Use of direct XRD pattern fitting to quantify clay mineral assemblage changes and unravel soil change processes

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Introduction

The studied soil is a polygenetic Cambisol developed onto a paleo-oxisol (INRA Lusignan, France). The profile is characterised by silty surface horizons (loess deposit) overlying a reddish paleosol. From field observations, the soil profile is divided into five horizons and degradation tongues are present through the three deeper ones (from 40 to 180 cm). The clay mineral assemblage was determined on the < 2 µm fraction for the soil horizons (matrix, 5 samples) and along soil tongues (6 samples). The aim of this study is to highlight the clay mineral assemblage modifications induced by the soil change processes from paleo-tropical climate to current temperate climate.

For this purpose we applied direct XRD pattern fitting approach that was developed for diagenetic clays (Lindgreen et al., 2000, Claret et al., 2004, Aplin et al., 2006, Lanson et al., 2009) and more recently on soil samples (Hubert et al., 2009) and afforded great improvements in the identification of the mixed layer minerals (MLMs). The crystallographic characteristics of the different clay mineral species are adjusted to directly fit the calculated 00ℓ reflections on the experimental XRD patterns (range from 3 to 35 °2θCuKα in the air-dried (AD) and ethylene glycol solvated (EG) states). When achieved, a semi-quantification of the different clay minerals species is obtained.

Results

Particle size distribution

Soil matrix texture (Table 1) varies along the soil profile with an increase of the < 2 µm fraction from 15.4% in surface to 33.4% at the top of the M horizon. Between S2 and S_{Fe} horizons, the < 2 µm fraction in the soil matrix is quite constant with respectively 29.1% and 31.9 %. S2 and S_{Fe} horizons correspond to the level within which tongues occur. Tongues texture follows similar trends to the soil matrix (Table 1). The < 2 µm fraction slightly increases with depth from 27.6% at 60 cm depth to 29.6% at 100cm depth. The top of the tongue at 50 cm depth present lower clay content (24.7%) compared to the matrix at the corresponding depth. It is due to sampling strategy: the value for the S2 horizon corresponds to a mean value of the horizon whereas the tongue sample at this depth corresponds to the transition between S1 and S2 horizons.

The clear similarity of < 2 µm fraction content between tongue and matrix is noticed in the deeper horizon M with 33.3% in tongue and 33.4% in matrix. As a result, no significant fine particles accumulation is noticeable in the deeper part of tongue.

Table 1. Texture of the soil and the degradation tongues.

Tongue Sample	Depth cm	Clay fraction %	Loam fraction %	Sand fraction %	Matrix Sample	Depth cm	Clay fraction %	Loam fraction %	Sand fraction %
					L	0-30	15.4	70.4	14.2
					S1	30-50	22.3	67.5	10.2
$T_{S2\text{-}50}$	50-60	24.7	61.7	13.6					
$T_{S2\text{-}60}$	60-70	27.6	58.7	13.7	S2	50-80	29.1	56.6	14.3
$T_{S2\text{-}70}$	70-80	27.2	56.1	16.7					
$T_{SFe\text{-}80}$	80-90	28.0	56.5	15.5	S_{Fe}	80-120	31.9	52.8	15.3
$T_{SFe\text{-}90}$	90-100	29.6	56.7	13.7					
$T_{M\text{-}130}$	130	33.3	54.3	12.4	M	130	33.4	48.9	17.7

Identification and quantification of the clay mineral assemblage

In the < 2 µm fractions, low CSDS (Coherent Scattering Domain Size, < 10 layers) clay species are mainly MLMs with: illite/smectite rich in illite (Ill/Sm^L R0 85/15), illite/smectite rich in smectite (Ill/Sm^H R0 60/40), kaolinite/illite (R1 segregated 79/21) and kaolinite (Fig.1).

High CSDS (> 10 layers) clay species are mainly discrete with: illite, chlorite, kaolinite and illite/chlorite/smectite MLM (R0 60/26/14) (Fig. 1).

Results indicate that the same clay mineral assemblage is relevant for all the soil samples studied both in soil matrix and in tongues (not shown). Only variations among the relative proportions occur (Tables 2 and 3).

