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Adsorption of Water on Nano-Ball Allophane as Affected by Dry Grinding

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Abstract: Water adsorption is one of the important physicochemical properties of clays and nano-ball allophane has extremely high water adsorption capacity due to its high specific surface. The water vapor adsorption on two nano-ball allophane samples with low and high Si/Al ratios (0.67: KyP; 0.99: KnP), under various Relative Humidities (RHs), generally decreased with dry grinding treatment. For KyP sample, water vapor adsorption at monolayer level on the nano-ball ($RH \leq 0.45$) decreased by 2 h grinding, but capillary water condensation between the nano-ball ($RH \geq 0.6$) was not affected. The little effect of the grinding on the capillary water condensation means no change in water vapor accessibility of outer surface in the hollow spherical allophane structure. On the other hand, decrease in water vapor adsorption at monolayer level indicates decrease in water vapor accessibility of the rest of total surface, i.e., pore region and inner surface of the hollow sphere. In case of KnP sample with higher Si/Al ratio, water vapor adsorption at monolayer level showed little change with the grinding, but capillary water condensation decreased. These results indicates that, with the grinding, allophane nano-balls in the KnP sample became more closer each other, but small space is still remained allowing monolayer water adsorption on the outer surface, pore region and inner surface. The small space remained is presumed to be due to accessorially attached silicate tails projected outward of the nano-ball, which prevented direct contact between nano-balls. The nano-ball in the KyP sample with few tails tended to contact directly even before the grinding and the grinding might caused connection between nano-balls via pore region which decreased water vapor accessibility to pore region and inner surface.

Key words: Allophane, water adsorption, dry grinding, Si/Al ratio

INTRODUCTION

The phenomenon of grinding is occurring in the natural soil environment. In the earth, abrasion of minerals is one of the principal weathering processes, recognized mainly in dry regions (Yariv and Cross, 1979). The agriculture system is experiencing grinding during cultivation practices. It attains maximum momentum when the seed bed is prepared during dry season in the irrigated area, or prior to rainfall in rain-fed cultivation.

Grinding of clay minerals is an important process occurring in industry and nature. Dry grinding, which is commonly used in sample preparation, causes clay minerals to undergo various changes (Grim, 1968; Sudo, 1974, 1978). The changes may or may not be favorable for intended aims, such as pulverization or mixing of the minerals. Grim (1968) stated that the susceptibility of clay minerals to alteration by grinding should definitely be considered in preparing samples. He also pointed out that clay minerals may yield divergent results due to variation in grinding techniques. Previous studies investigated the effects of grinding on the physicochemical properties of many clay minerals, for example kaolinite (Kristoff *et al.*, 1993; Suraj *et al.*, 1997; Stepkowska *et al.*, 2001), talc (Liao and

Senna, 1992; Sanchez-Soto *et al.*, 1997), pyrophyllite (Perez-Rodriquez and Sanchez-Soto, 1991; Wiewiora *et al.*, 1993; Uhlík *et al.*, 2000) and smectite (Mingelgrin *et al.*, 1978; Cicel and Kranz, 1981; Volzone *et al.*, 1987) and chrysotile (Papirer and Roland, 1981).

According to Yariv and Lapidés (2000), grinding change the surface and colloid properties of clay minerals. For example, (1) grinding increases the ion exchange capacity of the minerals, (2) in the first grinding stage, the particle size decreases and the clay surface area increases, but with further grinding, particles are stuck one to another and the surface area decreases, (3) prolonged grinding leads to the reaggregation of the amorphous material and the formation of spherical particles with a zeolite structure, (4) grinding increases the adsorption of water from the atmosphere and (5) grinding increases the plastic and dispersion properties of clays.

