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Evidence of short-term clay evolution in soils under human impact

Évolution rapide des argiles des sols sous l'impact des activités humaines

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ABSTRACT

Clay minerals are still often considered as stable in soils over a century to millennium time scale despite a few examples of rapid evolution. Indeed, recent advances in X-ray diffraction pattern treatment combined with studies of soil sequences, demonstrated that changes in clay mineralogy were faster than commonly thought. In this article we present the evidence for rapid clay evolution based on X-ray diffraction pattern decomposition of soil samples collected along land-use sequences chosen to represent the main route of clay evolution in temperate soils (interlayer ion exchanges, weathering and transport).

RÉSUMÉ

Les minéraux argileux sont généralement considérés comme stables dans les sols à l'échelle du siècle ou du millénaire et ce, malgré des exemples d'évolution rapide de ces minéraux. Des développements récents dans le traitement des diffractogrammes des rayons X, acquis sur des séquences de sols, mettent en évidence des évolutions des minéraux argileux à la suite de changements d'usage des terres ou de pratiques agricoles. Dans cet article, nous présentons des exemples d'évolutions rapides des argiles mises en évidence par décomposition des diffractogrammes de rayons X dans des séquences de sols soumises à des changements d'occupation des sols ou d'aménagement agricole et choisies pour représenter les principales voies d'évolution des argiles en milieu tempéré (changement de cation interfoliaire, altération et transfert).

1. Introduction

Soil evolves permanently under the impact of fluxes of matter and energy (Chadwick and Chorover, 2001). Rates of soil processes remain poorly known, although their knowledge is a key-point to model soil pedogenesis. Soil formation is classically considered as a slow process. Wilkinson and Humphreys (2005) give 10^4 to 10^5 years as an average of soil ages. However, some studies demonstrated rapid soil evolutions in various pedological contexts. As an example, Burt and Alexander (1996), studying a chronosequence of podzolic soils, reported that

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the formation of the organic O-horizon was completed within 38 years only while the E/Bhs layering was macromorphologically identified within 70 years.

Other authors observed even faster mineralogical changes in soils like significant feldspar dissolution within 3 years only in Podzols and Cambisols (Augusto et al., 2000) or permanent kaolinite dissolution/precipitation with significant evolutions in time scales as short as 6 months in tropical soils (Cornu et al., 1995; Lucas et al., 1996) or illite formation in a season time scale in the rhizosphere (Calvaruso et al., 2009). Despite these few examples, soil mineralogy is still considered as stable in soils over a century to millennium time scale.

Clay minerals represent a key compartment of soils, as they are responsible for most of the soil functions. Different types of soil processes are acting on clay minerals: some are acting on the distribution of clay minerals within the soil as eluviation and illuviation, while others are acting on the formation/dissolution/transformation of these minerals. Classically, those evolutions were studied along soil profiles or soil sequences for long-term pedogenesis (e.g., Egli et al., 2001; Fritsch et al., 2011; Lucas, 1989; Righi et al., 1999; among others) or using test minerals (Ranger et al., 1991; Righi et al., 1988).

As uncertainties on initial state and on past environmental conditions inconstancy increased with the pedogenesis duration as well as possibilities of overlapping soil processes and non-linear dynamics, the analysis of soil clay-mineral evolutions on such a time-scale is mostly qualitative and the kinetics of the processes are therefore poorly addressed. By contrast, the use of human-induced soil evolutions on shorter time scales resulting from a change in land use or from specific agricultural practices can be easily dated and described thanks to historical or even prehistorical records.

Recent advances in numerical analysis of X-ray diffraction (XRD) patterns allow better clay minerals identification (Hughes et al., 1994; Lanson, 1997) and more recently quantification (Alves and Omotoso, 2009; Hillier, 2002; Hubert et al., 2009, 2012).

In this work, we took advantage of the combined use of two dated soil anthroposequences and numerical analysis of X-ray patterns. The considered soil sequences were previously studied by Cornu et al. (2007, 2008) and Montagne et al. (2008). They identified changes in pH, eluviation and initiation of podzolization on time scales ranging from a few tenths of years to a few centuries. All these geochemical and pedological processes are known to act on soil clay mineralogy on large time scale (Dixon and Weed, 1989; Fichter et al., 1998; Jamagne, 1973; Righi et al., 1999; Robert, 1973 among others). We conducted here a systematic analysis of clay minerals in these two soil sequences to determine if these processes induced clay mineral modifications at a short time scale and, if so, specify the kinetics of such modifications.

2. Material and methods

2.1. Site description and sampling

2.1.1. The Albeluvisols under forest and agriculture including drainage

Cornu et al. (2007) studied Albeluvisols cultivated for at least 200 years and showed that:

- cultivation increased the pH from 5 to about 8 due to liming (Table 1) and;
- bleaching was more pronounced under forest than under agriculture.

Montagne et al. (2008), studying a soil sequence perpendicular to a drain line in the same site, showed that 16 years of drainage increased eluviation at the vicinity of the drain.

These Albeluvisols developed in silty deposits of Quaternary age were sampled in a geographically restricted plateau setting – in order to ensure that climate and parent material remain constant – in the southern part of the "Gâtinais de l'Yonne" in France (South East Parisian Basin). Two adjacent plots, one forested and one cultivated for at least 200 years were selected. The cultivated plot has been drained by a subsurface drainage network since 1988 (16 years before sampling). The studied Albeluvisol comprises four horizons whatever the considered plot: a silty, brown surface horizon ploughed under cultivation; a silty grey E-horizon equally partly ploughed under cultivation; and two horizons composed of a complex mixture of several soil volumes of distinctive colours. The most abundant soil volumes are silty and white-grey (10YR8/2 to 10YR7/1) to pale-brown (10YR7/4) in the upper horizon, whereas there are clayey and ochre (10YR5/6 to 10YR5/8) in the lower horizon. Black Fe-Mn concretions and impregnations occur in the core of these latter volumes. For convenience, we call hereafter the upper horizon the E&Bt-horizon, whilst the lower one is

Table 1
Basic pedological properties of the two Albeluvisols sampled under forest and under culture respectively.

