Stability of coprecipitated natural humic acid and ferrous iron under oxidative conditions

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ABSTRACT

Goethite and lepidocrocite are considered the stable species of Fe oxyhydroxides formed from Fe^{2+} oxidation in mildly acidic soil environments, while maghemite is formed in mildly alkaline conditions. Complexing ligands, especially humic acid (HA), can change the pathway formation of these iron oxyhydroxides from Fe^{2+} oxidation. This research aimed to assess the influence of HA on Fe^{2+} oxidation and its effect on crystalline Fe mineral products. Ferrous iron was added to HA at increasing initial COOH/Fe(II) charge ratios (R) at pHs of 5.0 and 8.0 and aged at 70 °C for 1 month and up to 8 years at room temperature. The precipitated products after aging were analysed using XRD, FT-IR, TEM and AFM. The results indicate that oxidation of Fe^{2+} at pH 5.0, in the presence of large amounts of HA (R = 0.1) promoted the formation of goethite together with ferrihydrite. Oxidation of Fe^{2+} in slightly alkaline conditions (pH 8.0) yielded maghemite with small amounts of goethite. Further, long-term aging of HA coprecipitated with Fe^{2+} perturbed the stacking of the Fe hydroxyl sheets at pH 5.0, favouring the formation of ferrihydrite. At pH 8.0 the presence of humic acid does not influence the crystallinity of the precipitation products and maghemite was still stable after 8 years of aging. This research confirms that the oxidation of Fe^{2+} in soil and its subsequent hydrolysis is a very common process of Fe hydroxides/oxide formation in acidic soil environments. The type of Fe oxide formed depends strictly on the pH and secondly on the rate of oxidation, especially on the presence and amount of organic compounds that inhibit crystal growth. Humic acid are the main organic molecules in soils, particularly in cool, humid weathering environments where they lead to a decrease in crystalline perfection and promote the formation of ferrihydrite instead of goethite or lepidocrocite. These results provide significant insights into the effect of the mobility of HA in association with Fe minerals.

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1. Introduction

Weathering of primary Fe minerals in soil environments releases Fe^{2+}, which readily oxidizes in aerobic condition and precipitates as ferrihydrite, the precursor of many other pedogenetic Fe oxides (Schwertmann, 1991). The nature of the hydrolytic products of Fe^{2+} oxidation is reported to vary with Eh and pH formation (Lindsay, 1988). In laboratory systems, the oxidation of Fe^{2+} solutions in the absence of complexing ligands yields goethite (α-FeOOH) and lepidocrocite (γ-FeOOH) in mildly acidic environments (pHs of 4.0–6.0) and magnetite (Fe_3O_4) in mildly alkaline conditions (pHs of 7.0–8.0) (Schwertmann and Taylor, 1989; Taylor and Schwertmann, 1974). In laboratory hydrothermal synthesis, many complexing ligands are capable of altering the rate of Fe^{2+} oxidation, resulting in different Fe precipitation products, namely green rust (Krishnamurti and Huang,

1989, 1991, 1993; Schwertmann and Fechter, 1994). Cornell and Schwertmann (1979) showed that citrate inhibited the conversion of ferrihydrite to goethite and promoted the crystal growth of lepidocrocite at the expense of goethite. These soluble organic compounds, such as citrate and malate, are dominant in root exudates, and they can solubilize and reduce Fe^{3+} of soil minerals to Fe^{2+} (Pédrot et al., 2011). The Fe^{2+} released to the soil solution rapidly transforms in the presence of soluble organic acids to lepidocrocite, especially in root channels and in soil concretions (Fan et al., 2002; Fitzpatrick et al., 1985; Loeppert et al., 1984). In addition, the Fe^{2+} oxidation is generally retarded in the soil solution and in natural waters which contain significant amount of complexing ligands as soluble humic substances (Theis and Singer, 1974). Humic substances can also affect ferrihydrite formation by an indirect mechanism involving the stabilisation of ferrihydrite by high molecular weight humic fractions, which thus tend to stabilise the poorly crystalline iron precipitate (Angelico et al., 2014; Colombo et al., 2014; Eusterhues et al., 2011; Mikutta, 2011). The presence of high concentrations of complexing ligands coprecipitated with Fe^{2+} ensures

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that ferrihydrite is thermodynamically very stable compared with other iron oxides (Navrotsky et al., 2008) due to the high surface areas (500–700 $m^2 g^{-1}$) and the small size of the nanoparticles (2–5 nm).

