the U-tube was changed. The vapour in the air which condensed in the U-shaped tube was weighed, and subsequently dissolved in 10 ml dioxan.

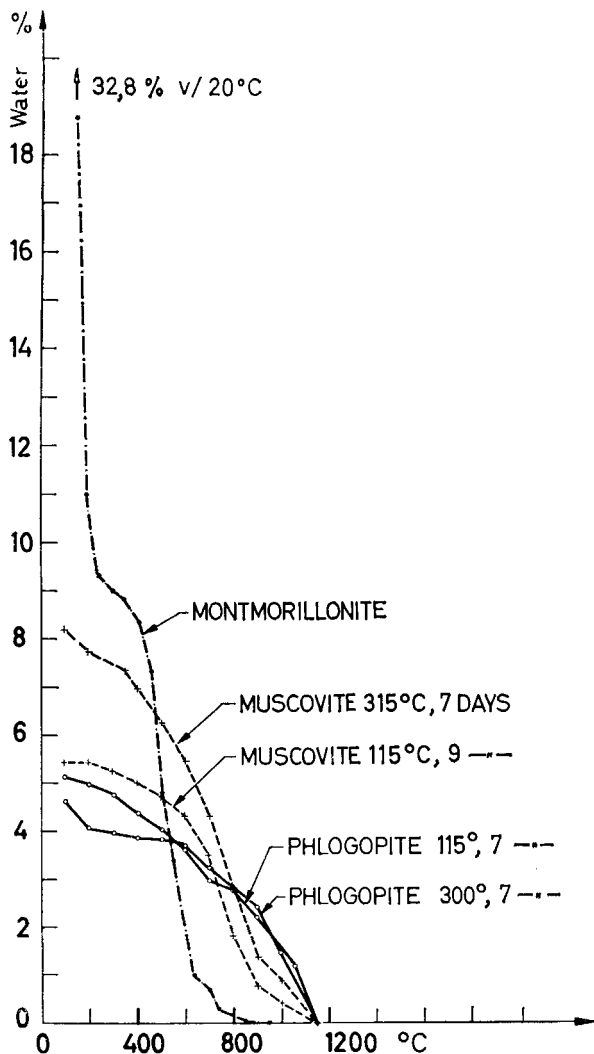


FIGURE 3.—Gravimetric records of the water contents of treated mica preparations at elevated temperatures.

The radioactivity of this dioxan-water solution was measured and compared with standard solutions containing 1 and 100 mg of tritium water and 10 ml

dioxan respectively. Figure 3 shows the cumulative weight curves of the water content of the minerals after heating at 7 to 9 days at 115–315°C in tritium water. For the sake of comparison the corresponding curve from a calcium montmorillonite from Namdalen is added.

Figure 4 shows the relative radioactivity of the various water fractions from samples of muscovite pretreated in various ways.

