Clay mineral dissolution following intensive cultivation in a tropical sandy soil

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Abstract

Sandy soils of Northeast Thailand are predisposed to high acidification rates due to leaching and the export of alkalinity is associated with crop removal in these intensive cropping systems. Despite significant acid release, soil pH generally remains stable at a threshold value of around 4.0. Low organic matter content and the absence of weatherable primary minerals would suggest that clay mineral dissolution is responsible for the high degree of buffering commonly observed in these soils. The objective of this study was to investigate changes in nature and organisation of clay minerals following intensive cultivation in a typical sandy soil from Northeast Thailand. Surface soils were sampled under a forest (FS) and an adjacent area cultivated for 50 years (CS); they were compared with parent material sampled at 3.5 meter depth (PM) with the aim of characterising the evolution of clay minerals through pedogenesis and cultivation. The proportion of small particles (mode 0.1 µm) decreased according to pedogenesis – from parent material to soil, and land use – from forest to crop. Under the cultivated and forest soils, particles of kaolinite appeared to be very small (0.02-0.10 µm), poorly crystallised and eroded, often organised as aggregates of 1-2 µm. Expandable 2:1 clay minerals were associated with kaolinite. Chemical data of individual particles revealed that kaolinite contained iron and that expandable 2:1 clay minerals were smectite, vermiculite and mixed-layer illite/smectite. X-ray diffraction patterns of <2 µm-fractions indicated that kaolinite was the main phase, 78%, 88% and 88% in CS, FS and PM respectively, smectite being a minor phase with 20%, 6% and 12% respectively. Our results suggest that the dissolution of kaolinite was accelerated in cultivated system (CS), with a correlative neoformation of smectite, which buffers potential declines in soil pH.

Introduction

Sandy soils are widespread in the tropics and constitute an important economic resource for agriculture despite their inherent low fertility (FAO, 1975). Such soils occupy a large area of the Northeast Thailand plateau (Ragland and Boonpuckdee, 1987). These soils are often characterised as being of a light sandy texture, acidic to depth (pH around 4.0 in $CaCl_2$) with very low exchange properties (CEC <2 $cmol_c$ kg^{-1}) and therefore a low nutrient supplying capacity (Imsamut and Boonsompoppan, 1999). Soil acidification is a major concern in tropical sandy soils since climate and high leaching rates are prevailing conditions for the development of this phenomenon. Intensive cultivation results often in accelerated acidification which has brought into question the long-term sustainability of agronomic production systems (Helyar, 1976).

In Northeast Thailand, degradation of acid sandy soils by further acidification under permanent agriculture has been clearly highlighted (Noble *et al.*, 2000). However accelerated acidification occurs sometime without pH drop in these acid sandy soils (Lesturgez *et al.*, 2005). Regarding the low organic matter content and the absence of other weatherable minerals, the authors suggested the role of clay minerals in buffering the soil pH.

In order to ascertain the role of clay minerals in buffering capacity, a mineralogical study has been conducted in Northeast Thailand with the objective to

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identifying changes in nature and properties of clay minerals possibly induced by 50 years of intensive cultivation. The study has been conducted on a forest soil, an adjacent cultivated area and the parental material of these soils in order to highlight (i) general clay properties of the soils, (ii) evolution following pedogenesis and (iii) changes induced by 50years of intensive cultivation.

Materials and methods

Site and sampling

The study was conducted on a representative upland sandy soil of Northeast Thailand. The site selection was based on previous studies (Lesturgez, 2005) and a paired site approach was conducted to quantify differences between Dipterocarp forest (undeveloped) and agricultural (developed) areas. The soil at the studied sites belongs to Warin soil series (N 16º16′; E 102º47′): Dipterocarp forest and adjacent cultivated land that was deforested 50years ago and used for cassava and sugarcane cultivation to date. The same soil type was observed in both areas with little topographical differences (i.e. slope) between these two areas. The undisturbed Dipterocarp forest, close to agricultural field, had a well-defined boundary to separate the two land use systems. Selected characteristics of the soil at the studied sites are presented in Table1. Samples were collected at 0-10cm depth both in the soil under forest (FS) and in adjacent cultivated area (CS) and at 3.5 m depth for parent material (PM). Samples were air-dried and passed through 2mm sieve.

