THE EXCHANGE OF DEUTERIUM BY HYDROGEN IN DEUTERIUM BRUCITE AND SOME DEUTERIUM SEPTECHLORITES

by

Takeshi KIKUCHI

(with 3 tables and 4 Text-figures)

(Contribution from the Department of Geology and Mineralogy,
Faculty of Science, Hokkaido University, No. 1132)

Abstract

Brucite, serpentine and some septechlorites (7 Å), of which hydroxyl position were occupied by $(OD)^-$ instead of $(OH)^-$, were synthesized. After these samples were put in H_2O at various temperatures and time durations under hydrothermal conditions, D_2O mol percent of resulted liquid was measured by gas chromatography. The reaction between heavy water and the natural clinochlore (14 Å) was also treated by the same method. Surface areas of powdered minerals used for samples were measured by BET method.

Exchange reaction occurred under hydrothermal conditions between hydrogen in H_2O and deuterium in brucite, serpentine, septechlorites and natural clinochlore (D_2O was added instead of H_2O).

It is concluded that this reaction proceeds to only several inner layers from crystal surfaces of these minerals. No remarkable difference was noticed according to the difference of minerals in the measurement of D_2O mol percent in H_2O derived from these minerals.

Contents

Introduction

Chemical properties of brucite, serpentine, some septechlorites (7 Å) and natural clinochlore (14 Å) under hydrothermal conditions are very important for the study on the mechanism of the crystallization of these minerals. An attempt to use heavy water as tracer was done to get some informations about the reaction between water and these minerals under hydrothermal conditions.

ROMO (1956) treated kaolinite hydrothermally at 300°C and 700 bars at various time duration in the presence of D_2O. He studied infrared spectra of the samples after runs with the results of the characteristic shift of absorption bands. The ratio of absorbances of OH/OD bands obtained with polarized light beamed parallel or perpendicular to the c-planes of vibration, was found to be the same in both cases. He found it is conveninent to plot the ratio of integrated areas of the absorptions peaks of the OH/OD versus time. He concluded that the rate of the exchange of hydroxyl groups with deuterium were characterized by two steps : first a predominant exchange on the surface hydroxyl followed by a process of diffusion into the intra-lattice hydroxyls.

ROY and ROY (1957) studied the exchange reaction of hydroxyl groups with deuterium on many clay minerals in identification by infrared method with corresponding shift of characteristic bands. They found that dickite reacted much more slowly in exchange than other clay minerals and that the exchange is very limited at room temperature into well-ordered hydroxyl positions, whereas it is prompt and intense above 190°C. They concluded that it was not possible to refer to " inner " or " outer " hydroxyl groups, exchanging H for D.

In the present investigation deuterium brucite and some deuterium septechlorites were synthesized and the reaction between water and these minerals was treated under hydrothermal conditions. Thereafter, D_2O mol percent of the resulted liquid was measured by gas chromatography with the results discussed in this paper.

Method of investigation

Throughout the present studies, hydrothermal runs were carried out using mainly " test-tube " type reactors, the inner volume of which is 8 ml and Morey-type bomb with the inner volume of 30 ml.

The temperatures were measured by an alumel-chromel thermocouple with an accuracy of ± 5°C. The pressures were measured by a Bourdon gauge with an accuracy of ± 20 bars. The time required to raise the temperature to the desired value was about 20 minutes. The time required for preheating occupied a large proportion in the durations of ordinary short runs. Heavy water supplied from Toshiba-Denko Co., the purity of which was 99.8 weight percent, was used to

synthesize deuterium brucite and deuterium septechlorites.

50 mg of reagent grade MgO with 80–100 mg of heavy water was placed in a silver tube welded in an end (0.3 mm in thickness, 3 mm in diameter and 45 mm in length). Then the other end was welded, while the large part of the tube was cooled with flowing water to prevent the vaporization. Silver capsule was kept at 300°C and 300 bars for 24 hours. It should be mentioned that the outer pressures applied to the silver capsule were produced by water vapor; a series of blank tests ascertained that no proton or H_2O could intrude in silver capsule, when the capsule was perfectly sealed. Careful weighing of each capsule before and after the hydrothermal run was carried out to examine possible cracking of the capsule, through which outer water vapour might be intruded during the experiment.