The effects of humic acids (HA) on the transformations of the hydrolytic products of Fe^{3+} have been extensively investigated (Cornell and Schwertmann, 2003). However, few studies have explored the influence of organic molecules, such as HA, on the oxidative products of Fe^{2+} after a long period of aging (Krishnamurti and Huang, 1991; 1993). Furthermore, the effect of insoluble HA on the kinetics of Fe^{2+} oxidation and the nature of the resultant hydrolytic products of Fe^{3+} in mildly alkaline pH have so far fully established.

Based on the knowledge outlined above, we hypothesise that the HA concentration influences the various pathways of formation of the Fe minerals produced during the Fe^{2+} oxidative processes. Therefore, the main objectives of this study were as follows: i) to determine the influence of HA at initial $COOH/Fe^{2+}$ charge ratios (R) of 0.0001, 0.001, 0.01, and 0.1 on the oxidative products of Fe^{2+}; ii) to evaluate the effects of coprecipitated HA products at pHs of 5.0 and 8.0 over short times (1 month at 70 °C) and after 8 years of aging at room temperature; iii) to characterise the final precipitates after aging formed during oxidation in the presence of HA using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), atomic force microscopy (AFM) and by chemical extraction.

2. Materials and methods

2.1. Humic acids extraction and characterisation

A volcanic soil under oak forest was sampled in the around of the Royal Palace in Portici (Italy). Humic acids (HA) were extracted from the Ap horizon with 0.1 M NaOH and purified following standard methods (International Humic Substances Society (IHSS), 1985). The HA ash content was 1.29%. The COOH was 3.27 and phenolic acidity 2.72 $mmol_c g^{-1}$, determined with acid–base tritations. Some characteristics of the extracted HA were reported previously by Amalfitano et al. (1995).

2.2. Preparation of the iron-humic acid sample

Appropriate amounts of solutions of 0.01 M Fe^{+2} perchlorate (Fe $(ClO_4)_2 \cdot 6H_2O$) (Aldrich Chemical Company Inc., USA) and HA were added to 750 ml of distilled and boiled water in polypropylene containers, in order to obtain the desired $COOH/Fe^{2+}$ charge ratios (R) of 0, 0.0001, 0.001, 0.01 and 0.1. The suspension, in which N_2 was continuously bubbled, was titrated to either pH 5.0 or 8.0 with 0.25 M NaOH at a feed rate of 1 ml min^{-1}. When the solution pH had stabilised, N_2 bubbling was replaced by air (300 ml min^{-1}) and the pHs were maintained for 16 h. No attempt was made to remove CO_2 from the air. The pHs were monitored and adjusted to the pre-set values twice a day for 6 days with 0.1 M NaOH or 0.1 M $HClO_4$ at room temperature using a Metrohm Titroprocessor (Model 672) in a set-mode. The final volume of all samples was adjusted to 1 l. The suspensions were aged for 1 month at 70 °C and, finally 8 years at room temperature without pH control, when the final precipitate was taken. Solids were separated after 6 days at 20 °C, after 30 days of aging at 70 °C, and after 8 years of aging by ultrafiltration with semipermeable membrane of 0.01 μm under an N_2 gas (Spectrum Molecular/Por type C membrane atmosphere, Amicon) and then freeze-dried for mineralogical and chemical analysis.

2.3. Characterisation of the precipitation products

The freeze-dried samples were examined by X-ray powder diffraction (XRD) on a Rigaku Geigerflex D/Max IIIC diffractometer using Fe-filtered Co-K_α radiation at 40 kV and 30 mA. Infrared spectra were collected on a Perkin Elmer 1720X spectrometer using the KBr pellet technique (1 mg of sample mixed with 200 mg of KBr). Transmission electron micrographs were obtained using a Philips CM120 microscope at 100 kV by depositing one drop of a water suspension of the sample onto a carbon-coated Formvar film Cu grid.