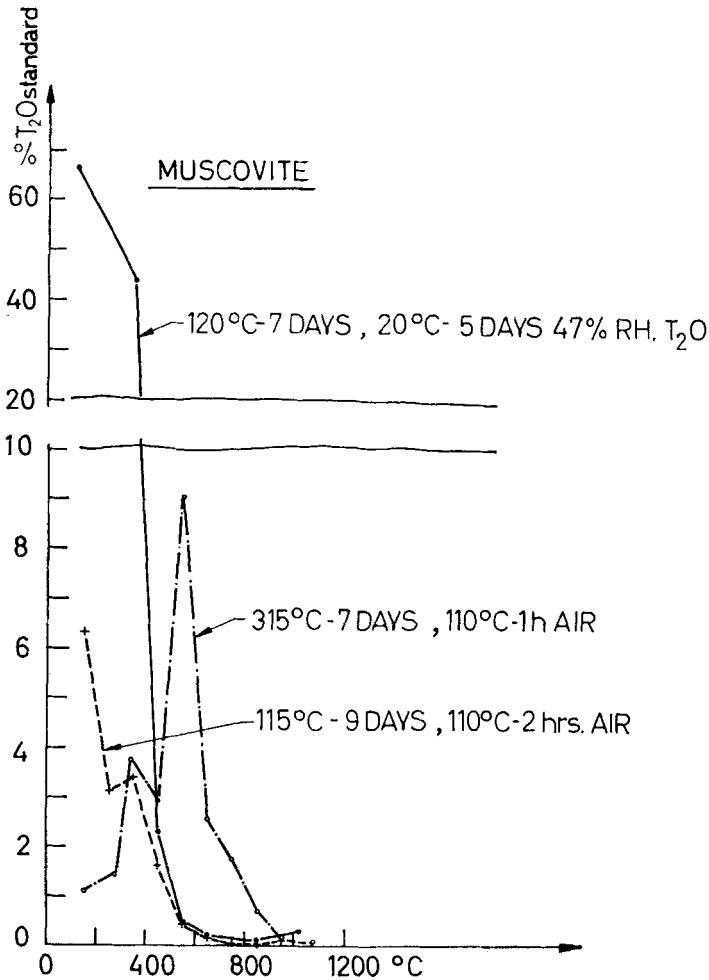


FIGURE 4.—Relative radioactivity of water fractions from pretreated hydro-muscovite.

Figure 5, A, B and C, shows the amounts of tritium in the various fractions collected. Each of the columns represents the tritium water independent of the

