

CLAYS DEVELOPED UNDER *SEQUOIA GIGANTIA* AND PRAIRIE SOILS: 150 YEARS OF SOIL-PLANT INTERACTION IN THE PARKS OF FRENCH CHÂTEAUX

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Abstract—The effect of plant species on soil-clay mineralogy has not been studied widely. In the present study, the clay mineralogy of top soils under *Sequoia gigantea* and grass regimes, maintained side by side for up to 150 y in the parks of several French châteaux, were investigated using X-ray diffraction (XRD) methods and chemical analyses of the clay fractions. The seven paired samples that were studied originated from soils developed on calcareous, granitic, and loess substrates. The XRD data indicated the presence of a trioctahedral chlorite with a trioctahedral hydroxy-Mg sheet in sequoia soils observed in four of seven of the sites whereas it was absent from the adjacent prairie-soil samples. Parent materials influenced the formation of magnesian chlorite as it was observed in all soils developed on granite and in none of the soils developed on limestone. The exchangeability of the interlayer hydroxy-Mg sheet replaced by K^+ from newly formed chlorite in a 14 y old sequoia-influenced soil suggests that the mineral was initially a hydroxy-interlayered mineral. Increased stability was observed in the older (100 and 150 y) soil chlorites, indicating a progression of polymerization of the Mg hydroxy-interlayered material. The small amount of chlorite in the whole clay assemblage impeded the observation of changes in Mg content by direct chemical measurements of the clay fractions but the systematically greater amount of exchanged Mg^{2+} ion measured under sequoia compared with adjacent prairie supports the formation of Mg magnesian chlorite.

The results presented indicate, on the one hand, the importance of plant regimes in controlling the soil chemistry and hence the clay mineralogy of surface soil horizons (magnesian chlorites were observed only under sequoia), and, on the other hand, that parent material modulates this plant influence (chlorite formation was observed on granite-derived soils).

Key Words—Chlorite, Plant Species, Sequoia Tree, Soil, X-ray Diffraction.

INTRODUCTION

The activities of plants determine to a large extent the physico-chemical conditions in soils. As a result, plants have a significant impact on clay mineralogy in the upper soil horizons. Plant regimes have been observed to increase clay weathering due to K^+ and Mg^{2+} uptake from phyllosilicate minerals (e.g. Hinsinger *et al.*, 1992, 1993; Khademi and Arocena, 2008) or through the acidifying action of their roots (Kelly *et al.*, 1998; Eick *et al.*, 2009). Conversely, the plant-mediated translocation of elements from deep soil to the surface (detailed in Jobaggy and Jackson, 2004) can stabilize certain types of clay minerals which would otherwise be lost by alteration processes. For example, Lucas *et al.* (1993) showed that Si translocation leads to the stabilization of kaolinite at the expense of gibbsite in the upper horizons of a Brazilian tropical soil and Barré *et al.* (2007a) observed that illite content usually increases near the surface of temperate grassland soils due to K^+ translocation. These past studies indicated that plant action can lead to the modification of the structure of the clay layer itself or to a modification of the occupancy of interlayer sites. Modifications of interlayer composition can be

very rapid. This was observed on a daily time scale under laboratory conditions (Hinsinger *et al.*, 1992, 1993), at the decade time scale (Barré *et al.*, 2008), or even at the monthly time scale under field conditions (Turpault *et al.*, 2008).

Since the pioneering work by Zinke (1962), several studies have supported the idea that single-tree stands can influence the physico-chemical properties (mostly pH and exchangeable cation quantities) of the surrounding soil (e.g. Boettcher and Kalisz, 1990; Amiotti *et al.*, 2000). As a result, they should influence clay mineralogy in different ways. However, species-related transformations of clays in soils have been little studied thus far. Recent work has indicated the importance of different plants (grass and forest regimes) on the clay minerals found in their soils (Madsen and Norberg, 1995; Tice *et al.*, 1996; Augusto *et al.*, 2001; Bain and Griffen, 2002). Nonetheless, little quantitative information has been gathered on the chemical and clay mineralogical changes induced by different plant regimes. Furthermore, the influence of time and parent-rock factors on clay mineralogy has usually not been considered. The parent-rock factor could be of particular importance for the observation of clay modifications. First, it influences the physico-chemical conditions of the soil and, second, some of the minerals it contains can be precursors for other minerals (e.g. high-charge phyllosilicates form illite-like minerals

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upon K⁺ saturation). The present study aims to fill parts of this information gap by comparing clay suites developed simultaneously under grass-regime soils and under *Sequoia gigantea* in a temperate Atlantic climate (central western France) on three types of soil substrates.

