MATERIALS AND METHODS

1. Sampling Sites

The soils were chosen on the basis of national soil mapping information to be fully representative of Thai Alfisols and Ultisols (Soil Survey Staff, 1993; Kheoruenromne, 1999). Soil series, parent materials and their taxonomic classes are summarized in Appendix Tables 1 and 2. Within Thailand there are diverse sedimentary, metamorphic and igneous rocks ranging in age from Precambrian to Recent (Department of Mineral Resources, 1987). Approximately one third of Thailand area is covered by unconsolidated Quaternary sediments consisting of silt, clay, sand and gravel within stream channels, flood plains and terraces together with residual lateritic materials (Department of Mineral Resource, 1987). The sampling sites related to rock and sediment regions is shown in Figure 1. One hundred and seven sites of Alfisols (32 sites) and Ultisols (75 sites) were selected as shown in Figure 2. A brief description of site parent materials and soil classification is shown in Appendix Tables 1 and 2 (Kheoruenromne, 1999; Soil Survey and Classification Division, 1999a, b, c and d; Soil Survey Staff, 1999; Soil Survey Staff, 2003).

2. Sample Preparation

Two groups of genetic horizons, topsoil and subsoil, were taken by a hand auger from depths ranging from 0-50 cm for topsoil and 50-100 cm for subsoil. Soil samples were air-dried, crushed using a ceramic mortar and pestle and then passed through a 2 mm stainless steel sieve. The resultant less than 2 mm air-dried samples were used for all laboratory analysis. The clods samples were used for physical analysis.