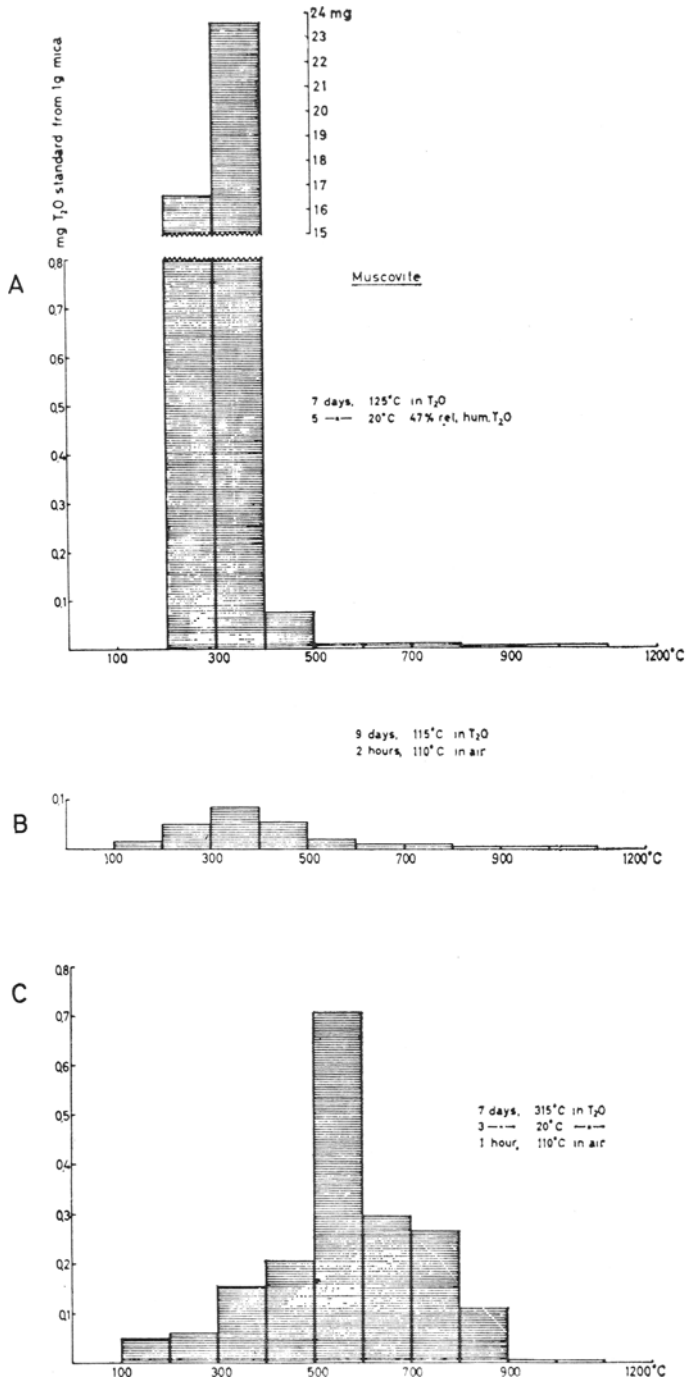


FIGURE 5.—Tritium water in water fractions from pretreated hydromuscovite.

total amount of water given off after 1 hr at each temperature, the temperature range being divided into intervals of 100°C each. (In Fig. 5A the column between 100° and 200° was lost. As seen from Fig. 4, however, this fraction has a very high relative radioactivity.)

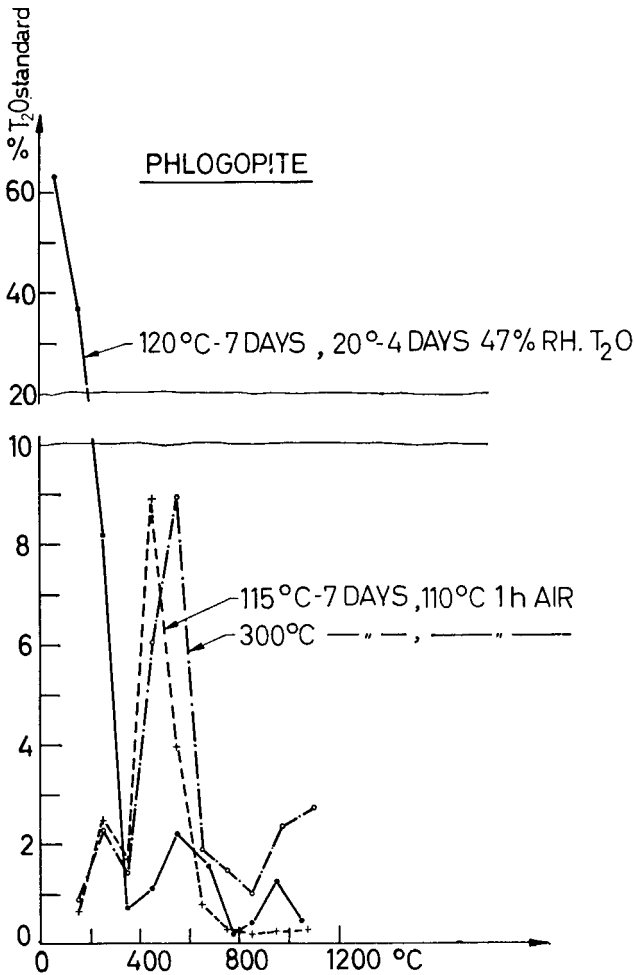


FIGURE 6.—Relative radioactivity of water fractions from pretreated phlogopite.

Figure 6 shows the relative amount of tritium in the various water fractions of the phlogopite, and Fig. 7, A, B and C, gives the amount of tritium standard in the various fractions of phlogopite corresponding to Fig. 5 in case of muscovite.

