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

by

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(with 3 tables and 4 Text-figures)

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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 H₂O at various temperatures and time durations under hydrothermal conditions, D₂O 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 H₂O and deuterium in brucite, serpentine, septechlorites and natural clinochlore (D₂O was added instead of H₂O).

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 D₂O mol percent in H₂O derived from these minerals.

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Introduction

Chemical properties of brucite, serpentine, some septechlorites (7 Å) and natural clinocllore (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 D₂O. 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 convenient 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 septe-chlorites were synthesized and the reaction between water and these minerals was treated under hydrothermal conditions. Thereafter, D₂O 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 $\pm 5^\circ\text{C}$. 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 H₂O 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 clinocllore composition (5MgO·Al₂O₃·3SiO₂) and amesite composition (4MgO·2Al₂O₃·2SiO₂) 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 clinocllore (14 Å) used in the study was collected from Kankyōnando, Korea (Hokkaido University collection No. 861), with a mineralogical description by HARADA (1936).

Synthesized deuterium brucite and deuterium septechlorites, in which OH⁻ position was completely occupied by OD⁻, were put in H₂O under hydrothermal conditions and the amount of D₂O in remained water was measured at various duration of reaction after runs were over.

The D₂O molecule which is contained in silicate minerals will be dissolved into H₂O 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. D₂O 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 D₂O molecule can be dissolved to H₂O. D₂O mol percent in H₂O 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 H₂O 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. D₂O 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 H₂O 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 $\text{Mg}(\text{OD})_2$ 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 helium 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 $\text{Fe}(\text{OH})_3$ 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. $\text{Mg}(\text{OD})_2 + \text{H}_2\text{O}$

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 $\text{Mg}(\text{OD})_2$ 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 $\text{Mg}(\text{OD})_2$ 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 $\text{Mg}(\text{OD})_2$ at 400°C and 500 bars, whereas, 46 percent D_2O from 15 mg of H_2O and 70 mg of $\text{Mg}(\text{OD})_2$ at the same condition. Dehydration of brucite at this temperature is most unlikely. The phase boundary of $\text{Mg}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}$ 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 $\text{Mg}(\text{OD})_2$ 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.

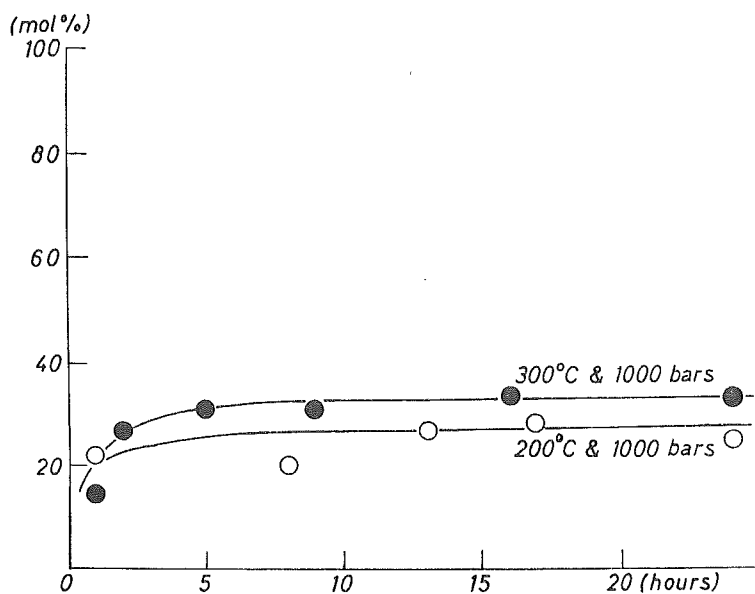


Fig. 1
Mol percent of D₂O derived from Mg(OD)₂ in H₂O against the duration of time.

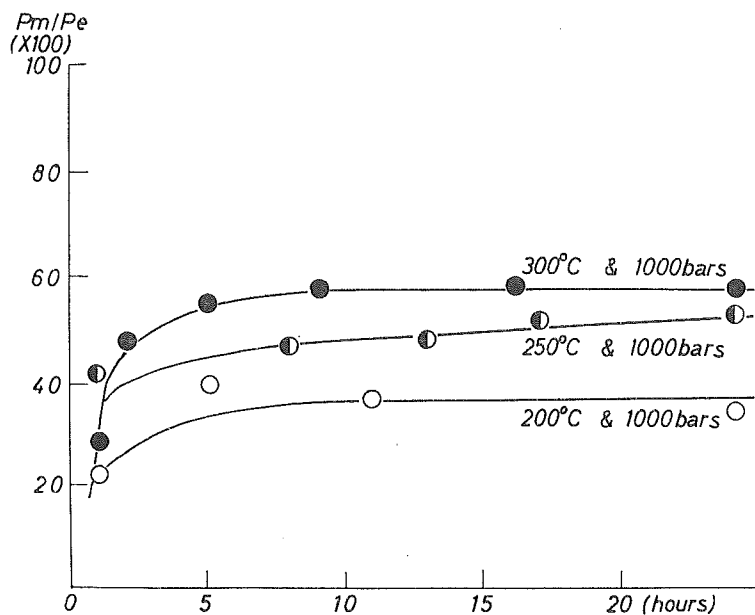


Fig. 2
Pm/Pe of Mg(OD)₂ against the duration of time.

Namely, measured mol percent of D_2O (abbreviated as "Pm" in this paper) was divided 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 $350^\circ C$ only one experiment, of which run duration was one hour was done at every required temperature. At about $500^\circ C$ 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 listed in Table 1.

