Smectite in Selected Thai Paddy Soils

N. Prakongkep[1], A. Suddhiprakarn[1,*], I. Kheoruenromne[1] and R.J. Gilkes[2]

[1]*Department of Soil Science, Faculty of Agriculture, Kasetsart University, Chatuchak, Bangkok 10900, Thailand*
[2]*School of Earth and Geographical Sciences (South), The University of Western Australia, 35 Stirling Highway-M087, Crawley, WA 6009, Australia*

**Corresponding author. Email: agrals@ku.ac.th*

Abstract

Eighteen widely distributed paddy soils from Northern, Northeastern, Central Plain and Eastern parts of Thailand were studied. Smectite is a dominant mineral in the clay fraction of soils in the Central Plain whereas soils in Northern, Northeastern and Eastern Thailand are kaolinitic and have none to moderate smectite contents. Therefore, of eighteen soils, four soils from Central Plain were selected for a detailed study of smectite.

Crack structure dominates the morphology of smectite-rich soils whereas illite and kaolinite paddy soils have a massive fabric. Microprobe analysis shows that chemical composition of the clay matrix of smectite-rich soils corresponds to beidellite.

The dioctahedral smectite in four smectite-rich paddy soils was investigated in detail. The swelling behavior of heated Li-saturated smectites demonstrated that the smectites are beidellitic. The layer charge of the smectites was estimated from the monolayer to bilayer transition on exchange with n-alkylammonium ions and ranges from 0.31 to 0.38 charge units per half unit cell formula. The structural formula of a calcium saturated soil smectite is: $(Ca_{0.38}K_{0.01})(Si_{6.83}Al_{1.17})$-$(Al_{3.20}Fe^{3+}_{0.80}Fe^{2+}_{0.01}Mg_{0.19})O_{20}(OH)_4$. This finding on beidellite in Thai paddy soils enhances basic knowledge required for optimizing paddy soil fertilizer management practices.

Keywords: alkylammonium method, layer charge, smectite, kaolin, paddy soil

Introduction

Paddy soils used for the intensive cultivation of rice in Thailand vary considerably in mineralogical and chemical composition (Yoothong et al., 1997). Smectite is commonly a dominant clay mineral in lowland paddy soils throughout the world but there has been no systematic study on this aspect of Thai paddy soils (Ghosh et al., 2006). The availability of several plant nutrient elements is likely to depend on the cation retention properties of the clay fraction which are poorly understood. Clay minerals possess net negative charge in their structures due to isomorphous substitution of cations within both the tetrahedral and octahedral sheets. The location of charge within the structure of clay minerals affects the retention of ions (Singh and Heffernan, 2002). In many natural smectites, the charge is distributed over both tetrahedral and octahedral sheets. Soil smectites with high amounts of tetrahedral substitution (e.g. beidellite) are believed to fix K and NH_4 more strongly than does montmorillonite and thus affect soil fertility (Laird et al., 1988).

The recognition of smectite species in soil clays is difficult. Hofmann and Klemen (1950) demonstrated that with Li saturation and heating at 200^{o}C, the negative octahedral charge can be neutralized by Li ions which diffuse into octahedral sites. The irreversible collapse of a smectite to ~1.0 nm after saturation with Li^+ and heating at 200-300^{o}C is a criterion for identifying montmorillonite (Singh and

Heffernan, 2002). On the other hand, expansion of a smectite to 1.78 nm with glycerol after Li-treatment and heating characterizes beidellite (Malla and Douglas, 1987). This test has not been applied to the smectites in Thai paddy soils.

Smectite rarely occurs in a pure form in soils so that direct measurement of layer charge of soil smectites is not possible, however, the alkylammonium method enables the determination of layer charge of smectites in samples containing mixed mineral assemblages (Senkayi et al., 1985). The alkylammonium ions are arranged in the interlayer space with their chains lying flat or tilted, the former being typical of low-charge smectites and the latter of high-charge smectites (Stul and Mortier, 1974).

The primary objective of this study was to use these criteria to characterize the smectite present in soils used for paddy rice in Thailand. This research is a component of a survey of the clay mineralogy, morphology and chemical composition of a large number of paddy soils which was intended to improve our knowledge of these soils and to help the development of optimum land management practices.

Materials and Methods

Soils

Topsoil and subsoil samples from eighteen widely distributed Thai paddy soils were used for this investigation (Figure 1). The soil samples were air-dried, gently crushed, and sieved to obtain the <2 mm fraction. Some physico-chemical properties of whole smectite-rich soils were determined using the procedures described by National Soil Survey Center (1996). Soil classification was based on soil taxonomy (Soil Survey Staff, 2006).

Mineralogical Characterization and Total Analysis of Clay

The clay fraction (<2 μm) was obtained by sedimentation. Organic matter was removed from the clay using the H_2O_2 oxidation method (Kunze, 1965). Free sesquioxides were removed with a solution of sodium dithionite and sodium citrate in a sodium bicarbonate-buffered system (Mehra and Jackson, 1960). Cation exchange capacity (CEC) of the clay fraction was measured by the Ag-thiourea method (Rayment and Higginson, 1992). A basally oriented Li-saturated clay was prepared on a ceramic plate, heated at 300^{o}C for 2 h, cooled in a dessicator and then glycerol solvated prior to XRD examination (Greene-Kelly, 1955).