Allophane formed in weathered volcanic ash and pumice has morphology of aggregates composed of fine hollow spherules with diameter of 3.5 to 5.0 nm (Ghoneim *et al.*, 2007). Chemical analysis showed that the amounts of Si and Al, which are the main elements of the spherules wall, differ from one sample to another and vary from 0.5 to 1.0 in terms of Si/Al atomic ratio (Parfitt and Henmi, 1980; Henmi *et al.*, 1981). Wall of the particles has open pores of about 0.35 nm in diameter (Wada and Wada, 1977; Wilson *et al.*, 1986). Because of the particle morphology and resultant high degree of surface activity, gases and liquids including water could be adsorbed easily onto inside, outside and pore region of the hollow sphere. The hydroxyl groups exist on the surface also increase the adsorption capacity for various adsorbates (Clark and McBride, 1984). We determined water vapor adsorption isotherm on nano-ball allophane in relation to detailed chemical structure of the allophane and found that the amount of monolayer water adsorption is close to the amount of functional groups exposed on the allophane structure. This indicates that water molecules are firstly connected to the functional groups such as silanol and aluminol groups on the allophane by hydrogen bonding. Molecular orbital calculations also showed that the adsorption affinity or strength of the hydrogen bonding of water molecule was greater for silanol groups than for aluminol groups (Khan *et al.*, 2006).

In case of nano-ball allophane, dry grinding is predicted to greatly change its water vapor adsorption characteristics, because grinding may cause close approach or bonding of each nano-balls, leading functional groups at inner and outer surfaces and pore region less accessible to the water molecules. Therefore purpose of this research was to investigate the effect of dry grinding on water vapor adsorption behavior of nano-ball allophane in relation to changes in chemical structure, aggregation state and water-accessible functional groups of nano-ball allophane. Further, the effect of grinding on water vapor adsorption may different between allophane samples with different Si/Al ratio, because the ratio has known to affect structural changes of allophane with dry grinding (Henmi *et al.*, 1983). Therefore two allophane samples with different Si/Al ratios were used in this experiment.

MATERIALS AND METHODS

Weathered pumice grains from two different locations in Japan were used in this experiment. The first sample with lower Si/Al ratio, KyP, was collected near Mt. Daisen in Kurayoshi, Tottori prefecture. The second sample with higher Si/Al ratio, KnP, was collected near Mt. Aso in Kakino, Kumamoto prefecture. To obtain nano-ball allophane samples without contaminants such as volcanic glasses, opaline silica, imogolite and organic matter, only the inner part of the pumice grain was used and fine clay fraction (<0.2 μm) was separated (Henmi and Wada, 1976). The separation was carried out by centrifugation after ultrasonification at 28 kHz and dispersion at pH 4 for KyP and at pH 9 for KnP (Henmi and Wada, 1976). The collected fine clay fraction was flocculated by NaCl, washed with water, freeze-dried and used as sample. The Si/Al atomic ratio of the samples were 0.67 for KyP and 0.99 for KnP, respectively. Figure 1 shows chemical structure of nano-ball allophane with lower and higher Si/Al atomic ratio: the KnP sample contains much more polymerized silanol groups at inside and pore region.

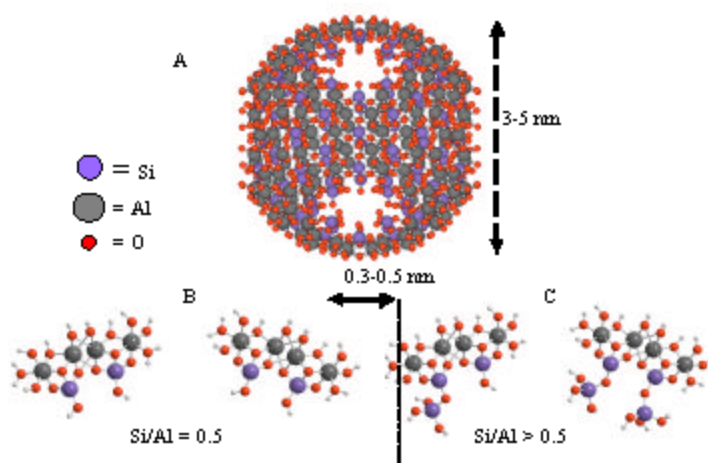


Fig. 1: Chemical structure of nano-ball allophane (A) Full structure, (B) and (C) Atomic arrangement in cross section at pore region

Dry grinding was carried out with mechanical agate mortar and pestle driven by electric motor, using 6.5 g portions of the original samples, for time period of 2 to 8 h. The grinding force was kept constant by always setting the mortar and the pestle in the same position.

