

NANOMETER-SCALE CHEMICAL MODIFICATION OF NANO-BALL ALLOPHANE

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Abstract—Nano-ball allophane is a hydrous Al silicate with a hollow-sphere morphology that contains some defects or pores along the spherule walls. Enlargement of the pore openings by dilute alkali treatment was confirmed by cation exchange capacity determinations using various alkylammonium cations as replacement cations. An allophane sample with a low Si/Al ratio (0.67) was equilibrated with 10 mM CaCl₂ (pH = 6.0) and the Ca²⁺ retained was extracted using aqueous 1 M NH₄Cl or alkylammonium chloride salts. The Ca²⁺ extracted by NH₄⁺ was 15.1 cmolc kg⁻¹, but CH₃NH₃⁺ (mean diameter = 0.38 nm) only extracted 7.9 cmolc kg⁻¹ of Ca²⁺. After 10 mM NaOH treatment (0.25 g:100 mL) of the allophane, the Ca²⁺ extracted by NH₄⁺ was 29.7 cmolc kg⁻¹, 29.6 cmolc kg⁻¹ by CH₃NH₃⁺, and 29.4 cmolc kg⁻¹ by (CH₃)₂NH₂⁺. The extraction of Ca²⁺ by the large C₂H₅NH₃⁺ cation (mean diameter = 0.46 nm) only decreased to 26.1 cmolc kg⁻¹, indicating that pore diameters were enlarged from ~0.35 to 0.45 nm. The significant increase in Ca²⁺ retention after NaOH treatment was attributed to the dissociation of increased numbers of newly exposed silanol groups in the enlarged pores. The low Si/Al ratio of the NaOH-dissolved material (0.35) and the decreased intensity of the 348 cm⁻¹ IR band also suggested selective dissolution of the pore region. For allophane with a high Si/Al ratio (0.99) and much accessory polymeric Si, dissolution of polymeric Si and of the pore region occurred simultaneously. Alkali treatment produced a smaller increase in pore size and Ca²⁺ retention for allophanes with large Si/Al ratios than for allophanes with small Si/Al ratios. It was concluded that by altering the dilute alkali treatment conditions and varying the Si/Al ratio of allophane, the extent of structural modification or pore enlargement of the hollow spheres might be controlled.

Key Words—Alkylammonium, Allophane, Dilute Alkali, Dissolution, Pore Size.

INTRODUCTION

Allophane is a naturally occurring Al silicate that has a hollow-sphere morphology with diameters of 2.5 to 5.0 nm (Henmi and Wada, 1976). Therefore, it is sometimes called nano-ball allophane. The sphere wall chemical structure is similar to an imogolite tube (imogolite sheet) which has orthosilicates bonded to the inside of vacant gibbsite sites (Shimizu *et al.*, 1988). The sphere wall, however, has some defects or pores that allow water and metal ions to penetrate into the inside of the sphere (Wada and Wada, 1977). The imogolite Si/Al ratio is usually close to 0.5 (Cradwick *et al.*, 1972), but natural and synthetic allophane Si/Al ratios vary between 0.5 and 1.0 (Parfitt and Kimble, 1989). Solid-state ²⁹Si NMR spectroscopy has shown that allophane samples with greater Si/Al ratios have excess Si attached to the main allophane structure (Si/Al = 0.5) to form polymerized silicates (Shimizu *et al.*, 1988). However, nano-ball allophanes with Si/Al ratios of <0.6 are very rare in both natural and synthetic samples. In a previous work (Abidin *et al.*, 2006), we proposed that the Si/Al

ratio of the main structure was close to 0.6. In allophane, the aluminol functional groups act as anion exchange sites and the silanol functional groups act as cation exchange and surface acid sites. The surface chemical properties together with the unique morphology suggest the possible uses of nano-ball allophane as adsorbents, catalysts and molecular sieves.

Due to the high surface chemical activity and specific surface area, allophane has a low tolerance to acidic and alkaline conditions and dissolution reagents such as oxalate and NaOH (Wada, 1989). We found that natural nano-ball allophane samples separated from volcanic pumice grains in Japan dissolved partly even in dilute NaOH solutions (pH <12), and presumed that the pore region of the hollow sphere was preferentially dissolved (Abidin *et al.*, 2004).

