AN ASPECT OF THE WATER IN CLAY MINERALS: 
AN APPLICATION OF NUCLEAR MAGNETIC RESONANCE 
SPECTROMETRY TO CLAY MINERALOGY 

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ABSTRACT 

Adsorbed water and structural hydroxyl groups in several clay minerals were 
studied by NMR spectrometry, infrared absorption spectrometry, proton exchange 
reaction by deuteron, and the substitution of hydroxyl group for fluoride ion. 
Kaolinite, air-dried at room temperature, has double line with wide-line NMR 
absorption with maximum slope line-width $\delta H_{\text{max}}$ of 0.3 and 4.5 gauss. The value 
of $\delta H_{\text{max}}$ is 0.18 gauss for adsorbed water of halloysite, and 0.13 gauss for that of 
montmorillonite, and adsorbed water seems to be different in these minerals. The 
infrared absorption band associated with $\mathrm{O}--\mathrm{H}$ stretching vibration in layer 
silicates distinguishes clearly the adsorbed water from the structural hydroxyl 
group, and the band for adsorbed water is also different between halloysite and 
montmorillonite. Layer silicates may be comparatively stable to fluoride. Protons 
exchanged with difficulty between adsorbed water and structural hydroxyl group, 
but in halloysite seem to be somewhat unstable. 

The absorption line width of wide-line NMR for water in the molecular sieve, 
type 4A, is 0.07 gauss $\delta H_{\text{max}}$, which is closer to the value for free liquid water, and 
increases only to 0.16 gauss on drying at 110°C. The adsorbed water may remain 
in the cavities, being slightly restricted after the drying. The infrared absorption 
band associated with $\mathrm{O}--\mathrm{H}$ stretching vibration of water in the molecular sieve 
is a broad band with maximum near 3400 cm$^{-1}$. 

The absorption line width of wide-line NMR with water in allophane, is 0.12 
gauss $\delta H_{\text{max}}$, and expands to 0.8 gauss on drying at 110°C. The infrared absorp-
tion spectrum of allophane shows a broad absorption band near 3480 or 3490 cm$^{-1}$ 
associated with $\mathrm{O}--\mathrm{H}$ stretching vibration. Protons in allophane are almost com-
pletely exchanged by deuterons, and a large number of the hydroxyl groups are 
released from allophane by fluoride. These results suggest for the properties of the 
water in allophane: comparatively unstable hydroxyl group, weak adsorption of 
water, continuous exchange of proton between adsorbed water and structural 
hydroxyl groups, and difference from so-called “zeolite water.” 

Exchangeable proton content is determined by high-resolution NMR spectrometry. 

INTRODUCTION 

The properties of adsorbed water and structural hydroxyl groups 
in clay minerals are very interesting, and their surface and atomic 
structures are important. Many scientists have studied their properties 
by differential thermal analysis, thermogravimetry, infrared absorption
spectrometry, proton exchange reaction by deuterons, substitution of hydroxyl group by various anions such as fluoride and phosphate, and Karl-Fischer analysis. Moreover, thermodynamic studies on clay-water systems have also been made by many scientists (Grim, 1968).

Recently, nuclear magnetic resonance (NMR) spectrometry has been widely applied to various fields of chemistry. Several researchers introduced NMR to the study of water adsorbed on powder specimens. Resing and his co-workers (1964, 1965, and 1967) studied by wide-line NMR the properties of water adsorbed on charcoal. Resing and Thompson (1969, 1970) applied NMR to the study of “zeolite water.” Woessner and Snowden, Jr. (1969a, b) studied the water adsorbed on montmorillonite by pulsed NMR. Woessner, Snowden, Jr., and Meyer (1970) discussed the application of pulsed NMR to the clay-water system. Anderson (1970) studied the water at phase boundaries in frozen soils by wide-line NMR spectrometry. Prebble and Currie (1970) measured the free water in soils by a wide-line NMR technique.

