

## CHEMICAL AND CRYSTALLOGRAPHIC PROPERTIES OF KAOLIN FROM ULTISOLS IN THAILAND

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**Abstract**—Eighteen purified kaolin samples from Thai Ultisols were studied by X-ray diffraction, X-ray fluorescence, transmission electron microscopy and BET methods. Minor amounts of inhibited vermiculite, quartz and anatase were general contaminants of the kaolins which had an average chemical composition of 403 g kg<sup>-1</sup> Al<sub>2</sub>O<sub>3</sub>, 550 g kg<sup>-1</sup> SiO<sub>2</sub>, 25.3 g kg<sup>-1</sup> Fe<sub>2</sub>O<sub>3</sub>, 15.6 g kg<sup>-1</sup> TiO<sub>2</sub> and 4.65 g kg<sup>-1</sup> K<sub>2</sub>O on an ignited basis. Appreciable concentrations of Mn, Co, Ni, Cu, Zn, As and Pb were present and most of the Ni, Cu and Zn in the original clay fraction was retained in the deferrated kaolin concentrate. It was not possible to determine if these elements are present as structural ions in kaolin crystals.

The kaolins exhibited a variety of crystal morphologies ranging from sub-micron, euhedral, hexagonal plates to anhedral plates and tubes. Their specific surface areas ranged from 15.9 to 61.4 m<sup>2</sup>g<sup>-1</sup> (mean 44.9 m<sup>2</sup>g<sup>-1</sup>) and surface area increased with decrease in crystal size. The cation exchange capacity of the kaolins ranged from 7.2 to 23.4 cmol<sub>c</sub> kg<sup>-1</sup> and surface charge density from 0.16 to 0.99 C m<sup>-2</sup> but these values are sensitive to the presence of contaminants. Structural iron ranged from 12.4 to 44.8 g kg<sup>-1</sup> Fe<sub>2</sub>O<sub>3</sub> and there was an increase in structural defects towards the soil surface associated with an increase in the amount of structural iron.

**Key Words**—Crystal Shape, Iron Substitution, Kaolin, Tropical Soil, Ultisols.

### INTRODUCTION

Kaolin is formed from the decomposition of silicates under moderate to strong acid leaching conditions which remove the more soluble metal ions such as Ca, Mg and Na and some Si. The residual Al and Si recrystallizes to form kaolin (Brady and Ray, 2002) and some trace elements may also be retained by kaolin, *e.g.* Cr (Singh and Gilkes, 1992a). Many soils of the tropics have clay fractions dominated by minerals of the kaolin subgroup (referred to hereafter as kaolin) with various amounts of sesquioxides (Juo, 1980; McCrea *et al.*, 1990).

Many properties of these soils are related, directly or indirectly, to the dominant kaolin mineralogy of the soils. The chemical properties include low-pH and weak-pH buffering, Al toxicity, low available P and high P-fixation capacity, deficiencies of Na, Ca, Mg, K and micronutrients, and low cation exchange capacity (CEC) (Schwertmann and Herbillon, 1992). Soil physical processes, particularly those relating to aggregation and dispersion, may depend on the crystal properties of kaolin and some kaolinitic soils exhibit poor structure (Dixon, 1989). However, despite the dominance of kaolin in soils of the tropics, little is known of the extent to which the properties of kaolin vary in tropical soils and how this variation affects soil properties.

The structure of kaolin is simple but it has complex crystal and surface chemistries. The CEC of kaolin is partly pH dependent (Ferris and Jepson, 1975), and is due to both ionic substitution and pH dependent surface charge on several distinct surfaces (Bolland *et al.*, 1976). The increase in CEC with increasing structural defects in kaolin can be associated with a greater surface charge density in high-defect kaolin (Tari *et al.*, 1999). Kaolin in highly weathered soils often incorporates many defects and thus has a low degree of structural order ('crystallinity') together with a small crystal size and large specific surface area (Hughes and Brown, 1979; Cases *et al.*, 1986; Montes *et al.*, 2002). Consequently, kaolin may provide an appreciable proportion and probably most of the cation exchange capacity in the solum of kaolin-rich tropical soils. The 'crystallinity', chemical and morphological properties of kaolin are considered to be mostly consequences of pedo-environmental factors of soil formation, although distinct parent-mineral influences can be recognized in some instances, *e.g.* epitactic and topotactic replacement of mica by kaolin (Gilkes and Suddhiprakarn, 1979; Singh and Gilkes, 1992a). Several workers have suggested that the degree of defect structure in kaolin may be due to the extent of replacement of Al<sup>3+</sup> by Fe<sup>3+</sup> ions (Mestdagh *et al.*, 1980; Brindley *et al.*, 1986). Parent rock type may also play an important role, as low-defect kaolin often occurs in subsoils of well drained soils over granitic or siliceous sedimentary rocks (Jungerius and Levelt, 1964; Webster, 1965; De Alwis and Pluth, 1976). Pedoclimate

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may affect the nature of soil kaolins, *e.g.* structural order decreases as the length of the dry season decreases (Hughes and Brown, 1979).

Very little is known of the crystal chemical properties of kaolin in Thai soils despite kaolin often being the dominant clay mineral. Recently Hart *et al.* (2003) investigated kaolin in purified samples from 10 Thai soils including Alfisols, Ultisols and Oxisols on parent materials as diverse as granite, basalt, sandstone, shale, limestone and mixed colluvium. They observed that very small, high-defect and Fe-substituted kaolin was the dominant form of this mineral but no systematic association of kaolin properties and soil type/parent rock could be identified due to the small number and great diversity of the soil samples. This paper is concerned only with the properties of kaolin in a single

soil order (Ultisols) on a range of parent materials. Ultisols are soils that have an argillic or kandic horizon and a subsurface horizon enriched with illuvial clay, with low base saturation (Soil Survey Staff, 1999). They occupy 229,930 km<sup>2</sup> of Thailand and are major agricultural soils within the Kingdom, yet little is known of their clay minerals apart from the dominance of kaolin (Yoothong *et al.*, 1997).

