

# Impact of clay mineralogy on stabilisation of organic matter in the clay fraction of a Neo-Luvisol and a Cambisol

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## Abstract

This study was focused on the identification and quantification of the clay mineral assemblage of the clay fraction of two surface soil samples from a Neo-Luvisol on loess deposit in the Parisian basin (France), and a Cambisol on ancient ferrallitic soil in south-west France in relation to their organic carbon content. The two soil samples exhibit contrasted mineralogy. In order to better characterize the clay mineralogy the < 2  $\mu\text{m}$  fraction was subsequently fractionated in sub-micronic fractions. The < 0.04  $\mu\text{m}$  fraction of the Neo-Luvisol is rich in smectite both as discrete and mixed layers while in the Cambisol, kaolinite is the dominant species. However the carbon content is larger in the < 0.04  $\mu\text{m}$  fraction of the Cambisol compared to the Neo-Luvisol. In the 0.2 – 2  $\mu\text{m}$  fraction organic carbon content is larger for the Neo-Luvisol. These preliminary results support the hypothesis that in the Cambisol the poorly crystallised kaolinite exhibits a large specific surface area that allows important organic matter sorption, and that in the Neo-Luvisol smectite favours, in addition to sorption, organic matter stabilisation within micro-aggregates that leads to larger content in organic carbon of the < 2  $\mu\text{m}$  fraction.

## Key Words

Clay mineralogy, XRD profile fitting, organic matter, particle size fractionation, smectite

## Introduction

The “clay fraction” of soils is commonly dominated by clay minerals which control to a large extent important soil chemical and physical properties (Dixon & Weed 1989). An accurate determination of soil clay mineralogy is required to better understand their role on soil properties. Several factors impede their precise identification: first, soil clay mineral assemblages are often mixtures of clay species with a variety of particle sizes, crystal-chemistries and mineralogy; second, soil clay minerals are often mixed layers with variable compositions (Righi & Elsass 1996). Mixed layer identification is performed from the comparison of experimental peak positions with those calculated using decomposition and Newmod simulation for mixed layers. Such a combination of XRD pattern decomposition and Newmod calculations has been successfully applied for several purposes in soil science. However, this dual procedure allows only an approximate characterisation of the mixed layers as the identification relies essentially on peak position. Consistently, profile fitting which allows fitting the complete reflection profiles including asymmetries results in a more reliable identification of mixed layers (Drits 2003). Profile fitting calculates a complete XRD pattern from a structure model optimized for each clay species present (Drits & Sakharov 1976; Drits 1997; Sakharov *et al.* 1999a, b). This method can be applied to mixed layers with more than two layer types and different layer stacking sequences and also provides quantitative phase analysis of complex clay assemblages (Drits 2003). This method used in burial diagenesis context has been applied to soil samples developed on loess deposits by Hubert *et al.* (2009).

## Methods

### *Soil profiles*

Two soil samples were used in this study: profile 1 is a “Neo-Luvisol” developed on loess deposits from the Closeaux Field Experiment, at the Station of the INRA de Versailles (France) and profile 2 a “Cambisol” developed on a relic of an ancient ferrallitic soil was sampled at the experimental site of the ORE ACBB (INRA de Lusignan, France). This study was focused on the surface horizons (L1) of these two profiles studied in details by Moni (2008), Hubert (2008) and Hubert *et al.* (2009).

### *Particle size fractionation and X-ray diffraction*

Soil samples were air dried and sieved at 2 mm to remove coarse fragments. 100 g of the fine earth were dispersed in osmosed water and disaggregated using agitation with glass balls. The < 50  $\mu\text{m}$  fraction was

separated by wet sieving and dispersed using ultrasonic treatment. The < 2 µm clay fraction was isolated from the silt one (2-50 µm) by repeated siphoning. An aliquot (1g) of the <2 µm fraction was sequentially fractionated into three sub-fractions (2-0.2 µm; 0.2-0.04 µm and <0.04 µm) according to the procedure employed by (Laird *et al.* 1991) using a Biofuge stratos centrifuge. Two dispersion procedures without destruction of organic matter were employed: 1) a dispersion using molar NaCl solution and washed until chloride-free and 2) dispersion into osmosed water. Between each centrifugation step, the sample was sonified in osmosed water (30 s at ~150 W for 40 ml). The particle-size fractions were collected using repeated centrifugation until the supernatant becomes clear (8 to 10 steps). The different fractions were flocculated and saturated four times with CaCl<sub>2</sub> (0.5 M), dialysed in osmosed water until chloride-free, freeze-dried and then weighted.