Tableau 1
Analyses pédologiques classiques des deux profils de Luvisols de l'Yonne échantillonnés sous forêt et sous culture.

Site	Horizon	Depth in cm	< 2 μm in %	CEC at soil pH[a] in cmol(c) kg^{-1}	% of exchangeable K in the CEC	pH_{water}
Forest	E&Bt	43–50	22	5.83	0.86	4.8
	Bt	60–70	33	11.5	1.56	5.3
Culture	E&Bt	40–50	28	12.8	3.59	8.0
	Bt	60–70	33	15.8	1.53	8.0

After Cornu et al., 2007.

[a] CEC at soil pH measured by the cobaltihexamine method.

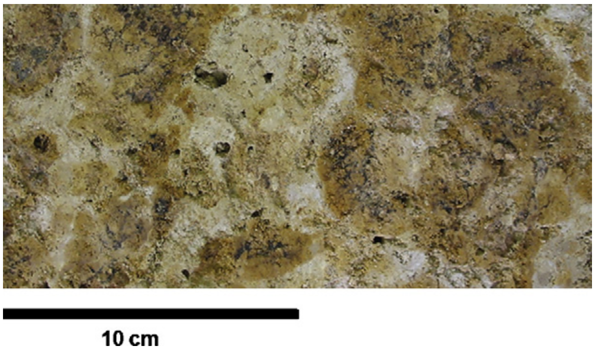

Fig. 1. The different soil volumes of the cropped Albeluvisol E&Bt-horizon.

Fig. 1. Les différents volumes pédologiques de l'horizon E&Bt de l'Albeluvisol cultivé.

called the Bt-horizon. Fig. 1 presents the E&Bt-horizon with the different soil volumes.

To analyse the soil evolution due to both cultivation and drainage, a 4-meter trench was dug perpendicularly to one of the drain in the cropped plot and a pit was dug in the forested plot. In both cases, undisturbed soil monoliths ($27 \times 15 \times 12$ cm) were collected in both the E&Bt- and the Bt-horizons at different distances from the drain for the cropped plot (namely at 60, and 400 cm). Particles were also collected at the outlet of the main drain. Back in the laboratory the different soil volumes defined by their colour as described above were manually sorted from the soil monoliths.

2.1.2. The Dystric Cambisol reforested 60 years ago

Cornu et al. (2008) studied Dystric Cambisols reforested 60 years ago and showed that forest initiated podzolisation on such a time scale (Table 2). These Dystric Cambisols developed in a slope colluvium of gneissic origin were sampled in the Monts de Lacaune in the southwestern Massif Central (France). Three plots, one under meadow, and two reforested about 60 years ago with spruce and Douglas-fir respectively, were selected in a geographically restricted zone so that exposure and slope were as similar as possible – in order to ensure that climate and parent material remain constant. One soil profile was dug in each plot. The studied soil comprises five horizons. The two upper horizons consist in a silty-sand, dark-brown (7.5YR3/2 to 10YR2/2), A-horizon containing small Fe-Mn concretions and a silty-sand, brown (7.5YR3/2) B-horizon slightly richer in clay and with a lighter colour than the upper A-horizon (see Cornu et al., 2008 for more details). The main differences among the different plots concern the texture and thickness of the surface horizons. Therefore, only those where sampled with a sample every 10 cm up to 50 cm depth.

2.2. XRD-analysis and treatments

XRD analyses were made on the < 2 μm fraction of all the samples. This fraction was separated from the bulk soil through sedimentation according to Stokes' law and then analysed on oriented slides according to the method described by Robert and Tessier (1974). For particles collected at the outlet of the drain and the soil volumes sampled from the cropped Albeluvisol, the < 0.1 μm fraction was also separated by centrifugation for XRD-analysis. Fractions < 2 μm and < 0.1 μm were Ca-saturated ($CaCl_2$ 0.5 M) or K-saturated (KCl 1 M). Oriented preparations were obtained by drying at room temperature (air dried: AD). Slides were also saturated with ethylene-glycol (EG) vapour at 50 °C for 16 h. K-Saturated slides were heated at 110, 330 and 550 °C. XRD-patterns were recorded on a Bruker D8 Advance diffractometer (Cu Kα radiation) from 2.5 to 35° 2θ with steps of 0.012° 2θ and a counting time per step of 96 s converted from scanning mode.

The AD X-Ray diffraction patterns were decomposed into elementary peaks by the method proposed by Lanson (1997) using DecompXR software over the 3–14° 2θ range. The decomposition procedure by DecompXR started with the removal of the baseline. The XRD-patterns were then decomposed into Gaussian or Lorentzian elementary curves. The number of elementary curves was progressively increased to obtain a reliable fit of the experimental pattern. The parameters of the elementary curves (position, full-width at half maximum – FWHM and maximum

Table 2
Basic pedological properties of the three Dystric Cambisols developed on gneiss under meadow or forested by Douglas-fir or Spruce.

Tableau 2
Analyses pédologiques classiques des trois Dystric Cambisols développés dans du gneiss et sous prairie, ou forêt de Douglas ou d'Epicéa.

Horizon	Depth in cm	< 2 μm in %	OC in %	pH_{water}	Exch. Al in %	Free Al[a] in %	Tot. Al in %	Free Fe[a] In %	Tot. Fe in %
Meadow									
Ao/Ah1	0–10	26	8.7	5.2	0.05	1.81	7.62	1.78	3.38
Ah2	10–25	21	4.9	5.2	0.05	1.95	8.02	1.94	3.36
Spruce									
Ah1	0–6	26	15	4.2	0.21	1.24	5.85	1.34	2.34
Ah2	10–20	18	4.6	4.5	0.08	1.64	7.22	1.66	2.56
Douglas									
Ah1	0–6/15	20	9.0	4.3	0.14	1.63	7	1.47	3.03
Ah2	6/15–38/43	13	2.6	4.7	0.05	2.22	8.09	2.13	3.17

After Cornu et al., 2008.