XRF analyses of fused discs of the Ca-saturated clay fractions were obtained using a Philips PW1400 X-ray fluorescence (XRF) spectrometer fitted with a rhodium tube. Zero point seven gram of Ca-saturated clay fraction was fused with 7.000 g of lithium meta/tetraborate flux at 1050°C in a platinum crucible. For this analysis, the clay fraction was Ca^{2+}-saturated by four centrifugal washings in 1 M $CaCl_2$ and then repeated washing with distilled water until free of $AgNO_3$ detectable chloride. These analyses were carried out on two clay samples (Ap and Bss3 horizons of Lop Buri series (Typic Haplustert)) based on XRD data that indicated dominance of smectite.

Layer Charge Characterization

The layer charge of smectites was estimated by XRD measurement of the (001) interplanar spacing of alkylammonium-clay complexes using alkylchains with 6, 7, 10, and 12 C alkyl number (n_c). Alkyl

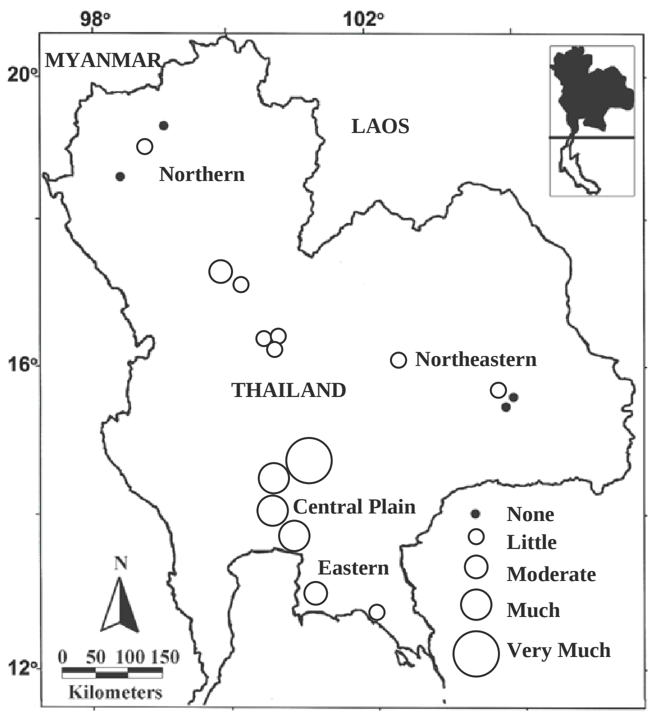

Figure 1 Locations of eighteen representative Thai paddy soils and the abundance of smectite in the clay fraction (None = 0%, Little = 1–5%, Moderate = 5–20%, Much = 20–60%, Very much = >60%).

solutions were prepared using a slight modification of the procedure of Lagaly (1994), which consisted of heating the solution containing the required amount of alkylamine salt, ethanol, water, and HCl at about 60°C for 1 h and adjusting the solution pH to 6.5-7.0 with 0.1 M HCl after cooling. One hundred milligrams of clay was dispersed in a capped tube using a vortex mixer with 1 mL for alkylammonium concentrations of >0.1 M (n_c<11) and 4 mL in the case of 0.05 M solutions (n_c>15), equilibrated overnight in a water bath at 65°C and centrifuged. The treatment was repeated once. The excess alkylammonium salt was removed by washing the samples 8 times with 3 mL of a water-ethanol mixture (2:1) followed by two washings with pure ethanol. Oriented specimens were prepared by thinly spreading the clay-ethanol slurry onto glass slides which were then dried in a desiccator containing P_2O_5 for 24 h prior to XRD analysis.

All XRD traces were obtained on a computer controlled Philips X-ray diffractometer using CuKα radiation and a focusing monochromator. The XRD traces of clay separates were recorded between 2 and 15° 2θ using a step size of 0.02° 2θ. The critical chain length used for the calculation of layer charge is the molecule with the alkylnumber n_c (general formula $C_nH_{2n+1}NH_3^+$) where the molecules attain the densest monolayer packing in the interlayer of the smectite. The spacings are mostly between 1.3 and 1.4 nm (monolayer) and 1.7 and 1.8 nm (bilayer). The procedure for calculating layer charge was given by Lagaly (1994).

SEM/EDS Analysis

Twelve slides of smectite-rich soils and twenty seven slides of other paddy soils were studied by polarizing microscope on thin sections of resin impregnated soils using standard micromorphological techniques (Bullock et al., 1985). Selected areas described under the petrographic microscope were submitted to SEM-EDS analysis. Soil matrix and pedofeatures, including clay coatings and iron oxide accumulations, were investigated using a JEOL 6400 scanning electron microscope coupled with an energy dispersive X-ray detector (SEM/EDS). The thin sections were analyzed for the elemental distribution of Si, Al and Fe.

Results and Discussion

The classification, parent materials and landform of Thai paddy soils are shown in Table 1. The geographical distribution of smectite in the soils shown in Figure 1 and a summary of the mineralogical composition of the clay fraction of the soils is shown in Figure 2. Smectite is a dominant mineral in the clay fraction of soils in the Central Plain whereas paddy soils in Northern, Northeastern and Eastern Thailand, contain none to moderate amounts of smectite. The Central Plain is a fault bounded basin that developed in the Plio-Pleistoscene epoch. The basin has been filled with Quaternary fluvial and swamp sediments reaching a thickness of almost 2000 m (Sinsakul, 2000). This area is naturally poorly drained and prior to drainage and agricultural development was saturated for a long period each year. Under this condition, some iron was reduced and dissolved ions including Si, Al and Mg were introduced from the adjacent leached uplands enabling the neoformation of smectite (Borchardt, 1989). The parent materials of some of these soils are associated with limestone derived alluvium and a deltaic environment. A favorable condition for smectites to precipitate exists close to dissolving limestones and in the lower positions of landscapes that receives alkaline seepage water from uplands (Borchardt, 1989). Smectite forms under brackish conditions where soil solution is enriched in silicon, magnesium and calcium (Dabbakula et al., 1992). Calcite is present in some paddy soils in the Central Plain due to authigenesis in this environment where dissolved ions accumulate. In contrast, most paddy soils in other part of Thailand are on terraces where leaching of Si and basic cations has occurred in the humid tropical climate. This condition favours formation of kaolin (Tardy et al., 1973) so that relatively little smectite is present. Seven samples representing clay fractions of four representative Central Plain Thai paddy soils have been studied in detail. The physical and chemical properties of the smectite-rich soil samples are shown in Table 2.

