



Research paper

Effects of oxalic and citric acids on three clay minerals after incubation

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ABSTRACT

The release of silicon (Si) from and the structural changes to clay minerals (i.e., kaolinite, montmorillonite (Mt), and illite) were investigated after being batch incubated with low-molecular-mass organic acids (i.e., oxalic and citric acids, LMMOA) of varying concentrations (0–0.5 mol L⁻¹) at 25 °C. Two mineral acids (i.e., HCl and H₂SO₄) with varying concentrations were also reacted with Ca-montmorillonite (Ca²⁺-Mt). With increasing reaction time, the Si released from kaolinite and illite reached its maximum level after incubation with the varying LMMOA concentrations for 15 days. Quantities of Si released from the clay minerals with the LMMOA ranged from 0.22 to 114.01 μg mL⁻¹ (Si). Quantity of Si released with oxalic acid was higher than that with citric acid. The Si released from the clay minerals increased with increasing organic acid concentrations. More Si was released from Mt than from kaolinite and illite when incubated with the same LMMOA concentration. With increasing organic acid concentrations, the X-ray diffraction (XRD) reflection intensities of the Mt weakened, and this trend was more remarkable in the clay treated with oxalic acid than citric acid. However, no relationship between the XRD reflection intensity and the acid concentrations was noticeable in the incubated kaolinite and illite. While incubating with hydrochloric acid (HCl) and sulfate acid (H₂SO₄) for 15 day incubation, amounts of Si released from Ca²⁺-Mt were generally higher than those reacting with organic acids, and more Si was released in the H₂SO₄ treatment than that of HCl. But the XRD reflection intensities of the Ca²⁺-Mt had no distinctly change compared with those treated with the organic acids.

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1. Introduction

Low-molecular-mass organic acids (LMMOA) are common in rhizosphere soils, especially in the immediate zone at the soil–root interface (Tani and Higashi, 1999; Wang et al., 2005; Wu et al., 2011). These acids primarily are derived from animal and plant residue decomposition, secretions from the plant root systems, microbial synthesis and organic matter applied for soil transformation (Lundegard and Kharaka, 1994; Strobel, 2001; Xu et al., 2005). Organic acids such as malate, citrate and oxalate are involved in many processes in the rhizosphere, including nutrient acquisition and metal detoxification, the alleviation of anaerobic stress in roots, mineral weathering and pathogen attraction (Huang et al., 2010; Jones, 1998; Li et al., 2006; Marschner, 1995). These acids possess one or more carboxyl and hydroxyl functional groups that can form complexes with elements in the soil, and thus play an important role in soil processes such as mineral weathering, nutrient mobilization and Al detoxification (Bolan et al., 1994; Chin and Mills, 1991; Drever and Stillings, 1997; Feng et al., 2004; Han and Jordan, 1995; Li et al., 2006; Xu et al., 2010).

The secretion of LMMOA by plants and microorganisms in the soil can destroy the soil's potassium feldspar and biotite lattice structure releasing elemental K and Si (Buss et al., 2007; Sheng and He, 2006; Song et al., 2007). Oxalic acid, citric acid and other LMMOA can effectively activate the structural K in muscovite and illite, and, to some extent, can dissolve the feldspar minerals (Bernier and Holdren, 1979). Dissolution rate of kaolinite was observed via the regression of the Si concentration versus the time during a steady state given the weaker affinity of Si for the kaolinite surface (Blake and Walter, 1999; Welch and Ullman, 2000). There was a decrease of CEC and Mg contents in naturally weathered montmorillonite (Mt) due to structural dissolution and precipitation of amorphous SiO₂ (Sucha et al., 2001). Organic acids had been implicated in the release of Mn from the rhizosphere (Godó and Reisenauer, 1980). Studies have reported that the swelling of Mt with hydrochloric, sulfuric or other inorganic acids, leads to the dissolution of Si, Al and other ions causing changes to the physical and chemical properties and structure of the minerals (Sanjay and Sugunan, 2008).