A detailed dissolution mechanism in the pore region was developed using the molecular orbital method where dissolution of three Al atoms and one Si atom was caused by nucleophilic attack on the Si atom by an hydroxyl ion (Abidin *et al.*, 2005). This dissolution mechanism causes the pore openings in the nano-ball allophane structure to enlarge which allows the interior space of the hollow sphere to accept larger ions and molecules. Also, allophane dissolution in the pore region increases the number of broken edge sites and increases the number of exposed functional groups. This leads to

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increases in the cation and anion exchange capacity and surface acid sites. Pore-opening enlargement is a nm-scale chemical modification of the structure that has important implications for allophane use as an adsorbent, catalyst or molecular sieve.

Therefore, the objective of this study was to prove that dilute NaOH treatment can enlarge the pore openings of nano-ball allophane. For this purpose, various alkylammonium cations were used to replace the index cation (Ca^{2+}) during cation exchange capacity (CEC) determinations. The use of progressively larger replacement cations should yield smaller CEC values because smaller pore openings might restrict access by larger cations to cation exchange sites inside the hollow spheres of nano-ball allophane.

MATERIALS AND METHODS

Two different weathered volcanic pumice samples that contain nano-ball allophane were gathered at field sites in Japan: (1) a pumice containing a low Si/Al-ratio allophane was collected near Mt. Daisen in Kurayoshi, Tottori prefecture (KyP); and (2) a pumice containing a higher Si/Al-ratio allophane was collected near Mt. Aso in Kakino, Kumamoto prefecture (KnP). The fine clay fraction ($<0.2 \mu\text{m}$) was separated from only the interior part of pumice grains in order to obtain nano-ball allophane samples without contaminants such as volcanic glass, opaline silica or imogolite (Henmi and Wada, 1976). The fine clay was separated by centrifugation of pumice samples ultrasonically dispersed (28 kHz) after adjustment to pH 4 (KyP) and pH 10 (KnP). The fine clay fractions were flocculated with NaCl, washed with water, and freeze dried. The samples were completely dissolved in acid oxalate solution and Si/Al ratios of 0.67 (KyP) and 0.99 (KnP) were measured (Higashi and Ikeda, 1974).

Allophane samples were partially dissolved by treatment with dilute NaOH solution. A 250 mg sample (KyP or KnP) was placed in a 250 mL polypropylene bottle containing 100 mL of 0 to 100 mM NaOH solution and shaken for 24 h at $30^\circ\text{C} \pm 0.1^\circ\text{C}$. After shaking, the bottle was centrifuged at 9000 g for 30 min and the supernatant liquid decanted. The supernatant liquid was then analyzed for Si and Al using a Hitachi Z-5000 (Hitachi Co., Tokyo, Japan) atomic absorption spectrophotometer (AAS). The material left in the centrifuge tube was designated 'NaOH-treated' after it was washed with distilled water and freeze dried.

The CEC values were measured on 50 mg samples of untreated or NaOH-treated allophane samples in pre-weighed 50 mL polypropylene centrifuge tubes. The allophane samples were Ca saturated using centrifugation to wash three times with 30 mL aliquots of 0.5 M CaCl_2 solution (pH 6.0). Subsequently, each sample was washed once using 30 mL of distilled water and five times using 30 mL of 10 mM CaCl_2 . After the last wash

using 30 mL of 10 mM CaCl_2 , each centrifuge tube was weighed to determine the residual amount of entrained 10 mM CaCl_2 solution. Each sample centrifuge tube was then washed five times using 30 mL of 1 M NH_4Cl or alkylammonium chloride solution for the replacement of exchangeable Ca. The amount of Ca extracted was determined using atomic absorption spectroscopy (AAS). The alkylammonium cations used were: methylammonium (MA), dimethylammonium (DMA), trimethylammonium (TMA), ethylammonium (EA), diethylammonium (DEA), and triethylammonium (TEA). The amount of Ca retained by each sample was calculated as the difference between extracted Ca and entrained Ca. For this calculation, the specific gravity of the entrained 10 mM CaCl_2 solution was assumed to be 1.0 kg dm^{-3} . The CEC determinations were carried out in triplicate.