## MATERIALS AND METHODS

### *Sampling sites and soil preparation*

The soils were chosen on the basis of national soil mapping information to be fully representative of Thai Ultisols (Soil Survey Division Staff, 1993; Kheoruenromne, 1999). Topsoil and subsoil materials

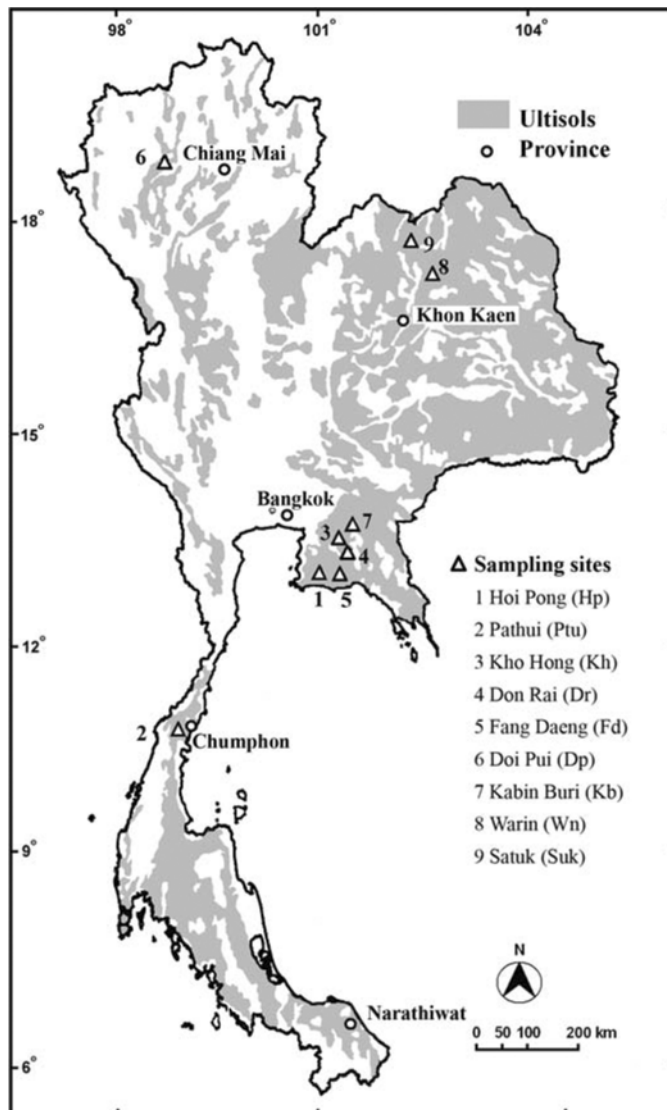


Figure 1. The distribution of Ultisols in Thailand. The numbers indicate sampling sites of soil series for the present study (Kheoruenromne and Kesawapitak, 1989).

were sampled at nine sites from physiographically distinct regions of Thailand (Figure 1). A brief description of site properties is provided in Table 1 and all soil profiles conformed to the Soil Taxonomy requirements for this soil order (Soil Survey Staff, 2003). At each site, samples were taken with a hand auger from depth intervals of 0–50 cm for the topsoil and 50–100 cm for the subsoil. All samples were air dried and passed through a 2 mm sieve prior to analysis.

#### Laboratory analysis

Particle-size distribution was determined by the pipette method (Gee and Bauder, 1986). Soil pH was determined using a soil:solution ratio of 1:1 with H<sub>2</sub>O (Thomas, 1996) and CEC by using 0.01 M silver thiourea solution at pH 4.7 (Rayment and Higginson, 1992). Extracted solutions were measured by atomic absorption spectrophotometry (Perkin Elmer AAnalyst 300). Minor elements (Mn, Co, Ni, Cu, Zn, As and Pb) in soil and kaolin concentrates were determined using an inductively coupled plasma mass spectrometer (Perkin Elmer ICP-MS), after digestion in concentrated HCl and HNO<sub>3</sub>.

Clay separation involved treating the soil with 30% hydrogen peroxide to remove organic matter (Gee and Bauder, 1986) prior to dispersion by shaking overnight in deionized water with 0.1 M NaOH. The sand fraction was retained on a 0.053 mm sieve, and the silt and clay fractions were separated by sedimentation. Free Fe oxides were removed from the clay fraction by repeated treatment with dithionite citrate bicarbonate (DCB) (Mehra and Jackson, 1960). The deferrated clay samples consisted mostly of kaolin and will henceforth be referred to as the soil kaolins.

#### X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) patterns of the soil kaolins were obtained using CuK $\alpha$  radiation with a Philips PW3020 diffractometer equipped with a graphite diffracted beam monochromator. The XRD patterns were recorded using a step size of 0.02°2 $\theta$  and a scan speed of 1.20°2 $\theta$  min<sup>-1</sup>. Patterns of the basally oriented clay fraction suctioned onto a ceramic plate were obtained after various pretreatments to enable the identification of clay mineral species (Brown and Brindley, 1980). The pretreatments consisted of variously saturating the clay

Table 1. Soil series, sampling sites, parent materials and some soil properties of Thai Ultisols.