In this paper, the properties of water in several clay minerals is discussed. The results obtained with wide-line NMR for protons are compared with the data obtained from infrared absorption spectra. Further, protons in clay minerals were exchanged by deuterons, and the exchangeable protons were detected by high-resolution NMR spectrometry. Paulsen and Cooke (1964a, b) proposed a method for quantitative determination of active hydrogen based on the exchange reaction of the group with heavy water and the determination of the exchanging protons by NMR spectrometry. Kula, Rabenstein, and Reed (1965) determined the water of crystallization in ethylenedinitrilotetraacetates with heavy water by NMR spectrometry. Fluoride ion was substituted for the hydroxyl group in clay minerals to examine the stability of their structural hydroxyl group.

Samples

One sample each of kaolinite, halloysite, montmorillonite, molecular sieve, and two of allophane were used.

Kaolinite was from Kaolin Dry Branch, Georgia, obtained from Ward’s Natural Science Establishment, Inc., Rochester, N.Y. The X-ray diffraction pattern indicated the clay fraction of the kaolin contained a small amount of mica minerals and 14 Å minerals as impurities. The halloysite was found in a clay bed altered from volcaniclastic material distributed near Numanoi, Tochigi, Japan. The results of examination by X-ray diffraction analysis, differential thermal analysis, and chemical analysis showed its clay fraction consisted of halloysite and accessory iron oxide. Montmorillonite used was Volclay Bentonite SPV, obtained from American Colloid Company, Skokie, Illinois. X-ray diffraction analysis revealed the clay fraction contained a small amount of quartz in addi-
tion to montmorillonite. Allophane samples were collected from two weathered pumice beds: one is the so-called Kanumatsuchi in Kanuma, Tochigi, Japan; and the other is Misokuchi in Iijima, Nagano, Japan. The results of X-ray diffraction analysis and chemical analysis indicated in both samples small amounts of iron oxide. The molecular sieve, type 4A was produced by Linde Company. The fraction minus 100 mesh was used.

For the clay mineral samples, except for the molecular sieve, the fraction less than 2 μm (clay fraction) was prepared by sedimentation; the fraction suspended in alkaline or acidic water was syphoned off at the required time according to Stokes' law. Kaolinite, halloysite, and montmorillonite were dispersed in NaOH-alkaline solution at pH 8.5; and allophane in HCl-acid solution at pH 3.5. Iron oxide in halloysite and allophanes was, then, removed by a dithionate-citrate system buffered with sodium bicarbonate after Mehra and Jackson (1959). After the above procedures, the samples saturated with hydronium ion were prepared; i.e. the clay fraction was washed with 0.02N HCl, water, ethanol, and acetone, air-dried, and pulverized.

**Experimental**

The water in the samples was determined by gravimetric analysis; namely, the loss in weight after heating at 110 and 1000°C was measured.

Before the measurement by wide-line NMR, two kinds of specimen were prepared; one air-dried at room temperature, and the other dried at 110°C for 72 hours in an oven. The wide-line NMR spectrum was obtained at 20°C using a Varian System WL-12, under the following condition: radio frequency, 7978 MHz; external magnetic field, 1862 gauss; modulation width, 0.079 gauss; sweeping rate, 0.25–0.5 gauss/min; and response time, 1 sec. The specimen was packed to about a 3 cm depth in a pyrex glass tube having a 15 mm outside diameter. From the chart, δHm,1 at 20°C was determined.

The infrared absorption spectrum was measured in the range of the absorption band associated with stretching and deformation vibrations of the hydroxyl group from 1200 to 4000 cm⁻¹ by using a Hitachi Model EPI-G2 infrared spectrometer. The tablet for measurement was prepared by pressing at 200 kg/cm² a mixture of 1 mg of specimen with 200 mg of KBr.

