

# Investigation of the Deuteration of Crystalline Layer Forms of Silica and Alumina in Liquid D<sub>2</sub>O

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**Abstract**—The mechanism of hydrogen–deuterium isotopic exchange was studied in crystalline layer forms of silica (hydrous and cation-substituted SiO<sub>2</sub>–X<sub>2</sub> and SiO<sub>2</sub>–Y varieties) and alumina (hydrargillite and boehmite) in contact with liquid D<sub>2</sub>O at temperatures of 20–200°C and saturated vapor pressure. Extensive exchange was observed between adsorbed H<sub>2</sub>O and D<sub>2</sub>O molecules via the self-diffusion mechanism in all silica varieties and boehmite at a temperature of 20°C. Deuterium substitution for hydrogen in structural OH groups was observed at 20°C only in the H-form of SiO<sub>2</sub>–Y (0.7%) and boehmite (1.2 or 17% with molecular deuteration). When the temperature of the hydrothermal treatment of samples was raised up to 200°C, the degree of structural deuterium exchange increased up to 12% (35% with molecular deuteration) in the former case and up to 34% in the latter case. In the former case, the process of isotopic exchange occurred by the nucleophile substitution S<sub>N</sub>i near surface silicon atoms, and in the latter case, the electrophile substitution E<sub>N</sub>i in surface OH groups.

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## INTRODUCTION

This study is connected with the purification of industrial waste water from the radioactive hydrogen isotope tritium and its long-term disposal in clay rocks and minerals [1–3]. In order to understand these processes, we investigated the mechanism of hydrogen–deuterium isotopic exchange in synthetic hydroxylated forms of silica and alumina, which can be regarded as isolated structural units of the aforementioned aluminosilicates. The use of deuterium in our study was related to its stability (in contrast to radioactive tritium), which makes it more convenient for experimental investigations. The SiO<sub>2</sub>–X<sub>2</sub> and SiO<sub>2</sub>–Y types of silica [4] and two alumina forms, hydrargillite and boehmite, were selected as model matrixes for deuterium capture (and, probably, tritium). Similar to clay minerals, they have a layer crystalline structure and extensive hydroxylated surfaces but, in contrast to natural clay minerals, they are chemically and structurally homogeneous. These phases can therefore be used as suitable models for the investigation of the mechanism of hydrogen–deuterium isotope exchange. It should also be noted that the eval-

uation of the mechanism of deuterium exchange in these silica and alumina forms will shed light on the molecular mechanism of hydration and hydroxylation of aluminosilicate rocks and minerals in ordinary water in geochemical environments.

## RESEARCH TARGETS

In this study we used hydrogen-bearing and cation-substituted forms of silica, SiO<sub>2</sub>–X<sub>2</sub> and SiO<sub>2</sub>–Y, obtained as transitional phases during the hydrothermal synthesis of quartz from amorphous silica. The conditions of their synthesis and properties were previously reported by Mitsuk [4]. The SiO<sub>2</sub>–X<sub>2</sub> and SiO<sub>2</sub>–Y varieties are layer phases with six- and eight-membered rings of SiO<sub>4</sub> tetrahedra in layers. The two silica types have different molecular structures of the interlayer space. The surface of layers is corrugated and undulating in the SiO<sub>2</sub>–X<sub>2</sub> form and smooth in SiO<sub>2</sub>–Y; the thickness of the Si–O frame of the elementary layer is 1.77 and about 1.16 nm, respectively. In both cases, the surface of layers is covered by hydroxyl groups, which form interlayer and intralayer hydrogen bonds. In addi-

**Table 1.** Influence of the preliminary annealing of silica and alumina samples on the degree of D<sub>2</sub>O substitution for adsorbed H<sub>2</sub>O at a temperature of 20°C

Sample	Air dried		After annealing at 160°C		After annealing at 240°C	
	total H <sub>2</sub> O content in sample before experiment, %	H <sub>2</sub> O content in D <sub>2</sub> O after 150-day experiment, %*	total H <sub>2</sub> O content in sample before experiment, %	H <sub>2</sub> O content in D <sub>2</sub> O after 90-day experiment, %	total H <sub>2</sub> O content in sample before experiment, %	H <sub>2</sub> O content in D <sub>2</sub> O after 75-day experiment, %
H-form of SiO <sub>2</sub> -Y	5.3	2.4	–	–	3.2	0.5
Na-form of SiO <sub>2</sub> -Y	14.1	7.8	8.3	1.2	3.9	0.6
Ca-form of SiO <sub>2</sub> -Y	7.3	5.1	–	–	–	–
H-form of SiO <sub>2</sub> -X <sub>2</sub>	6.4	4.1	3.8	1.3	2.6	1.3
K-form of SiO <sub>2</sub> -X <sub>2</sub>	7.8	4.9	5.0	1.3	2.3	1.2
Na-form of SiO <sub>2</sub> -X	12.1	5.4	6.1	1.2	3.3	1.3
Ca-form of SiO <sub>2</sub> -X	10.0	7.9	4.6	2.4	3.2	3.0
Hydrargillite	34.6	0.2	–	–	–	–
Boehmite	25.6	8.8 (10 d)	18.2	1.8 (10 d)	–	–

\* The concentration of water in D<sub>2</sub>O was taken into account for the evaluation of PMR spectra.

tion, the hollows in the layers of SiO<sub>2</sub>-X<sub>2</sub> (interlayer channels) accommodate water molecules. The treatment of samples of these silica forms with various alkaline solutions resulted in that their surface was covered with respective cations owing to ion exchange. In this study we used K-, Na-, Ca-, and H-forms of both silica varieties.

