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LAYER-CHARGE CHARACTERISTICS OF SMECTITE IN THAI VERTISOLS

NATTHAPOL CHITTAMART[1], ANCHALEE SUDDHIPRAKARN[1,]*, IRB KHEORUENROMNE[1], AND ROBERT J. GILKES[2]

[1] Department of Soil Science, Faculty of Agriculture, Kasetsart University, Bangkok 10900, Thailand
[2] School of Earth and Environment, Faculty of Natural and Agricultural Sciences, University of Western Australia, Crawley, WA 6009, Australia

Abstract—The fertility of soils with respect to K^+ and NH_4^+ is often difficult to measure, but is essential for achieving effective agronomic practices. This problem is especially important in the Vertisols of Thailand. The purpose of the study reported here was to characterize the composition and layer-charge behavior of Thai Vertisols in order to understand better their K^+ and NH_4^+ fertility. Topsoil and subsoil clay of 12 representative highly smectitic Vertisols from Thailand were studied. Interlayer swelling of smectite with alkylammonium cations, cation exchange capacity (CEC), and chemical composition were determined. These data and the re-expansion on glycerol treatment of Li-saturated, heated smectite demonstrated that high-charge, Fe-rich beidellite is the major clay mineral in these soils. The beidellite has a heterogeneous layer-charge distribution as measured by the alkylammonium method, with mean values ranging from 0.43 to 0.62 charges per half unit cell. The layer charge determined by CEC and structural formula methods for some almost pure smectites is smaller (0.32−0.54) and greater (0.46−0.69), respectively, than determined by the alkylammonium method. The structural formulae of beidellite confirm that the layer charge originates mostly in the tetrahedral sheet.

Key Words—Layer-Charge Characterization, High-charge Fe-rich Beidellite, Smectite Properties, Vertisols, Tropical Soils, Thailand.

INTRODUCTION

Layer charge is an important characteristic of 2:1 phyllosilicates. It is responsible for much of the soil's capacity to retain cations and the selectivity that soils exhibit for various cations during exchange reactions including fixation of K^+ and NH_4^+. Layer charge also affects the shrink-swell properties of smectite. Layer charge is an essential criterion in the identification, characterization, and classification of 2:1 phyllosilicates (Guggenheim *et al.*, 2006).

Smectite is commonly an abundant clay mineral in Vertisols and various smectite species have been identified (Bouabid *et al.*, 1996; Moore and Reynolds, 1997; Wilson, 1999). High-charge beidellite has been reported as the dominant clay mineral in many Vertisols (Badraoui and Bloom, 1990; Math and Murthy 1994; Bühman and Schoeman, 1995; Righi *et al.*, 1995, 1998; Pai *et al.*, 1999; Singh and Heffernan, 2002). Soil smectites with large tetrahedral charge fix K^+ and NH_4^+ more strongly than does montmorillonite, which will influence the availability of these cations to plants (Bajwa, 1981a, 1981b; Badraoui and Bloom, 1990). Alkylammonium sorption provides a method for determining the layer charge of expandable minerals (Senkayi *et al.*, 1985; Lagaly, 1994). The Greene-Kelly test to identify the location of charge is used to distinguish montmorillonite from beidellite and nontronite (Greene-Kelly, 1953, 1955) and the calculation of structural formulae also identifies the location of layer charge. These procedures have been applied in this research to characterize smectite in Thai Vertisols.

Vertisols in Thailand cover an area of ~336,500 hectares, which constitutes ~0.65% of the total area of the country (Panichapong, 1982; Vijarnsorn, 1982). The soils have a high potential for crop production, which is being used mostly for intensive cultivation of paddy rice, but they are also used for upland crops including maize, cotton, mung bean, banana, and fruit trees (Vijarnsorn, 1982) with high rates of application of NPK fertilizers. Variations in the agronomic efficiency of ammonium and K fertilizers are of concern to farmers and may relate to smectite-cation interactions.

The objectives of this study were: (1) to determine the mineral composition of representative Thai Vertisols; and (2) to characterize the layer-charge properties of smectite in Thai Vertisols.

MATERIALS AND METHODS

Samples

Following an extensive survey of the mineralogy of a large number of Thai Vertisols, 12 representative smectite-rich soil profiles on various parent materials were sampled for use in this investigation (Table 1). The soil samples were air-dried, gently crushed, and sieved to obtain the fine-earth fraction (<2 mm). Twenty four soil samples from topsoil and subsoil horizons that contained much smectite were used for layer charge characterization and chemical analysis.

* E-mail address of corresponding author:
agrals@ku.ac.th
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Table 1. Classification, landform, parent material, and site location of Thai Vertisols.

Soil series	Classification	Landform	Parent material	Site location
Lowland Vertisols				
Ban Mi (Bm)	Ustic Endoaquert, fine, smectitic, isohyperthermic	Lower footslope	Wash and local alluvium derived from weathered limestone	Phra Phutthabat, Saraburi
Chong Khae (Ck)	Ustic Endoaquert, very fine, smectitic, isohyperthermic	Semi-recent terrace	Mixed alluvium and local alluvium derived from limestone	Soa Hai, Saraburi
Lop Buri 1 (Lb1)	Calcic Endoaquert, fine, smectitic, isohyperthermic	Local alluvial plain	Local alluvium derived from limestone	Phra Phutthabat, Saraburi
Lop Buri 2 (Lb2)	Ustic Endoaquert, very fine, smectitic, isohyperthermic	Toeslope	Local alluvium derived from limestone	Muang, Lop Buri
Upland Vertisols				
Buri Ram (Br)	Typic Haplustert, very fine, smectitic, isohyperthermic	Dissected lower footslope	Local alluvium derived from limestone	Chai Badan, Lop Buri
Chai Badan 1 (Cd1)	Calcic Haplustert, very fine, smectitic, isohyperthermic	Dissected upper footslope	Local alluvium derived from lime-containing rocks	Chai Badan, Lop Buri
Chai Badan 2 (Cd2)	Typic Haplustert, fine, smectitic, isohyperthermic	Lower middle slope basalt corrosion plain	Residuum derived from weathered basalt	Nong Phai, Phetchabun
Lop Buri 3 (Lb3)	Typic Haplustert, very fine, smectitic, isohyperthermic	Lower footslope	Local alluvium derived from limestone	Kok Samrong, Lop Buri
Samo Thod 1 (Sat1)	Chromic Haplustert, fine, smectitic, isohyperthermic	Dissected upper footslope	Local alluvium on residuum derived from both weathered andesite and limestone	Buengsamphan, Phetchabun
Samo Thod 2 (Sat2)	Chromic Haplustert, very fine, smectitic, isohyperthermic	Upper footslope	Local alluvium derived from limestone on residuum derived from weathered andesite	Buengsamphan, Phetchabun
Wang Chomphu 1 (Wc1)	Chromic Haplustert, fine, smectitic, isohyperthermic	Lower footslope	Local alluvium mixed wash over residuum derived from calcareous rocks	Nong Phai, Phetchabun
Wang Chomphu 2 (Wc2)	Typic Haplustert, fine, smectitic, isohyperthermic	Lower dissected footslope	Local alluvium derived from calcareous rocks	Muang, Phetchabun

Physicochemical analyses

Soil pH was measured in 1:1 soil:solution in H_2O (National Soil Survey Center, 1996). Organic matter was calculated from the organic carbon determined by the Walkley and Black method (Nelson and Sommers, 1996). The CEC was measured by saturating the exchangeable sites with 1 M NaOAc at pH 8.2 and displacing Na with 1 M NH_4OAc at pH 7.0 (National Soil Survey Center, 1996). Electrical conductivity was determined in a soil:water saturation extract. Particle-size distribution was determined by the pipette method (Gee and Bauder, 1986). The coefficient of linear extensibility (COLE) was measured by the method of Schafer and Singer (1976) and is required for soil classification.

Mineralogical characterization

Calcium carbonate was removed from soils (<2 mm) using 1 M NaOAc buffered at pH 5.0 (National Soil Survey Center, 1996). Clay was separated by dispersing soil in deionized water using sodium hexametaphosphate and the <2 μm fraction was obtained by sedimentation and siphoning. The clay was flocculated in saturated sodium chloride solution. Excess sodium chloride was removed by dialysis. Dialyzed clay fractions were oven-dried at 60ºC and crushed. To preserve the redox status of structural Fe and Mn, so as to not alter layer-charge density and avoid the alteration of clay structure (Stucki *et al.*, 1984; Manceau *et al.*, 2000; Mikutta *et al.*, 2005; Stucki and Kostka, 2006), the clays were not chemically treated to remove organic matter or free Fe and Mn oxides prior to X-ray diffraction (XRD) analysis.