Infrared (IR) spectra were collected using KBr disks prepared by mixing and grinding 2 mg allophane samples with 200 mg of spectroscopic-grade KBr. For each sample KBr disk, 100 scans were averaged and recorded from 300 to 4000 cm^{-1} using a Shimadzu FTIR-8300 (Shimadzu Co., Kyoto Japan) with a resolution of 4 cm^{-1} .

The differential thermal analysis (DTA) curves of the samples were obtained using 10 mg of the samples against 10 mg Al_2O_3 as the reference material. The samples were analyzed with a heating rate of $20^\circ\text{C}/\text{min}$ using the Rigaku Thermo Plus TG 8110 instrument (Rigaku Co., Tokyo Japan).

RESULTS AND DISCUSSION

Change in structure of allophane with dilute NaOH treatment

The 24 h dilute NaOH treatments dissolved Si and Al in all cases. The total amount of dissolved Si and Al was greater for KyP than for KnP at both concentrations of dilute NaOH (Table 1). It is known that nano-ball allophane samples with larger Si/Al ratios have a greater tolerance to thermal and grinding treatments (Henmi, 1980; 1985) and to dilute acid solutions (Henmi *et al.*, 2001). This greater tolerance is attributed to the larger content of attached polymerized Si in the larger Si/Al-ratio allophane samples which might act to protect the main allophane structure. The substantial amounts of Si and Al dissolved from two samples by 100 mM NaOH treatment suggest the collapse of the hollow-sphere morphology.

The 10 mM NaOH treatment of KyP preferentially dissolved more Al than Si. This is reflected by the smaller Si/Al ratio (0.35) of the dissolved material from KyP than the untreated (0.67) sample ratio (Table 1). Two possible reasons might explain preferential Al dissolution: (1) dissolution of outer surface Al-OH-Al bonds; and (2) dissolution of the pore region. However, as noted by Abidin *et al.* (2005), it can be reasonably

Table 1. The Si and Al dissolved from untreated and dilute NaOH-treated allophane samples: Si/Al ratios and percent Si and Al dissolved.

NaOH concentration	Si/Al residue		Si/Al dissolved		%Al dissolved		%Si dissolved	
	KyP	KnP	KyP	KnP	KyP	KnP	KyP	KnP
Untreated	0.67	0.99	—	—	—	—	—	—
0	0.68	0.98	1.97	5.13	0.22	0.17	0.64	0.90
10 mM	0.75	0.99	0.35	1.05	10.51	6.64	5.38	6.06
100 mM	0.85	1.10	0.50	0.83	38.96	28.12	27.85	22.91

argued that dissolution at the broken edges (pore region) would release 2 or 3 Al atoms for each Si atom. Therefore, allophane nano-balls in the 10 mM NaOH-treated KyP sample might have larger pore openings than the untreated sample and the enlarged pore region in the treated sample might contain newly-exposed silanol and aluminol groups.

The Si/Al ratio (1.05) of the dissolved material from the 10 mM NaOH-treated KnP sample is close to that of the untreated (0.99) sample, but does not necessarily mean congruent dissolution. Because KnP contains a large amount of accessory polymeric-Si that increases the Si/Al ratio, polymeric Si dissolution in alkaline solution (Table 1) or dilute acids (unpublished data) would act to reduce the Si/Al ratio in the residual solid. Therefore, it is more reasonable to suggest that simultaneous dissolution of accessory Si and the pore region occurred during 10 mM NaOH treatment to produce the Si/Al ratios observed in the dissolved material. The smaller Si/Al ratio in the dissolved material from the 100 mM NaOH treatment (0.83) compared to the 10 mM NaOH treatment (1.05) suggests greater hydroxyl ion attack of the main allophane structure relative to accessory Si dissolution. Accessory Si might act to protect the main allophane structure from dissolution by more dilute NaOH treatments.

Changes in the chemical structure of the allophane samples after NaOH treatment was also examined using IR spectroscopy (Figure 1). The IR spectra of untreated and NaOH-treated allophane samples were generally similar. Small but distinct changes were, however, observed for the absorption bands at 348 cm^{-1} and near 1000 cm^{-1} .