Deuterium septechlorites were synthesized from oxide mixtures of clinochlore composition ($5MgO \cdot Al_2O_3 \cdot 3SiO_2$) and amesite composition ($4MgO \cdot 2Al_2O_3 \cdot 2SiO_2$) with heavy water at 400°C and 400 bars for 7 days. Reagent grade γ alumina for chromatography was converted to α alumina by heating at 1400°C and was used for the making of septechlorite. Quartz powder, the purity of which was 99.8 weight percent was used to synthesize these minerals.

Natural clinochlore (14 Å) used in the study was collected from Kankyônando, Korea (Hokkaido University collection No. 861), with a mineralogical discription by HARADA (1936).

Synthesized deuterium brucite and deuterium septechlorites, in which OH^- position was completely occupied by OD^-, were put in H_2O under hydrothermal conditions and the amount of D_2O in remained water was measured at various duration of reaction after runs were over.

The D_2O molecule which is contained in silicate minerals will be dissolved into H_2O by three possible ways. In the first case, the mineral is dissolved in accordance with its solubility at the temperature during the run. This case can be applied to any hydrothermal conditions so far as the mineral exists stably at the temperature studied. D_2O mol percent in water after the run remains the same as that during the run and is very small because of its very small solubility in water at even high temperatures. In the second case, the mineral will be dehydrated in a certain P-T field where the mineral cannot exist stably. Therefore, all of D_2O molecule can be dissolved to H_2O. D_2O mol percent in H_2O after the run remains the same as that during the run even if the rehydration of the mineral occurs when sample is cooled. In the third case, exchange reaction occurs between H^+ or OH^- in H_2O and D^+ or OD^- in crystals during the run. In this case, the diffusion velocity of H^+ or OH^- in crystals will determine the rate of reaction. D_2O mol percent after run remains also the same as that during the run.

A silver capsule in which about 80 mg of $Mg(OD)_2$ and about 20 mg of H_2O were placed was kept at required temperature. After the run, the capsule was opened at its top and was placed in a glass vessel of about 20 ml capacity, connected

to a vacuum system by a tap. The tap to the vacuum system was opened, while the vessel was cooled by liquid nitrogen. When the state of vacuum was attained, the tap was closed and the other tap to the trap was opened. The vessel was kept at room temperature and water in the capsule was allowed to distil into the trap cooled by liquid nitrogen. The distillate is not pure H_2O but contain D_2O derived from $Mg(OD)_2$ by some kind of reaction mechanism. The molar fraction of D_2O in the extracted liquid was measured as follows by a gas chromatographic device. The mixture was passed through a column of powdered zinc at about 350°C to be reduced to H_2, HD and D_2. Then the gases were carried by herium gas to gas chromatographic column. D_2 can be separated from HD and H_2 by a column of the mixture of γ alumina and $Fe(OH)_3$ at the temperature of liquid nitrogen (Moore and Ward 1960). The fractions of H_2, HD, and D_2, in the order mentioned, were passed through a column of CuO at 350°C to be oxidized to H_2O, HDO and D_2O, respectively. Their molecular proportions were recorded on a recorder chart by a thermal conductivity cell. Their molecular proportions were then calculated by measuring the weight of each peak area cut out from the recorder chart. Inevitable admixture of H_2O and HDO among these two peaks were separated empirically. The surface areas of the samples for these experiments were measured by BET method with use of nitrogen adsorption at temperature of liquid nitrogen.

Results

1. $Mg(OD)_2+H_2O$

Mol percent of D_2O against the duration of time at 250°C and 300°C and 1000 bars were plotted in Figure 1. It is noticed that molar proportions of D_2O in water became to be almost constant for each temperature and that molar proportions at higher temperatures were larger than that at lower temperatures. Therefore, it seems likely at first that these values were derived from solubility of $Mg(OD)_2$ to H_2O. But it is not the case, since it is not sufficient for explaining such large mol percent of D_2O. Further, a relation was found in these experiments that molar proportion of D_2O in water is proportional to the amount of $Mg(OD)_2$ and is inversely proportional to the amount of H_2O added. For example, 56 percent D_2O was obtained from 15 mg of H_2O and 150 mg of $Mg(OD)_2$ at 400°C and 500 bars, whereas, 46 percent D_2O from 15 mg of H_2O and 70 mg of $Mg(OD)_2$ at the same condition. Dehydration of brucite at this temperature is most unlikely. The phase boundary of $Mg(OH)_2=MgO+H_2O$ determined by many authors lies above 500°C at about 1000 bars. Moreover, greater proportion of D_2O should be expected than the measured values if $Mg(OD)_2$ is dehydrated. Therefore, only the exchange reaction is regarded as the most possible kind of reaction in these experiments.