Water adsorption was measured by putting each 1 g sample into a glass weighing bottle. The bottle was placed in desiccator with saturated solution of different salt for establishing desired humidity levels at constant temperature ($20 \pm 1^\circ\text{C}$) and the mass was checked every 5 h until a constant value had reached. The various salts used for the humidity control were LiCl (Relative Humidity (RH) = 0.15), CH_3COOK (0.20), CaCl_2 (0.31), KNO_3 (0.45), $\text{Na}_2\text{Cr}_2\text{O}_7$ (0.52), NaNO_2 (0.66), NaClO_2 (0.75), $(\text{NH}_4)_2\text{SO}_4$ (0.81), ZnSO_4 (0.90) and $\text{Pb}(\text{NO}_3)_2$ (0.98). The RH of 0 was achieved through continuous evacuation with P_2O_5 powder.

To investigate structural changes of allophane samples with the dry grinding treatments, samples before and after the dry grinding treatment were subjected to IR spectroscopy, XRD and DTA analysis. IR spectra of the sample was obtained with KBr disk, where 2 mg of sample was mixed with 200 mg of spectroscopic grade KBr, ground and pressed into a disk. IR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer. Powder XRD analysis was performed with a Rigaku Miniflex X-ray diffractometer using $\text{Cu-K}\alpha$ radiation generated at 30 kV and 10 mA. DTA was carried out on a 10 mg sample at a heating rate of $20^\circ\text{C}/\text{min}$ up to 1020°C , using a Rigaku ThermoPlus TG 8120 with micro type sample holder unit. Aluminum oxide was used for temperature calibration.

RESULTS AND DISCUSSION

Change in the Nano-ball Allophane Structure by Dry Grinding

The induced changes by the dry grinding in the IR spectroscopy and XRD in nano-ball allophane samples, KnP and KyP, are shown in Fig. 2 and 3, respectively. With the grinding, both the nano-ball allophane samples showed the same progressive changes in IR spectra (especially in the $300\text{-}1300\text{ cm}^{-1}$ region) and XRD patterns. These changes indicate that the allophane structure is modified appreciably by the dry grinding. According to Kitagawa (1971) and Henmi *et al.* (1983), grinding collapsed the hollow spherules morphology of nano-ball allophane and changed into large thin films. With increase in grinding time the IR spectra became increasingly similar to those of synthetic aluminosilicate precipitates, referred to as hydrous feldspathoids (Famer *et al.*, 1979). The absorption

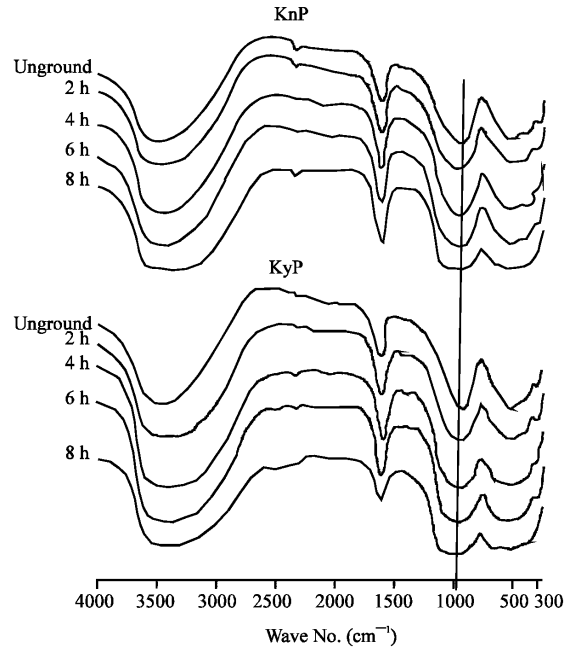


Fig. 2: Infrared absorption spectra of allophane samples unground and ground up to 8 h