The 348 cm^{-1} peak position for KyP did not change after 10 mM NaOH treatment, but the intensity of this band decreased (Figure 2a). Because the 348 cm^{-1} band is related to the Al–OH–Al bonds in the ‘imogolite structure’ (Farmer *et al.*, 1977), the decreased intensity of this band suggests preferential dissolution of Al relative to Si. This is consistent with the smaller Si/Al ratio (0.35) of the dissolved material (Table 1). The peak position of the 970 cm^{-1} band did not change after 10 mM NaOH treatment (Figure 2b). The peak position of the 970 cm^{-1} band, which is attributed to Si(Al)–O stretching vibrations, shifts to higher wavenumbers with

increases with the polymeric Si content in allophane (Parfitt *et al.*, 1980; Parfitt and Henmi, 1980). The higher wavenumber position of the 970 cm^{-1} band in the untreated KnP sample (997 cm^{-1}) is due to the greater polymeric Si content (Figure 2b). The lack of change in peak position for the 970 cm^{-1} band suggests that very little dissolution of accessory polymeric Si occurred. This suggests that dissolution of the KyP sample occurred largely in the pore region.

However, the 997 cm^{-1} KnP peak shift to 984 cm^{-1} after 10 mM NaOH treatment (Figure 2b) suggests that some of the large polymeric Si content of this sample was dissolved. The 348 cm^{-1} band peak position was not changed, but the peak intensity decreased slightly after 10 mM NaOH treatment (Figure 2a). The decreased peak intensities of the 348 cm^{-1} band for KnP and KyP were similar and suggest dissolution of the allophane pore region. These changes in both the

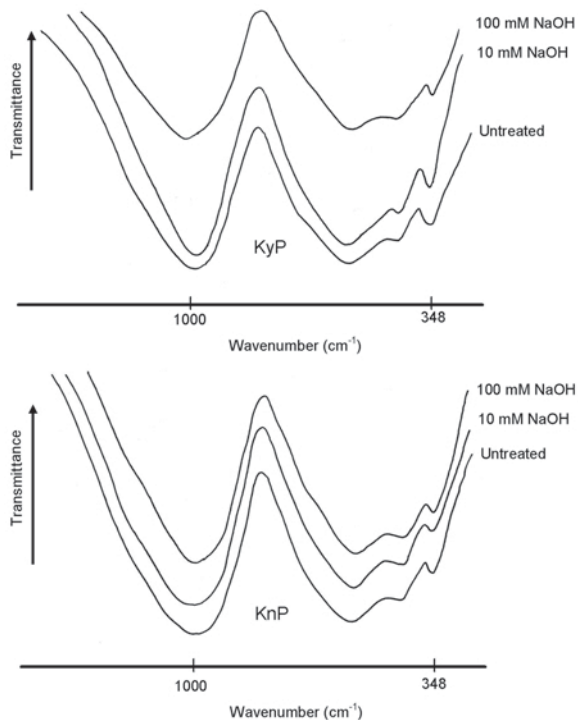


Figure 1. Change in IR spectra of allophane samples (KyP:Si/Al = 0.67 and KnP:Si/Al = 0.99) with NaOH treatment.

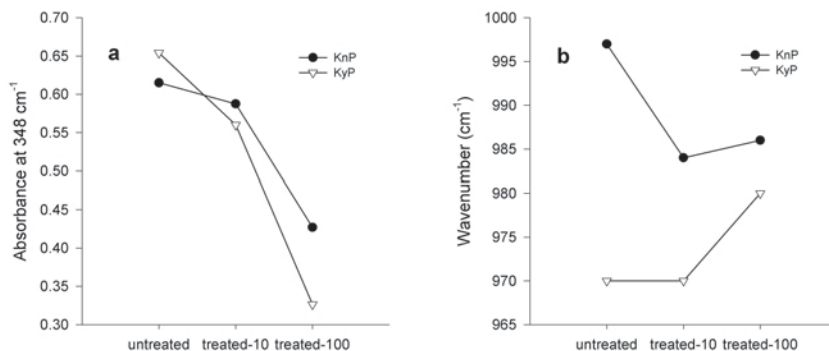


Figure 2. Detailed examination of IR spectra from Figure 1: (a) changes in 348 cm⁻¹ absorbance, and (b) changes in peak position of the band near 1000 cm⁻¹.