In addition, we synthesized and investigated two hydrogen-bearing crystalline forms of alumina, hydrargillite Al(OH)<sub>3</sub>, and boehmite AlOOH. Both varieties have layer structures [5, 6]. The conditions of their synthesis were reported in [7].

## METHODS

All samples were treated as suspensions in liquid 99.8% D<sub>2</sub>O at temperatures of 20–200°C in hermetically sealed glass vessels or autoclaves with Teflon inserts in experiments of various durations. The degree of D<sub>2</sub>O–H<sub>2</sub>O exchange was controlled by proton magnetic resonance (PMR) from the content of H<sub>2</sub>O in initial D<sub>2</sub>O, and the fraction of deuterium substituting for protons in surface OH groups was estimated from the IR spectra recorded on an UR-20 spectrometer in the region 400–4000 cm<sup>-1</sup>.

## EXPERIMENTAL RESULTS AND DISCUSSION

### *H–D Isotopic Exchange on Layer Silica Varieties*

In the experiments of various durations with silica forms in contact with liquid D<sub>2</sub>O at a temperature of 20°C, deuterium substitution was observed in practically all samples. However, as can be seen from Table 1, the degree of deuterium substitution in air-dried samples estimated from the PMR data was always lower

than their total water contents, which is indicative of a pure molecular exchange between adsorbed H<sub>2</sub>O and D<sub>2</sub>O and the lack of exchange in structural OH groups. This is also supported by the IR spectroscopy of these samples.

The degree of molecular deuteration of the Na-forms of silica determined from the amount of water in the D<sub>2</sub>O phase was significantly lower than that of other cation-substituted forms. This is probably related to the fact that strongly bonded water molecules in the coordination sphere of Na cations (to a smaller extent, K cations) are not substituted by D<sub>2</sub>O via the molecular mechanism. This suggestion was supported by the data obtained for samples preliminarily annealed at temperatures of 160 and 240°C, when only the most strongly bonded H<sub>2</sub>O molecules were retained in the coordination sphere. It should be noted that in such a case D<sub>2</sub>O molecules can be additionally incorporated into the coordination sphere by the deuteration of surface silica cations dehydrated during annealing.

On the other hand, the IR spectroscopy of samples of various SiO<sub>2</sub>-X<sub>2</sub> and SiO<sub>2</sub>-Y forms conducted after their prolonged treatment in liquid D<sub>2</sub>O (260 days) showed that the substitution of deuterium for protons in the structural OH groups of the surface is possible, but was observed only for the H-form of SiO<sub>2</sub>-Y. The degree of deuteration of the surface of this sample determined from the ratio of the areas of corresponding absorption bands in the IR spectra was not higher than 1.3%, and the fraction of structural OD groups was about 0.7%.

The hydrothermal treatment of samples of the H-form of SiO<sub>2</sub>-Y in liquid D<sub>2</sub>O resulted in a much higher degree of H–D exchange, which depended on the temperatures and duration of experiments (Table 2).

The maximum value of 35% was obtained for a sample treated at a temperature of 200°C for 10 d. An increase in temperature up to 250°C changed the rate of H–D exchange from 3.5% (at 200°C) to 35% per day (at 250°C). However, an increase in the duration of the treatment at this temperature should inevitably result in a decrease in the degree of deuterium exchange owing to the progressive dehydroxylation of surface layers at the expense of interlayer condensation accompanied by the formation of interlayer Si–O–Si bonds [4] and decreasing accessibility of the remaining OH groups. An increase in the temperature of a hydrothermal treatment up to 285°C produced the same structural transformations in the sample and hampered H–D exchange (Table 2), although the content of the remaining interlayer OH groups was about 13% of their initial amount.

As can be seen in Fig. 1, the IR spectra of deuterated samples of the H-form of SiO<sub>2</sub>–Y display two intense absorption bands at about 2580 and 2680 cm<sup>-1</sup>, which correspond to the stretching vibrations of the OD groups. The more intense band at 2580 cm<sup>-1</sup> is characteristic of liquid D<sub>2</sub>O [8, 9] and corresponds to OD group vibration in D<sub>2</sub>O molecules adsorbed on the active centers of the silica surface. The second intense band at 2680 cm<sup>-1</sup> can be assigned to the stretching vibrations of structural OD groups (in the region of OH vibrations, it corresponds to the band at 3660 cm<sup>-1</sup> [4]). The IR spectrum of the H-form of SiO<sub>2</sub>–Y subjected to deuteration at a temperature of 200°C for 10 d suggests that the amount of fixed structural OD groups is about two times lower than that of adsorbed D<sub>2</sub>O molecules, 12 and 23%, respectively.