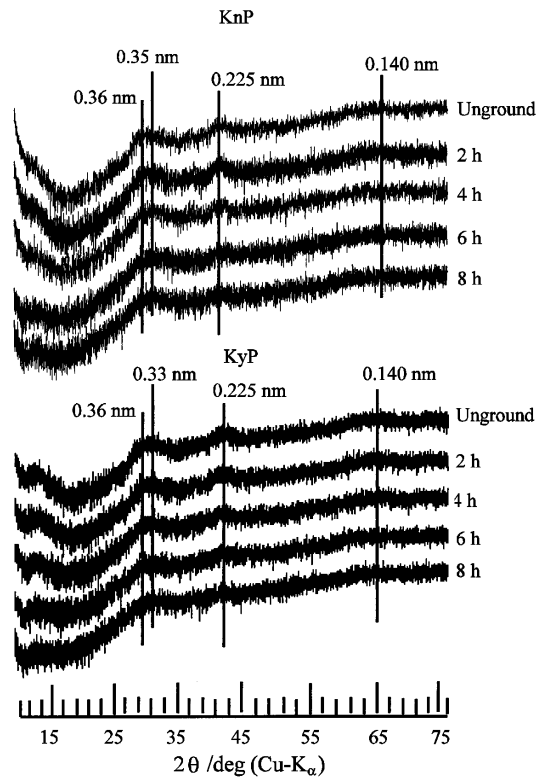


Fig. 3: Effect of dry grinding on X-ray powder diffraction patterns of allophane samples

band at 348 cm^{-1} became weaker with increasing grinding time and disappeared completely after 8 h grinding (Fig. 2). This band has been related to structural domains where imogolite structural units are present in the walls of allophane spherules (Parfitt and Henmi, 1980). The disappearances of the 348 cm^{-1} band therefore indicate that grinding destroyed the imogolite-like structures in the allophane samples. The Si-O stretching band shifted from about 1000 cm^{-1} towards higher frequencies (Fig. 2), indicating increasing polymerization of SiO tetrahedra, which is probably associated with breakdown of some Si-O-Al linkages. Such changes in bonding status of SiO tetrahedra is strongly supported by an accompanying increase in intensity of the absorption band near 450 cm^{-1} , which is assignable to O-Si-O bending vibration of condensed silicates (Moenke, 1974). Simultaneously with these changes in IR absorption bands, the XRD peak heights with maxima at 0.140 and 0.225 nm decreased and disappeared almost completely after 8 h grinding (Fig. 3). The diffraction band at 0.33-0.35 nm shifted to 0.36 nm and the XRD patterns gradually resembled the patterns of synthetic silica gels where most SiO tetrahedra are highly polymerized.

There were, however, differences in the changes of IR spectra (Fig. 2) between the two nano-ball allophane samples with different Si/Al ratios. The absorption bands near 1000 cm^{-1} due to Si-O stretching vibration shifted towards higher frequencies more rapidly with grinding for the sample with low Si/Al ratio (KyP) than that with higher Si/Al ratio (KnP). This shift towards higher frequencies indicates polymerization of SiO tetrahedra and suggests that allophane rich in silica has mechanically stronger structural framework than allophane rich in alumina. These results are in line with Henmi *et al.* (1983).