The introduction of the sequoia tree into France followed its 'discovery' in the 1850s by European botanists. Newly renovated parks around chateaux and grand estates in the romantic gardening style led to their placement in the middle of grass or lawn areas. Such trees have been in place since that time and the grass has been mowed continuously around them, maintaining a prairie-type vegetation. This situation allows one to observe the development of the soil clays under two much contrasted plant regimes over the 150 y period in the same starting clay materials since their introduction into the parks. In the region of study, essentially three major types of geological units are apparent, limestone of Mesozoic age (edge of the Paris basin), granite-schist basement of Precambrian age (Armorican massif), and loess or Tertiary clay-rich materials. The old alteration sequences were affected variously by glacial action in the area studied (Central Western France), usually removing the surface-soil portion resulting in a truncated soil profile. Subsequently, loess was deposited and reworked depending on the topography. Hence, the soil profiles in this area are heterogeneous in terms of their history. Further, the creation of the parks where the sequoia-lawn pairs were planted was often made from a slightly remodelled landscape where levelling and soil additions were practiced to give a more harmonious aspect to the landscape. The soil type and any nomenclature one could propose for the different sampling sites are, thus, subject to caution. However, the one common trait for the plant regime pairs investigated here is the simultaneous development of clays from the same starting point.

The aim of the present study was to observe the clay-mineral modifications induced by the introduction of sequoia. To that end, the clay mineralogy and soil-clay chemical compositions of five 150 y old and one 100 y old and one 14 y old sequoia-grass pairs (three

developed on granite, two on limestone, and two on loess or siliceous clay-rich deposits) were investigated. Based on the pioneering work by Zinke (1962) on the influence of sequoia trees on soil physico-chemical properties and some other studies, the following differences between the clays in prairie and sequoia soils were expected: (1) greater clay content under grassland due to lesser weathering intensity of secondary phyllosilicates and greater translocation of Si from depth to the surface by grasses (Hodson *et al.*, 2005); (2) greater hydroxy-interlayered vermiculite content under Sequoia due to its acidifying activity; (3) greater illite content under grassland due to translocation of more K from depth by grasses; and (4) modulation of these effects according to parent material.

MATERIALS AND METHODS

Sampling sites

The sampling was from the upper 10 cm of the mineral soil (litter excluded). The scientific reason for this sampling strategy relies on the fact that plant influence (root activity and element translocation through litter deposits) is greater near the surface and decreases with depth (Jobbagy and Jackson, 2004; Schenk and Jackson, 2002). Studying this zone, therefore, maximizes the probability of observing a plant effect. The practical reason for this sampling technique was that the proprietors of the châteaux often did not wish to have a deeper and larger hole dug in their gardens or parks. At each sampling location (Table 1), two soil samples of ~200 g were taken, one under the sequoia and the other in the prairie 10 m from the sequoia trunk. In addition to the 0–10 cm sample, a 0–1 cm sample and a 4–6 cm sample were obtained at La Percerie where the youngest of the seven sequoias was planted. Soil samples were air dried and sieved to <2 mm.

Soil properties and analysis methods

Particle-size distribution (PSD), pH, and exchangeable cations were measured at the INRA 'Laboratoire d'Analyses des Sols d'Arras' (France). The PSD was

Table 1. Description of sampling sites (based on a map taken from <http://www.hist-geo.com/>).

Letter	Site	Sequoia age (years)	Soil substrate	Chlorite under sequoia
R	Richelieu	150	Limestone	
LH	Les Herbiers	100	Granite	X
V	Villedieu	150	Loess	
S	Secondigny	150	Granite	X
P	Pontlevoiy	150	Limestone	
B	Bressuire	150	Granite	X
LP	La Percerie	14	Cherty clay sediment	X



determined according to the norm NF X 31-107 (Baize, 1995; AFNOR, 1999). The pH was measured in water (5:1 v/v water:soil) according to the norm NF ISO 10390. Exchangeable cations were extracted using ammonium acetate (norm NF X 31-108; AFNOR, 1999) and measured by absorption flame spectrometry.

Clay-fraction extraction

The soil samples were treated in the following manner in order to preserve the initial, natural state of the clays. For each sample, 20 g of each soil was shaken with 100 mL of de-ionized water at 175 rpm on a shaking plate over 16 h. Clay fractions were recovered by the extraction of the <2 μm size fraction after gravity sedimentation. The supernatant containing the clay fraction was poured into a beaker. This procedure was repeated until the supernatant was quite clear. All the supernatants collected for a given soil sample were pooled. The suspension was then flocculated using a dilute (0.01 M) SrCl_2 solution. Subsamples of flocculated samples were saturated with K^+ using a 1 M KCl solution.

X-ray pattern acquisition and numerical treatment

Oriented preparations were made by pouring several drops of the clay suspension onto a glass slide. Air-dried, glycol-treated clay mounts were analysed using a PANalytical Xpert Pro diffractometer. The instrument was set in the θ/θ Bragg-Brentano configuration, with an optical system defined using the following settings and parameters: anti-scatter and diffusion slits of 0.25 and $0.5^\circ 2\theta$, respectively, Soller slits of 0.04 radians, Ni filter for Cu radiation, and an Xccelerator detector counting simultaneously over an angular range of $2^\circ 2\theta$. The resulting XRD patterns were then decomposed (after background subtraction and a four-point smoothing routine) using the *Decomp* program (Lanson, 1997). Peak areas were determined as the product of peak height and width at half height. The center of gravity position of the XRD patterns in the 001 2:1 clay area was calculated according to Barré *et al.* (2007b). This indicator gives an insight into the total amount of layers “closed” to 10 Å: the smaller the center of gravity position, the greater the number of 10 Å layers (as discrete illite or in mixed-layered minerals).