The frequency and intensity of two main OD bands in the IR spectra were not changed by the subsequent heating of the deuterated samples in air to a temperature of 200°C, boiling in normal water at 100°C, and soaking in water at 20°C for 120 d. These observations indicate a high strength of deuterium bonds in the exchange positions of the surface of the H-form of SiO<sub>2</sub>–Y.

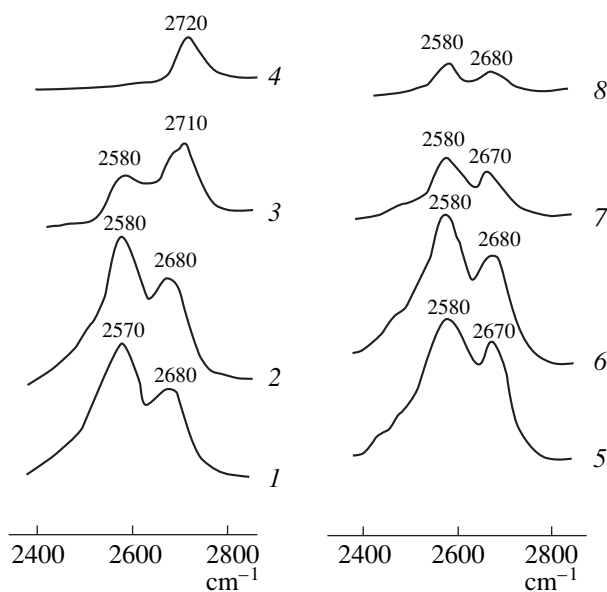
However, when a sample with an initial degree of deuteration of 35% was heated in air at a temperature of 250°C for 3 h, the area of the spectra of OD groups decreased by about 15%, while the relative intensities of bands at 2580 and 2680 cm<sup>-1</sup> remained unchanged. Further heating of the sample at 400°C for 2 h reduced the total area of the bands of stretching vibrations of the OD groups by 60% compared with the starting sample.

Considerable changes were observed in the IR spectrum of OD groups. Compared with the IR spectrum of the initial sample, the intensity of the 2580 cm<sup>-1</sup> band corresponding to OD vibration in D<sub>2</sub>O molecules decreased by a factor of 3. Its intensity became two times lower than that of the absorption band of structural OD groups at 2680 cm<sup>-1</sup>, which shifted to higher frequencies of 2700–2710 cm<sup>-1</sup> (Fig. 1). The latter effect could be related to the desorption of a significant portion of D<sub>2</sub>O molecules, which can probably be

**Table 2.** The influence of the conditions of preliminary treatment of samples of the H-form of SiO<sub>2</sub>–Y in liquid D<sub>2</sub>O on the degree of deuterium substitution

No.	Conditions of treatment		Degree of deuterium substitution, %
	temperature, °C	duration, day	
1	20	60	0
2	20	260	1.3
3	150	5	8
4	150	10	20
5	170	0.8	7
6	170	1	12
7	175	3	20
8	200	10	35
9	250	0.8	28
10	285	3	0

regarded, taking into account the high temperature of their removal, as strongly bonded coordination molecules near surface silicon atoms bearing structural OD groups (by analogy with normal water [10, 11]). This was accompanied by the redistribution of electron density in Si–OD bonds, which increased the frequency of stretching vibrations of structural OD groups.



**Fig. 1.** IR spectra of a deuterated sample of the H-form of SiO<sub>2</sub>–Y: (1) initial sample obtained by treatment in D<sub>2</sub>O at T = 200°C for 10 d; (2) after annealing at 250°C for 3 h; (3) after annealing at 400°C for 2 h; (4) after annealing at 500°C for 1.5 h; (5) after soaking in H<sub>2</sub>O at 20°C for 12 d; (6) after soaking in H<sub>2</sub>O at 100°C for 2 h; (7) after hydrothermal treatment in H<sub>2</sub>O at 200°C for 3 d; and (8) after hydrothermal treatment in H<sub>2</sub>O at 200°C for 8 d.

A further increase in the temperature of annealing of the initial deuterated sample up to 500°C for 1.5 h resulted in a complete disappearance of OD vibrations at 2580  $\text{cm}^{-1}$ , a decrease in the intensity of the second band of OD groups, and its shift to a frequency of 2720  $\text{cm}^{-1}$ . Compared with the initial 2680  $\text{cm}^{-1}$  band, the intensity of the 2720  $\text{cm}^{-1}$  band is two times lower, and its total area decreased by 90%.

These observations suggest that the annealing completely eliminated  $\text{D}_2\text{O}$  molecules coordinated to surface silicon atoms, which is in agreement with the data on the thermal stability of normal water coordinated to silicon atoms [10, 11]. Simultaneously, part of structural OD groups were removed, which resulted in the appearance of a sharp band of free structural OH groups at 3680  $\text{cm}^{-1}$  in the spectrum of stretching vibrations of OH groups.