Oriented clay specimens were prepared for XRD analysis after various pretreatments. After dispersion in deionized water in an ultrasonic bath for 20−30 min, clay suspension was transferred onto a ceramic tile which was placed under suction. The clay was next saturated with Mg by two washings with 5 mL of 2 M $MgCl_2$ followed by six washings with deionized water to remove excess salt. The specimens were air-dried prior to XRD analysis after which the same Mg-saturated specimen was glycerol solvated by two washings with a 1:1 glycerol:deionized water mixture followed by three washings with deionized water while the ceramic tile was still under suction. After this, the ceramic tile was placed in a desiccator over silica gel, stored for at least 12 h and then analyzed by XRD.

The Greene-Kelly test (Greene-Kelly, 1953, 1955) was used to distinguish between montmorillonite (octahedral charge smectite) and beidellite (tetrahedral charge smectite). In this test, clays were saturated with 3 M LiCl, deposited onto a ceramic tile, washed, heated at 300ºC for 2 h, and then glycerol solvated. After heating, the basal spacing of all smectites collapsed to ~1 nm and, after subsequent glycerol saturation, beidellite expanded to ~1.7 nm, but montmorillonite remained at 1.0 nm.

Chemical composition analyses

Prior to total chemical analysis by X-ray fluorescence spectrometry (XRF), organic matter was first removed from the clay fraction (<2 μm) using the H_2O_2 oxidation method (Kunze and Dixon, 1986). Free sesquioxides were also removed with a solution of sodium dithionite and sodium citrate in a sodium bicarbonate-buffered system (Mehra and Jackson, 1960). These clay fractions were Ca saturated by four washings with 1 M $CaCl_2$ and then repeatedly washed with deionized water followed by ethanol until free of $AgNO_3$-detectable chloride. They were then oven dried at 60ºC and crushed. 700 mg of Ca-saturated clay was fused with 7.000 g of lithium metatetraborate flux at 1050ºC in a platinum crucible. The XRF analyses of fused discs of the Ca-saturated clay fraction were obtained using a Philips PW1400 X-ray fluorescence spectrometer fitted with a rhodium tube. The CEC of the untreated Na-saturated clay was determined by the silver thiourea ($AgTU^+$) method (Rayment and Higginson, 1992). This method allows a relatively fast CEC determination and only one extraction step is necessary (Searle, 1986) due to the very high selectivity for the silver-thiourea complex (AgTU) as compared to the natural exchangeable cations (Cremers and Pleysier, 1973). The method is appropriate for measuring the CEC of smectite-rich clay (Pleysier and Cremers, 1975).

Layer-charge characterization

Twenty-four representative clay samples (<2 μm) from topsoil and subsoil horizons were intercalated with each of 12 alkylammonium cations with carbon atom number (n_c) ranging from 6 to 18, but excluding 17. Standard Upton Wyoming bentonite (John C. Lane Tract, Wards Clay Mineral Standard) was used as a reference material in this investigation. Alkylammonium solutions were prepared following the procedure of Lagaly (1994), which consisted of making a solution containing the required amount of alkylamine salt, ethanol, and water and then adjusting the solution pH to 6.5−7.0 with 0.1 M HCl. The alkylammonium clay intercalation followed the method of Rühlicke and Kohler (1981). Approximately 100 mg of clay was treated with 2 mL of 0.1 M alkylammonium solution in a 5 mL tightly capped centrifuge tube. About 1 mL of alkylammonium solution was used for concentrations >0.1 M (n_c <11). For 0.05 M alkylammonium solutions (n_c>15) 4 mL was used. The clays were dispersed in these solutions and held in an oven at 65ºC overnight. The solid was separated by centrifugation, washed with 95% ethanol, and again dispersed in fresh alkylammonium solution. After a second incubation, the alkylammonium derivatives were separated by centrifugation. Excess alkylammonium salt was removed by washing the sample ~8 times with 95% ethanol in a centrifuge tube in an ultrasonic bath until the supernatant was free of $AgNO_3$-detectable chloride. An oriented specimen was prepared by depositing the clay-ethanol slurry onto a glass slide which was then dried overnight in a desiccator containing P_2O_5 prior to XRD analysis. The layer-charge calculation was based on basal spacings and followed the method of Lagaly (1994). The upper and lower limits of layer charge value were estimated from the bilayer to pseudotrimolecular (1.76 to 2.2 nm) transition and a mean value of layer charge was calculated. The following equation was used for layer-charge calculation:

$$\xi = 23.3\ \lambda \div (5.7\ (n_c) + 14)$$

where ξ is average layer-charge density in mol(−)/($O_{10}(OH)_2$), λ = 1 for monolayer to bilayer, and λ = 2 for bilayer to pseudotrilayer transition, n_c = carbon atom numbers in alkylammonium, and 23.3 comes from the clay surface area representing a single negative charge (A_e) where $A_e = (d_{100})(d_{010})/2$ and $(d_{100})(d_{010}) = 0.466\ nm^2$ for the dioctahedral clay minerals (Lagaly, 1994).

All XRD traces were obtained on a computer-controlled Philips X-ray diffractometer using CuKα radiation and a focusing monochromator. Lorentz-polarization (LP) factor correction, curve fitting, and deconvolution were used following the methods of Stanjek and Friedrich (1986) and Stanjek *et al.* (1992) to accurately locate the 001 reflection of alkylammonium smectite derivatives and to separate overlapping reflections. The LP-factor correction was programmed in *Microsoft Excel* 2003, and *Traces* software version 5.0.5 was used for curve fitting and deconvolution using a modification of the method of Stanjek *et al.* (1992).

RESULTS AND DISCUSSION

Environment and physicochemical properties of soils

Local alluvium derived from limestone was the most common parent material of the lowland Vertisols (Ustic Endoaquert: Ban Mi (Bm), Chong Khae (Ck), Lop Buri (Lb2); Calcic Endoaquert: Lop Buri (Lb1)), but for upland Vertisols (Typic Haplusterts: Buri Ram (Br), Chai Badan (Cd2), Lop Buri (Lb3), Wang Chomphu (Wc2); Chromic Haplusterts: Samo Thod (Sat1, Sat2), Wang Chomphu (Wc1); Calcic Haplustert: Chai Badan (Cd1)) the parent materials were various mixtures of local alluvium, wash, and residuum derived from limestone, andesite, and basalt (Table 1). These soils are on flat to undulating (1 to 2% slope) sites and most developed at low positions in the local landscape. Dissolved cations from limestone and mafic rocks accumulated in these low positions and induced the neoformation of smectite (Borchardt, 1989; Wilson, 1999).

Soils were mildly acidic to alkaline with pH (H_2O) ranging from 6.3 to 8.2 for topsoils and 5.2 to 8.5 for subsoils (Table 2). The soils had low to moderate organic-matter contents ranging from 15.9 to 51.5 g kg^{-1} in topsoils and 5.3 to 19.3 g kg^{-1} in subsoils. Cation exchange capacity ranges from 27.3 to 83.5 cmol kg^{-1}. The soluble salt content of these soils was generally low with the electrical conductivity value of saturation extracts ranging from 0.11 to 2.29 dS m^{-1}. Most of these soils had a clayey texture with clay content ranging from 316 to 902 g kg^{-1}. Sand content ranged from 21 to 490 g kg^{-1} and silt from 59 to 461 g kg^{-1}. The coefficient of linear extensibility ranged from 0.09 to 0.30; these values were in the defined range for the Vertisol classification which requires wide (1 cm) and deep (50 cm) cracks, a COLE value of at least 0.09, and a clay content >30% (Soil Survey Staff, 1999).