With increase in grinding time the large endothermic peak height around 150°C , resulting from removal of adsorbed water molecules (Wada, 1977) decreased. This indicates that the water adsorption capacity reduced by the grinding. The exothermic peak at around 1000°C persisted with practically no change in intensity and sharpness, but a small decrease in peak temperature was noticed with the increase in grinding time (Fig. 4). A high temperature exothermic peak has been taken as an indication of the presence of Si-O-Al linkages in non crystalline aluminosilicate materials (Wada, 1977). The decrease in exothermic peak temperature with increase in grinding time might be caused by the deformation of Si-O-Al bonds produced by mechanical forces. These results are in line with Kristof *et al.* (1993).

Change in Water Adsorption of Allophane with Dry Grinding

Water vapor adsorption isotherms of two nano-ball allophane samples, unground and ground up to 8 h are shown in Fig. 5. The isotherms indicate that the amounts of water adsorbed by allophane samples increased with increasing RH or water vapor pressure. For unground samples, the water adsorption isotherms were type II (sigmoidal function curve) as commonly found for the sorption of water vapor by clay minerals (Newman, 1987).

From the water adsorption isotherms it is clear that the water adsorption increased relatively rapidly until $\text{RH} = 0.3$, increased gradually between $\text{RH} = 0.3-0.6$ and again increased rapidly above $\text{RH} = 0.6$. The water adsorption until RH of about 0.5 was attributed to monolayer water adsorption onto functional groups at inner surface (Si-OH), outer surface (Al-OH-Al) and pore region (Al-OH₂, Si-(OH₂) and Si-O-Al) of the nano-ball allophane structure (Khan *et al.*, 2006). From molecular orbital method simulations, the water adsorption at inner surface and pore region were estimated to be stronger than at outer surface and occurred first followed by adsorption at outer surface region (Khan *et al.*, 2006). However, in nano-ball allophane structure, the calculated proportion of the inner surface and pore region to the total surface is approximately one sixth and the rest is the outer surface (Abidin *et al.*, 2006). Therefore even at lower RHs, water adsorption might occur almost simultaneously at all the surfaces although inner surface and pore region were more preferred. This is the reason for the relatively gentle increase of the isotherms at lower RHs (Fig. 5) as compared with those of materials with micropore such as zeolites.

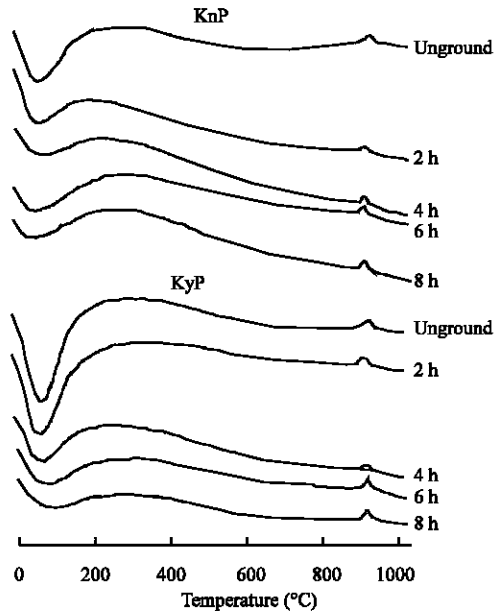


Fig. 4: Differential thermal analysis curves of allophane samples unground and ground up to 8 h

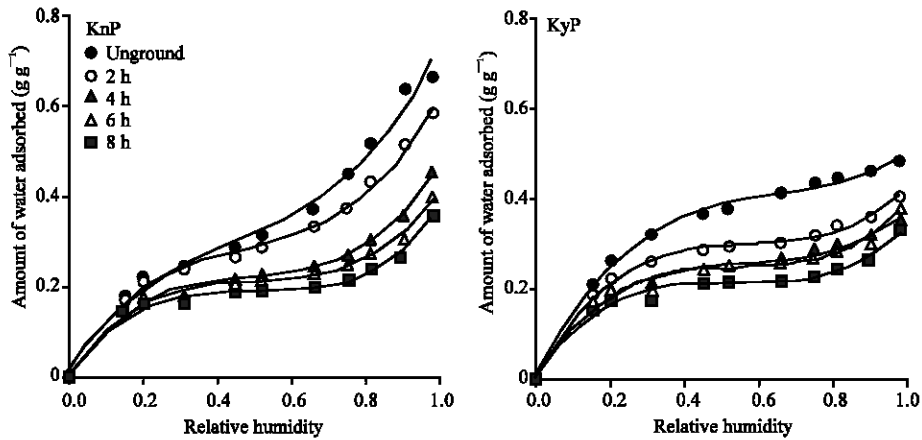


Fig. 5: Adsorption isotherms of water vapor on two allophane samples (KnP and KyP) as affected by dry grinding

