



Sorption of phosphates on Al-pillared smectites and mica at acidic to neutral pH

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Abstract

To investigate sorption behaviors and mechanisms of phosphates, phosphate sorption (hereafter, P sorption) experiments were carried out for synthetic montmorillonite, beidellite, saponite, and fluor-tetrasilicic expandable mica pillared with cationic, Keggin ion-like, Al clusters (Al_{clst}). The P sorption experiments were done in the final pH range of 3 to 7 at room temperature and at an initial concentration of 3.2 mmol/l P. The P sorption maxima for the Al_{clst} samples were 0.66–0.87 mmol/g, which are higher by about 2 orders of magnitude than those for smectites without Al_{clst} pillars. The sorption ability of the Al_{clst} samples is nearly as high as that of Al-bearing minerals and materials such as boehmite and amorphous Al hydroxide, which are regarded as effective absorbents to remove P from water. Examinations by X-ray diffraction analysis, infrared spectroscopy, scanning electron microscopy, and analytical transmission electron microscopy indicated that the P sorption is mostly related to the OH functional groups of the Al_{clst} pillars, but little to the P species in solution, the reactive sites on the edge surface of smectites and mica, or possible precipitates. The P sorption maxima increased with increasing an amount of Al_{clst} pillars in the Al_{clst} samples, suggesting that the P sorption maximum is determined by the number of the OH functional groups of the Al_{clst} pillars and is independent of the structures and chemical compositions of the host phases.

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1. Introduction

Increase of phosphates in water promotes growth of microorganisms such as algae and cyanobacteria, which results in loss of dissolved oxygen because of high biological oxygen demand levels (e.g., Fox and Malati, 1993; Sharpley et al., 1994; Ruan and Gilkes, 2000). Behaviors and mechanisms of phosphate sorption (unless otherwise described, phosphate sorption

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is hereafter referred to as P sorption) on soils and minerals have been investigated extensively from environmental and geological standpoints (e.g., Parfitt, 1978; Goldberg and Sposito, 1985; Sharpley et al., 1994). The most effective minerals for P sorption are Al-bearing minerals such as boehmite and gibbsite, Fe-bearing minerals such as ferrihydrite, goethite and hematite, and kaolinite (e.g., Barrow, 1985; Parfitt, 1989; Fontes and Weed, 1996). The sorption is credited to the presence of Al–OH and Fe–OH functional groups on the mineral surface.

Two important mechanisms for P sorption to Al–OH functional groups have been proposed. One is an ion-exchange mechanism that involves surface OH groups (Parfitt, 1978, 1989; Nanzyo, 1984; Goldberg and Sposito, 1985; Fox and Malati, 1993; He et al., 1994; Fontes and Weed, 1996; Tang et al., 1997; Lookman et al., 1997). Parfitt (1978) has suggested that phosphate is adsorbed on mineral surface forming binuclear complexes. The other is a precipitation mechanism that forms P-bearing materials, which is accompanied by dissolution of Al-bearing minerals and materials (Nanzyo, 1987; Lookman et al., 1994, 1997; Tang et al., 1997). This reaction plays an important role in P sorption at low pH or high P concentration (Tang et al., 1997; Lookman et al., 1997).

Smectite, abundant at the earth surface, has characteristics of permanent negative charge, large surface area, and profound reactive surface sites and has high ability for cation sorption, e.g., a large cation exchange capacity (CEC). The pillaring of Keggin ions, $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ (hereafter, Al_{13}), and cationic Al clusters with Keggin ion-like structures (e.g., $[\text{Al}_{13}\text{O}_4(\text{OH})_{30}(\text{H}_2\text{O})_6]^+$) into smectite results in increases in basal spacing, surface area, and pore and produces a structure with two-dimensional micropores (e.g., Pinnavaia et al., 1984; Plee et al., 1985; Schoonheydt et al., 1993). The sorption capacities of Al_{13} -pillared smectites for cations such as Cd, Cu, Zn, and Ni are as high as those of nonpillared smectites (Matthes et al., 1999; Jobstmann and Singh, 2001; Cooper et al., 2002).

On the other hand, smectite hardly sorbs anions such as phosphates. Phosphate sorption by smectite is lower by about 2 orders of magnitude than that by Al-bearing minerals and materials because of less amount of reactive sites such as Al–OH (Fox and Malati, 1993; Tang et al., 1997; Lookman et al., 1997). Al-

bearing minerals show high P sorption because of the presence of Al–OH and Al–H₂O (e.g., Parfitt, 1978; Tang et al., 1997; Lookman et al., 1997) which are also contained in the Al_{13} pillars and Keggin ion-like Al clusters. This implies that Al_{13} -pillared smectites and smectites with Keggin ion-like Al clusters possibly have high affinity for P sorption. The purpose of the present study is to elucidate sorption behaviors and mechanisms of phosphates on the smectites and expandable mica pillared with Keggin ion-like Al clusters that are more stable than Al_{13} (Schoonheydt et al., 1993). The Keggin ion-like Al clusters are hereafter referred to as Al_{clst} and pillars with the Al_{clst} as Al_{clst} pillars.