A correction was made to get constant value as the function of D_2O mol percent.

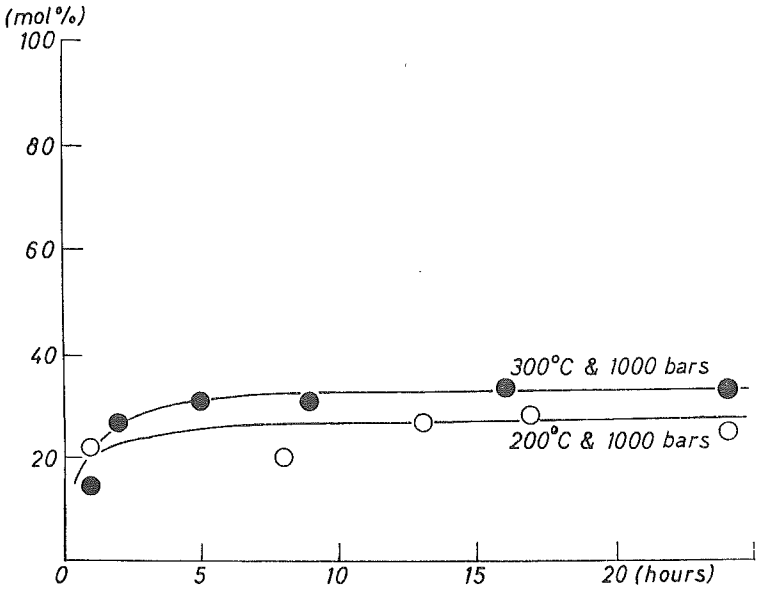

Fig. 1
Mol percent of D_2O derived from $Mg(OD)_2$ in H_2O against the duration of time.

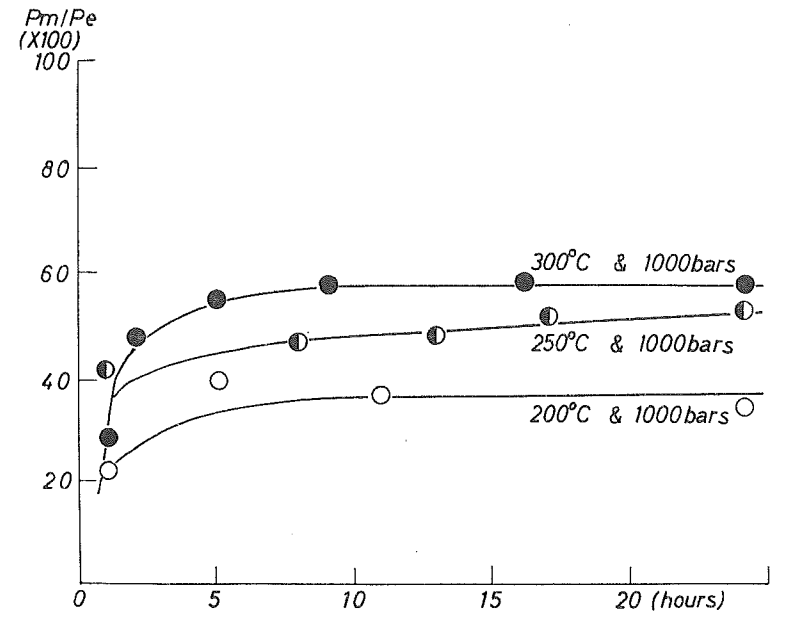

Fig. 2
Pm/Pe of $Mg(OD)_2$ against the duration of time.

Namely, measured mol percent of D_2O (abbreviated as " Pm " in this paper) was devided by the mol percent of D_2O (abbreviated as " Pe"), obtained by calculation on hypothetical equilibrium where given mg of $Mg(OD)_2$ and given mg of H_2O exchange their proton and deuterium each other until any parts of the crystals and liquid have the same molar proportion of D_2O. This correction can be made to minimize the effect of proportion of sample to water. Pm/Pe is plotted against duration of time in Figure 2 and Pm/Pe versus temperatures is shown in Figure 3. Above 350°C only one experiment, of which run duration was one hour was done at every required temperature. At about 500°C or above, it may be possible to dehydrate $Mg(OD)_2$. Hence large proportion of Pm/Pe may be resulted owing to the dehydration. These data are lised in Table 1.