Table 1 Classification, parent material and landform of soils investigated.

Soil series	Classification (Soil Survey Staff, 2006)	Parent material	Landform
Tha Tum (Tt1, 2, 3)	Plinthic Endoaqualf	Mixed alluvium over residuum	Low terrace
Kula Ronghai (Ki)	Typic Natraqualf	Wash over residuum derived from clastic sedimentary rock	Erosional plain
Mae Sai (Ms)	Aeric Endoaqualf	Alluvium	Low intermontane terrace
Hang Dong (Hd)	Typic Endoaqualf	Mixed local alluvium over residuum derived from weathered clastic metasedimentary rocks	Low erosional intermontane terrace
San Sai (Sai)	Typic Endoaquult	Wash deposits on residuum derived from weathered granite	Upper part of low erosional intermontane terrace
Chiang Rai (Cr1, 2)	Plinthic Paleaqualf	Old alluvium	Higher part of low alluvial terrace
Chum Saeng (Cs1, 2, 3)	Aeric Endoaqualf	Alluvium (semi-recent)	Low terrace
Chon Buri (Cb)	Typic Endoaqualf	Mixed alluvium derived mainly from granite	Higher part of low terrace
Klaeng (Kl)	Typic Plinthaquult	Alluvium	Low terrace-floodplain transition
Lop Buri (Lb)	Typic Haplustert	Local alluvium derived from limestone	Toeslope of limestone mountain
Tha Rua (Tr)	Chromic Vertic Endoaqualf	Alluvium over old local alluvium	Low terrace
Khok Krathium (Kk)	Ustic Endoaquert	Recent alluvium	Flood plain
Bang Phae (Bph)	Typic Endoaquoll	Marine deposits mixed with riverine alluvium	Deltaic fringe

Table 2 Selected physical and chemical characteristics of smectite-rich Thai paddy soils.

Soil_Horizon	Depth	Sand	Silt	Clay	pH 1:1 H_2O	OM	Exchangeable bases				CEC soil	CEC clay
							Ca	Mg	K	Na		
	(cm)	(--------- g kg^{-1}		----------)		(g kg^{-1})	(---------------------- cmol kg^{-1}					------------------------)
Lop Buri series: Typic Haplustert												
Lb_Ap	0-23	70	326	604	8.0	24.0	62.8	2.2	0.9	0.9	29.6	84.0
Lb_Bss3	90-110	84	284	632	7.8	7.6	61.1	0.7	0.4	0.6	38.0	87.8
Tha Rua series: Chromic Vertic Endoaqualf												
Tr_Apg1	0-18	82	350	568	8.2	11.0	37.8	6.4	2.1	1.5	24.6	45.5
Khok Krathium series: Ustic Endoaquert												
Kk_Apg1	0-10	19	281	700	5.5	24.7	23.8	4.4	2.9	1.6	33.6	42.4
Kk_Bssg2	100-120	14	214	772	8.2	2.8	31.6	4.2	1.4	3.2	38.0	54.1
Bang Phae series: Typic Endoaquoll												
Bph_Apg1	0-6	39	369	592	5.4	20.4	16.3	5.8	0.5	15.2	32.5	37.9
Bph_Bg2	80-115	97	387	516	7.8	10.3	11.5	4.5	0.3	15.8	17.0	32.1

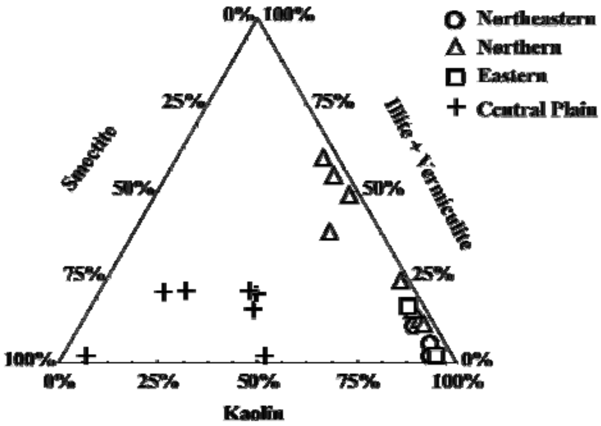

Figure 2 The mineralogical composition of the clay fraction of the soils.

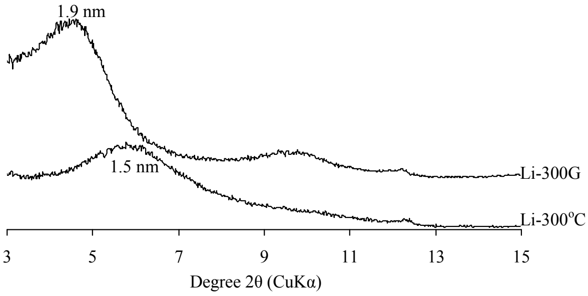

Figure 3 X-ray diffraction patterns of basally oriented clay from the Lop Buri soil (Ap horizon, 0-23 cm); Li-300°C = Li-saturated and heated at 300°C; Li-300 G = Li-saturated, heated at 300°C and glycerol solvated.

