



Nanoclays from an Andisol: Extraction, properties and carbon stabilization

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ABSTRACT

Soils contain an abundance of nano-size particles. Because of their tendency to aggregate and associate with organic colloids, however, soil nanoparticles are difficult to obtain and characterize. Here we report on a simple and rapid method of extracting mesoporous nanomaterials from the clay fraction of an Andisol with narrow size distribution. The clay and nanoclay were characterized by elemental analysis, pyrolysis GC/MS, electron and atomic force microscopy, infrared spectroscopy, and electrophoresis. The nanoclay dominantly consists of hollow allophane spherules forming globular aggregates of about 100 nm in diameter. The nanoclay contains more organic matter (carbon and nitrogen) with a larger proportion of polysaccharides and nitrogen containing compounds, and has a lower isoelectric point, than the clay. Treatment with hydrogen peroxide causes a large decrease in the organic matter contents of both nanoclay and clay. The aggregates of allophane nanoparticles retain a significant amount (~12%) of carbon against intensive peroxide treatment. Thus, besides playing an important role in carbon stabilization, these naturally occurring nanomaterials are potentially useful for developing a low-cost carbon sequestration technology.

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1. Introduction

Increased burning of fossil fuels and intensive deforestation have released an increasing amount of greenhouse gases into the environment (Angulo-Brown et al., 2009; Glasby, 2006; Schulp et al., 2008; Thomson et al., 2008). It has been suggested that nanoparticles, with their large surface-to-volume ratio, could be highly effective in carbon sequestration (Khedr et al., 2006). Many functional nanoparticles have been synthesized as candidates for environmental applications (Garrido-Ramírez et al., 2010). However, synthetic nanomaterials, especially those with a narrow size distribution, can be expensive and difficult to obtain. For this reason, much effort is being directed at developing simple methods for designing and synthesizing low-cost nanomaterials (Bendall et al., 2008, 2010; Plank et al., 2009). Nanoparticles occur widely in the natural environment (Klaine et al., 2008; Yuan, 2004). In this respect, soils can potentially provide an abundance of inexpensive nano-size

materials (Besoain and Sepúlveda, 1985; Calabi-Floody et al., 2009; Parfitt et al., 1983, 1988; Theng and Yuan, 2008; Wada, 1987).

Soils contain about three times more carbon than the above-ground vegetation, and approximately 75% of the terrestrial carbon pool. As such, soils play a key role in the global carbon cycle (Schlesinger, 1986). The clay fraction of soils derived from volcanic ash (Andisols) contains a range of inorganic nanoparticles, among which allophane is the most abundant (Theng and Yuan, 2008; Wada, 1987). Allophane is a non-crystalline or 'short-range order' aluminosilicate with an Al/Si ratio between 1 and 2. Irrespective of chemical composition and origin, the unit particle of allophane is a hollow spherule (Fig. 1) with an outer diameter of 3.5–5.0 nm (Abidin et al., 2007; Creton et al., 2008). The 0.7–1.0 nm thick spherule wall is composed of an outer Al octahedral (gibbsitic) sheet and an inner Si sheet. Defects in the wall structure give rise to perforations of ~0.3 nm in diameter (Brigatti et al., 2006; Hashizume and Theng, 2007; Parfitt, 1990).

The external (interspherule) and internal (intraspherule) surface area of allophane, calculated on the basis of unit particle size and density, is about 1000 m² g⁻¹, while values of 700–900 m² g⁻¹ are obtained by retention of ethylene glycol and ethylene glycol monoethyl ether (Hall et al., 1985; Wada, 1989). Allophane spherules ('nano-balls') tend to form porous nano-size aggregates (Calabi-Floody et al., 2009; Garrido-Ramírez et al., 2010) with physical characteristics similar to those of synthetic mesoporous silica.

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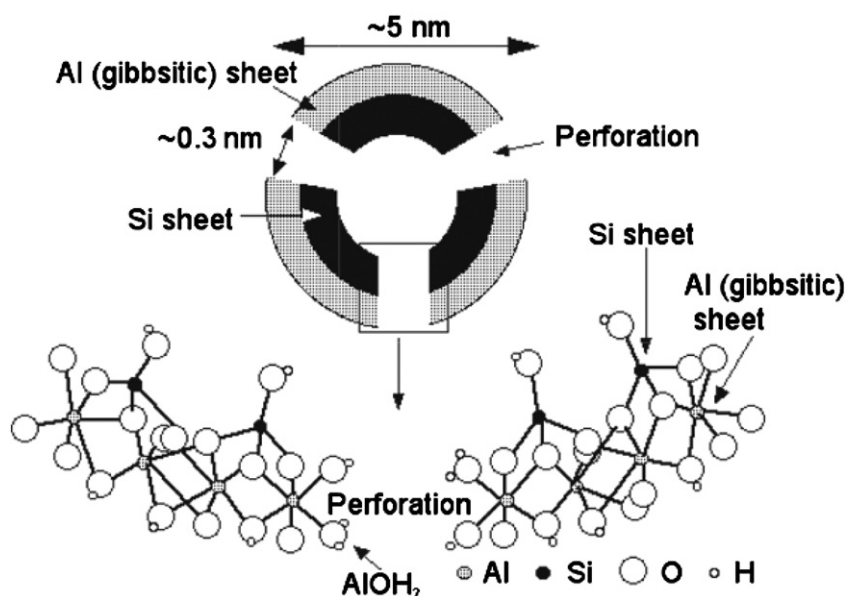


Fig. 1. Diagram showing the structure and size of an allophane 'nano-ball' (from Hashizume and Theng, 2007).