2. Experimental procedures

2.1. Sample preparation

Three synthetic Na-smectites, montmorillonite (Na-Mont), beidellite (Na-Beid), and saponite (Na-Sap), and a synthetic Na-fluor-tetrasilicic mica (Na-TSM) were used as host materials. Na-TSM provided by Topy Industries is an expandable mica. The smectites were prepared as described below according to the methods by Yamada et al. (1991, 1999). Starting glasses were quenched from a mixture of Na_2CO_3 , Al_2O_3 , MgO, and SiO_2 with stoichiometric dehydrated Na-smectite compositions corresponding to Na-Mont, Na-Beid, and Na-Sap. The glasses were crushed and fractionated at $< 10 \mu\text{m}$ by hydraulic classifier. One hundred milligrams of each pulverized glass and 100 mg of distilled water were sealed in a gold tube and reacted at a hydrothermal pressure of 100 MPa for 7 days in a rapid-quench type hydrothermal apparatus (Yamada et al., 1988). The synthetic temperatures for Na-Mont, Na-Beid, and Na-Sap were 325, 375, and 350 °C, respectively.

The pillaring of the Al_{clst} into the interlayers of the four samples was made by the method described in Yamada et al. (1995) who slightly modify the method by Schoonheydt et al. (1993). The Al solution for pillaring was prepared by adding 0.4 M NaOH dropwise to 0.4 M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solution with stirring. The OH/Al ratio was 2. The solution was refluxed for 24 h before it was mixed with the Na-smectites and Na-TSM. A suspension with 1 wt.% of each solid sample

was added to 10 times more of the refluxed Al solution than was required to satisfy the CEC of each sample. The suspension was stirred at room temperature for 24 h. Then, the suspension was filtered, washed by distilled water, and dried at 70 °C for 24 h in oven to obtain a sample pillared with the Al_{clst} (hereafter, Al_{clst} sample). Al_{clst}-pillared montmorillonite, beidellite, saponite, and fluor-tetrasilicic mica are hereafter referred to as Al_{clst}-Mont, Al_{clst}-Beid, Al_{clst}-Sap, and Al_{clst}-TSM, respectively. The formation of the Al_{clst} pillars in the interlayers of the Al_{clst} samples was confirmed by the change in basal spacings of the Al_{clst} samples prepared randomly on glass slides. The basal spacings were measured by X-ray diffractometry (XRD, Rigaku RINT2200) with monochromatized CuK α radiation operated at 40 kV and 20 mA.

The surface areas were measured by the BET (Shimadzu FlowSorbII 2300) method using nitrogen gas after removal of physically adsorbed water at 150 °C for 4 h. The chemical formulas and the Al amounts in the interlayers of the Al_{clst} samples were obtained from chemical analyses determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Nippon Jarrell-Ash IRIS AP). A solution for ICP-AES measurement was prepared by the following procedure: for Si, Al, and Mg, 10 mg of each Al_{clst} sample was mixed with a Na₂CO₃ and H₃BO₃ powder. After melting the mixture by heating, the mixture was dissolved by a HNO₃ solution, and finally pure water was added to the solution to make 100 ml of a final solution. For Na, 10 mg of each Al_{clst} sample was immersed in H₂SO₄ and then HF solutions and dissolved. After the solution was evaporated, the dried residual was dissolved by heating it in an HNO₃ solution, and pure water was added to the solution to make 50 ml of a final solution.

2.2. Phosphate sorption experiments

The P sorption experiments were carried out at room temperature in the final pH range of 3 to 7 at an initial concentration of 3.2 mmol/l P. Thirty milligrams of each Al_{clst} sample was mixed with 15 ml of 3.2 mmol/l H₃PO₄ and 10 mmol/l NaNO₃ solution. NaNO₃ worked as background electrolyte. The initial pH was adjusted by adding an HNO₃ or NaOH solution to the above reactant solution. Each Al_{clst} sample reacted with the solution in a polypro-

pylene vessel for 24 h by rotating the vessel at 20 rpm. The polypropylene vessel was used to avoid Si contamination. Solutions after P sorption were separated from solids by centrifugation at 30,000 rpm for an hour and then filtrated through a 0.22- μ m filter. The solids were separated using a membrane filter of 0.45 μ m to remove excess solution and dried at room temperature.

The pHs of the product solutions were measured immediately after the separation, and then the solutions were analyzed for P, Si, and Al by ICP-AES (Seiko Ins., SPS4400). A sorption amount of P was calculated from the difference of P concentrations between the initial and product solutions. Phase change of the Al_{clst} samples and precipitation during P sorption were checked by XRD analysis, field emission scanning electron microscopy (SEM, Hitachi S4500) equipped with an energy dispersive X-ray spectrometer (EDS), and analytical transmission electron microscopy (TEM) (JEOL JEM2010 operated at 200 kV).

To examine sorption sites for phosphates, Fourier transform-infrared spectroscopy equipped with a unit for diffuse reflectance (DR-FTIR, Perkin Elmer Ins. SPECTRUM2000) was employed. We carried out additional P sorption experiments for DR-FTIR measurements; 50 mg of each Al_{clst} sample reacted with 15 ml of H₃PO₄ solution for 3 days. The P concentrations and pHs of the initial solutions were 0.30 mmol/l and 3.3, 1.0 mmol/l and 2.9, 2.0 mmol/l and 2.8, and 3.0 mmol/l and 2.8. Background electrolyte was not used and pH was not adjusted. The different initial P concentrations were adopted to observe changes in absorbance bands, which could be related to the sorption sites, with changes in P sorption amounts. Ten milligrams of each of the Al_{clst} samples before and after P sorption and the Na samples were mixed with 190 mg of KBr powder and analyzed by DR-FTIR.