[a] Free Al and Fe are extracted by 1 mol L^{-1} hydroxylamine in acetic acid solution at 90 °C for 3 h (see Cornu et al. (2008) for the detailed method).

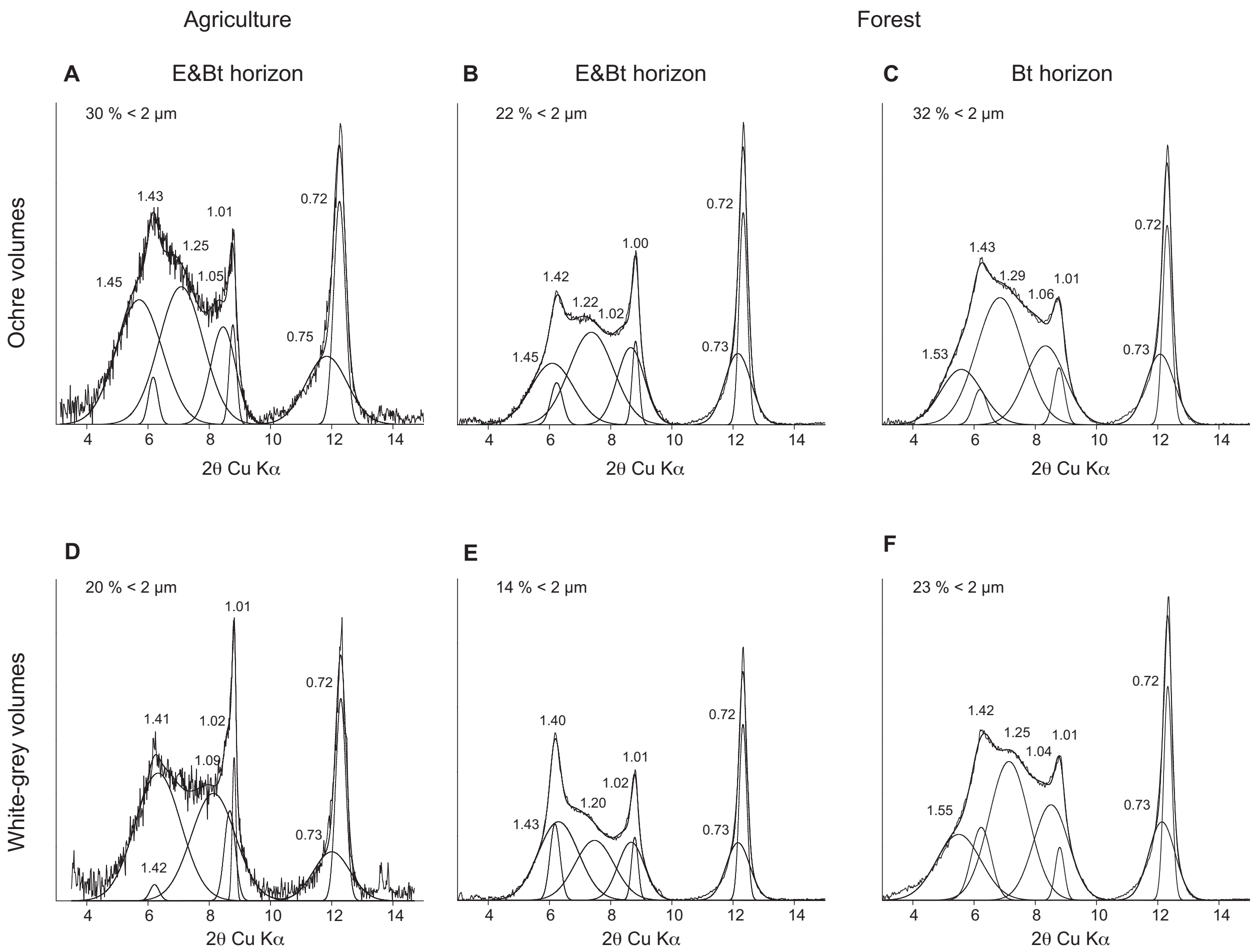

Fig. 2. Decomposition of the air-dry XRD-patterns of the < 2 μm fractions of the different soil volumes (A, B, C: ochre and D, E, F: white-grey) of: A and D – the E&Bt horizon of a cropped and drained Albeluvisol at 400 cm to the drain; B and E – the E&Bt horizon of the same Albeluvisol under forest; C and F– the Bt-horizon of the forested Albeluvisol.

Fig. 2. Décomposition des diffractogrammes de rayons X de la fraction < 2 μm séchée à l'air (AD) de différents volumes de sols (A, B, C : ocre et D, E, F : gris-blanc) de l'horizon E&Bt (A et D) de l'Albeluvisol drainé et cultivé à 400 cm du drain ; des horizons E&Bt (B et E) et Bt (C et F) du même sol sous forêt.

intensity) were used to identify the soil clay mineral species according to Righi et al. (1995) and Velde (2001).

3. Results

3.1. Differences in clay mineralogy in Albeluvisols under forest and agriculture including drainage

XRD experimental patterns from the < 2 μm fractions of the three Albeluvisol profiles and of the particles collected at the drain outlet display in AD and EG similar rational peak series at 1.00, 0.50, 0.333 nm; 0.715, 0.358 nm and 1.41, 0.71, 0.354 nm which correspond to illite, kaolinite and chlorite, respectively. In addition, decomposition results exhibit wide band at 1.02–1.09 and 1.20–1.30 nm that shift to 1.50–1.55 nm after EG treatment, respectively. These positions, widths and peak displacements plead for the presence of two Mixed-Layers Minerals (MLM) containing swelling layers (I/S MLM), with some differences in terms of respective abundance of the different layers (Figs. 2–4). Discrete smectite is also present and evidenced by its 001 reflection at 1.45–1.55 nm in AD that shifts at 1.55–1.65 nm in EG.