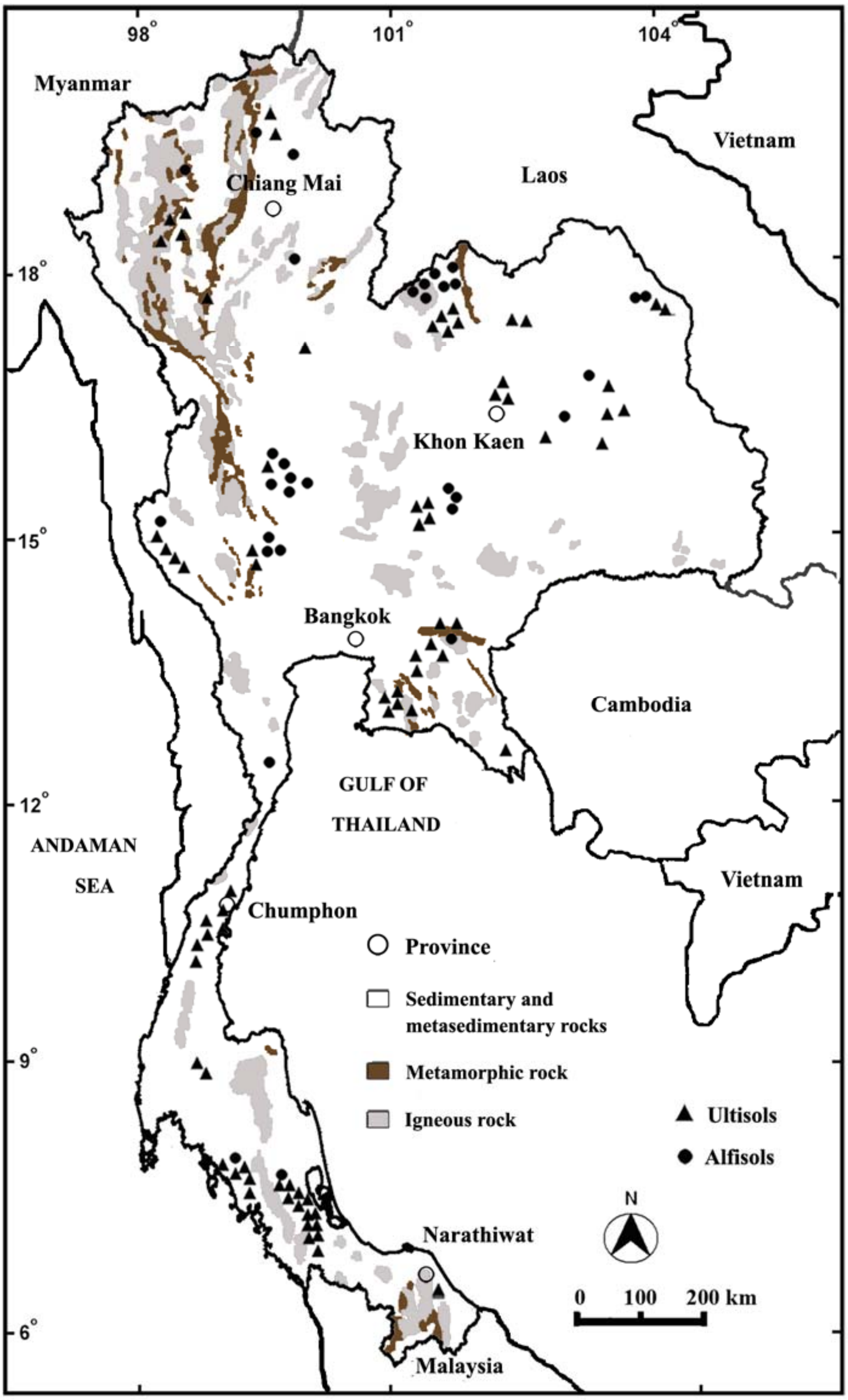

Figure 1 Geological map of Thailand showing the three main geological and soil sampling sites.

Source: Department of Mineral Resources (1987)