Protons of the water or hydroxyl group in clays were exchanged with deuterons by the following method; 0.2 g of the specimen was suspended in a covered centrifuge tube containing 5 ml of heavy water with dissolved 0.146 g of NaCl at room temperature, and the specimen was allowed to stand for 20, 50, 230, or 1430 minutes and then centrifuged for 10 minutes at 200 rpm. Heavy water used in this experiment had a 99.75 percent purity and was made by Merck Company. Proton amount removed into the supernatant liquid was determined by high-resolution NMR spectrometry. To prepare the standard for the calibration curve, aliquots of water were mixed with the heavy water containing the dissolved 0.146 g NaCl; less than 9 mol of water was added to a liter of the heavy water; 9 mol of water is equivalent to 18 mol of proton. The high-resolution NMR spectrum was obtained at a radio frequency of 60 MHz; sweeping rate, 1 Hz/sec; temperature during the measurement was 25°C; by using a Varian System T-60, and DSS (2,2-dimethyl-2-silapentane-5-sulfonate) was employed as a standard substance. A pyrex glass tube with 4 mm outside diameter was filled to a depth of 3 cm with the supernatant liquid to make the absorption measure-
ment. The intensity of the absorption line was determined from the value of the integral curve of the absorption spectrum drawn on the strip chart.

The amount of hydroxyl group in clays removed by fluoride was determined by the following method: 0.5 g of specimen saturated with ammonium ion was suspended in a centrifuge tube with 80 ml of 0.5, 1.0, or 2.0 N ammonium fluoride solution, kept in a thermostat at 30°C for 24 hours, and centrifuged at 2000 rpm for 10 minutes. Supernatant liquid (20 ml each) was titrated with 0.1 N H$_2$SO$_4$ using bromthymolblue indicator, and the amount of hydroxyl group released from the specimen was calculated.

**RESULTS AND DISCUSSION**

**Water Content**

The content of water in specimens determined from loss in weight on heating at 110 and 1000°C is shown in Table 1. Weight loss was only 1.2 percent in the kaolinite on drying at 110°C, but about 7 percent was lost in the halloysite, despite the fact it belongs to the same mineral group as kaolin. Both minerals lost about 13 weight percent on heating to 1000°C. Two thirds of the total water in montmorillonite was lost at 110°C. Montmorillonite lost an additional 5 percent of its weight after heating to 1000°C, the value is lower than that for kaolin minerals. The water content of these layer silicates agrees well with the values obtained by other analysts (Grim, 1968). The molecular sieve, type 4A had a comparatively high content of water, and about 70 percent of the total water was lost while drying at 110°C. This result suggests that considerable amount of the water in the molecular sieve remains in an adsorbed form, for no hydroxyl group is found in the structural lattice of this mineral according to Reed and Breck.

**Table 1. Loss of Weight on Heating at 110 and 1000°C, and Proton Content Calculated from Weight Loss**

<table>
<thead>
<tr>
<th>Loss of weight (percent)</th>
<th>Proton content (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>110°C</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1.2</td>
</tr>
<tr>
<td>Halloysite</td>
<td>7.1</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>10.3</td>
</tr>
<tr>
<td>Molecular sieve, 4A</td>
<td>14.5</td>
</tr>
<tr>
<td>Allophane, Kamaru</td>
<td>21.1</td>
</tr>
<tr>
<td>Allophane, Misotsuchi</td>
<td>24.1</td>
</tr>
</tbody>
</table>

* Loss of weight corresponds to water content.
Both specimens of allophane have a great deal of water, and \( \frac{3}{4} \) of the total water in the specimens was lost on drying at 110°C. This will be discussed later.

**Wide-line NMR and Infrared Absorption**

The NMR absorption line for protons obtained from each specimen are shown in Figures 1–3. They are differential curves. In the figures, the transition of the external magnetic field is shown on the abscissa, where zero indicates the center of the resonance, and the distance of

![Graphs showing derivatives of wide-line NMR absorption line for montmorillonite air-dried (MWo), halloysite air-dried (HNo), kaolinite air-dried (KGo), and kaolinite dried at 110°C (KGh).](image)

**Fig. 1.** Derivatives of the wide-line NMR absorption line: montmorillonite air-dried (MWo); halloysite air-dried (HNo); kaolinite air-dried (KGo); and kaolinite dried at 110°C (KGh).
Fig. 2. Derivatives of the wide-line NMR absorption line of molecular sieve, type 4A: air-dried (L4Ao); and dried at 110°C (L4Ah).

Fig. 3. Derivatives of the wide-line NMR absorption line of allophanes: Misotsuchi air-dried (AMo); Misotsuchi dried at 110°C (AMh); Kanuma air-dried (AKo); and Kanuma dried at 110°C (AKh).
the magnetic field between maximum and minimum is the maximum slope line width, $\delta H_{\text{mat}}$.

