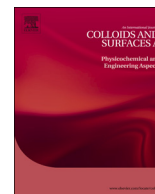




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Impact of organic matter types on surface charge and aggregation of goethite

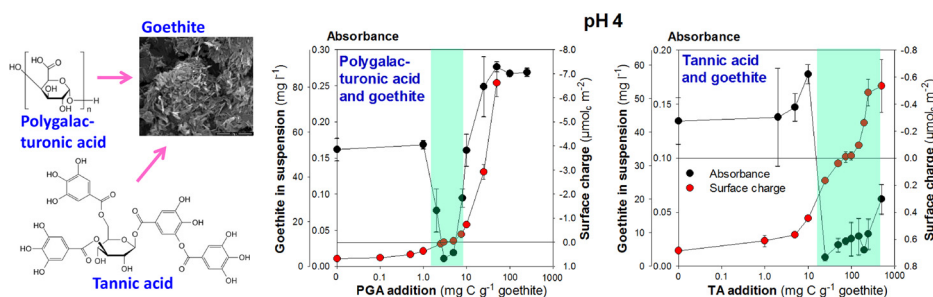


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GRAPHICAL ABSTRACT



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ABSTRACT

In order to assess the mobility and function of Fe oxihydroxides in terrestrial and aquatic environments, knowledge of the parameters and conditions determining aggregation and the size of formed aggregates is crucial. Here we study the impact of different organic matter (OM) types on the aggregation of goethite (α -FeOOH) with particular focus on the relevance of surface charge (SC). Synthetic goethite was reacted with galacturonic acid (GA), polygalacturonic acid (PGA), and tannic acid (TA) as model substances as well as with natural dissolved OM (DOM) from a litter (Oi-DOM) and a humified horizon (Oa-DOM). The SC of goethite was adjusted at pH 4 and 6 by the adsorption of organic acids and DOM to equal positive and negative SC as well as point of zero charge (*pzc*). Aggregation was traced by laser light scattering and sedimentation experiments. Aggregation of all goethite-OM associations depended on OM type and could well be explained by SC. Associations of goethite with OM rich in acidic groups (PGA, Oi-DOM, and Oa-DOM) followed the aggregation behavior of pure goethite. Largest aggregates with diameters up to 7 μm formed at *pzc*, whereas smaller ones ($\sim 0.4 \mu\text{m}$) developed at positive or negative SC. Organic substances rich in acidic functional groups interacted strongly with goethite at high additions, thus favoring charge reversal and limiting aggregate growth. For OM with low acidity (TA and GA), adsorption on goethite was incomplete even at high additions. These associations remained close to *pzc* and, hence, were susceptible to aggregation with maximum diameters at 6 μm . Aggregation was possibly also promoted by the exposure of less polar moieties exposed at the goethite-OM interface. Our data suggest that aggregation in environmental systems such as soils is driven by the nature and acidity of ubiquitous OM, which determines SC by the extent of adsorption to mineral surfaces.

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1. Introduction

Soil microaggregates are organized in structural units even at the smallest scale $< 2 \mu\text{m}$, the so-called building units [1], which can be composed of different silicates, metal oxyhydroxides, organic matter (OM) as well as microbial biomass [2]. Microaggregates of a size up to $250 \mu\text{m}$ are well known to play a decisive role in the stabilization of soil OM as they limit the access of microbial decomposers to the organic substrate [3]. Despite microaggregation is a common feature of most soils, the underlying factors controlling how compounds are bound together are not well understood [1]. A basic assumption is that microaggregation is primarily controlled by differences in surface charge (SC) of the interacting soil constituents. While layer silicates and OM represent predominantly negatively charged soil constituents, Fe and Al oxyhydroxides exhibit a high point of zero charge (pzc) typically at pH 6.5–9 [4]. Because of their small particle sizes even a few mass percent of metal oxyhydroxides can contribute significantly to the total soil surface area [5]. At $\text{pH} < \text{pH}_{pzc}$ their positive charge enables attraction of negatively charged constituents such as clay minerals, rendering metal oxyhydroxides a potential key factor for aggregation at the micron scale.

At pzc the number of positively and negatively charged surface sites is balanced and particle-particle interactions mainly depend on van der Waals forces [6]. The kinetic energy of Brownian motion can overcome weak electrostatic repulsive barriers, resulting in aggregation. With increasing deviation from pzc towards positive and negative charges, electrostatic repulsive forces between colloids increase, thus resulting in dispersion. Besides pH, the SC of metal oxyhydroxides can be further modified by inorganic anions and cations as well as natural dissolved OM (DOM) present in soil solution. Adsorption of multivalent anions like PO_4^{3-} , CO_3^{2-} , or SO_4^{2-} on Fe oxyhydroxides driven by electrostatic attraction can decrease SC and shift pzc to lower pH, whereas adsorbed multivalent cations can increase SC and shift pzc to higher pH [7–9]. At high surface coverage of goethite by OM, aggregation can be also promoted by the preferred sorption of nonpolar moieties of OM to goethite surfaces from aqueous solution [10]. Hence, for polymeric OM with high aromaticity, hydrophobic interactions may further promote aggregation [11].