The water adsorption beyond RH of about 0.6 is due to capillary condensation at inter-particle region of the hollow spherical allophane unit particles. When compared the two unground allophane samples, water adsorption at this region increased more steeper for KnP than for KyP. This means, even for the unground sample, more aggregation or attachment between hollow spherical particles have occurred for the KyP sample with lower Si/Al ratio, leading water molecules less accessible to the inter-particle region.

After grinding, the amount of water adsorption of the samples decreased with increasing grinding time through all RH levels. For KyP and KnP, the decrease was steep until dry grinding treatment for 2 and 4 h, respectively and became gradual until 8 h (Fig. 5). However, as shown in the IR and

XRD data, dry grinding more than 8 h completely destroyed the chemical structure of nano-ball allophane, therefore we confined the investigations up to 8 h grinding.

For all combinations of allophane samples and dry grinding treatments, the isotherm data points until RH of 0.45 fitted well to the Langmuir equation, indicating strong monolayer water adsorption on allophane. The water adsorption data for the two allophane samples until RH of 0.45 were then plotted according to the linear form of Langmuir equation below.

$$C/X = 1/X_m K + C/X_m$$

Where,

C = RH (unitless).

X = Amount of water adsorbed on allophane (g g^{-1}).

X_m = Maximum water adsorption (g g^{-1}) and

K = A constant related to binding energy (unitless).

The calculated X_m and K values are shown in Table 1. The X_m value decreased with increasing the grinding time for both the two allophane samples and this decrease in X_m value is attributed to less surface area available to the water molecules after the dry grinding. As has been mentioned, there are three different water adsorption sites exist in the nano-ball allophane structure, i.e., outer and inner surfaces and pore region. By grinding, allophane hollow spherical particles came close and were stuck each other and therefore the outer surface of some particles was blocked by adjacent particles. In this case water molecules are not able to go near the blocked outer surface. This might be one of the reasons for lower water adsorption at monolayer level after the grinding treatment. Another reason for the decrease in water adsorption with the grinding treatment is blocking the pore region of allophane particle, because water adsorption to the inner surface of allophane particle requires penetration of water molecules from the pore. If the pore was blocked by adjacent particles, the pore region and also the inner surface become unavailable to water molecules. As a whole, monolayer water adsorption on allophane decreased due to close approach between allophane particles with the dry grinding treatment.

On the other hand, for the both samples, the Langmuir K value tended to increase with increasing the grinding time (Table 1), indicating increase in water adsorption energy after the grinding treatment. With the grinding, allophane particles came close and were stuck each other and the outer surface and pore region became less accessible to water molecules. However, the grinding treatment might cause partial destruction of the hollow spherical wall and exposed new broken edges on the samples. This is the reason for the increasing K value with increasing grinding time, because the newly formed broken edges are expected to have greater affinity for water molecules than the original outer surface has.

The decrease in monolayer water adsorption with the grinding treatment was greater for KyP sample with lower Si/Al atomic ratio: the X_m values of KnP and KyP samples decreased by 0.047 g g^{-1} and 0.101 g g^{-1} , respectively, with grinding for 2 h (Table 1), as compared with corresponding unground samples. However, decrease in water adsorption at higher RHs, where inter-particle capillary water condensation occurred was greater for KnP sample (Fig. 5). These mean that the blocking effect of the outer and inner surfaces and pore region of allophane particles toward water molecules and way of the close approach between particles with grinding are different between KyP and KnP samples.