348 cm⁻¹ and 970 cm⁻¹ IR bands of KnP suggest that pore region and accessory Si dissolution occurred simultaneously during 10 mM NaOH treatment. The intensity of the 348 cm⁻¹ band for both allophane samples (Figure 2a) was greatly diminished after 100 mM NaOH treatment due to dissolution of much of the Al and collapse of the allophane sphere.

The differential thermal analyses of the allophane samples that were carried out to examine the water content have been summarized in Figure 3. The original allophane samples showed broad endothermic peaks at 87.2 and 90.7°C for KyP and KnP, respectively. The endothermic peaks are due to dehydration and dehydroxylation (Wada, 1989; Mitchell *et al.*, 1964), and allophane samples with larger Si/Al ratios show greater endothermic peaks than samples with smaller Si/Al ratios (Henmi, 1980). This order in the intensity of endothermic peaks corresponds to the increased amounts of silanol groups, which strongly adsorb water, in allophanes with increased Si/Al ratios. The endothermic peak areas from 30 to 250°C were 5.5 and 6.0 cm²/mg for KyP and KnP samples, respectively. The endothermic peak area was correlated with the amount of water adsorbed to the allophane samples.

With alkali treatment, the endothermic peaks shifted to higher temperatures as shown in Figure 3a. This peak

shift might be due to the exposure of new silanol and aluminol functional groups, especially in the pore region, after dissolution by the alkali treatment. By using molecular orbital analysis, Khan *et al.* (2006) observed that water adsorption to allophane was stronger to functional groups in the pore region than to the wall region. The alkali treatment also increased the amount of water adsorption. Figure 3b shows that the endothermic peak area changes from 30 to 250°C for two allophane samples. With 10 mM NaOH treatment, the endothermic peak areas increased by 25.5 and 22.4% for KyP and KnP samples, respectively, in comparison to untreated samples. This result, together with the endothermic peak shifts (Figure 3a), strongly support our assumption that the pore size was enlarged and new functional groups were exposed.

CHANGES IN ALKYLAMMONIUM CATION ADSORPTION AFTER NaOH TREATMENT

The CEC values (Figure 4) were determined from the difference between the Ca²⁺ concentrations in the NH₄Cl or alkylammonium chloride solution extracts and the Ca²⁺ present in the entrained 10 mM CaCl₂ solution (pH = 6.0) for both untreated and 10 mM NaOH-treated allophane samples. The CEC values were designated

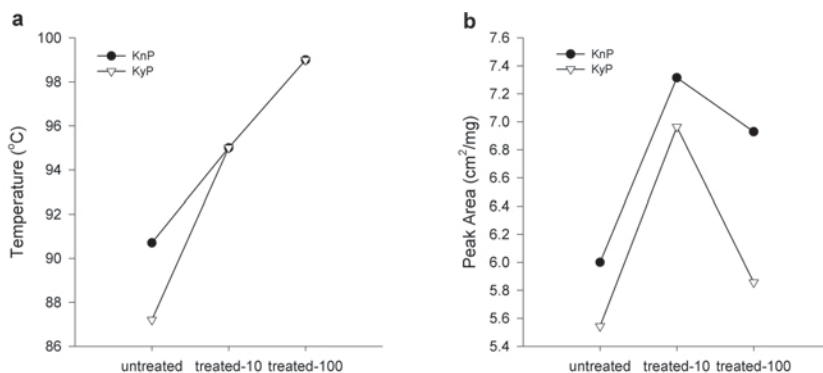


Figure 3. Shifts in endothermic peak temperature (a) and changes in endothermic peak area (b) of allophane samples after alkali treatment.