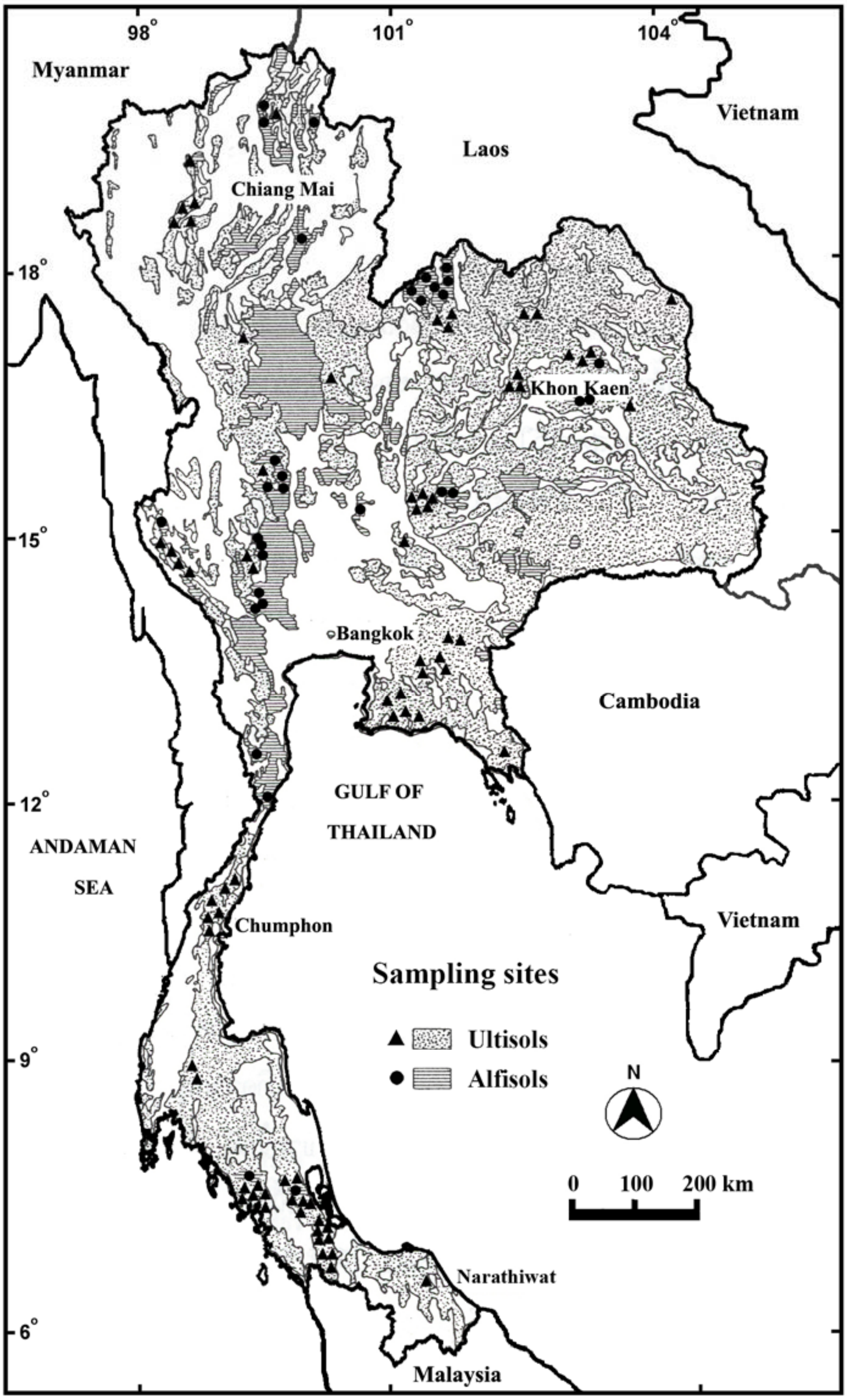

Figure 2 Distribution of Ultisols and Alfisols in Thailand and soil sampling locations.
Source: Kheoruenromne and Kesawapitak (1989)

3. Laboratory Analysis

3.1 Analysis of bulk soil samples

3.1.1 Physical analysis

Particle size analysis

A mass of 10 g air dried soil sample was pretreated with 30% hydrogen peroxide to remove organic matter. For dispersion of soil, the suspension was placed in a milk shake container and 10 milliliter of 5% sodium hexametaphosphate, a dispersing agent, was added. The volume of the contents was made up to about 200 milliliter with deionized water. The contents were stirred for 15 minutes on a milk shake mixer and then sieved through a 300-mesh (0.047 mm) sieve into a one litre cylinder and volume was made up to 1000 milliliter with deionized water. The sand grains that remained in the sieve were dried at 105°C for overnight and were weighed. The suspension in the cylinder was stirred well with an agitator in an up-down motion for 30 s. The pipette method was used as a direct sampling procedure. Twenty milliliter of suspension was pipetted out from a depth of 10 cm for clay at appropriate times based on Stoke's Law (i.e. at 28°C for <0.002 mm sized fraction sampling time at 10 cm depth the time is 6.5 hrs). Suspensions were dried at 105°C and weighed (Gee and Bauder, 1986). The amounts of sand, silt and clay were calculated. The percentage of clay (<2 μm), silt (0.002 to 0.05 mm) and sand (0.05 to <2 mm) were plotted on ternary plots, and soils were classified using soil textural triangle classes (Soil Survey Staff, 1993).

Bulk density (BD)

Bulk density is the mass of dry solid per unit bulk volume of the soil (Brady and Ray, 2002). The undisturbed clod sample (size of about 40 g oven-dry weight) was oven dried at 105 °C. The clod and attached thread were weighed in air, the clod was then dipped into paraffin wax. The paraffin wax-coated clod was weighed in air and in water. The difference in these weights provides the weight of water that has the same volume as the bulk volume of the paraffin wax-coated clod.

The density of water and paraffin, weights of oven-dry clod, in air, clod plus paraffin coating in air and in water were used to calculate the bulk density which is reported in units of Mg m^{-3} (Blake and Hartge, 1986).

3.1.2 Chemical analysis

Soil reaction (pH)

Soil pH was determined in water and 1N KCl at a solid to solution ratio of 1:1. The contents were stirred with a glass rod for 30 minutes before measuring the pH using a standardized pH meter (Thomas, 1996; National Soil Survey Centre, 1996).