X-ray diffraction (XRD)

40g sub-samples of air -dried material were dispersed in water overnight by shaking. Clay fractions (<2 μm) were obtained by sedimentation from the initial samples after organic matter oxidation (H_2O_2-treated clay). Mineralogical analysis was performed by X-ray diffraction on oriented samples obtained by sedimentation of the <2 μm fractions on glass slides and air-dried. Samples were run in a Siemens D5000 system with CoKα radiation. The diffraction patterns were decomposed into elementary curves using the program DECOMPXR (Lanson, 1997) in order to quantify the proportion of different clay minerals. The decomposition was done on the 1st order diffraction peaks for kaolinite, illite and smectite (or vermiculite).

Table 1. Selected properties of the studied soils

Horizon	Depth (cm)	Particle size distribution (%)			pH	Bulk density ($Mg.m^{-3}$)
		Sand	Silt	Clay		
Forest soil (FS)						
A	0-15	78.7	18.5	2.8	5.4	1.4
E	15-65	74.9	18.0	7.1	5.2	1.4
B1	65-120+	67.9	15.3	16.8	4.9	1.5
Cultivated soil (CS)						
Ap	0-15	80.5	16.8	2.7	4.6	1.6
E	15-65	71.2	16.9	11.9	4.8	1.6
B1	65-120+	64.0	15.2	20.8	4.6	1.5
Parent material (PM)						
PM	350	77.4	9.5	13.1	–	–

Laser granulometry (LG)

Particle size distributions (PSD) were measured on <2 μm fractions dispersed in distilled water (ultrasound ~15 min).The quantity of material was adjusted in order to obtain adequate particle concentration (obscuration = 45%). PSD was produced using a LS-230 Beckman-Coulter laser grain-size analyser, with a range of particle size from 0.04 to 2000 μm, divided into 116 fractions. PSD was performed under agitation of clay suspension in the measuring cell. Three repeated measurements were undertaken in each sample.

Analytical transmission electron microscopy (TEM-EDS)

Dispersed clay suspensions were deposited on collodion-coated Cu grids and air-dried. Images were produced in a Philips 420 STEM transmission electron microscope operated at 120kV and equipped with a Megaview II CDD camera. Magnification at 10500x covered the particle-size ranged from 0.5-2.0 μm and magnification at 31000x ranged from 0.05 μm-1.00 μm.

Microanalyses were performed using an Oxford INCA energy dispersive spectrometer (EDS) with an ultrathin windowed Si (Li) detector connected to the microscope. In order to limit irradiation damages, analyses were done using a probe spot 100nm in diameter (Romero *et al.*, 1992). The chemical compositions (Al, Si, K, Ca, Mg, Fe, Na and Ti) were determined on individual particles selected regarding dispersion. A minimum of 100 particles was analysed for each sample in order to get a representative set of data. Minerals were identified by their chemical compositions, on the basis of calculated structural formula expressed in number of constituting cations. Quantitative discriminations were used to sort particle analyses into mineralogical classes (Figure1).

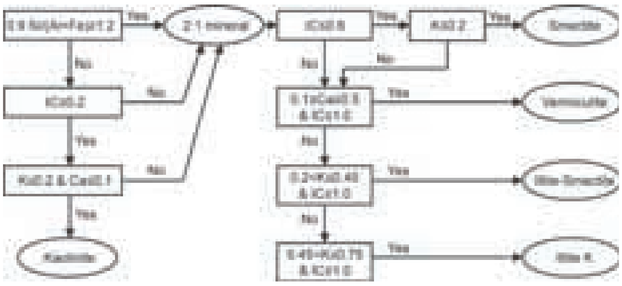

Figure 1. Procedure for identifying clay minerals using analytical data from TEM-EDS. Numbers of atoms in structural formulae are calculated on the basis of 11 and 7 oxygen atoms per half cell for 2:1 and 1:1 clay minerals, respectively. Si, Al, Fe, K, Ca: number of atoms in the calculated structural formula. IC: Interlayer Charge Value (Ca^{2+} + Na^{2++} K^{+}) of the particle