Figure 1 shows the curves for the layer silicates, kaolinite, halloysite and montmorillonite. The absorption line in kaolinite is the double line consisting of 0.3 gauss and 4.5 gauss lines for $\delta H_{\text{mat}}$. The intensity of the wider absorption line may be far stronger than the narrower one, because the intensity is the value obtained from twice the integration of the derivative curve. Only the narrower line has disappeared on drying at 110°C. This result suggests that the narrower line is associated with the adsorbed water, and the wider one corresponds to the structural hydroxyl group. From the viewpoint of NMR, protons in kaolinite, air-dried at room temperature, may be separated into two independent systems, and protons in different systems may not be mutually exchanged. The absorption line for halloysite was 0.18 gauss and narrower than that for kaolinite. The absorption line disappeared on drying at 110°C. This seemed to be associated with the release of the adsorbed water on halloysite, but the adsorption energy of the water may be lower than in the case of kaolinite. The signal due to the hydroxyl group in the halloysite lattice was not observed in the measurement. This may be due to a strong absorption line from the adsorption water compared with that of the structural hydroxyl group. The adsorption line of wide-line NMR for water in montmorillonite was 0.13 gauss in $\delta H_{\text{mat}}$, and also disappeared after drying at 110°C. The water adsorbed on montmorillonite seems to be more like a liquid than the water in halloysite, because montmorillonite has a double layer sheet of water in the space between the structural layers, while halloysite has a monolayer sheet of water in its interlayer space. The wide-line NMR absorption also suggests this difference in the structure.

These results are contrasted with the infrared absorption spectra shown in the left side of Figure 4. Kaolinite had absorption bands with four distinct peaks at 3700, 3670, 3650, and 3620 cm$^{-1}$ associated with O—H stretching vibrations of the structural group, but a few signals from adsorbed water were found. Halloysite has an infrared absorption band at 1640 cm$^{-1}$ associated with the deformation vibration of adsorbed water, besides absorption bands with double peaks at 3700 and 3600 cm$^{-1}$ associated with stretching vibrations of the structural hydroxyl group. The absorption band between 3600 cm$^{-1}$ and 3200 cm$^{-1}$ may be associated with stretching vibrations of adsorbed water in halloysite. Montmorillonite also had two kinds of infrared absorption bands due to adsorbed water and the structural hydroxyl group; 3630 cm$^{-1}$ due to the stretching vibration from the structural hydroxyl
group; 3430 and 1630 cm\(^{-1}\) due to the stretching vibration and deformation vibration, respectively, of adsorbed water. The absorption band associated with the stretching vibration of adsorbed water in montmorillonite was shifted to a lower wave number than the absorption band in halloysite. This result may be related to the state of adsorbed water in both minerals as mentioned in the discussion of wide-line NMR. The infrared absorption band associated with the O—H stretching vibration of the structural hydroxyl group in layer silicates has already been studied in detail by many researchers in relation to the position and direction of the hydroxyl group (Serratosa and Bradley, 1958; Lyon and Tuddenham, 1960; and Hidalgo and Vinas, 1962).

The wide-line NMR spectrum of protons in the molecular sieve, type 4A, showed very sharp absorption with \(\delta H_{\text{rel}}\) 0.07 gauss at room temperature. The absorption line expanded on drying at 110\(^\circ\)C, and \(\delta H_{\text{rel}}\) increased to 0.16 gauss. This suggested that the water in the molecular sieve was closer to free liquid, and a considerable amount of water was also adsorbed on the mineral even after 72 hours of heating at 110\(^\circ\)C. The drying resulted in the expansion of the line width, possibly be-

![Image](https://example.com/figure4.png)

**Fig. 4.** The infrared absorption spectra of kaolinite (KG), halloysite (HN), montmorillonite (MW), molecular sieve, type 4A (L4A), allophane, Kanuma (AK), and allophane, Misotsuchi (AM).
cause binding forces between water molecules and the surface of the molecular sieve became stronger with a decrease of absorbed water. In the infrared absorption spectrum for the molecular sieve, type 4A, shown in the right side of Figure 4, a broad absorption band was found at 3400 cm\(^{-1}\) associated with O—H stretching vibrations, and another band was clearly found at 1660 cm\(^{-1}\) due to the O—H deformation vibration. This suggested that the absorbed water of the molecular sieve is at several energy levels.