Soil series	Parent material	Horizon	pH (H <sub>2</sub> O)	CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	Total Fe (g kg <sup>-1</sup> )	Sand (g kg <sup>-1</sup> )	Silt (g kg <sup>-1</sup> )	Clay (g kg <sup>-1</sup> )
Typic Kandiuults, fine*								
Hoi Pong (Hp)	Colluvium and alluvium from granite and quartzite	topsoil	4.1	1.09	8.4	756	164	80
		subsoil	4.5	1.50	12.0	604	316	80
Pathui (Ptu)	Sandstone, limestone	topsoil	6.8	2.89	16.7	718	198	84
		subsoil	5.0	3.10	40.0	500	152	348
Typic Kandiuult, coarse-loamy								
Kho Hong (Kh)	Alluvium	topsoil	6.0	1.18	5.0	787	161	52
		subsoil	5.1	1.42	6.9	728	140	132
Typic Kandiuult, fine-loamy								
Don Rai (Dr)	Old alluvium on middle terraces	topsoil	4.5	1.26	9.2	669	243	88
		subsoil	4.8	2.29	10.4	552	244	204
Rhodic Kandiuult, fine-loamy								
Fang Daeng (Fd)	Granite, quartzite and phyllite	topsoil	5.9	1.55	18.5	680	200	120
		subsoil	5.1	1.17	27.7	534	346	120
Typic Palehumult, fine								
Doi Pui (Dp)	Residual soils derived from granite, gneiss or schist	topsoil	5.5	5.53	95.4	119	641	240
		subsoil	5.5	5.97	107	103	547	440
Typic Plinthudult, clayey-skeletal								
Kabin Buri (Kb)	Residual soils derived from shale	topsoil	5.4	3.44	79.9	360	260	380
		subsoil	5.2	3.58	104	200	190	610
Typic Kandiuult, fine-loamy								
Warin (Wn)	Old alluvium (middle and high terrace)	topsoil	5.3	0.44	3.9	480	480	40
		subsoil	5.1	1.98	12.1	670	130	200
Typic Paleustult, fine-loamy								
Satuk (Suk)	Old alluvium (middle and high terrace)	topsoil	5.9	1.28	3.1	850	94	56
		subsoil	4.7	3.18	13.7	648	76	276
Mean			5.2	2.38	3.2	553	250	197
SD			0.6	1.49	3.6	218	145	154

\*Taxonomic class (Soil Survey Staff, 1999).

with Mg, Mg and glycerol, K and saturating the clay with K followed by heating at 550°C for at least 2 h. Random powder patterns were obtained from 3 to 70°2 $\theta$  to identify minerals other than clay minerals and to determine the degree of ‘crystallinity’ of the kaolins as expressed by the HB index (Hughes and Brown, 1979). The XRD patterns were interpreted with the aid of XPAS analytical software (Singh and Gilkes, 1992b), which enables calculation of the coherently scattering domain size (CSD) using the Scherrer equation (Klug and Alexander, 1954). Oriented clay XRD patterns were also used to determine the asymmetry index (AI) and to provide an accurate measure of the basal spacing for the 001 and 002 reflections of kaolin (Singh and Gilkes, 1992c).

#### *Transmission electron microscopy (TEM)*

A very dilute suspension of the <2  $\mu\text{m}$  size fraction of the kaolin samples was dispersed by ultrasonic treatment. A drop of suspension was deposited on a carbon coated grid and dried at room temperature. The samples were studied on a Philips 430 transmission electron microscope operated at 300 kV which was equipped with an X-ray energy dispersive analytical system (EDS).

#### *X-ray fluorescence (XRF) analysis*

Major and minor elements in the soil and kaolin samples were determined using a Philips PW1400 XRF spectrometer fitted with a Rh tube. Samples were fused with lithium meta/tetraborate flux at 1050°C (Norrish and Chappell, 1977). The elemental composition was calculated using a matrix correction procedure and validated by comparison with analyses of certified reference materials.

#### *Specific surface area (SSA)*

The surface area of the kaolin samples was determined by the BET method. Samples were degassed overnight at 373°K and measurements made using a Micromeritics Gemini III 2375 surface area analyzer by N<sub>2</sub> adsorption (Aylmore *et al.*, 1970). Surface charge densities (CD) were derived from CEC and BET surface area.

## RESULTS AND DISCUSSION

#### *General properties of Thai Ultisols*

The properties of the investigated soils are given in Table 1 including a set of abbreviations for the sampling sites. The texture ranged from loamy sand to clay with most soils being sandy in texture. In some soil profiles there is a substantial increase in clay content in subsurface horizons, indicating that some of the Ultisols are duplex (texture contrast) soils (Stace *et al.*, 1965).

The soils are all acidic, with pH values in water that mostly range from extremely to moderately acid

(4.1–6.0). The Pt<sub>u</sub> series has a near neutral pH in the topsoil that is possibly due to addition of colluvial limestone. The CEC of these soils is low to very low which is consistent with the mostly low organic matter content (results not given), low pH, sandy texture and kaolin-dominated clay.

#### *Properties of the soil kaolins*

*Clay mineralogy.* From XRD powder patterns the approximate abundance of kaolin in the samples was calculated based on the relative peak areas of the 001 kaolin reflection for soil kaolin and reference Georgia kaolin (MP#5). The approximate amounts of the impurities quartz, vermiculite and anatase were also calculated from the XRD pattern, by comparing peak areas from powder patterns with those of patterns of standard quartz (101 reflection), vermiculite (001) and anatase (101). It was assumed that errors due to differences in X-ray absorption coefficients would be small because all samples and standards had similar X-ray absorption coefficients (Klug and Alexander, 1954). The properties of the kaolins are given in Table 2.

The 001 spacing of the kaolins range from 0.716 to 0.725 nm with a mean value of 0.719 nm. The range of values of the 002 spacing was narrower than for the 001 reflection with a mean value of 0.357 nm. The mean basal spacings are slightly higher than those for the Georgia kaolin (Table 2). The spacing of the 001 reflection increases with decreasing CSD due to displacement of the 001 reflection towards smaller 2 $\theta$  as CSD decreases (Trunz, 1976) (Figure 2a). There is no corresponding relationship for  $d_{002}$ .

The asymmetry of the 001 reflection was greater than for the 002 reflection. Perfectly symmetrical reflections would have an asymmetry index of zero whereas values for the 001 reflections for the soil kaolins, excluding the Suk, Dr and Dp topsoils are greater than zero. This is a consequence of both small crystal size and the rapid increase of the angular Lorentz-Polarization factor towards small 2 $\theta$  values in the region of  $d_{001}$  (MacEwan and Wilson, 1980). Some asymmetry could also be due to interstratification of kaolin with a small proportion of other clay minerals such as smectite, vermiculite or illite but the extent of such interstratification must be small as there is little or no displacement of  $d_{001}$  to higher spacings and no sensitivity to glycerol solvation or K saturation and heating. The kaolins show a very large range of asymmetry values but there is no significant difference between the mean value of the AI for soil kaolins and that for the reference kaolin for both the 001 and 002 reflections. The asymmetry index for the 002 reflection is near zero as angular variations in both Lorentz-Polarization and structure factor are small at this 2 $\theta$  angle (MacEwan and Wilson, 1980).

