



Research paper

Hydroxy-interlayered minerals in the Holocene paleosol on the southernmost Loess Plateau, China

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ABSTRACT

The presence and formation of hydroxy-interlayered minerals in the Holocene paleosol at the Wugong profile on the southernmost Chinese Loess Plateau were investigated by examining the $< 1 \mu\text{m}$ and $1\text{--}2 \mu\text{m}$ clay fractions of the 50–150 cm horizon by Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Prior to the analyses free Al and Fe phases were removed by dithionite-citric-bicarbonate (DCB) extraction. XRD patterns were obtained with air-dried, Mg-saturated, Mg-saturated with glycerol solvation (Mg-glycerol) and K-saturated and heated at 110, 250, 350, 450 and 550 °C samples both before and after hydroxy-interlayered materials removal by sodium citrate extraction. The absorption bands at 3699 and 3430 cm^{-1} in the FTIR spectra of both sub-fractions indicated the presence of hydroxy-interlayered minerals. The K-saturated and heated XRD patterns confirmed this by the progressive collapse of the 1.4 nm reflection to a 1.0 nm reflection. After removal of the hydroxy-interlayered materials no obvious increase of the relative XRD intensity of the 1.8 nm reflection in Mg-glycerol pattern was observed and the 1.4 nm reflection exhibited a stronger collapse to 1.0 nm after K-saturation and increasing temperature treatment. This indicated that the hydroxy-interlayered minerals in the Holocene paleosol were mainly composed of hydroxyl-interlayer vermiculite. The hydroxyl-interlayer vermiculite was formed by the polymerization of Al/Fe-hydroxy materials within the interlayer space of vermiculite. Shoulder-like reflection at 1.2 nm in the K-550 °C pattern of the $1\text{--}2 \mu\text{m}$ fraction indicated a higher degree of Al/Fe-hydroxylation in the coarse fraction than in the fine fraction, which was consistent with the lower extractable Al and Fe in the coarse fraction. The reflection at 1.38 nm in the K-550 °C pattern could be interpreted as pedogenic chlorite. Thus, transformation of vermiculite into hydroxy-interlayered vermiculite and finally into a chlorite-like mineral (pedogenic chlorite) has occurred in the Holocene paleosol on the southernmost Chinese Loess Plateau.

1. Introduction

Soil profiles reflect the successive stages of mineralogical evolution depending on the various environmental conditions that have prevailed during soil formation (Turpault et al., 2008). The thick loess-paleosol sequences of the Chinese Loess Plateau are therefore a unique record of the terrestrial paleoclimate and Asian monsoon changes through the Quaternary age (An et al., 1991). By studying the degree of alteration of pre-existing minerals and the composition of the neo-formed clay minerals in loess-paleosol, the evolution of the local environmental

conditions along with global climatic changes can be characterized (see Gylesjö and Arnold, 2006; Han et al., 1998; Huang et al., 2011, 2012; Li et al., 2008). Illite is the dominant clay mineral in the loess-paleosol sequences, but also chlorite, vermiculite, smectite and kaolinite may be present. However, on the southernmost Chinese Loess Plateau also trace amounts of hydroxy-interlayered minerals have been found in the Holocene paleosol (Huang et al., 2011).

The hydroxy-interlayered minerals may result from the polymerization of hydroxyl-materials in the expandable interlayers of layer-silicates (Meunier, 2007) or from the degradation of chlorite (Carnicelli

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et al., 1997). In moderately acidic soils with frequent wetting and drying cycles and low organic matter, the Al dissolution and subsequent adsorption and polymerization of hydroxyl-Al in the interlayer space of expandable 2:1 clay minerals (vermiculite and smectite) is facilitated and may lead to hydroxy-interlayered minerals formation (Meunier, 2007; Rich, 1968). Hydroxy-interlayered minerals may be present as hydroxy-interlayered vermiculite and hydroxy-interlayered smectite, which have been considered as intermediate mineral phases in the solid-solution series between pure Al-chlorite and pure vermiculite and smectite (Barnhisel and Bertsch, 1989).

Hydroxy-interlayered vermiculite is an important component of hydroxy-interlayered minerals in soils of tropical to subtropical China (Chiang et al., 1999; Huang et al., 2007; Li et al., 2002; Yin et al., 2014). As the intensity of soil formation and evolution increases from north to south there is a gradual transformation of vermiculites to hydroxy-interlayered vermiculite in the subtropical soils (especially in Alfisols and Ultisols) of China (Chiang et al., 1999; Huang et al., 2007).

Based on pollen analysis, the Holocene paleosol in the arid and semi-arid regions of the Chinese Loess Plateau is generally regarded as forest-steppe soil (or steppe soil) formed under semi-arid climatic conditions (e.g. Zhao et al., 2009). However, pollen in the southernmost Chinese Loess Plateau (semi-humid region) was characterized by small amounts of temperate to subtropical deciduous broad-leaved trees, in spite of general dominance of steppe through the Holocene (Tang and He, 2004). Hence, the pollen evidence signified a forest dominated landscape paleoecology and an acidic paleosol environment. In the southernmost Chinese Loess Plateau the soil environment during the pedogenesis of the Holocene paleosol was therefore suited for the formation of the hydroxy-interlayered minerals (Huang et al., 2011).

To further investigate the hydroxy-interlayered minerals of the Chinese Loess Plateau, with the aim of improving our understanding of the formation of hydroxy-interlayered minerals, the mineralogy of the Wugong Holocene paleosol on the southernmost Chinese Loess Plateau was studied by Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) with particular attention to presence of hydroxy-interlayered minerals (hydroxy-interlayered vermiculite and/or hydroxy-interlayered smectite). Different size-fractions often have different relative abundances of clay phases (Viennet et al., 2015). To facilitate the detection of hydroxy-interlayered minerals the mineralogical investigations were carried out by separating the clay fraction of the paleosol horizon in a fine (< 1 μm) and a coarse (1–2 μm) sub-fractions.