Thermodynamic calculations were carried out to estimate the activities of dissolved species and to evaluate possible formation of precipitates from the solutions. For the calculations, a Visual MINTEQ program, a Windows version of MINTEQA2 released by the United States Environmental Protection Agency and produced by J.P. Gustafsson of Kungl Tekniska Högskolan, was used. The formation of precipitates was estimated by calculating $\log(Q/K)$ where Q is the ion activity product and K is the

equilibrium constant of a dissolution reaction; when a value of $\log(Q/K)$ is larger than zero, the solution is supersaturated with respect to a precipitate.

3. Results

3.1. Formation of Al_{clst} pillars in the interlayers of synthetic smectite and mica samples

Chemical formulas, Al amounts in the interlayers, basal spacings, and surface areas of the Na and Al_{clst} samples are given in Table 1. The basal spacings of the Al_{clst} samples were slightly smaller than those reported by previous studies (Pinnavaia et al., 1984; Plee et al., 1985; Schoonheydt et al., 1993, 1994; Moreno et al., 1997), but significantly larger than the basal spacings of the respective Na samples. The chemical analyses indicate that the Al amounts in the interlayers of the Al_{clst} samples were similar to or more than those reported by Schoonheydt et al. (1994) (Table 1). By the comparison of the basal spacings and the Al amounts in the interlayers between the Na and Al_{clst} samples, it was confirmed that the Al_{clst} pillars were formed in the interlayers of the Al_{clst} samples.

The apparent grain size of the samples was not changed significantly, which was confirmed by SEM. Therefore, the significant increase in surface area after pillaring the Al_{clst} (Table 1) cannot be explained by an increase in the surface areas of the sample grains themselves, but by an increase in accessibility to the

surface of the Al_{clst} pillars for nitrogen that was used for the BET measurements. The basal spacings, surface areas, and Al amounts in the interlayers after pillaring the Al_{clst} are similar to those of smectites after pillaring Al_{13} (Pinnavaia et al., 1984; Plee et al., 1985; Schoonheydt et al., 1993, 1994; Yamada et al., 1995; Moreno et al., 1997). Therefore, the Al_{clst} pillars are similar in structure to the pillars with Keggin ions, Al_{13} pillars, that contain Al–OH and Al–H₂O (Schoonheydt et al., 1993; Yamada et al., 1995; Moreno et al., 1997).

3.2. Phosphorus species in the initial solution

The abundances of P species in the initial solution of 3.2 mmol/l H₃PO₄ and 10 mmol/l NaNO₃ at pH 3–7 were calculated by Visual MINTEQ and are given in Fig. 1. The coexisting P species were H₂PO₄[−] and H₃PO₄ at acidic pH, and H₂PO₄[−], HPO₄^{2−}, and NaHPO₄[−] at neutral pH (Fig. 1). Among the P species, H₂PO₄[−] was predominant in the pH range examined except for pH 6.5–7.0.

3.3. pH dependency of phosphate sorption

The P sorption to the Al_{clst} samples strongly depended on pH: the sorption had reverse s-shaped curves and was larger at lower pHs (Fig. 2A). The P sorption amounts were different between the Al_{clst} samples in the pH range of 3.0–4.2 where the P sorption amounts were at maximum, whereas they were similar at pHs 5.6–6.6 where the P sorption

Table 1

Chemical formulas, Al amounts in the interlayers, basal spacings, and surface areas of the samples used

Sample name ^a	Derived unit-cell formula/O ₁₀ (OH) ₂ or O ₁₀ F ₂	Al amount in the interlayer (mmol/g) ^b	Basal spacing (nm)	Surface area (m ² /g)
Na-Mont	Na _{0.36} (Al _{1.67} Mg _{0.33})(Si _{3.99} Al _{0.01})	0	1.25	27.3
Na-Beid	Na _{0.36} Al _{1.99} (Si _{3.66} Al _{0.34})	0	1.23	24.0
Na-Sap	Na _{0.37} Mg _{2.99} (Si _{3.67} Al _{0.33})	0	1.25	39.7
Na-TSM	Na _{1.01} Mg _{2.32} Si _{4.00}	0	1.23	2.5
Al_{clst} -Mont	[Al ₁₃] ⁷⁺ _{0.040} (Al _{1.67} Mg _{0.33})(Si _{3.99} Al _{0.01}) ^c	1.41	1.77	156
Al_{clst} -Beid	[Al ₁₃] ⁷⁺ _{0.058} Al _{1.99} (Si _{3.66} Al _{0.34}) ^c	2.05	1.72	274
Al_{clst} -Sap	[Al ₁₃] ⁷⁺ _{0.057} Mg _{2.99} (Si _{3.67} Al _{0.33}) ^c	1.90	1.67	148
Al_{clst} -TSM	[Al ₁₃] ⁷⁺ _{0.060} Mg _{2.20} Si _{4.00} ^c	2.03	1.89	166

^a See text for the abbreviation of the samples names.

^b Al amount pillared into the interlayers in 1 g of smectite or mica.