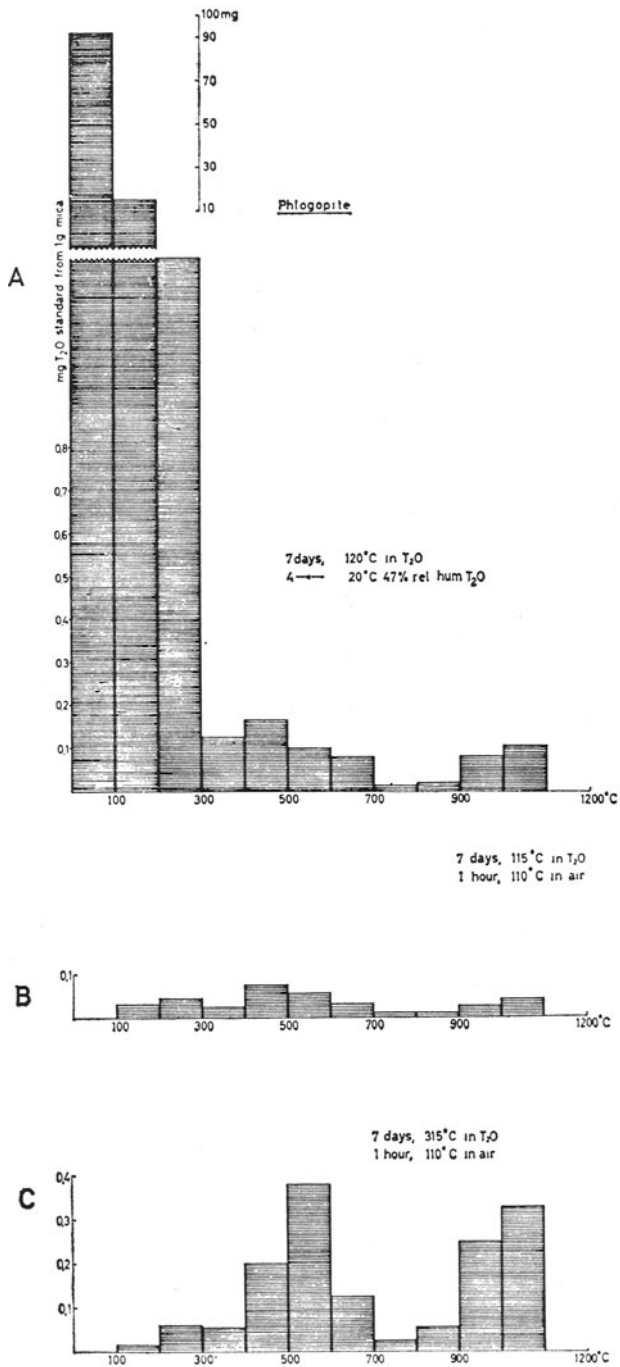


FIGURE 7.—Tritium water in water fractions from pretreated phlogopite.

## COMMENTS TO THE TRITIUM DATA

As demonstrated by Figs. 5 and 7, the fine-grained mica powder which has been kept in an atmosphere of 47 per cent relative humidity until equilibrium, has a considerable amount of tritium which is removed at temperatures below 300°C. This tritium is, however, present in such a state that one hr heating at 110°C in normal moist atmosphere removes the major part of it, although the amount of water given off in the temperature range from 100–300°C is still considerable. For instance, in the case of muscovite 2.5 mg of water is given off in this range from 1 g, whereas the tritium content in the water corresponds to less than 0.1 mg of the standard. We thus have to deal with a type of hydrogen for which the bonding conditions permit an easy establishment of equilibrium with the hydrogen of the vapour in the surrounding atmosphere. This fraction of the water given off at temperatures below 300°C is obviously of the same nature as the water given off below 100°C, i.e. *adsorbed water*.

We thus have a method to distinguish between water of adsorption and water of constitution. This distinction is not possible solely from the loss of water curve, as some of the constitutional water is given off in the same temperature range. The constitutional water, on the other hand, is clearly demonstrated to be present in two states, namely the part of water which is given off in the temperature interval between 100 and 600° (chiefly between 300 and 400°C). It is characteristic for the samples treated with tritium oxide at 115°C for 9 days, and subsequently permitted to exchange adsorbed water with normal water of the laboratory atmosphere (Fig. 5B), that  $\frac{2}{3}$  of the tritium content is given off in the temperature interval between 200 and 500°C, although only 17 per cent of the total hydrogen content is lost within the temperature range. The hydrogen given off in this water fraction clearly distinguishes itself in several ways from the OH groups of the mineral phase. The hydrogen present as such groups is mainly given off in the temperature range 600–1100°C.

