



Research paper

Characteristics of clay minerals in soil particles of two Alfisols in China

Zhi Yi Zhang^a, Li Huang^{a,*}, Fan Liu^a, Ming Kuang Wang^b, Qing Ling Fu^a, Jun Zhu^a^a Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtze River), Ministry of Agriculture, Huazhong Agricultural University, Wuhan 430070, China^b Department of Agricultural Chemistry, National Taiwan University, Taipei 10617, Taiwan

ARTICLE INFO

Article history:

Received 18 August 2015

Received in revised form 17 November 2015

Accepted 22 November 2015

Available online 1 December 2015

Keywords:

Alfisols

Clay mineral

Nanoparticles

Evolution of clay minerals

ABSTRACT

The composition, structure and transformation characteristics of clay minerals in various size particles (<2000, 450–2000, 100–450 and 25–100 nm) of two Alfisols (Haplustalf and Hapludalf) in China were investigated by elemental analysis, X-ray diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FT-IR) and ²⁷Al and ²⁹Si Magic-angle Spinning Nuclear Magnetic Resonance (MAS NMR). The clay minerals in <2000, 450–2000 and 100–450 nm size particles of the two soils were illite, vermiculite, smectite, kaolinite and kaolinite interstratified minerals. In Haplustalf, vermiculite was dominant clay mineral in 450–2000 nm particles and illite was dominant clay mineral in 100–450 nm particles. In Hapludalf, kaolinite (and kaolinite interstratified minerals) predominated in all size particles. With decreasing particle sizes, the two clays showed a decrease in K₂O, Na₂O, MgO and SiO₂ contents and an increase in Al₂O₃ content, with the minimum molar ratio of SiO₂ to Al₂O₃ observed in nanoparticles (25–100 nm). Meanwhile, the smectite and vermiculite contents decreased or disappeared, leaving illite and kaolinite (and kaolinite interstratified minerals) as the main clay minerals in the two soil nanoparticles. Additionally, with decreasing particle sizes, the clay mineral structures were transformed from well crystalline to poor crystalline, with illite being the poor crystalline in nanoparticles of the soils. The hydroxyl groups between the tetrahedral and octahedral structures of the 2:1 clay minerals and the surface of kaolinite gradually broke down, and ^{IV}Al of the tetrahedral structure gradually reduced. In nanoparticles, Al mainly appeared in the octahedral structure as ^{VI}Al, and Si in the structure of Q³ (Si linked to three other Si atoms via oxygen). The composition and structure of clay minerals in different size particles showed that the clay minerals weathered from larger particles (>100 nm) were an important mineral source of nanoparticles, and the 1:1 clay minerals were mainly inherited from the minerals in larger particles and transformed from 2:1 clay minerals into nanoparticles.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Clay minerals are widely distributed in the surface of earth with the characteristics of small size, and they significantly affect the physical, chemical and biological processes of soils (Owliaie et al., 2006; Velde and Meunier, 2009; Cébron et al., 2015). Additionally, clay minerals undergo spontaneous modification and transformation with the change of environmental conditions, which can be illustrated by the structures and types of clay minerals (Wilson, 2004; Turpault et al., 2008). In recent years, studies have begun to focus on the clay minerals of soil nanoparticles (Waychunas et al., 2005; Wilson et al., 2008; Li et al., 2012; Regelink et al., 2013; Ismadji et al., 2015) other than soil colloids (<2000 nm) (Pai et al., 1999; Egli et al., 2001; Deepthy and Balakrishnan, 2005).

"Nanoparticle" refers to particles with a size between 1 and 100 nm, whose composition and properties will be changed by the impact of particle size (Banfield and Zhang, 2001). When compared with other soil clay fractions, the amount of Fe and Al was higher in nanoparticles

(Van Veen and Kuikman, 1990). The mineral structure of soils will also be changed in the nanoscale (Banfield and Zhang, 2001; Gilbert et al., 2007; Hochella et al., 2008). Compared with bulk samples (<2000 nm), the Si to Al molar ratio was increased in nanoparticles, and significantly distinguished in surface area, morphology, crystallinity, surface atomic structure, and framework structure (Tsao et al., 2011). When the muscovite changed into illite of nanoscale, the interlayer K⁺ ions and layer charge would decrease. Similarly, the 2M mica would convert into the 1Md polytype under the influence of particles with nano division in soil (Wilson, 1999). Tsao et al. (2013) studied clay minerals of various size particles in red soil, and found that quartz and feldspar mainly existed in the particles of <2000 and 450–2000 nm, and illite and kaolinite were the major clay minerals in nanoparticles. In volcanic soils, the allophane nanoparticles were short-range order minerals (Parfitt, 1990).