Smectite Properties

The clay content is high in all seven Central Plain soil samples (>500 g kg^{-1}), the CEC values range from 17-38 cmol kg^{-1} soil and the CEC values of the clay fraction vary between 32-88 cmol kg^{-1} clay (Table 2). Smectite is the dominant clay mineral with trace to moderate amounts in kaolin and a little illite present in some samples. The clay fractions of samples from the Lop Buri series (Typic Haplustert) are almost pure smectite (Table 3). XRD patterns of random powder of all the smectitic clays give a strong 060 reflection at 0.150 nm indicating that the smectite is dioctahedral (Badraoui and Bloom, 1990). The lithium-saturated and heated at 300°C samples give an approximately 1.5 nm diffraction peak which on glycerol solvation expanded to 1.9 nm (Table 4, Figure 3). After saturation of smectite with lithium ions and heating, the lithium ions migrate to vacant sites in the octahedral sheet to correct charge imbalance, consequently montmorillonite loses its capacity to expand after Li saturation and heating. However, beidellite has dominantly tetrahedral charge and lithium ions cannot migrate to tetrahedral sheets which do not contain cation vacancies, therefore beidellite continues to expand after Li saturation, heating and glycerol solvation. Thus the charge in smectites in these Thai paddy soils is more tetrahedral than octahedral in origin and the smectite resembles beidellite, not montmorillonite (Greene-Kelly, 1955).

Table 3 Semiquantitative mineralogical composition of the clay fraction of Thai paddy soils[1/].

Sample	Depth (cm)	Sme	Ill	Kao	Qtz	Fel
Lb_Ap	0-23	xxxx	-	tr	tr	-
Lb_Bss3	90-110	xxxx	-	tr	tr	-
Tr_Apg1	0-18	xx	x	xx	tr	-
Kk_Apg1	0-10	xxx	-	xx	tr	-
Kk_Bssg2	100-120	xx	x	xx	tr	-
Bph_Apg1	0-6	xxx	x	xx	tr	tr
Bph_Bg2	80-115	xxx	x	x	tr	tr

[1/] Based on integrated areas under the diffraction peaks and the use of mineral standards; xxxx = Dominant (>60%), xxx = Much (40-60%), xx = Moderate (20-40%), x = Little (5-20%), tr = Trace (<5%); - = Not detected, Sme = Smectite, Ill = Illite, Kao = Kaolin, Qtz = Quartz, Fel = Feldspar.

The XRD patterns for the various alklyammonium derivatives of the smectites in the seven samples provided evidence for the existence of (1) monolayer forms which had a 1.4 nm basal spacing, (2) bilayer forms which had a 1.9 nm basal spacing, and (3) monolayer-bilayer transition forms which had irrational sequences of basal reflections with values of d(001) between 1.5 to 2.0 nm. For example, the basal spacings for alkylammonium-clay complexes of the smectite in the Apg1 sample of the Tha Rua series (Chromic Vertic Endoaqualf) are shown in Figure 4 where the d(001) interplanar spacing is plotted against the number of C atoms in the alkyl chain. The ~1.45 nm reflection persists up to C7 and possibly up to C8 or C9 (not evaluated in this work) corresponding to an interlayer charge of 0.33 mol of charge per half unit cell formula if layer charge is calculated from the end of the monolayer plateau (n_c = 7). The monolayer-bilayer transition (C7-C10) gives a range of calculated charge of 0.33 to 0.43 with a mean value 0.38 charge per half unit cell. Values of charge calculated from the mono to bilayer transition are similar averaging around 0.37 charge per half unit cell for smectite in all seven samples (Table 5) (Calvet and Prost, 1971). These results are within the range of typical montmorillonite of 0.25-0.40 charge per half unit cell formula (Mermut and Lagaly, 2001). Natural beidellite typically has a layer charge near 0.33 charge per half unit cell (Ross and Hendricks, 1945) although the layer charge of beidellite in Vertisols and Mollisols from Morocco ranges from 0.36-0.55 charge per half unit cell (Badraoui and Bloom, 1990) and for beidellite in a Vertic Haplaquoll from Northwestern Minnesota ranges from 0.37-0.50 charge per half unit cell (Badraoui et al., 1987).

The results of chemical analysis of two almost pure Ca saturated smectites from the Ap and Bss3 horizons of Lop Buri series (Table 6) are consistent with the interpretation of a beidellitic character for smectite in Thai paddy soils based on the Li saturation procedure (Table 4). Satisfactory structural formulae can be calculated from the chemical composition of the Lop Buri smectites by assuming the ideal anion composition of smectite, that almost all Fe is present as Fe3+ and subtracting the elemental contributions of the minor impurity minerals. The structural formulae of Ca-saturated smectite samples

Table 4 The d_{001} spacing for Li saturated and heated (300°C) smectites before and after glycerol solvation.

Sample	d_{001} interlayer spacing (nm)		
	Li300°C	Li300°C/G	Smectite type[1/]
Lb_Ap	1.52	1.92	B
Lb_Bss3	1.44	1.86	B
Tr_Apg1	1.41	1.98	B
Kk_Apg1	1.43	1.89	B
Kk_Bssg2	1.47	1.88	B
Bph_Apg1	1.43	1.94	B
Bph_Bg2	1.43	1.85	B

[1/] B = beidellite; Li300°C = Li-saturated, heated at 300°C; Li300°C/G = Li-saturated, heated at 300°C and glycerol solvated.