^c The structural formulas of the Al_{clst} samples were determined on the assumption that their interlayers were occupied with Keggin ions [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺ (abbreviated as [Al₁₃]⁷⁺) because the exact nature of the Al_{clst} pillars was unknown.

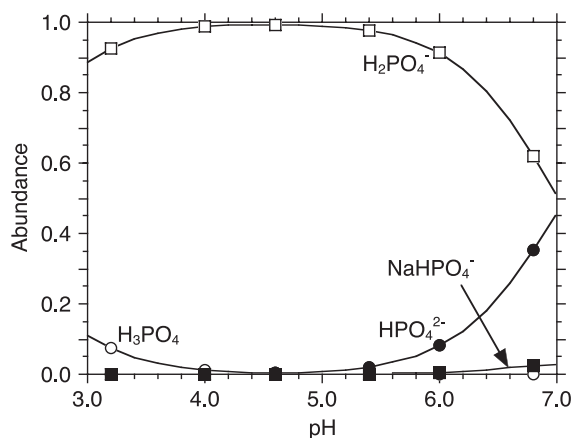


Fig. 1. Thermodynamically calculated abundance of P species in the initial solution of 3.2 mmol/l H_3PO_4 and 10 mmol/l NaNO_3 at pH 3–7 and 25 °C.

amounts were at minimum. The P sorption amounts of the Al_{clst} samples increased sharply at around pH 6 toward lower pHs (Fig. 2A). This is consistent with the results by Bergaoui et al. (1999) who show that the points of zero charge of Al_{13} -pillared montmorillonite and saponite are at around pH 6. The sorption behavior of the Al_{clst} samples as a function of pH was significantly different from that of smectites (Fox and Malati, 1993) and that of Na-Beid and Na-TSM that did not sorb P even in the pH range of 3–4 (Fig. 2A).

The comparison of pHs in solution between before and after the P sorption is shown in Table 2. The pHs after the P sorption are always higher than those before the P sorption, suggesting that the sorption reaction results in the release of OH^- to solution.

During the sorption experiments, small amounts of Si and Al were released from the Al_{clst} samples to solution (0.02–0.30 and 0.00–0.38 mmol/l, respectively). The released amounts increased gradually with a decrease in pH (Fig. 2B and C). If the Al_{clst} samples were dissolved congruently, Al would be released according to the Al/Si ratios of the Al_{clst} samples and would be more in solution than observed. However, the observed release amounts of Al were much lower or Al was not detected at pH higher than 4.4 (Fig. 2C), indicating that Al released from the Al_{clst} samples could precipitate as solid phases such as amorphous Al-phosphates and Al-(oxy)hydroxides (Chen et al., 1973; Veith and Sposito, 1977; Nanzyo, 1984, 1987; Lookman et al., 1997; Tang et al., 1997).

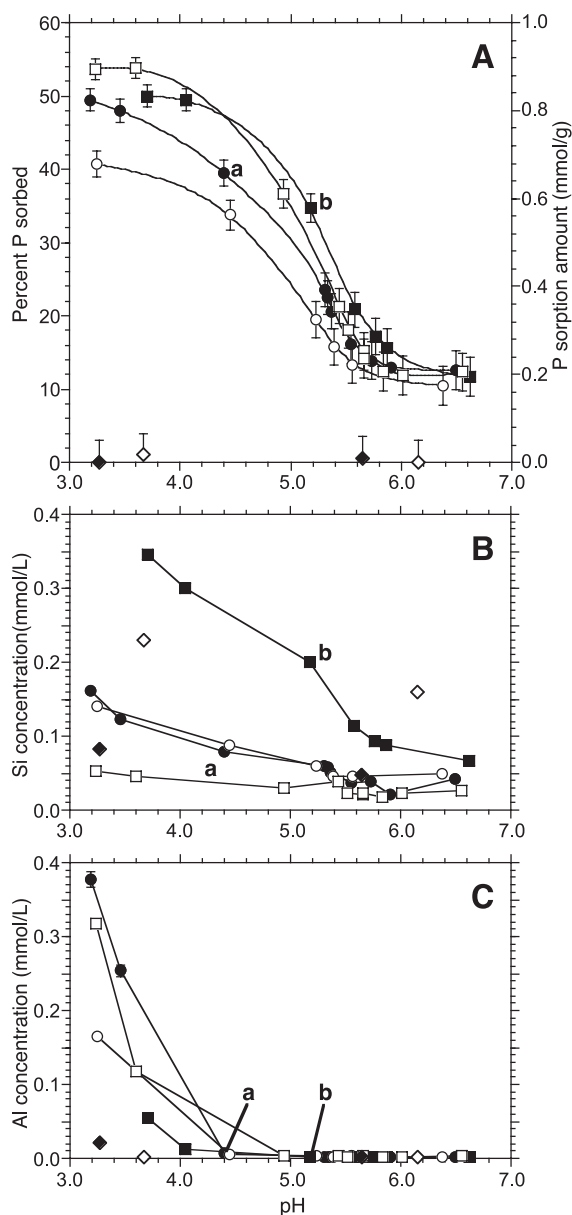


Fig. 2. Phosphate sorption of the Al_{clst} samples, Na-Beid, and Na-TSM as a function of pH (A), and concentrations of Si and Al released from the Al_{clst} samples, Na-Beid, and Na-TSM to solution during the P sorption (B and C, respectively). Initial P and NaNO_3 concentrations are 3.2 and 10 mmol/l, respectively. Open circles are Al_{clst} -Mont, solid circles Al_{clst} -Beid, open squares Al_{clst} -TSM, solid squares Al_{clst} -Sap, open diamonds Na-TSM, and solid diamonds Na-Beid. The data points 'a' and 'b' show Al_{clst} -Beid at pH 4.4 and Al_{clst} -Sap at pH 5.2, respectively (see Figs. 3 and 4).