Mineralogy of soil clays determined by XRD analysis

The clay mineralogy was relatively uniform consisting predominantly of smectite with lesser amounts of kaolinite, vermiculite, and illite (Table 3). Illite (5 to 20%) only occurred in the Ck profile. Kaolinite was a common associated clay mineral being present in all clays and with moderate amounts (20−40%) occurring in Ck and the topsoil horizon of Sat2. Minor amounts of vermiculite occurred in Sat1, Sat2, and Cd2, which had developed on mixed alluvium, wash, and residuum of calcareous rocks, andesite, and basalt, respectively. A trace amount of calcite occurred in the clay of the subsoil horizon of Lb1 which is a carbonate accumulation horizon (Bk horizon). Quartz was present in trace amounts in all clay samples. Smectite is known to predominate in the clay fraction of Vertisols in Lop Buri province, Thailand (Kosayodom, 1986). Vermiculite, illite, and kaolinite were present in the clay fraction of these soils and also in Vertisols in the Mae Klong Basin in Thailand. The presence of smectite in these soils was attributed to the large Ca and Mg contents of the parent materials (Vijarnsorn, 1982; Chaipanich, 1988).

Smectite properties

In the Mg-saturated, air-dried state (Mg-sat), the smectite basal spacing ranged between 1.45 and 1.77 nm and shifted to between 1.79 and 1.94 nm after glycerol solvation (Table 4). The large expansion due to glycerol solvation (Mg-gly) indicated that the dominant mineral was smectite and not vermiculite (Walker, 1958; Whittig and Allardice, 1986; Malla and Douglas, 1987a) (Figure 1a). Glycerol can form a double layer complex (1.8 nm) in the interlayer of some vermiculites (Malla and Douglas, 1987a) but the absence of a clear 1.4 nm peak for Mg-saturated and glycerol-solvated samples indicated that vermiculite was not present. For Sat1, Sat2, and Cd2, the Mg-saturated and glycerol-solvated clays showed the presence of a clear 1.43 nm reflection, indicating that minor vermiculite was present (Malla, 2002).

After applying the Greene-Kelly test, re-expansion of Li-saturated clays after glycerol treatment (Li-300-gly) occurred for all soil smectites (Figure 1b). The smectites

Table 2. Physicochemical properties of topsoil and subsoil of Thai Vertisols.

Horizons	Depth (cm)	pH	OM ($g\ kg^{-1}$)	CEC ($cmol\ kg^{-1}$)	EC-sat ($dS\ m^{-1}$)	PSD Sand ($g\ kg^{-1}$)	PSD Silt ($g\ kg^{-1}$)	PSD Clay ($g\ kg^{-1}$)	COLE (Lm/Ld)
Lowland Vertisols									
Ban Mi (Bm)									
Apkg	0–20	7.7	26.1	36.3	1.56	234	318	449	0.17
Bsskg2	63–84	7.7	9.7	45.1	0.35	131	343	526	0.20
Chong Khae (Ck)									
Apg	0–27	6.8	17.8	34.1	0.44	46	391	563	0.25
Bssg2	75–105	5.2	6.2	37.1	0.18	21	296	684	0.30
Lop Buri 1 (Lb1)									
Apkg	0–12	7.8	51.5	58.3	0.22	121	229	650	0.25
Bkg2	33–55	8.3	8.5	34.5	0.44	99	329	572	0.19
Lop Buri 2 (Lb2)									
Apg	0–20	7.8	32.6	66.8	1.08	44	147	809	0.23
Bssg3	65–90	7.7	9.4	64.0	2.29	44	142	813	0.27
Upland Vertisols									
Buri Ram (Br)									
Ap	0–20	7.6	20	63.5	0.4	87	168	746	0.30
Bss2	60–90	6.8	10.9	71.7	0.34	54	170	776	0.26
Chai Badan 1 (Cd1)									
Apk	0–20	7.9	24.9	83.5	0.31	36	83	880	0.28
Bss2	80–110	8.0	14.9	79.5	0.31	39	59	902	0.24
Chai Badan 2 (Cd2)									
Ap	0–15	6.8	25.4	50.7	0.29	199	224	577	0.22
Btc	40–40/70	7.4	13.4	52.2	0.22	276	214	510	0.19
Lop Buri 3 (Lb3)									
Apk	0–25	8.1	27	58.0	0.67	135	461	404	0.22
Bssk2	70–93	8.5	14.3	56.2	0.88	132	156	712	0.21
Samo Thod 1 (Sat1)									
Apk	0–20	8.2	15.9	37.0	0.34	291	237	473	0.19
Bt3	70–90	8.3	6.3	39.1	0.3	218	200	582	0.25
Samo Thod 2 (Sat2)									
Apk	0–18/20	8.0	19.2	51.0	0.32	112	167	721	0.26
Btk2	40–60	8.3	19.3	48.0	0.35	86	172	742	0.25
Wang Chomphu 1 (Wc1)									
Ap	0–20	6.3	21.5	27.3	0.2	490	194	316	0.09
Btc1	45–75	5.8	5.3	30.6	0.11	446	208	346	0.14
Wang Chomphu 2 (Wc2)									
Ap	0–25	6.3	30.3	33.8	0.2	364	214	422	0.10
2Btk2	100–130	8.2	5.5	44.5	0.4	165	122	713	0.25

OM = organic matter, CEC = cation exchange capacity, EC-sat = electrical conductivity (saturated), PSD = particle-size distribution, COLE = coefficient of linear extensibility, Lm = length of moist soil, Ld = length of dry soil

collapsed to basal spacings (d_{001}) from 0.98 to 1.38 nm after Li saturation and heating at 300ºC (Li-300) (Table 4); such peak shifts are indicative of the charge location in smectite as Li ions migrate from the interlayer position to vacant octahedral sites on heating, with a consequent neutralization of negative charge originating in the octahedral sheet due to divalent cation substitution (Jaynes and Bigham, 1987; Malla and Douglas, 1987b). Only beidellite, where charge originates in the tetrahedral sheet, re-expands with glycerol after Li saturation and heating at 300ºC (Li-300-gly). Basal spacings of all Li-300 treated soil smectites after glycerol solvation ranged from ~1.51 nm to ~2.78 nm. Thus, layer charge originated mainly within the tetrahedral sheet and the smectite in these Thai Vertisols is beidellite (Greene-Kelly, 1953, Brindley and Brown, 1980).

Layer-charge characteristics

The layer charge of reference Upton Wyoming montmorillonite (John C. Lane Tract, Wards Clay Mineral Standard) was estimated from the monolayer (1.34 to 1.36 nm) to bilayer (1.76 to 2.2 nm) transition

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Table 3. Semi-quantitative XRD estimation of the mineralogical composition of the clay fraction of topsoil and subsoil of Thai Vertisols.

Sample	Depth (cm)	Sm	Kao	Ill	Vm	Qtz	Cal
Lowland Vertisols							
Ban Mi (Bm)							
Apkg	0–20	xxxx	tr	–	–	tr	–
Bsskg2	84–106	xxxx	tr	–	–	tr	–
Chong Khae (Ck)							
Apg	0–27	xxx	xx	x	–	tr	–
Bssg2	75–105	xxxx	xx	x	–	tr	–
Lop Buri 1 (Lb1)							
Apkg	0–12	xxxx	tr	–	–	tr	–
Bkg2	33–55	xxxx	tr	–	–	tr	x
Lop Buri 2 (Lb2)							
Apg	0–20	xxxx	tr	–	–	tr	–
Bssg3	65–90	xxxx	tr	–	–	tr	–
Upland Vertisols							
Buri Ram (Br)							
Ap	0–20	xxxx	tr	–	–	tr	–
Bss2	60–90	xxxx	tr	–	–	tr	–
Chai Badan 1 (Cd1)							
Apk	0–20	xxxx	tr	–	–	tr	–
Bss2	80–110	xxxx	tr	–	–	tr	–
Chai Badan 2 (Cd2)							
Ap	0–15	xxxx	x	–	tr	tr	–
Btc	40–40/70	xxxx	x	–	x	tr	–
Lop Buri 3 (Lb3)							
Apk	0–25	xxxx	tr	–	–	tr	–
Bssk2	70–93	xxxx	tr	–	–	tr	–
Samo Thod 1 (Sat1)							
Apk	0–20	xxxx	x	–	x	tr	–
Bt3	70–90	xxxx	x	–	tr	tr	–
Samo Thod 2 (Sat2)							
Apk	0–18/20	xxxx	xx	–	tr	tr	–
Btk4	40–60	xxxx	x	–	tr	x	–
Wang Chomphu 1 (Wc1)							
Ap	0–20	xxxx	x	–	–	tr	–
Btc1	45–75	xxxx	x	–	–	tr	–
Wang Chomphu 2 (Wc2)							
Ap	0–25	xxxx	x	–	–	tr	–
2Btk2	100–130	xxxx	x	–	–	tr	–

xxxx = dominant (>60%), xxx = large (40–60%), xx = moderate (20–40%), x = small (5–20%), tr = trace (<5%), – = not detected, Sm = smectite, Kao = kaolinite, Ill = illite, Vm = vermiculite, Qtz = quartz, Cal = calcite

on saturation with alkylammonium ions (Lagaly, 1994). The layer-charge density ranged between 0.22 and 0.36 with a mean layer-charge density of 0.29 mol(–)/($O_{10}(OH)_2$) which is typical for Wyoming montmorillonite which has reported values of 0.2–0.4 charge per half unit cell (Mermut and Lagaly, 2001). The procedure used in the present study, therefore, probably determined the layer charge correctly.