The shape of the wide-line NMR curves was almost the same for the two specimens of allophane (Fig. 3). The specimens, air-dried at room temperature, had 0.12 gauss \(8H_{\text{mol}}\). The line width in allophanes was wider than for the type 4A molecular sieve, but narrower than in montmorillonite. The absorption line in allophanes expanded to 0.8 gauss \(8H_{\text{mol}}\) on drying at 110°C. The infrared absorption spectra of allophanes showed the absorption bands associated with the O—H stretching vibrations at 3490 and 3480 cm\(^{-1}\) in Kanuma allophane and Misotsuchi allophane, respectively, and the other band due to O—H deformation vibrations at 1630 cm\(^{-1}\) in both specimens (Fig. 4). The absorption band associated with the stretching vibration of adsorbed water was located at the higher side of the wave number than the bands for the molecular sieve and montmorillonite, despite the result of wide-line NMR. This suggests that the water molecules are adsorbed more strongly on allophane than they are on the molecular sieve. The water remaining in allophane after drying at 110°C was more like a liquid, rather than a structural hydroxyl group in kaolinite, based on the fact that \(8H_{\text{mol}}\) in the former was less than 1 gauss. Many have studied the dehydration of allophane by means of thermogravimetry since Ross and Kerr (1934), and found that allophane releases water slowly in the temperature between 200 to 1000°C.

**Proton Exchange Reaction and Substitution of Hydroxyl Group**

The proton content in heavy water was determined from the high-resolution NMR spectrum using DSS as a standard. Chemical shift due to the protons in water was 2.1 ppm of the \(\delta\) value. The calibration curve of the concentration of protons in heavy water versus the peak intensity obtained from the integral curve drawn in the chart is shown in Figure 5, with a good straight line within the concentration range tested.

The amount of protons in the specimens exchanged by deuterons is shown in Table 2. The exchange reaction was complete within 30 minutes in all specimens except in montmorillonite. The protons in montmorillonite exchanged slowly. This may be due to the jelly-like
consistency of the montmorillonite suspension in water so that the water around the mineral is stagnant. The protons in kaolinite was not exchanged, but the protons in halloysite were exchanged to a greater extent than the water lost on drying at 110°C. This suggests that the protons of the structural hydroxyl group in halloysite are partially exchangeable. In the molecular sieve, type 4A, almost all protons were changed by deuterons. The protons in allophane were exchangeable in spite of the high water content. The protons seem to be continuously exchanged between adsorbed water and the structural hydroxyl group in allophane. Wada (1966) found this phenomenon by infrared absorption spectrometry of clay minerals.

The results of substitution by fluoride showed that a few hydroxyl groups in kaolinite and montmorillonite were released; 0.3 mmol/g in kaolinite and 0.6 mmol/g in montmorillonite were released with 2N ammonium fluoride treatment. From halloysite, 1.5 mmol/g of hydroxyl group was released using 0.5N ammonium fluoride, and the amount of hydroxyl group released by fluoride increased as the concentration of ammonium fluoride solution increased. Hofmann et al. (1956) found that a marked increase of the hydroxyl group released from kaolin

Fig. 5. The calibration curve between the peak intensity of high-resolution NMR associated with water-state proton versus the amount of proton added to heavy water.
minerals occurred as the concentration of the ammonium fluoride solution exceeded 1N. Most of the hydroxyl groups released by fluoride from kaolinite and montmorillonite seem to be from the edges of the structural units.

On the other hand, abundant hydroxyl groups were released from allophane with ammonium fluoride solutions: 7.0, 11.9, and 14.4 mmol/g with 0.5, 1.0, and 2.0N solutions, respectively. The hydroxyl groups in allophane may be more reactive to fluoride ion even at comparatively low concentration. The increase, in hydroxyl groups released from allophane, levels off in ammonium fluoride solutions of about 2N concentration, according to Egawa et al. (1960). The stability of the structural hydroxyl group in clay minerals to fluoride ion may be closely related to the exchangeability of protons in the structural lattice.