Clay-mineral nomenclature

In the present study the differences in clay mineralogy were probably not due to a dissolution-recrystallization process because the periods of time involved were much too short. Hence, one should consider less drastic methods of changing the clay-mineral compositions. The first obvious change is that of cationic occupation in the interlayer ion site. In a 2:1 clay mineral with a certain charge on the silicate structure, a certain amount of change of interlayer ions is known to occur by different treatments in the laboratory. These chemical variations

lead to different responses in cell dimension and, hence, in identification of the clay phase. Essentially, one can find four types of 2:1 clay phases in soils based on variations in interlayer ion occupation: (1) illite with an anhydrous layer of potassium (10 Å interlayer spacing) and no changes occur upon glycol treatment; (2) smectites with a hydrous interlayer cation population with a 15.2 Å spacing in the air-dried state for Sr^{2+} saturation (two water-layer hydration state); the spacing changes to 17 Å upon treatment with glycol; (3) hydroxy interlayered (HI) ion structure (soil vermiculite) with a 14.2 Å interlayer spacing – such minerals can include soil chlorites; no change occurs upon glycol treatment; and (4) mixed-layer HI chlorite/illite mineral (see Li *et al.*, 2003); peaks are found near 12 Å and 11.8 Å depending on the relative proportion of illite and HI layers, and changes do occur upon glycol or K^+ treatments.

In the case of smectites, or smectite layers in interstratified clays, a certain proportion of the layers can become illite-like upon K^+ saturation (see Velde, 2001, for examples). The same is true for HI minerals. This can lead to the formation of ‘illite’ minerals with peaks at 10 Å for well crystallized illite (WCI) (see Lanson, 1997) or peaks near 10.4 Å for poorly crystallized illite (PCI) with fewer coherent diffracting layers in the crystallite. Shifts in the peak position of the mixed-layered minerals indicate the presence of newly formed anhydrous K layers.

To delve more deeply into the identification of HI phases, X-ray patterns were calculated for different types of HI and chlorites with different combinations of interlayer hydroxy cations and 2:1 site occupancies (E. Ferrage, University of Poitiers, pers. comm.). For details on the method, refer to Ferrage *et al.* (2005). These calculations allowed a better characterization of the chlorite-type minerals which were observed in this study. The chlorite-type minerals are abbreviated as follows in the present work: ‘di,tri’, ‘di,di’, ‘tri,di’, and ‘tri,tri’ referring to dioctahedral interlayer and trioctahedral 2:1 layer, dioctahedral interlayer and dioctahedral 2:1 layer, trioctahedral interlayer and dioctahedral 2:1 layer, and trioctahedral interlayer and trioctahedral 2:1 layer, respectively.

Extraction of the hydroxy-interlayered cations

When the formation of magnesian chlorite under sequoia was reported, the extraction of the hydroxy-Mg sheet was attempted using 1 M KCl solution, which is common for exchangeable hydroxy-Al ions (Norfleet and Smith, 1989).

Elemental composition of the clay fraction

Sub-samples of the clay fractions were compacted into disks 6 mm in diameter and 2 mm thick using a hand press and mounted on glass slides, coated with carbon, and then subjected to electron microbeam irradiation.

The resulting X-ray fluorescence radiation was analyzed for major elements using an SEM (scanning electron microscope, EDS-X-ray fluorescence analysis): for details, see Velde (2006). Values for K₂O were considered to be accurate to within 8% of the amount present or near 0.2 wt.%.

Statistical analysis

Data from sequoia and prairie soils were compared in an Excel[®] spreadsheet using a pairwise t-test.

RESULTS

Soil characteristics

The clay contents, pH, and amount of exchangeable ions in the different soils are listed in Table 2. The clay contents were slightly greater on average under prairie than under sequoia but the difference was not statistically significant. The pH was slightly greater on average in sequoia soils than in the adjacent prairie soils, though again, the difference was not significant. Exchangeable cations other than Na⁺ and Mg²⁺ were rather indifferent to the planting regime. The amounts of exchangeable Na⁺ and Mg²⁺, however, were significantly greater under sequoia compared with the adjacent prairie. As the quantity of Na⁺ was small compared to the other cations and Na⁺ is not usually a determining factor in mineral stability, its role could be assumed to be anecdotal. The significantly greater amount of exchangeable Mg²⁺, however, was important for the minerals found, as described below. On average, the K₂O content in the clay fraction under sequoia was greater but this difference was not significant. Otherwise, no trend was observed (Table 3).

General description of clay assemblages observed on the different sites

Clay-mineral assemblages observed in this study look much like other assemblages classically described in temperate-region soils (e.g. Velde, 2001), either prairie or forest vegetation (Figures 1, 2). Two illite peaks and two types of illite-smectite (one with a proportion of smectite (S/I) and another with an illitic composition (I/S)) were commonly identified. Kaolinite was also present in all samples, and HI minerals were observed in the clay fractions recovered from the Bressuire, Secondigny, Les Herbiers, and La Percerie samples. These kinds of assemblages seem typical of temperate soils either under prairie or forest (Velde, 2001). The effect of sequoia on the clay mineralogy was variable but distinct compared to adjacent prairie soils. Decomposition methods of the X-ray patterns were used in order to better differentiate the specific minerals in the clay assemblages.