Table 2
Comparison of pHs in solution between before and after P sorption

Sample name	P sorption (1) ^a		P sorption (2) ^a		P sorption (3) ^a	
	Before	After	Before	After	Before	After
Al _{clst} -Mont	3.0	4.5	4.0	5.4	5.0	5.6
Al _{clst} -Beid	3.0	4.4	4.0	5.4	5.0	5.6
Al _{clst} -Sap	3.0	5.8	4.0	5.8	5.0	5.9
Al _{clst} -TSM	3.0	4.9	4.0	5.5	5.0	5.7

^a Data selected from Fig. 2A.

3.4. Thermodynamically calculated precipitates

The thermodynamic calculations for possible precipitates were carried out assuming that Al was dissolved according to the Al/Si ratios of the Al_{clst} samples. The dissolved amounts of Al were calculated based on the observed release amounts of Si (Fig. 2B). The P, Na⁺, and NO₃⁻ concentrations were the initial ones, 3.2, 10, and 10 mmol/l, respectively. The calculated results indicated that amorphous Al(OH)₃, boehmite [AlO(OH)], gibbsite [Al(OH)₃], diaspore [AlO(OH)], berlinite [AlPO₄], and quartz [SiO₂] could be precipitated at pH higher than 4.4. The precipitation of one or more of the above materials could explain the absence or nearly absence of Al in the solutions at pH higher than 4.4 (Fig. 2C). At pH lower than 4.4, the solutions were undersaturated with respect to Al and Al- and P-bearing materials. All the observed solutions were undersaturated with respect to amorphous SiO₂ (Fig. 2B). Thermodynamic calculations were not carried out for variscite [AlPO₄], metavariscite [AlPO₄·2H₂O], or amorphous Al(OH)₂H₂PO₄ because their thermodynamic data were not available (Chen et al., 1973; Veith and Sposito, 1977; Nanzzyo, 1987; Tang et al., 1997).

3.5. Characterization of the Al_{clst} samples after P sorption

XRD profiles of the Al_{clst} samples before and after P sorption revealed that the crystal structures of the Al_{clst} samples were not changed significantly and any precipitates were not found after sorption. Because no changes in the basal spacings of the Al_{clst} samples were observed after P sorption, the structures of the Al_{clst} pillars were probably preserved.

SEM images of Al_{clst}-Beid before sorption and after sorption at pH 4.4 (a sample designated by 'a' in Fig. 2) are shown in Fig. 3, where both samples have a morphology of aggregates with scale-like particles. Thus, the morphology did not change after sorption. As was for Al_{clst}-Beid, no morphological changes were observed after P sorption for Al_{clst}-Mont, Al_{clst}-Sap, and Al_{clst}-TSM. Any precipitates were not found in any Al_{clst} samples examined by SEM.

TEM images and EDS spectra of Al_{clst}-Beid at pH 4.4 (a sample designated by 'a' in Fig. 2) and Al_{clst}-Sap at pH 5.2 (a sample designated by 'b' in Fig. 2) after P sorption are shown in Fig. 4. Smectite observed by TEM generally has a wavy shape and a stacking sheet that has a thickness of a few nanometers to several tens of nanometers (e.g., Kasama et al., 2001). Therefore, we can easily distinguish smectite from other minerals. Elemental analysis by EDS showed that P was present in and/or on Al_{clst}-Beid and

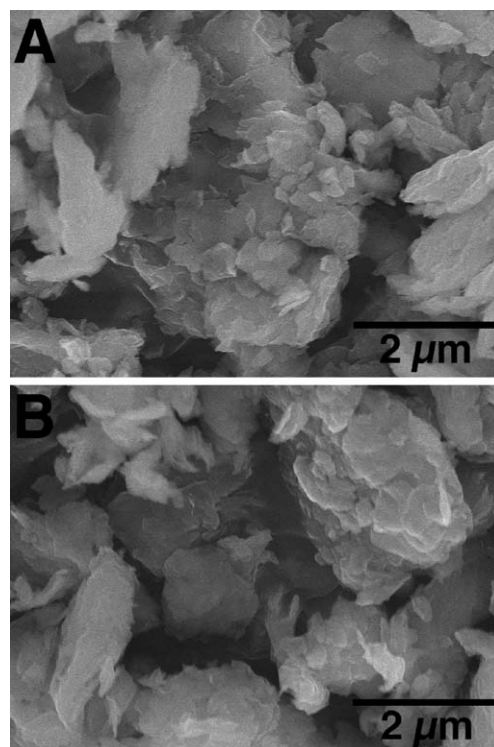


Fig. 3. SEM images of Al_{clst}-Beid before sorption (A) and after sorption at pH 4.4 (B) (a sample designated by 'a' in Fig. 2).