In order to evaluate the reversibility of H–D exchange, the sample of the H-form of  $\text{SiO}_2\text{--Y}$  exposed in liquid  $\text{D}_2\text{O}$  at 200°C for 10 d was treated under similar hydrothermal conditions in pure normal water. It was found that already in a 3-day experiment there was a significant synchronous decrease in the intensity of the 2580 and 2680- $\text{cm}^{-1}$  bands corresponding to the stretching vibrations of the OD group (Fig. 1) and an increase in the intensity of bands due to the stretching vibration of OH groups at 3480 and 3630  $\text{cm}^{-1}$ . The total area of OD bands decreased by 70%. An increase in the duration of the hydrothermal treatment of the sample up to 8 d resulted in more pronounced hydration and hydroxylation of the surface and a simultaneous decrease in the intensity of the bands of stretching vibration of OD groups at 2580 and 2680  $\text{cm}^{-1}$ . The total area of the bands of OD groups decreased by 85%.

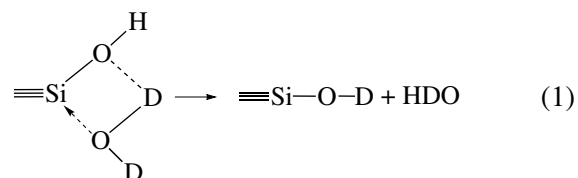
These data suggest the reversibility of the processes of H–D and D–H exchange on the H-form of  $\text{SiO}_2\text{--Y}$  occurring intensely only at a high temperature by the same mechanism. This mechanism includes the weakening of interlayer hydrogen (deuterium) bonds at an increase in temperature. This is accompanied by an increase in the access of  $\text{D}_2\text{O}$  ( $\text{H}_2\text{O}$ ) molecules into the interlayer space and, consequently, into the coordination sphere of surface silicon atoms, which enhances H–D or D–H exchange in structural hydroxyl or deuterioxy groups.

It should be noted that a hydrothermal treatment in liquid  $\text{D}_2\text{O}$  of hydrogen-bearing and cation-substituted  $\text{SiO}_2\text{--X}_2$  varieties and cation-substituted  $\text{SiO}_2\text{--Y}$  varieties did not result in a deuterium exchange in structural OH groups.

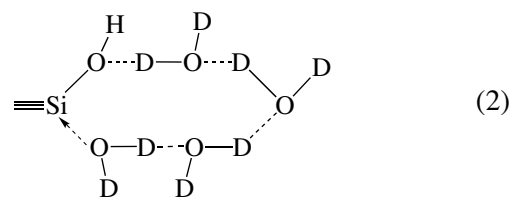
Consequently, it can be suggested that the H–D exchange that occurs only on the H-form of  $\text{SiO}_2\text{--Y}$  is controlled by some structural features of the surfaces of layers and a specific mechanism of interaction between  $\text{D}_2\text{O}$  molecules and silicon atoms on the surface of this silica variety.

Indeed, the surface of  $\text{SiO}_2\text{--X}_2$  is characterized by a corrugated structure, i.e., this phase contains interlayer channels, in contrast to  $\text{SiO}_2\text{--Y}$ , the layers of which have smooth surfaces [4]. The channels of  $\text{SiO}_2\text{--X}_2$  accommodate  $\text{H}_2\text{O}$  molecules, which are connected by a strong coordination bond to surface silicon atoms [10, 11].

This is sterically impossible in  $\text{SiO}_2\text{--Y}$ . Therefore, while the vacant 3d-electron orbitals of surface silicon atoms in  $\text{SiO}_2\text{--X}_2$  are saturated at the expense of poorly exchangeable adsorbed  $\text{H}_2\text{O}$  molecules, they are empty in  $\text{SiO}_2\text{--Y}$ , which has a different molecular structure of the surface, and its Si atoms are not coordinatively bonded to water molecules at an ambient temperature. However, an increase in the temperature of liquid  $\text{D}_2\text{O}$  weakens and breaks intralayer hydrogen bonds, which makes Si atoms accessible for  $\text{D}_2\text{O}$  molecules. As a result,  $\text{D}_2\text{O}$  can form coordination bonds with surface silicon atoms. This, in turn, leads to the redistribution of electron density in the Si–OH bonds, which enables deuterium exchange and formation of Si–OD deuterioxy groups replacing structural hydroxyl groups by the mechanism of  $\text{S}_{\text{N}}1$  nucleophile substitution at silicon atoms, which was invoked by us for the description of silica dissolution and condensation in normal water [12], according to the scheme



Transitional cyclic complexes are formed at the expense of additional deuterium and coordination bonds shown by dashed lines and facilitate the deuteration of a silica surface in liquid  $\text{D}_2\text{O}$ . A softer redistribution of electron density at the minimum charge separation in the process of breaking and forming new bonds occurs during the formation of more complex transitional cyclic complexes (clusters) involving several  $\text{D}_2\text{O}$  molecules linked to each other by deuterium bonds, for example, by the mechanism



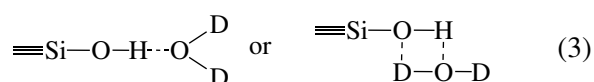
The formation of such polynuclear clusters was supported by the results of combined IR spectroscopic and thermogravimetric investigations of molecular  $\text{H}_2\text{O}$  adsorption on amorphous silica samples preliminarily annealed in vacuum [11].