At present, the study of the effect of LMMOA on mineral damage has focused on primary minerals, with little research into secondary clay minerals. Kaolinite, Mt and illite are typical layered silicate minerals found in soils (Chefetz et al., 2011; Chin and Mills, 1991; Huang et al., 2010; Huertas et al., 1999; Laszlo, 1987; Sparks, 1995). Due to their fine particle sizes (<2 μm) and unusual intercalation properties, they

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provide a large surface area for the adsorption of organic and inorganic moieties (Huang et al., 2010; Pinnavaia, 1983). Their dissolution and precipitation are important to the genesis and degradation of the soils and the maintenance of soil fertility (Huertas et al., 1999; Vicente-Rodríguez et al., 1996). LMMOA is widely distributed throughout rhizosphere and influence its evolution, the properties of the rhizosphere soil and, to varying degrees, the nutrients released from the soil (Li et al., 2006; Strobel, 2001; Tani and Higashi, 1999; Xu et al., 2005, 2010). Silicon is a key element in the structures of clay minerals and plays an important role in the geochemical processes of weathering and mineralogical evolution (Mavris et al., 2011, 2012). Therefore, the effect of LMMOA on phyllosilicate weathering is necessary to examine the soil's mineral transformation.

In this paper, the effects of the concentration and reaction time of oxalic and citric acids on the release of Si from kaolinite, Mt and illite, and the changes to the minerals before and after the reaction were investigated. Mt treated with two mineral acids (HCl and H₂SO₄) and the two organic acids were compared and their effects were studied. The aims of the study were (i) to identify elemental migration from the clay minerals, (ii) to observe the structural transformation processes in the clay minerals affected by the LMMOA, and (iii) to reveal the ability of the organic acids induce the modification of the clay structures. The results will help gain insight into the function of LMMOA in rhizosphere to soil mineral weathering from one side.

2. Materials and methods

2.1. Materials

The kaolinite, Ca-montmorillonite (Ca²⁺-Mt), and illite were purchased from the Fengcheng Reagent Factory (Shanghai City, China), the Sanding Factory (Zhejiang Province, China) and the Hongfa Building Materials Factory (Shanxi Province, China), respectively. The clay minerals were separately dispersed in deionized distilled water (ddH₂O), adjusted to pH 10.0 with 0.01 mmol L⁻¹ NaOH or HCl using a thermometric titrator (907 Titrand, Metrohm, Switzerland) and dispersed via occasional sonication. The electric conductivity of ddH₂O was 7.48 μS cm⁻¹ at room temperature. The <2 μm clay fractions were separated by sedimentation after dispersion according to Stokes Law (Pansu and Gautheyrou, 2006). The kaolinite, Ca²⁺-Mt, and illite particles were flocculated with 0.5 M CaCl₂, washed in ddH₂O and ethanol to remove any Cl, then air dried (Huang et al., 2010). Cation exchange capacity (CEC) of kaolinite, Ca²⁺-Mt and illite was 13.73, 111.80, and 14.04 cmol kg⁻¹, respectively (determined according to the method described by Jackson (1979)).

2.2. Methods

Varying concentrations of oxalic acid and citric acid solutions with 0 (check, CK), 0.025, 0.05, 0.10, 0.25, and 0.50 mol L⁻¹ were prepared; 20 mL of each concentration was added separately to 50 mL centrifuge tubes containing 0.200 g of the test mineral particles and incubated in an oscillator (200 rpm) for 3, 7, or 15 days (d) at 25 °C. After incubation, the tubes were centrifuged (9000 rpm) for 15 min in a Beckman Super-Speed refrigerated centrifuge, the supernatant solutions were filtrated through a 0.45-μm microporous membrane, and soluble Si content in the supernatant was determined. Ca²⁺-Mt particle was incubated separately using various concentrations (CK, 0.025, 0.05, 0.10, 0.25, and 0.50 mol L⁻¹) of hydrochloric acid (HCl) and sulfuric acid (H₂SO₄) for 3, 7, or 15 d at 25 °C. Treatments of Ca²⁺-Mt incubated by mineral acids were the same as those of the organic acids.

The samples were washed several times with ddH₂O after incubation until the electrical conductivity of the dispersions decreased to 20 μS cm⁻¹. The samples were air-dried and ground through a 100-mesh sieve (0.15 mm) for X-ray diffraction (XRD) analysis. All experiments were performed in triplicate.