The stability of organic matter in soil has been ascribed to interactions with inorganic nanoparticles, and physical protection within micropores of clay domains and interlayers (Chenu and Plante, 2006; Lehmann et al., 2008; Theng and Yuan, 2008; Theng et al., 1992). More recently, Monreal et al. (2010) have shown that the organic matter in a cultivated Black Chernozem is stabilized in nano-size structures. Because of their strong interaction with organic matter, nanoclays are difficult to isolate from soil.

Here we describe the extraction and spatial arrangement (i.e., form, shape, and size) of clays and nanoclays from an Andisol in Southern Chile. The organic matter, associated with the clay and nanoclay particle size fraction, was characterized using various instrumental techniques, and their stability against treatment with hydrogen peroxide was determined. The results of this investigation can provide insight into the long-term stabilization of organic matter in volcanic ash soils.

2. Materials and methods

2.1. Soil preparation and clay extraction

The soil used was an Andisol of the Piedras Negras Series in Southern Chile (40°20'S 72°35'W). Five samples of about 1 kg each were taken from the top 20 cm of the soil horizon. The samples were pooled, passed through a 2 mm mesh sieve, and dried in air (2–3 days at room temperature). A portion of the air-dried material was used for clay fractionation. Thus, 20 g of soil was ultrasonically dispersed in water by applying 7500 J g^{-1} , using a Sonics Vibra Cell model VC 750 equipment. The soil suspension was placed in a one-liter measuring cylinder, from which the clay fraction ($<2 \mu\text{m}$ equivalent spherical diameter), was obtained (390 g clay from 1 kg of soil) by sedimentation under gravity, following Stokes' law. The separated clay suspension was concentrated by evaporation (of the water) in a rotary evaporator at 60°C . A portion of the concentrated suspension was set aside for subsequent nanoclay extraction, while another portion was freeze-dried for further analysis.

2.2. Nanoclay extraction

The nanoclay fraction was extracted using a modified method as described by Li and Hu (2003). Briefly, 5 g of the clay was suspended in 100 mL of 1 M NaCl, ultrasonicated at 4280 J g^{-1} , (selected from

3000 to 5000 J g^{-1} range tested) for 3 min, and centrifuged in a Sorvall Instrument RC-SB refrigerated superspeed centrifuge at 654 g for 40 min and 25°C . The centrifugation speed was the same as used by Li and Hu (2003). The average diameter of the particles was less than 100 nm when the first-round supernatant was discarded in order to remove mineral impurities. The pellet was suspended in 50 mL of deionized water with moderate stirring for 40 min and centrifuged again. The supernatant was collected, while the pellet was resuspended (in deionized water) and centrifuged. This procedure was repeated 11 more times. The collected supernatants, containing the nanoclay, were dialyzed (1000 kDa membrane) against deionized water until the conductivity of the water reached $0.5\text{--}0.8 \mu\text{S cm}^{-1}$. The dialyzed material was freeze-dried to yield solid nanoclay.

2.3. Hydrogen peroxide treatment and organic matter removal

A portion of the clay and nanoclay was treated with 30% hydrogen peroxide (H_2O_2) to partially remove the associated organic matter. Peroxide treatment was selected (over potassium dichromate oxidation) because we wanted to preserve the integrity of the clay and nanoclay minerals, and isolate the refractory (recalcitrant) organic matter (Eusterhues et al., 2005; Monreal et al., 2010; Plante et al., 2004; Theng et al., 1992). The procedure involved adding H_2O_2 to the clay or nanoclay suspension (2 mg mL^{-1} suspension concentration) at a H_2O_2 :suspension ratio of 1:2, acidifying to pH 2 with 0.1 M HCl, and heating at 60°C for 16 h with stirring. The suspensions were neutralized by adding NaOH (0.1 M) and dialyzed (1000 kDa membrane) against deionized water to remove excess H_2O_2 .

2.4. Structural and chemical characterization

2.4.1. Elemental composition and chemical characterization of soil organic matter

The carbon and nitrogen contents of the clay and nanoclay fractions, before and after peroxide treatment, were determined on samples that had been dried at 60°C for 2 h, using a dry combustion method and an Analysis EuroEA3000 series instrument. The molecular composition of the organic matter, associated with the clay and nanoclay fractions, was determined by analytical pyrolysis, using samples that had been freeze-dried and ground to a fine powder. Curiepoint pyrolysis was carried out with a pyrolysis unit (GSG Curiepoint Pyrolyser 1040 PSC) coupled to a gas chromatograph

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