All XRD patterns of alkylammonium derivatives were corrected by dividing the intensities by the Lorentz and polarization (LP) factor and curve fitting (Stanjek and Friedrich, 1986; Stanjek *et al.*, 1992). The effect of the LP-correction upon apparent *d* values and intensities is illustrated for Bm soil (Bm-Bsskg2) (Figure 2). The relative intensities of all peaks changed considerably following the LP-correction and higher-angle peaks became more clearly resolved. Weakly developed shoulders in the uncorrected XRD patterns became symmetrical and peaks were clearly visible after the correction, allowing the use of a fitting and

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Table 4. Basal spacing (d_{001}) of smectite in the clay fraction after various pretreatments: Mg-saturated (Mg-sat); Mg-saturated and glycerol solvated (Mg-gly); Li-saturated-heated at 300ºC (Li-300); and Li-saturated-heated at 300ºC and glycerol solvated (Li-300-gly). All smectites behave as beidellite. Upper and lower limits, and mean values of layer charge of smectite estimated by the alkylammonium-intercalation method (bilayer to pseudotrimolecular transition).

Sample	Basal spacing (d_{001}) (nm)				Layer charge [mol(−)/$O_{10}(OH)_2$]		
	Mg-sat	Mg-gly	Li-300	Li-300-gly	Lower limit	Upper limit	Mean
Lowland Vertisols							
Ban Mi (Bm)							
Apkg	1.54	1.91	1.34	1.76	0.53	0.66	0.59
Bsskg2	1.52	1.83	1.33	1.87	0.53	0.71	0.62
Chong Khae (Ck)							
Apg	1.56	1.85	1.25	1.56	0.50	0.66	0.58
Bssg2	1.56	1.85	1.38	1.59	0.44	0.66	0.55
Lop Buri 1 (Lb1)							
Apkg	1.52	1.88	1.2	1.97	0.50	0.66	0.58
Bkg2	1.58	1.86	1.32	1.77	0.44	0.57	0.50
Lop Buri 2 (Lb2)							
Apg	1.59	1.81	1.31	1.98	0.53	0.66	0.59
Bssg3	1.56	1.91	1.22	1.78	0.53	0.66	0.59
Upland Vertisols							
Buri Ram (Br)							
Ap	1.65	1.9	1.33	1.98	0.53	0.66	0.60
Bss2	1.71	1.94	1.03	1.99	0.44	0.57	0.50
Chai Badan 1 (Cd1)							
Apk	1.59	1.79	1.09	1.95	0.53	0.66	0.60
Bss2	1.75	1.84	1.16	1.94	0.53	0.57	0.55
Chai Badan 2 (Cd2)							
Ap	1.77	1.86	1.23	1.6	0.44	0.66	0.55
Btc	1.45	1.87	1.28	2.6	0.40	0.47	0.43
Lop Buri 3 (Lb3)							
Apk	1.73	1.83	1.34	1.51	0.44	0.61	0.53
Bssk2	1.66	1.84	1.37	1.68	0.53	0.61	0.57
Samo Thod 1 (Sat1)							
Apk	1.45	1.9	0.98	2.4	0.44	0.57	0.51
Bt3	1.51	1.84	1.02	1.93	0.47	0.50	0.48
Samo Thod 2 (Sat2)							
Apk	1.45	1.88	1.23	1.77	0.44	0.61	0.53
Btk2	1.49	1.89	1.18	1.86	0.40	0.66	0.53
Wang Chomphu 1 (Wc1)							
Ap	1.52	1.79	1.22	2.77	0.44	0.57	0.50
Btc1	1.53	1.82	1.07	2.78	0.40	0.47	0.43
Wang Chomphu 2 (Wc2)							
Ap	1.52	1.85	1.21	2.19	0.44	0.57	0.50
2Btk2	1.56	1.85	1.03	2.73	0.40	0.57	0.48
Mean					0.47	0.60	0.54
Min					0.40	0.47	0.43
Max					0.53	0.71	0.62

deconvolution program to accurately locate peak positions. Small overlapping peaks of vermiculite (d_{001}) which were hardly visible in the uncorrected patterns changed to a distinct shoulder for most samples. Importantly, a consistent shift of the peak position of smectite to smaller spacings was observed after correction (marked with dashed vertical line in Figure 2). Some published *d* values for intercalated smectite may have been based on broad reflections that were not corrected for LP displacement; the effect of error in *d* spacings on values of layer-charge density was discussed by Stanjek *et al.* (1992).

The minor amount of vermiculite present in clay from Sat1, Sat2, and Cd2 (Table 3) generated a 001 peak partially overlapping with smectite 001 and a distinct second-order peak for n_c 6−18 with *d* values for 001

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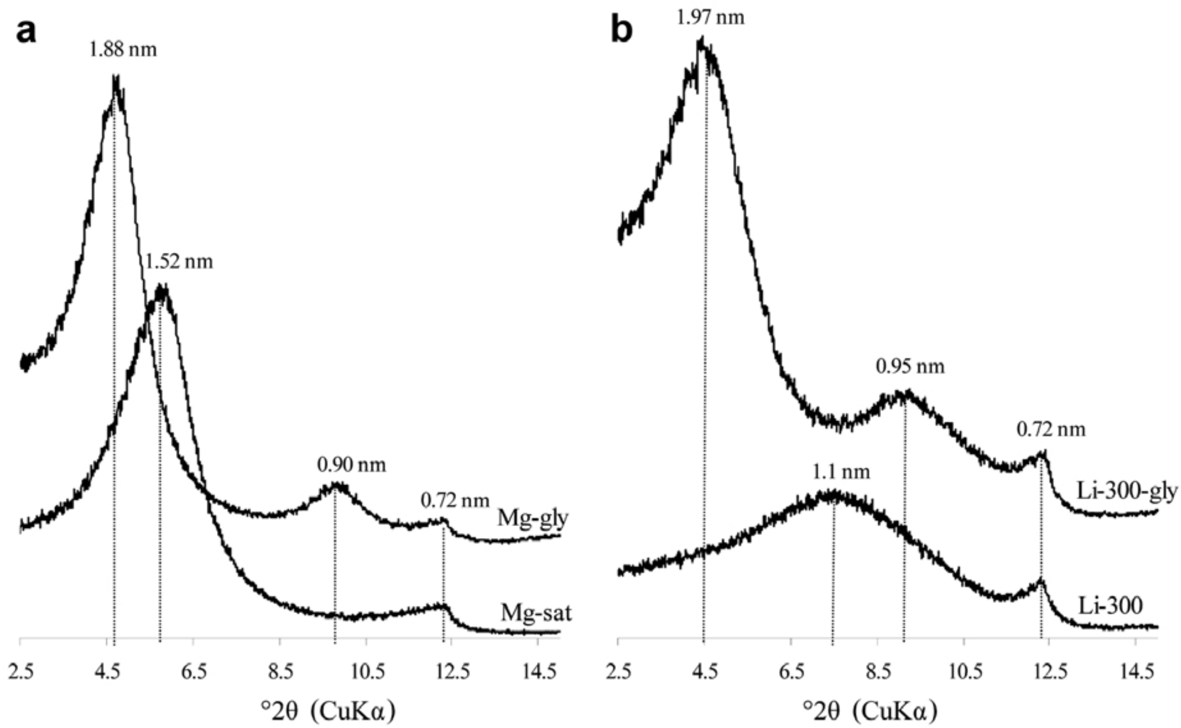

Figure 1. XRD patterns showing basal spacings of clay minerals in basally oriented clay from the Lb1-Apkg horizon: (a) after Mg-saturation and glycerol solvation; and (b) after the Greene-Kelly test. The re-expansion after glycerol solvation (Li-300-gly) to 1.97 nm indicates the presence of beidellite (tetrahedral charge).

increasing linearly with increasing n_c. Smectite in this clay had a broad 001 peak and a distinct second-order 002 peak for n_c = 16 or 18 (Figure 3a). Smectite in Cd1 (Cd1-Bss2) generated much sharper peaks for alkylammonium clay with distinct second-order peaks for long carbon chains (C13, C16, and C18) (Figure 3*b*). Smectite in Lb1, Lb2, Lb3, Bm, Br, Wc1, and Wc2 had similar characteristics to the smectite in Cd1-Bss2 with sharp smectite XRD peaks when n_c >9.