Table 5 Interlayer charge characterization of Thai soil smectites determined from the mono/bilayer transition with alkylammonium.

Sample	Xmin	Xmax	Xmean
	(---------Charge per half unit cell-------)		
Lb_Ap	0.33	0.43	0.38
Lb_Bss3	0.28	0.48	0.38
Tr_Apg1	0.33	0.43	0.38
Kk_Apg1	0.28	0.48	0.38
Kk_Bssg2	0.28	0.48	0.38
Bph_Apg1	0.33	0.43	0.38
Bph_Bg2	0.28	0.33	0.31

$$X = \frac{\lambda 23.25}{5.67 n_c + 14}$$

n_c = number of C atoms in the alkyl chains
λ = number of alkylammonium layers
X = charge (mol of charge/(Si, Al)$O_{10}OH_2$)
Xmax = beginning of the transition
Xmin = end of the transition
Xmean = (Xmax + Xmin)/2

Table 6 Elemental composition of Ca-saturated smectites from two horizons of a Thai paddy soil (ignited basis).

Elemental composition (g kg^{-1})	Soil_Horizon	
	Lb_Ap	Lb_Bss3
SiO_2	557.0	556.2
Al_2O_3	307.8	309.9
Fe_2O_3[1/]	85.3	84.9
TiO_2[2/]	10.8	11.0
MgO	10.2	9.5
K_2O	0.5	0.3
CaO	28.4	27.9
MnO	0.7	0.6

[1/] All Fe expressed as Fe_2O_3.
[2/] Anatase impurity.

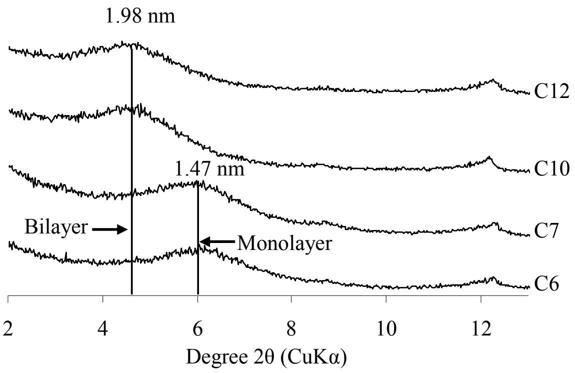

Figure 4 X-ray diffraction patterns of basally oriented smectite from the Apg1 horizon of the Tha Rua series (Chromic Vertic Endoaqualf) treated with various chain length (carbon number) alkylamine salts (carbon chain length specified at right). The range for the monolayer to bilayer transition is indicated by the arrows.

from the Ap and Bss3 horizons of the Lop Buri series are almost identical, being on average $(Ca_{0.38}K_{0.01})(Si_{6.83}Al_{1.17})(Al_{3.20}Fe^{3+}_{0.80}Fe^{2+}_{0.01}Mg_{0.19})$-$O_{20}(OH)_4$. This formula indicates that negative charge originates only in the tetrahedral layer. It is quite different from the smectite in Vertisols in New South Wales, $(Ca_{0.30}K_{0.06})(Si_{7.75}Al_{0.25})(Al_{2.92}Fe^{3+}$-$_{0.80}Mg_{0.23})O_{20}(OH)_4$ (Singh and Heffernan, 2002) which has less total layer charge, considerable octahedral charge and little tetrahedral charge. It is also very different from the smectite in the Bt1 horizon of the Zwingle pedon in Iowa, $(Ca_{0.34})(Si_{8.02})(Al_{2.72}Fe^{3+}_{0.12}Ti_{0.02}Li_{0.32}Mg_{1.18})O_{20}(OH)_4$ which has no tetrahedral charge (Laird et al., 1989). Smectite in the fine clay fraction of Chaouia Vertisols and Mollisols $(Na_{1.08}K_{0.15})(Si_{7.18}Al_{0.82})$-$(Al_{2.55}Fe^{3+}_{0.76}Mg_{0.84})O_{20}(OH)_4$ is more similar to the Lop Buri smectite but has a less beidellitic character (Badraoui and Bloom, 1990).

As is commonly the case with calculated structural formulae some uncertainly exists regarding the allocation of minor TiO_2 some of which is present as free anatase and minor FeO may be present in the smectite structure (Brown et al., 1978) but this will not significantly affect the formula. The calculated layer charge of the Lop Buri smectites of 0.38 charge per half unit cell is identical with the value of 0.38 obtained by solvation with alkylammonium ions (Table 5).

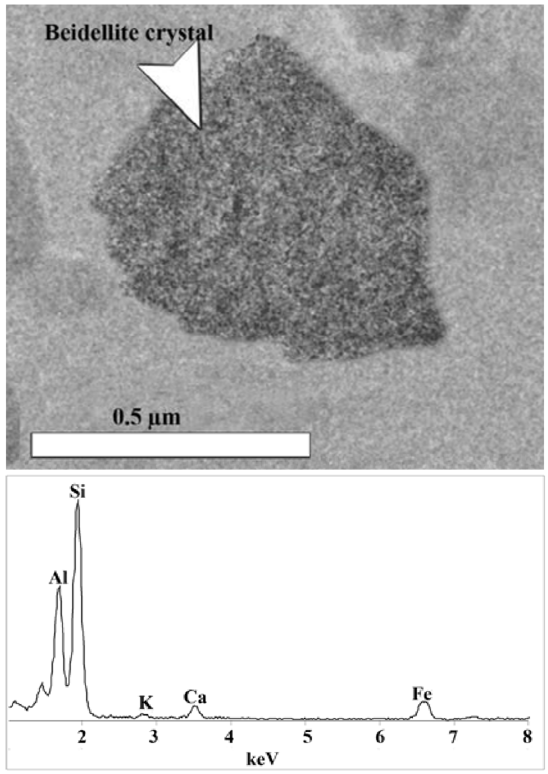

Figure 5 Transmission electron micrograph showing an irregular, platy smectite crystal from the Bg2 horizon of the Bang Phae series (Typic Endoaquoll). The EDX spectrum confirms the beidellitic composition of the smectite. Note that the appearance of the crystal has been computer enhanced, surrounding non-enhanced crystals of low contrast are also smectite.