Formation of magnesian chlorite in some soils influenced by sequoia

At first sight, all clay assemblages contained illite, I/S materials, HI minerals, and kaolinite. A closer inspection of the XRD patterns near 7 Å revealed, however, the presence of a sharp peak at 7.08 Å for the sequoia soil samples (Figure 3). This peak is the 002 second order peak of the 14.2 Å basal spacing and indicates the presence of a chlorite where the interlayer cation sites are complete with few or no vacancies (see Meunier, 2007, for details). A similar sharp peak at 7.08 Å was observed in the sequoia soils at Bressuire, Les Herbiers, Secondigny, and La Percerie in the

Table 2. Selected soil characteristics in sequoia and prairie soils.

Site	Vegetation	Clay content (%)	pH	Exchangeable cations (cmol+/kg)						
				Ca	Mg	Na	K	Fe	Mn	Al
Richelieu	Prairie	22.10	6.81	25.50	1.00	0.07	0.34	0.02	0.02	0.05
Richelieu	Sequoia	11.90	7.91	17.00	1.10	0.20	0.67	0.03	0.00	0.07
Les Herbiers	Prairie	19.70	5.82	6.04	1.62	0.14	0.26	0.01	0.28	0.13
Les Herbiers	Sequoia	18.40	5.57	13.70	2.60	0.46	0.24	0.01	0.75	0.14
Villedieu	Prairie	38.20	5.76	12.10	1.65	0.18	0.31	0.01	0.12	0.15
Villedieu	Sequoia	29.90	4.86	11.10	2.79	0.70	0.75	0.01	0.27	0.42
Secondigny	Prairie	21.80	5.07	6.13	0.90	0.08	0.65	0.02	0.19	0.48
Secondigny	Sequoia	23.10	5.30	7.97	2.04	0.35	0.62	0.01	0.38	0.26
Pontlevoy	Prairie	17.40	6.81	13.90	0.85	0.06	0.83	0.01	0.09	0.05
Pontlevoy	Sequoia	22.50	7.29	20.70	1.79	0.42	0.98	0.01	0.03	0.04
Bressuire	Prairie	17.40	5.12	6.72	0.98	0.07	0.15	0.01	0.10	0.27
Bressuire	Sequoia	13.80	4.88	4.15	1.13	0.48	0.87	0.01	0.13	0.61
La Percerie	Prairie	27.60	5.37	8.83	1.95	0.10	1.23	0.02	0.39	0.15
La Percerie	Sequoia	24.40	6.40	14.40	3.39	0.20	0.53	0.01	0.02	0.03

Table 3. Oxide wt.% of major elements in the clay fractions of the samples studied.

Site	Vegetation	Oxide wt.% abundances in clay fractions								
		Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	MnO	FeO
Richelieu	Prairie	0.17	2.42	16.63	64.32	0.21	2.83	2.71	0.01	10.72
Richelieu	Sequoia	0.11	1.41	18.12	60.97	0.14	2.67	7.57	0	9.01
Les Herbiers	Prairie	0.52	1.75	27.36	56.72	0.03	2.84	1.69	0.04	9.04
Les Herbiers	Sequoia	0.73	2.02	26.45	57.28	0.17	3.99	1.29	0.08	7.98
Villedieu	Prairie	0.31	2.35	26.07	59.05	0.2	4.44	1	0.01	6.56
Villedieu	Sequoia	0	2.39	26.47	58.47	0.2	4.94	0.89	0.01	6.62
Secondigny	Prairie	0.14	3.21	31.89	50.04	0.32	2.1	0.66	0.02	11.61
Secondigny	Sequoia	0.55	3.02	27.91	55.08	0.26	2.6	1.01	0.05	9.53
Pontlevoy	Prairie	0.17	1.23	21.85	64.82	0.21	2.97	1.72	0.01	7.02
Pontlevoy	Sequoia	0.56	1.6	20.49	58.78	0.25	2.79	9.27	0	6.26
Bressuire	Prairie	0.11	1.41	18.12	60.97	0.14	2.67	7.57	0	9.01
Bressuire	Sequoia	0.11	1.26	28.94	59.08	0.36	3.41	0.6	0.04	6.2
La Percerie	Prairie	0.28	0.42	15.04	74.43	0.17	1.94	0.54	0.04	7.13
La Percerie	Sequoia	0.24	0.51	14.83	74.23	0.11	1.97	0.83	0.05	7.23

0–1 cm samples but not in the 0–10 cm samples. This peak was not reported either under sequoia at the three other sites or in any of the seven grassland soils. Further, in the older samples (100–150 y of sequoia growth) the 060 peak region showed the presence of a 1.54 Å peak under sequoia on granite, indicative of a trioctahedral mineral, but which was essentially absent under prairie (Figure 4). The 1.54 Å peak is normally seen in chlorite structures only when both the interlayer and 2:1 octahedral sites are magnesian (see Brindley and Brown, 1980).