For large n_c values, a distinct second-order vermiculite reflection occurred, corresponding to a basal spacing of 1.54 nm (C18, Figure 2) and indicating that vermiculite is present. Vermiculite can form a double layer complex with glycerol which is not distinguished from smectite by Mg-gly treatment (Rühlicke and Neiderbudde, 1985; Malla and Douglas, 1987a). They can be distinguished by high n_c alkylammonium intercalation. Some illites could also be expanded by the alkylammonium cation and would produce low-angle peaks that could be difficult to distinguish from the peak of alkylammonium vermiculite (Laird *et al.*, 1987). Smectite in Ck was associated with much kaolinite and significant amounts of illite. The expandable phase peaks were broad, which is interpreted as the contribution of expandable illite caused by K-depletion by exchange of K with the alkylammonium ion (Laird *et al.*, 1987).

The gradual transition in *d* spacing as shown by the bilayer (*d* = 1.76 nm) to pseudotrimolecular layer (*d* = 2.20 nm) transition (Figure 4) indicated that these smectites have heterogeneous charge distributions. The corresponding total layer charge values (Table 4) and the distribution of layer charge values for eight representative smectites (Figure 5) were calculated using the procedure of Lagaly (1994). A broad range of layer-charge values was obtained (*e.g.* 0.5−0.7 charges per half unit cell). The layer-charge density of the smectites has been taken to be the mean of upper and lower limit values. The layer-charge density of smectite in topsoils ranged from 0.50 to 0.60 mol(−)/$O_{10}(OH)_2$ with a mean value of 0.55 mol(−)/$O_{10}(OH)_2$ and the layer-charge density of smectite in subsoils ranged from 0.43 to 0.62 mol(−)/$O_{10}(OH)_2$ with a mean value of 0.52 mol(−)/$O_{10}(OH)_2$. The layer-charge density for lowland Vertisols (Bm, Ck, Lb1, and Lb2) varied in a narrow range from 0.50 to 0.62 mol(−)/$O_{10}(OH)_2$ whereas upland Vertisols (Br, Cd1, Cd2, Lb3, Sat1, Sat2, Wc1, and Wc2) exhibited a wider range of 0.43 to 0.60 mol(−)/$O_{10}(OH)_2$ for both topsoils and subsoils.

The mean layer-charge values for all smectites examined (ranging from 0.43 to 0.62 mol(−)/$O_{10}(OH)_2$) were within the range for smectite of 0.2 to 0.6 defined by Guggenheim *et al.* (2006). These Thai smectites could be considered to be high-charge smectites with respect to the limits of >0.45 charge per half unit cell and a value between 0.45 and 0.60 (Tessier and Pedro, 1987). The expansion of the basal spacing of smectite upon

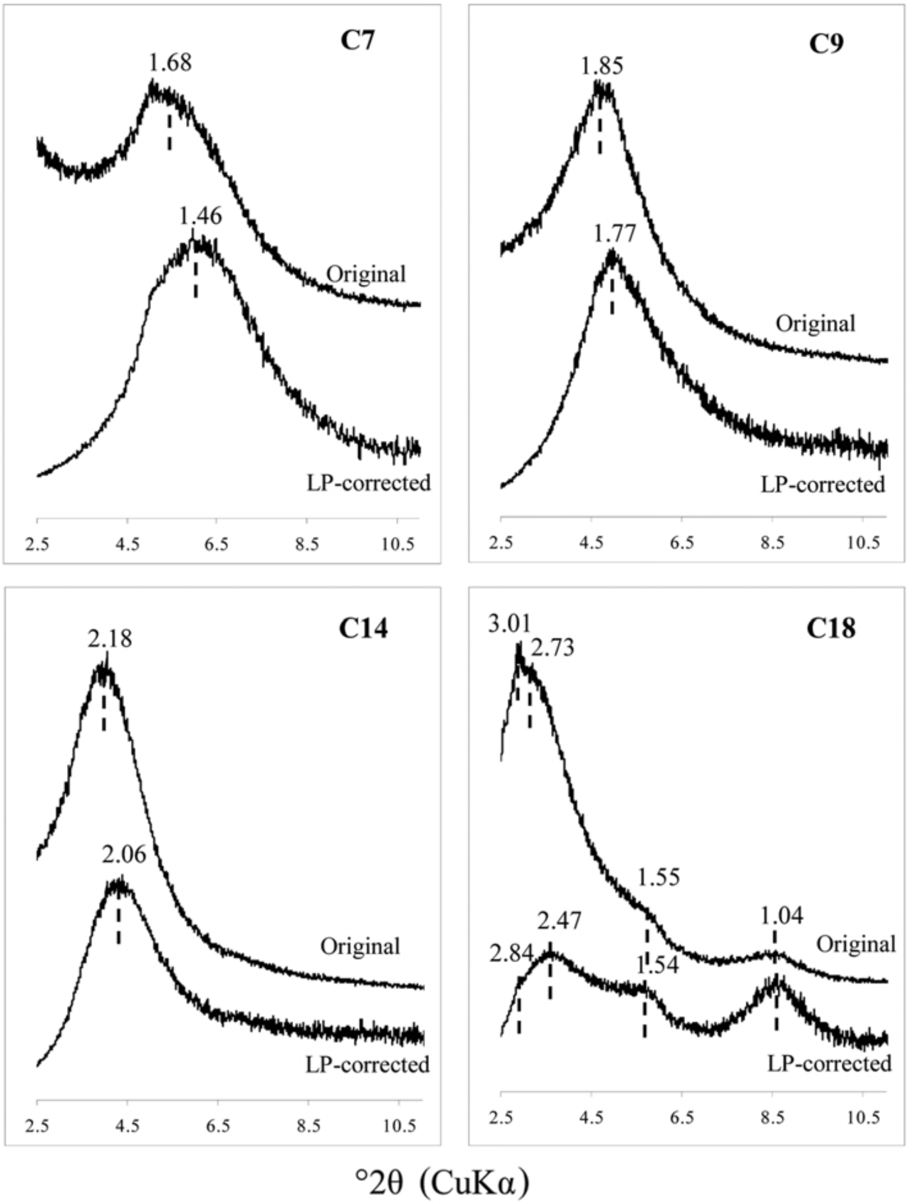

Figure 2. Comparison of uncorrected and Lorentz- and polarization-corrected (LP) XRD patterns and corrected *d* values after curve fitting for the Bm-Bsskg2 clay sample treated with alkylammonium with $n_c = 7, 9, 14$, and 18. Dashed vertical lines indicate *d* values of peak maxima (nm).

dodecylamine intercalation (C12) with *d* values ranging from 1.76 to 2.20 nm confirms the high-charge density of these smectites (Olis *et al.*, 1990). The smectites in these Thai Vertisols can thus be classified as high-charge beidellites which exhibit a range of layer-charge values. These smectites thus resemble smectites from a Vertic Haplaquoll in northwestern Minnesota for which the layer charge ranged from 0.4 to 0.5 mol(−)/$O_{10}(OH)_2$ (Badraoui *et al.*, 1987), smectite in Vertisols from New South Wales, Australia (0.55 to 0.67 mol(−)/$O_{10}(OH)_2$) (Singh and Heffernan, 2002), high-charge beidellite in Vertisols and Mollisols in the High Chaouia Region of Morocco (0.55 to 0.66 mol(−)/$O_{10}(OH)_2$) (Badraoui and Bloom, 1990), and smectite in Fe-rich calcareous and black soils in Taiwan (0.43 to 0.52 mol(−)/$O_{10}(OH)_2$) (Pai *et al.*, 1999).