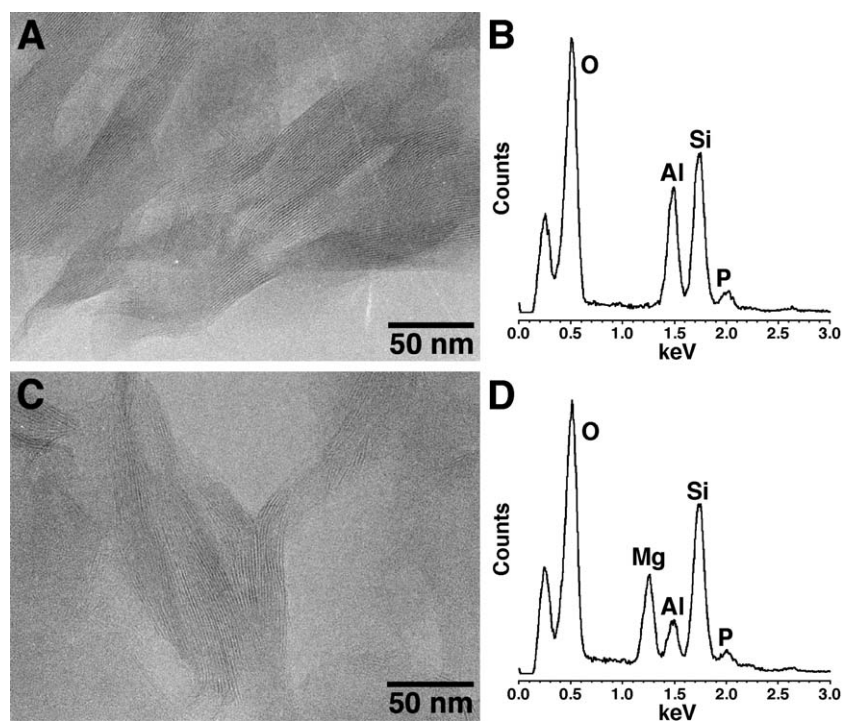


Fig. 4. TEM images and EDS spectra of Al_{clst} -Beid at pH 4.4 (a sample designated by 'a' in Fig. 2) (A and B) and Al_{clst} -Sap at pH 5.2 ('b' in Fig. 2) (C and D) after P sorption.

Al_{clst} -Sap (Fig. 4B and D). No precipitates were observed even at the nanometer level. Al_{clst} -Mont and Al_{clst} -TSM showed the same microstructural and chemical features as those of Al_{clst} -Beid and Al_{clst} -Sap. The TEM observations revealed that the Al_{clst} samples retained their microstructures and that P was accommodated in and/or on the Al_{clst} samples.

3.6. DR-FTIR characterization of P sorption

The results of the additional P sorption experiments for DR-FTIR measurements are given in Table 3. Fig. 5 shows DR-FTIR spectra of Al_{clst} -TSM before and after sorption and that of Na-TSM. DR-FTIR spectra of Al_{clst} -Mont, Al_{clst} -Beid, and Al_{clst} -Sap and their Na counterparts are not presented because they are almost the same as those of Al_{clst} - and Na-TSM. Comparison of DR-FTIR spectra between the Al_{clst} and Na samples revealed that the peaks at approximately 3520, 3450, 3310, 3200, and 760 cm^{-1} occurred after pillaring of the Al_{clst} (Fig. 5). The two bands at around 3520 and 3450 cm^{-1} were

associated with OH functional groups resulted from the Al_{clst} pillars (Chevalier et al., 1994; Kloprogge and Frost, 1999). However, these OH functional groups were probably not related to the P sorption because the intensities of the two bands at around 3520 and 3450 cm^{-1} remained unchanged with increasing P sorption amount (Fig. 5A). The very broad bands at 3310 and 3200 cm^{-1} were assigned to water molecules both in the Al_{clst} pillars and on the

Table 3

Sorption amounts of P (mmol/g) with final pHs for the additional sorption experiments for DR-FTIR measurements

Sample name	(1) ^a		(2) ^a		(3) ^a		(4) ^a	
	P	pH	P	pH	P	pH	P	pH
Al_{clst} -Mont	0.08	6.4	0.26	6.1	0.50	5.2	0.71	3.9
Al_{clst} -Beid	0.09	4.9	0.30	4.7	0.58	4.2	0.82	3.6
Al_{clst} -Sap	0.09	6.2	0.28	5.9	0.51	4.9	0.71	4.5
Al_{clst} -TSM	0.08	6.1	0.27	5.7	0.52	4.9	0.77	4.5

^a Initial solution conditions: (1) 0.30 and 3.3, (2) 1.0 and 2.9, (3) 2.0 and 2.8, and (4) 3.0 and 2.8 for a P concentration (mmol/l) and pH, respectively.