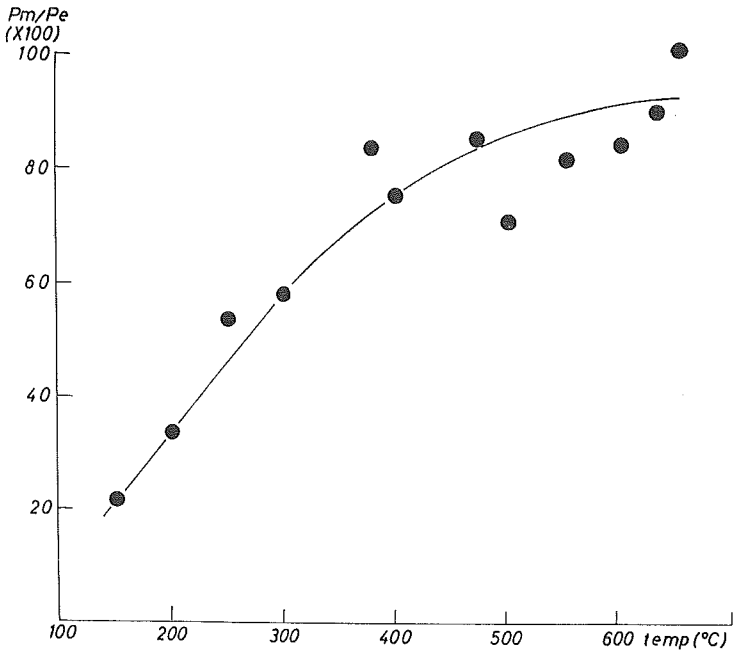

Fig. 3
Pm/Pe of $Mg(OD)_2$ versus temperatures.

2. *Deuterium serpentine and septechlorites*+H_2O

Since weight percent of D_2O in serpentine and septechlorite is smaller than that in brucite, smaller amount of H_2O was added to samples of these silicates to keep similar value of Pe as the case of $Mg(OD)_2$. Pm/Pe is plotted against temperatures in

Table 1. $Mg(OD)_2+H_2O$

Temp. (°C)	Pres. (bars)	Time (hours)	H_2O (mg)	Sample (mg)	Pm	Pe	Pm/Pe×100
150	1000	2	19.5	83.5	12.1	56.1	21.6
200	1000	1	18.7	78.5	12.1	55.6	21.8
200	1000	5	18.8	80.5	22.0	56.1	39.2
200	1000	11	19.2	81.5	20.0	55.9	35.7
200	1000	24	19.1	75.7	18.5	54.2	34.1
250	500	1	19.5	75.8	18.9	53.7	35.2
250	1000	1	19.8	54.5	22.0	52.9	41.6
250	1000	8	25.5	64.9	20.2	43.2	46.7
250	1000	13	15.8	65.7	26.5	55.4	47.8
250	1000	17	15.9	60.7	28.0	53.3	52.5
250	1000	24	23.3	68.2	24.9	46.6	53.4
300	1000	1	19.4	79.9	15.9	55.1	28.9
300	1000	2	19.4	79.2	26.6	54.9	48.5
300	1000	5	18.6	79.3	31.0	56.0	55.4
300	1000	9	20.5	80.3	31.3	53.9	58.1
300	1000	16	19.3	81.3	32.5	55.7	58.3
300	1000	24	19.9	84.5	32.4	55.9	58.0
350	1000	1	20.0	76.5	21.3	53.3	40.0
375	1000	2	20.5	80.5	45.0	54.0	83.4
400	1000	1	18.2	80.7	42.5	57.0	74.6
400	500	1	14.7	143.2	50.2	75.2	74.7
400	500	1	14.8	69.1	45.9	58.2	78.8
400	350	24	20.0	71.0	39.8	51.4	77.3
470	1000	1	14.8	80.7	52.6	61.9	84.9
500	1000	1	19.3	80.5	39.1	55.5	70.5
550	1000	1	14.7	79.8	50.2	61.8	81.1
600	1000	24	20.5	61.0	39.3	47.0	83.6
630	1000	1	17.5	116.7	59.3	66.6	89.1
650	1000	1	19.8	103.2	70.8	60.9	116.2

Figure 4. It is evident that serpentine, clinochlore, amesite and also $Mg(OD)_2$ show similar Pm/Pe values at each temperature. Similar curve of Pm/Pe against time duration will be expected in the case of $Mg(OD)_2$, since the value of Pm/Pe measured at 300°C for one hour was 0.68, whereas that value measured at 300°C for 17 hours was 0.61. These data are listed in Table 2.