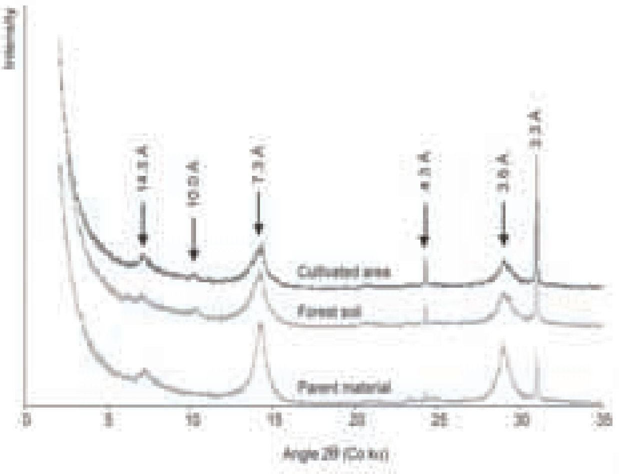

Figure 2. X-ray diffractograms (Co kα) of clay fractions (<2 µm) for cultivated soil, forest soil, and parent material

Results

Mineralogical determination of clay fraction by XRD

XRD patterns indicated the presence of quartz (4.3 and 3.3 Å), kaolinite (7.3 and 3.6 Å) and 2:1 clay minerals (illite at 10.0 Å and smectite at 14.3 Å) in all three samples (Figure 2).The intensity of quartz peaks (4.3 and 3.3Å) was higher in soils (CS and FS) than in parent material (PM). According to peak intensity, kaolinite was the main crystalline phase with 78%, 88% and 88% in CS, FS and PM, respectively (Table 2). On the other hand, the proportion of smectite was only of 20%, 6% and 12% in CS, FS and PM respectively. The diffraction intensity of illite was significant only in FS (6%). As the peaks of kaolinite were very large compared to a reference kaolinite (Brindley and Brown, 1980), they have been decomposed into three elementary peaks modelling crystallinity, each peak position corresponded to a structural order: highly disordered (7.37Å), slightly disordered (7.22Å) and well ordered (7.15 Å). The proportion of the three types of peaks within the kaolinite fraction has been recalculated and expressed in percentage of total peak surface (Table3). The proportion of highly disordered kaolinite was equivalent for CS and FS (40%) but lower in PM (34%). The slightly disordered kaolinite was correlatively more important in PM (66%) while the well ordered kaolinite was present only in CS (3%).

Table 2. Selected characteristics of the clay fractions (<2 µm) for parent material, forest and cultivated soil

	Parent material	**Forest soil**	**Cultivated soil**
Mineralogical determination by modelling the XRD diffractograms. Peak surface (%)			
Highly disordered kaolinite (7.37 Å)	30	35	31
Slightly disordered kaolinite (7.22 Å)	58	53	45
Well ordered kaolinite (7.15 Å)	0	0	2
Total kaolinite	88	88	78
Illite (10 Å)	0	6	2
Smectite (14.3 Å)	12	6	20
Particle size distribution by laser granulometry. Particle surface area vs. particle diameter (%)			
0.04-0.30 µm (%)	86	49	37
Mode value (µm)	0.088	0.117	0.106
0.30-10.00 µm (%)	14	51	63
Mode value (µm)	0.775	0.755	0.755
Quantitative mineralogy by analytical transmission electron microscopy (TEM-EDS). Particle number (%)			
Kaolinite	82	42	34
Smectite	10	29	54
Al-vermiculite	1	12	1
Mixed layer illite/smectite	5	14	3
Illite	2	2	8

Particle size distribution by laser granulometry (PSD)

Particle size distribution (PSD) was expressed in particle surface area (SA) as a function of the particle equivalent diameter. Average and standard deviation of the three replicates are presented in Figure3. Particle size distributions were bimodal shape in all samples. For PM, the main particle size mode was around 0.1 µm (0.04-0.30 µm) and covered 86% of total SA (Table2). PSD for CS and FS had two strong modes around 0.1 µm and 1.0 µm, thus appearing very different from PM. The SA of small particles (mode 0.1 µm) strongly decreased from PM to FS and CS. When comparing FS and CS, the SA of small particles decreased from FS to CS.

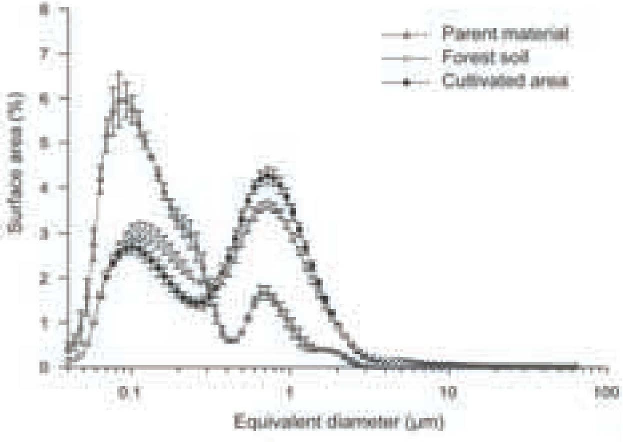

Figure 3. Particle size distributions of clay fractions (<2 µm) for cultivated soil, forest soil, and parent material by laser granulometry