The CSD size calculated from the 001 reflections of the soil kaolins (Table 2) range from 9.6 to 29.2 nm, with a mean value of 15.4 nm which is similar to values

Table 2. Properties of the soil kaolins.

Soil	Kaolin (%)	CEC* (cmol <sub>c</sub> kg <sup>-1</sup> )	SSA* (m <sup>2</sup> g <sup>-1</sup> )	CD* (C m <sup>-2</sup> )	HB* index	<i>d</i> value (nm)		Asymmetry index		CSD* (nm)	
						001	002	001	002	001	060
Hp-top*	95.7	16.2	36.5	0.44	6	0.716	0.357	0.33	0.14	19.6	21.4
Hp-sub*	94.4	9.6	37.1	0.26	7	0.719	0.358	0.33	0.33	20.1	19.9
Ptu-top	91.7	17.5	44.0	0.40	7	0.718	0.358	0.33	0.00	29.2	18.5
Ptu-sub	91.4	10.1	50.9	0.20	5	0.716	0.357	0.33	0.00	24.8	19.2
Kh-top	99.1	11.8	59.8	0.20	6	0.717	0.356	0.14	0.00	11.4	17.2
Kh-sub	99.3	12.5	61.4	0.21	6	0.724	0.357	0.17	0.00	11.3	15.3
Dr-top	99.6	20.7	53.1	0.38	5	0.720	0.356	0.00	0.33	14.2	19.2
Dr-sub	97.9	19.3	50.8	0.39	4	0.718	0.356	0.18	0.00	12.8	18.7
Fd-top	95.4	15.7	15.9	0.99	4	0.717	0.357	0.20	0.20	18.6	19.7
Fd-sub	93.7	15.7	22.7	0.69	4	0.717	0.357	0.27	0.00	19.5	21.6
Dp-top	97.7	23.4	45.7	0.57	5	0.719	0.357	0.00	0.11	10.0	10.4
Dp-sub	93.3	20.1	42.9	0.47	5	0.724	0.357	0.11	0.11	9.6	18.5
Kb-top	96.1	18.9	40.8	0.46	9	0.720	0.357	0.43	0.14	16.1	14.7
Kb-sub	94.8	9.3	39.5	0.24	8	0.717	0.356	0.25	0.14	13.9	21.0
Wn-top	91.2	7.2	44.4	0.16	4	0.723	0.357	0.41	0.14	13.0	14.7
Wn-sub	91.1	10.1	48.9	0.21	5	0.721	0.357	0.25	0.14	11.3	19.9
Suk-top	95.1	20.1	59.8	0.34	6	0.721	0.357	0.00	0.00	10.7	15.6
Suk-sub	92.1	15.1	54.0	0.28	6	0.725	0.358	0.11	0.11	10.4	15.9
Mean	95.0	15.2	44.9	0.38	6	0.719	0.357	0.21	0.11	15.4	17.8
SD	2.9	4.7	12.1	0.21	1	0.003	0.001	0.14	0.11	5.5	2.9
Georgia kaolin (MP#5)	–	2.3	18.0	0.18	28.2	0.715	0.356	0.26	0.03	37.5	31.5

\*CEC: cation exchange capacity; SSA: specific surface area; CD: surface charge density; HB: Hughes and Brown (HB) index; CSD: coherently scattering domain size; top: topsoil; sub: subsoil. (Sampling site abbreviations as in Figure 1 and Table 1.)

for soil kaolins from other locations (Table 3). There is an inverse exponential relationship between CSD<sub>001</sub> and Fe<sub>2</sub>O<sub>3</sub> concentration (Figure 2b) as was also observed by Hart *et al.* (2003). The CSD values for the 060 reflection (mean 17.8 nm) are larger than for the 001 reflection which is consistent with the platy morphology of kaolin crystals. Values of CSD determined for the kaolin 060 reflection must be treated with caution as several kaolin reflections occur at ~0.15 nm and may coalesce. These reflections are also split into K $\alpha_1$  and K $\alpha_2$  components and the relative intensities of these reflections also depend on the extent of three-dimensional order as several of the reflections are prism ( $h, k, l \neq 0$ )

reflections that are highly sensitive to defects. Consequently the measured width at half height (WHH<sub>060</sub>) is often too large so that the calculated CSD<sub>060</sub> is much smaller than the true plate dimension of crystals which can be observed by TEM (Hart *et al.*, 2003).

The HB 'crystallinity' index for soil kaolins ranged from 4 to 9 with a mean value of 6 which is indicative of kaolin with a high-defect structure (Hughes and Brown, 1979). The values are similar to those found by other authors (Table 3). Commonly, the degree of defect structure in kaolin is related to the amount of structural Fe. For these soil kaolins the range of values of both the

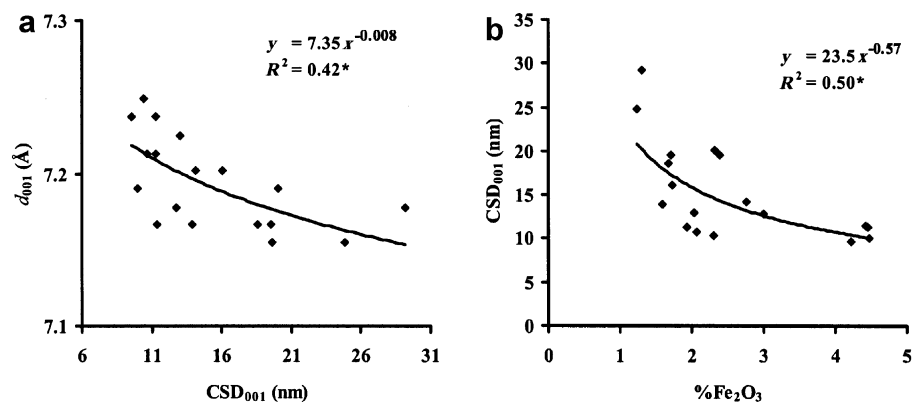


Figure 2. Bivariate relationships for soil kaolins (a)  $d_{001}$  vs. CSD<sub>001</sub> and (b) CSD<sub>001</sub> vs. % Fe<sub>2</sub>O<sub>3</sub>.