This does not occur in the cation-substituted forms of  $\text{SiO}_2\text{--Y}$ , because the access of  $\text{D}_2\text{O}$  molecules into

the coordination sphere of surface silicon atoms is limited in response to an increase in the electron density in Si–O(Cat) bonds compared with the Si–OH bond. As a result, the electron-acceptor properties of silicon atoms decrease owing to a significant shift of the electron density to vacant  $3d$  orbitals of silicon due to  $d_{\pi}$ – $p_{\pi}$  conjugation.

In silica of the  $\text{SiO}_2$ – $\text{X}_2$  type, the sites of the coordination sphere of surface silicon atoms are occupied by water molecules, which are not substituted by  $\text{D}_2\text{O}$  molecules (similar to the Na-forms of  $\text{SiO}_2$ – $\text{Y}$  and  $\text{SiO}_2$ – $\text{X}_2$ , the strongly bonded coordination of water which is not substituted by  $\text{D}_2\text{O}$  molecules) (Table 1). Therefore, there is not a nucleophile exchange near silicon atoms via mechanisms (1) and (2).

In such a case, hydrogen bonds can only be formed by the mechanisms



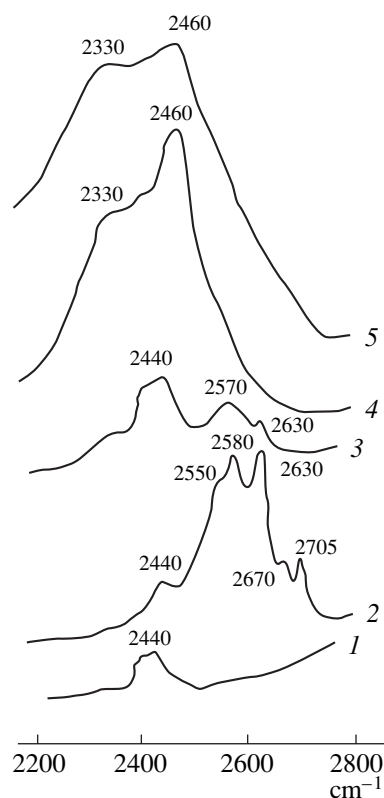
However, the degree of electron density redistribution in bonds in such a case is insufficient for the occurrence of H–D isotopic exchange through the mechanism of  $\text{E}_{\text{N}}\text{i}$  electrophile substitution [11].

Thus, the substitution of deuterium for hydrogen in liquid  $\text{D}_2\text{O}$  was observed only for the H-form of  $\text{SiO}_2$ – $\text{Y}$  and does not occur in its cation-substituted varieties, as well as in similar forms of  $\text{SiO}_2$ – $\text{X}_2$ . The different behavior of these two silica phases is related to the specific features of the molecular structure of their surface layers.

#### Isotopic H–D Exchange on Layer Varieties of Alumina

The degree of deuterium substitution (PMR data) in the alumina varieties hydrargillite and boehmite at a temperature of  $20^\circ\text{C}$  was much lower than the total water content in them for air dried samples and for a boehmite sample preheated at  $160^\circ\text{C}$  (Table 1). Additional investigations showed that the concentration of weakly bound physically adsorbed water removed during heating up to  $100^\circ\text{C}$  is about 0.1% for hydrargillite synthesized by us and about 8% for boehmite. It can therefore be supposed that hydrargillite underwent slight deuterium substitution in structural OH groups, whereas molecular deuterium exchange prevailed in the air dried boehmite.

However, our IR investigation of hydrargillite samples after their treatment in liquid  $\text{D}_2\text{O}$  did not confirm the possibility of deuterium substitution in structural OH groups, even in experiments lasting for 260 d. On the other hand, the IR spectra of an air dried boehmite sample treated in liquid  $\text{D}_2\text{O}$  for only 6–7 d showed a weak wide band at  $2330$ – $2360\text{ cm}^{-1}$  and a more intense absorption band at  $2400$ – $2440\text{ cm}^{-1}$  (Fig. 2). These bands can be attributed to the stretching vibrations of structural OD groups, because they are typical of syn-



**Fig. 2.** IR spectra of samples of air dried boehmite treated with liquid  $\text{D}_2\text{O}$  at (1)  $T = 20^\circ\text{C}$  for 7 d and (2)  $20^\circ\text{C}$  for 260 d; (3) boehmite preliminarily annealed at  $300^\circ\text{C}$  after treatment in  $\text{D}_2\text{O}$  at  $20^\circ\text{C}$  for 10 d; (4) boehmite after hydrothermal treatment in  $\text{D}_2\text{O}$  at  $200^\circ\text{C}$  for 3.5 d; and (5) boehmite synthesized from hydrargillite during its hydrothermal treatment in  $\text{D}_2\text{O}$  at  $200^\circ\text{C}$  for 3.5 d.

thetic deutero-boehmite,  $\text{AlOOD}$  [6]. The degree of sample deuteration in an experiment with a duration ( $\tau$ ) of 7 d was about 1.2% (Table 3).