The Si in the supernatant was determined using the silicon molybdenum blue spectrophotometric method (American Public Health Association, 1995; Galhardo and Masini, 2000). The specific surface area (SSA) of the clay minerals was determined via BET measurement with N₂ gas adsorption using a specific surface apparatus (Autosorb-1, JEDL-6390/LV, Quantachrome Corporation, Philadelphia, PA). After incubation, the powdered clay samples were analyzed via XRD at room temperature using CuKα radiation generated at 40 kV and 15 mA with a Bruker X-ray diffractometer (D8 Advance, Bruker Corporation, Karlsruhe, Germany). The XRD spectra were recorded in a continuous mode from 2θ = 3° to 85° with 0.01° steps at a scanning rate of 10° min⁻¹.

The statistical analysis was conducted with the STATISTICS software package (Jackson, 1993). A value of P = 0.05 was taken as the significance level.

3. Results and discussion

3.1. The effect of a prolonged reaction time on the release of Si

The clay minerals were incubated with various oxalic and citric acid concentrations for 3, 7 and 15 d. With increasing reaction time, the released Si from the kaolinite incubated with oxalic acid exhibited an upward trend (Fig. 1A) and reached a maximum at 15 d. As the oxalic acid concentration increased, the quantities of Si released were 0.86, 30.41, 34.98, 42.27, 49.91, and 48.63 μg mL⁻¹, demonstrating a significant relationship between the amount of released Si and the oxalic acid concentration (P < 0.05). Release of Si from kaolinite dispersions correlated to the organic acid concentrations. The trend is similar to that from a previous study on the kaolinite dissolution induced by three types of organic acids (citric, oxalic, and malic acids) (Wang et al., 2005). After incubation with various concentrations of oxalic acid for 7 and 15 d, the quantity of Si released from the kaolinite was 2.04 to 2.27, and 2.71 to 3.65 times higher than that released after 3 d of incubation, respectively.

When the concentration of oxalic acid ranged from 0.025 to 0.05 mol L⁻¹, the quantity of Si released by the Mt increased similarly to the trend with prolonged reaction period (Fig. 2A). After incubation with different concentrations of oxalic acid for 7 and 15 d, the quantity of Si released from the Ca²⁺-Mt ranged from 0.76 to 0.78 μg mL⁻¹, which is from 1.80 to 1.86 times higher than the amount released after 3 d of incubation. When the oxalic acid concentration changed from 0.10 to 0.25 and 0.50 mol L⁻¹, with increasing reaction period, the Ca²⁺-Mt released the most Si on the 7 d of incubation (110.69, 101.59 and 77.71 μg mL⁻¹, respectively), demonstrating a significant relationship between the Si released by Mt and the oxalic acid concentration. When the oxalic acid concentration was increased, the quantity of Si released by the illite increased with prolonged reaction time (Fig. 3A). With prolonged reaction period, the quantity of Si released by the illite showed no significant difference after treatment with 0.25 and 0.50 mol L⁻¹ oxalic acid, but the Si released at the other oxalic acid concentrations changed significantly. After incubation with varying concentrations of oxalic acid for 7 and 15 d, quantity of Si released by the illite ranged from 0.60 to 0.64 μg mL⁻¹, which is from 1.42 to 1.53 times higher than that released after 3 d of incubation.

Quantities of Si released after prolonged reaction period with citric acid concentrations of 0.025, 0.05, 0.10 and 0.25 mol L⁻¹ from the kaolinite, Mt and illite are shown in Figs. 1B, 2B and 3B, respectively. When the kaolinite, Mt and illite are incubated at 3, 7, 15 d, respectively, with 0.50 mol L⁻¹ citric acid, the quantity of released Si ranges from 0.22 to 1.14, 5.60 to 8.69 and 0.32 to 0.93 μg mL⁻¹, respectively, which is a result similar to that with the CK.

3.2. The release of Si affected by the organic acid concentrations

In the oxalic and citric acid reaction systems, the quantities of Si released by the clay minerals first increased and then decreased

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