Morphology and chemical composition of particles by TEM-EDS

Examples of TEM images are shown for FS (Figure4). The shape and size of particles were similar in CS and FS. The size of particles observed on TEM images allowed discrimination between quartz grains and clay minerals. Most of quartz grains were the large particles while clay minerals were much smaller (Figure4-A). A significant proportion of small particles was organised into aggregates of 0.5-2.0 µm (Figure4-B). Dispersed kaolinite particles appeared to be eroded both in CS and FS and constituted the majority of PM ranging between 40 and 120 nm. A great diversity of particle shapes was observed in Figure4-C.

Analytical transmission electron microscopy (TEM-EDS) revealed that kaolinite contained iron. The 2:1 clay minerals were smectite and mixed-layer illite/smectite in all samples, vermiculite was in FS and illite was only in CS. Smectite was associated with kaolinite in aggregates. Particles of titanium and iron were also detected. The main 2:1 clay mineral was smectite with 54, 29 and 10% in CS, FS and PM, respectively (Table2). Mixed-layer illite/smectite was low in proportion with 3, 14 and 5% in CS, FS and PM, respectively. Al-vermiculite developed mainly in FS (12%). The repartition of clay minerals was determined by EDS following the marked trends between samples, but their proportions were markedly different from XRD determinations.

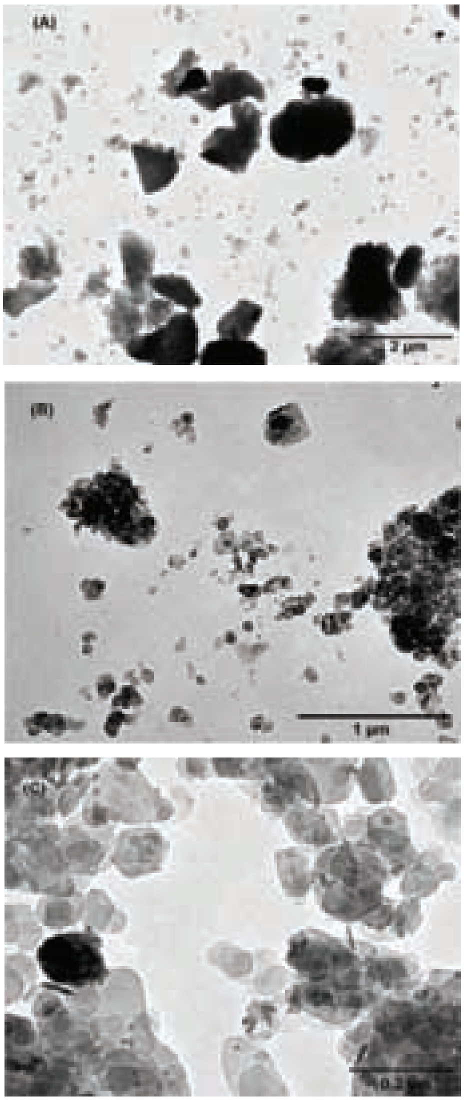

Figure 4. TEM images of clay fractions (<2 µm) for cultivated soil, forest soil, and parent material at magnification ×10500 (A), ×31000 (B) and ×105000 (C)

Discussion

Methodological aspects

When comparing results obtained by XRD and EDS analyses, the discrepancy between quantitative data relates to two essential methodological aspects:

- XRD detected the diffraction ability of minerals, which depended on their crystallinity and chemical composition. It is worthy of note that kaolinite contains iron and the presence of this element strongly enhances the structure factor, i.e. the diffraction intensity. Furthermore, XRD technique is not suitable for poorly crystallised phases and not able to produce diffraction peaks for amorphous material or loose monolayers such as smectite, and even for loose bilayers (Dudek *et al.*, 2002).
- EDS analyses were sorted using strict rules applied to calculated structural formulae, discarding from the kaolinite group, all particles containing Mg and having a high interlayer-charge (K and Ca). Such particles are thus identified as 2:1 clay minerals.

XRD detected well crystallised phases of clay minerals in parent material but it was underestimated for the fine neoformed phases as well as dissolution products in soils. The discrepancy between XRD and EDS is not a trivial issue, but suggests a transition from 1:1 to 2:1 clay minerals in a significant part of the clay fraction.