Table 3. Comparative data for soil kaolins.

Location	CSD size (nm)		HB index		SSA (m <sup>2</sup> g <sup>-1</sup> )		d <sub>001</sub> value (nm)		l dimension (nm)		Fe <sub>2</sub> O <sub>3</sub> (g kg <sup>-1</sup> )		CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	
	001 mean	060 mean	range	mean	range	mean	range	mean	range	range	mean	range	range	mean
Thailand <sup>1</sup>	19.3	17.9	4.1–11.4	6.7	35.3–80.6	47.4	0.721	20–750	5.4–31.2	19.6	4.4–17.4	8.3		
W. Australia <sup>2</sup>	22.9	34.5	3.1–10.7	5.6	33.6–67.8	50.8	0.721	60–120	21.6–33.4	25.7	2.9–7.6	5.0		
Indonesia <sup>3</sup>	10.8	11.9	4.5–7.1	5.6	59–88*	72.8	0.721	20–70	15.2–37.2	25.4	5.2–12.9	9.4		
Nigeria <sup>4</sup>	—	—	4.3–13.7	8.0	—	—	—	—	—	—	—	—		
Brazilian Ultisols <sup>5</sup>	—	—	10.1–18.5	14.1	44–66	45.8	0.719	57–80	—	19.6	—	—		

<sup>1</sup>Hart *et al.* (2002, 2003); <sup>2</sup>Singh and Gilkes (1992c); Hart *et al.* (2002, 2003); <sup>3</sup>Hart *et al.* (2002, 2003); <sup>4</sup>Hughes and Brown (1979); <sup>5</sup>Melo *et al.* (2001); mean kaolin content of 85.4%

HB index and structural Fe (12.4 to 44.8 g kg<sup>-1</sup>Fe<sub>2</sub>O<sub>3</sub>) are too small to exhibit a clear relationship between these parameters.

*Specific surface area.* The specific surface area of the kaolins is large, ranging between 15.9 and 61.4 m<sup>2</sup>g<sup>-1</sup> with a mean value of 44.9 m<sup>2</sup>g<sup>-1</sup> (Table 2). These kaolins have greater surface areas than most standard kaolins (5 to 28 m<sup>2</sup>g<sup>-1</sup>) (Hart *et al.*, 2002) but are similar to soil kaolins from Brazil, Western Australia, and Thailand. Values of SSA are mostly smaller than for Indonesian soil kaolins on volcanic tuff (Table 3). Values of the surface charge density (CD) calculated from CEC and SSA range from 0.16 to 0.99 C m<sup>-2</sup> in comparison to 0.18 C m<sup>-2</sup> for the Georgia kaolin (Table 2). The greater values of CD for soil kaolins are likely to reflect the presence of small amounts of impurities (*e.g.* inhibited vermiculite) which contribute to high CEC values but it is likely that the surface charge density of soil kaolins is not constant.

*Morphology of kaolin crystals.* The size and shape of the kaolin crystals in representative samples were determined by TEM, and typical micrographs are shown in Figure 3 which clearly demonstrate the small size and diverse morphologies of kaolin crystals in these Ultisols. These observations were quantified by determining the morphology of ~200 crystals for each sample (Table 4). Most of the kaolins consist of mixtures of particles with very different morphologies including large euhedral crystals (common in Hp and Fd series), small subhedral–euhedral crystals (Ptu series) and small anhedral platy crystals (Kh, Dr, Kb, Wn and Suk series); a few samples also contained tubular halloysite crystals (to a maximum of 34% in the Dp subsoil). All samples contained some rounded platy particles with no euhedral (*hk*) faces (9–80% of crystals). The percentage of platy kaolin crystals with six euhedral (*hk*) faces varied from 0 to 47%. The dimensions of the kaolin crystals varied greatly both within and between samples. The longest axis (henceforth called the l dimension) and the shortest axis (the w dimension) were measured for about 200 platy crystals in each sample (Table 4). The ratio l/w is defined as the axial ratio (AR) and a regular hexagonal crystal would have an axial ratio of 1.12. The mean values of the AR for the kaolins (1.15–1.34) were similar to the value for Georgia kaolin (1.17) (Singh and Gilkes, 1992c) and indicate that substantially elongated crystals (*i.e.* laths) are rare. The mean l dimension of the platy crystals of the soil kaolins varies from 100 to 218 nm; a range similar to published data (Table 3). The median size of platy crystals of three Georgia reference kaolins determined by Hart *et al.* (2003) using the same procedure as followed here are 180, 280 and 370 nm. The size of soil kaolin crystals in these Ultisols is inversely related to their specific surface area (Figure 4). Kaolin in the Kh series topsoil had the smallest mean crystal size (100 × 83 nm) which is

Table 4. Distribution of various crystal forms and dimensions determined by TEM for the soil kaolins.

Soil series	% of platy crystals with euhedral faces										% Total platy	% Tubes (length, diameter, nm)	Crystal length (l) (nm)			Crystal width (w) (nm)			Axial ratio (l/w)
	0 face	1 face	2 faces	3 faces	4 faces	5 faces	6 faces	Max	Min	Mean			Max	Min	Mean				
Hp-top	9	6	17	19	7	4	29	90	10 (112, 29)	392	29	133	373	29	110	1.20			
Hp-sub	13	9	24	23	9	2	19	99	1 (250, 50)	475	24	135	350	24	114	1.19			
Ptu-top	24	9	9	21	12	6	18	97	3 (96, 41)	373	24	110	353	24	89	1.23			
Ptu-sub	24	9	9	21	12	6	18	97	3 (101, 44)	373	24	110	353	24	89	1.23			
Kh-top	27	1	2	5	16	11	39	100	0	275	30	100	235	30	83	1.20			
Kh-sub	26	5	9	14	4	5	39	100	0	471	39	141	392	20	114	1.24			
Dr-top	26	14	16	16	9	5	15	100	0	324	28	103	269	19	78	1.34			
Dr-sub	28	11	15	21	10	1	16	100	0	293	24	110	220	24	90	1.22			
Fd-top	18	17	21	21	7	4	14	100	0	667	48	218	524	48	180	1.24			
Fd-sub	11	16	20	28	7	3	14	100	0	451	59	162	373	39	134	1.21			
Dp-top	10	5	7	17	19	13	31	100	0	317	37	110	256	24	94	1.18			
Dp-sub	12	3	7	12	12	7	12	66	34 (125, 40)	275	29	123	235	29	100	1.23			
Kb-top	80	10	10	0	0	0	0	100	0	183	61	107	152	55	87	1.22			
Kb-sub	36	36	18	0	9	0	0	100	0	183	69	119	171	56	92	1.32			
Wn-top	40	10	20	10	10	0	10	100	0	244	73	124	232	49	98	1.34			
Wn-sub	20	40	20	10	0	0	10	100	0	130	74	103	130	60	90	1.15			
Suk-top	20	5	6	18	6	7	39	100	0	294	37	114	235	37	93	1.23			
Suk-sub	21	2	3	4	6	20	47	100	0	294	29	115	255	29	96	1.20			