2. Material and methods

2.1. Sample preparation

The Holocene paleosol at the Wugong site is located in the southernmost Chinese Loess Plateau (N 34° 19' 17", E 108° 07' 07") at an altitude of about 500 m, see Fig. 1. The present climate of this region is a warm temperate semi-humid continental monsoon with mean annual rainfall of 650–750 mm and mean annual temperature of 12–14 °C. The modern zonal soil in this region belongs to the 'Anthrosols (World Reference Base for Soil Resources) and more specifically to the Eum-Orthic Anthrosols (Chinese Soil taxonomy). Huang et al. (2011) deduced that the 'optimum' Holocene paleosol profile was observed in the 50–150 cm horizon with silty clay texture, firm and prismatic structure. Four samples at 60–70 cm, 80–90 cm, 100–110 cm and 120–130 cm horizons were collected for the characterization of the phyllosilicate minerals and the hydroxy-interlayered minerals in particular. The basic physiochemical properties of the four soil samples were summarized in Table 1 together with the properties of the overlying and underlying loess layers.

Each soil sample was air-dried and sieved at 2 mm to remove the coarse fragments. The < 2 mm fractions were treated with, respectively, diluted H₂O₂ and acetic acid solution (buffered with sodium

acetate at pH = 5.0) to remove organic matter and calcium carbonate. To remove excess ions from these fractions several washings with distilled water were applied. The < 1 μm and 1–2 μm fractions were then collected by a stepwise sedimentation technique according to Stokes' law using repeated siphoning until the withdrawn suspension became clear. The obtained sub-fractions were concentrated by flocculation of the suspensions with 0.5 mol/L CaCl₂ (about 25 mL in 25 L suspension) and centrifugation (10 min at 5000g) and then dried at 50 °C.

2.2. Analytical methods

Prior to the analytical measurements, the free Al and Fe phases present in the sub-fractions removed by using the dithionite-citric-bicarbonate (DCB) method (McKeague et al., 1971). Fourier-transform infrared (FTIR) spectra of the < 1 μm and 1–2 μm fractions after the free Al and Fe phases removal were collected by means of a Bruker Vertex70 FTIR spectrometer for random powder specimens dispersed in KBr pellets. The sub-fractions were first dried by heating at 180 °C for 24 h and then grounded in an agate mortar. The KBr powder was pre-heated at 550 °C for 24 h. The sample/KBr ratio of the pellets was 1/100. For each sample 64 scans were collected in the range from 400 to 4000 cm⁻¹ with a resolution of 2 cm⁻¹.

Removal of hydroxy-interlayered materials of sub-fractions (< 1 μm and 1–2 μm clay fractions) was carried out by the procedure of Pai et al. (2004) after DCB extraction. This treatment consisted of heating 50 mg of a sub-fraction at 80 °C for 16 h in 10 mL 0.3 M sodium citrate. The citrate solution was renewed hourly after centrifugation and decantation. The concentrations of Al and/or Fe in the supernatants were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, VARIAN VISTA-MPX). The identification of the minerals in the pre-treated fine (< 1 μm) and coarse (1–2 μm) sub-fractions before and after hydroxy-interlayered materials removal was made by X-ray diffraction (XRD) analysis of the oriented samples. Four types of XRD patterns were acquired: oriented air-dried, Mg-saturated, Mg-saturated with glycerol solvation, K-saturated and heated (110, 250, 350, 450 and 550 °C) samples. The XRD analysis was carried out on a Bruker D8 Advance diffractometer equipped with a 1° divergence silt, 4° incident- and diffracted beam Soller silts, and a CuK α radiation (λ = 0.15418 nm) generated at 40 kV and 40 mA. The XRD patterns were recorded from 3 to 30° (2 θ) at a scanning speed of 10° (2 θ) min⁻¹.

3. Results and discussion

3.1. FTIR of the sub-fractions in the different horizons

Typical FTIR spectra of the < 1 μm and 1–2 μm fractions isolated from the four horizons of the Holocene paleosol have been depicted in, respectively, Fig. 2a and b. The results of Fig. 2a and b indicated that the four spectra of the two sub-fractions were very similar. The FTIR spectra showed the presence of two weak absorption bands in the OH stretching region at \sim 3699 cm⁻¹ and \sim 3625 cm⁻¹ indicating the small amounts of kaolinite and di-octahedral 2:1 minerals (Szymański et al., 2014; Yin et al., 2014). The presence of these minerals in both sub-fractions was also confirmed by absorption bands in the Si–O stretching and OH bending regions (bands at \sim 1035, 1008, 915, 753, 695, 647, 530, 467, and 428 cm⁻¹) (Szymański et al., 2014). However, it should be noted that the weak band at \sim 3699 cm⁻¹ and the O–H stretching vibration at 3430 cm⁻¹ also could be due to the presence of Al/Fe-hydroxy sheets within the interlayers of 2:1 expanding clay minerals (Brydon and Kodama, 1966). Therefore, the FTIR spectra allowed the presence of Al/Fe-hydroxy interlayers in the sub-fractions, but the presence of kaolinite obscured their unambiguous determination. The \sim 1640 cm⁻¹ band originated most likely from aromatic C=C vibration and C=O vibration of carboxylic acid anions, while the \sim 1405 cm⁻¹ band was related to aliphatic C–H deformation of CH₂ and CH₃ bending and C–OH deformation of COOH groups (e.g.

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