Under forest, the differentiation of the clay mineral assemblages from the reference Bt-horizon to the E&Bt-horizon was more pronounced for the white-grey volumes than for the ochre ones (Fig. 2). Whatever the considered soil volume, the swelling after ethylene-glycol (EG) solvation was less pronounced and K-saturation followed by heating does not induce the complete collapse of the 1.43–1.45 nm peak to 1 nm. The 1.0 nm reflection was characterized by a shoulder at 1.05–1.10 nm supporting the presence of Al-interlayered 2:1 clay minerals. Chlorite identified in the E&Bt-horizons should at least partly correspond to hydroxy-aluminium-interlayered vermiculite (HIV) or hydroxy-aluminium-interlayered smectite (HIS) (Dixon and Weed, 1989). The swelling observed for the Bt horizon support the hypothesis that Al-interlayering was absent or less pronounced. The difference of pH recorded between the two horizons was in agreement with

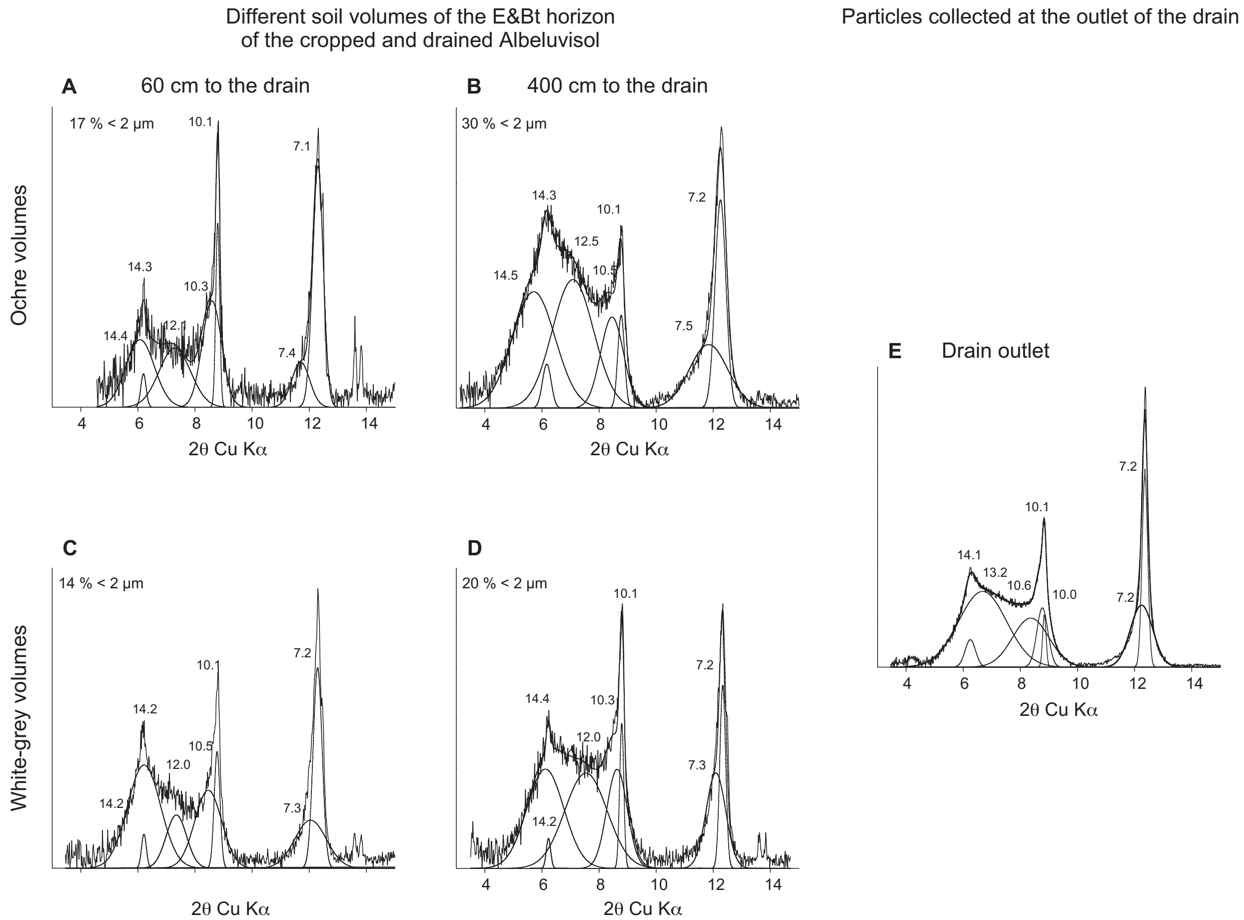

Fig. 3. Decomposition of the air-dry XRD-patterns of the < 2 μm fractions of: A to D – the different soil volumes (A, B: ochre and C, D: white-grey) of the E&Bt-horizon of a drained Albeluvisol for two distances to the drain (A, C: 60 cm and B, D: 400 cm); E – the particles collected at the outlet of the main drain.

Fig. 3. Décomposition des diffractogrammes de rayons X de la fraction < 2 μm séchée à l'air (AD) de : A à D – différents volumes de sols (A, B : ocre et C, D: gris-blanc) de l'horizon E&Bt de l'Albeluvisol drainé pour deux distances au drain (A, C : 60 cm et B, D : 400 cm) ; E – particules collectées à la sortie du drain.

this difference (Table 1). To summarize, under forest, we observed that the white-grey and the ochre volumes of the E&Bt-horizon were characterised by:

- a loss of about 10% in < 2 μm fraction;
- a decrease of the relative abundance of I/S MLM and smectite and;
- an increase in illite and chlorite compared to the Bt-horizon (Fig. 2).

By comparison, the E&Bt-horizon under agriculture was characterised by an increase in the abundance of illite in white-grey volume and of smectite in the ochre volume. These changes were only qualitative as the amounts of < 2 μm fractions of the different soil volumes remained constant between the E&Bt-horizon under agriculture and the reference (Fig. 2).