E. Ferrage (pers. comm.) calculated the X-ray patterns for different configurations of 2:1 minerals, including trioctahedral and dioctahedral 2:1 layer

structures with hydroxyl-Al and hydroxyl-Mg interlayers (Figure 5). The greatest difference between the peak intensities for the 001 and 002 (14 and 7 Å) reflections occurs in the Mg interlayer, dioctahedral 2:1 (Al) structure (tri,di) chlorite, for which the 14/7 Å peak ratio is ~0.35. Magnesium interlayer, trioctahedral (Mg) 2:1 structure (tri,tri) chlorite has a 14/7 Å ratio of 0.78. A larger Al content increases the 14 Å peak intensities, causing the all-Al interlayer, trioctahedral (Mg) structure (di,tri) chlorite to have a 14/7 Å ratio of >1. In the La Percerie sample, the ratio was 0.4, while in the calculated XRD pattern for magnesian interlayer tri,di-chlorite the ratio was 0.35 (Table 4). Reported activity under sequoia, therefore, apparently produced mostly

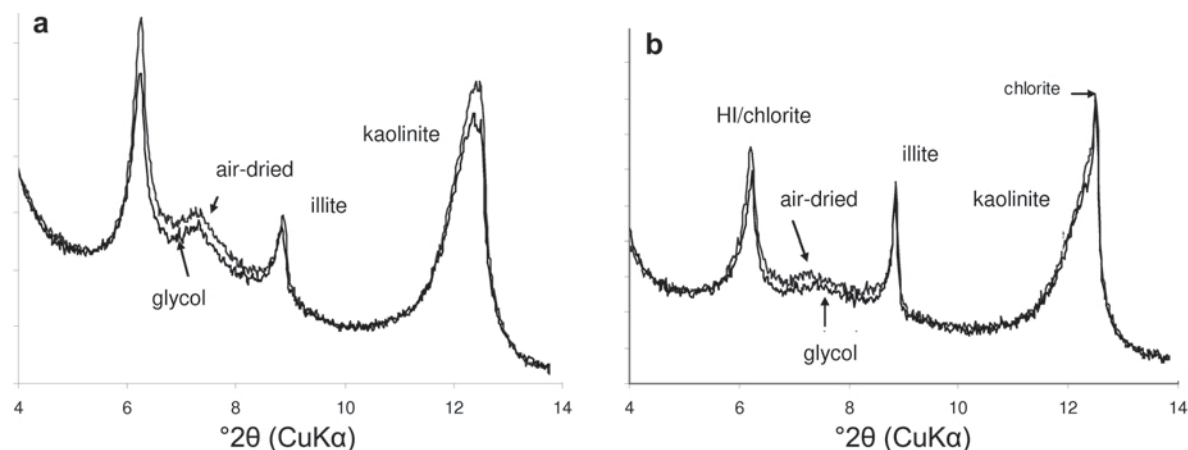


Figure 1. XRD patterns of soil-clay fractions sampled at Secondigny in air-dried and glycolated (glycol) states under prairie (a) and sequoia (b).

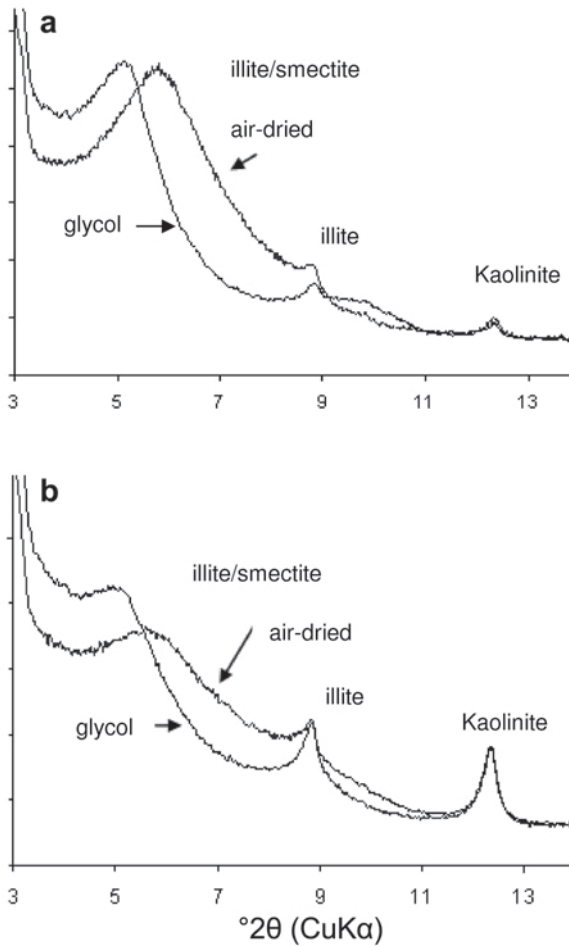


Figure 2. XRD patterns of soil clay fractions sampled at Richelieu in air-dried and glycolated (glycol) states under prairie (a) and sequoia (b).

tri,di-chlorite with a magnesian interlayer at this location. In the Segondigny sample, the ratio was 0.70, a value which could indicate either a greater Al³⁺ content in the interlayer cation sites (with Mg²⁺ still the dominant cation) or a trioctahedral 2:1 mineral structure.