To observe in more detail the effect of dry grinding on water adsorption of allophane samples, decrease in water adsorption after 2 h grinding for the two samples were plotted in Fig. 6. From the plots, the difference in the effect of dry grinding between the two samples became more clear. For KyP sample with lower Si/Al ratio, the decrease in water adsorption with grinding continues until about RH

Table 1: Langmuir parameters for water adsorption on allophane samples

Sample	Grinding time (h)	Xm (g g ⁻¹)	K
KnP	0	0.393	5.783
	2	0.346	7.220
	4	0.272	7.855
	6	0.250	9.416
	8	0.213	13.458
KyP	0	0.545	4.442
	2	0.444	4.076
	4	0.397	5.344
	6	0.295	8.169
	8	0.237	12.048

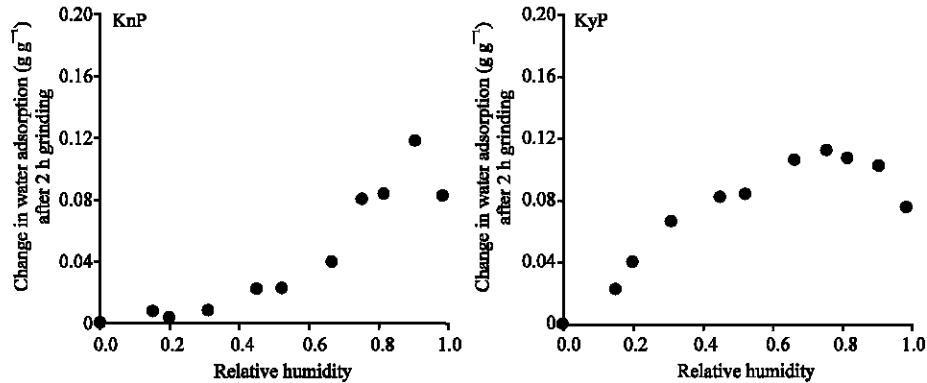


Fig. 6: Change in water adsorption of allophane samples with dry grinding after 2 h

of about 0.7 and at higher RH region, the decrease stopped. This means that for KyP sample, 2 h grinding treatment caused decrease in water adsorption at monolayer level, but water adsorption due to capillary condensation was little affected by the grinding. On the other hand, for KnP sample with higher Si/Al ratio, the decrease in water adsorption started from RH of about 0.4 and the decrease became steeper after RH of about 0.6 (Fig. 6). This means, for KnP sample, the 2 h grinding treatment little affected the water adsorption at monolayer level, but affected capillary water condensation.

For KyP sample, the little effect of 2 h grinding on the capillary water condensation (Fig. 6) indicates little change in aggregation state of allophane hollow spherical particles with the grinding. As it has been mentioned, the hollow spherical particles in the original, unground KyP sample are more closely attached each other than those in the unground KnP sample (Fig. 5). Therefore, more approach of the particles with the 2 h grinding occurred only a little and water adsorption at the capillary condensation region was not affected by the grinding (Fig. 6). This also indicates that accessibility of water molecules to outer surface region did not decrease by the grinding. However, water adsorption at monolayer level decreased (Fig. 6), which leads us to the conclusion that the water accessibility of the pore region and inner surface decreased. The decreased water accessibility of the pore region and inner surface might be caused by direct attachment between pores and between pore and wall of adjacent particles, with the grinding. The above direct attachment prevented water molecules to contact the pore region and to penetrate into the inner surface.

On the other hand for KnP sample, the observed greater decrease in water adsorption at capillary condensation region (Fig. 6) indicates closer approach between allophane hollow spherical particles occurred with the 2 h grinding. The approach is, however, not a direct one. Because the effect of 2 h grinding was very small at monolayer level water adsorption (Fig. 6), indicating the outer surface is still available for water molecules. Therefore, some space is still remaining allowing monolayer water adsorption on the outer surface, in addition to pore region and inner surface, after the grinding.