Chemical properties of smectite

The CEC of soil clays measured using AgTU and expressed on an anhydrous basis (*i.e.* no interlayer water) ranged from 84 to 139 cmol kg^{-1}. The small values belong to clays which have a relatively large kaolinite content and to illite minerals which have smaller CEC values than does smectite (Bühmann and

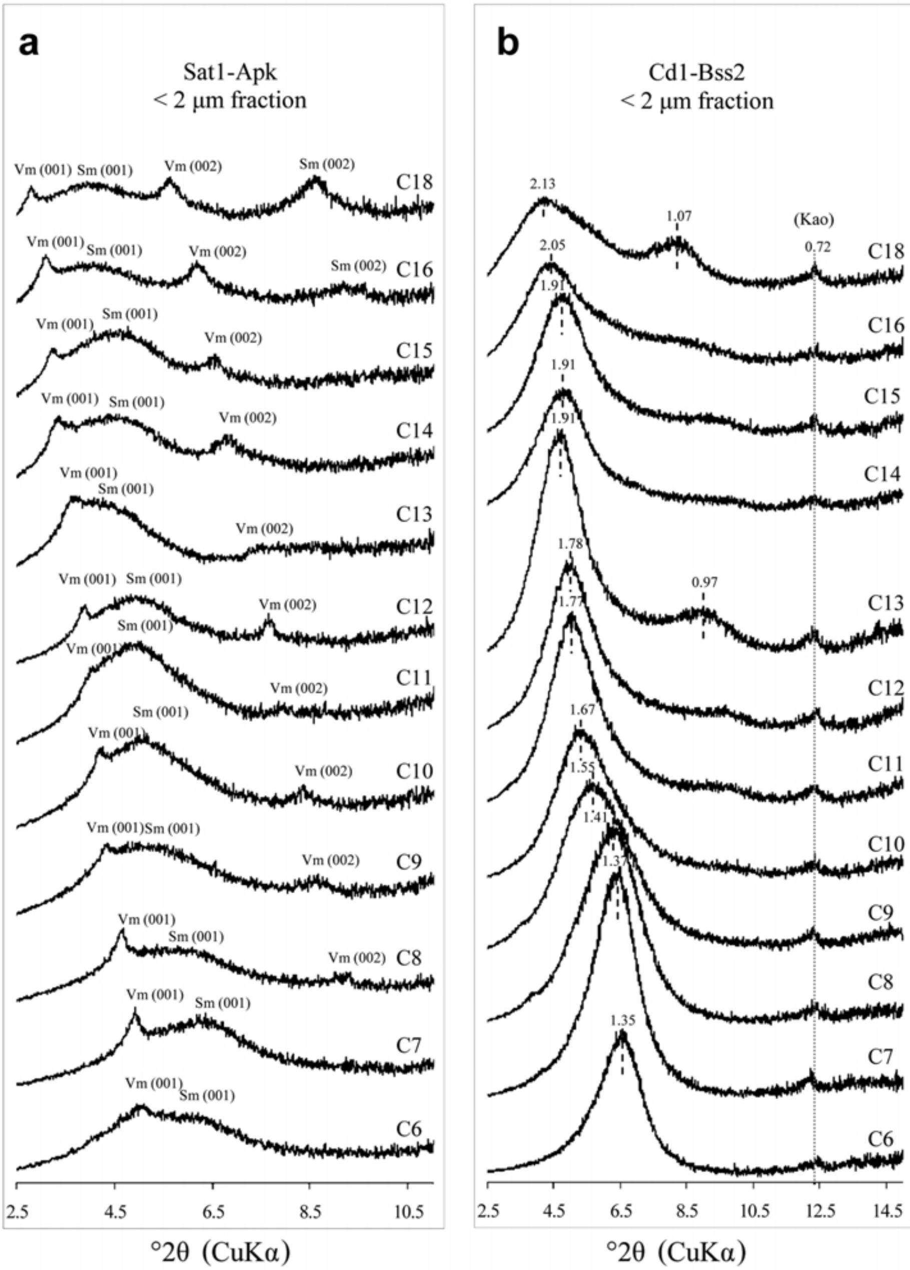

Figure 3. LP-factor corrected XRD patterns of two basally oriented clays treated with alkylammonium (n_c= 6–18): (a) high-charge smectite from an upland Vertisol (Sat1-Apk) with a small amount of vermiculite (Vm); (b) high-charge smectite from an upland Vertisol (Cd1-Bss2) with a small amount of kaolinite (Kao, 0.72 nm). Spacings in nanometers (nm).

Schoeman, 1995). The CEC values for most clays were within the typical range for smectite proposed by Wolters *et al.* (2009) and similar values (80–120 cmol kg^{-1} clay) for soil smectite were observed by Bühmann and Schoeman (1995). The CEC values of highly smectitic clays were converted into values of layer-charge density using the equation given by Mermut and Lagaly (2001) where the molecular mass of anhydrous smectite was assumed to be 385 g mol^{-1}, to generate the so-called CEC-charge density (Table 5). These values were in the range 0.32 to 0.54 mol(–)/$O_{10}(OH)_2$ and are systematically smaller than the values of mean layer charge (0.50 to 0.62 mol(–)/$O_{10}(OH)_2$) determined by the alkylammonium method.

For these smectites, the agreement of alkylammonium-based values of charge density with values calculated from CEC of the clay fraction ranged from

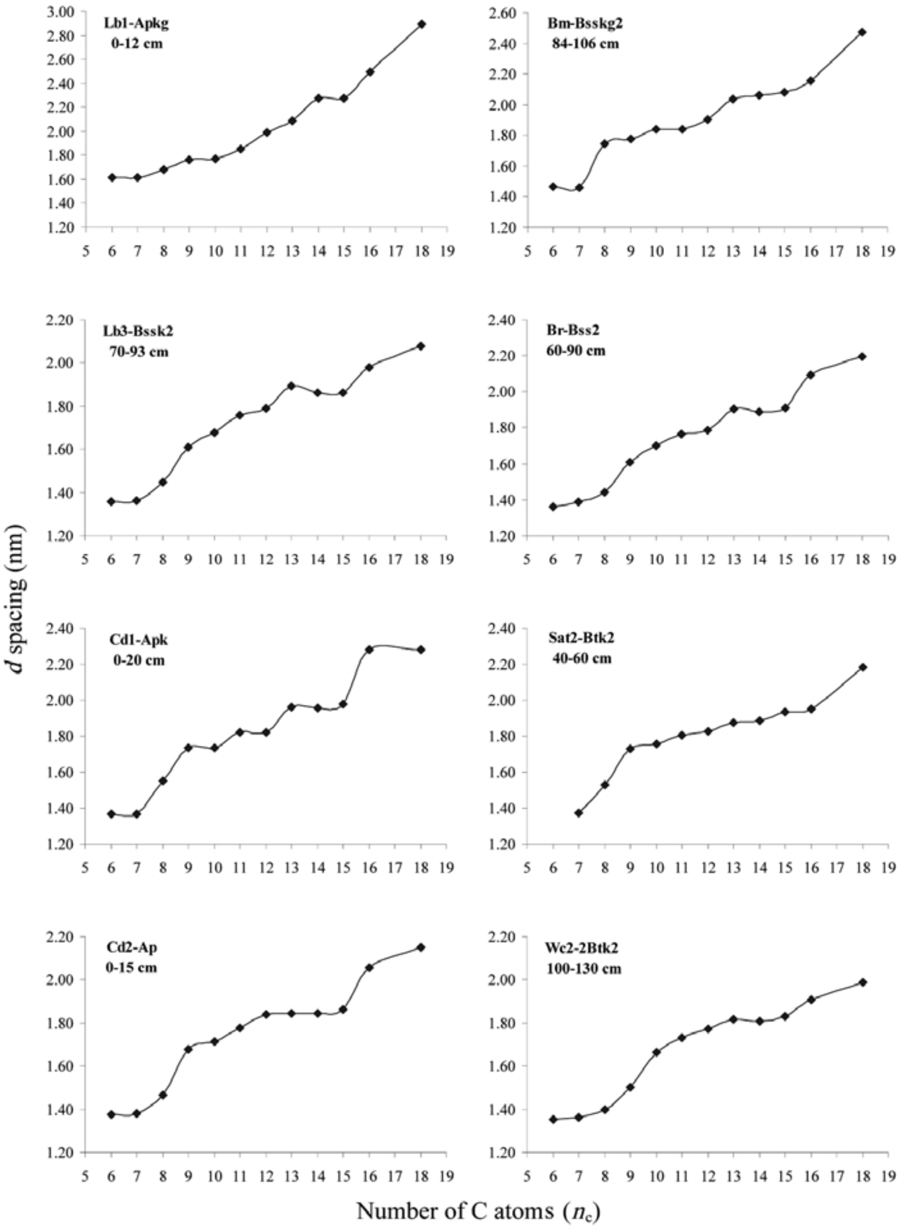

Figure 4. Relations between d_{001} values derived from XRD data after LP correction and curve fitting *vs.* alkylammonium chain length (n_c) for eight alkylammonium-intercalated smectites from Thai Vertisols.

good to poor (Table 5). Many of the clay fractions contained considerable amounts of minerals other than smectite, which greatly decreased the calculated values of charge density.