Table 4. 14/7 Å peak intensities for the chlorites in the sequoia soils and the different values for the simulated chlorite XRD patterns. Mg and Al refer to the composition of the interlayer hydroxyl sheet.

Sample	14/7 Å intensity
La Percerie	0.40
Segondigny	0.70
Les Herbiers	0.72
tri,di Mg	0.23
di,di Al	2.00
tri,tri Mg	0.78
di,tri Al	2.45

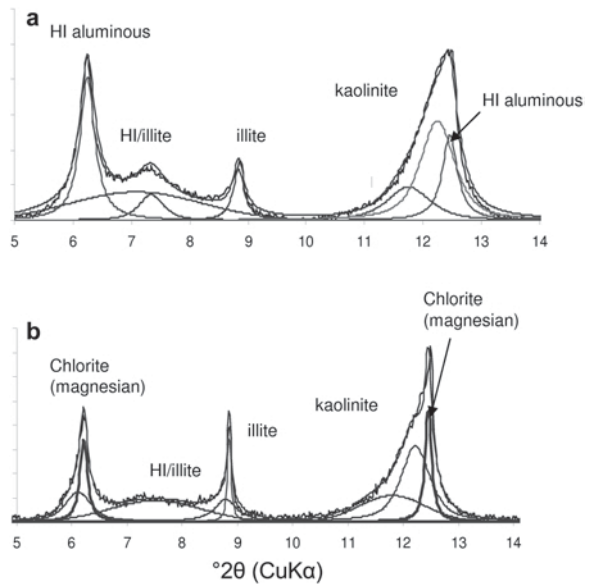


Figure 3. Decomposed XRD patterns of the clay fraction recovered in grassland (a) and sequoia (b) soils at Segondigny. A sharp peak at 7.08 Å is seen in the sequoia soil but not in the grassland soil.

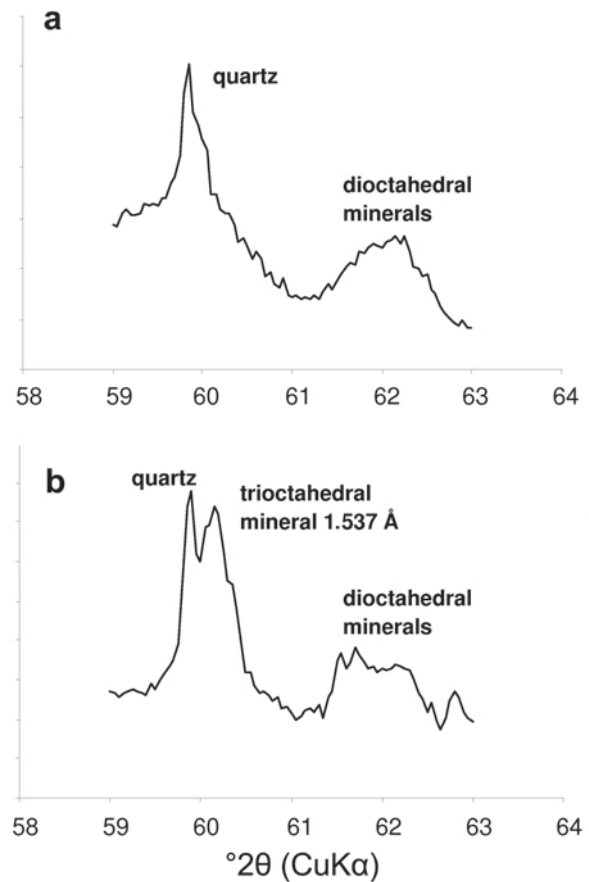


Figure 4. XRD patterns of soil clay fractions sampled at Segondigny in the 060 peak region under prairie (a) and sequoia (b).