top: topsoil; sub: subsoil. (Sampling site abbreviations as in Figure 1 and Table 1.)

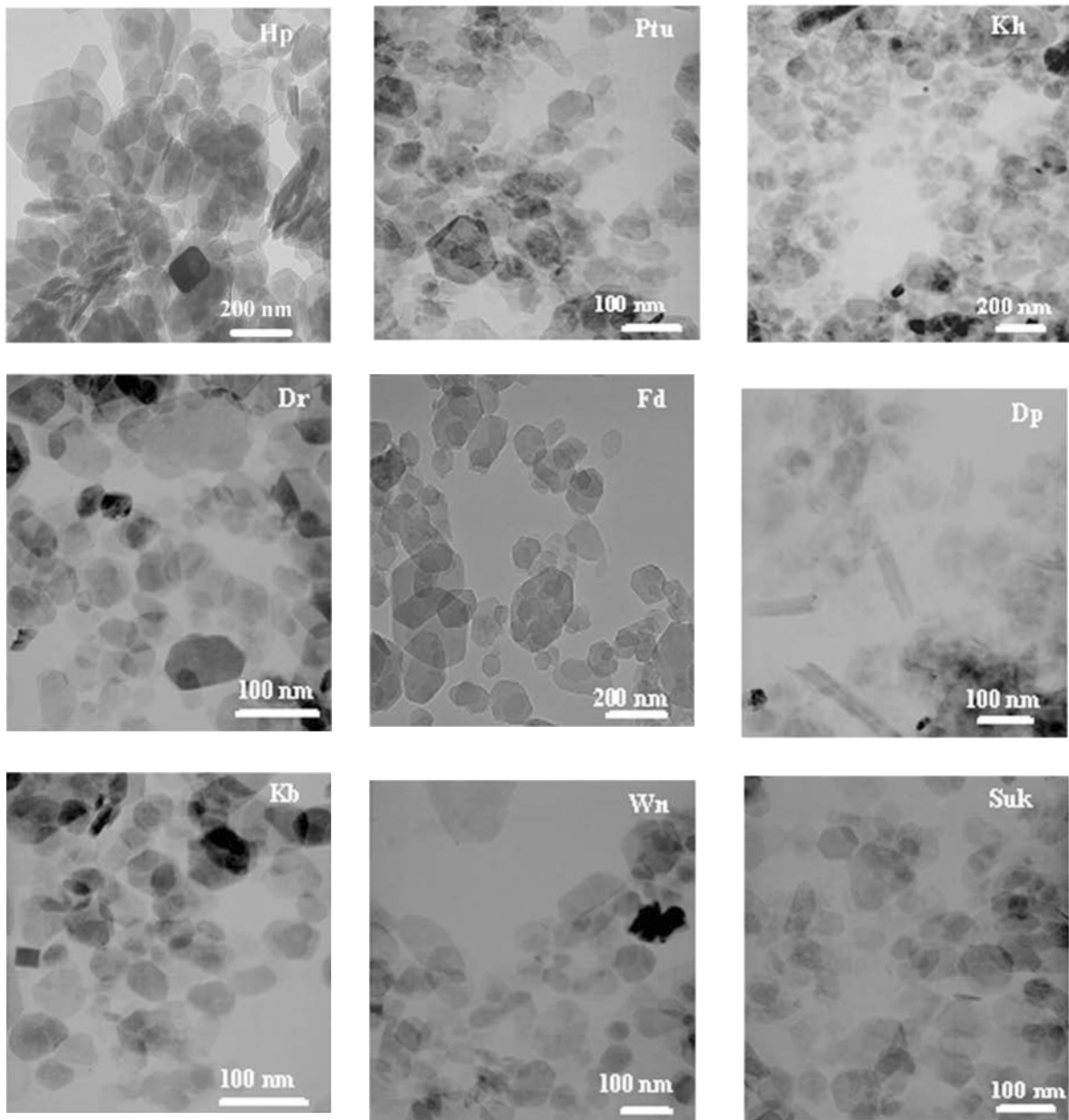


Figure 3. TEM images of some of the soil kaolins (sampling site abbreviations as in Figure 1 and Table 1).

consistent with its large SSA ( $59.8 \text{ m}^2 \text{ g}^{-1}$ ). Exchange capacity is expected to increase with decreasing crystal size (Suraj *et al.*, 1997) but there is no systematic statistical relationship between these two attributes for these soil kaolins ( $R^2 = 0.05$ ).