Organic matter

The organic matter content of soil was indirectly estimated through multiplication of the organic carbon concentration by 1.724. The organic carbon was determined according to the Walkley and Black wet oxidation procedure (Walkley and Black, 1934). This involved wet combustion of organic carbon with a mixture of potassium dichromate and sulfuric acid. After reaction the residual dichromate was titrated against ferrous sulphate (Nelson and Sommers, 1996). A weight of 0.5 g of soil (<0.5 mm) was placed in a 250 milliliter Erlenmeyer flask. Five milliliter of 1N $K_2Cr_2O_7$ was added and the flask was swirled gently to disperse the soil into suspension. Then 10 milliliter of concentrated H_2SO_4 was added to the flask, swirled gently until the soil and reagents were mixed. The solution took on a greenish cast and then changed to dark green. The flask was allowed to stand with occasional swirling for 30 minutes. Then 30 milliliter of deionized water was added to the flask, swirled gently then 3-4 drops of o-phenolphthalein indicator were added and the solution was titrated with 1N $FeSO_4$ until the colour changed to a red end point.

Total nitrogen

Total nitrogen was determined by the Kjeldahl method (Jackson, 1965). This procedure which is generally employed for determination of total nitrogen involves two steps: (i) The soil is digested in concentrated H_2SO_4 with a catalyst mixture to raise the boiling temperature and to promote the conversion from organic-N to ammonium-N and (ii) determination of NH_4^+-N in the digest. A weight of 1 g of soil (<2mm) was placed in a digestion tube. A sample was dissolved in 5 milliliter digestion mixture (potassium sulfate-catalyst mixture) at 300°C for 2 hrs. After completion of digestion, allow the aqua regia to cool. The volume was made to 20 milliliter before filtering it with filter paper into acid washed vials. Ten milliliter of the filtrate was pipetted into a distillation flask and 5 milliliter L of 10 N NaOH added. The distillate was collected in saturated H_3BO_3; and then titrated with dilute H_2SO_4 to pH 5 until the colour of the solution changed from green to pink.

Available phosphorus

Available phosphorus was determined by the Bray II method (Bray and Kurtz, 1945). Three grams of soil were placed into a 250 milliliter erlenmeyer flask and 30 milliliter of extracting solution added. The container was shaken 40 seconds, and the contents filtered through Whatman no. 42 paper. Ten milliliter of the filtrate was pipetted into a 25 milliliter volumetric flask and made up to 25 milliliter. After 15 minutes, the solution was measured species photometrically at 882 millimicrons wavelength. A standard curve for 0, 0.2, 0.4, 0.6, 0.8, and 1.0 mg P kg^{-1} was prepared.

Extractable bases

The bases (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were extracted by 0.01 M silver thiourea solution at pH 4.7. The extracting solution was analysed using an atomic absorption spectrophotometer (AAS) (Rayment and Higginson, 1992).

Extractable acidity

Extractable acidity was determined as the acidity released from the soil by barium chloride-triethanolamine solution buffer ($BaCl_2$-TEA) at pH 8.2 (Thomas, 1982). It includes all acidity generated by replacement of the hydrogen and aluminum ions from permanent and pH-dependent exchange sites. A soil sample of 5 g was placed in an Erlenmeyer flask and 15 milliliter of buffer solution at 8.2 (0.5N

$BaCl_2 \cdot H_2O$ and 0.2 N triethanolamine) were added. The contents were stirred and allowed to equilibrate for 30 minutes before filtering using the Buchner funnel procedure. The contents were given 3 additional washings with 20 milliliter buffer solution and 5 washings with 20 milliliter of the replacing solution (0.5N $BaCl_2$ H_2O and 0.4 milliliter of buffer solution in 1 liter). The volume of the extracts was made up to 100 milliliter and 5 drops of mixed indicator (bromocresol green and methyl red in 95% ethyl alcohol) were added. The extract was titrated with 0.17N HCl. The acid was added drop by drop until the colour changed from green to an end point of purplish red colour. The amount of HCl consumed was used to calculate the extractable acidity expressed as cmol H^+ kg^{-1}.

Cation exchange capacity (CEC)

Cation exchange capacity were measured using 0.01 M silver thiourea solution at pH 4.7 displacing the exchangeable cations (Rayment and Higginson, 1992). A weight 2 g of soil was placed into acid washed vials and 20 milliliter of 0.01 Ag $(TU)^+$ were added. The contents were shaken for 16 hrs. Centrifuged and pipetted 1 milliliter of soil extraction into 100 milliliter volumetric flask, added 10 milliliter of 1% La-chloride and 5 milliliter of 5% HNO_3 and made up to 100 milliliter with deionised water. The concentration of Ag in solution was determined by using atomic absorption spectrophotometry (AAS).