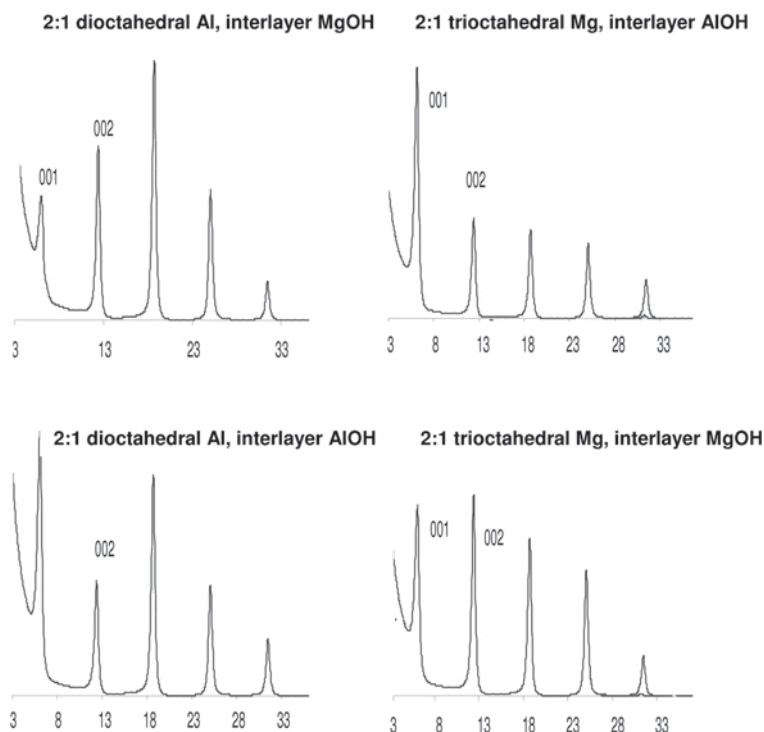


Figure 5. Calculated XRD patterns for different compositional configurations of 2:1 hydroxy-interlayered minerals (calculations by Eric Ferrage, University of Poitiers, see Ferrage *et al.*, 2005 for details) where dioctahedral and trioctahedral ion occupancy (Mg^{2+} ions) are permuted.

The position of the 060 peaks for the Segondigny samples indicated the presence of a trioctahedral mineral. Thus, the 14.2 Å mineral in the sequoia soil here is considered to be a magnesian tri,tri-chlorite. The HI peaks in the Les Herbiers sample under sequoia were similar to those in Segondigny sequoia samples. The peaks in the Bressuire sequoia sample were not of sufficient intensity to extract the 14 Å reflection from the HI mineral assemblage present and, hence, no peak ratios were determined.

Extraction of the hydroxy interlayer cations using 1 M KCl solution was successful for the hydroxy-Mg sheet in the clay fraction of the 14 y old La Percerie sequoia sample (planted in the lawn), in the location where the influence of sequoia was most recent (Figure 6). No effect was noted for the older Segondigny, Les Herbiers, and Bressuire samples (150 y of sequoia), suggesting the presence of a stable magnesian tri,tri-chlorite.

Sequoia trees and accumulation of K: do they promote illite-layer formation?

Barré *et al.* (2008) reported that K-cycle modification can rapidly affect the proportion of “illite-like” layers in soil-clay assemblages at the field scale. Chemical data for the clays under sequoia and prairie regimes indicated a trend of concentration of K^+ under sequoia, especially for granite soils (Table 3). However, this trend led to no

significant clay modifications either when all soils were considered or when the analysis was restricted to granite soils. Indeed, no significant differences between prairie and sequoia soils were observed in terms of illite peak area (PCI+WCI) or center of gravity position (Table 5).

DISCUSSION

The sharp peak at 7.08 Å representing the 002 second-order peak of the 14.2 Å basal spacing was observed in four of seven sites under a sequoia regime. Even if it has not been observed under every sequoia, the fact that it was not observed in any of the clay suites of prairie soils suggests that its origin is related to the presence of sequoia. The data from the La Percerie site indicate that the sequoia influence on clay mineralogy occurs rapidly, *i.e.* after <14 y. As the influence of sequoia decreased with depth at La Percerie (1 cm compared to 10 cm depth), the influence of sequoia is probably related to the physico-chemical conditions imposed by the decomposing above-ground litter and dissolved matter in rain water falling through the tree branches.

X-ray data provided several strong arguments supporting the conclusion that the chlorite formed under sequoia is tri,tri-magnesian chlorite: (1) a sharp peak at 14.2 Å unmodified by glycol treatment; (2) 14/7 Å peak ratio close to those calculated for fully tri,tri-chlorite;

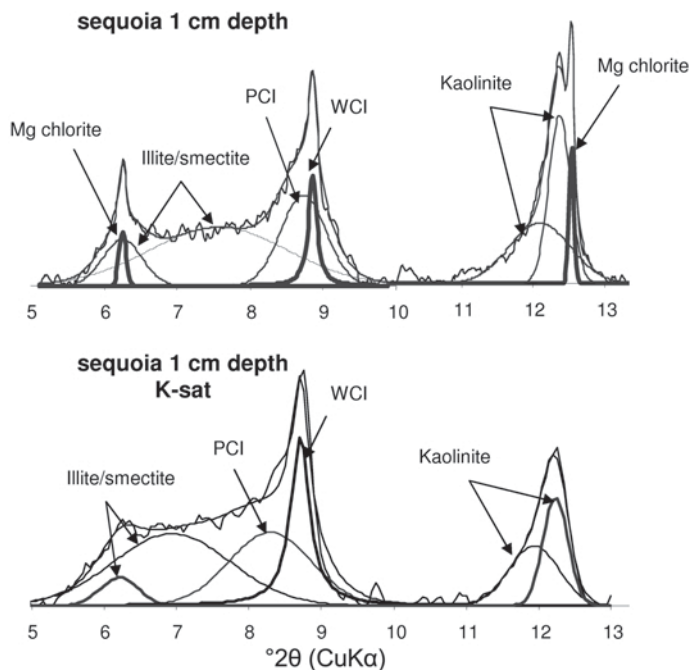


Figure 6. Decomposed XRD patterns of soil samples (taken from depths of 1 cm) at La Percerie, under sequoia in air-dried and K^+ -saturated (K-sat) states.