In soil formation process, the 1:1 type clay minerals were formed as follows: (1) the primary minerals evolved to secondary minerals, which were transformed through 2:1–2:2–1:1 or 2:1–1:1 pedogeochemical reactions; (2) 1:1 type clay minerals would also directly form through hydrolysis of the primary minerals (Pedro, 1982; Wilson, 1999). A previous study showed that the major results of clay mineral evolution

* Corresponding author.

E-mail address: huang_lj62@aliyun.com (L. Huang).

were from colloidal particles of less than 2000 nm, but with the particle size decreased to nanoscale, the composition and structure of clay minerals would change significantly (Banfield and Zhang, 2001). However, these studies did not report the 1:1 type clay minerals of nanoparticles from the above processes or other sources. Alfisols are widely spread in China with frequent movement and accumulation of soil minerals (Huang et al., 2007, 2008). The evolution process of clay minerals under nanoscale in Alfisols remains to be elucidated. The objectives of the present study were to (1) identify the elementary composition of clay minerals in various size particles (<2000, 450–2000, 100–450 and 25–100 nm) in Haplustalfs and Hapludalfs in China; (2) investigate the characteristics of tetrahedral and octahedral crystals in clay minerals and their structure changes in different size soil particles; and (3) discuss the evolution path of clay minerals from micro-particles (450–2000, 100–450 nm) to nanoparticles (25–100 nm) in Alfisols.

2. Materials and methods

2.1. Description of the sites

Two profiles of Alfisols were collected from eastern China, which were Haplustalfs (Alf-1) and Hapludalfs (Alf-2) according to Key to Soil Taxonomy (Soil Survey Staff, 2014). Alf-1 was collected from Tai'an City (N 36°05' and E 117°24') in Shandong Province, and Alf-2 was collected from Luotian City (N 30°47' and E 115°24') in Hubei Province (Lu et al., 2015). The Alf-1 site was located in a warm temperate zone, at 163 m above sea level, with an annual mean temperature and precipitation of 13 °C and 697–730 mm, respectively. The vegetation in the Alf-1 site was *Triticum aestivum* L. and the parent material was gneiss. For the profile of Alf-1, the Munsell color of all horizons was strong brown (7.5 YR 5/6), some white pebbles appeared below 20 cm depth, C horizon was between 58 and 73 cm, and rock layers could be seen under 73 cm. The Alf-2 site was located in a subtropical climate zone of China, at 158 m above sea level, with an annual mean temperature and precipitation of 15.5 °C and 1300 mm, respectively. The vegetation in this area was *Castanea mollissima* B, and the parent material of Alf-2 was granite. The profile of Alf-2 formed naturally, with the Munsell color of the profile followed by 7.5 YR 5/6, 2.5 Y 6/3 and 2.5 Y 8/5 from eluvial horizon to parent material, the soil layer was thick and hard, and some rocks could be seen clearly in the deep layer (80 cm). At each site, the soil samples of A horizon (Alf-1, 0–19 cm and Alf-2, 0–25 cm) were collected. The samples were air-dried and ground to pass 2, 0.85, 0.25 and 0.15 mm sieves.

2.2. Collection of nanoparticles

Organic matter in the soil samples was removed by hydrogen peroxide (30%). Then, the clay (<2000 nm) fractions were collected by sedimentation according to Stokes' Law. The suspension of <2000 nm size fraction was centrifuged to collect the suspension of <450 nm size fraction, which was further centrifuged to obtain the <100 nm size fraction. The suspension of <100 nm size fraction was collected and filtered to obtain the 25–100 nm size fraction by an automated ultrafiltration device ((AUDII), Tony nano-techno, Taiwan), using the Millipore ultrafiltration disk membrane (Filter type: 25 nm VSWP). Details concerning the separation and collection of various particle-size fractions have been reported previously (Tsao et al., 2009).

2.3. Analytical methods

Soil pH was measured at a soil to water ratio of 1:2.5. The soil organic matter content was determined by the $K_2Cr_2O_7$ oxidation method (Nelson and Sommers, 1996). The cation-exchange capacity (CEC) of the soils was determined using the buffered ammonium acetate method

(Rhoades, 1982). Texture was determined by the pipette method (Gee and Bauder, 1986).