Oriented preparations for quantitative XRD analysis were obtained by pipetting the Ca-saturated suspensions on a glass slide (sample length: 3 cm, sample density: 3 mg cm<sup>-2</sup>) and drying at room temperature (AD). XRD patterns were obtained using a Panalytical X'pert Pro diffractometer equipped with an X'celerator detector (CuK<sub>α1+2</sub>) in air-dried state (AD) at room humidity conditions (~35% RH) and following vapour ethylene glycol (EG). Diffraction data was recorded in a scanning mode and converted to a step pattern (step of 0.017°2θ from 2.5 to 35°2θ, using a 200 s counting time per step). Organic carbon content of the different particle-size fractions were determined by dry combustion (NF ISO 10694).

#### *X-ray diffraction profile modelling method*

XRD patterns were modelled, in both AD and EG states, using the Sybilla© software developed by Chevron™ (Aplin *et al.* 2006) and using the algorithm developed by Drits & Sakharov (1976) and used recently on soil samples by Hubert *et al.* (2009). The modelling allows the direct comparison between experimental and calculated XRD profiles, the latter being the sum of all elementary contributions which have been identified. Details on the modelling procedure are given in Hubert *et al.* (2009). For each mixed layer, the number, nature, proportion and stacking sequences of the different layer types were considered as adjustable parameters. Optimization was performed using a trial-and-error approach without automatic refinement of the parameters. To ensure the reliability of the modelling, both AD and EG patterns of a given sample were fitted with a unique set of structural parameters. The relative proportions of the different clay species in these complex assemblages were also optimized with Sybilla©. The multi-specimen approach requires these proportions to be similar in both AD and EG states.

## **Results**

### *Particle size distribution and organic carbon repartition*

The percentages are based on gravimetric recoveries of each fraction that were > 92.9 % and have been normalised to 100% (Table 1). Particle-size fractionation shows that the dominant fraction of Neo-Luvisol is 0.2-2 µm for both dispersion methods. For the Cambisol the dominant fraction is 0.2-2 µm with water dispersion whereas Na dispersion results in approximate same proportion for the 3 fractions. For both profiles Na dispersion induces a doubling of the < 0.4 µm fraction proportion principally at the expense of the 0.2 -2 µm one.

**Table 1. Sub-micronic particle size distribution of the two soil samples with both dispersion technique.**

	Dispersion method	< 0.04 µm (%)	0.04 - 0.2µm (%)	0.2 - 2 µm (%)
Neo-Luvisol	water	8	36	56
	NaCl	15	38	47
Cambisol	water	17	39	44
	NaCl	35	33	32

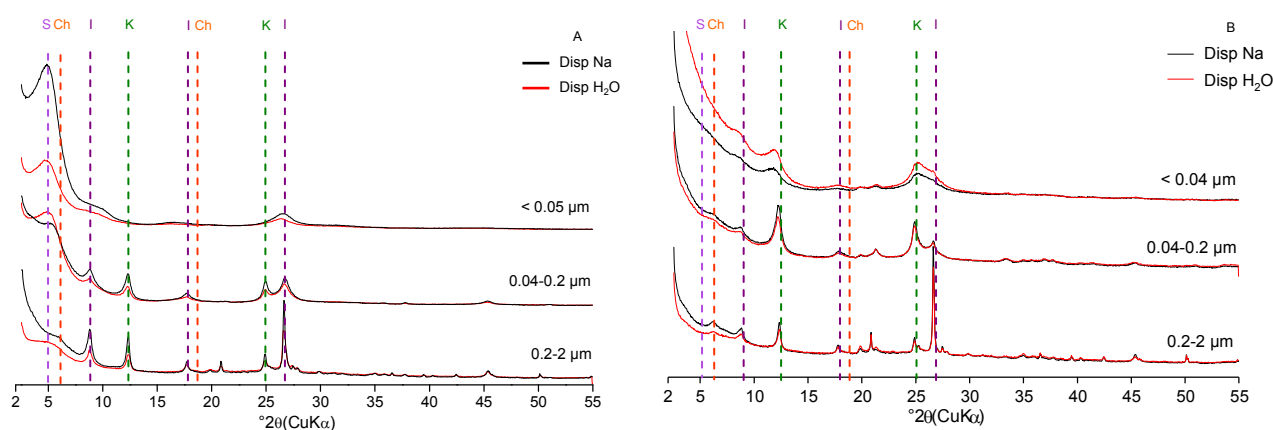
Organic carbon measurements highlights that the richest fraction is the 0.2 – 2 µm fraction for the Neo-Luvisol and the < 0.04 µm for the Cambisol with the both dispersion method (Table 2). Taking into account the mass percentage of the different fraction in both samples the 0.2 - 2µm fraction contains the larger amounts in organic carbon (Table 2). The < 0.04 µm fraction of the Cambisol is richer in organic carbon compared to the Neo-Luvisol one with respectively 44.9 g/kg and 35.0 g/kg.