An increase in the duration of the treatment of the air dried boehmite sample up to 260 d resulted in a dramatic change in its IR spectrum (Fig. 2) and the appearance (in addition to the  $2330$ – $2360$ ,  $2400$ , and  $2440\text{ cm}^{-1}$  bands) of a number of new intense well-resolved absorption bands at  $2550$ ,  $2580$ , and  $2630\text{ cm}^{-1}$  and weak bands at  $2670$  and  $2705\text{ cm}^{-1}$  (Table 3). Among them, the  $2580\text{ cm}^{-1}$  band is observed in free liquid  $\text{D}_2\text{O}$  [8, 9], and the other band can be also attributed to  $\text{D}_2\text{O}$  molecules tightly bound in the interlayer space of the sample. Similar bands were observed in the IR spectra of cordierite after its treatment in  $\text{D}_2\text{O}$  at a temperature of  $700^\circ\text{C}$  and a pressure of 200 MPa [13]:  $2540$ ,  $2630$ ,  $2675$ , and  $2705\text{ cm}^{-1}$ . Bul'bak et al. [13] assigned them to the stretching vibrations of OD in two types of  $\text{D}_2\text{O}$  molecules substituting for intrachannel  $\text{H}_2\text{O}$  molecules of types I and II by the mechanism of self-diffusion.

The data presented allow us to suggest that, in addition to deuterium substitution in structural OH groups

**Table 3.** Influence of the preliminary treatment of boehmite samples in liquid D<sub>2</sub>O on the frequency of stretching vibrations of OD groups and degree of deuterium substitution

No.	Initial state of sample	Treatment conditions		Frequency of the stretching vibrations of OD groups, cm <sup>-1</sup>	Degree of deuterium substitution, %
		T, °C	τ, day		
1	Air dried	20	6	2400–2440	1.1
2	Air dried	20	7	2330–2360, 2400–2440	1.2
3	Air dried	20	260	2330–2360, 2400, 2440, 2550, 2580, 2630, 2670, 2705	17
4	Dehydrated at 150°C	20	4	2400–2440	0.7
5	Dehydrated at 300°C	20	1	No bands	
6	Dehydrated at 300°C	20	10	2330–2360, 2400, 2440, 2570, 2630	8.5
7	Air dried	170	0.8	2330–2370, 2470	28
8	Air dried	175	3	2340–2370, 2470	30
9	Air dried	200	3.5	2330–2360, 2400, 2460	34
10	Hydrargillite	150	10	2340–2370, 2460 (hydrargillite + boehmite, tr.)	6
11	Hydrargillite	200	3.5	2330–2360, 2460 (boehmite)	53
12	Hydrargillite	200	10	2330–2360, 2470 (boehmite)	53

of the surface layers of boehmite, D<sub>2</sub>O molecules can be incorporated into the interlayer space by the exchange mechanism in prolonged experiments. This is supported by the high degree of deuterium substitution, which is up to 17% according to the data of IR spectroscopy (Table 3). The degree of deuterium substitution in structural OH groups is about 1.2%, whereas the degree of H<sub>2</sub>O–D<sub>2</sub>O molecular exchange approaches 15.8%.

The influence of the duration of the treatment in liquid D<sub>2</sub>O on the character of IR spectra suggests different mechanisms of boehmite deuteration at a temperature of 20°C depending on the time of exposure to D<sub>2</sub>O. Because of this, we studied the influence of the temperature of annealing of a boehmite sample preliminarily deuterated in liquid D<sub>2</sub>O for 260 d on the character of the IR spectra. It was found that the annealing of the sample at 100°C for 2 h changed considerably only the intensity of the 2440-cm<sup>-1</sup> absorption band in the low-frequency segment of the spectrum. When the annealing temperature increased to 200°C, the 2440-cm<sup>-1</sup> band disappeared, whereas the intensities of the 2550, 2580, 2630, 2670, and 2705-cm<sup>-1</sup> bands did not change and they even became more distinct and sharp. The latter completely disappeared after further sample annealing at a temperature of 270°C for 1.5 h.

The obtained results suggest the existence of several centers of deuterium fixation differing in nature and activity in the boehmite structure. The most accessible centers are those already saturated within the first 6–7 d of exposure to liquid D<sub>2</sub>O and associating with the bands at 2330–2360 and 2400–2440 cm<sup>-1</sup> related to the stretching vibrations of structural OD groups [6]. However, the fact that their intensity begins decreasing already at a temperature of 100°C and they disappear completely at 200°C suggests that the surface structural

OD groups are unstable and labile. Other bands of the IR spectra related to D<sub>2</sub>O molecules are more stable during sample heating and disappear only at a temperature of about 270°C, which is in agreement with the presence of strongly bonded adsorbed water in the starting boehmite. According to our thermogravimetric investigation, this water accounts for about 3% and is completely eliminated at a temperature of 250°C.

This is related to the character of the molecular structure of boehmite layers, which contain double chains of AlO<sub>6</sub> octahedra separated in a layer by empty spaces, the width and thickness of which are similar to those of the double AlO<sub>6</sub> octahedra [6, 14]. In fact, they form channels (voids) in the interlayer space. The layers are connected with each other by bent and therefore strained hydrogen bonds. Structural OH groups are located on the outer side of a layer, and the intralayer channels hosting oxygen atoms are free of hydrogen atoms. Because of this, D<sub>2</sub>O molecules are fixed in the structural channels, similarly to cordierite [13]. This is responsible for the striking similarity observed in the IR spectra of deuterium-treated samples of cordierite and boehmite in the area of OD vibrations, although this occurs at a temperature of 700°C and a pressure of 200 MPa in the former case, but already at 20°C in the latter case.