### Table 2. Proton Exchanged by Deuteron

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>0.5</th>
<th>1</th>
<th>4</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>(hours)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>tr</td>
<td>tr</td>
<td>tr</td>
<td>tr</td>
</tr>
<tr>
<td>Halloysite</td>
<td>9.4</td>
<td>9.4</td>
<td>10.9</td>
<td>10.5</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>3.3</td>
<td>2.8</td>
<td>10.5</td>
<td>10.0</td>
</tr>
<tr>
<td>Molecular sieve, 4Å</td>
<td>20.0</td>
<td>19.2</td>
<td>20.5</td>
<td>19.2</td>
</tr>
<tr>
<td>Allophane, Kanuma</td>
<td>33.6</td>
<td>33.3</td>
<td>34.4</td>
<td>34.7</td>
</tr>
<tr>
<td>Allophane, Misotsuchi</td>
<td>40.8</td>
<td>35.0</td>
<td>37.5</td>
<td>36.6</td>
</tr>
</tbody>
</table>

### Table 3. Hydroxyl Group Released in Ammonium Fluoride Solution

<table>
<thead>
<tr>
<th>Concentration of</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄F (normality)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Halloysite</td>
<td>1.5</td>
<td>1.9</td>
<td>2.8</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>0.4</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Allophane, Misotsuchi</td>
<td>7.0</td>
<td>11.9</td>
<td>14.4</td>
</tr>
</tbody>
</table>
The energy levels of water are clearly distinguished between adsorbed water and structural hydroxyl groups in layer silicates such as kaolinite, halloysite, and montmorillonite, but such differentiation of water in zeolite and allophane is very difficult. Especially in allophane, this is difficult because its atomic structure is as yet not clearly understood. The results of proton-exchange reactions and substitution of hydroxyl groups by fluoride suggest that all hydroxyl groups in allophane are exposed on the surface.

Fransdorff and Kington (1958) found from the infrared absorption spectrum of synthetic zeolite, type 4A, that the absorption band at 1650-1660 cm\(^{-1}\), associated with the O—H deformation vibration, does not change but the peak of the absorption band associated with the O—H stretching vibration shifts from 3486 cm\(^{-1}\) to 3377 cm\(^{-1}\) as water is added to the zeolite, and it becomes more like liquid water, 3390 cm\(^{-1}\). In the liquid H\(_2\)O—D\(_2\)O system, the absorption band associated with O—H stretching vibration is situated at 3388 cm\(^{-1}\), and OH—O distance is 2.85 Å, according to Van Eck, Mendel, and Fahrenfort (1958). Reed and Breck (1956) reported that molecular sieves, type A series, have two kinds of cavities; large ones are 11.4 Å in diameter, and small ones are 6.6 Å. The adsorbed water in the molecular sieve, type 4A, may be kept in the cavities. On the other hand, Kitagawa (1971) proposed that allophane consists of close-packed “unit particles” 55 Å in diameter. On that basis, allophane has also two kinds of cavities among the particles; large ones are about 23 Å in diameter and small ones are about 12 Å; larger than the cavities in the molecular sieve. A part of the adsorbed water in allophane is kept within the cavities but a great deal of adsorbed water surrounds the allophane particles. The proton in adsorbed water is continuously exchanged with proton in the structural hydroxyl group. Accordingly, the absorption line of wide-line NMR and infrared absorption spectrum in allophane may be different from those in molecular sieve, type 4A. The water adsorbed on allophane and the molecular sieve is slowly released at temperatures higher than 200°C, but the water in allophane may be essentially different from so-called “zeolite water.”

The structural hydroxyl group of allophane is different from that of kaolinite; protons in allophane are continuously exchanged between the structural hydroxyl group and adsorbed water, but protons in the kaolinite structure are stable to the exchange reaction. This may be related to the position and the direction of the hydroxyl group in the different mineral structures.
The properties of water in allophane present an interesting study, and it will be an important problem in the future.

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