Characteristics of soil kaolin on various parent materials in Thailand

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Abstract
The nature of kaolin in Thai soils developed on sandstone, shale/limestone, granite and basalt has been investigated. Mineralogical, chemical and morphological properties of kaolins were determined using X-ray diffraction, transmission electron microscopy, and chemical analysis. Clay concentrates from Thai soils consist of >70% kaolin group minerals with minor amounts of inhibited vermiculite, illite, interstratified clay mineral, gibbsite, quartz and anatase. Soil kaolins exhibit a wide range of crystal sizes, (0.02-0.83 μm, median 0.02 μm) with a variety of morphologies including euhedral platy crystals, laths and tubes. Euhedral hexagonal platy crystals predominate in soils derived from sandstone, lath-shaped crystals in soils derived from basalt and anhedral crystals in soils on shale/limestone.
There are considerable variations in other soil kaolin properties; d(001) ranged from 0.7121-0.7275 nm, coherently scattering domain size (CSD001) 10.3-43.7 nm, Hughes and Brown crystallinity index (HB) 4.1-11.7, specific surface area 34-76 m^2/g and cation exchange capacity 4.2-13.9 cmol/kg. Kaolin in soils on sandstone has the highest value of HB index and largest crystal size, in contrast to kaolin in soils on basalt which has the lowest values of crystallinity index and crystal size. The CEC of soil kaolin (median 9.4 cmol/kg) did not differ systematically between parent materials but was much higher than values for reference mineral kaolin (3.2 cmol/kg). The median value of structural Fe_2O_3 in soil kaolin is 1.84% being highest for soils developed on basalt (median 2.67%) and lowest for soils on shale/limestone (1.39).

Key Words
XRD, TEM, clay mineral, tropical soil

Introduction
Highly weathered soils of the tropics often consist mostly of kaolin group minerals, oxides of Fe, Al and Ti and resistant minerals such as quartz and zircon inherited from the parent material. Chemical properties of these soils reflect this mineralogy as they have low CEC, high zero point of charge, high P sorption and low nutrient reserves (Schwertmann & Herbillon 1992). Kaolin is the most common clay mineral in soils that cover about 47% of the total area in Thailand. Throughout tropical regions plant yield on these soils is highly dependent on fertilization and liming (Yoothong *et al.* 1997). With the growing demand for food, optimum utilization of these common tropical soils will be an important factor in the development of most tropical countries. Consequently the influences of soil mineralogy on agricultural production and land management need to be identified.
Sixty three representative soil samples which developed on sandstone, shale/limestone, granite or basalt, were chosen after screening by XRD for the dominance of kaolin group minerals henceforth the deferrated clay is referred to as '*kaolin*'. These soils are representative of the soils that are extensively used for agriculture in Thailand and elsewhere in the tropics. The sites are nearly flat to undulating with slopes of 2-8%. The soils are classified as belonging to the kaolinitic mineralogical classes of Ultisols, Oxisols and Alfisols.

Methods
Prior to analysis the soil samples were air-dried, crushed using a ceramic mortar and pestle and then passed through a 2 mm stainless steel sieve. The purified soil kaolins were analysed as followings:
1. Mineral composition of the kaolins was determined for random powders and basally oriented clay on ceramic plates using X-ray diffraction with CuKα radiation and a Philips PW3020 diffractometer equipped with a diffracted beam graphite monochromator.
2. Accurate XRD measurement of basal spacings was made using both quartz and octacosane as internal standards (Brindly & Wan 1974).
3. Coherently scattering domain size (CSD) was calculated from the width at half height of the XRD patterns of kaolins via the Scherrer equation (Klug & Alexander 1974).

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4. A random powder XRD pattern was used to determine the HB index (Hughes & Brown 1979).
5. The size and shape of kaolin crystals were obtained from electron micrographs using a JEOL 3000F Field Emission Gun TEM.
6. Cation exchange capacity was measured using 0.01M silver thiourea solution at pH 4.7 to displace the exchangeable cations (Rayment & Higginson 1992).
7. Specific surface area was measured using the N_2-BET method (Aylmore *et al.* 1970) with a Micrometrics Gemini III 2375 surface area analyser.

Results and discussion

General soil characteristics

Field soil texture of the soils ranged from sandy loam to clay, some soils contained minor amounts of particles larger than 2 mm. Particle size analysis confirmed the field observations, the soils developed on sandstone and granite generally contained much sand whereas those on shale/limestone and basalt mostly have more than 50% clay. Values of soil pH in water ranged from 3.8 to 7.7 (mean 5.0). Some of the surface soils were near neutral with a pH in water of 6.0-7.7, this may be due to applications of lime that is used in agriculture in these areas.