X-ray fluorescence (XRF) analysis for bulk soil samples

Total major and minor elements in soil samples were determined using a Philips PW 1400 XRF spectrometer fitted with a rhodium tube. Soil samples were dried overnight at 105°C to release absorbed water and then 0.700 gram of sample was fused with 7.000 gram of lithium meta/tetraborate flux at 1,050°C in a platinum crucible. The molten mixture was cast into a disc in a platinum-gold alloy mold. The elemental composition was determined by XRF and compared with analyses of certified reference materials used to check on the accuracy of the results. The minimal spectrometer drift was corrected by regular measurement of an external monitor (Norrish and Hutton, 1964; Wilklins, 1983; Karathanasis and Hajek, 1996).

Inductively Coupled Plasma-Mass Spectrometry

Trace element content was determined using inductively coupled plasma-mass spectrometry (ICP-MS). For aqua regia digestion, 0.2 gram of sample was dissolved in 2 milliliter of conc. HNO_3 and 6 milliliter of conc. HCl at 95-100^{o}C for 4 hrs. The volume was made to 20 milliliter before filtering it with No. 42 Whatman filter paper into acid washed vials. The 0.5 milliliter aliquots of the digestions were made up to the 10 milliliter mark with a 10 µg kg^{-1} rhodium internal standard (1:20 dilution ratio) acidified solution (1%HNO_3) with <2% total dissolved solids (TDS), using an automated dilutor. An analysis was carried out on a Perkin Elmer Elan 6000 ICP-MS for Li, Be, P, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Mo, Ag, Cd, Cs, Pb, Bi and U. Blanks and standard samples were analysed at the beginning and the end of each sample run. Additional blanks and 200 µg kg^{-1} multi-element standard were included after every 25 samples and analysed as for the samples (Soltanpour *et al.*, 1996; Lynch, 1999).

3.1.3 Mineralogical analysis

X-Ray Diffraction (XRD) for clay fraction

The clay fraction for mineralogical analysis was separated by using a sedimentation procedure. Pre-treatments of the 2 mm soil to dissolve $CaCO_3$ by using 1M sodium acetate at pH 5.0, and to remove organic carbon by using H_2O_2 (Gee and Bauder, 1986). A weight of 40 grams or an appropriate amount of soil to obtain ~ 10 gram of clay fraction was used, 40 milliliter of 0.1M NaOH solution was added to the soil in a milk shake container with deionised water to make up the volume in the container to approximately 250 milliliter. The contents were stirred for 15 minutes on a milk shake mixer. The contents were transferred into the litre measuring cylinder. The suspension was stirred well with an agitator, 20 milliliter suspension was pipette at approximate times based on Stokes Law (i.e. at 20°C for <0.02 mm and < 0.002 mm size fractions sampling time at a 10 cm depth was 4 minutes 48 seconds and 8 hours, respectively).

The clay size suspension in the measuring cylinder was transferred into a plastic cylinder. The suspension containing the clay size fraction was removed by several cycles of dispersion and then flocculated by adding excess solid NaCl, the supernatant was decanted. The concentrated flocculated clay was transferred into presoaked 10 cm diameter cellulose dialysis tubing and placed in a bucket containing ~50 L of deionised water to remove excess salts. The deionised water in the bucket was changed frequently until the conductivity of water after equilibrium was equal to that of deionised water. About 50 milliliter suspension of this Na-saturated clay fraction was transferred from the analysis tube into plastic bottles for use in the preparation of oriented specimens for clay mineral analysis by XRD. The remaining suspension was dried in an oven at 40 °C and this clay fraction was used for detailed investigation of the properties of clay minerals (Singh, 1991).