**Chemical composition.** The major element concentrations of the kaolins are given in Table 5. The mean concentrations of  $403 \text{ g kg}^{-1} \text{ Al}_2\text{O}_3$  and  $550 \text{ g kg}^{-1} \text{ SiO}_2$  differ substantially from those of ideal kaolin which contains  $459 \text{ g kg}^{-1} \text{ Al}_2\text{O}_3$  and  $541 \text{ g kg}^{-1} \text{ SiO}_2$ . The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio for soil kaolins ranges from 1.20 to

1.76 with a mean of 1.38 which is greater than the values of 1.17 for ideal kaolin and 1.20 for the reference Georgia kaolin, due mostly to the presence of quartz and to some Al in soil kaolin being replaced by Fe. Minor inhibited vermiculite of unknown composition but probably containing interlayer Al-OH polymers was present in most samples and may have affected the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, though, as pointed out by Hart *et al.* (2003), the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of inhibited dioctahedral vermiculite with aluminous interlayers is similar to that of kaolin. The deferrated clay from the two horizons in the profile Dp contained no quartz or vermiculite and the



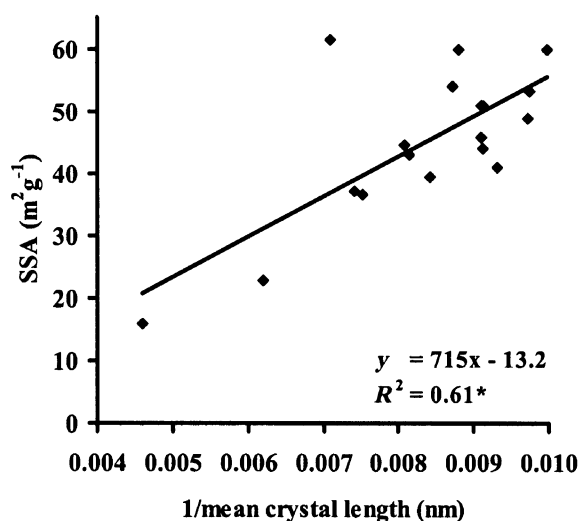


Figure 4. Bivariate relationship of SSA vs. the reciprocal of mean crystal length determined by electron microscopy for soil kaolins.

topsoil and subsoil have  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 1.32 and 1.38, respectively, much greater than the value for ideal kaolin; consequently, it is likely that these kaolins contain structural Fe. Small amounts of anatase were present in all samples as indicated by a distinct XRD reflection at 0.352 nm and anatase crystals were

observed by TEM. The kaolin clay concentrate contains small amounts of K (mean  $\text{K}_2\text{O} = 4.65 \text{ g kg}^{-1}$ ) but there are no mica or feldspar reflections in the XRD patterns. For these  $\text{K}_2\text{O}$  concentrations, each sample would have  $<5\%$  illite as a discrete impurity or as interstratified layers in kaolin (Ma and Eggleton, 1999). A consistent difference between the soil kaolins and the standard kaolin (Georgia kaolin, MP#5) is the much larger amount of Fe in the former with a mean value of  $25.3 \text{ g kg}^{-1}$  compared to  $6.9 \text{ g kg}^{-1}$   $\text{Fe}_2\text{O}_3$  for the Georgia kaolin. The  $\text{Fe}_2\text{O}_3$  content of the soil kaolins (Table 5) ranges from 12.4 to  $44.8 \text{ g kg}^{-1}$ . The values are similar to those for kaolins from other soils (Table 3), from Nigeria,  $18.6 \text{ g kg}^{-1}$ ; Rwanda,  $23.2 \text{ g kg}^{-1}$  and Cuba,  $15.2 \text{ g kg}^{-1}$  (Mestdagh *et al.*, 1980). The published data indicate that increasing Fe concentration in kaolins is commonly related to reduced crystal size ( $\text{CSD}_{001}$ ) as is also indicated by the present data (Figure 2b).

**Cation exchange capacity.** The CEC of the kaolins ranged from 7.2 to  $23.4 \text{ cmol}_c \text{ kg}^{-1}$  (Table 2). These values are similar to those for other Thai and Indonesian soil kaolins and are approximately twice those for Western Australian soil kaolins (Table 3). Koppi and Skjemstad (1981) reported values of 9.3 to  $30.5 \text{ cmol}_c \text{ kg}^{-1}$  for Queensland soil kaolins and Ma and Eggleton (1999)

Table 5. The major element composition of kaolin concentrates from nine Thai Ultisols (ignited, exchangeable cation free basis).

Soil series	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{TiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{K}_2\text{O}$	$\text{MgO}$	$\text{P}_2\text{O}_5$	$\text{SiO}_2/\text{Al}_2\text{O}_3$
	(----- g kg <sup>-1</sup> -----)								
Hp-top	422	535	15.8	23.8	0.24	3.11	0.00	0.46	1.27
Hp-sub	431	530	13.2	23.3	0.00	2.61	0.00	0.32	1.23
Ptu-top	368	596	18.1	13.1	0.12	3.85	0.00	0.68	1.62
Ptu-sub	404	566	13.6	12.4	0.58	2.88	0.00	0.00	1.40
Kh-top	374	563	11.5	44.2	1.86	4.89	0.12	0.31	1.51
Kh-sub	377	559	10.8	44.6	3.85	4.43	0.00	0.14	1.48
Dr-top	370	576	22.4	27.6	0.41	4.19	0.00	0.24	1.56
Dr-sub	392	557	16.2	30.0	0.13	4.28	0.00	0.23	1.42
Fd-top	421	540	20.9	16.8	0.14	0.82	0.00	0.31	1.28
Fd-sub	434	531	17.2	17.0	0.13	0.52	0.00	0.25	1.22
Dp-top	407	536	7.1	44.8	0.12	3.29	2.07	0.00	1.32
Dp-sub	396	548	6.9	42.1	0.12	5.47	1.07	0.00	1.38
Kb-top	429	529	17.3	17.4	0.24	5.59	0.48	0.44	1.23
Kb-sub	438	525	15.6	15.9	0.35	4.90	0.00	0.07	1.20
Wn-top	427	520	21.1	20.3	5.05	6.16	0.49	0.46	1.22
Wn-sub	415	538	19.5	19.3	0.47	5.82	0.70	0.58	1.30
Suk-top	342	602	19.5	20.7	2.63	10.5	2.03	0.66	1.76
Suk-sub	404	546	14.4	23.0	0.00	10.3	2.00	0.36	1.35
Mean	403	550	15.6	25.3	0.91	4.65	0.50	0.31	1.38
Ideal kaolin	459	541	—	—	—	—	—	—	1.17
Georgia kaolin (MP#5)	442	532	16.4	6.9	1.30	1.20	0.10	0.80	1.20
Thai soils	355	452	19.9	19.6	0.40	2.80	6.00	—	1.27
W. Australian soils	—	—	—	25.7	—	—	—	—	0.96
Indonesian soils	—	—	—	25.4	—	—	—	—	0.98
Brazilian Ultisols	360	417	3.2	19.6	—	0.70	0.80	—	1.16

top: topsoil; sub: subsoil. (Sampling site abbreviations as in Figure 1 and Table 1.)