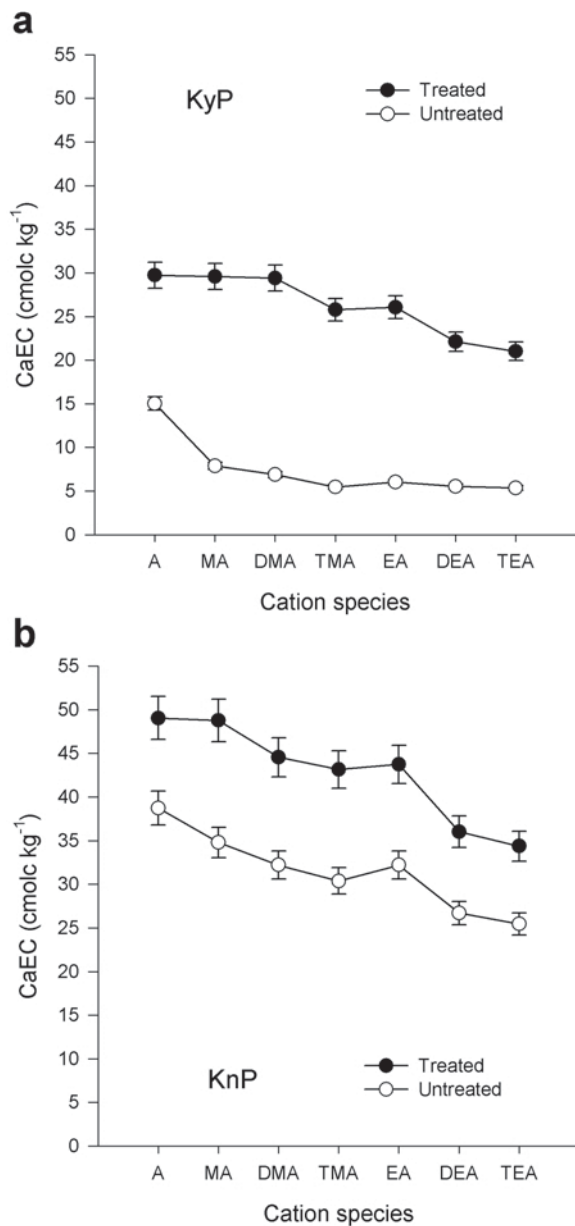


Figure 4. Calcium exchange capacities (CaEC) of untreated and 10 mM NaOH-treated allophane (KyP:Si/Al = 0.67 and KnP:Si/Al = 0.99) samples based on the amount of Ca extracted using ammonium (A) and alkylammonium cations of progressively greater size increasing from methylammonium (MA) to triethylammonium (TEA). Error bars indicate means and standard errors ($n = 3$).

A-CEC for the NH_4Cl extraction and similarly for the alkylammonium chloride extractions. The untreated KyP sample had an A-CEC value of $15.1 \text{ cmolc kg}^{-1}$. The A-CEC values were considered to be equivalent to the total amount of exchangeable Ca^{2+} retained by each sample. The MA-CEC value decreased to $7.9 \text{ cmolc kg}^{-1}$ suggesting that the larger CH_3NH_3^+ cation (mean diameter = 0.38 nm) had restricted access to the interior space of allophane hollow spheres due to

the limited size of the pore openings. Therefore, the CEC decrease ($15.1 - 7.9 = 7.2 \text{ cmolc kg}^{-1}$) was assigned to exchangeable Ca^{2+} retained inside the hollow spheres and the MA-CEC value ($7.9 \text{ cmolc kg}^{-1}$) was assigned to exchangeable Ca^{2+} retained outside the spheres. As the size of the alkylammonium cation was increased, the CEC values gradually decreased to the $5.4 \text{ cmolc kg}^{-1}$ value for $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ (TEA-CEC). The gradual CEC decrease might be a steric effect. The larger alkylammonium cations might have had restricted access to interior cation exchange sites due to the small size of the pore openings. These results suggest that the diameters of the pore openings of the KyP-allophane hollow spheres was $\sim 0.3\text{--}0.4 \text{ nm}$ as reported by Wada and Wada (1977). About half of the exchangeable Ca^{2+} was retained inside the hollow spheres and the other half retained in the pore region.