In order to elucidate the role of adsorbed H<sub>2</sub>O in boehmite deuteration, experiments with a preliminarily dehydrated boehmite sample were conducted. The sample was annealed at 300°C, immediately mixed with D<sub>2</sub>O, and kept at a temperature of 20°C. The treatment of the dehydrated sample in D<sub>2</sub>O for 10 d resulted in the appearance of several absorption bands at 2330–2360, 2400, 2440, 2570, and 2630 cm<sup>-1</sup> (Table 3) in its IR spectrum (Fig. 2). The 2400 and 2440 cm<sup>-1</sup> bands cor-

responding to structural OD groups were much more intense than the 2570 and 2630  $\text{cm}^{-1}$  bands due to  $\text{D}_2\text{O}$  molecules. The degree of sample deuteration was 8.5%, and the fraction of structural OD groups was about 5.5%. An air dried boehmite sample showed opposite intensity relations of these bands and corresponding distribution of OD groups in the structural and molecular states.

Thus, it can be concluded that the preliminary complete elimination of adsorbed water and part of structural OH groups from the boehmite sample heated to 300°C resulted already in short experiments in a more extensive deuteration of the interlayer surface at the expense of the formation of structural OD groups. The penetration of  $\text{D}_2\text{O}$  molecules into the interlayer structural channels is less pronounced.

In order to increase the degree of boehmite deuteration and elucidate its mechanism, samples were hydrothermally treated in pure liquid  $\text{D}_2\text{O}$  at temperatures of 170–200°C. As can be seen from Table 3, the hydrothermal treatment of an air dried boehmite sample at 170°C for 0.8 d resulted in a degree of deuterium substitution of 28%. However, an increase in the duration of a treatment to 3 d at 175°C and 3.5 d at 200°C had only a small influence on the maximum degree of deuterium substitution, 30 and 34%, respectively. Thus, an increase in the temperature of deuteration of air dried boehmite samples up to 170–200°C resulted in a dramatic increase in the degree of deuterium substitution.

The IR spectra of these samples show only two intense bands in the region of stretching vibrations of OD groups at 2330–2370 and 2460–2470  $\text{cm}^{-1}$  (Fig. 2), which correspond to structural OD groups. The absorption bands of molecular  $\text{D}_2\text{O}$  are missing in the spectra, which is in agreement with the intense desorption of  $\text{H}_2\text{O}$  molecules from the air dried boehmite samples already during short-term annealing at temperatures of 100–200°C. Therefore, under conditions of prolonged hydrothermal deuteration of boehmite, the exchange adsorption and fixation of  $\text{D}_2\text{O}$  molecules in structural channels are impossible.

It should be noted that the position and intensity of the adsorption bands of OD groups may vary depending on the conditions of boehmite synthesis. Our samples were prepared by heating synthetic hydrargillite in air at a temperature of 300°C for 4 h. In addition, we studied the possibility of deuterium substitution in an aluminous material during hydrargillite–boehmite phase transitions in hydrothermal experiments with liquid  $\text{D}_2\text{O}$  at temperatures of 150 and 200°C.

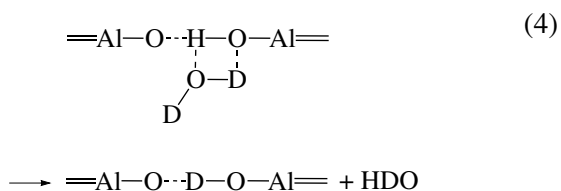
The IR spectrum of the sample obtained after hydrargillite treatment at 150°C for 10 d displays two weak absorption bands at 2340–2370 and 2460  $\text{cm}^{-1}$ , which are characteristic of structural OD groups. The degree of deuterium substitution was only 6% (Table 3), which is indicative of the initial stage of the hydrargillite–boehmite transformation. An increase in the exper-

imental temperature to 200°C at run durations of 3.5 and 10 d resulted in a complete phase transformation of hydrargillite into boehmite, and the intensities of the aforementioned bands at 2320–2360 and 2460–2470  $\text{cm}^{-1}$  in the IR spectra of both samples strongly increased (Fig. 2). The corresponding degree of deuterium substitution was identical and equal 53% independent of experiment duration.

Thus, there is a significant difference in the degree of deuterium substitution in the initial boehmite sample (34%) and boehmite synthesized through the transformation of hydrargillite during hydrothermal deuterium treatment (53%) under the same temperatures and run durations. This could be related to the direct participation of  $\text{D}_2\text{O}$  molecules in phase transformation accompanied by the breaking and appearance of new chemical bonds during the formation of the structural unit of boehmite (more accurately, boehmite–deuteroboehmite solution). In contrast, the hydrothermal treatment in  $\text{D}_2\text{O}$  of preliminarily synthesized boehmite,  $\text{D}_2\text{O}$  molecules can participate only in the processes of sorption and exchange on a previously formed surface.