Organic matter is typically present in the same environments as Fe oxyhydroxides, but has broad variations in composition and concentration [12]. Adsorption of DOM on Fe oxyhydroxides occurs fast and almost complete at small DOM additions, implying that mineral surfaces of Fe oxides in soil environments are typically coated by OM [13]. The adsorption of DOM to goethite ($\alpha\text{-FeOOH}$), the most common Fe oxyhydroxide in temperate soils, can markedly decrease SC, depending on the amount adsorbed [7,14]. Ligand exchange between carboxyl/hydroxyl functional groups of OM and Fe oxide surfaces is thought to be the dominant interaction factor, especially at acidic pH (Gu et al., 1994). Subsequent aggregation is affected here not alone by modification of SC properties (reversal of charge, change of SC density) but also by functional groups and changes of molecular scale surface roughness. Depending on the DOM source, its composition, such as the proportion of carboxyl-rich lignin-derived aromatics and that of sugars of different source can vary strongly. These components exhibit different affinities towards mineral surfaces, resulting in preferential adsorption of specific DOM moieties [15]. For example, goethite favors the adsorption of high-molecular weight aromatic constituents rich in carboxylic groups and has a lower affinity towards OM dominated by carbohydrates and aliphatic compounds [16–18]. Due to the heterogeneous nature of DOM, information on the effect of adsorbed DOM on aggregation of goethite is sparse and difficult to generalize. However, such interactions between OM and metal oxyhydroxides may play a profound role for colloid transport and the migration of nutrients and pollutants down the soil profile [19].

The main objectives of the present study, therefore, were (i) to clarify the relevance of SC for aggregation of a variety of goethite-OM

associations at different pH values, (ii) to determine the effect of OM type and adsorption on the aggregation of goethite, and (iii) to elucidate the aggregation kinetics in goethite-OM systems as proxy for the vulnerability of goethite for being transported in soil. For this purpose, we used defined model compounds representing different sources and decomposition stages of OM: polygalacturonic acid (PGA) as a polymeric plant pectin representing mucilage-type OM, monomeric galacturonic acid (GA) representing the respective hydrolysis product, and the aromatic organic polymer tannic acid (TA), constituting a polyphenolic part of terrestrial plants. For comparison, DOM extracted from a fresh litter (Oi) and well decomposed (Oa) organic horizon under forest was used as natural OM sources, reflecting the extremes with respect to OM age, decomposition stage, and chemical composition. Organic model compounds and DOM were added to goethite at pH 4 and 6 in different amounts and the respective aggregation was analyzed over time by particle sizing using dynamic light scattering and sedimentation tests [20,21]. For identification of the role of added OM types for aggregation, the SC of goethite was adjusted by the addition of organic acids and DOM to positive and negative SC of the same absolute value. The resulting goethite-OM associations with positive SC thus have small OM additions and those with negative SC high OM additions, while the quantity of charged surface sites was the same. This novel approach, normalizing the total SC to defined values, allows to determine the impact of different OM types and amounts on aggregation and, hereby, improve prognosis of the mobility of Fe oxides in soils.

2. Material and methods

2.1. Goethite preparation and characterization

Goethite ($\alpha\text{-FeOOH}$) was synthesized by addition of 10 M NaOH to a 0.5 M FeCl_3 solution ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Merck AG) under continuous stirring up to pH 12. The suspension was kept at 55°C for 120 h, to convert the formed ferrihydrite to goethite. After adjusting the suspension to pH 6 by addition of 0.1 M HCl, the goethite was washed with deionized water until the electrical conductivity was $< 10 \mu\text{S cm}^{-1}$. The resulting suspension with $59.7 \text{ g goethite l}^{-1}$ was used to prepare a stock suspension with 2.00 g l^{-1} , which was kept at 4°C in the dark. One aliquot of the suspension was freeze-dried for further analyses. The X-ray diffraction pattern indicated well-crystalline goethite (data not shown). The C content determined with a TOC analyzer (LiquiTOC Trace, Elementar, Germany) was 4 mg g^{-1} , indicating contamination of the synthetic goethite with carbonate anions. The Brunauer-Emmett-Teller specific surface area (SSA) measured by N_2 adsorption (Nova 4000e, Quantachrome, USA) was $65.2 \pm 2.3 \text{ m}^2 \text{ g}^{-1}$. In backscattered electron images (Quanta 200, FEI, USA) goethite crystallites showed the typical needle-like habitus, with an average length of $0.84 \pm 0.55 \mu\text{m}$ and thickness of $0.21 \pm 0.08 \mu\text{m}$. The mean hydrodynamic diameter of dispersed primary goethite particles, determined in a 100 mg l^{-1} suspension by a particle sizer (ZetaPals, Brookhaven, USA) in presence of a dispersant (0.01 mM $\text{Na}_4\text{P}_2\text{O}_7$, pH 8) and after 30 s sonication (Labsonic M, Sartorius Stedim) was $0.23 \pm 0.01 \mu\text{m}$. This diameter was integrated over the length and thickness of particles.

2.2. Solutions with dissolved organic matter

Solutions of organic acids were prepared using polygalacturonic acid (Sigma Aldrich, Switzerland), D(+)-galacturonic acid monohydrate (Fluka Analytical, Slovakia), and tannic acid (Riedel de Haen, Germany). For preparation of DOM solutions the Oi layer, consisting of relatively undecomposed plant material (Oi-DOM) and the Oa layer, representing decomposed OM (Oa-DOM) of a granite-derived Podzol under spruce (Waldstein, Fichtelgebirge, Germany; $50^\circ 7' 44'' \text{ N}$, $12^\circ 51' 18'' \text{ E}$) were used. DOM was extracted from air-dried samples at a sample-to-water ratio of 1:10 by shaking suspensions on a horizontal shaker at room temperature for 24 h. Suspensions were pre-filtered

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