The AFM images were taken by using a NanoScope III atomic force microscope with a Multiplode SPM unit (Digital Instrument, Inc.). The images were taken in air using a J model, with 125 nm × 125 nm scan size, and an A model, with 400 nm × 400 nm scan size according the procedure of Colombo et al. (2012b). The cantilever used had a wedge-shaped silicon nitride (Si_3N_4) tip with a force constant of 20–100 N/m in tapping mode (T-AFM). The images were collected at scan rate of 1.00 Hz and the set point voltage was approximately 0.77 V.

Total iron (Fe_t), after dissolution with 6 M HCl, and the ammonium oxalate-extractable Fe at pH 3 (Fe_o) were determined by atomic absorption on a Perkin Elmer 3130 spectrophotometer (Schwertmann, 1964).

3. Results and discussion

Visual observations of the precipitation process as Fe^{2+} was oxidized with air as the purge gas over 16 h provided a good indication of the sequence of crystallization events. At pH 5.0, a green solution developed within 30 min, which then changed to yellow orange and finally to a well-defined yellow brown precipitate after an additional 2 h of reaction. At pH 8.0 the green solution rapidly changed to a yellow brown precipitate after 30 min, and in time the Fe-oxide transformed to a dense brown sediment. All the Fe products were completely precipitated and oxidized after 16 h, after which the precipitates were separated by ultrafiltration for further characterisation.

3.1. X-ray powder diffraction

X-ray diffraction patterns of the products are shown in Fig. 1. In the absence of HA (R = 0), the precipitation product formed at pH 5 after aging at 70 °C for 1 month was predominantly poorly crystalline goethite (α-FeOOH) along with smaller amounts of maghemite (β-Fe_2O_3) (Fig. 1a). The XRD pattern for R = 0 at pH 5.0, in Fig. 1a shows the characteristic peaks of goethite at 0.418, 0.269, 0.246, 0.225, 0.219 and 0.156 nm, and trace amounts of maghemite with very weak peaks at 0.295 and 0.251 nm. For R = 0.001, trace amounts of lepidocrocite are indicated by very weak peaks at 0.332, 0.192 nm and 178 nm. In the presence of increasing amounts of HA at pH 5.0 small amounts of ferrihydrite occurred along with goethite (Fig. 1a). After eight years of aging at pH 5.0 in the absence of HA (Fig. 1b), a reduction of a poorly crystallized compound and a mixture of goethite, ferrihydrite and small amount of lepidocrocite may be observed with the presence of two sharp peaks at 0.332, 0.192 nm only at R = 0.0001. In the absence of HA, after 8 years of aging, an abundant amount of the poorly crystalline phase as a "2-line ferrihydrite" (the two broad lines at 0.252 and 0.172 nm), the most disordered state for this type of compound (Carlson and Schwertmann, 1990) (Fig. 1b).

The oxidation of 0.01 M ferrous perchlorate at pH 8.0 yielded maghemite at R = 0 with characteristic d-spacings observed at 0.492, 0.296, 0.252, 0.209, 0.171, and 0.161 nm. With increasing HA concentration, small amounts of goethite (a weak broad XRD peak at d-spacings of 0.419, 0.269, 0.222, and 0.187 nm, Fig. 1c) formed at R = 0.001. The XRD pattern for R = 0.1 at pH 8.0, in Fig. 1d shows the characteristic peaks of maghemite with very weak peaks of goethite at 0.492 and 0.296 nm. From the XRD data it is difficult to distinguish magnetite from maghemite in the final products at pH 8.0. Thus it is also possible that the product formed is magnetite surrounded by secondary maghemite, which produces overlapping peaks not resolved in the diffraction patterns. From XRD data the presence of HAs does not seem to influence the nature of Fe oxides formed at pH 8.0, but the oxidation of Fe^{2+} produced magnetite with small amounts of goethite. This effect was clearer during aging, where the presence of goethite increases the HA concentration rise (Fig. 1d).