During the hydrargillite  $\rightarrow$  boehmite phase transformation, the most important role was probably played by the reactions of nucleophile substitution of the  $\text{S}_{\text{N}}\text{i}$  type near surface aluminum atoms, which activate the rearrangement of chemical bonds. The atoms of Al become accessible and are readily attacked by nucleophile oxygen atoms of  $\text{D}_2\text{O}$  following mechanisms similar to Eqs. (1) and (2). This results in extensive deuteration of the newly formed interlayer surface.

Because of the sterical difficulties for a direct attack of the oxygen atom of  $\text{D}_2\text{O}$  on coordinationally saturated aluminum atoms and the strains of bent interlayer hydrogen bonds, the deuteration of preliminarily synthesized boehmite occurs by the mechanism of  $\text{E}_{\text{N}}\text{i}$  electrophile substitution [11] following the schematic reaction



This process is accompanied by the redistribution of electron density in transitional cyclic complexes formed by donor–acceptor hydrogen and deuterium bonds (shown by dashed lines in the scheme), which is favorable for the breakage of  $\text{AlO-H}$  groups and formation of new  $\text{AlO-D}$  groups. Similar to  $\text{Al-OH}$  groups, the latter form strained bent interlayer deuterium bonds. Because of this, they begin breaking down already at a temperature of 100°C and completely disappear at about 200°C.

Indeed, the annealing in air of boehmite samples deuterated at a temperature of 200°C both during the hydrargillite  $\rightarrow$  boehmite phase transformation



(degree of deuterium substitution of 53%) and during the deuterium treatment of previously formed boehmite (degree of substitution of 34%) at a temperature of 100°C for 1.5 h resulted in a dramatic decrease in the intensity of the 2330–2360 and 2460 cm<sup>-1</sup> absorption bands corresponding to structural OD groups. The degree of deuterium substitution decreased simultaneously by a factor of 2.6 and was about 20% in the former case and 13% in the latter case. An increase in the duration of annealing of these samples by 1.5 h resulted in a further decrease in the degree of substitution to 12 and 10.5%, respectively. The annealing of initial samples at a temperature of 200°C for 2 h reduced the degree of exchange to 2% in both cases. This was accompanied by the disappearance of both absorption bands in the former case and the appearance of a weak sharp band at 2395 cm<sup>-1</sup>. In the latter case, the position of these bands did not change, but their intensity became very low. This suggests that deuteration during the hydrargillite–boehmite transformation produced Al–OD bonds, which are missing in the deuterated sample of initial boehmite.

Thus, in agreement with the data obtained for deuterated boehmite, it can be suggested that during the heating of initial air dried boehmite, structural OH groups were eliminated already at a temperature of about 100°C with physically adsorbed weakly bound water molecules.

## CONCLUSIONS

(1) The mechanism of hydrogen–deuterium isotopic exchange was studied in synthetic hydroxylated crystalline layer forms of silica (SiO<sub>2</sub>–X<sub>2</sub> and SiO<sub>2</sub>–Y) and alumina (hydrargillite and boehmite) treated with liquid D<sub>2</sub>O at temperatures of 20–200°C and saturated vapor pressure.

(2) It was found that practically all silica and boehmite samples experienced extensive molecular exchange between adsorbed H<sub>2</sub>O molecules and D<sub>2</sub>O via the self-diffusion mechanism at a temperature of 20°C. The substitution of deuterium in structural OH groups was detected only in the H-form of SiO<sub>2</sub>–Y and in boehmite, and the degree of hydrogen–deuterium exchange was about 0.7 and 1.2%, respectively. The degree of deuterium substitution in boehmite increases with increasing run duration (from 7 to 260 d) up to 17% at the expense of additional exchange incorporation of D<sub>2</sub>O molecules into the intralayer structural channels.

(3) The intensity of deuterium substitution in structural OH groups increased sharply in samples of the H-form of SiO<sub>2</sub>–Y and boehmite hydrothermally treated in pure D<sub>2</sub>O at a temperature of 200°C, reaching 12% (35% with molecular deuteration) and 34%, respectively. However, boehmite synthesized through the transformation of initial hydrargillite during a deuterium treatment at a temperature of 200°C showed a

degree of structural deuterium substitution of 53%. This is related to the direct participation of D<sub>2</sub>O molecules in phase transformations accompanied by the breakage and appearance of new chemical bonds during the formation of structural units of boehmite (in fact, deuteroboehmite–boehmite solution).

(4) Based on the obtained experimental data, a mechanism of H–D exchange was proposed accounting for the donor–acceptor electron properties of the Si–O and Al–O bonds. It was shown that deuterium substitution in the H-form of SiO<sub>2</sub>–Y occurs by the mechanism of S<sub>N</sub>i nucleophile substitution near surface silicon atoms with the formation of transitional active cyclic complexes. A similar mechanism involving Al atoms is characteristic of deuterium substitution accompanying the hydrargillite–boehmite phase transformation during high-temperature deuterium treatment. In contrast, when a previously formed boehmite sample is subjected to deuteration, H–D exchange occurs by the mechanism of E<sub>N</sub>i electrophile substitution in surface OH groups.

(5) It was demonstrated that boehmite and the H-form of SiO<sub>2</sub>–Y are the most promising varieties among the silica and alumina phases that can be used for the disposal of tritium-bearing waters.

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