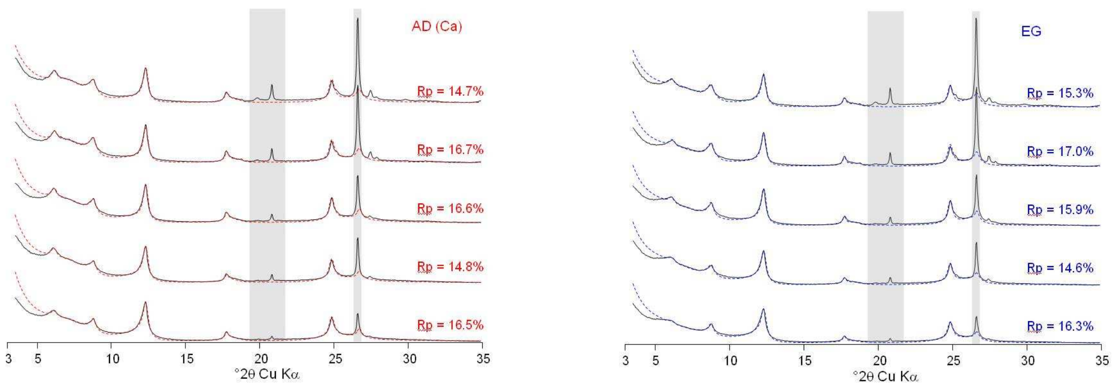

Fig. 1. Complete calculated XRD patterns of the < 2 µm fraction of L, S1, S2, S_{Fe} and M soil horizons. Experimental XRD patterns are shown as solid gray lines and calculated ones as dashed red line in AD state (left) dashed blue lines (right). Rp values are calculated from 3.5 to 35 °2θCuKα. Gray area corresponds to part of the diffractogram not taken into account for calculation of the quality of the fit (Rp).

Table 2. Calculated estimations of clay mineral phases for soil horizon samples.

Sample	State	MLM Ill/Sm^L (%)	MLM Ill/Sm^H (%)	MLM Ill/Ch/Sm (%)	Illite (%)	Chlorite (%)	Kaolinite (high CSDS) (%)	Kaolinite (low CSDS) (%)	MLM K/Ill (%)
L	AD	<5*	14	22	17	3	19	7	17
	EG	<5	15	23	16	<5	19	7	17
S1	AD	<5	14	20	21	<5	20	7	13
	EG	<5	15	19	20	<5	21	7	14
S2	AD	<5	10	22	16	<5	21	9	13
	EG	<5	10	25	16	<5	20	10	13
S_{Fe}	AD	6	11	22	12	<5	19	13	14
	EG	6	12	21	13	<5	20	12	15
M	AD	5	9	17	15	<5	18	20	14
	EG	5	7	16	16	<5	18	21	16

*: < 5 % mean that the clay mineral cannot be quantified due to low amounts. The presence is however detected and necessary for fitting the patterns in corresponding angular domain.

In soil matrix, the large relative content of high CSDS kaolinite (~20%) and the increase of low CSDS kaolinite with depth from 5% at soil surface to 20% in the deepest horizon are characteristics of the paleo-oxisol (Table 2). Illite, chlorite and illite/chlorite/smectite MLM slightly decrease with depth and seem to originate from the incorporation of silt material (i.e.: loess). Smectite/illite MLM relative content is low (~5%) and its distribution along the soil profile indicates leaching. In comparison to soil matrix, tongue clay mineral assemblage is depleted in kaolinite and smectite/illite MLM relative contents due to higher leaching (Table 3).

Tongue zone of the studied soil presents similarity with degradation tongues observed in soils developed on loess deposit according to the increase in quartz, illite, chlorite and associated MLM's and, to a shorter extent, the decrease in fine particles rich in clays with expandable layers.

Conclusion

In the present study, clay mineral quantification confirmed that the soil firstly developed under a 'ferrallitic' weathering environment that induced the formation of large amounts of low CSDS kaolinite in the deepest horizon. More recent deposit of silt, mainly composed of illite, chlorite and MLM illite/chlorite/smectite, was progressively incorporated in the soil without important mineralogical changes. The current pedogenesis under temperate climate does not induce significant modifications of the clay minerals at the crystal scale. Most importantly, results of the modelling highlights that the active pedogenic processes induce a redistribution of the clay minerals at the profile scale due to tongue formation.

In addition, this work highlights that profile fitting that allow a semi quantification of the clay minerals in the < 2 µm fraction is a valuable tool to clarify complex pedogenic processes.

Table 3. Calculated estimations of clay mineral phases for tongue samples.

Sample	State	MLM Ill/Sm^L (%)	MLM Ill/Sm^H (%)	MLM Ill/Ch/Sm (%)	Illite (%)	Chlorite (%)	Kaolinite (high CSDS) (%)	Kaolinite (low CSDS) (%)	MLM K/Ill (%)
T_{S2-50}	AD	<5*	10	24	23	5	16	5	14
	EG	<5	10	25	24	<5	17	5	13
T_{S2-60}	AD	<5	8	25	24	5	16	7	12
	EG	<5	8	28	23	<5	15	7	12
T_{S2-70}	AD	<5	9	23	24	5	16	6	13
	EG	<5	8	27	25	<5	14	7	12
T_{SFe-80}	AD	<5	8	26	21	<5	15	5	17
	EG	<5	7	27	21	<5	16	5	18
T_{SFe-90}	AD	<5	10	24	19	<5	15	8	18
	EG	<5	9	26	17	<5	16	8	19
T_{M-130}	AD	<5	9	23	18	<5	17	14	13
	EG	<5	8	26	15	<5	16	17	13

*: < 5 % mean that the clay mineral cannot be quantified due to low amounts. The presence is however detected and necessary for fitting the patterns in corresponding angular domain.

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