Since as much as  $\frac{1}{3}$  of the non-adsorbed tritium is expelled by moderate heating, mainly in the temperature range around 350°C, it is improbable that this hydrogen is present as  $H_3O^+$  groups. The cracking of such a group would statistically give off  $\frac{2}{3}$  of its hydrogen as water, whereas the third proton will have to stick to the mineral lattice and be lost at higher temperatures. Thus the tritium exchange data fit with the infrared investigation of the deuterium-treated sample.

In the case where the muscovite powders had been treated for 7 days at 315°C, the general picture of the tritium content in the water fractions is fundamentally different. In this case we have obtained a marked maximum in the temperature range from 450–800°C, and even in the water lost at temperatures above 800°C the tritium content is considerable. The tritium content in the fractions between 450°C and 800°C makes about 73 per cent of the total tritium, whereas 18 per cent is given off at temperatures below 400°C, and 9 per cent above 800°C. The curve in Fig. 3 shows that 28 per cent of the

total water content is given off in the temperature interval between 450°C and 800°C, 19 per cent between 100 and 450°C, and 53 per cent above 800°C.

Thus it seems as if a new hydrogen-bearing phase has developed as a result of the hydrogen-thermal treatment. As far as we are able to judge, this phase must be of a type which gives off the majority of its water in the temperature range from 450 to 800°C. This is in very good agreement with a dioctahedral montmorillonite (compare the dehydration curve for the dioctahedral montmorillonite from Namdalen Fig. 3). X-ray data and differential-thermal analyses have not as yet made it possible to ascertain the nature of the hydrothermally formed phase. The results by Garrels and Howard (1959) do, however, suggest the possibility that the new-formed phase may be kaolinite. In the samples treated at low temperatures no such new-formed phase seems to have developed.

The data clearly show that the rate of exchange for the three types of hydrogen is very different. The adsorbed hydrogen exchanges rapidly. The next type of hydrogen exchanges to several percent within a week at 115°–120°C, whereas the third type of hydrogen, certainly present as OH groups, only exchanges to a very low percent after such treatment.

If we assume that the water lost at temperatures above 800°C solely derives from the OH groups of the mica structure, we find that the amount of tritium in this position is roughly 30 times higher after 7 days of hydrothermal treatment at 315°C than after 7 days at 125°C. The activation energy calculated on basis of these two figures gives the very low value of 3.2 kcal/mol.

For the trioctahedral phlogopites we have several similarities with the results found for the hydro-muscovite, but also marked differences (compare Figs. 4 and 6). The first striking feature of the phlogopite data is the marked maximum in the tritium content in the water lost at temperatures around 450°C, whereas the muscovite had the corresponding maximum at a temperature of 350°C. The phlogopite as well as the muscovite seems to develop a new phase after hydrothermal treatment at 350°C. This phase has a maximum in the loss of water at 550°C. At the same time even after 7 days at 115–120°C, and in a much more accentuated way after 7 days at 350°C, we have tritium fixed in a position which corresponds to the loss of water in the temperature interval 800–1100°C. Especially in the highest part of this range, between 900 and 1100°C, the tritium content is marked. Whether this corresponds to hydroxyl ions in the octahedral layers of the trioctahedral micas or in the new phase is not possible to ascertain. The minimum in tritium content found between 650°C and 900°C (although the phlogopite gives off more than 25 per cent of its water in this interval) seems to indicate that either the hydroxyl ions of the phlogopites are not present in equivalent positions, or (more probably) that we have to assume a new phase. The equivalency of the hydroxyl ions is assumed in the recognized crystal structure. Serratos and Bradley's (1958) investigations of the stretching frequencies of the OH bonds in the trioctahedral micas point in the same direction. On the other hand, it is difficult to point to any distinct known mineral corresponding to the values

found. The amount of tritium given off in the temperature interval around 900°C corresponds to roughly 5 per cent of the total mica. At present we think it most probable that vermiculite has been formed, giving off its "talc water" at a high temperature.