A representative TEM micrograph of beidellite from a Thai paddy soil is presented in Figure 5 together with the corresponding EDX spectrum. The crystal which has enhanced contrast in this micrograph for clarity is an irregular, thin plate as has been observed by other workers (Badraoui and Bloom, 1990). The chemical composition of the crystal is indicated by the EDX spectrum and is consistent with the calculated beidellite formula.

Micromorphology of Smectitic Paddy Soils

Voids are mainly present as cracks in the smectite-rich paddy soils (Figure 6a) whereas voids in soils containing major illite or kaolin are vughs of various sizes (Figure 6). The crack micro-structures dominate in smectite-rich soils because

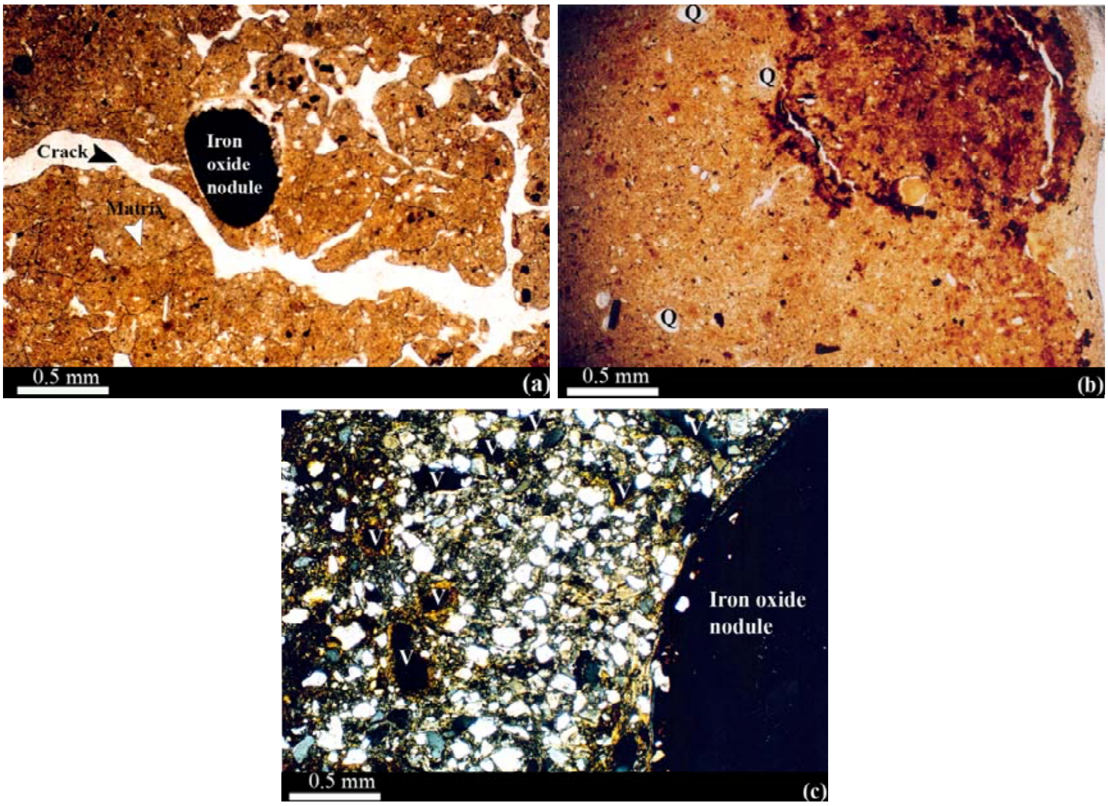

Figure 6 Optical micrographs of paddy soils showing the different types and abundance of voids associated with differences in clay mineralogy (a) Btg1 horizon (35-60 cm) of Tha Rua series which consists of major smectite with a crack structure, (b) Btg3 horizon (70-93 cm) of Mae Sai series (Aeric Endoaqualf) which consists of major illite with a vughy structure and (c) Btg horizon (30-48 cm) of Kula Ronghai series (Typic Natraqualf) which consists of major kaolin with vughs in a quartz rich compact grain structure (Q = quartz, V = void).

of the considerable shrinking and swelling of these soil materials due to the smectitic mineralogy. In dry conditions, these soils crack deeply but these cracks close when the soils become wet either due to rain or irrigation water. Numerous SEM-EDS single point analyses of the clay matrix of the smectite-rich soils indicate the major constituent of the clay matrix has the composition of beidellite (Figure 7).

Conclusions

Thai paddy soils vary in the types of clay minerals they contain. Smectite is a dominant mineral in the Central Plain, where a high water table has persisted and ions leached from adjacent uplands have accumulated resulting in the authigenesis of smectite and also calcite. Crack structure dominates in the beidellite-rich soils and vugh-structure in kaolin/illite soils.