3. *Natural clinochlore*+D_2O

D_2O was added to powdered natural clinochlore and molar proportion of H_2O in D_2O derived from sample were measured. There might be large errors in the data since H_2O in the air may be introduced in the system during the whole process

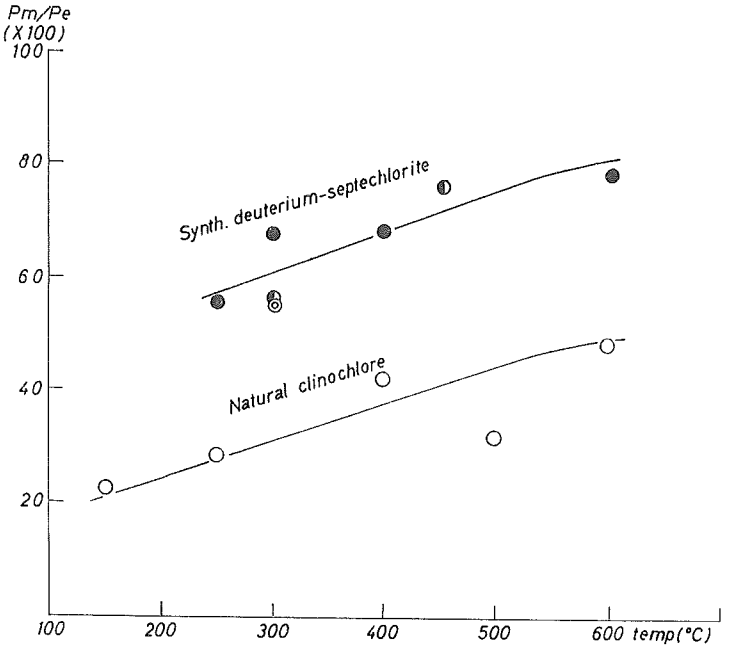

Fig. 4
Pm/Pe of deuterium septechlorites and natural clinochlore versus temperatures. Solid circles are synthetic deuterium clinochlore, half solid circles are synthetic deuterium amesite, and double circle is synthetic deuterium serpentine. Open circles are natural clinochlore.

Table 2. Deuterium septechlorites+H_2O

Comp.	Temp. (°C)	Time (hours)	H_2O (mg)	Sample (mg)	Pm	Pe	Pm/Pe×100
C	250	1	15.0	67.0	20.2	36.3	55.6
C	300	1	14.6	79.4	27.7	41.0	67.6
C	300	17	16.5	98.5	26.5	43.3	61.4
C	400	1	15.3	75.7	26.6	38.7	68.7
C	600	1	14.3	73.5	31.3	39.6	78.9
A	300	1	15.0	85.3	23.5	42.0	55.8
A	450	1	14.5	72.2	29.8	38.8	76.8
S	300	1	14.8	77.4	23.7	42.7	55.5

All runs were made under the pressure of 1000 bars.
C : Composition of clinochlore
A : Composition of amesite
C : Composition of pure serpentine

Table 3. Natuual clinochlore+D_2O

Temp. (°C)	Time (hours)	D_2O (mg)	Sample (mg)	Pm	Pe	Pm/Pe×100
150	10	15.0	112.5	11.8	51.8	22.8
250	1	19.5	81.5	10.7	37.5	28.5
400	1	17.0	84.5	17.8	41.6	42.8
500	1	15.3	92.7	14.6	46.5	31.4
600	1	18.0	81.0	19.1	39.2	48.7

All runs were made under the pressure of 1000 bars.

of experiment, to become large proportion to true value. Mol percent of H_2O derived from sample might be smaller than the measured value. All runs were made for 1 hour except the run at 150°C, which were made for 10 hours. Pm/Pe is plotted against temperatures in Figure 4 and these data are given in Table 3.

4. *Surface areas of the samples*

Surface areas of $Mg(OD)_2$, deuterium clinochlore (7 Å) and natural clinochlore (14 Å) were measured by BET method, with the following results.