Structural formula of smectite

The major-element composition of highly smectitic soil clays which was not corrected for minor amounts of mineral impurities is given in Table 6. CaO (1.87−3.48%) and Na_2O (0.10−0.88%) were considered to represent the exchange cation content. The SiO_2:Al_2O_3 ratio (mean = 2.0:1) of these smectites was substantially less than that for Vertisols from New South Wales, Australia (mean SiO_2:Al_2O_3 = 3.2:1) (Singh and Heffernan, 2002), the High Chouia Region of Morocco (mean SiO_2:Al_2O_3 = 2.6:1) (Badraoui and Bloom, 1990), and Italy (mean SiO_2:Al_2O_3 = 3.44:1) (Righi *et al.*, 1995) but the Fe_2O_3 concentration was similar to values for those Vertisols. The relatively small silica to alumina ratio of the smectite studied may to some extent reflect the presence of impurity kaolinite and the contribution of Fe substitution in the octahedral sheet, which results in less Al in the smectite.

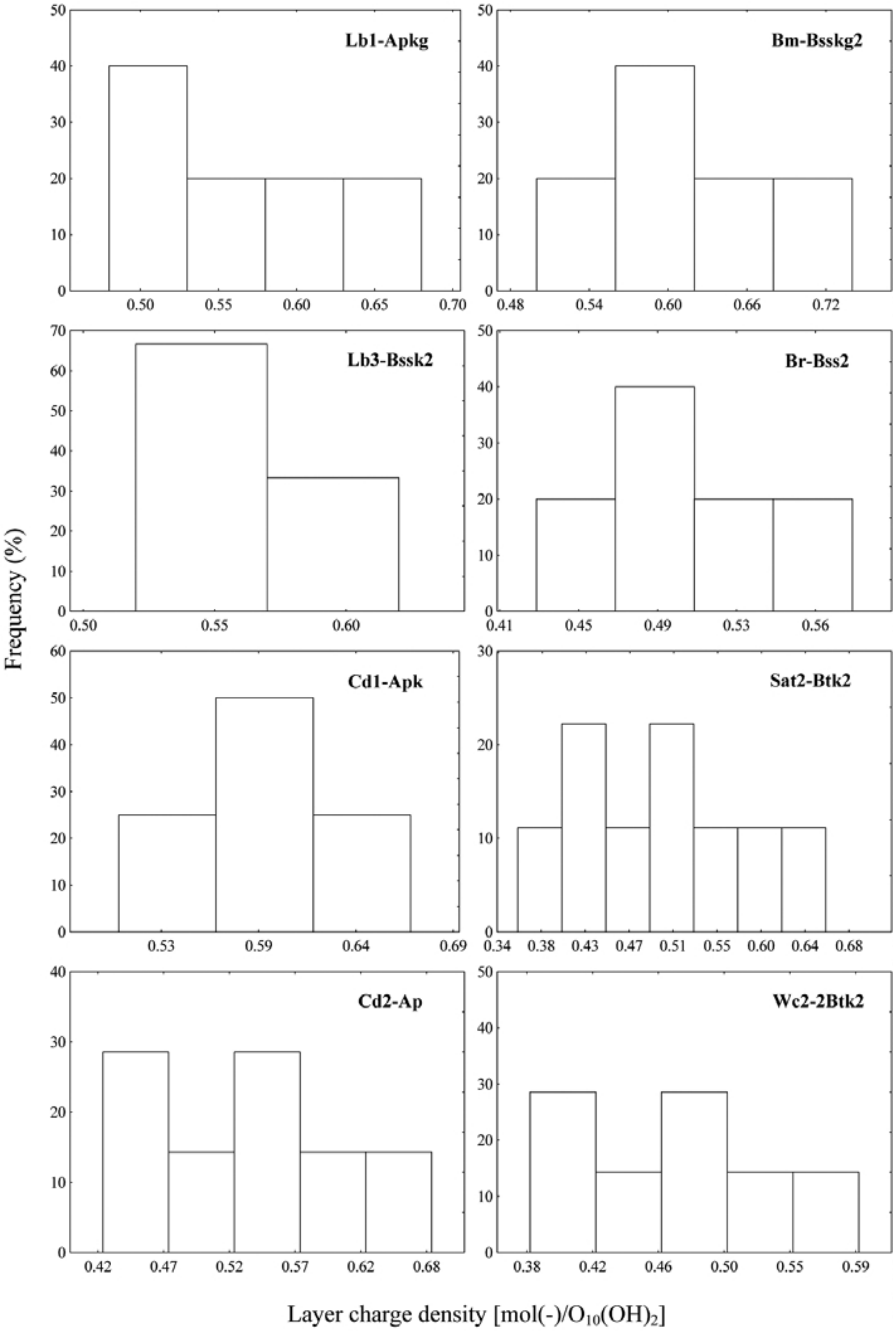

Figure 5. Distribution of layer-charge values derived from spacings of alkylammonium-treated samples (*e.g.* as in Figure 4) for eight smectites from Thai Vertisols.

The minor elemental contributions from kaolinite and quartz that were determined semi-quantitatively by XRD were subtracted from the analyses. Iron was assumed to be present only as Fe^{3+}. The minor TiO_2 was omitted from the structural-formula calculation as free anatase occurs in most soil clays (Brown *et al.*, 1978) and the structural formula calculation followed the method proposed by Laird (1994).

The smectites in these Thai Vertisols from widely dispersed sites had remarkably similar structural formulae (Table 7). Silicon in the tetrahedral sites was substantially substituted by Al^{3+} occupying 9.9–18.2% of tetrahedral cation sites to produce tetrahedral negative charge ranging from 0.40 to 0.73 charges per half unit cell. Aluminum was the major octahedral cation. The concentration of Fe in the octahedral sheet ranged from

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Table 5. A comparison of values of charge density of smectite determined by the CEC, alkylammonium, and structural formula methods.

Sample	Depth (cm)	Approximate % smectite in clay	CEC-clay[a] (cmol kg^{-1})	Calculated CEC-charge density[b]	Mean layer charge density[c] (alkylammonium)	Structural charge density
				——— mol(−)/$O_{10}(OH)_2$ ———		
Lowland Vertisols						
Ban Mi (Bm)						
Apkg	0–20	80	86	0.33	0.59	0.48
Bsskg2	84–106	80	107	0.41	0.62	0.49
Lop Buri 1 (Lb 1)						
Apkg	0–12	95	113	0.44	0.58	0.53
Bkg2	33–55	85	97	0.37	0.50	–
Lop Buri 2 (Lb2)						
Apg	0–20	95	84	0.32	0.59	0.48
Bssg3	65–90	95	92	0.35	0.59	0.47
Upland Vertisols						
Buri Ram (Bm)						
Ap	0–20	95	100	0.38	0.60	0.46
Bss2	60–90	95	91	0.35	0.50	0.47
Chai Badan 1 (Cd1)						
Apk	0–20	95	139	0.54	0.60	0.60
Bss2	80–110	95	132	0.51	0.55	0.69
Lop Buri 3 (Lb3)						
Apk	0–25	95	112	0.43	0.53	–
Bssk2	70–93	95	121	0.47	0.57	–

[a] CEC values of clay fraction are expressed on a water-free basis.
[b] CEC-charge density values are low as clays contain impurities.
[c] Mean layer-charge density values calculated from bilayer to pseudotrilayer transition.

Table 6. Major element composition of 60ºC dried, deferrated, OM-free, Ca-saturated soil clays (not corrected for impurities).