**Table 2. Organic carbon content and proportion of total carbon in the particle size fractions.**

	Dispersion	< 0.04 $\mu\text{m}$		0.04-0.2 $\mu\text{m}$		0.2-2 $\mu\text{m}$	
		C org. (g/kg)	% C tot (%)	C org. (g/kg)	% C tot (%)	C org. (g/kg)	% C tot (%)
Neo-Luvisol	water	32.5	8	23.8	24	44.7	69
	NaCl	35.0	16	32.5	36	35.6	49
Cambisol	water	45.4	23	27.7	33	32.9	44
	NaCl	44.9	46	31.2	30	26.3	24

### Identification of the clay mineral assemblage

A qualitative description of the X-ray diffraction patterns of the different particle size fractions (Figure 1) show that the two samples present contrasted clay mineralogy. The clay minerals assemblage of the Neo-Luvisol is composed of kaolinite, illite mica, smectites and mixed layers illite/smectite with broad peaks displacing following ethylene glycol solvation (not shown). By contrast, the clay mineral assemblage of the Cambisol is composed of kaolinite, illite, chlorite in addition to low amounts of mixed layers containing expandable layers. In both samples quartz and feldspars are present. The average trend with decrease in particle size is an increase in swelling minerals particularly for the Neo-Luvisol. Na dispersion also induces an increase in swelling minerals in the 0.04 – 0.2  $\mu\text{m}$  and < 0.04  $\mu\text{m}$  fraction of the Neo-Luvisol.



**Figure 1. X-ray diffraction patterns of the particle-size fraction of the surface horizon of the Neo-Luvisol (A) and of the Cambisol (B) following EG solvation (red line: dispersion with water, black line: dispersion with NaCl).**

XRD profile modeling were performed on the <0.05  $\mu\text{m}$  which presents the most contrasted clay mineralogy and organic carbon content. The clay mineral assemblage of the L1 horizon of the Neo-Luvisol is composed of discrete smectite, two random-ordered mixed layers illite/smectites: one rich in illite (R0 90/10) and one rich in smectite (R0 65/35), and a random-ordered kaolinite/smectite mixed layers. The proposed mineral assemblage closely reproduces the experimental patterns in the EG state, and provides an acceptable fit in AD state (not shown). The optimum XRD patterns fits of <0.05  $\mu\text{m}$  fraction of the Cambisol in AD and EG states were obtained with three mixed layer clays dominated by kaolinite, illite and smectite layers, respectively. The first interstratified corresponds to kaolinite-illite (R0 77/23) not commonly described in soils samples. The second clay mineral is a smectite-rich randomly interstratified illite-smectite (R0, 30/70) and the third clay type corresponds to illite-rich mixed layer clay containing three components: illite (75%), smectite (17%) and chlorite (8%) layers. The employed clay mineral assemblage provides good quality of the fit in EG state and an acceptable one in AD state (not shown).

### Conclusion

The two soil profiles present contrasted clay mineralogy especially in the < 0.04  $\mu\text{m}$  fraction. However the < 0.04  $\mu\text{m}$  fraction of the Cambisol on palaeo-oxisol which is dominated by kaolinite minerals has larger content in organic carbon than the same fraction of the Neo-Luvisol rich in smectitic minerals. These results supports the hypothesis that in the Cambisol the poorly crystallised kaolinite minerals exhibit a large surface area that allows sorption of larger quantity of organic matter than in the Neo-Luvisol.

By contrast, the 0.2 – 2  $\mu\text{m}$  fraction of the Neo-Luvisol is richer in organic matter most probably due to the impact of smectite on micro-aggregation that allows physical protection of carbon which is not observed in

the Cambisol. However to complete these preliminary results we have to check the role of iron oxides in both samples by estimating their amounts by chemical dissolution.

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