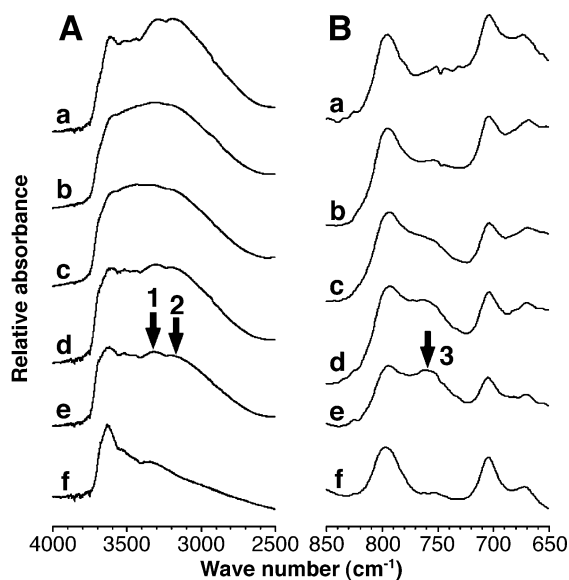


Fig. 5. DR-FTIR spectra in the hydroxyl stretching region (A) and the low-frequency region (B) of Al_{clst} -TSM at P sorption amounts of 0.77 mmol/g (a), 0.52 mmol/g (b), 0.27 mmol/g (c), 0.08 mmol/g (d), before sorption (e), and Na-TSM (f). Numbers with arrows show the band positions of (1) 3310 cm^{-1} , (2) 3200 cm^{-1} , and (3) 760 cm^{-1} .

surface of the Al_{clst} samples (Kloprogge and Frost, 1999; Johnston et al., 1992). The intensities of the bands at about 3310 and 3200 cm^{-1} increased with increasing P sorption amount (1 and 2 in Fig. 5A, respectively). Boehmite to which the Al_{clst} pillars are similar in respect of chemical components and local structures has bands at $748\text{--}761\text{ cm}^{-1}$ which are assigned to OH-bending vibration (Ryskin, 1974; Frost et al., 1999). Therefore, the band at 760 cm^{-1} of the Al_{clst} samples is probably related to Al–OH vibration. The intensity of the band at 760 cm^{-1} decreased gradually with increasing P sorption amount (3 in Fig. 5B).

Although we found small bands at approximately 1515 , 1410 , and 1310 cm^{-1} in the Al_{clst} samples after P sorption, we could not find any relationships between the changes of the spectra and P amounts in the Al_{clst} samples. The bands assigned to P–O stretching vibration of P-sorbed alumina gel are observed at $1130\text{--}1140\text{ cm}^{-1}$ and $1040\text{--}1050\text{ cm}^{-1}$ (Nanzyo, 1984). Several bands associated with $Al(H_2PO_4)_3$ that partly has an Al– H_2PO_4 structure appear at around $900\text{--}1300\text{ cm}^{-1}$ (Arlidge et al., 1963; Nanzyo,

1989). Our DR-FTIR spectra did not show these bands because they were entirely overlapped with very strong bands due to Si–O stretching vibration at around $900\text{--}1200\text{ cm}^{-1}$.

4. Discussion

4.1. Phosphate sorption maxima of the Al_{clst} samples

The P sorption maxima of Al_{clst} -Mont, Al_{clst} -Beid, Al_{clst} -Sap, and Al_{clst} -TSM are 0.66, 0.79, 0.81, and 0.87 mmol/g, respectively, at an initial concentration of 3.2 mmol/l P in the pH range of 3–7 (Fig. 2 and Table 4). On the other hand, phosphates sorbed by the Na samples were not detected. Fox and Malati (1993) have shown that the sorption amount of P by smectite is about 3×10^{-3} mmol/g at an initial concentration of 3.23 mmol/l P and pH 4–6. Thus, the P sorption by the Al_{clst} samples is higher by at least 2 orders of magnitude than that by nonpillared smectites. This suggests that the significant increase of P sorption results from the pillaring of the Al_{clst} into the smectites and mica.

Comparison between the Al_{clst} samples and various Al-bearing minerals and materials in respect of P sorption amounts is given in Table 4. Although there

Table 4

Comparison between the Al_{clst} samples and various Al-bearing minerals and materials in respect of P sorption amounts

Mineral or material name	pH	P initial concentration (mmol/l)	P sorption amount (mmol/g)	Reference ^a
Al_{clst} samples	3–4	3.2	0.66–0.87	1
Boehmite	3	2	0.12–1.22	2
Boehmite	3	4	1.04	3
Al hydroxide gel	3	4	1.00	3
Al_{clst} samples	6–7	3.2	0.17–0.21	1
Boehmite	6.5	2	0.06–0.80	2
Boehmite	6.8	8.32	0.70	4
Al hydroxide gel	6.8	8.32	0.17	4
Al hydroxide gel	1.2	8.32	0.29	4
Boehmite	1.2	8.32	0.22	4
Amorphous Al hydroxide	n.d.	3	1.3	5
Gibbsite	n.d.	3	0.42	5

n.d. = no data.

^a 1 = This study, 2 = Watanabe et al. (2002), 3 = Tang et al. (1997), 4 = Nishida et al. (1990), and 5 = Lookman et al. (1997).

are differences in experimental conditions such as initial P concentration and pH, the Al_{clst} samples have broadly similar capacity of P sorption to that of the Al-bearing minerals and materials which are regarded as effective absorbents to remove P from water (e.g., Parfitt, 1978).