The A-CEC of KyP increased to $29.7 \text{ cmolc kg}^{-1}$ (Figure 4a) after 10 mM NaOH treatment. This implies that new silanol groups were exposed in the pore region as suggested by the Si and Al dissolution data. The MA-CEC ($29.6 \text{ cmolc kg}^{-1}$) and DMA-CEC ($29.4 \text{ cmolc kg}^{-1}$) values were nearly equal to the A-CEC value, but the EA-CEC was slightly smaller at $26.1 \text{ cmolc kg}^{-1}$. These CEC values suggest that after NaOH treatment, the smallest alkylammonium cation rejected by the pore openings changed from MA (mean diameter = 0.38 nm) to EA (mean diameter = 0.46 nm) due to pore opening enlargement. The pore opening diameter was roughly estimated to have increased from 0.35 nm to 0.45 nm . The $3.6 \text{ cmolc kg}^{-1}$ difference between the A-CEC (29.7) and EA-CEC (26.1) values for KyP was attributed to Ca^{2+} retained inside the hollow spheres that was not accessible to $\text{C}_2\text{H}_5\text{NH}_3^+$ cations, whereas the $26.1 \text{ cmolc kg}^{-1}$ (EA-CEC) was attributed to Ca^{2+} retained outside the hollow spheres. After NaOH treatment, the amount of Ca^{2+} retained inside the hollow spheres decreased from 7.2 to $3.6 \text{ cmolc kg}^{-1}$ and Ca^{2+} retained outside the hollow spheres increased significantly from 7.9 to $26.1 \text{ cmolc kg}^{-1}$ because the average pore circumference increased and the wall area decreased with pore enlargement. The larger alkylammonium cations, TMA, DEA and TEA, gave slightly smaller CEC values compared to the EA-CEC (Figure 4a) due to steric effects at the pore region.

It was concluded from dissolution data, IR spectra, thermal analysis, and other observations noted above, that 10 mM NaOH treatment of KyP caused preferential pore-region dissolution which enlarged the pore openings and increased the number of exposed silanol groups. Figure 5 illustrates possible changes in pore-opening size in relation to changes in CEC values that were induced by treating KyP with 10 mM NaOH. Possible changes in the hollow spherical allophane particles of untreated and NaOH-treated samples are compared.

As noted above, the particles of KyP are very similar to nano-ball allophane particles without accessory

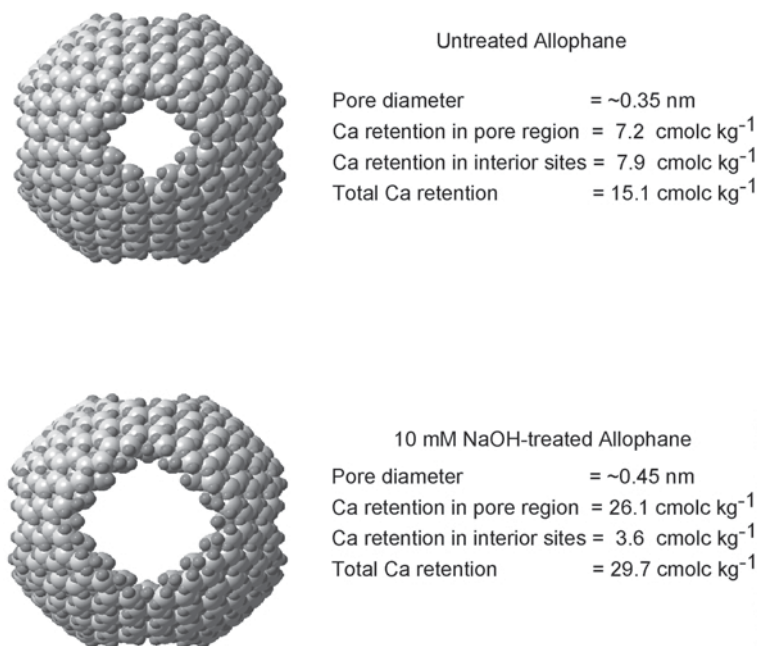


Figure 5. Possible morphological changes in KyP nano-ball allophane particles caused by 10 mM NaOH treatment inferred from changes in CEC measured by Ca extracted using ammonium and progressively larger alkylammonium cations.

polymeric Si. The increased size of the pore openings and increased CEC values illustrated in Figure 5 were caused by chemical modification and suggest the possible use of modified nano-ball allophanes as adsorbents, catalysts and molecular sieves. The degree of modification, especially the increased size of pore openings, can be controlled by varying the NaOH concentration and the reaction conditions.