Elementary composition of different size particles (<2000, 450–2000, 100–450 and 25–100 nm) was determined by the microwave digestion method (US EPA, 1996). Concentrations of Si, Al, Fe, Ca, Mg, Mn and Ti were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES Visata-MPX, Varian, California, USA), and K and Na were tested by a Flame Photometer (M410, Sherwood, UK).

Deferrated clay samples were saturated with Mg-glycerol (Mg-gly) and K. The Mg-gly samples were examined at 25 °C. The K-saturated samples were examined at 25 °C, and after heating at 110, 250, 350, 450 and 550 °C for 2 h (Jackson, 1979). The oriented samples were measured with an X-ray diffractometer (D8 Advance, Bruker, Rheinstetten, Germany) with $CuK\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) generated at 40 kV and 40 mA. Semi-quantitative estimations of clay minerals were performed as reported by Brindley (1980) and Pai et al., (1999).

The d_{060} region was studied on random mounts and then step-scanned from 58 to 64°2 θ with a scanning speed of 1°2 $\theta \text{ min}^{-1}$ (Egli et al., 2008).

Synchrotron XRD patterns of nanoparticles in Mg-gly and K-saturated oriented samples at 25 °C were collected at the Shanghai Synchrotron Radiation Facility (SSRF) of China. The synchrotron XRD was 18 keV (BL14B1 beamline). The incident X-ray wavelength (λ) was 0.6887 Å. The data were recorded by a NaI scintillation detector. Based on Bragg's Law, d values of synchrotron radiation were converted into d values of Cu target ($\lambda = 1.5418 \text{ \AA}$).

Various particle size samples (<2000, 450–2000, 100–450 and 25–100 nm) were ground and mixed with a dry spectroscopic grade of KBr powder (1 mg of sample and 100 mg of KBr) and pressed into disk. The infrared spectrum was collected with the resolution of 4 cm^{-1} using 128 scans by a Bruker Vertex-70 (Germany) Infrared Spectrometric Analyzer.

The solid-state ^{27}Al and ^{29}Si NMR experiments were performed on a Varian Infinity-plus 400 NMR Spectrometer (California, USA) operating at a frequency of 104.31 and 79.47 MHz for ^{27}Al and ^{29}Si , respectively. ^{27}Al NMR spectra were recorded with a short pulse length (0.36 μs) and 1 s recycle delay. The probe was used with a spinning frequency of 10.1 kHz. ^{27}Al chemical shifts were referenced using $\text{Al}(\text{NO}_3)_3$. For ^{29}Si , the MAS speed was 8 kHz, and ^{29}Si NMR spectra were recorded with a single pulse excitation using a short tip angle ($\pi/4$) to obtain quantitative results, and a recycle delay of 10 s. The ^{29}Si chemical shifts were determined using a solid external reference kaolin resonate at -91.5 ppm relative to tetramethylsilane (TMS).

3. Results

3.1. Soil properties

The two soils were acidic with the pH ranging from 5.2 to 5.6 (Table 1). The OM contents of Alf-1 and Alf-2 were 9.7 and 16.4 g kg^{-1} , respectively. Alf-1 soil was higher than Alf-2 in terms of CEC, exchangeable K^+ , Na^+ , Ca^{2+} and Mg^{2+} . The two soils had a high sand content of about 741–771 g kg^{-1} and the texture was sandy loam.

SiO_2 , Al_2O_3 and Fe_2O_3 were the main chemical components of the two soils, with the highest content of SiO_2 in 450–2000 nm size particles and the lowest content in nanoparticles (Table 2). The SiO_2 content was ranged from 46.3 to 51.6% in 450–2000 nm size particles, and about 43% in nanoparticles (Table 2). The Al_2O_3 and Fe_2O_3 contents showed an opposite trend to that of SiO_2 in various size particles, and gradually increased with the decrease of the particle size. The Al_2O_3 content was 32.0 and 38.5% in Alf-1 and Alf-2 nanoparticles, respectively. The K_2O , Na_2O and MgO contents were higher in 450–2000 nm size particles than in 100–450 nm particles and nanoparticles. In the two soils, the molar ratios of SiO_2 to Al_2O_3 and SiO_2 to R_2O_3 ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) in 450–2000 nm particles were about 2.75 and 2.30 in Alf-1 and Alf-2, respectively. The SiO_2 to Al_2O_3 molar ratio was 2.32 and 1.95, and the SiO_2 to

Download English Version:

<https://daneshyari.com/en/article/1694174>

Download Persian Version:

<https://daneshyari.com/article/1694174>

[Daneshyari.com](https://daneshyari.com)