Mineralogical properties of soils in Northeast Thailand

The studied soils contained a very small quantity of clay minerals. The clay fraction consisted of a mixture of 1:1 (kaolinite) and 2:1 clay minerals (illite and smectite), and contained a significant proportion of small quartz grains as noted in other soils of this region (Bruand et al., 2004). Kaolinite showed crystal disorder (XRD) and appeared to be dissolved (TEM) in soils as well as in parent material. Some iron was detected in kaolinite as a lattice substitution for Al. XRD patterns and EDS analysis confirmed the presence of expandable 2:1 clay minerals especially smectite, but EDS also identified mixed-layer illite-smectite and Al-vermiculite in small proportion. Kaolinite appeared to be disordered in these soils as well as in parent material since the XRD peak around 7Å was very lar ge.

Evolution through pedogenesis

To investigate in more detail changes in crystallinity between the different samples, the “kaolinite” XRD peaks have been decomposed. The proportion of highly disordered kaolinite is equivalent in CS and FS but more important in soils than in PM, and slightly disordered is correlatively more important in PM (Table3). Crystal disorder is probably related to kaolinite dissolution. This may be consistent with the hypothesis that kaolinite in parent material was poorly crystallised and this phenomenon has been accentuated by weathering through pedogenesis.

Table 3. Normalised proportions of disordered kaolinite species in kaolinite fraction

	Parent material	Forest soil	Cultivated soil
Highly disordered kaolinite/Total kaolinite	34	40	40
Slightly disordered kaolinite/Total kaolinite	66	60	58
Well ordered kaolinite/Total kaolinite	0	0	3

Particle size distributions of clay fractions showed the loss of finer particles (mode 0.1 µm) in soils when compared to those in PM. The value corresponding to the loss was 50% for CS and 37% for FS. On the other hand, EDS result indicated a higher proportion of kaolinite in PM (82%) than in the soils (34% in CS and 42% in FS). TEM images showed that the fine particles (mode 0.1 µm) corresponded to fine grained kaolinite. These results strongly suggested that a disappearance (completely dissolved) of the small particles of kaolinite may be due to their dissolution when buffering acid addition and/or their leaching to depth. On the other hand, EDS detected a much higher proportion of 2:1 clay minerals in soils than in parent material, suggesting that the clay neoformation may possibly occur on the basis of degraded kaolinite.

Evolution of mineralogy due to intensive cultivation

Particle size distributions of <2 µm fractions revealed a decrease of finer particles (mode 0.1 µm) in CS compared to FS. On the other hand, EDS analysis revealed a discrepancy in the content of mixed-layer illite/smectite and Al-vermiculite between CS (4%) and FS (26%) and a correlative discrepancy in the content of smectite between CS (54%) and FS (29%). These results pointed out the difference between these two soils: kaolinite dissolution was associated with a neoformation of smectite which appeared to be accentuated in CS.

Conclusion

The aim of this study was to evaluate the evolution of clay minerals, especially kaolinite and 2:1 clay minerals, in acid sandy soils of Northeast Thailand subjected to intensive cultivation. Our results have shown that the main clay mineral is kaolinite. Quartz is also present in all clay fractions but its grain size is coarser compared to clay minerals (TEM images). The presence of expandable 2:1 clay minerals has been highlighted, especially smectite as well as mixed-layer illite/smectite and vermiculite, though in smaller proportions. With respect to kaolinite, the great diversity of morphological shapes, very small particle size and the presence of iron in crystal structure were consistent with a dissolution process due to soil acidification. Kaolinite is thus characterised by fragility under acidic conditions.

Results also indicate, by using three different analytical methods (especially TEM-EDS analysis), that fine kaolinite particles become scarcer with increasing pedogenesis whereas 2:1 clay minerals tend to be neoformed. The first phenomenon may be related to dissolution of fine grained kaolinite particles and/or their leaching to depth. The second phenomenon can be linked to the properties of 2:1 clay minerals which are less readily eluviated.

The neoformation of smectite containing Ca as exchangeable cation appeared to dominate in cultivated soil, whereas in forest soil it appeared to be associated with neoformation of other 2:1 clay minerals such as Al-vermiculite and mixed-layer illite/smectite. Further studies, focusing on the clay evolution in soil profiles, are needed to validate these hypotheses and to investigate the role of smectite in soil pH buffering.

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