Table 6. Minor element concentrations in soil and kaolin concentrates of Thai Ultisols and percentage retention (ret.) of minor elements by the kaolin concentrate.

Soil series	Mn		Co		Ni		Cu		Zn		As		Pb		
	soil (mg kg <sup>-1</sup> )	kao ret. %	soil (mg kg <sup>-1</sup> )	kao ret. %	soil (mg kg <sup>-1</sup> )	kao ret. %	soil (mg kg <sup>-1</sup> )	kao ret. %	soil (mg kg <sup>-1</sup> )	kao ret. %	soil (mg kg <sup>-1</sup> )	kao ret. %	soil (mg kg <sup>-1</sup> )	kao ret. %	
Hp-top	56	43	0.5	1.2	19	3	54	127	3	17	46	2	2	8	45
Hp-sub	20	28	0.5	1.5	24	5	38	63	3	16	46	2	1	6	27
Ptu-top	371	35	4.3	4.4	9	7	39	45	6	16	22	28	31	9	15
Ptu-sub	146	38	2.7	3.9	50	14	36	93	9	20	82	58	36	22	16
Kh-top	117	86	1.3	5.5	22	1	37	149	2	28	60	0.7	0.4	3	71
Kh-sub	16	57	0.4	2.7	88	3	47	238	3	30	136	0.8	0.1	1	27
Dr-top	432	49	1.7	4.2	22	3	21	59	4	13	28	2.7	0.8	2	31
Dr-sub	90	41	1.1	3.1	58	5	23	96	5	10	47	1.1	0.5	9	17
Fd-top	608	80	1.3	2.5	23	6	37	76	8	42	61	2.8	2.4	10	32
Fd-sub	607	93	1.9	2.2	14	10	57	69	6	17	34	4.6	2.4	6	24
Dp-top	566	32	16.6	5.3	8	49	84	41	42	36	21	16	6	9	24
Dp-sub	436	28	10.6	4.2	18	48	63	58	45	27	26	14	4	12	12
Kb-top	886	88	11.3	4.7	16	15	39	100	27	33	46	13	3	8	17
Kb-sub	1134	52	7.4	4.6	38	17	34	125	34	37	66	11	3	18	124
Wn-top	56	92	0.3	3.9	52	1	53	164	2	19	42	0.5	0.1	1	38
Wn-sub	29	29	0.4	1.3	63	4	29	151	3	6	34	1.5	1.1	14	36
Suk-top	78	75	0.3	4.7	88	2	39	128	1	33	141	0.4	2.8	39	7
Suk-sub	20	38	0.7	4.6	182	7	34	137	4	37	236	1.2	3.2	75	13
Mean	315	55	3.5	3.6	44	11	42	107	11	24	65	9	6	14	26
SD	336	24	4.8	1.4	43	14	15	51	15	10	55	14	10	18	16

top: topsoil; sub: subsoil. (Sampling site abbreviations as in Figure 1 and Table 1.)

values of 16 to 34 cmol<sub>c</sub> kg<sup>-1</sup> for thin (15 nm) high-defect kaolins. Kaolins in the Wn series soil had the lowest CEC, possibly because of the relatively large amount of quartz in these samples, although the Hp and Pt soil clays have similar amounts of quartz. The CEC of kaolin is considered to be primarily due to pH-dependent charge arising from broken bonds along the edges of crystals with some contribution from basal surfaces (Yong *et al.*, 1992). The abundance of this charge should therefore increase as the size of kaolin crystals decrease (Ma and Eggleton, 1999). However, no systematic relationship exists for the present data ( $R^2 = 0.03$ ). The presence of small amounts of inhibited vermiculite could have increased the CEC of some of the clays (Yong *et al.*, 1992), e.g. kaolin from the Kb topsoil contains the most inhibited vermiculite (~5%) and has a high CEC.

*Minor element concentrations.* The concentrations of minor elements in the clay fractions of the Ultisols were determined before (on whole clay fraction) and after removal of free Fe oxides by DCB treatment (kaolin concentrate) (Table 6). The concentrations of minor elements have been expressed as the percentage of minor elements retained in deferrated clay after DCB treatment. Concentrations of Mn, Ni, Cu, Zn and Pb in the clay are significant and the average percentage retained by the deferrated clay is >50% for Ni, Cu and Zn. Most Mn, Co, Pb and As (>75%) was removed from the clay fraction by DCB treatment so these elements were probably mostly associated with the Fe and Mn oxides dissolved by DCB solution. The concentrations of minor elements in the soil kaolins could be present in minor accessory minerals including anatase or even in sulfides precipitated during the DCB treatment. However, these data are consistent with soil kaolin containing appreciable proportions of the Ni, Cu and Zn and some of the Co and Pb present in these highly weathered soils.

## CONCLUSIONS

The deferrated clay fraction of Thai Ultisols consists mostly of kaolin with lesser inhibited vermiculite, illite and anatase and so resembles other tropical soils including those Thai soils investigated by Hart *et al.* (2003). The large surface area and chemical reactivity of soil kaolin, which results from the small size and defect structure will be important for sorption reactions in these soils which are often sandy and contain little organic matter to adsorb plant nutrients and other ions. Consequently, kaolin may provide a substantial part of the capacity of the soil profile to retain anions and cations. This research has also identified a possible role for kaolin as a host for minor elements as structural ions which has significant implications for soil fertility and geochemical exploration. Although not investigated in this research, the physical properties of Ultisols may also

reflect their kaolin-dominated clay mineralogy. There is a need to identify the properties of kaolin in all the major soils of tropical regions where this mineral is dominant as it has the potential to play an important role in determining soil chemical and physical properties.

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