The XRD patterns of the clay fraction were obtained using CuKα radiation with a Philips PW 3020 diffractometer equipped with a graphite diffracted beam monochromator. Basally oriented clay samples were prepared on ceramic plates by a suction method and XRD pattern from 3-30° 2θ were obtained after standard pretreatments (Mg saturated, Mg saturated and glycerol solvated, K saturated and K saturated and heated at 550 °C) to aid identification (Brown and Brindley, 1980). Accurate measurements of d-values were made using quartz as an internal standard (Brindley and Wan, 1974). The random powder patterns were obtained from 3-70° 2θ to identify minerals other than clay mineral.

3.1.4 Statistical analysis

Factor analysis, a widely used multivariate statistical method, was employed to interpret data. This technique reveals the correlation structure of the geochemical variables allowing the identification of affinity groups of elements and samples. The statistical analyses of the geochemical data were performed using the Statistica Program (Version 6.1) (Shine *et al*., 1995; Evans *et al.,* 1996; Bakac and Kumra, 2001; Kumru and Bakaç, 2003).

3.2 Analysis of kaolin samples

3.2.1 Kaolin concentration

Nine soil series from different regions of the country had kaolins as the sole clay mineral which enabled the kaolin to be concentrated. The location of these soils are as follows: Doi Pui from the North, Warin and Satuk from the Northeast, Hoi Pong, Kho Hong, Don Rai, Fang Daeng and Kabin Buri from Ssoutheast Coast and Pathio from the Peninsular region. Soil samples were air-dried, crushed using a ceramic mortar and pestle and then passed through a 2 mm stainless steel sieve.

Organic carbon and $CaCO_3$ were removed from the soils using H_2O_2 and sodium acetate (buffer to pH 5.0 with acetic acid), respectively (Gee and Bauder, 1986), the < 2 mm fraction was dispersed by shaking with 0.01 M NaOH and collecting the clay fraction (< 2 μm) by sedimentation. Free iron oxides were removed from the clay fraction by repeatedly treating with dithionite citrate bicarbonate following the procedure of Mehra and Jackson (1960). These purified kaolin samples were used to study various properties of kaolin using a variety of techniques.

3.2.2 Physical analyses

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 were made using a Micromeritics Gemini III 2375 surface area analyzer by N_2 adsorption (Aylmore *et al.,* 1970). Surface charge densities (CD) were derived from CEC and BET SSA values.

3.2.3 Chemical analyses

Cation exchange capacity (CEC)

Cation exchange capacity and extractable bases were measured using 0.01 M silver thiourea solution at pH 4.7 to displace the exchangeable cations (Rayment and Higginson, 1992). A weight 0.5 gram of kaolin was placed into acid washed vials and 15 milliliter of 0.01 Ag $(TU)^+$were added. The contents were shaken for 16 hrs, centrifuged and 1 milliliter of soil extract pipetteed into a 100 milliliter volumetric flask, 10 milliliter of 1% La-cholride and 5 milliliter of 5% HNO_3 were added and made up the solution to 100 milliliter with deionised water. The solution was analysed for Ag, Na, K, Ca and Mg by using atomic absorption spectrophotometry (AAS).

X-ray fluorescence (XRF) analysis

Total major and minor elements in kaolin samples were determined using a Philips PW 1400 XRF spectrometer fitted with a rhodium tube. Kaolin samples were oven dried overnight at 105 °C to release water and then 0.700 gram of sample was fused with 7.000 gram of lithium meta/tetraborate flux at 1,050 °C in a platinum crucible. The molten mixture was cast into a disc in a platinum-gold alloy mold. The elemental composition was determined by comparison with certified reference material and the minimal spectrometer drift corrected by regular measurement of an external monitor samples (Norrish and Hutton, 1964; Norrish and Chappell, 1977; Karathanasis and Hajek, 1996).

3.2.4 Mineralogical analyses

X-ray diffraction (XRD) for kaolin samples

X-ray diffraction (XRD) patterns of the soil kaolins were obtained using CuKα 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°2θ and a scan speed of 1.20 °2θ min^{-1}. XRD patterns of the basally oriented clay fraction on 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 with magnesium, magnesium and glycerol, potassium and saturating the clay with potassium followed by heating at

550 °C for at least 2 hours. Random powder patterns were obtained from 3 to 70°2θ 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).