Sample	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	MnO	CaO	K_2O	MgO	Na_2O	Si/Al ratio
	———	———	———	———	(%)	———	———	———	———	
Bm-Apkg	26.43	48.78	0.32	8.57	0.05	2.80	0.20	0.96	0.13	1.85
Bm-Bsskg2	26.92	48.65	0.26	8.34	0.03	2.86	0.09	0.89	0.23	1.81
Br-Ap	23.92	50.64	0.70	9.24	0.04	2.72	0.06	1.40	0.16	2.12
Br-Bss2	21.65	49.34	0.99	8.89	0.05	2.78	0.06	1.47	0.12	2.28
Cd1-Apk	18.91	47.82	0.73	8.35	0.08	2.77	0.12	2.24	0.88	2.53
Cd1-Bss2	18.87	47.57	0.39	8.42	0.07	3.48	0.09	2.15	0.78	2.52
Cd2-Ap	22.14	46.11	0.63	11.12	0.03	2.60	0.05	1.80	0.26	2.08
Cd2-Btc	22.53	45.48	0.86	10.79	0.03	2.39	0.03	1.72	0.10	2.02
Lb1-Apkg	24.87	49.43	0.67	8.85	0.07	2.97	0.11	1.27	0.18	1.99
Lb2-Apg	26.24	49.51	0.78	8.04	0.04	2.51	0.09	0.94	0.18	1.89
Lb2-Bssg3	25.65	47.93	0.75	8.12	0.03	2.55	0.04	0.93	0.19	1.87
Sat1-Bt3	25.00	47.60	0.61	8.37	0.03	2.41	0.42	1.14	0.17	1.90
Sat2-Btk4	26.25	44.34	0.48	6.68	0.02	3.33	0.59	1.15	0.35	1.69
Wc1-Btc1	23.86	47.23	0.73	8.42	0.02	2.21	0.04	1.32	0.28	1.98
Wc2-Ap	24.28	46.63	0.42	7.71	0.03	1.87	0.24	1.45	0.62	1.92
Wc2-2Btk2	24.21	48.67	0.66	6.37	0.01	2.30	0.40	1.82	0.37	2.01
Min	18.87	44.34	0.26	6.37	0.01	1.87	0.03	0.89	0.1	1.69
Max	26.92	50.64	0.99	11.12	0.08	3.48	0.59	2.24	0.88	2.53
Mean	23.86	47.86	0.62	8.52	0.04	2.66	0.16	1.42	0.31	2.03

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Table 7. Structural formulae of some Ca-saturated Thai Vertisol smectites after correction of analyses for contents of kaolinite and quartz, compared with literature values.

Sample	- Interlayer -			- Tetrahedral -			- Octahedral -			Charge
	Ca^{+2}	Na^{+}	K^{+}	Si^{+4}	Al^{+3}	Al^{+3}	Fe^{+3}	Mg^{+2}	Mn^{+2}	$Mol/O_{10}(OH)_2$
Lb1-Apkg	0.25	0.03	0.01	3.39	0.61	1.41	0.51	0.15	0.005	−0.53
Bm-Apkg	0.22	0.02	0.02	3.34	0.66	1.51	0.48	0.11	0.003	−0.48
Bm-Bsskg2	0.23	0.03	0.01	3.35	0.65	1.52	0.46	0.10	0.002	−0.49
Lb2-Apg	0.22	0.02	0.01	3.27	0.73	1.50	0.50	0.12	0.003	−0.48
Lb2-Bssg3	0.22	0.03	0.00	3.31	0.69	1.51	0.49	0.11	0.002	−0.47
Br-Ap	0.21	0.02	0.01	3.46	0.54	1.42	0.51	0.15	0.003	−0.46
Br-Bss2	0.22	0.02	0.01	3.52	0.48	1.39	0.50	0.16	0.003	−0.47
Cd1-Apk	0.23	0.13	0.01	3.60	0.40	1.27	0.48	0.26	0.005	−0.60
Cd1-Bss2	0.28	0.11	0.01	3.59	0.41	1.26	0.48	0.24	0.005	−0.69
Average	0.23	0.05	0.01	3.43	0.57	1.42	0.49	0.15	0.003	−0.52

Representative formula	$[Ca_{0.23}Na_{0.05}K_{0.01}][Si_{3.43}Al_{0.57}][Al_{1.42}Fe_{0.49}Mg_{0.15}]O_{10}(OH)_2$	(1/2 unit cell)[a]
Examples		
India[b]	$M^{+}_{0.43}[Si_{3.74}Al_{0.26}][Al_{1.24}Fe_{0.42}Mg_{0.46}]O_{10}(OH)_2$	Vertisol
Morocco[c]	$[Na_{0.54}K_{0.07}][Si_{3.59}Al_{0.41}][Al_{1.28}Fe_{0.38}Mg_{0.42}]O_{10}(OH)_2$	Vertisol
	$[Na_{0.59}K_{0.04}][Si_{3.56}Al_{0.44}][Al_{1.23}Fe_{0.40}Mg_{0.46}]O_{10}(OH)_2$	Mollisol
Turkey[d]	$M^{+}_{0.56}[Si_{3.55}Al_{0.45}][Al_{1.21}Fe_{0.54}Mg_{0.33}]O_{10}(OH)_2$	Vertisol
Italy[e]	$[Ca_{0.15}Na_{0.01}K_{0.15}][Si_{3.64}Al_{0.36}][Al_{1.41}Fe_{0.39}Mg_{0.24}Mn_{0.01}]O_{10}(OH)_2$	Vertisol
Australia[f]	$[Ca_{0.15}Na_{0.01}K_{0.03}][Si_{3.87}Al_{0.13}][Al_{1.45}Fe_{0.40}Mg_{0.11}Mn_{0.01}]O_{10}(OH)_2$	Vertisol

[a] Data obtained in this study, [b] Mathy and Murthy (1994), [c] Badraoui and Bloom (1990)
[d] Ozkan and Ross (1979), [e] Righi *et al.* (1995), [f] Singh and Heffernan (2002)

22 to 25% of total octahedral cations, indicating that these smectites are Fe-rich beidellites which resemble the high-charge beidellite in Vertisols of the High Chaouia Region of Morocco in which octahedral Fe ranged from 16 to 21% of total octahedral cations (Badraoui and Bloom, 1990) and Indian Vertisols where it ranged from 18 to 25% (Math and Murthy, 1994). The representative structural formulae of smectite for Thai Vertisols indicate that the negative charge originates mainly in the tetrahedral sheet with some excess positive charge originating in the octahedral cation site for some samples (*e.g.* Lb1). Other samples had some negative charge originating in the octahedral cation site (*e.g.* Cd1). Smectites in the clay fraction of Chouia Vertisols (M1F), Mollisols (M7F) (Badraoui and Bloom, 1990), Indian Vertisols (Math and Murthy, 1994), Turkish Vertisols (Ozkan and Ross, 1979), and Italian Vertisols (Righi *et al.*, 1995) differ from smectite in Thai Vertisols in having much less tetrahedral charge. Thus, the smectite in Thai Vertisols has a much more beidellitic character than the smectite in these published examples. However, with the exception of the Australian Vertisols (average 0.34) of Singh and Heffernan (2002), the total layer charge of Thai Vertisol smectite (0.46−0.69) is similar to the above published values (0.43−0.62).

The layer charge of smectite in Thai Vertisols derived from the structural formula was mostly less than the average layer charge determined by the alkylammonium method. Values of layer-charge density derived from the CEC were even smaller (Table 5). Different values of layer charge obtained by various methods may, to some extent, relate to sample impurities and the assumption regarding the oxidation state of structural Fe (Laird, 1994).

CONCLUSIONS

Thai Vertisols developed from local alluvium derived from limestone and residuum of andesite and basalt contain abundant smectite which is remarkably uniform being a high-charge, Fe-rich beidellite. The average layer charge determined by the alkylammonium method ranges from 0.43 to 0.62 $mol(-)/O_{10}(OH)_2$ and the smectite has a heterogeneous charge distribution. The layer-charge value of smectite determined by the alkylammonium method is significantly greater than that determined using CEC and the structural formula methods.

High-charge beidellite with a large CEC may play an important role in the fixation and release of K^+ and NH_4^+ in these soils (Weir, 1965; Bajwa, 1981a, 1981b; Bouabid *et al.*, 1991).

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