Mineralogy of the deferrated clay fraction

Kaolin is the major clay mineral (70-90%) present in the deferrated clay fraction of 63 soil samples. Small or trace amounts of inhibited vermiculite, illite, interstratified clay minerals, quartz, gibbsite and anatase occur in most kaolin samples with quartz, gibbsite and/or illite being moderate constituents of 11 samples. Clays from soils developed on basalt contain less inhibited vermiculite and illite compared to soils developed from other parent materials. A relatively high amount of quartz is present for the soils developed on sandstone. Gibbsite is present only in some soils derived from granite, sandstone and shale/limestone which possibly indicating that they are more highly weathered. Anatase is relatively abundant in most of the soils derived from basalt which may be due to the relative abundance of Ti in mafic rocks and it is concentrated considerably during weathering (Anand & Gilkes 1987).

XRD Measurements of soil kaolin

Basal spacing

The 001 spacing (d001) of Thai soil kaolins ranges from 0.7121 to 0.7293 nm (mean 0.7209 nm) which is slightly higher than for standard Georgia kaolin (0.7180 nm). Values of d001 for the soil kaolins developed on basalt (mean 0.7233 nm) were higher than those on granite (0.7208 nm), shale/limestone (0.7204 nm) and sandstone (0.7197 nm), respectively. Linear correlation coefficients (r) for relationships between properties of purified soil kaolins are shown in Table 1. There is a highly significant positive linear relationship between 001 spacing of kaolin and structural Fe concentration (r = 0.50***) so the higher basal spacing of kaolin may be partly due to isomorphous substitution of Fe affecting unit cell dimensions (Brindley & Brown 1980). However the 001 spacing of these kaolins increases with decreasing crystal size (r = -0.62*** for CSD001 and r = -0.49** for CSD060).

Table 1. Linear correlation coefficients (*r*) for relationships between properties of Thai soil kaolins.

Properties		1	2	3	4	5	6
1	d 001	1.00					
2	CSD 001	**-0.62*** **					
3	CSD 060	**-0.49*** **	**0.47*** **				
4	HB	-0.22	**0.43*** **	0.22			
5	Structural Fe	**0.50*** **	**-0.59*** **	**-0.51*** **	**-0.27***		
6	CEC	**0.30***	**-0.31***	**-0.38** **	**-0.52*** **	**0.33***	
7	SSA	**0.40** **	**-0.53*** **	**-0.52*** **	**-0.50*** **	**0.46*** **	**0.79*** **

Number of samples for properties 1-5 (n=63), 6 (n=35), 7 (n=49) which does not include data that would be affected by the presence of moderate amounts of impurities). *** Significant at P = .001, ** P = 0.01 and * P = 0.05
d = d spacing, CSD = crystal size dimension, HB = Hughes & Brown index, CEC = cation exchange capacity, and SSA = specific surface area

Coherently Scattering Domain size (CSD)

Values of the CSD of these kaolins, calculated from 001 and 060 reflections, range from 9.3 to 43.7 nm (mean 17.2 nm) and 10.7 to 25.2 nm (19.1 nm), respectively. The kaolin in soils developed on shale/limestone had the largest CSD001 (mean 20.5 nm) followed by sandstone (18.5 nm), granite (15.6 nm) and basalt (12.6 nm), respectively. CSD for both 001 and 060 reflections decreased with increasing structural Fe (r = -0.59*** for CSD001, and r = -0.51*** for CSD060) (Table 1).

Crystallinity Index

Values of the Hughes and Brown index (HB) for Thai soil kaolins range from 4.1 to 11.7 (mean 6.4). The Thai soil kaolins developed on basalt that has the lowest value of HB index (range 4.7-7.6, mean 5.6) whereas the highest values were for soils on shale/limestone (4.7-11.4, 7.0) followed by sandstone (4.1-11.7, 6.6) and granite (5.4-7.5, 6.3). There is a very weak inverse linear relationship between HB index and Fe content for the kaolins (r = -0.27*) (Table 1).

Transmission electron microscopy investigation of single crystals of soil kaolin

Sizes of platy kaolin crystals expressed as the longest dimension (width), ranged from 0.02-0.84 μm. Some Thai kaolins contain large crystals (>0.4 μm) similar to those in the standard Georgia kaolin (0.4-0.8 μm) but for those soil kaolins, the median size is smaller than 0.2 μm. The largest crystal sizes are for the soil kaolins derived from sandstone (0.023-0.829 μm (median 0.108 μm) followed by those for shale/limestone 0.017-0.835 μm (0.098 μm), granite 0.040-0.364 μm (0.099 μm) and basalt 0.015-0.657 μm (0.106 μm), respectively. Thai kaolins consist mostly of platy crystals (ranging from euhedral and anhedral), some are lath-shaped and there are rare tubular crystals as shown in Figure 1.