At last, we compared the mineralogical composition of the < 2 μm and < 0.1 μm particles sampled at the outlet of a drain with that of the < 2 μm and < 0.1 μm fractions of two Albeluvisol sola located respectively at 400 cm and 60 cm to the drain. For the < 2 μm fraction, an enrichment in kaolinite was observed in the exported particles compared to all soil volumes (Fig. 3). Conversely, these particles were impoverished in illite compared to the ochre volumes at 60 cm and the white-grey ones at 400 cm and in smectites and I/S MLM compared to the ochre volumes at 400 cm. Their mineralogy was close to that of the white-grey volume at 60 cm.

For the < 0.1 μm fraction collected at the outlet of the drain, enrichment in smectite compared to all soil volumes was observed (Fig. 4). This enrichment increased with the decreasing of the distance to the drain and from the white-grey volumes to the ochre ones. Conversely, the < 0.1 μm fraction at the outlet of the drain was impoverished in I/S MLM compared to all soil volumes and in illite mainly compared to the white-grey volumes at 60 cm.

3.2. Differences in clay mineralogy among Dystric Cambisols reforested 60 years ago and residual original meadow

The different Dystric Cambisols present a similar clay mineralogy in their < 2 μm fraction whatever the treatment considered (meadow, spruce or Douglas-fir). Peaks at

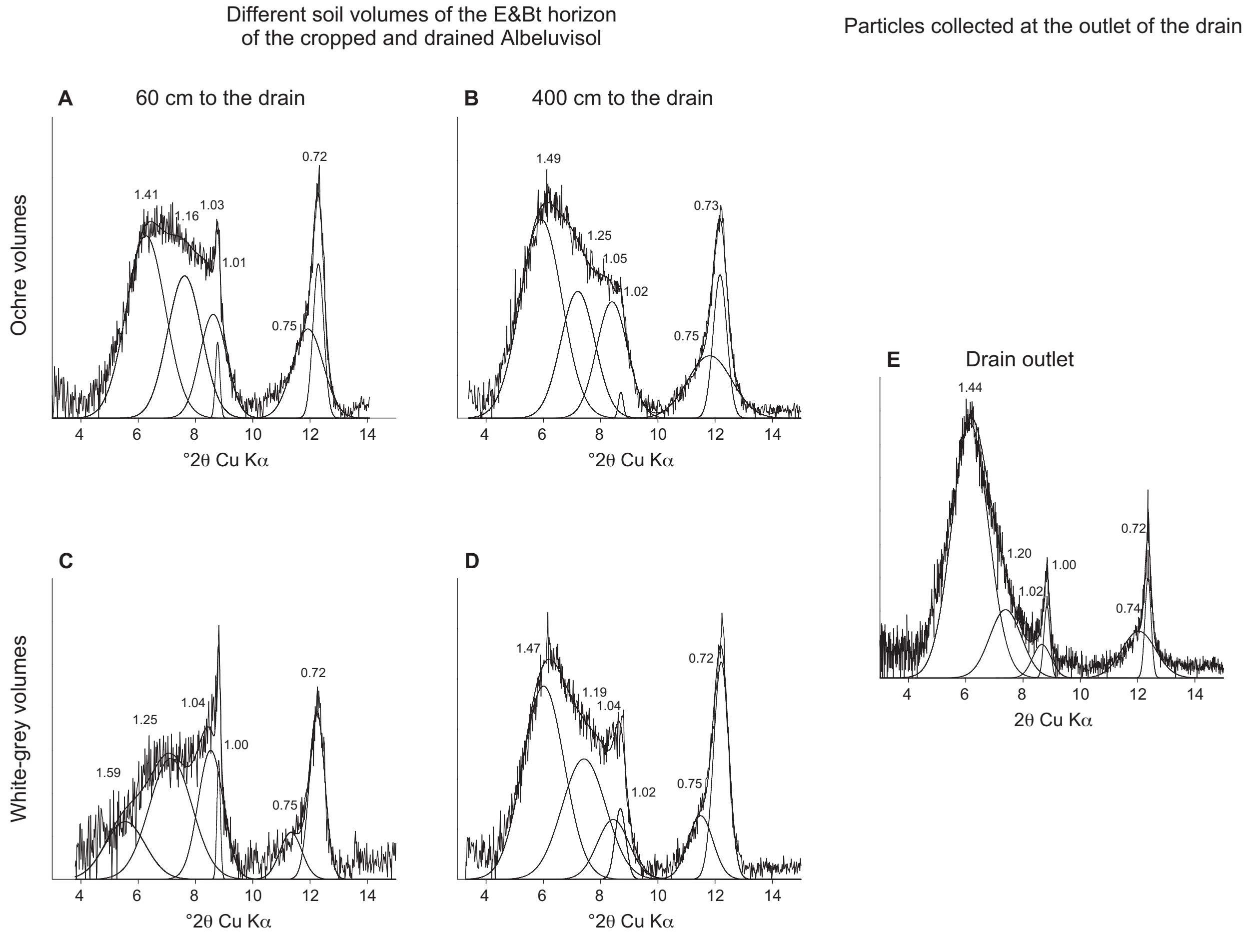

Fig. 4. Decomposition of the air-dry XRD-patterns of the < 0.1 μm fractions of: A to D – the different soil volumes (A, B: ochre and C, D: white-grey) of the E&Bt-horizon of a drained Albeluvisol for two distances to the drain (A, C : 60 cm and B, D : 400 cm); E – the particles collected at the outlet of the main drain.

Fig. 4. Décomposition des diffractogrammes de rayons X de la fraction < 0.1 μm séchée à l'air (AD) de : A à D – différents volumes de sols (A, B : ocre et C, D : gris-blanc) de l'horizon E&Bt de l'Albeluvisol drainé pour deux distances au drain (A, C : 60 cm et B, D : 400 cm) ; E – particules collectées à la sortie du drain.