The smectite in these paddy soils is beidellitic with a mean layer charge of about 0.38 charge units per half unit cell formula which differs from soil smectites described by some other workers that are montmorillonitic in nature. The availability of ammonium and potassium to plants depends on the clay mineral species and particularly on the layer charge characteristics of 2:1 phyllosilicate in soils. Ammonium and potassium are among the most important nutrients used to fertilize paddy soils and smectites have the ability to fix and exchange both ions. The location of layer charge in smectite is important in the release and fixation of K^+ and NH_4^+ (Chen et al., 1989) with beidellite clays in lowland Philippine rice soils fixing more than 90% of the applied NH_4^+ under hydromorphic conditions,

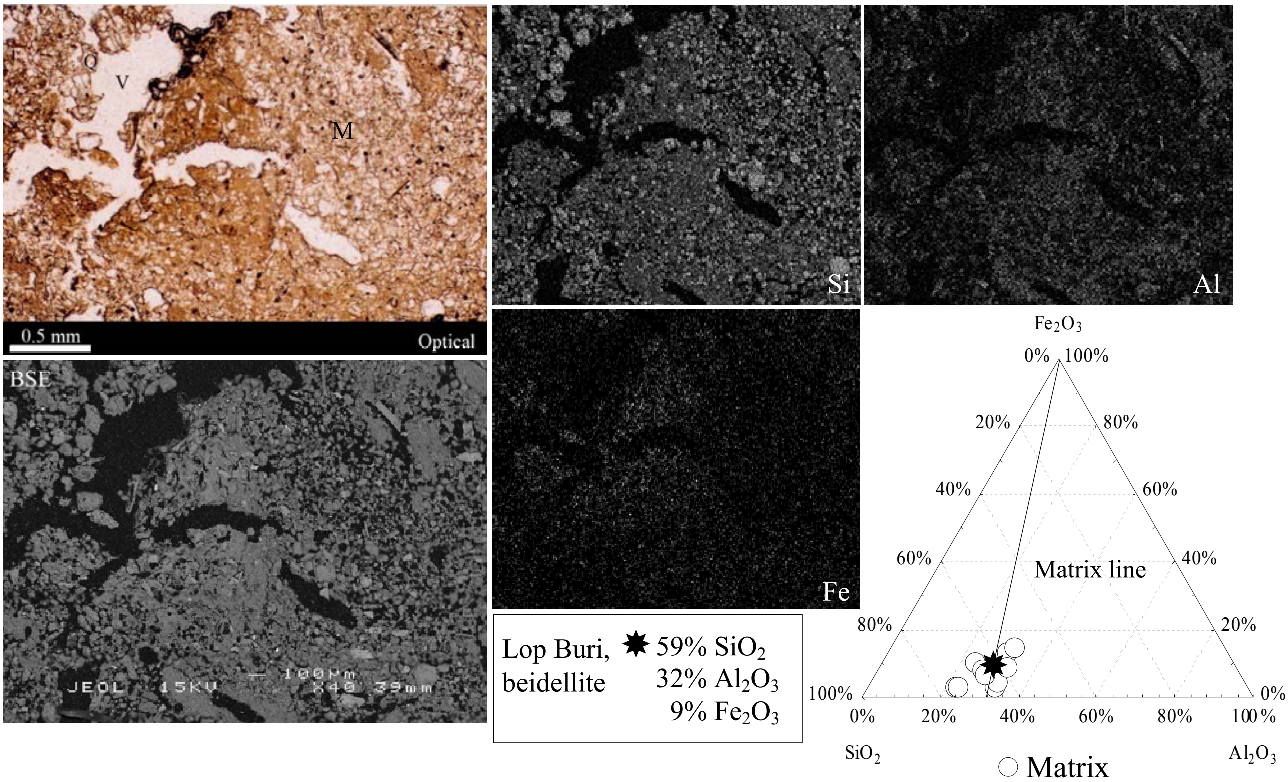

Figure 7 Optical and backscattered electron micrographs, element maps (Si, Al and Fe) and normalized composition triangular graph for the matrix of the Bg3 (115-150 cm) horizon of Bang Phae series. The matrix consists of much smectite and minor other clay minerals (Q = quartz, V = void, M = matrix). The composition of beidellite in the Lop Buri series falls on the matrix line in the triangular graph indicating that the matrix is beidellitic.

while montmorillonite clay fixed only 50% of the applied NH_4^+ (Bajwa, 1982). Soils dominated by beidellite will also fix K much more readily than montmorillonite soils (Badraoui et al., 1987). Under the alternate wetting and drying condition such as experienced by paddy soils, clays with more than 50 percent beidellite are major fixers of K fertilizers (Bajwa, 1981). As beidellite is the dominant smectite in the Thai paddy soils effective fertility management practices for paddy rice need to consider its properties in relation to the choice of forms and application practices for both nitrogen and potassium fertilizers.

Acknowledgments

Financial support was supplied by the Royal Golden Jubilee Ph.D. Program of The Thailand Research Fund. The authors are grateful to staff of School of Earth and Geographical Sciences and the Center for Microscopy and Microanalysis (CMM), The University of Western Australia for their kind assistance.

References

Badraoui, M. and P.R. Bloom. 1990. Iron-rich high charge beidellite in Vertisols and Mollisols of the high Chaouia region of Morocco. Soil Sci. Soc. Am. J. 54:267-274.

Badraoui, M., P.R. Bloom and R.H. Rust. 1987. Occurrence of high-charge beidellite in a Vertic Haplaquoll of Northwestern Minnesota. Soil Sci. Soc. Am. J. 51:813-818.