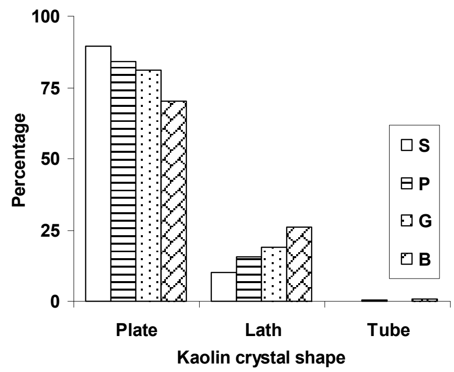

Figure 1. Median values of crystal shape measured from electron micrographs for kaolin in soils on various parent materials. (S = sandstone, P = shale/limestone, G = granite, B = basalt).

Specific Surface Area (SSA)

Values of SSA for the soil kaolins range from 34 to 76 m^2/g (median 50 m^2/g) which are similar to values for kaolins from Western Australian soils (44-56 m^2/g) (Singh & Gilkes 1992) and Indonesian red soils (59-88 m^2/g) (Siradz 2000). The Thai soil kaolins developed on basalt had a high SSA (47-76 m^2/g, mean 62 m^2/g) compared to those for the soils developed on shale/limestone (34-66 m^2/g, 48 m^2/g), granite (39-55 m^2/g, 47 m^2/g), and sandstone (4-60 m^2/g, 45 m^2/g), respectively.

Cation Exchange Capacity (CEC)

CEC of these kaolins ranges from 4.2 to 17.4 cmol/kg (mean 9.2 cmol/kg) whereas the Thai soil kaolins developed on basalt had the highest values of CEC (5.9-17.4 cmol/kg, mean 10.5 cmol/kg) followed by those on sandstone (4.2-12.4 cmol/kg, 9.3 cmol/kg), shale/limestone (4.4-14.3 cmol/kg, 8.9 cmol/kg) and granite (4.9-11.0 cmol/kg, 8.2 cmol/kg), respectively. The CEC of the Thai kaolins had a wider range of values compared to those for Western Australian soils (2.9-8.2 cmol/kg) (Singh & Gilkes 1992) and Indonesian red soils (5.2-12.9 cmol/kg) (Siradz 2000). There is a strong positive linear relationship between CEC and surface area for these Thai soil kaolins (R^2 = +0.62) as shown in Figure 2.

Conclusion

Kaolin group of clay mineral dominated in the deferrated clay fractions with minor amounts of inhibited vermiculite, illite, interstratified clay mineral, quartz, gibbsite and anatase, only those developed on basalt contained less inhibited vermiculite and illite whereas quartz is present highly in the soils on sandstone.

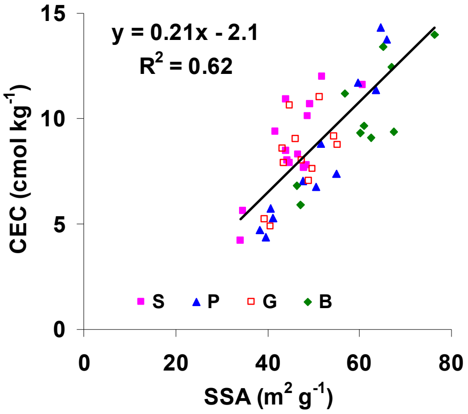

Figure 2. Relationships between CEC and SSA for Thai soil kaolins of soils developed on various parent materials (n=49). (S = Sandstone, P = Shale/limestone, G = Granite, B = Basalt).

Anatase is relatively abundant in most of the samples particularly in those derived from basalt. The larger crystal sizes for soil kaolins, the larger of crystal order exists especially for the soil kaolin of soils developed on sandstone. In contrast to the soil kaolins derived from basalt which have small crystal size, low crystallinity, high SSA, CEC and structural Fe concentration, this may be because of Fe substitution for Al in kaolin crystal. Higher Fe content, higher variation for kaolin properties can be observed for Thai soil kaolins. Electron micrographs show that these Thai soil kaolins consist of a wide variation of crystal sizes and shapes. High content of platy kaolin crystals are mostly found in kaolins of soils developed on sandstone, inversely to lath-shape crystals in those on basalt. Lath-shaped crystal mostly found for the soil kaolins derived from basalt.

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