However, the greater than three-fold increase in A-CEC (Figure 5) values was much greater than the calculated increase in pore circumference (0.45/0.35, 1.3 times). This suggests that NaOH treatment exposed new Si atoms near the pores with a greater number of more strongly dissociated OH groups. For example, by analogy with organic acids, the first dissociation reaction of Si-OH would be more likely to occur for =Si(OH)₂ groups than for ≡SiOH groups.

The 10 mM NaOH treatment also enlarged the pore openings of KnP, which has a large amount of accessory polymeric Si. The untreated KnP allophane had an A-CEC of 38.7 cmolc kg⁻¹, an MA-CEC of 34.8 cmolc kg⁻¹, and CEC values that decreased progressively as the size of the alkylammonium cation was increased to TEA (Figure 4b). This suggests that the untreated KnP nano-ball allophane has a pore-opening size between 0.3 and 0.4 nm, similar to that of untreated KyP. All the CEC values using NH₄⁺ and the alkylammonium cations were greater for the 10 mM NaOH-treated allophane samples than for the untreated allophane samples (Figures 4a, 4b). The DMA-CEC (44.6 cmolc kg⁻¹) of KnP was less than the MA-CEC

(48.8 cmolc kg⁻¹) and the A-CEC (49.1 cmolc kg⁻¹), but the A-CEC, MA-CEC, and DMA-CEC values for KyP were similar (Figure 4a). This suggests that the degree of pore-opening enlargement for the nano-ball allophanes was greater for the KyP sample than for the KnP sample. The 10.4 cmolc kg⁻¹ increase in the A-CEC for KnP was also smaller than the 14.6 cmolc kg⁻¹ increase for KyP. The percent increase in A-CEC was much smaller for KnP (27%) than for KyP (97%). The smaller increases in pore size and A-CEC for KnP were due to polymeric Si dissolution during 10 mM NaOH treatment. Some of the NaOH that might otherwise have attacked the pore region instead dissolved polymeric Si. The loss of polymeric Si eliminated some of the cation exchange sites.

Polymeric Si formation in the allophane structure is known to result in increased CEC values and greater surface acidity (Nartey *et al.*, 2001; Matsue and Henmi, 1993). However, it is difficult to determine experimentally the detailed chemical arrangement of accessory polymeric Si and the arrangement differs from one sample to another. The retention of Ca²⁺ in the pore region estimated from MA-CEC values was 34.8 cmolc kg⁻¹ for untreated KnP, but only 7.9 cmolc kg⁻¹ for untreated KyP. Also, the difference (3.9 cmolc kg⁻¹) between A-CEC and MA-CEC values used to estimate Ca²⁺ retention inside the inner surfaces was smaller for KnP than for KyP (7.2 cmolc kg⁻¹). These differences suggest that most accessory polymeric Si exists in the nano-ball allophane pore region where Si acts to increase cation retention.

CONCLUSIONS

Nano-ball allophane has hollow-sphere morphology with pores and is frequently found in volcanic ash soils, in pumice samples, and can be prepared synthetically. The pores are needed to form allophane hollow spheres from imogolite sheets. The pores act to limit larger ion and molecule access to the interior surfaces of the hollow spheres where silanol groups are exposed. This study has demonstrated that dilute alkali treatment of nano-ball allophane can enlarge pore openings and increase CEC.

Dilute alkali treatment (10 mM NaOH, sample/solution ratio = 2.5 mg/mL) of nano-ball allophane sample KyP selectively dissolved the pore region and some polymeric Si. The diameter of pore openings was increased from ~0.35 nm to 0.45 nm and total Ca²⁺ retention increased from 15.1 cmolc kg⁻¹ to 29.7 cmolc kg⁻¹. The increased CEC was attributed to greater numbers of silanol groups in the pore region that more readily dissociate to form exchange sites. For the KnP allophane sample, which has much polymeric Si, the dissolution of both polymeric Si and the pore region leads to smaller increases in pore-opening size and CEC.

The greater pore-opening size of nano-ball allophane after alkali treatment allows larger ions and molecules to penetrate inside the hollow spheres. The increased CEC might increase the nano-ball allophane adsorptive and catalytic capacities. Pore-opening sizes and CEC values of nano-ball allophanes might be controlled by adjusting the conditions of the dilute alkali treatment.

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