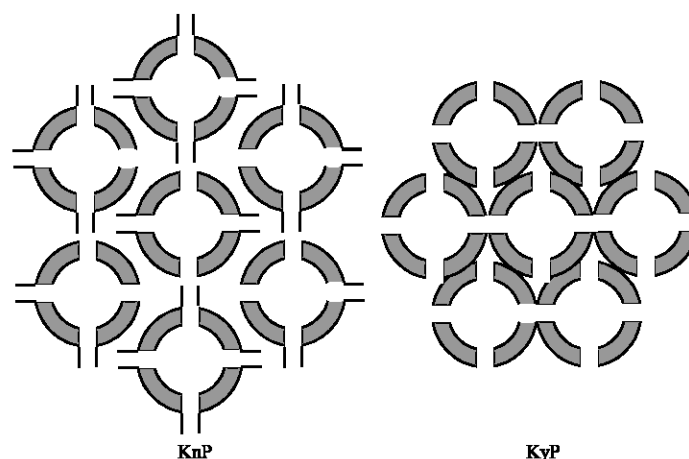


Fig. 7: Aggregation state of KnP and KyP samples after dry grinding

The distinct difference between the two allophane samples in the mode of contact between hollow spherical particles is supposed to be due to Si tetrahedra attached accessorially on the allophane structure. It is already shown that fundamental structure of allophane is that with Si/Al = 0.5 and allophane samples with higher Si/Al ratio, such as KnP, contain polymeric Si tetrahedra in their structure (Shimizu *et al.*, 1988). The accessory Si attach not only to the inner Si-OH, but also to Si-(OH₂), Al-OH₂ and Si-O-Al groups at the pore region to create polymerized Si tetrahedra. If the polymerized Si was formed at the pore, the hollow spherical allophane particles become possess tails projected outward. The polymerized tails possessing negative charge generate a repelling force between the particles. These create a wider space between the particles in KnP sample, where more water molecules were condensed prior to grinding at higher RH. This is the reason for steeper water vapor adsorption isotherm of KnP than for KyP sample before grinding (Fig. 5).

With grinding, for KnP sample, the tailed polymeric Si tetrahedra were broken and collapsed some, leaving less space between two allophane particles (Fig. 7). Therefore the capillary water condensation decreased with the grinding (Fig. 6). However, small tails were still remained after the 2 h grinding and the small tails prevented direct attachment between hollow spherical particles leaving the outer surface, pore region and inner surface of the particles accessible to water molecules. In case of KyP sample the tails are very few and small and with the grinding, the hollow spherical particles attached directly each other through pore (Fig. 7). As has been described, the direct connection between particles is already seen in the unground KyP sample (Fig. 5). In the natural allophane sample preparation processes, it was noticed that allophane samples with lower Si/Al ratio tended to coagulate by air-drying and also by freeze-drying (unpublished data).

CONCLUSIONS

Nano-ball allophane exists in nature and can be synthesized and this material plays important roles in agriculture and environmental conservation through its high surface physicochemical reactivities such as surface area, adsorptive capacity including water and cation and anion exchange capacities. The cation and anion exchange capacities of allophane are well known to be affected by the Si/Al atomic ratio of the sample. In this study, water adsorption behavior and its change with dry grinding have also been shown to be different with the Si/Al ratio of allophane samples and the difference has been interpreted by silicate tails projected outward of the hollow spherical particles. In case of allophane

with higher Si/Al ratio, mild dry grinding such as in sample preparation and in nature causes very small effect on monolayer adsorption of adsorbates like water molecules onto surface of allophane nano-ball. However, similar grinding treatment on allophane samples with lower Si/Al ratio and few tails may decrease accessibility of adsorbates to pore and inner surface of the nano-ball. Therefore it is important to know the Si/Al ratio of allophane sample used, when the material is investigated as an adsorbate both in natural and artificial conditions.

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