Summarizing, we may state that by *hydro-muscovites* we have water present in three different states:

1. "Low-temperature water I" in equilibrium with the humidity of the atmosphere after very short time. This adsorbed water at 47 per cent relative humidity is given off at temperatures below 400°C.
2. "Low-temperature water II" in equilibrium with humid atmosphere after a long time. This water is given off at temperatures between 200 and 500°C.
3. "High-temperature water" given off at temperatures between 500°C and 1150°C. This is the majority of the water, probably in equilibrium with the humidity of atmosphere after a very long time.

In *phlogopite* we have:

4. In trioctahedral micas subdivisions of the water similar to the dioctahedral micas can be seen. The difference is mainly seen in the amount of exchanged water given off in the temperature range from 900°C to 1100°C.
5. The marked difference between the hydro-muscovite and the hydro-phlogopite is most clearly seen by minerals which had been subjected to hydrothermal treatment at the highest temperature, i.e. 315°C for 7 days.

## COMPARISON OF INFRARED AND TRITIUM DATA

The result of the infrared examination correlated to the tritium determination shows that a part of the water is given off in the temperature range from 0 to 400°C. This water is in extremely quick exchange equilibrium with the vapour of the surrounding atmosphere, but in a very slow exchange equilibrium with the rest of the hydrogen atoms of the mineral. Conventionally we call this water, adsorbed. Depending upon the relative humidity of the atmosphere, the amount and bonding conditions of this water are variable. The faint infrared absorption band at 2900  $\text{cm}^{-1}$ , Fig. 1, seems to represent this water. If this is a correct interpretation, it represents very strong hydrogen bonds between the water and the oxygen network of the mineral surface. The abnormally strong bathochromic shift indicates the intensity of the hydrogen bonds.

Fripiat, Chaussidon and Touillaux (1960) showed that the OH stretching frequency of water adsorbed in montmorillonite and vermiculite was decreased below that in normal water when the amount of free water is lower than corresponding to monolayer. Very strong hydrogen bonding to the surface oxygen of the mineral may be reason for the strong bathochromic shift in the O-H stretching frequency.



The next type of water represented by the O–D frequency at  $2650\text{ cm}^{-1}$ , which nearly disappeared after 5 hr at  $300^\circ\text{C}$ , corresponds to the water given off in the tube furnace around  $400^\circ\text{C}$  after 1 hr. This water is in intermediate exchange equilibrium with the surrounding atmosphere, i.e. in the course of weeks. It seems to correspond to the alkali deficit in the mica molecules. It is in very slow exchange equilibrium with the rest of the hydrogen. As nearly all deuterium which had entered the powder after 180 days could be driven off at  $300^\circ\text{C}$  in 5 hr, the conclusion arrived at is that this hydrogen must be present as neutral  $\text{H}_2\text{O}$ , and not as  $\text{H}_3\text{O}^+$  groups. In the latter case we would have  $\frac{2}{3}$  of the water driven off at the distinct temperature, and not more than 90 per cent as seen from Fig. 1.

The rest of the hydrogen corresponds to the OH of the structural formula.

### DISCUSSION IN LIGHT OF THE MICA STRUCTURE

The present investigations indicate that hydrous micas based on tri-octahedral backbone sheets differ fundamentally from dioctahedral micas. Most probably they represent some kind of mixed layer minerals of phlogopite and vermiculite, whereas hydrous micas based on the muscovite structure may either be hydro-muscovites or 1 M illites, or mixtures of these elements with montmorillonite interstratifications. The conclusion arrived at is:

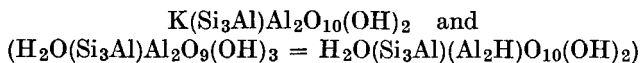
1. Hydrous micas may be derived from the muscovite structure by substituting some of the interlayer cations with neutral water molecules.
2. In order to equalize the charges between the backbone sheet and the interlayer cations and water molecules, a proton may be added to one of the oxygens in the tetrahedral layer or other changes may take place.
3. The negative charge of the backbone sheet is reduced proportionally to the leaching of interlayer ions, by an addition of a proton in the backbone sheet. The most probable position for this seems to be at the tri-coordinated oxygen in the apex of the tetrahedrons (the oxygen shared between the octahedral and the tetrahedral layer). The difference between trioctahedral and dioctahedral micas makes such a position for a proton possible, filling up the empty position in the octahedral layer, or just by transforming the apical oxygen into a OH group.

These oxygen atoms have three nearest cation neighbours in the muscovite structure, as compared to four in the phlogopite structure. In the muscovite structure, three of the four shared oxygen atoms fully satisfy the electrostatic valency rule by  $4/4$  valencies towards Si and  $2 \times 3/6$  valencies towards Al ( $\Sigma = 2$ ). The last oxygen has 3 Al as the next neighbours, and does not fully satisfy the electrostatic valency rule, as the valencies towards the next neighbour make  $3/4 + 2 \times 3/6$  ( $\Sigma = 1.75$ ).

If a proton enters the structure, it seems most reasonable to derive the dioctahedral hydrous mica structures from the muscovite structure by adding a proton to the top oxygen atoms of the  $\text{AlO}_4$  tetrahedron. In this way this tetrahedron will be  $\text{AlO}_3\text{OH}$ . This oxygen and the nearest apical oxygen in the opposite tetrahedral layer are at a distance which in itself could give possibilities for hydrogen bonds. If the valency of such a bond is set equal to  $1/2$ , the discrepancy from the electrostatic valency rule for this oxygen would be reduced to  $1/4$ , by use of the fourth orbital in the oxygen atoms. However, the angular discrepancy from linearity for the direction of the orbital by such a hypothetical hydrogen bond would be very large, of the order of  $50^\circ$ , thus making such a hydrogen bond less probable. On the other hand, the direction towards the next nearest neighbour in the opposite tetrahedral layer is favourable for hydrogen bonds. In this case, however, the O-O distance is of the order of  $4 \text{ \AA}$ , which will probably rule out the probability for hydrogen bonds. The most probable assumption is therefore that the intensity of an hypothetical hydrogen bond must be very low, and the infrared spectra do not indicate any bonding of this type.

In case of the phlogopite structure, we have no free orbital in the oxygen in the apex of the tetrahedrons. If these trioctahedral micas should permit a certain substitution of  $\text{H}_2\text{O}$  in the cation positions, the valency balance must be due to an oxidation of the iron on the octahedral layer, or a substitution Mg by Al. In both cases we will decrease the negative charge of the backbone sheet, which may counterbalance the loss of alkali ions from the dodecahedral layers, thus permitting neutral water to take this place. By a substitution of  $1/3$  of the central atoms in the trioctahedral structures by a trivalent ion, the electrostatic valency rule is satisfied for the oxygen in the apex of the tetrahedral layers surrounding Al in the following way from bivalent ions:  $2 \times 2/6 + 3/6$  from the trivalent ion in the tetrahedral layer +  $3/4$  from the silicon ( $\Sigma = 23/12$ ), or very close to 2.

However, the tritium substitution may, as stated above, be satisfactorily explained by assuming an interstratified structure, or partial mixed layer with phlogopite and vermiculite. The trioctahedral hydrous micas are still obscure, whereas the present investigations indicate that dioctahedral hydrous micas partly represent *mixed crystals* between the following ideal end members:



The hydro-muscovites and true illites have compositions fairly close to that of potassium muscovite, and the pure hydro end member is never found.

This structure type may explain why the illites seem to break up in montmorillonitic and illitic elements when the alkali deficit exceeds 50 per cent. The Brown and Norrish formula, on the other hand, will not in the same way explain this feature, as their formula involve the same charge distributions for illites and ideal muscovite.

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