1.00, 0.50, 0.333 nm; 0.715, 0.358 nm and narrow peaks 1.41–1.43, 0.71, 0.354 nm correspond to illite, kaolinite and chlorite respectively. The wide peak at 1.43 nm and wide bands between 1.05 and 1.35 nm were attributed to vermiculite and illite/vermiculite MLM with different proportions of the two layers, respectively (Fig. 5). Note that vermiculite is identified here as no variation of peak positions was observed following EG solvation. After progressive heating up to 550 °C, the peaks shifted to ~1.0 nm. However, the collapse was incomplete under forest and the peak presented a shoulder at 1.05–1.1 nm, while this was not observed under meadow. This behaviour was indicative of partial Al-interlayering of the 2:1 clay minerals. Vermiculite present in these samples may partly correspond to HIV. This result was coherent with the increase in exchangeable Al observed in the top horizon under forest (Table 2). Forest plantation also induced a decrease of the contribution of chlorite (narrow peaks at 1.42 and 0.71 nm) at 0–6 cm and 30–36 cm for spruce and at 30–38 cm depth of the Douglas-fir (Fig. 5). In the same horizons there is an increase of the peak at 1.25 nm and the occurrence of a peak at ~2.5 nm (super reflection) which partly shift to ~1.27 and 1.35 nm, respectively after EG solvation. These two peaks indicate the presence of an ordered illite/vermiculite or I/S MLM.

4. Discussion

Soil processes modifying the clay mineralogy are either acting on the nature of the interlayer cations, the dissolution/new formation or transformations of clay minerals or on the transfer of clay minerals within the soil. While these evolutions were extensively studied in the past, their velocity still remains poorly known. The selected human-induced soil-sequences were chosen in order to study the velocity of the different clay evolution routes in temperate soil. The discussion will be organised according to the different clay evolutions routes: evolution of interlayer cation occupancy in different pH ranges, podzolisation and eluviation and

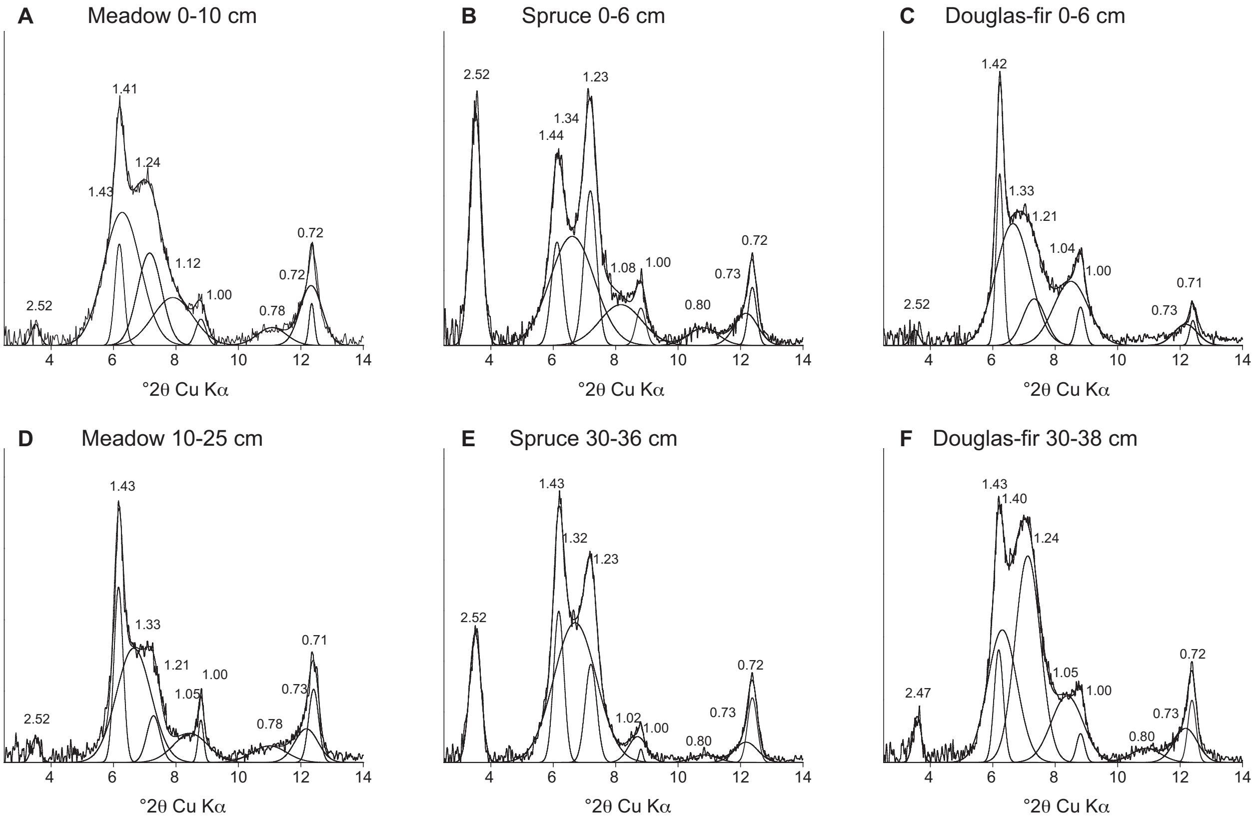

Fig. 5. Decomposition of the air-dry XRD-patterns of the < 2 μm fractions of the top horizons of a Dystric Cambisol developed on gneiss, under meadow (A, B), under Spruce forest (C, D) and under Douglas-fir forest (E, F).

Fig. 5. Décomposition des diffractogrammes de rayons X de la fraction < 2 μm séchée à l'air (AD) des horizons de surface d'un Dystric Cambisol développé sur gneiss, sous prairie (A, B), sous épicéa (C, D) et sous douglas (E, F).

compared to previously reported kinetics summarised in Table 3.