$Mg(OD)_2$	8.9 ± 0.2 m²/g
Deuterium clinochlore	7.9 ± 0.2 m²/g
Natural clinochlore	4.1 ± 0.2 m²/g

It is worthy of note that the surface area of natural clinochlore is about a half of other two samples.

Discussions

Main reaction mechanism between samples and added water is considered as an exchange reaction between H_2O and $(OD)^-$ or D^+ of these crystals. The relation between D_2O mol derived from sample and duration time seems not to be logarithmic, but rapid increase of D_2O in H_2O occurs within about one hour, followed by a very slow increase. Therefore it is evident that crystal surface determine the rate of these reaction. The data of surface area of the samples support this opinion.

If it is assumed that surface area of $Mg(OD)_2$ is composed only of $(OD)^-$ ions, mol gram of D_2O which composes surface area of $Mg(OD)_2$ can be calculated by the following method.

Let the measured surface area be a regular triangle in form. Then, each length can be calculated as follows.

$$3/4\ a^2=8.9\ m^2/g, \qquad a=450\ cm$$

If ionic radius of $(OD)^-$ is assumed to be 1.4 Å, number of $(OD)^-$ ions which compose a length of the triangle is:

$$450/(1.4\times10^{-8}) = 3.2\times10^{10}.$$

In addition, if these $(OD)^-$ ions are assumed to be arranged in two-dimentional hexagonal closed packing, then total number of $(OD)^-$ ions is calculated as;

$$(3.2\times10^{10})^2/2 = 5.2\times10^{20}.$$

Since one molecule of D_2O derived from two $(OD)^-$ ions, mol gram of D_2O which composes surface area is:

$$(5.2\times10^{20})/(2\times6\times10^{23}) = 4.3\times10^{-5}\ \text{mol/g}.$$

If this value is applied to several inner layers of $Mg(OD)_2$ and exchange reaction occurs only in these layers, then the following equation can be given:

$$(4.3\times10^{-5}\cdot Ws\cdot N)/(4.3\times10^{-5}\cdot Ws\cdot N+M_H) = Pm,$$

Where Ws is the weight of sample (g), N is number of layers, M_H is mol gram of added H_2O and Pm is measured mol percent of D_2O in water.

Thus calculated number of layers taking part in reaction is 7 to 8 at 250°C. This value is regarded as very reasonable, and therefore, it is inferred that the above-mentioned assumptions seem not to be so unlikely. Furthermore, this value can explain well the form of the curves in Figure 2, i.e. H_2O was introduced to sample from sample surface by some kind of mechanism and the reaction was almost stopped at only several tens Å from crystal surface. It may be due to the difference of chemical properties between the surface and the interior of the crystal. The fact that Pm/Pe values of septechlorite and serpentine and also those of natural clinochlore (taking the value of surface area in consideration) are similar to those of $Mg(OD)_2$ seems to indicate similarity of their crystal structures.

It is concluded that $(OH)^-$ or H^+ composing brucite or layer magnesium hydrosilicate near their crystal surfaces is always exchangeable with other $(OH)^-$ or H^+ in crystals and in H_2O under hydrothermal conditions, and that the surfaces of these minerals are chemically very active under these conditions.

Acknowledgements

The author wishes to express his sincere thanks to Professor K. YAGI of this Department for his unfailing guidance and discussions throughout this work and critical reading of the paper in manuscript, and to Professor K. TANABE of Department of Chemistry for his helpful discussions. Thanks are also given to Associate Professor M. EN-YO of Research Institute of Catalysis, Hokkaido University for his

helpful advice about the measurement of the concentration of D_2O, and to Doctor M. GOTO for his kind discussions.

References cited

HARADA, Z. (1936): Chemische Analysenresultate von japanischen Mineralien. J. Fac. Sci. Hokkaido Univ. Ser. IV, **3**, 221–262.

MOORE, W. R. and WARD, H. R. (1960): Gas-solid chromatography of H_2, HD, and D_2. Isotopic separation and heats of adsorption on alumina. J. Phys. Chem. **64**, 832.

ROMO, L. A. (1956): The exchange of hydrogen by deuterium in hydroxyls of kaolinite. J. Phys. Chem. **60**, 987–989.

ROY, D. M. and ROY, R. (1957): Hydrogen-Deuterium exchange in clays and problems in the assignment of infra-red frequencies in the hydroxyl region. Geochim. et Cosmochim. Acta **11**, 72–85.

(Manuscript received on 3, April, 1969)