Diversity of Natural Nanoparticles in Soils

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Ferrihydrite

Properties of ferrihydrite

• Granular at the nanometer scale
• XRD peaks are very broad; 2 to 6 depending on crystallinity
• High phosphate adsorption
• Closely associated with lepidocrocite in some soils
Rice field in the spring in southeast Texas when soils are drying & iron oxides are forming
Lepidocrocite on the surface of a Vertisol: moist (L) & dry (R)
Lepidocrocite laths with ferrihydrite granules
Lattice fringes of lepidocrocite
Properties of lepidocrocite-ferrihydrite mixtures

- Form and dissolve seasonally in soils of rice paddy culture
- Visible color change in a few weeks
- Prominent coatings on ped surfaces, tillage surfaces, and in pores
- Bright colors of iron oxides orange to dark red in common terms
- Influence the phosphate fixation and dissolution in Vertisols cropped to rice in southeast Texas
This goethite is a twin or aggregate of four crystals

The spot pattern indicates multiple crystals

Dixon, 1999
This enlargement shows numerous lattice fringes & crystal faces at the edges

This nm scale particle of goethite particle is well crystallized

Dixon, 1999
Vertisol from Oklahoma: lattice fringes of goethite
Goethite occurs in soils as very complex crystalline aggregates that influence soil structure.

This example is from a Vertisol.

Dixon, 1999
Todorokite: a Mn oxide

- Forms in nodules of a Vertisol of central America
- Forms on siderite boulders exposed in lignite mines of east Texas
- Has fibrous morphology, tunnel structure, & twins
- Has 1 nm lattice fringes that help identify it in soil clays with TEM
a. Birnessite (cultured), b. todorokite (siderite coating),
c. todorokite (soil), and d. lithiophorite (Oxisol, macro particle)

Golden et al., 1992

Senkayi et al., 1986

Golden et al., 1993
Section of soil nodule containing Fe and Mn oxides: small crystals in aggregate: thus oxides with high surface area

Concentric banding of oxides

White & Dixon, 1996
Todorokite twinning

Slickenside surface in Vertisol: Central America
Palygorskite fibers on calcite crystals in Israel

Palygorskite fibers deposited on a quartz grain in Australian soil
Petrified log composed of silica minerals, College Station, TX
Cross section of petrified log with nanoparticle zone at the top:
fine white powder
a. Nanoparticles of opal-CT formed on the outside of the petrified log

b. Quartz particles with nanoparticles of opal-CT in the background Senkayi et al., 1985
Properties of colloidal opal-CT

- Bright white color
- Readily dispersed: seldom seen on exposed petrified wood.
- Identifiable by XRD in many soils of Texas
Allophane spheres or circles and imogolite fibers: 50 nm scale

Wada, 1989
Allophane and imogolite properties

• They often occur together in volcanic soils e.g. Andisols
• They produce very broad XRD peaks
• They form a jell that commonly has a distinctive color brownish or reddish yellow
• They yield water when massaged between the fingers
• “Cottage cheese-like soils”
a. Smectite with folds indicated by lattice fringes
b. Also, folds on the edges below.

Folds indicate flexibility of some smectite particles

Dixon, 2002
Langmuir adsorption isotherms of aflatoxin B1 for three bentonite clays

Kannewischer et al, 2006
Smectite clay has the familiar 2:1 structure & the aflatoxin molecule is almost planar with localized charge.
Aflatoxin molecules between smectite layers: exchange cations and water molecules are not shown.
Colloidal gold with protective layer of thiol

- Why do colloidal crystals stay small? This study answers the question with a protective monolayer.
- Au in gold; S in blue; C in white; red electron density.
Common properties of nanoparticles in soils and soil systems

• High surface area
• Rapid chemical reactions
• Dispersible
• Often exhibit colloidal behavior
• Adsorb abundant water and organics
• Resemble small organic particles: starch, casein
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