4.1. Rapid evolution of interlayer cation occupancy

4.1.1. Exchange of interlayer K under neutral to slightly acidic pH conditions

The comparison between the Albeluvisol Bt-horizon under forest, considered as a reference stage, and the E&Bt-horizon of the same soil under agriculture illustrates the impact of pH conditions close to neutrality. After at least 200 years of cultivation, a higher abundance of illite is observed under agriculture that may be attributed to fertilisation and collapse of 2:1 clays minerals following K exchange. This was in agreement with the higher proportion of K on the cation exchange capacity (CEC) under agriculture than under forest (Table 1). The reversible transformation of vermiculite or smectite layers into illite in surface horizons was already observed on time scale ranging from 3 months at the rhizospheric scale to 83 years in other environments (see Table 3 for details). Therefore, despite a consensus on the rapidity of this transformation (from tenths of years to a century, or even more rapid locally, Table 3), large discrepancy in velocity remains in the literature. This might be due:

- to differences in efficiency of the considered environment in recycling K either due to the soil properties or to the plant specificity or;
- to a lack of samples to properly define the kinetic of the process and;
- to the heterogeneity of the 2:1 swelling clay minerals and their response to K supply.

4.1.2. Formation of hydroxy-interlayered-minerals

The increasing abundance of Al-interlayered 2:1 clay minerals from the Bt-horizon to the E&Bt-horizon in the forested Albeluvisol on one hand and from the Dystric Cambisol under meadow to the forested ones on the other hand, illustrates the impact of acidic conditions ($pH < 5$) on clay evolution.

In both examples, under the forest, soils undergo progressive acidification and interlayer calcium (or magnesium) is progressively replaced by aluminium on time scale of a few decades. This was due to the release of aluminium (Al^{3+} or hydroxylated forms) under acidic conditions (pH 4 to 5). However, apart from the study by Calvaruso et al. (2009) who worked on rhizospheric soil samples, the rapidity of this process (a few decades) was rarely demonstrated (Table 3).

Table 3
Time scales of clay mineral evolution due to different processes.
Tableau 3
Durées d'évolution des minéraux argileux sous l'impact de différents processus.

Clay evolution route	Soil type	Change induced by	Duration	Reference
K exchange		Continuous corn cropping	80 yrs	Velde and Peck, 2002
Illite - > smectite or vermiculite	Ferralsol	Agriculture without K input	10 yrs	Bortoluzzi et al., 2005
	Experimental alteration of phlogopite	Roots of Italian ryegrass	32 days	Hinsinger and Jaillard, 1993
	Marsh soils	Polders of different ages	80 to 330 yrs	Righi et al., 1995
	Albeluvisol developed on loess	Liming	> 200 yrs	This study
Smectite or vermiculite - > illite	Mesic Aquic Argiudoll	Continuous corn cropping	80 yrs	Velde and Peck, 2002
	Luvisol	K-fertilisation	70 yrs	Pernes-Debuyser et al., 2003
	Luvisol	K-fertilisation	40 yrs	Barré et al., 2008
	Ferralsol	Eucalyptus plantation	33 years	Mareschal et al., 2011
	Not specified	Forest monoculture	41 yrs	Tice et al., 1996
	Inceptisols with gleying on schist	Forest, grass land and cropping	50 yrs	Bain and Griffen, 2002
	Typic Dystrochrepts on volcanic tuff	Rhizosphere	3 months	Turpault et al., 2008
Al exchange: formation of HIV or HIS	Typic Dystrochrepts on granite	Rhizosphere	Not specified	Calvaruso et al., 2009
	Forest acid soils (Humods, Orthods, Ultisols, Oxisols, Dystrochrepts)	In situ resin and test mineral bag experiment	1–12 mths	Ranger et al., 1991
	Albeluvisol developed on loess	Forest	> 200 yrs	This study
	Dystric Cambisol developed on gneiss	Reforestation	60 yrs	This study
	Young poorly differentiated soils	Chronosequence on unconsolidated sandy sediment	40 yrs	Caner et al., 2010
Podzolisation: weathering of chlorite and illite and formation of smectite	Cambisol on sandstone	Forestation	81 yrs	Herbauts and de Buyls, 1981
	Soils on dunes	Afforestation with pine and spruce	80–100 yrs	Stützer, 1998
	Soils developed on recessional moraines	Glacier retreat	38 yrs	Burt and Alexander, 1996
	Acid soils on moraines	Glacier retreat	80 to 3000 yrs	Righi et al., 1999
	Dystric Cambisol developed on gneiss	Reforestation	60 yrs	This study

4.2. Rapid clay dissolution and new formation by podzolisation

The forestation of the meadow 60 years ago led to soil acidification which increased:

- the weathering of chlorite and mica compared to the residual meadow;
- the subsequent formation of ordered illite/vermiculite MLM and;
- the release of aluminium.

In this pH range, aluminium was partly exported into soil solution (Cornu et al., 2008) or incorporated into 2:1 clay minerals to form hydroxy-aluminium minerals (Dixon and Weed, 1989).

This pathway is classical of the weathering of mica (usually biotite) and chlorite in acidic soils and for incipient podzolisation (Robert, 1973).

In addition, in this study we showed that the two tree-species did not affect the clay minerals at the same depth. Under spruce, the transformations occurred in the surface horizon (0–6 cm) and at higher depth while under Douglas-fir the transformations mainly occurred at 30–38 cm. These differences may be attributed to different litter composition and/or to different roots systems of the species. Spruce litter is known to decay very slowly and produce high amounts of organic acids inducing weathering from the soil surface, while Douglas-fir litter is rapidly decayed with lower production of organic acids and enhances nitrification and subsequent production of HNO_3 (Andrianarisoa et al., 2010). Under this latter, tree species weathering at higher depth may be related to the root activity. The approach used here was however not quantitative enough to determine a relative kinetic among the two tree species.

These results are in agreement with previous works concerning the rapid development of podzolisation in a few tenths of years after a change in vegetation or the forestation of young material poor in nutrients (see Table 3 for details). Among these studies, Caner et al. (2010) demonstrated a clear and rapid impact on clay mineralogy.