Bajwa, M.I. 1981. Soil clay mineralogy in relation to fertility management: effect of soil clay mineral composition on potassium fixation under conditions of upland rice soils. Nutrient Cycling in Agroeco-systems 2:193-197.

Bajwa, M.I. 1982. Soil clay mineralogies in relation to fertility management: effect of clay mineral types on ammonium fixation under conditions of wetland rice culture. Agron. J. 74:143-144.

Borchardt, G. 1989. Smectite, pp. 675-728. *In* J.B. Dixon and S.B. Weed, (eds.), Minerals in Soil Environments. SSSA, Madison, Wisconsin, USA.

Brown, G., A.C.D. Newman, J.H. Rayner and A.H. Weir. 1978. The structures and chemistry of soil clay minerals, pp. 29-178. *In* D.J. Greenland and M.H.B.

Hayes, (eds.), The Chemistry of Soil Constituents. John Wiley and Sons, London.

Bullock, P.N. and M.L. Thompson. 1985. Micromorphology of Alfisols, pp. 17-47. *In* L.A. Douglas and M.L. Thompson, (eds.), Soil Micromorphology and Soil Classification. SSSA Special Publication, Madison, USA.

Calvet, R. and R. Prost. 1971. Cation migration into empty octahedral sites and surface properties of clays. Clays Clay Minerals 19:175-186.

Chen, C., F.T. Turner and J.B. Dixon. 1989. Ammonium fixation by high-charge smectite in selected Texas Gulf Coast soils. Soil Sci. Soc. Am. J. 53:1035-1040.

Dabbakula, M., P. Moncharoen, K. Yoothong, P. Vijarnsorn, L. Moncharoen and H. Eswaran. 1992. Microvariability in Vertisols, pp. 60. *In* C.J. Chartes, (Ed.), Proc. 7th Working Meet, Soil Micromorphology. Townsville, Australia.

Ghosh, A.K., D. Sarkar, P. Bhattacharyya, U.K. Maurya and D.C. Nayak. 2006. Mineralogical study of some arsenic contaminated soils of West Bengal, India. Geoderma 136:300-309.

Greene-Kelly, R. 1955. Dehydration of the montmorillonite minerals. Mineralogical Magazine 30:604-615.

Hofmann, U. and R. Klemen. 1950. Verlust der Austauschfahigkeit von Lithiumionen and Bentonit durch Erhitzung. Zeitschrift für anorganische und allgemeine Chemie. 262:95-99.

Kunze, G.W. 1965. Pretreatment for mineralogical analysis, pp. 568-577. *In* C.A. Black, (ed.), Methods of Soil Analysis, Part I. Physical and Mineralogical Properties Including Statistics of Measurement and Sampling. Agronomy. Am. Soc. Agron., Madison, WI.

Lagaly, G. 1994. Layer charge determination by alkylammonium ions, pp. 1-46. In A.R. Mermut, (ed.), Layer Charge Characteristics of 2:1 Silicate Clay Minerals, CMS Workshop Lectures, Volume 6. The Clay Minerals Society, USA.

Laird, D.A., A.D. Scott and T.E. Fenton. 1989. Evaluation of the alkylammonium method of determining layer charge. Clays Clay Minerals 37:41-46.

Laird, D.A., T.E. Fenton and A.D. Scott. 1988. Layer charge of smectites in an Argialboll-Argiaquoll sequence. Soil Sci. Soc. Am. J. 52:463-467.

Malla, P.B. and L.A. Douglas. 1987. Problems in identification of montmorillonite and beidellite. Clays Clay Minerals 35:232-236.

Mehra, O.P. and M.L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays Clay Minerals 7: 317-327.

Mermut, A. and G. Lagaly. 2001. Baseline studies of the clay minerals society source clays: layer-charge determination and characteristics of those minerals containing 2:1 layers. Clays Clay Minerals 49:393-397.

National Soil Survey Center. 1996. Soil Survey Laboratory Methods Manual. Soil Survey Investigation No. 42, Version 3.0. United States Department of Agriculture, Natural Resource Conservation Service.

Rayment, G.E. and F.R. Higginson. 1992. Australian Laboratory Handbook of Soil and Water Chemical Methods. Inkata Press, Australia.

Ross, C.S. and S.B. Hendricks. 1945. Minerals of the montmorillonite group: their origin and relation to soils and clays. United States Geological Survey Professional Paper 205:23-79.

Senkayi, A.L., J.B. Dixon, L.R. Hossner and L.A. Kippenberger. 1985. Layer charge evaluation of expandable soil clays by an alkylammonium method. Soil Sci. Soc. Am. J. 49:1054-1060.

Singh, B. and S. Heffernan. 2002. Layer charge characterristics of smectites from Vertosols (Vertisols) of New South Wales. Aust. J. Soil Res. 40:1159-1170.

Sinsakul, S. 2000. Late Quaternary geology of the Lower Central Plain, Thailand. J. Asian Earth Sci. 18:415-426.

Soil Survey Staff. 2006. Keys to Soil Taxonomy. 10th Ed. United States Department of Agriculture, Natural Resources Conservation Service, USA.

Stul, M.S. and W.J. Mortier. 1974. The heterogeneity of the charge density in montmorillonites. Clays Clay Minerals 22:391-396.

Tardy, Y., G. Bocquier, H. Paquet and G. Millot. 1973. Formation of clay from granite and its distribution in relation to climate and topography. Geoderma 10:271-284.

Yoothong, K., L. Moncharoen, P. Vijarnsorn and H. Eswaran. 1997. Clay mineralogy of Thai soils. Appl. Clay Sci. 11:357-371.

Manuscript received 1 October 2007, accepted 5 December 2007