4.2. Phosphate sorption mechanisms

The P sorption by the Al_{clst} samples increased sharply from pH about 6 to lower pHs and attained maximum at pH 3.0–4.2 (Fig. 2A). In the pH range of 3 to 6, H₂PO₄⁻ was a dominant P species (> ~ 90%, Fig. 1). In the pH range of 6 to 7, although the P sorption did not change among the Al_{clst} samples (Fig. 2A), the abundance of the P species significantly changed (Fig. 1). Thus, there is no proportional relationship between the P sorption and the P species abundance; the P sorption amounts by the Al_{clst} samples are not directly affected by the P species or the P species abundance. Similarly, the edge surfaces that contain Si–OH and Al–OH functional groups play little role in P sorption because the Al_{clst} samples and Na samples that are similar in edge structure showed the large difference in sorption (Fig. 2A).

The Al_{clst}, similar to Keggin ions, in the interlayers have functional groups such as Al–OH and Al–H₂O that provide reactive sites for phosphates (Parfitt, 1978, 1989; Bergaoui et al., 1999). The TEM observation revealed that a significant amount of P occurs in and/or on the Al_{clst} samples (Fig. 4), which strongly suggests that phosphates are sorbed to the Al_{clst} samples. The DR-FTIR analysis indicated that the band associated with the vibration of Al–OH in the Al_{clst} pillars (760 cm⁻¹) decreases in intensity gradually with increase in amount of sorbed phosphates. Namely, the number of Al–OH bonds in the Al_{clst} pillars decreases with P sorption. In addition, the values of pH after the P sorption experiments increase compared with those before the experiments: 3.0 to 4.4–5.8 and 4.0 to 5.4–5.8 at acidic pH, and 5.0 to 5.6–5.9 at neutral pH (Table 2). The above results along with the sorption data (Fig. 2A) are completely consistent with an ion exchange model: Al–OH + H₂PO₄⁻ → Al–H₂PO₄⁻ + OH⁻ (e.g., Tang et al., 1997). Thus, the OH groups of the Al_{clst} are exchanged mainly for H₂PO₄⁻, the dominant P species in solution.

We will discuss the effects of probable precipitates on the P sorption before we conclude that the ion exchange mechanism is predominant. The P sorption to Al-bearing precipitates such as amorphous Al(OH)₃ could occur (Nishida et al., 1990; Lookman et al., 1997; Tang et al., 1997). However, any precipitates containing P were not detected in any Al_{clst} samples after P sorption, as revealed by XRD, SEM, and TEM (Figs. 3 and 4). The thermodynamic calculations revealed that no Al-bearing precipitates could occur at acidic pH, and amorphous Al(OH)₃, boehmite, gibbsite, diasporite, and berlinite could precipitate at pH higher than 4.4. Because the P sorption of all Al_{clst} samples increased remarkably at around pH 6 and was at maximum at pH lower than 4 (Fig. 2A), the above minerals do not play a major role in the P sorption.

Because of no available data, thermodynamic calculations were not made for variscite, metavariscite, and amorphous Al(OH)₂H₂PO₄ that could precipitate (Chen et al., 1973; Veith and Sposito, 1977; Nanzyo, 1984, 1987; Lookman et al., 1997; Tang et al., 1997) and thus could be another possibility to affect the P sorption. In the present study, the P sorption amounts by the Al_{clst} samples were similar to one another over the observed pH range (Fig. 2A). However, the Al amounts released from the Al_{clst} samples were entirely different among the Al_{clst} samples (Fig. 2C). If the precipitation of the above Al- and P-bearing materials would be predominant for the P sorption, the P sorption amount by the Al_{clst}-Sap that had the least released Al would be least among the Al_{clst} samples. In addition, the precipitation of the Al- and P-bearing materials is quite slow in comparison with sorption reaction (Chen et al., 1973; Veith and Sposito, 1977; Tang et al., 1997). No proportional relationship between the P sorption and the Al amounts released from the Al_{clst} samples suggests that the precipitation of the Al- and P-bearing materials does not play an important role in the P sorption for the present study even if the precipitation reaction occurs.

It is thus shown that the P species abundance in solution, the edge surfaces containing Si–OH and Al–OH functional groups, or Al-bearing and Al- and P-bearing materials do not significantly affect the P sorption. It is concluded that the main mechanism of the P sorption by the Al_{clst} samples is ion exchange of the OH groups of the Al_{clst} in the interlayers for H₂PO₄⁻.

4.3. Relationship between the number of Al_{clst} pillars and P sorption

The P sorption curves are similar to one another between the Al_{clst} samples, whereas the sorption maxima are different (Fig. 2A). Because there is no significant difference in structure between the Al_{clst} pillars of the Al_{clst} samples as confirmed by XRD, DR-FTIR, and TEM, the sorption maxima are not related to the structures of the Al_{clst} pillars. The order of the sorption maximum is $Al_{clst}\text{-TSM} > Al_{clst}\text{-Beid} \geq Al_{clst}\text{-Sap} \gg Al_{clst}\text{-Mont}$ (Fig. 2A), which is exactly the same as that of the number of Al_{clst} pillars in the Al_{clst} samples (Table 1). Bergaoui et al. (1999) indicates that smectites with more Al_{13} pillars sorb more Cd. The ion-exchange mechanism for the P sorption and the relationship between the number of Al_{clst} pillars and sorption maxima suggest that the sorption maxima are determined by the number of OH functional groups on the Al_{clst} pillars, but independent of structures and chemical compositions of the host minerals after pillaring.

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