and (3) the observation of a 060 peak position of a trioctahedral mineral when the presence of the magnesian chlorite was suspected. Moreover, the increase in exchangeable Mg^{2+} under sequoia provided a chemical argument supporting the formation of a magnesian chlorite under sequoia. If the larger amount of HI minerals under sequoia was expected, the presence of a tri,tri-magnesian chlorite mineral is rather surprising. Indeed, to the authors' knowledge, the occurrence of this kind of mineral has not been reported previously. Initial stages of formation appear to be explained relatively easily in that the hydroxy-Mg sheet present in the interlayer sites can be extracted with KCl during the early stages of its formation (after 14 y). This indicates the presence of charged Mg hydroxide cations. Thus, the Mg would apparently enter the interlayer sites as a charged ion complex which can be exchanged under

conditions of high chemical activity of another cation, such as K^+ . Even though this theory needs to be confirmed on a larger number of sequoia-grassland paired samples, the polymerization of these cation complexes into a hydroxy-Mg sheet is apparently a function of time, the exchangeable chlorites being only 14 y old while the stable chlorites found in the sequoia soils are 100 or 150 y old (Secondigny sample). This would mean that the polymerization process of the magnesian chlorites is similar to that of hydroxy-Al interlayered minerals (commonly called soil chlorites) described by Meunier (2007).

The fact that the formation of tri,tri-magnesian chlorite was preferred in soils developed on granite suggests that the parent material influences its formation. Granite often contains an easily weatherable trioctahedral mineral, biotite. The release of K from

Table 5. XRD data and K content of samples.

Site	Clay K_2O content (wt.%)		Total illite (WCI+PCI) (%)		XRD peak center of gravity (\AA)	
	Sequoia	Prairie	Sequoia	Prairie	Sequoia	Prairie
Richelieu	2.7	2.8	34	2	13.61	14.2
Les Herbiers	4	2.8	44	11	11.92	13.31
Villedieu	5	4.4	49	43	12.06	11.74
Secondigny	2.6	2.1	17	14	12.58	13.25
Pontlevoy	2.8	3	18.5	18	13.32	14.82
Bressuire	3.4	2.7	32	36	12.38	12.07
La Percerie	2	1.9	42	44	11.51	11.47

the biotite leads to its vermiculitization. This vermiculitized biotite, which is also hydroxy-Al interlayered, appears to be transformed into a tri,tri-magnesian chlorite by the adsorption into the interlayers of exchangeable Mg^+ ions, the presence of which is promoted by the sequoia. In this case, the biotite would act as a chlorite precursor in the soils developed on granite. The absence of this precursor would explain why, in spite of increased Mg activity, tri,tri-magnesian chlorite did not form in the other soils which are based on limestone.

150 y (or even 14 y) is a very short period of time considering the normal time (on the order of thousands to a million years depending upon the climate conditions) necessary to form an alteration sequence which could be called a soil (Meunier and Velde, 2008). The presence of the tri,tri-magnesian chlorite indicates the power of plants to change the clays in their proximity. The time required to produce chlorite can be compared with that needed to destroy chlorite, changing it into mixed-layer smectite-illite, reported by Velde and Church (1999). In a Delaware Bay salt marsh grass environment, chlorite disappears from the incoming sediment in a period of tens of years. Hence, the reaction of destabilization and stabilization appears to occur over similar time periods in the cases of soil-plant interaction.

The formation of chlorite was the most striking mineral modification induced by sequoia introduction. Two of the hypotheses proposed in the introduction, however, were not substantiated; no significant difference in clay content between sequoia and prairie soils was observed and the illite content was not systematically larger in prairie soil. The larger amount of exchangeable Na^+ under sequoia can be explained by a greater weathering intensity that would increase its release from primary minerals, as proposed by Amiotti *et al.* (2000). However, this possible weathering increase under sequoia did not lead to an observable decrease in soil-clay content, indicating that the time scale was too short to observe such a difference. Contrary to expectations, grasses failed to increase illite and K^+ in soil-clay fractions compared to sequoia soils, suggesting that the introduction of sequoia did not modify the K^+ cycle significantly or the K^+ -cycle modifications induced by sequoia are too small to be observed at this time scale.

CONCLUSIONS

Previous work on soil K^+ cycles (Tributh *et al.*, 1987; Velde and Peck, 2002; Barré *et al.*, 2008) showed that the apparent soil "illite-like" clay content, as revealed by X-ray measurements, depends on K^+ concentration in the soil solution, which is largely controlled by plants. Observations from the present study indicate that this factor may also be responsible for the appearance of chlorite layers. Thus, chlorite, illite, and smectite clay

minerals, as seen from XRD techniques, can be 'created' by manipulation of the cation site occupancy (hydroxy-interlayer sheet, anhydrous K^+ , or hydrated cations) of 2:1 structures. Results emphasized the important roles of both plant activity and the native clay mineralogy determined by parent material. The consequences of short-term changes in clay mineralogy should be reflected in changes in soil fertility, including modifications in soil cation exchange capacity (decreases as chlorite or illite-like layer formation increases at the expense of smectite) and nutrient availability (the availability of elements stored in illite and chlorite-like interlayers to the different plant species is unknown). These effects could be significant and should be studied further.

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