4.3. Rapid modification of the soil clay mineralogy by eluviation

For the soil sequence on Albeluvisol described above, we observed that both under forest and close to the drain the white-grey volume mainly but also the ochre volume, in the E&Bt-horizon, were characterised by:

- a loss of < 2 μm fractions;
- a decrease of the abundance of I/S MLM and smectite and;
- an increase in illite and chlorite.

These changes in the clay mineralogy as a function of depth were attributed to eluviation that is considered as selective of smectite (Jamagne, 1973). The higher impact of eluviation on clay mineralogy of the white-grey volume was attributed to the combining effect of:

- the more advanced stage of eluviation in the white-grey volume (14% in < 2 μm) than in the ochre ones (22% in < 2 μm);
- the higher quantity and velocity of water flowing through the white-grey volume compared to the ochre one (Frison et al., 2009) and;
- iron oxides acting as cement in the ochre volume while their lack in white-grey volume favoured eluviation.

These changes were significant after only 16 years of drainage showing the rapidity of the process. As mentioned above, eluviation is classically considered as selective of smectite (Jamagne, 1973). However, controversial results exist in the literature on that point. Indeed, while results by Mercier et al. (2000) and Rousseau et al. (2004) – who analysed the 0.1 μm fraction at a drain outlet and particles collected from undisturbed Luvisol column submitted to simulated rainfall – showed that eluviation was selective of smectite, Pernes-Debuyser et al. (2003) showed that losses of < 2 μm particles from the E horizon of Luvisol did not induce any mineral change in the considered horizon. The results obtained here showed that the < 2 μm particles collected at the outlet of the drain had a mineralogy close to that of the white-grey volume at 60 cm from the drain and thus originated most likely from this soil volume. This showed that the observed process is active on a short distance to the drain and not really selective, except for kaolinite. This conclusion is in agreement with results of Pernes-Debuyser et al. (2003). On the opposite, the analysis of < 0.1 μm particles collected at the outlet of the drain showed that the process was highly selective of smectites as described by Mercier et al. (2000), and that particles were close in mineralogy from all soil volumes except the white-grey volumes at 60 cm. Particles in that case may have a further origin than the entire < 2 μm fraction.

Therefore, the apparent contradiction of the results observed in the literature is due to the considered particle size fraction as the selectivity is only observed on the finest fraction. In some soils, this fraction can be occulted while analysing the < 2 μm fractions only (Hubert et al., 2012; Righi and Elsass, 1996).

4.4. Rapid change observed but some uncertainty on the kinetics remains

Our results and previous studies (Table 3) showed that soil clay mineral modifications (modification of the interlayer site occupation, dissolution/precipitation or eluviation) can occur rapidly. However, the time scale needed for these processes is still rather large ranging from a few months to hundreds of years. This large discrepancy has two explanations:

- only integrated kinetics are available due to the poor resolution in time of the studied soil sequences that moreover covered various time spans ranging from some months to several centuries, such time-dependant mean kinetics does not allow a proper kinetic approach of soil evolution;
- differences into the environment where the process occurs may also influences their velocity. It is, for example, well known that micro-sites in soils, as the plant rhizosphere or the drilosphere, are especially reactive chemical environment enhancing clay transformation (Calvaruso et al., 2009, Jouquet et al., 2005, 2007). At a broader spatial scale, the presence of aluminium-interlayered minerals in podzols developed on gneiss (this study) has to be related to the composition of the parent material. Indeed gneiss has a higher reserve in weatherable minerals, compared to the sediments studied in other cited works, which buffers strong acidification by mineral weathering and release of aluminium. Another explanation involved in this large time-scale discrepancy might be due to synergy or antagonisms among processes as illustrated by the example of the forested Albeluvisol in which smectites are lost due to eluviation and partially transformed into HIS. By contrast, under agriculture Luvisols, liming provides calcium (and magnesium) limiting the intensity of eluviation. In addition, calcium may be partly bound to the 2:1 clay minerals allowing them to swell depending on the amount of expansible (smectite) layers. On the other hand, K-fertilisation revert smectite into illite. At last, close to the drain, eluviation is reactivated.

A last source of uncertainty is due to the semi-quantification that hinders inter-site comparison studies. Thus, quantitative method of XRD-analysis is needed. In that frame, the full XRD profile fitting of experimental XRD-patterns based on one-dimension XRD calculations, initially developed for studies on burial diagenesis series (Lanson et al., 2009; McCarty et al., 2008) and recently first applied to soils (Hubert et al., 2009, 2012) is particularly helpful to assess clay phase quantification and their properties.

5. Conclusion and outlook

Thanks to recent advances in XRD-pattern treatment by DecompXR (Lanson, 1997) notably, semi-quantitative analyses of clay assemblage evolution along soil chronosequences or dated soil anthroposequences were performed. This study demonstrates that significant clay mineralogy changes occurs on time scales as short as a few tenths of years as a result of a great diversity of soil processes including ion exchange, partial dissolution or eluviation. The observed changes are more rapid than the velocity classically admitted for such evolution in the literature, which are based on the results of laboratory-experiments. The discrepancies observed between laboratory-determined and some rapid field weathering has two main explanations:

- the clay minerals generally used in these experiments are better crystallised than the ones encountered in soils;
- the existence in soils of reactive micro-sites in soils (e.g. rhizosphere).

However, the time scale found for these processes is still rather large ranging from a few months to hundreds of years. This might be due to differences into the environment where the process occurs. The study of other well-documented soil sequences using quantitative clay mineral determination should allow significantly reducing the uncertainty on the rates of clay minerals evolution in soils.

Finally, considering on one side, the rapidity of change in the clay mineralogy in soils and, on the other side, the key role of the clays in most soil services (soil organic matter storage, water retention, nutrient supply, pollutant filtration, physical stability...), impact of human activities on these minerals and their consequences should be studied with more attention. This is a pre-requisite to develop sustainable agriculture or to propose agricultural practices to mitigate the impact of climate change on soils.

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