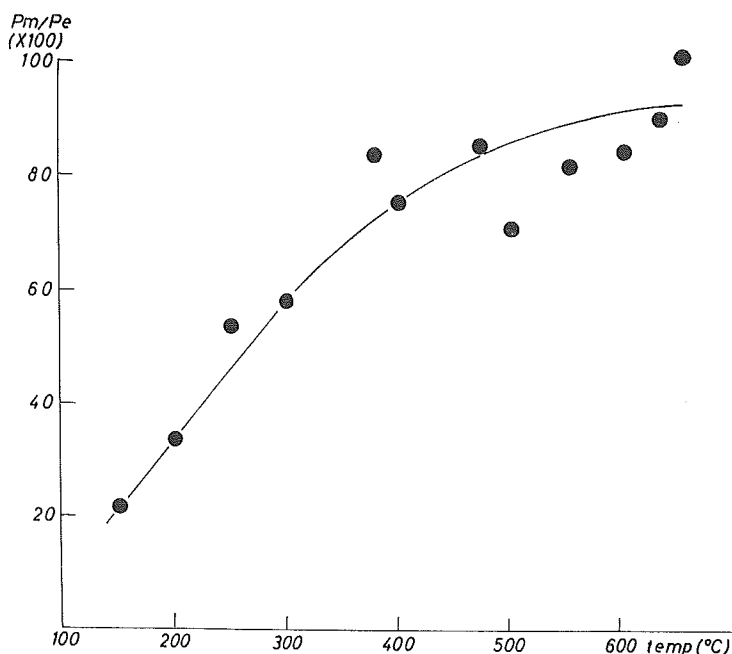


Fig. 3
Pm/Pe of $Mg(OD)_2$ versus temperatures.

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. $\text{Mg}(\text{OD})_2 + \text{H}_2\text{O}$

Temp. (°C)	Pres. (bars)	Time (hours)	H_2O (mg)	Sample (mg)	Pm	Pe	Pm/Pe $\times 100$
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 $\text{Mg}(\text{OD})_2$ show similar Pm/Pe values at each temperature. Similar curve of Pm/Pe against time duration will be expected in the case of $\text{Mg}(\text{OD})_2$, 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

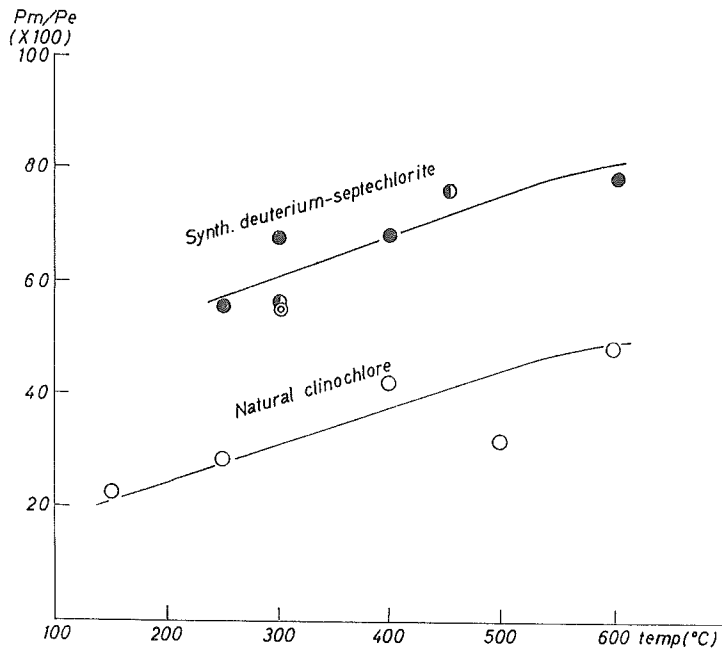


Fig. 4

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+H₂O

Comp.	Temp. (°C)	Time (hours)	H ₂ O (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. Natural clinochlore + D₂O

Temp. (°C)	Time (hours)	D ₂ O (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 H₂O 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 m ² /g
Deuterium clinochlore	7.9 ± 0.2 m ² /g
Natural clinochlore	4.1 ± 0.2 m ² /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 H₂O and (OD)⁻ or D⁺ of these crystals. The relation between D₂O mol derived from sample and duration time seems not to be logarithmic, but rapid increase of D₂O in H₂O 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 D₂O 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.

$$3/4 a^2 = 8.9 \text{ m}^2/\text{g}, \quad a = 450 \text{ cm}$$

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

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

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

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

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

$$(5.2 \times 10^{20})/(2 \times 6 \times 10^{23}) = 4.3 \times 10^{-5} \text{ mol/g.}$$

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

$$(4.3 \times 10^{-5} \cdot W_s \cdot N)/(4.3 \times 10^{-5} \cdot W_s \cdot N + M_H) = P_m,$$

Where W_s is the weight of sample (g), N is number of layers, M_H is mol gram of added H_2O and P_m 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 \AA 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 P_m/P_e values of septechlorite and serpentine and also those of natural clinocllore (taking the value of surface area in consideration) are similar to those of $\text{Mg}(\text{OD})_2$ seems to indicate similarity of their crystal structures.

It is concluded that $(\text{OH})^-$ or H^+ composing brucite or layer magnesium hydrosilicate near their crystal surfaces is always exchangeable with other $(\text{OH})^-$ 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.

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